INVESTIGATION OF THERMAL ELECTRON ATTACHMENT TO ORGANIC ACETATES AND AROMATIC HALOGEN DERIVATIVES

A Thesis

Presented to the Faculty of the Department of Chemistry College of Arts and Sciences University of Houston

In Partial Fulfillment of the Requirements for the Degree Master of Science

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> > by

Joe Charles Steelhammer

August, 1968

DEDICATION

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This thesis is dedicated to my wife.

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ACKNOWLEDGEMENT

I am especially grateful to Dr. W. E. Wentworth who made this work possible. I also want to thank Dr. E. C. Chen for his helpful discussions.

A special word of thanks goes to Mrs. Sharon Sloan, Mrs. Lynn George and Mr. Robert George for assistance in the computer programming. I would also like to thank Mr. W. T. Ristau for his assistance.

I am very grateful to my wife, Debbie, for her understanding.

The financial support of this work was made possible partly through the generous support of the Robert A. Welch foundation, to whom grateful acknowledgement is made.

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ABSTRACT

A new thermal electron attachment mechanism is proposed. The importance of this mechanism is that the activation energy for dissociative thermal electron attachment is equal to the change in internal energy for the process. It is therefore possible to determine electron affinities for radicals and bond dissociation energies providing one of these quantities is known. The results of three compounds leading to the electron affinity of the acetate radical are presented. The electron affinity of the acetate radical determined by this technique compares favorably with the electron impact value.

Thermal electron attachment studies to some aromatic halogen derivatives are also presented. In particular, the thermal electron attachment of 3'- and 4'- chloroacetophenone shows a unique temperature dependence involving three different phenomena. This adds further support to the thermal electron attachment mechanism proposed earlier for the aromatic halogen derivatives.

The relationship between thermal electron attachment and electron beam studies of dissociative electron attachment to the aromatic halogen derivatives is also shown. An empirical negative ion potential energy function is used to show this relationship. Use of this potential energy function permits a more quantitative representation of the thermal electron attachment mechanisms previously proposed. In some cases, the mechanisms have been altered from the earlier qualitative interpretation. Although the modes of electron attachment

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are quite different, the two techniques of studying dissociative electron attachment appear to be essentially in complete agreement.

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INTRODUCTION I.

INTRODUCTION

A. Thermal Electron Attachment Studies

Electron attachment to molecules is generally considered to occur by either of two processes represented by the chemical equations 1

$$AB + e^- \rightarrow AB^-$$

$$AB + e^- \rightarrow A \cdot + B^-$$

The latter process is called dissociative electron attachment in contrast to the former, nondissociative, process.

For many years electron attachment processes have been studied mainly by two experimental methods: electron swarm and electron beam. In recent years, a pulse sampling technique has been developed to study thermal electron attachment to molecules.²

The pulse sampling technique has been described in detail previously.^{3,4} The details of the operational parameters have also been reported.² In a gas mixture of argon-ten percent methane, presumably thermal or near thermal electron energies are obtained. Indirect support for this has been reported.^{5,6} The pulse sampling technique, in addition to its simplicity in operation and design, has another direct advantage since it can be used in conjunction with a gas chromatograph.

Although electron attachment to molecules is generally classified as above, it is convenient to discuss these two processes in a slightly different manner with regards to thermal electron attachment studies. In previous publications^{2,5,7} three mechanisms for thermal electron attachment to molecules have been proposed. These mechanisms involve: (I) formation of a stable negative molecular ion, (II) a single bimolecular electron attachment step followed by immediate dissociation into a negative ion and a radical by way of a dissociative potential energy curve, (III) a two-step dissociative process which first involves the formation of a negative molecular ion intermediate followed by a dissociative step giving generally a negative halide ion and an organic radical by way of a dissociative potential energy curve.

Both dissociative and nondissociative thermal electron attachment processes have been previously studied utilizing the pulse sampling technique. From these studies the following molecular parameters may be derived directly: molecular electron affinities, rate constants for dissociative and nondissociative thermal electron attachment, and activation energies for thermal electron attachment, detachment and dissociation.

B. <u>Electron Swarm and Electron Beam Studies of Electron Attachment Pro-</u> cesses

In swarm experiments, electrons are drawn through a gas by means of an electric field. The gas pressure is high enough (several Torr) to allow a large number of collisions. A steady state is attained in which the electrons gain energy from the electric field and lose energy in the course of collisions with molecules. The velocity at

which the electrons drift through the gas under definite electric field and pressure conditions is related to their energy losses to the gas. Since the electrons make many collisions with the gaseous medium through which they travel, their energies are spread over a wide range. Electron swarm experiments are much easier to carry out than are electron beam experiments, but are more difficult to interpret. In the swarm experiments, the quantities measured, e.g., the rates of electron attachment, are the average of many encounters and are thus averaged over the entire electron energy distribution. One problem in swarm experiments is that they do not generally lead to the identification of the various negative ions formed.

In beam experiments, the electrons are emitted in a vacuum and formed into a beam by a system of electrodes and slits. The electrons in the beam are then given a definite energy by accelerating them in a known electric field. The electrons are then passed into a chamber where they collide with gas molecules. The gas pressure in the chamber is very low (-10^{-5} Torr) so that the events that occur are due to single collisions between the electrons and the molecules. The negative ions are then withdrawn by an electrostatic field so that a mass analysis can be performed to identify the negative ions formed. The ion current, corresponding to a particular negative ion, is measured as a function of electron energy. Although the electrons are not truly monoenergetic, the difference ion current (first derivative of the ion current) as a function of electron energy can be regarded, to a first approximation, as the shape of the electron capture cross sections as a function of

electron energy. The cross section is basically a measure of the probability that a given type of reaction will occur under given conditions.⁸

Until several years ago, the data obtained in the low energy electron region (<2 ev) by either swarm or beam methods were not satisfactory. This was due to unknown energy distributions in the electron swarms and the poor energy resolution and uncalibrated energy scale in the electron beam experiments. A combined swarm-beam technique⁹ has been developed which utilizes known energy distributions in the electron swarms and a quasi-monoenergetic electron beam with a negative ion timeof-flight mass spectrometer for the study of low energy interactions with molecules. This technique is used to adjust the electron energy scale of the beam experiments and calculate the absolute capture cross sections as a function of electron energy.

Previously, the electron energy scale in the beam experiments was calibrated by using the resonance-capture process in sulfur hexafluoride, SF_6 , which yields a maximum in the difference negative ion current near .03 ev¹⁰. The swarm-beam method can establish the electron energy scale without the use of a calibrating gas. The actual energy at which the capture cross section is a maximum is neither the energy calculated from the swarm data nor the energy found in the beam experiments, but the beam value plus a correction factor. This correction factor is obtained by adjusting the difference negative ion current curves obtained by beam studies to obtain agreement between the calculated capture rates computed from beam data and the experimental rates obtained from swarm experiments.⁹ When the appearance potential as determined by the beam

method alone has a positive value, the new appearance potential determined from the swarm-beam combination is more likely to be correct. However, in cases where the appearance potential is zero as found by beam data alone and a positive energy shift is required upon application of the swarm-beam method, the appearance potential determined by the swarm-beam method is questionable.⁹

With this combined swarm-beam technique, the data obtained in the low-energy electron region are much improved. This technique has recently been used to investigate dissociative electron attachment to some aromatic halogen derivatives.¹¹

C. Comparison of Electron Beam and Thermal Electron Attachment Studies

Dissociative electron attachment has been studied by both the electron beam and pulse sampling techniques. Absolute agreement between the energy of maximum capture cross section obtained by beam experiments and the activation energy for dissociation measured by thermal electron studies is not possible since the modes of electron attachment for the two methods are quite different. In the beam experiments, a high energy electron collides with a molecule in the ground state and therefore a vertical transition from the neutral molecule to the dissociative negative ion state occurs. In the electron capture cell used in the pulse sampling technique, the molecules are thermally excited so that low lying vibrational levels of the neutral molecule become occupied to the point where the potential energy curve for the neutral molecule crosses that for the dissociative state.

Although the modes of electron attachment are different, a correlation should exist between the energy of maximum capture cross section and the activation energy if both techniques are investigating the same dissociative process. A correlation has not been previously attempted because the electron beam data in the low-energy electron region were not satisfactory. With the combined swarm-beam technique⁹, the data are now more reliable.

A previous study investigating thermal electron attachment to several aromatic halogen derivatives postulated the formation of a negative molecular ion intermediate prior to dissociation (Mechanism III)^{5,12} This has been confirmed with a unique type of electron beam experiment,¹³ in which the SF₆ peak is monitored in a mixture of SF₆ and an aromatic halogen derivative. New SF₆ peaks occur at energies above the usually observed SF₆ peak near zero energy. This is explained by the formation of a temporary negative molecular ion state of the aromatic halogen derivative followed by autoionization to give thermal electrons. The thermal electrons are then scavenged by SF₆ to give SF₆ peaks at a different energy than normal. The energy of the new SF₆ peaks will then correspond to the same energy as the dissociative electron capture resonances for the aromatic halogen derivatives. Intermediate negative molecular ions have been postulated for F-benzene, o-Cl-toluene, Cl-benzene, Br-benzene, o-Br-toluene and o-dichlorobenzene.¹³

D. Statement of the Problem

There were two purposes of this study. The first was to present data supporting a fourth mechanism (IV) for thermal electron attachment to molecules. This fourth mechanism is important since either bond dissociation energies or electron affinities for radicals can be determined providing one of these quantities is known.

The second purpose of this study was to investigate dissociative thermal electron attachment to some aromatic halogen derivatives (Mechanism III) and to correlate the results with those obtained from experiments that utilized the combined swarm-beam technique. II. EXPERIMENTAL

EXPERIMENTAL

The experimental technique for obtaining thermal electron attachment measurements has been reported in previous studies.^{2,5} A description of the electron capture cell and the pulse sampling technique has also been given previously.^{2,14} A tritium-embedded titanium foil with an activity of ~.1 Curie was used in the electron capture cell. A square-wave potential of 40 volts was applied across the cell by means of a Datapulse generator, Model 102. A pulse width of .5 µsec at an interval of 1000 µsec was employed in the electron capture cell to collect the free electrons.

Solutions of the compounds under investigation were prepared to give suitable peak sizes (about 60% capture), and linearity in response to the concentrations used. The solutions were prepared by volume measurements for the compounds that were liquid. Concentrations in moles per liter were then calculated from known densities and molecular weights. The solutions of the solid compounds were prepared by weighing the solute on a Cahn electrobalance. The solvents used were Mallinckrodt Nanograde benzene and toluene. The ethyl trifluoroacetate was obtained from Pierce Chemical Co....The acetic anhydride was Baker reagent grade and all other compounds were Eastman Red Label grade. It was not necessary to carry out a purification of the compounds since this was accomplished satisfactorily in the gas chromatograph prior to measurement in the electron capture cell. The Microtek 2000-R gas chromatograph was used for all compounds. Two gas chromatographic columns were used: a 225 foot - 1/16 inch stainless steel capillary column coated with polyphenyl ether, and a 3 foot - 1/8 inch stainless steel column packed with 20% Carbowax 20M on terepthalic acid.

The temperature of the electron capture cell was generally elevated to the highest temperature (~220°C) and measurements were made at successive intervals as the temperature was allowed to drop. In the case of the acetic anhydride, the data at low temperatures were obtained at a later date than the high temperature data. The low temperature data were adjusted to the high temperature data by the data points which were common to both regions.

The areas under the chromatographic peaks were obtained by using a Leeds and Northrup analog computer.¹⁴ In all cases the span correction b^0/b was used;² however, the correction was generally on the order of 1.5 or less.

The temperature dependence of the electron-capture coefficient,² K, was studied and ln $KT^{3/2}$ versus 1/T graphs^{2,5} were constructed from the data (Appendix A). The compounds investigated were:

(a) organic acetates: acetic anhydride $[(CH_3CO)_2O]$, benzyl acetate ($CH_3COOCH_2C_6H_5$), ethyl acetate ($CH_3COOC_2H_5$), ethyl trichloro-acetate ($CCl_3COO-C_2H_5$), and ethyl trifluoroacetate ($CF_3COOC_2H_5$).

(b) aromatic halogen derivatives: o-bromofluorobenzene (o-BrFC₆H₄), m-bromobenzotrifluoride (m-BrCF₃C₆H₄), o-bromotoluene (o-CH₃C₆H₄Br), 3'-chloroacetophenone (m-CH₃COC₆H₄Cl), 4'-chloroacetophenone (p-CH₃COC₆H₄Cl), chlorobenzene (C₆H₅Cl), 1-chloronapthalene (1-C₁₀H₇Cl), o-chlorotoluene (o-CH₃C₆H₄Cl), and o-dichlorobenzene (o-C₆H₄Cl₂).

(c) others: 1'-acetonapthone ($CH_3COC_{10}H_7$), biacetyl [(CH_3CO)₂], diacetylbenzene [p-C₆H₄(CH_3CO)₂], nitromethane (CH_3NO_2), and terepthal-aldehyde [p-C₆H₄(CHO)₂].

o-Dichlorobenzene had previously been investigated, but not over a sufficient temperature range.

III. RESULTS

RESULTS

The results for all the compounds run are given in Table I. The graphs of ln $KT^{3/2}$ versus 1/T for the organic acetates appear in Figure 1. Similar graphs for the aromatic halogen derivatives appear in Figures 2 and 3. The graphs of ln $KT^{3/2}$ versus 1/T shown in Figure 4 are for other compounds investigated during the course of this work.

The data in Table I were obtained by a least-squares fit⁵ of the experimental data (Appendix B). R is the gas constant. The solid lines in Figures 1 - 4 are the least-squares adjustments to the data. For the compounds that undergo nondissociative electron attachment, a common intercept of 14.79 \pm .11 was used in the least-squares adjustment of the data. This common intercept least-squares adjustment has been explained in a previous publication.¹⁵

Tables II, III, and IV give the temperature dependence of the electron capture coefficients for the organic acetates, aromatic halogen derivatives and the other compounds studied, respectively.

Table V gives the experimentally determined molecular electron affinities, EA, activation energies for dissociative electron attachment, E_{\perp}^{*} , and activation energies for nondissociative electron attachment, E_{\perp}^{*} (Appendix B).

TABLE I

LEAST-SQUARES ADJUSTMENT OF THE TEMPERATURE DEPENDENCE OF THE ELECTRON-CAPTURE COEFFICIENTS

| · · · · · · · · · · · · · · · · · · · | | | | |
|---------------------------------------|------------------------|---------------------------|--|--|
| Compound | ∆E = slope x R, kcal. | Intercept | | |
| Organic Acetates: | | | | |
| Acetic Anhydride | -7.82±.12 | 34.86 ±.14 | | |
| Benzyl Acetate | -10.27±.44 3.88±.15 | 33.76 ±.49 14.79 ±.11 | | |
| Ethyl Acetate | 3.66±.10 | 14.79 ±.11 | | |
| Ethyl trichloroacetate | -1. 97±.40 | 35.06 ±.52 | | |
| Ethyl trifluoroacetate | -8.15±.94 10.59±.13 | 37.50 ±1.06 14.79 ±.11 | | |
| Aromatic Halogen Derivative | s: | | | |
| o-Bromofluorobenzene | -4.44±.10 | 34.41±.12 | | |
| m-Bromobenzotrifluoride | -2.28±.10 | 35.93 ±.10 | | |
| o-Bromotoluene | -7.64±.12 | 34.61±.13 | | |
| 3'-Chloroacetophenone | -5.40±.61 13.45±.13 | 35.46±.61 14.79±.11 | | |
| 4'-Chloroacetophenone | -7.97±.66 13.07±.12 | 37.94±.66 14.80±.11 | | |
| Chlorobenzene | -10.62±.28 | 32.92±.31 | | |
| l'-Chloronaphthalene | -11.01±.25 6.39±.14 | 40,55±.29 14.83±.21 | | |
| o-Chlorotoluene | -11.65±.63 | 33.24±.6 8 | | |
| o-Dichlorobenzene | -8.67±.34 | 37.59±.39 | | |

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TABLE I CONTINUED

LEAST-SQUARES ADJUSTMENT OF THE TEMPERATURE DEPENDENCE OF THE ELECTRON-CAPTURE COEFFICIENTS

| Compound | ΔE = slope x R, kcal. | Intercept |
|------------------|-------------------------------|------------------------|
| Others: | | |
| 1'-Acetonapthone | 13.37±.13 | 14.77±.11 |
| Biacetyl | 14.16±.11 -1.10±.16 | 14.79±.11 34.06±.23 |
| Diacetyl benzene | -2.16±.10 | 34.89±.11 |
| Phthalaldehyde | -3.17±.15 | 33.76±.18 |
| Nitromethane | -12.58±.43 | 37.17±.45 |

FIGURE 1

LN $\mathrm{kt}^{3/2}$ versus 1/T for the organic acetates

- ♥ Ethyl trichloroacetate
- ∧ Ethyl trifluoroacetate
- ♥ Acetic anhydride
- Benzyl acetate
- 🖸 Ethyl acetate



..

FIGURE 2

LN $kT^{3/2}$ VERSUS 1/T FOR THE AROMATIC HALOGEN DERIVATIVES



• • • • •

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LN ${\rm KT}^{3/2}$ VERSUS 1/T FOR THE AROMATIC HALOGEN DERIVATIVES





LN $\mathrm{KT}^{3/2}$ VERSUS 1/T FOR SOME CARBONYL AND NITRO DERIVATIVES



| COMPOUND | T,° K | 1/T x 10 ³ , °K ⁻¹ | 1n KT ^{3/2} | L.S. 1n KT ^{3/2} |
|--------------------------|--------------|--|----------------------|---------------------------|
| Acetic | 505 | 1.98 | 27.05 | 27.06 |
| Anhydride (first data | 503 | 1.99 | 26.96 | 27.03 |
| set) | 500 | 2.00 | 26.86 | 26.98 |
| | 499 | 2.00 | 27.03 | 26.97 |
| , | 496 | 2.02 | 26.89 | 26.92 |
| | 495 | 2.02 | 26.92 | 26.91 |
| | 489 | 2.04 | 26.89 | 26.81 |
| | 476 | 2.10 | 26.63 | 26.58 |
| | 473 | 2.11 | 26.56 | 26.53 |
| | 468 | 2.14 | 26.39 | 26.44 |
| | 461 | 2.17 | 26.27 | 26.31 |
| | 454 | 2.20 | 26.19 | 26.19 |
| | 449 | 2.23 | 26.06 | 26.08 |
| | 438 | 2.28 | 25.88 | 25.87 |
| | 427 | 2.34 | 25.71 | 25.64 |
| • | 420 | 2.38 | 25.52 | 25.49 |
| | 410 | 2.44 | 25.32 | 25.26 |
| | 397 | 2.52 | 25.01 | 24.95 |
| | 387 | 2.58 | 24.74 | 24.69 |
| | 379 | 2.64 | 24.41 | 24.47 |
| | 369 | 2.71 | 24.21 | 24.19 |
| | 356 | 2.81 | 23.75 - | 23.79 |
| | 348 | 2.87 | 23.45 | 23.53 |
| . • | 342 | 2.92 | 23.23 | 23.34 |
| | 333 | 3.00 | 23.01 | 23.03 |

ELECTRON CAPTURE COEFFICIENTS AT VARIOUS TEMPERATURES FOR THE ORGANIC ACETATES
ELECTRON CAPTURE COEFFICIENTS AT VARIOUS TEMPERATURES FOR THE ORGANIC ACETATES

| COMPOUND | T,°K | 1/T x 10 ³ , °K ⁻¹ | 1n KT ^{3/2} | L.S. 1n KT ^{3/2} |
|------------------------|------------------|--|----------------------|---------------------------|
| · · · | 321 | 3.12 | 22.56 | 22.58 |
| | 318 | 3.14 | 22.49 | 22.49 |
| | 315 | 3.17 | 22.51 | 22.36 |
| (second data | a | | | |
| set: low te peratures) | em- 429 | 2.33 | 25.75 | |
| | 386 | 2.59 | 24.63 | |
| · | 375 | 2.67 | 24.31 | |
| | 362 | 2.76 | 23.94 | |
| | 353 | 2.83 | 23.67 | |
| | 344 | 2.91 | 23.41 | |
| | 331 | 3.02 | 23.00 | |
| | 319 | 3.13 | 22.80 | |
| | 306 | 3.27 | 22.49 | |
| | 299 | 3.34 | 22.25 | |
| • | 293 | 3.41 | 22.17 | |
| | 285 | 3.50 | 21.98 | |
| | 279 | 3.58 | 21.87 | |
| | 271 | 3.69 | 21.85 | |
| | 264 | 3.79 | 21.85 | |
| | 258 _. | 3.88 | 21.78 | |
| Benzyl | | | | |
| acetate | 497 | 2.01 . | 23.52 | 23.36 |
| | 490 | . 2.04 | 23.31 | 23.21 |
| | 476 | 2.10 | 23.02 | 22.90 |

ELECTRON CAPTURE COEFFICIENTS AT VARIOUS TEMPERATURES FOR THE ORGANIC ACETATES

| COMPOUND | T,°K | $1/T \times 10^3$, °K ⁻¹ | ln KT ^{3/2} | L.S. 1n KT ^{3/2} |
|----------|-------------|--------------------------------------|----------------------|---------------------------|
| | 467 | 2.14 | 22.63 | 22.68 |
| | 456 | 2.19 | 22.26 | 22.41 |
| | 444 | 2.25 | 21.94 | 22.11 |
| | 431 | 2.32 | 21.46 | 21.76 |
| | 417 | 2.40 | 21.36 | 21.36 |
| | 4 04 | 2.48 | 21.08 | 20.96 |
| | 391 | 2.56 | 20.74 | 20.54 |
| | 3 76 | 2.66 | 20.46 | |
| | 3 58 | 2.79 | 20.29 | 20,25 |
| | 347 | 2.88 | 20.41 | 20.42 |
| | 333 | 3.00 | 20.62 | 20.66 |
| Ethvl | | | · | |
| acetate | 506 | 1.98 | 20.57 | |
| | 500 | 2.00 | 20.44 | |
| | 496 | 2,016 | 20.51 | |
| | 488 | 2.05 | 20.36 | |
| | 475 | 2.11 | 20.15 | |
| • | 458 | 2.18 | 19,89 | |
| · | 438 | 2.28 | 19.79 | |
| | 417 | 2.40 | 19.83 | |
| | 395 | 2.53 | 19.91 | |
| | 366 | 2.73 | 19.90 | |
| | 346 | 2.89 | 20.13 | 20.11 |
| | .332 | 3.01 | 20.31 | 20.32 |

ELECTRON CAPTURE COEFFICIENTS AT VARIOUS TEMPERATURES FOR THE ORGANIC ACETATES

| · | | | | |
|------------|-------------|--|----------------------|---------------------------|
| COMPOUND | T,°K | 1/T x 10 ³ , °K ⁻¹ | 1n KT ^{3/2} | L.S. 1n KT ^{3/2} |
| Ethyl tri- | | | | |
| tate | 482 | 2.07 | . 33.05 | 33.00 |
| | 478 | 2.09 | 33.00 | 32.99 |
| | 473 | 2.11 | 32.97 | 32.97 |
| | 469 | 2.15 | 32.96 | 32.96 |
| | 457 | 2.19 | 32.88 | 32.88 |
| | 447 | 2.24 | 32.84 | 32.84 |
| | 435 | 2.30 | 32.76 | 32.78 |
| | 429 | 2.33 | 32.72 | 32.74 |
| | 413 | 2.42 | 32.68 | 32.66 |
| | 403 | 2.48 | 32.59 | 32.59 |
| | 397 | 2.52 | 32.55 | 32.56 |
| | 392 | 2.55 | 32.53 | 32.53 |
| | 378 | 2.65 | 32.41 | 32.43 |
| | 368 | 2.72 | 32.36 | 32.36 |
| | 362 | 2.76 | 32.32 | 32.32 |
| | 348 | 2.87 | 32.22 | 32.21 |
| | 341 | 2.93 | | 32.14 |
| | 329 | 3.04 | 32.06 | 32.05 |
| | 321 | 3.12 | 32.00 | 31.97 |
| | 316 - | 2.16 | 31.95 | 31.93 |
| Ethyl tri- | | | | |
| tate | 453 | 2.21 | 28.43 | 28.43 |
| | 447 | 2.24 | 28.34 | 28.32 |

.

ELECTRON CAPTURE COEFFICIENTS AT VARIOUS TEMPERATURES FOR THE ORGANIC ACETATES

| Т , °К | 1/T x 10 ³ , °K ⁻¹ | ln KT ^{3/2} | L.S. 1n KT ^{3/2} |
|---------------|---|--|--|
| 441 | 2.27 | 28.22 | 28.19 |
| 435 | 2.30 | 28.06 | 28.06 |
| 430 | 2.33 | 27.92 | |
| 422 | 2.37 | 27.85 | |
| 415 | 2.41 | 27.92 | |
| 410 | 2.44 | 28.03 | 27.79 |
| 403 | 2. 48 | 28.20 | 28.00 |
| 395 | 2.53 | 28.34 | 28.27 |
| 390 | 2.56 | 28.45 | 28.43 |
| 383 | 2.61 | 28.53 | 28.69 |
| 376 | 2.66 | 28.68 | 28.96 |
| | 441 435 430 422 415 410 403 395 390 383 376 | 441 2.27 435 2.30 430 2.33 422 2.37 415 2.41 410 2.44 403 2.48 395 2.53 390 2.56 383 2.61 376 2.66 | 4412.2728.224352.3028.064302.3327.924222.3727.854152.4127.924102.4428.034032.4828.203952.5328.343902.5628.453832.6128.533762.6628.68 |

TABLE III

.

ELECTRON CAPTURE COEFFICIENTS AT VARIOUS TEMPERATURES FOR THE AROMATIC HALOGEN DERIVATIVES

| COMPOUND | T,°K | 1/T x 10 ³ , °K ⁻¹ | ln KT ^{3/2} | L.S. 1n KT ^{3/2} |
|--------------|------------------|--|----------------------|---------------------------|
| o-Bromofluor |)- | A AA | | |
| benzene | 454 | 2.20 | 29.52 | 29.49 . |
| | 446 _. | 2.24 | 29.43 | 29.40 |
| | 439 | 2.28 | 29.34 | 29.32 |
| | 432 | 2.31 | 29.26 | 29.24 |
| | 426 | 2.35 | 29.16 | 29.17 |
| | 419 | 2.39 | 29.06 | 29.08 |
| | 412 | 2.43 | 28.99 | 28.99 |
| | 406 | 2.46 | 28.89 | 28.91 |
| | 401 | 2.49 | 28.81 | 28.84 |
| | 394 | 2.54 | 28.64 | 28.74 |
| | 381 | 2.62 | 28.50 | 28.54 |
| | 367 | 2.72 | 28.30 | 28.32 |
| | 3 56 | 2.81 | 28.15 | 28.13 |
| | 333 | 3.00 | 27.84 | 27.70 |
| | 3 32 | 3.01 | 27.68 | 27.67 |
| | 325 | 3.07 | 27.47 | 27.53 |
| m-Bromobenzo | | | | |
| trifluoride | 469 | 2.13 | 33.51 | 33.49 |
| | 463 | 2.16 | 33.50 | 33.46 |
| | 458 | 2.18 | 33.46 | 33.41 |
| | 454 | 2.20 | 33.43 | 33.41 |
| | 447 | 2.24 | 33.36 | 33.37 |
| | 440 | 2.27 | 33.35 | 33.33 |
| | 434 | 2.30 | 33.26 | 33.29 |
| | | | • | • |

23

ELECTRON CAPTURE COEFFICIENTS AT VARIOUS TEMPERATURES FOR THE AROMATIC HALOGEN DERIVATIVES

| | | | | • • |
|-------------|-------|--|----------------------|---------------------------|
| COMPOUND | Τ,°Κ | 1/T x 10 ³ , °K ⁻¹ | 1n KT ^{3/2} | L.S. 1n KT ^{3/2} |
| • | 429 | 2.33 | 33.25 | 33.26 |
| | 423 | 2.36 | 33.21 | 33.22 |
| | 416 | 2.40 | 33.15 | 33.18 |
| | 408 | 2.45 | 33.09 | 33.12 |
| | 403 | 2.48 | 33.07 | 33.09 |
| | 398 | 2.51 | 44.04 | 33.05 |
| | 392 | 2.55 | 32.97 | 33.01 |
| | 386 | 2.59 | 32.93 | 32.96 |
| | 381 | 2.62 | 32.92 | 32.92 |
| | 372 | 2.69 | 32.83 | 32.85 |
| | 366 | 2.73 | 32.81 | 32.80 |
| | 362 | 2.76 | 32.78 | 32.77 |
| | 353 | 2.83 | 32.72 | 32.69 |
| | 348 | 2.87 | 32.68 | 32.64 |
| o-Bromotolu | ene | 0.00 | 00 70 | 26.02 |
| | 494 | 2.02 | 20.73 | 20.82 |
| | 492 | 2.03 | 26.73 | 26.79 |
| | . 486 | 2.06 | 26.70 | 26.70 |
| | • 479 | 2.09 | 26.61 | 26.58 |
| | | | | |

ELECTRON CAPTURE COEFFICIENTS AT VARIOUS TEMPERATURES FOR THE AROMATIC HALOGEN DERIVATIVES

| COMPOUND | Т , °К | 1/Т x 10 ³ , °К ⁻¹ | 1n KT ^{3/2} | L.S. 1n KT ^{3/2} |
|--------------------------|---------------|--|----------------------|---------------------------|
| | 471 | 2.12 | 26.51 | 26.45 |
| | 463 | 2.16 | 26.35 | 26.31 |
| | 456 | 2.19 | 26.21 | 26.18 |
| | 448 | 2.23 | 26.04 | 26.03 |
| | 441 | 2.27 | 25.91 | 25.89 |
| | 433 | 2.31 | 25.74 | 25.73 |
| | 425 | 2.35 | 25. 58 | 25.56 |
| · | 417 | 2.40 | 25.40 | 25.39 |
| | 409 | 2.44 | 25.21 | 25.21 |
| | 402 | 2.49 | 25.03 | 25.04 |
| | <u>.</u> 395 | 2.53 | 24.85 | 24.87 |
| | 389 | 2.57 | 24.69 | 24.72 |
| 3'-chloroacet phenone | 0- 507 | 1.97 | 30.08 | 30.10 |
| | 504 | 1.98 | 30.05 | 30.06 |
| | 502 | 1.99 | 30.05 | 30.05 |
| | 498 | 2.01 | 30.07 | 30.01 |
| | 494 | 2.02 | 29.99 | 29.96 |
| | 492 | 2.03 | 29.92 | 29.93 |

•

ELECTRON CAPTURE COEFFICIENTS AT VARIOUS TEMPERATURES FOR THE AROMATIC HALOGEN DERIVATIVES

| COMPOUND | Т , °К | 1/T x 10 ³ , °K ⁻¹ | ln KT ^{3/2} | L.S. 1n KT ^{3/2} |
|----------|------------------|--|----------------------|---------------------------|
| | 489 | 2.04 | 29.90 | 29.90 |
| | 485 | 2.06 | 29.88 | 29.86 |
| | 480 | 2.08 | 29.78 | 29.79 |
| | 476 | 2.10 | 29.76 | |
| | 472 | 2.12 | 29.71 | |
| • | 466 | 2.15 | 29.73 | |
| | 461 | 2.17 | 29.73 | |
| | 457 | 2.19 | 29.77 | |
| | 447 | 2.24 | 29.96 | |
| | 443 | 2.26 | 30.16 | 30.07 |
| | 439 | 2.28 | 30.24 | 30.21 |
| | 434 | 2.30 | 30.44 | 30.37 |
| | 424 | 2.36 | 30.79 | 30.75 |
| | 420 | 2.38 | 31.06 | 30.91 |
| | 416 | 2.40 | 31.19 | 31.16 |
| | 411 _. | 2.43 | 31.26 | 31.26 |
| | 407 | 2.46 | 31.39 | 31.41 |
| | 401 · | 2.49 | 31.49 | 31.66 |

ELECTRON CAPTURE COEFFICIENTS AT VARIOUS TEMPERATURES FOR THE AROMATIC HALOGEN DERIVATIVES

| COMPOUND | Т , °К | 1/T × 10 ³ , °K ⁻¹ | 1n KT ^{3/2} | L.S. 1n KT ^{3/2} |
|------------------------|---------------|--|----------------------|---------------------------|
| | 396 | 2.53 | 31.62 | 31.88 |
| | 391 | 2.56 | 31.69 | |
| | 384 | 2.60 | 31.87 | |
| | 376 | 2,66 | 31.94 | |
| | 369 | 2.71 | 32.10 | |
| | 362 | 2.76 | 32.16 | |
| | 354 | 2.82 | 32.21 | |
| | 347 | 2.88 | 32.27 | |
| • | 340 | 2.94 | 32.26 | |
| | 331 | 3.02 | 32.11 | |
| | 324 | .3.09 | 32.38 | |
| 4'-chloroac phenone | eto- 505 | 1.98 | [.] 29.99 | 29.99 |
| | 502 | 1.99 | 29.98 | 29.94 |
| | 498 | 2.01 | 29.87 | 29.88 |
| | 496 | 2.02 | 29.83 | 29.84 |
| | 492 | 2.03 | 29.80 | 29.79 |
| | 488 | 2.05 | 29.72 | 29.71 |
| | · 479 | 2.09 | 29.62 | |

ELECTRON CAPTURE COEFFICIENTS AT VARIOUS TEMPERATURES FOR THE

AROMATIC HALOGEN DERIVATIVES

| COMPOUND | T,°K | 1/T x 10 ³ , °K ⁻¹ | 1n KT ^{3/2} | L.S. 1n KT ^{3/2} |
|----------|-------|--|----------------------|---------------------------|
| | 475 | 2.11 | 29.64 | |
| | 469 | 2.13 | 29.69 | |
| | 465 | 2.15 | 29.71 | |
| | 461 | 2.17 | 29.69 | |
| | 456 | 2.19 | 29.72 | |
| | 450 | 2.22 | 29.82 | |
| | 445 | 2.25 | 29.92 | 29.58 |
| | 441 | 2.27 | 30.01 | 29.72 |
| | 434 | 2.30 | 30.08 | 29.96 |
| | 434 | 2.30 | 30.10 | 29,96 |
| | 428 | 2.34 | 30.23 | 30.17 |
| | 422 | 2.37 | 30.36 | 30.38 |
| | 417 | 2.40 | 39.49 | 30.57 |
| | 412 | 2.43 | 30.69 | 30.75 |
| | 406 | 2.46 | 30.82 | 30.99 |
| | 400 | 2.50 | 31.01 | 31.24 |
| | 394 | 2.54 | 31.24 | 31.49 |
| L | . 391 | 2.56 | 31.26 | |

ELECTRON CAPTURE COEFFICIENTS AT VARIOUS TEMPERATURES FOR THE AROMATIC HALOGEN DERIVATIVES

| | | | | · |
|--------------|-----------|--|----------------------|---------------------------|
| COMPOUND | Τ,°Κ | 1/Т x 10 ³ , °К ⁻¹ | 1n KT ^{3/2} | L.S. 1n KT ^{3/2} |
| - | 387 | 2.58 | 31.34 | |
| | 381 | 2.62 | 31.39 | |
| | 372 | 2.69 | 31.59 | |
| | 367 | 2.72 | 31.69 | |
| | 360 | 2.78 | 31.81 | |
| | 350 | 2.85 | 31.87 | |
| | 343 | 2.92 | 32.05 | |
| | 329 | 3.04 | 32.08 | |
| | 324 | 3.09 | 32.10 | |
| | 311 | 3.22 | 32.02 | |
| | 304 | 3.29 | 32.07 | |
| Chlorobenzei | ne 495 | 2.02 | 22.03 | 22.12 |
| | 491 | 2.04 | 22.03 | 22.03 |
| | 483 | 2.07 | 21.92 | 21.86 |
| | 477 | 2.10 | 21.77 | 21.72 |
| | 468 | 2.14 | 21.54 | 21.51 |
| | 459 | 2.18 . | 21.27 | 21.27 |
| • | 449 | 2.23 | 21.00 | 21.01 |
| | | | | |

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ELECTRON CAPTURE COEFFICIENTS AT VARIOUS TEMPERATURES FOR THE AROMATIC HALOGEN DERIVATIVES

| COMPOUND | Т , °К | 1/T x 10 ³ , °K ⁻¹ | ln KT ^{3/2} | L.S. 1n KT ^{3/2} |
|-------------------------|---------------|--|----------------------|---------------------------|
| | 441 | 2.26 | 20.76 | 20.79 |
| | 432 | 2.31 | 20.55 | 20.54 |
| | 421 | 2.38 | 20.24 | 20.23 |
| | 410 | 2.44 | 19.98 | |
| | 400 | 2.50 | 19.80 | |
| | 390 | 2.56 | 19.44 | |
| | 381 | 2.62 | 18.37 | |
| | 373 | 2.68 | 19.24 | - |
| | 367 | 2.72 | 19.15 | |
| l-chloronap- thalene | 504 | 1.98 | 29.43 | 29.55 |
| | 497 | 2.01 | 29.38 | 29.39 |
| | 488 | 2.05 | 29.25 | 29.20 |
| | _480 | 2,08_ | 29_25 | 29.00 |
| | 473 | 2.11 | 28.93 | 28.83 |
| | 461 | 2.17 | 28.42 | 28.52 |
| | 456 | 2.19 | 28.37 | 28.39 |
| | 446 | 2.24 | 28.,12 | 28.11 |
| | 439 | 2.28 | 27.91 | 27.92 |
| | | | | |

ELECTRON CAPTURE COEFFICIENTS AT VARIOUS TEMPERATURES FOR THE AROMATIC HALOGEN DERIVATIVES

| | | | | ·· ·· · · · · |
|-------------|---------------|--|----------------------|---------------------------|
| COMPOUND | Τ , °Κ | 1/T x 10 ³ , °K ⁻¹ | 1n KT ^{3/2} | L.S. 1n KT ^{3/2} |
| | 431 | 2.32 | 27.75 | 27.70 |
| | 423 | 2.36 | 27.40 | 27.44 |
| | 414 | 2.42 | 27.11 | 27.16 |
| | 405 | 2.47 | 26.79 | 26.86 |
| | 394 | 2.54 | 26.43 | 26.58 |
| | 381 | 2.62 | 26.08 | 26.14 |
| | 370 | 2.70 | 25.69 | 25.57 |
| - | 361 | 2.77 | 25.19 | |
| • | 332 | 3.01 | 24.88 | |
| | 332 | 3.01 | 24.84 | 24.51 |
| | 319 | 3.13 | 25.00 | 24.91 |
| | 3 08 | 3.25 | 25.32 | 25.27 |
| | 297 | 3.37 | 25.43 | 25,66 |
| <u> </u> | 293 | 3.41 | 25.58 | 25.79 |
| | 2 89 | 3.46 | 25.95 | 25.95 |
| o-Chlorotol | uene | 0.00 | 01 01 | 01 06 |
| | 494 | 2.02 | 21.31 | 21.30 |
| | 487 | 2.05 | 21.30 | 21.20 |
| • | · 482 | 2.07 | 21.08 | 21.07 |
| | | | | |

ELECTRON CAPTURE COEFFICIENTS AT VARIOUS TEMPERATURES FOR THE AROMATIC HALOGEN DERIVATIVES

| - | | | | |
|------------------------|-------|--|----------------------|---------------------------|
| COMPOUND | Τ, °K | 1/T x 10 ³ , °K ⁻¹ | ln KT ^{3/2} | L.S. 1n KT ^{3/2} |
| - | 473 | 2.11 | 20.81 | 20.83 |
| | 464 | 2.16 | 20.53 | 20.59 |
| | 453 | 2.21 | 20.32 | 20.29 |
| | 444 | 2.25 | 20.04 | 20.03 |
| | 433 | 2.31 | 19.82 | |
| • | 422 | 2.37 | 19.67 | |
| | 410 | 2.44 | 19.40 | |
| | 400 | 2.50 | 19.29 | |
| | 381 | 2.62 | 19.15 | |
| o-Dichloro- benzene | 480 | 2.08 | 28.62 | 28.50 |
| | 476 | 2.10 | 28.51 | 28.42 |
| | 476 | 2.14 | 28.31 | 28.25 |
| | 459 | 2.18 | 28.11 | 28.08 |
| | 444 | 2.25 | 27.56 | 27.76 |
| | 439 | 2.28 | 27.50 | 27.66 |
| | 428 | 2.34 | 27.36 | 27.39 |
| | 419 | 2.39 . | 27.11 | 27.17 |
| · | 410 | 2.44 | 26.93 | 26.94 |
| | | | | |

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ELECTRON CAPTURE COEFFICIENTS AT VARIOUS TEMPERATURES FOR THE AROMATIC HALOGEN DERIVATIVES

| • | | | | • • • • • |
|----------|---------------------------|--|----------------------|---------------------------|
| COMPOUND | Τ , [°] Κ | 1/Т x 10 ³ , °К ⁻¹ | 1n KT ^{3/2} | L.S. 1n KT ^{3/2} |
| | 401 | 2.49 | 26.70 | 26.71 |
| | 389 | 2.57 | 26.39 | 26.37 |
| | 372 | 2.69 | 25.99 | 25.86 |
| | 348 | 2.87 | 25.38 | |
| | 325 | 3.08 | 24.87 | |
| | 306 | 3.27 | 24.30 | |
| | | | | |

TABLE IV

ELECTRON CAPTURE COEFFICIENTS AT VARIOUS TEMPERATURES FOR SOME CARBONYL AND NITRO DERIVATIVES

| COMPOUND | Т , °К | 1/T × 10 ³ , °K ⁻¹ | 1n KT ^{3/2} | L.S. 1n KT ^{3/2} |
|-----------|---------------|--|----------------------|---------------------------|
| l'-Aceto- | | 44-149-79-1 _{9-−-} | | |
| napthone | 500 | 2.00 | 27.89 | 28.23 |
| | 492 | 2.03 | 28.01 | 28.45 |
| | 487 | 2.05 | 28.35 | 28.58 |
| | 478 | 2.09 | 28.57 | 28.85 |
| | 473 | 2.11 | 28.80 | 28.99 |
| | 459 | 2.18 | 29.50 | 29.43 |
| | 453 | 2.21 | 29.75 | 29.62 |
| - | 445 | 2.25 | 30.13 | 29.88 |
| | 432 | 2.31 | 30.78 | 30.35 |
| | 415 | 2.41 | 31.32 | 31.00 |
| | 400 | 2.50 | 31.95 | 31.59 |
| | 381 | 2.62 | 32.19 | 32.43 |
| | 369 | 2.71 | 32.26 | |
| | 362 | 2.76 | 32.22 | |
| Biacetyl | | | | |
| · | 463 | 2.16 | 29.93 | 30.18 |
| | 449 | 2.23 | 30.69 | 30,65 |
| | 431 | 2.32 | 31.45 | 31.31 |

ELECTRON CAPTURE COEFFICIENTS AT VARIOUS TEMPERATURES FOR SOME CARBONYL AND NITRO DERIVATIVES

| | | • | | • • • |
|---------------------|---------------|--|----------------------|---------------------------|
| COMPOUND | Τ , °K | 1/T × 10 ³ , °K ⁻¹ | ln KT ^{3/2} | L.S. 1n KT ^{3/2} |
| | 414 | 2.42 | 32.05 | 31.99 |
| | 398 | 2.51 | 32.42 | |
| | 386 | 2.59 | 32.66 | 32.64 |
| | 375 | 2.67 | 32.57 | 32.59 |
| | 345 | 2.90 | 32.47 | 32.47 |
| | 341 | 2.93 | 32.41 | 32.44 |
| | 320 | 3.13 | 32.36 | 32.35 |
| Diacetyl Benzene | 496 | 2.02 | 32.68 | 32.68 |
| | 495 | 2.02 | 32.59 | 32.67 |
| | 487 | 2.05 | 32.64 | 32.64 |
| | 478 | 2.09 | 32.62 | 32.61 |
| | 469 | 2.13 | 32,59 | 32,56 |
| • | 462 | 2.17 | 32,56 | 32.53 |
| | 450 | 2.22 | 32.53 | 32.47 |
| | 438 | 2.28 | 32.42 | 32.40 |
| | 435 | 2.30 | 32.43 | 32.39 |
| | 422 | 2.37 | 32.29 | 32.30 |
| | - 421 | 2.38 | 32.34 | 32.30 |

ELECTRON CAPTURE COEFFICIENTS AT VARIOUS TEMPERATURES FOR SOME CARBONYL AND NITRO DERIVATIVES

| | | • | | <i>.</i> |
|--------------|---------------|--|----------------------|---------------------------|
| COMPOUND | Т , °К | 1/T x 10 ³ , °K ⁻¹ | ln KT ^{3/2} | L.S. 1n KT ^{3/2} |
| | 406 | 2.46 | 32.16 | 32.20 |
| | 403 | 2.48 | 32.17 | 32.18 |
| | 385 | 2.60 | 32.03 | 32.05 |
| | 372 | 2.69 | 32.00 | 31.96 |
| | 364 | 2.75 | 31.85 | 31.81 |
| Nitromethane | 509 | 1.97 | 24.89 | |
| | 505 | 1.98 | 24.74 | |
| • | 500 | 2.00 | 24.61 | |
| | 494 | 2.03 | 24.37 | 24.31 |
| | 489 | 2.05 | 24.21 | 24.19 |
| | 486 | 2.06 | 24.09 | 24.12 |
| | 481 | 2.08 | 23.98 | 23.99 |
| • | 473 | 2.12 | 23.75 | 23.75 |
| | 464 | 2.16 | 23.50 | 23.50 |
| | 456 | 2.19 | 23.33 | 23.31 |
| | 448 | 2.23 | 23.10 | |
| | 436 | 2.29 | 23.48 | |
| | •440 | 2.28 | 23.34 | · · · |
| | | | | |

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ELECTRON CAPTURE COEFFICIENTS AT VARIOUS TEMPERATURES FOR SOME CARBONYL AND NITRO DERIVATIVES

| COMPOUND | Τ , [°] Κ | 1/Т x 10 ³ , °К ⁻¹ | 1n KT ^{3/2} | L.S. 1n KT ^{3/2} |
|---------------|---------------------------|--|----------------------|---------------------------|
| | 430 | 2.33 | 23.25 | |
| | 422 | 2.37 | 23.17 | |
| | 413 | 2.42 | 23.36 | |
| | 407 | 2.46 | 23.43 | |
| | 397 | 2.52 | 23.68 | |
| | 389 | 2.58 | 23.94 | |
| | 376 | 2.66 | 24.44 | |
| | 351 | 2.85 | 25.50 | |
| • | 341 | 2.94 | 25.95 | |
| Pthalaldehyde | 497 | 2.01 | 30.54 | 30.52 |
| | 491 | 2.04 | 30.40 | 30.50 |
| | 490 | 2.04 | 30.55 | 30.46 |
| | 483 | 2.07 | 30.50 | 30.38 |
| | 472 | 2.12 | 30.40 | 30.33 |
| | 464 | 2.16 | 30.29 | 30.25 |
| | 454 | 2.20 | 30.25 | 30.18 |
| | 444 | 2.25 | 30.14 | 30.13 |
| | 439 | 2.28 | 30.04 | 30.04 |

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ELECTRON CAPTURE COEFFICIENTS AT VARIOUS TEMPERATURES FOR SOME CARBONYL AND NITRO DERIVATIVES

| COMPOUND | Т, °К | 1/T x 10 ³ , °I | K ⁻¹ ln KT ^{3/2} | L.S. 1n KT ^{3/2} | |
|----------|-------|----------------------------|--------------------------------------|---------------------------|--|
| | 429 | 2.33 | 30.07 | 30.02 | |
| | 426 | 2.35 | 29.99 | 29.90 | |
| | 413 | 2.42 | 29.76 | 29.85 | |
| | 408 | 2.45 | 29.73 | 29.80 | |
| | . 390 | 2.56 | 29.66 | 29.67 | |
| | 375 | 2.67 | 29.57 | 29.52 | |
| | 366 | 2.73 | 29.45 | 29.41 | |
| · | | | | | |

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TABLE V

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ELECTRON AFFINITIES AND ACTIVATION ENERGIES FOR DISSOCIATION AND

ELECTRON ATTACHMENT

| Compound . | EA (ev) | E*(kcal) | E _l *(kcal) |
|-------------------------------|---------|----------|------------------------|
| Organic Acetates: | - | | |
| Acetic Anhydride | - | 6.56 | - |
| Benzyl Acetate | .168 | 8.94 | ** |
| Ethyl Acetate | .158 | 9.79 | ** |
| Ethyl trichloroacetate | - | 0.76 | - |
| Ethyl trifluoroacetate | .459 | 6.85 | - |
| Aromatic Halogen Derivatives: | | | |
| o-Bromofluorobenzene | - | 3.25 | - |
| m-Bromobenzotrifluoride | - | 1.05 | - |
| o-Bromotoluene | - | 6.31 | - |
| 3'-Chloroacetophenone | .583 | 4.00 | - |
| 4'-Chloroacetophenone | .566 | 6.57 | - |
| Chlorobenzene | - · | 9.25 | - |
| l'-Chloronaphthalene | .277 | 9.87 | - |
| o-Chlorotoluene | - | 10.26 | - |
| o-Dichlorobenzene | - | 7.37 | - |
| • | | | |

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ELECTRON AFFINITIES AND ACTIVATION ENERGIES FOR DISSOCIATION AND

| ELECTRON ATT | ACHMENT |
|--------------|---------|
|--------------|---------|

| Compound | EA (ev) | E*(kcal) | E _l *(kcal) |
|-------------------|---------|----------|------------------------|
| Others: | | | |
| 1'-Acetonaphthone | .580 | - | - |
| Biacetyl | .614 | - | .05 |
| Diacetyl benzene | - | - | 1 .16 |
| Pthalaldehyde | - | - | 2.17 |
| Nitromethane | - | 9.86 | |
| | | | |

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IV. GENERAL KINETIC MODEL

GENERAL KINETIC MODEL

Since a complete discussion of the reactions occurring in the electron capture cell has been reported in previous publications^{2,5}, only the electron attachment and negative ion reactions will be presented here. The reaction steps that are essential to the various thermal electron attachment mechanisms are:

$$AB + e^{-} \xrightarrow{k_{1}} AB^{-} \qquad (I) \qquad (1)$$

$$AB + e^{-} \xrightarrow{k_{12}} A \cdot + B^{-}$$
 (II) (2)

$$AB^{-} \xrightarrow{k_{2}} A^{+} B^{-} (III)$$

$$AB^{-} + B^{-} (IV)$$
(3)

$$e^{-} + P^{+} \xrightarrow{k_{N}^{\prime}} neutrals$$
 (4)

$$e^- + R \cdot \xrightarrow{k_R^+} R^- \xrightarrow{p^+}$$
 neutrals (5)

$$AB^- + P^+ \xrightarrow{k_{N1}}$$
 neutrals (6)

$$AB^{-} + R \cdot \xrightarrow{k_{R1}^{+}} AB + R^{-} \xrightarrow{p^{+}} neutrals$$
 (7)

The Roman numerals to the right of Equations 1-3 refer to the reactions which are the most important for that particular mechanism.

It should be pointed out that this kinetic model is only applicable at high pressures, as is the case in the electron capture cell. When the pressure is low, as in the electron beam experiments, the kinetic model must be altered slightly. Consider, for example, nondissociative electron attachment (Equation 1)

$$AB + e^{-} \frac{k_{1}^{\prime}}{k_{-1}^{\prime}} (AB^{-})^{*} \frac{Z(m)}{Z_{-1}(m)} AB^{-}$$
 (8)

where (AB⁻)* is a vibrationally excited negative molecular ion and Z(m) and $Z_{-1}(m)$ represent the rate of stabilization and detachment, respectively. The "effective" forward rate constant, k_1 , would therefore be

$$k_{1} = k_{1}^{\prime} \left(\frac{Z(m)}{Z(m) + k_{-1}^{\prime}} \right)$$
 (9)

and for the reverse

$$k_{-1} = Z_{-1}(m) \left(\frac{k'_{-1}}{Z(m) + k'_{-1}} \right)$$
 (10)

If the pressure is sufficiently high, $Z(m) >> k_{-1}$, then $k_1 = k_1$. The rate constant, k_{-1} , represented in Equation 1, reduces to

$$k_{-1} = \frac{Z_{-1}(m)}{Z(m)} \quad k_{-1}'$$
 (11)

at sufficiently high pressures.

The conditions under which the thermal electron attachment studies are carried out have been described in detail.^{2,5} Assuming steady state for the concentration of electrons and the negative molecular ions, and an excess concentration of positive species, P^+ , radical species, $R \cdot$, and capturing species, [AB] = a, the following expression can be derived for the response of the electron capture cell as a function of concentration²

$$\frac{b - [e^-]}{[e^-]} = K a \qquad (12)$$

where [e⁻] and b are the concentration of electrons with and without the capturing species present, respectively. K is defined as the electron capture coefficient.

The electron capture coefficient for the general case involving Equations 1-3 can be expressed in terms of the rate constants 5

$$K = \frac{1}{k_D} \left[k_{12} + \frac{k_1(k_2 + k_L)}{(k_1 + k_2 + k_L)} \right]$$
(13)

In Equation 13, $k_L = k_{N1} + k_{R1}$ and $k_D = k_N + k_R$, where k_{N1} , k_{R1} , k_N , and k_R are pseudo first order rate constants, e.g., $k_N = k'_N[P^+]$. The first term in Equation 13 corresponds to the dissociative electron attachment process represented by Equation 2. This mechanism (II) can be considered completely independent of the second term in Equation 13 or it can be derived from the second term letting k_2 become extremely large. Then k_1 would become analogous to k_{12} . Equation 2 has been included in the general kinetic model to differentiate this dissociative process from the one that involves a negative molecular ion intermediate which has a measureable lifetime (Equation 3). In this present work, only the dissociative process represented by Equation 3 was mainly considered, i.e., $k_{12} = 0$. Thus, K will have the form

$$K = \frac{1}{k_{D}} \left[\frac{k_{1}(k_{2} + k_{L})}{k_{-1} + k_{2} + k_{L}} \right]$$
(14)

Assuming Arrhenius expressions for the rate constants, the general form for the temperature dependence of Equation 14 is

$$K = \frac{T^{-3/2}A_{1}e^{-E_{1}^{*}/RT}(A_{2}e^{-E_{2}^{*}/RT} + k_{L})}{k_{D}(A_{-1}e^{-E_{-1}^{*}/RT} + A_{2}e^{-E_{2}^{*}/RT} + k_{L})}$$
(15)

The rate constants k_{L} and k_{D} have been assumed to be temperature independent. E_{1}^{*} , E_{-1}^{*} , and E_{2}^{*} are the activation energies for electron attachment, detachment, and dissociation of the negative molecular ion, respectively. A_{1} , A_{-1} , and A_{2} are the frequency factors associated with the rate constants k_{1} , k_{-1} , and k_{2} , respectively. The T^{-3/2} pre-exponential term for k_{1} in Equation 15 has been inserted to agree with the equilibrium expression for electron attachment-detachment.⁷ Consistent with this equilibrium expression, $\ln KT^{3/2}$ versus 1/T is conveniently plotted. The T^{-3/2} pre-exponential term is actually appropriate only when k_{-1} is predominant in the denominator, but for comparative purposes $\ln KT^{3/2}$ is plotted in all cases.

When certain rate constants are predominant or certain rate constants are zero (no reaction) the expression for K will acquire various forms. These various expressions for K will now be discussed in relationship to the type of temperature dependence expected for the various thermal electron attachment mechanisms.

Mechanism I: Stable Negative Molecular Ion Formation

$$k_2 = 0$$

 $K = \frac{k_1 k_L}{k_D (k_{-1} + k_L)}$ (16)
 $k_{12} = 0$

Equation 14 can acquire three forms depending upon the relative magnitude of k_{-1} , k_2 and k_L . If k_2 is zero or extremely small, then a stable negative molecular ion is formed. Equation 16 is a general expression for this mechanism. Two different temperature dependencies may be observed corresponding to

| High Temperature | | Low Temperatur | <u>e</u> |
|--|------|----------------------------|----------|
| k_1 > kL > k2 = | - 0 | $k_{L} > k_{-1} > k_{2} =$ | 0 |
| $K = \frac{k_L}{k_D} \frac{k_1}{k_{-1}}$ | (17) | $K = \frac{k_1}{k_D}$ | (18) |

According to the principle of microscopic reversibility, k_1/k_{-1} in Equation 17 can be equated to the equilibrium constant for Equation 1, which in turn can be expressed in terms of the electron affinity through the statistical thermodynamic expression for an ideal gas.⁷ The partition functions for the negative molecular ion and the neutral molecule are assumed to cancel except for the statistical weight of two. Equating k_1/k_{-1} in terms of the equilibrium constant, the expression for the electron capture coefficient in Equation 17 becomes

$$K = \frac{k_L}{k_D} \frac{A}{T^{3/2}} e^{+EA/RT}$$
(19)

Comparing Equation 15 with Equation 19 under these approximations, $A = A_1/A_{-1}$ and $EA = -(E*_1 - E*_1)$. A is a constant which can be evaluated from fundamental constants and the mass of the electron. As a result of Equation 19, ln $KT^{3/2}$ versus 1/T is plotted and the positive slope times R gives the molecular electron affinity.

Frequently k_1 is relatively temperature independent and the ln KI^{3/2} plot is characterized by a large positive slope at high temperatures and a zero or slightly negative slope at low temperatures. Several examples of this type of temperature dependence have been reported,^{2,15} in which E^{*}₁ is zero. Figure 5 shows a series of curves calculated from Equation 15 (Appendix C) with the electron affinity fixed and a variable E^{*}₁. 2,4,6-Trimethylacetophenone¹⁶ is given as an example.

Mechanism II: Dissociative Thermal Electron Attachment

As mentioned earlier, the dissociative mechanism leading directly to $A \cdot + B^{-}$ can be considered from only the first term of Equation 13 where

$$K = \frac{k_{12}}{k_D}$$
(20)

FIGURE 5

TEMPERATURE DEPENDENCE FOR MECHANISM I

E^{*} variable; EA = 10.9 kcal

 $E_1^* = (1) -1, (2) 0, (3) 1, (4) 3.1, (5) 5 kcal$

0 Represents experimental data for 2,4,6-trimethylacetophenone



If the temperature dependence of k_{12} is taken as the Arrhenius expression, a simple ln K versus l/T plot will be linear with a single negative slope. A ln KT^{3/2} versus l/T plot is also linear and several examples of this have been reported.^{5,17}

Mechanisms III and IV: Dissociative Thermal Electron Attachment Preceded

by a Negative Molecular Ion Intermediate

The fourth mechanism (IV), proposed in this study, is identical to Mechanism III except that dissociation does not occur along a dissociative potential energy curve. The activation energy for dissociation in Mechanism IV, E*, is equal to the change in internal energy for the process; ΔE . ΔE is equal to the difference in the bond dissociation energy (D_{AB}) and the electron affinity of the radical (EA_A). Since Mechanism IV does not alter the kinetic model, the expected temperature dependence will be discussed along with Mechanism III. Support for Mechanism IV will be given later.

In discussing the expected temperature dependence for Mechanism III, it is necessary to consider the magnitude of E_1^* . The activation energy, E*, for Mechanism III is generally equal to $(E_2^* + E_1^* - E_{-1}^*)$, unless E_1^* is greater than $(E_2^* + E_1^* - E_{-1}^*)$ in which case $E_1^* = E^*$, i.e., the activation energy for electron attachment is greater than the energy required for dissociation. It is necessary to consider two cases for Mechanism III: (a) $k_1 k_2 / k_{-1}$ and (b) k_1 . Mechanism IV has only one case, which is equivalent to case (a) of Mechanism III.

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(a) $k_1 k_2 / k_{-1}$ case: $E^* = (E_1^* + E_2^* - E_{-1}^*)$

The discussion for this case of Mechanism III also applies to Mechanism IV. When k_2 is not zero, Equation 14 can take on three possible expressions which could be observed in different temperature regions.

| <u>High Temperature</u> | Intermediate Temperature | Low Temperature |
|---|---|---|
| k ₋₁ > k ₂ > k _L | $k_{-1} > k_{L} > k_{2}$ | k _L > k ₋₁ > k ₂ |
| $K = \frac{1}{k_D} \left(\frac{k_1 k_2}{k_{-1}} \right)$ (| (21) $K = \frac{k_L}{k_D} \frac{k_1}{k_{-1}}$ | $K = \frac{k_1}{k_D}$ |

The intermediate and low temperature expressions for K are identical to the two regions of Mechanism I. For the intermediate temperature region, a positive slope related to the molecular electron affinity is observed in the ln $\mathrm{KT}^{3/2}$ versus l/T plot. For the low temperature region, a negative or zero slope related to the activation energy for electron attachment, E_1^* , is observed. The high temperature region is associated with a negative slope of a ln $\mathrm{KT}^{3/2}$ versus l/T plot. This negative slope is related to the activation energy for dissociation (E* = E_1^* + E_2^* - E_{-1}^*).

Mechanisms III(a) and IV can take on the appearance of Figure 6 where all three linear regions may be observed. In Figure 6, the molecular electron affinity was varied and $(E_2^{\star} - EA)$ was held constant with E_1^{\star} equal to zero. The deviations from linearity in the transition between linear regions should be noted. Use of data over a temperature span which appears to be linear could lead to serious errors in the

FIGURE 6

TEMPERATURE DEPENDENCE FOR MECHANISMS III(a) AND IV

 $(E_2^* - EA) = 4.4$ kcal; $E_1^* = 1.4$ kcal; EA = (1) 12, (2) 8, (3), 6, (4) 4, and (5) 0 kcal.

0 Represents experimental data for 3'-chloroacetophenone. Solid line through data obtained by using the parameters:

 $E_2^* = 17.8$ kcal, EA = 13.4 kcal, $E_1^* = 0$ kcal.



slopes. Figure 7 contains a series of curves varying E_2^* with EA held constant and E_1^* equal to zero. Again the range of linearity should be noted. The purpose of the family of curves in Figures 6 and 7 is to show how good the approximations are that lead to the linear regions and to show the limitations of using only the data in the "linear" regions. In some cases, the linear regions are almost nonexistent.

(b) k_1 case: $E^* = E_1^*$ $k_2 > k_{-1} > k_L$ $K = \frac{k_1}{k_D}$

For the k_1 case, a single negative slope in the ln $KT^{3/2}$ versus l/T plot would be observed. This negative slope is related to the activation energy for dissociation.

Mechanisms III and IV cannot be differentiated on a kinetic basis. However, in Mechanism IV the activation energy for dissociation is equal to the change in internal energy (ΔE). In Mechanism III, E* is greater than ΔE . Mechanisms III and IV can also be distinguished quite precisely on the basis of their potential energy curves. Mechanism IV involves only a single negative ion potential energy curve, whereas Mechanism III involves two negative ion potential energy curves leading to different negative ions upon dissociation.

A complete summary of the four thermal electron attachment mechanisms is shown in Figure 8. Representative two dimensional potential energy curves are drawn to illustrate the reaction paths. The appropriate kinetic expressions for the capture coefficient and a representation of the type of temperature dependence are also shown in
TEMPERATURE DEPENDENCE FOR MECHANISMS III(a) AND IV EA = 7.7 kcal; $E_1^* = 0$ kcal; $E_2^* = (1)$ 6.4, (2) 8.4,

(3) 10.4, (4) 14.4, (5) 18.4 kcal.



REPRESENTATIVE POTENTIAL ENERGY CURVES AND TEMPERATURE DEPENDENCE FOR THE VARIOUS THERMAL ELECTRON ATTACHMENT MECHANISMS



Figure 8 for each mechanism. The various classes of compounds assigned to the different thermal electron attachment mechanisms are also given in Figure 8 as are the molecular parameters which can be derived from each case.

As mentioned earlier, nondissociative electron attachment is characterized by a positive slope in the ln $KT^{3/2}$ versus 1/T plot. As shown in Figure 8, this type of electron attachment can also occur with compounds which undergo dissociative electron attachment according to Mechanism III(a) or IV. This is strong evidence for assuming a negative molecular ion intermediate for Mechanisms III(a) or IV. The reasons for assuming a negative molecular ion intermediate for Mechanism III(b) will be discussed later.

The potential energy curves shown in Figure 8, being two dimensional, are approximations or cross sections of the actual multi-dimensional potential energy surface that is necessary to represent a polyatomic molecule. For some polyatomics, the two dimensional representation may be satisfactory if the configurational change from the neutral molecule to the negative ion is principally a lengthening of a specific bond.

V. NEGATIVE ION POTENTIAL ENERGY FUNCTION

NEGATIVE ION POTENTIAL ENERGY FUNCTION

There are numerous empirical two dimensional potential energy functions which have been proposed for representing a neutral diatomic molecule.^{18,19} The best known of these functions is the Morse potential. This function is considered to be generally satisfactory for a three parameter function. Referenced to zero energy at infinite internuclear separation, the Morse function has the form

$$U(AB) = -2D_{AB}^{\circ} e^{-\beta(r-r_{0})} + D_{AB}^{\circ} e^{-2\beta(r-r_{0})}$$
(22)

where the first term represents the attractive term and the second term represents the repulsive term. D_{AB}° is the bond dissociation energy referenced to the minimum of the function, i.e., $D_{AB}^{\circ} = D_{AB} + 1/2 \text{ hv}_{0}$, r_{0} is the equilibrium internuclear distance, $\beta = v_{0}\sqrt{\frac{2\pi^{2}\mu}{D_{AB}^{\circ}}}$, v_{0} is the fundamental vibrational frequency for the A-B stretching mode, μ is the reduced mass, and h is Planck's constant.

A two dimensional potential energy function has been proposed to represent the negative ion potential energy curves discussed earlier (Figure 8).¹⁷ This function is the Morse function with an additional parameter, k, that modifies only the attractive term of Equation 22. The general form for the negative ion potential energy function is

$$U(AB^{-}) = -2kD_{AB}^{\circ} e^{-\beta(r-r_{0})} + D_{AB}^{\circ} e^{-2\beta(r-r_{0})} - EA_{A \text{ or } B}$$
 (23)

where EA_A or B is the electron affinity of the appropriate radical, depending upon whether A⁻ or B⁻ is the dissociative product.

The arguments supporting Equation 23 are numerous 17 and only a few will be discussed. First, the repulsive term is the same in both the neutral molecule and negative ion potential energy functions, Equations 22 and 23, respectively. Since most of the repulsive term probably arises from the core electrons and the positive nuclei, the addition of a single electron would not alter this significantly. This would be especially true for higher atomic number elements. Linnet has shown that the repulsive term for several diatomic positive ions is the same as that of the neutral molecule.²⁰ The deviation which he observed for three diatomics was only 6%. Secondly, the exponential function of internuclear displacement in the attractive and repulsive terms of Equation 23 are identical to those for the neutral molecule. This can be rationalized by considering the valence bond approximation for a localized A-B bond. The energies for the symmetric and unsymmetric wave functions, neglecting the overlap integral, are determined by the sign of the exchange integral and hence the functional dependence of the internuclear distance is the same.²¹ On this basis one might expect the same exponential function of internuclear displacement for the neutral molecule and its negative ion.

As mentioned earlier, electron beam studies yield the distribution of relative capture cross sections as a function of electron energy. The capture cross sections refer to the electron capture process occurring with no change in internuclear distance, i.e., vertical transitions. The parameter k in Equation 23 can be determined from these measured electron energies. At some A-B internuclear separation, the energy of

the vertical transition, E_v , is given by the difference between Equation 23 and the bond dissociation energy of the molecule.

$$E_{v} = -2kD_{AB}^{\circ} e^{-\beta(r-r_{o})} + D_{AB}^{\circ} e^{-2\beta(r-r_{o})} - EA_{A \text{ or } B} + D_{AB}$$
(24)

The vertical energy of maximum cross section occurs when $(r-r_0)$ equals zero and can be expressed in terms of k by the expression

$$E_{v,max} = 2(1-k)D_{AB}^{\circ} - EA_{A \text{ or } B} - 1/2 hv_0$$
 (25)

The parameter k in Equation 23 can be calculated from Equation 25 if the vertical energy of maximum cross section is known.

Assuming the Franck-Condon principle, the probability of the vertical transition occurring is a function of the energy of the transition, the energy of the electron, and the overlap integral for the two vibrational states involved (for the neutral molecule and the negative molecular ion). An approximation for the probability of the vertical transition occurring can be obtained by considering only the probability that the neutral molecule will have a particular internuclear distance²², i.e., consider only the vibrational state of the neutral molecule. For the neutral molecule, the probability of a particular internuclear distance is given by the harmonic oscillator solution.²³

$$P(r-r_{o}) = \frac{\left(\frac{\alpha}{\pi}\right)^{1/2}}{2^{n}n!} [H(\xi)]^{2} e^{-\xi^{2}} dr$$
(26)

where $H(\xi)$ is the Hermite polynomial, $\alpha = (\mu f/h^2)^{1/2}$, f = force constant, $\mu = reduced$ mass, n is the vibrational quantum number, and $\xi = \sqrt{\alpha} (r-r_0)$. Differentiating Equation 24 respect to $(r-r_0)$, one obtains $dE_v = k D_{AB}^{\circ} e^{-\beta(r-r_0)} - 2D_{AB}^{\circ} e^{-2\beta(r-r_0)} dr$ (27)

Rearranging Equation 27 to obtain dr as a function of E_{y} ,

$$dr = \frac{dE_{v}}{2 D_{AB}^{\circ} e^{-\beta(r-r_{o})} (e^{-\beta(r-r_{o})} - k)}$$
(28)

Substitution of Equation 28 into Equation 26 gives

$$P(E_{v}) = \frac{\left(\frac{\alpha}{\pi}\right)^{1/2} [H(\xi)]^{2} e^{-\xi^{2}}}{2^{n} n! 2D_{AB}^{\circ} e^{-\beta(r-r_{0})} (e^{-\beta(r-r_{0})} - k)} dE_{v}$$
(29)

Equation 29 can be used to calculate the relative capture cross sections as a function of vertical energy. $H(\xi)$ is obtained from the harmonic oscillator solution.²³

The bond dissociation energy for the negative molecular ion can be calculated from the expression 17

$$D^{\circ}_{AB^{-}} = k^2 D^{\circ}_{AB}$$
(30)

where D_{AB}° is the bond dissociation energy for the negative molecular ion referenced to the minimum of the function, i.e., $D_{AB}^{\circ} = D_{AB}^{\circ} + 1/2hv_{0,AB}^{\circ}$ where $v_{0,AB}^{\circ}$ is the stretching frequency of the A-B bond in the negative molecular ion. The equilibrium internuclear distance for the negative molecular ion can be calculated from the expression¹⁷

$$r_0^{AB^-} = \frac{-\ln k}{\beta} + r_0^{AB}$$
(31)

Equations 22, 23 and 29 have been programmed in Fortran IV so that the potential energy curves and relative cross section distributions could be calculated and compared to the experimental data for several diatomics which undergo dissociative electron attachment (Appendices D and E). Equation 23 was used to represent the negative ion curve and k was calculated from the energy for the vertical process by Equation 25. The relative cross section distributions were calculated from Equation 29 and compared to the experimental difference ion current curves, which can be used, to a first approximation, as a representation for the shape of the relative cross section distributions. Comparison of predicted and experimental relative cross section distributions have been done previously for the hydrogen halides.²⁴ The diatomics considered in this study were: H_2 , O_2 , CO, and HCI. The parameters used in constructing the potential energy curves and the distributions are given in Table VI. The experimental distributions were obtained from the references for $E_{v, max}$. Figures 9, 10, 11, and 12 show the potential energy curves and the calculated and experimental relative cross section distributions. There is good agreement between the calculated and experimental cross section distributions only for oxygen and carbon monoxide. For hydrogen and hydrogen chloride, the approximation that the neutral molecule and negative ion have the same repulsive term is probably invalid.

As mentioned earlier, the use of a two dimensional potential energy function may be satisfactory in some cases to represent a polyatomic molecule. One specific case is in the consideration of dissociative thermal electron attachment to a molecule, where the configurational change is principally the lengthening of a specific bond.

TABLE VI

PARAMETERS USED TO CALCULATE POTENTIAL ENERGY CURVES AND RELATIVE CROSS SECTION DISTRIBUTIONS FOR DIATOMICS

| Compound Negative Formed | and Ion | EA,kcal | E _{v,max} kcal | , r _o ,Å | D _{AB} ,kcal | 1/2hv ^b , kcal ⁰ , | β,Å-1 | αçÅ-2 | k ^j |
|----------------------------------|------------|------------------------|----------------------------|---------------------|-----------------------|---|-------|--------|----------------|
| H ₂ (H ⁻) | | H∙=17.29 ^d | 86.5 ^e | .742 | 103.19 | 6.29 | 1.933 | 65.40 | .497 |
| HC1(C1 ⁻) | | Cl⋅=83.16 ^f | 17.8 ^g | 1.274 | 102.13 | 4.27 | 1.861 | 86.53 | .505 |
| 0 ₂ (0 ⁻) | | 0•=33.56 ^h | 161.4 ¹ | 1.207 | 117.10 | 2.26 | 2.659 | 306.99 | .163 |
| CO(0 ⁻) | | 0·=33.56 ^h | 228.0 ¹ | 1.128 | 254 | 3.10 | 2.304 | 441.00 | .485 |

^aE.A. Moelwyn-Hughes, <u>Physical Chemistry</u>, Pergamon Press, Oxford, 1964
^bν_o from reference a.
^c force constants from reference a.
^dC. L. Pekeris, <u>Phys. Rev.</u>, <u>112</u>, 1649 (1958)
^eG. J. Schulz and R. K. Asundi, <u>Phys. Rev. Letters</u>, <u>15</u>, 946 (1965).
^fR. S. Berry and C. W. Riemann, <u>J. Chem. Phys.</u>, <u>38</u>, 1540 (1963).
^gD. C. Frost and C. A. McDowell, <u>J. Chem. Phys.</u>, <u>29</u>, 504 (1958).
^hF. M. Page, <u>Trans. Faraday Soc.</u>, <u>57</u>, 359 (1961).
ⁱD. Rapp and D. D. Briglia, <u>J. Chem. Phys.</u>, <u>43</u>, 1485 (1965).
^jCalculated from Equation 25.

POTENTIAL ENERGY CURVES AND RELATIVE CROSS SECTION DISTRIBUTION FOR DISSOCIATIVE ELECTRON ATTACHMENT TO HYDROGEN

 $\boldsymbol{\Theta}$ Represents electron beam results

- -

-- Calculated



POTENTIAL ENERGY CURVES AND RELATIVE CROSS SECTION DISTRIBUTION FOR DISSOCIATIVE ELECTRON ATTACHMENT TO HYDROGEN CHLORIDE

- 0 Represents electron beam results
- -- Calculated



POTENTIAL ENERGY CURVES AND RELATIVE CROSS SECTION DISTRIBUTION FOR DISSOCIATIVE ELECTRON ATTACHMENT

TO OXYGEN

Represents electron beam results-- Calculated



POTENTIAL ENERGY CURVES AND RELATIVE CROSS SECTION DISTRIBUTION FOR DISSOCIATIVE ELECTRON ATTACHMENT TO CARBON MONOXIDE

0 Represents electron beam results

-- Calculated



Dissociative thermal electron attachment to the aliphatic halides, Mechanism II, is assumed to arise from the electron adding to an antibonding sigma orbital. Thus the negative ion state is essentially dissociative and the lifetime of the negative molecular ion is considered to be on the order of a vibration (10^{-12} sec) . The aliphatic halides show a unique linear relationship between the activation energy, E*, and the change in internal energy, ΔE , for dissociative thermal electron attachment.¹⁷ ΔE is equal to the bond dissociation energy for the carbonhalogen bond minus the electron affinity of the dissociating halide (EA_B).

$$E^* = I + (D_{AB} - EA_B)$$
 (32)

Equation 23 has been used to explain this unique relationship.¹⁷ The activation energy is interpreted as the intersection of the negative ion potential energy curve with that of the neutral molecule about the zero-point level of the neutral molecule. Solving Equation 22 and 23 for the intersection, one can obtain an expression which can be readily equated to Equation 32.¹⁷ From this expression, k can be written in terms of I.

$$k_{\rm B} = \frac{1}{2} - \frac{I - \frac{EA_{\rm B}}{(D^{\circ}_{\rm AB})^{1/2}} [D^{\circ}_{\rm AB} - (EA_{\rm B} - I)]^{1/2}}{2(EA_{\rm B} - I)}$$
(33)

I has been determined experimentally to be 15.3 kcal.¹⁷ k_B represents k in Equation 23. Rewriting Equation 23, the expression for the dissociative negative ion potential energy curve for the aliphatic halides is

$$U(AB^{-}) = -2k_{B}D_{AB}^{\circ} e^{-\beta(r-r_{0})} + D_{AB}^{\circ} e^{-2\beta(r-r_{0})} - EA_{B}$$
 (34)

The reason for rewriting Equation 23 in this form will be seen later.

Equation 23 can also be applied to Mechanism IV. This case is the same as that for Mechanism II since only one negative ion potential energy curve is involved; however, it is not a dissociative curve but has an appreciable minimum. In Mechanism IV, the activation energy for dissociation is equal to the change in internal energy for the process and is not interpreted to be the intersection of the neutral and negative ion potential energy curves above the zero-point level of the neutral molecule. If electron beam data is available, k can be calculated from Equation 25. A relationship between k and the molecular electron affinity can also be developed. The expression for the molecular electron affinity in terms of the potential energy curves for the neutral molecule and the negative molecular ion is

$$EA_{AB} = -D_{AB} + D_{AB} - + EA_A$$
(35)

Substituting $E^* = D_{AB} - EA_A$ and the expression for D_{AB}° - from Equation 30, the expression for k becomes

$$k^{2} = \frac{EA_{AB} + E^{*} + 1/2h_{\nu_{0},AB}}{D_{AB}^{\circ}}$$
(36)

Figure 13 shows a representative set of potential energy curves for Mechanism IV calculated from Equations 22 and 23. The E^{*}₁ in Figure 13 is

POTENTIAL ENERGY CURVES FOR MECHANISM IV



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the activation energy for dissociation discussed in Mechanism III(b); however, the activation energy for dissociation in Mechanism IV is equal to $(E_2^* + E_1^* - E_{-1}^*)$.

Equation 23 can also be applied to Mechanism III although two negative ion potential energy curves leading to different products upon dissociation are involved (Figure 8). Since the aromatic halogen derivatives are the only compounds that have been classified as Mechanism III, this discussion will be specifically for them.

Mechanism III involves a dissociative negative ion curve leading to the products of an aromatic radical and a halogen negative ion. This dissociative negative ion curve is assumed to arise from the electron adding to an antibonding sigma orbital. This was the same interpretation used in Mechanism II for the aliphatic halides. On this basis, Equation 34 can be used to represent the dissociative negative ion potential energy curve for Mechanism III, with k_B being calculated from Equation 33.

The second negative ion potential energy curve for Mechanism III is assumed to arise from the electron adding to a pi orbital. The dissociation products for this negative ion curve are a halogen atom and an aromatic negative ion. Rewriting Equation 23 in a slightly different form to represent this second negative ion potential energy curve, one gets

 $U(AB^{-}) = -2k_{A} D_{AB}^{\circ} e^{-\beta(r-r_{o})} + D_{AB}^{\circ} e^{-2\beta(r-r_{o})} - EA_{A}$ (37) where EA_A is the electron affinity of the aromatic radical.

Since the antibonding sigma orbitals are generally higher in energy than the pi orbitals, the dissociative negative ion potential energy curve, Equation 34, will be the higher energy negative ion curve near the equilibrium internuclear separation of the neutral molecule. This is in agreement with the experimentally observed results that, other factors being the same, the activation energy for dissociative electron attachment is lower for Mechanism III than for Mechanism II.^{5,17} Except for iodobenzene,⁵ the aromatic halogen derivatives do not fit the relationship expressed for the aliphatic halides in Equation 32. If the dissociative negative ion curve was the lower of the two negative ion curves, then the aromatic halogen derivatives might be expected to follow Equation 32.

Considering Equation 37 to represent the lower of the two negative ion potential energy curves, k_A can be calculated from the lowest vertical transition observed by electron beam studies by Equation 25. If the molecular electron affinity is known, k_A can also be calculated from the expression

$$k^{2} = \frac{EA_{AB} + D_{AB}^{\circ} - EA_{A} - 1/2 h(v_{0,AB} - v_{0,AB})}{D_{AB}^{\circ}}$$
(38)

Equations 37 and 38 apply for both cases of Mechanism III.

The activation energy for Mechanism III(a) is interpreted as the intersection of the two negative ion potential energy curves above the zero-point energy level of the neutral molecule. The expression for the

activation energy can be derived by solving for this intersection. The resulting expression is

$$E^{*} = \frac{-k_{A}(EA_{A} - EA_{B})}{(k_{B} - k_{A})} + \frac{(EA_{A} - EA_{B})^{2}}{4D_{AB}^{\circ}(k_{A} - k_{B})^{2}} - EA_{A} + D_{AB}$$
(39)

A representative set of potential energy curves for Mechanism III(a) is shown in Figure 14. Equations 22, 34 and 37 were used to calculate the potential energy curves.

For Mechanism III(b), the activation energy is interpreted as the intersection of the negative ion curve, Equation 37, and the potential energy curve for the neutral molecule above the zero-point energy level of the neutral molecule. Solving for this intersection, one obtains

$$E^{*} = \frac{EA_{A}}{(k_{A} - 1)} + \frac{(EA_{A})^{2}}{4D_{AB}^{\circ}(k_{A} - 1)^{2}} + D_{AB}$$
(40)

A representative set of potential energy curves calculated from Equations 22, 34, and 37 are shown in Figure 15 for Mechanism III(b).

The activation energies calculated in Equations 39 and 40 are defined in relationship to the crossing points of the potential energy curves. The actual (measured) activation energy is an average quantity and is larger than that calculated from either Equation 39 or 40. If one assumes the Boltzmann distribution to represent the distribution of activation energies near the crossing point of the potential energy curves and the harmonic oscillator



POTENTIAL ENERGY CURVES FOR MECHANISM III(a)







distribution function for the internuclear separation of either the neutral molecule or negative molecular ion, the actual activation energy, \overline{E}^* , can be approximated by

$$\overline{E}^{*} = \frac{\int E^{*}[(\frac{\alpha}{\pi}) / 2^{n}n! [H(\xi)]^{2} e^{-\xi^{2}} e^{-E^{*}/RT} dE^{*}]}{\int \frac{(\frac{\alpha}{\pi})^{1/2}}{2^{n}n!} [H(\xi)]^{2} e^{-\xi^{2}} e^{-E^{*}/RT} dE^{*}}$$
(41)

 \overline{E}^* can be calculated only when the vibrational spacing of the neutral molecule or negative molecular ion is known.

Consideration should be given to the "non-crossing" rule²⁵ in regards to the two negative ion potential energy curves of Mechanism III. If the two negative ion curves are of the same symmetry, they will not cross as shown in Figures 14 and 15 but will split. This fact will not be taken in to account since the symmetries of the two curves are not known. If the "non-crossing" rule is operative, Figure 14 would now have the appearance shown in Figure 16. If the two negative ion curves do not cross, the relative cross section distributions calculated from Equation 29 would not be affected since in most cases the energy difference between the two curves is quite large near the equilibrium internuclear distance for the neutral molecule. The splitting of the two curves at this point would be negligible. The calculation of the activation energy for Mechanism III(b) would not be affected for the same reason. However, the calculation of the activation energy for Mechanism III(a) would be affected since the energy difference between

POTENTIAL ENERGY CURVES FOR MECHANISM III(a) WITH

"NON-CROSSING" RULE APPLIED



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the two negative ion curves is quite small near their crossing point and the splitting would be large. This would lead to activation energies calculated from Equation 39 being larger than they would be if the splitting of the two negative ion curves was taken into account. The effect on the activation energy can be seen by comparing Figure 14 with Figure 16.

VI. DISCUSSION

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DISCUSSION -

A. Thermal Electron Attachment to the Organic Acetates - Mechanism IV

The fourth mechanism for thermal electron attachment to molecules is important since the activation energy (E*) for dissociative electron attachment is a direct measure of the difference in bond dissociation energy (D_{AB}) and the electron affinity of the radical If the compound being studied is sufficiently volatile, the $(EA_{\Delta}).$ activation energy can generally be determined with a standard error of $\pm 0.2 - 0.4$ kcal/mole. Therefore, if one knows the bond dissociation energy rather precisely, thermal electron attachment studies utilizing the pulse sampling technique would permit a precise determination of the electron affinity of the radical. On the other hand, if the electron affinity of the radical was previously known, the bond dissociation energy could be determined. In another paper¹⁷ a technique for the determination of bond dissociation energies of some aliphatic halides is presented. However, that technique involves an empirical linear relationship between E* and (D_{AB} - EA_{B}), where B refers to the halide, which is necessarily an indirect method.

Of the existing experimental methods for the determination of the electron affinity for a radical, probably the two most important are the electron impact and the magnetron methods. The magnetron method was first developed by Sutton and Mayer²⁶ and refined more recently by Page²⁷. The precision of the electron impact method is generally on the order of $\pm 2 - 5$ kcal/mole. The magnetron method is generally more precise than the electron impact method; however, interpretation of the results is often complicated by a complex mechanism which must be established and hence is always subject to error. If the correct mechanism is selected, then the magnetron method can give excellent results. The technique proposed in this study should yield results which are both simple to interpret and have the desired precision.

Three compounds leading to the electron affinity of the acetate radical were investigated by thermal electron attachment utilizing the pulse sampling technique. This radical was selected since a rather reliable estimate of the electron affinity has been established²⁸.

The compounds acetic anhydride, benzyl acetate, and ethyl acetate were run in this study and the temperature dependence results are shown in Figure 1. The data for acetic anhydride at higher temperatures define a linear ln $KT^{3/2}$ versus l/T plot with a negative slope corresponding to the dissociative mechanism. At lower temperatures, there is an upward trend of the data away from the negative slope. This deviation in slope will be discussed more thoroughly later. The data for benzyl and ethyl acetates likewise show a negative slope at higher temperatures; however, the departure at lower temperatures leads to a positive slope in both cases. This is in agreement with the temperature dependence expected for Mechanism IV.

Since only the acetate radical has a sufficiently large electron affinity relative to the bond dissociation energy in these compounds,

only a single negative ion potnetial energy curve is expected in the vicinity of the ground state of the neutral molecule. This electron attachment phenomena involving a single negative ion potential energy curve has been classified as Mechanism IV.

The two regions of temperature dependence shown in Figure 1 are important in distinguishing this mechanism from Mechanism II. In Mechanism II the activation energy for electron attachment, E_1^* , is greater than $\Delta E = (D_{AB} - EA_B)$ and dissociation should occur almost immediately upon electron attachment to the vibrationally active molecule. For Mechanism II only a single negative slope should be observed for the temperature dependence. In Mechanism IV, $E_1^* < \Delta E$ and the intermediate negative molecular ion should form prior to dissociation.

As stated previously, according to Mechanism IV, $E^* = (D_{AB} - EA_A)$. Hence with an experimental E^* and knowledge of the bond dissociation energy, the electron affinity of the acetate radical can be calculated. These results are shown in Table VII. The -(negative slope x R) was determined by a least-squares adjustment^{2,5} for acetic anhydride and benzyl acetate, and E^* corresponds to the activation energy for no pre-exponential temperature term⁵, i.e., the energy of activation from a ln K versus 1/T graph. The data for ethyl acetate does not define the negative slope well and the line in Figure 1 was drawn with an assumed intercept of 32. In general, the intercepts for the dissociative mechanism fall in the region of 32 - 36. A

| | TAB | LE | V1 | Ι |
|--|-----|----|----|---|
|--|-----|----|----|---|

EA CH3CO2 EACH3CO2 Compound Intercept -(Negative Molecular E* Ε* D_{AB},298° 298°, slope x R), EA, ev 298° ev 0° ev kca1 kca] kcal kcal (1) (2) (3) (4) (5) (6) (7)(8) (9) 6.93±.12 Acetic $34.86 \pm .14$ 7.82 6.56 _ _ _ _ Anhydride (81.6±3.6)^e 3.13±.16 3.10±.16 0.168±.004 8.94 9.38±.44 Benzyl $33.76 \pm .49$ 10.27 Acetate 32.00±2.00 11.25 Ethy1 Acetate weighted average $= 3.36 \pm .16$

EVALUATION OF ELECTRON AFFINITY OF ACETATE RADICAL

** Error estimated

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FOOTNOTES FOR TABLE VII

- ^aBond diss. E. in parentheses were calculated by: D_{AB} = ΔH^o_f(A,g) + ΔH^o_f(B,g) ΔH^o_f(AB,g). ΔH^o_f of all radicals except acetyl were obtained from C. T. Mortimer, "Reaction Heats and Bond Strengths," Addison-Wesley Pub. Co., Reading, Massachusetts, 1962, Chap. 7; ΔH^o_f Acetyl Radical from R. I. Reed and J. C. D. Brand, Trans. Faraday. Soc., <u>54</u>, 478-82 (1958).
- ^bΔH°(AB,g) from H_{comb}, H_{vap} in "Handbook of Chemistry and Physics," Chemical Rubber Publishing Co., Cieveland, Ohio, 1962.
- ^CΔH^o₄(AB,g) from H_{comb} from reference b and H_{vap} from John Perry, ed., "Chemical Engineer's Handbook," McGraw-Hill Book Co., New York, 1963, Sec. 3.
- ^d∆H^o_f(AB,g) from reference.c.
- ^eΔH_f(AB,g) from H_{RX}, Mario Fiorani, Giorgio Barbieri, and Luigi Riccoboni, Ricerca Sci., <u>28</u>, 11-30 (1958).
 H_{vap} from V. V. Serpinski, S. A. Vortkevich, N. Yu. Lyuboshits, Zhur. Fiz. Khim., <u>28</u>, 810-13 (54).

 $f_{\Delta H_{f}^{e}(AB,g)}$ from reference c.

^gD_{AB} calculated from appearance potential and ionization potential. IP from F. A. Elder, C. Giese, M. G. Inghram, and B. Steiner, ASTM Committee E-14 on Mass Spectrometry, 9th Annual Meeting, Chicago, Illinois, June 4-9, 1961. AP from Reference

relatively large error in the slope has been assigned to the E* for ethyl acetate which is to account for the error in the assumed intercept. The correction of E* to 298°K is given in column six and was made with $\Delta C_v = 3/2$ R. This ΔC_v was derived assuming ideal gas behavior, complete activation of the rotational modes, cancellation of the vibrational contributions of the molecule with those in the radical and negative ion products and neglect of the vibrational mode leading to dissociation. The bond dissociation energies are given in column seven of Table VII. In some cases, values from more than one source are given when it is uncertain which value is to be preferred. The difference of columns six and seven leads to the electron affinity of the acetate radical at 298°K and is given in column eight. Finally, the electron affinities corrected to 0°K are given in column nine using $\Delta C_v = 3/2$ R for the difference in translational and rotational contributions to the heat capacities. One should note that the electron affinity for the acetate radical obtained from the various compounds are consistent within the experimental error. Furthermore, the weighted average of these values is $3.36 \pm .16$ ev which aggrees favorably with the electron impact value of 3.3 ev obtained by Tsuda and Hamill.²⁸ This agreement clearly shows that E* is equal to the change in internal energy for the process, $(D_{AB} - EA_A)$, and gives strong support for the proposed mechanism for dissociative electron attachment (IV).

The molecular electron affinity estimates for benzyl acetate and ethyl acetate are also given in column four of Table VII. They were obtained from the limited amount of data in the region suggestive of a positive slope. A least squares adjustment using the common intercept discussed earlier was carried out. The molecular electron affinity values themselves are not of any specific significance in regards to the proposed mechanism (IV). However, the fact that the data definitely suggests the formation of a stable negative ion at lower temperatures adds further support to Mechanism IV. With the data for acetic anhydride it is difficult to establish a reliable estimate of the molecular electron affinity.

The data for acetic anhydride in Figure 1 does not appear to agree with Mechanism IV since a definite positive slope does not exist. However, upon closer examination of Equation 15, the data are consistent with the mechanism. In the previous discussion concerning the temperature dependence for Mechanism IV, three approximations were made which resulted in distinct linear regions in the ln KT^{3/2} versus 1/T plot. However, under certain conditions these regions are not so distinct. A family of curves was generated using Equation 15 in conjunction with the empirical negative ion potnetial energy function, Equation 23. The electron affinity of the acetate radical was held constant and k varied to give molecular electron affinities ranging from 0 - 12 kcal. The activation energies E_1^* , E_{-1}^* , and E_2^* (Figure 13) for each of these molecular electron affinities were then evaluated from the negative molecular ion potential energy curve relative to the neutral molecule. The family of curves is shown in Figure 17. It should be noted that three distinct linear regions are observed only when the molecular electron affinity is large and E_1^* is small. However, as k decreases and the molecular electron affinity correspondingly decreases, E^{*} becomes larger and the region of the positive slope becomes smaller. Figure 18 shows the potential energy curves corresponding to several ln $\mathrm{KT}^{3/2}$ versus l/T plots in Figure 17. Note the change in E_1^* as the molecular electron affinity, and thus k, increases. Furthermore, the positive slope cannot always be used to calculate the molecular electron affinity, e.g., EA = 6 kcal in Figure 17 for curve 4. Eventually at lower k values, Et exceeds Et and the process converts from Mechanism IV to Mechanism II. For the curves intermediate to these mechanisms in Figure 17, the intercept is lower than that drawn for curves 1 - 3 since k_{-1} and k_2 both contribute to the denominator in Equation 14. Again it should be emphasized that Equation 15 should be used to rigorously represent the electron capture coefficient as a function of temperature. The approximate expressions which can be derived from this general equation may be useful in evaluating the molecular parameters; however, caution should be exercised. The approximate expressions are useful for a qualitative assignment of the mechanism. The curve for EA = 4.4 kcal in Figure 17 fits the experimental data for acetic

| FIGURE 1 | 7 |
|----------|---|
|----------|---|

TEMPERATURE DEPENDENCE FOR MECHANISM IV

| Plot Number | E *, kcal | EA, kcal | k |
|-------------|------------------|----------|-----|
|] | .43 | 12 | .47 |
| 2 | 1.54 | 10 | .44 |
| 3 | 2.87 | 8 | .42 |
| 4 | 4.40 | 6 | .39 |
| 5 | 5.76 | 4.4 | .36 |
| 6 | 6.13 | 4 | .35 |
| 7 | 7.07 | 3 | .34 |
| · 8 | 8.06 | 2 | .32 |
| 9 | 9.12 | · 1 | .30 |
| 10 | 10.66 | . 0 | .28 |

0 Represents experimental data for acetic anhydride displaced down the ln ${\rm KT}^{3/2}$ scale by .15 units.

E^{*} = 6.56 kcal



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FIGURE 18

POTENTIAL ENERGY CURVES FOR MECHANISM IV WITH k VARIED

1,3,6, and 10 corresponds to the ln $\mathrm{KT}^{3/2}$ versus 1/T graphs of the same number in Figure 17.

(1) k = .47, Mechanism IV

(3) k = .42, Mechanism IV

(6) k = .35, Mechanism IV

(10) k = .28, Mechanism II



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anhydride quite well if it was displaced along the ln $\mathrm{KT}^{3/2}$ axis by .15 units. This could be accomplished by the adjustmnet of A in Equation 15. In Figure 17, the experimental data for acetic anhydride were displaced .15 units along the ln $\mathrm{KT}^{3/2}$ axis instead.

Two substituted acetates were also investigated: ethyl trichloroacetate and ethyl trifluoroacetate. The activation energies for dissociation were determined to be .76 kcal and 6.85 kcal, respectively. For ethyl trichloroacetate, the dissociative process is probably by Mechanism II where the bond that is broken is a carbon-chlorine bond. The bond dissociation energies for carbon tetrachloride and chloroform are 67.9 \pm 3 ²⁹ and 71.4 \pm 2 ²⁹ kcal, respectively. One would expect the carbon-chlorine bond in ethyl trichloroacetate to be near these values. The electron affinities for the chlorine atom and the acetate radical are on the same order of magnitude. Since the C-O bond in ethyl trichloroacetate probably has a bond dissociation energy nearly the same value it has in ethyl acetate, 87.6 kcal, the bond that would be broken in the electron attachment process would be the carbon-chlorine bond. Ethyl trichloroacetate appears to fit Equation 32 for the aliphatic halides and has been assigned to Mechanism II.

The data for ethyl trifluoroacetate in Figure 1 shows two temperature dependent regions, thus establishing the formation of a negative molecular ion intermediate prior to dissociation. On this basis, ethyl trifluoroacetate could be assigned to Mechanism III-a or IV. The electron affinities of the fluorine atom and the acetate radical are on the same order of magnitude. Since the bond dissociation energies for the carbon-fluorine bond in carbon tetrafluoride and fluoroform are 121 ± 4 ²⁹ and 108 ± 5 ²⁹ kca., respectively, compared to the carbon-oxygen bond in ethyl acetate of 87.6 kcal, Mechanism III-a can be eliminated. This assigns ethyl trifluoroacetate to Mechanism IV. Assuming the bond dissociation energy for ($CF_3CO-C_2H_5$) to be the same as ($CH_3CO-C_2H_5$), 87.6 kcal, the electron affinity for the trifluoroacetate radical would be 3.50 ± .13 ev.

B. Thermal Electron Attachment to the Aromatic Halogen Derivatives

The aromatic halogen derivatives have previously been assumed to follow dissociative electron attachment according to Mechanism III-a^{5,12}. Assignment to Mechanism III-a was based primarily on the fact that the activation energies for dissociative electron attachment for the aromatic halogen derivatives were lower than that for the aliphatic halides (Mechanism II) for the same change in internal energy, $(D_{AB}-EA_B)$. The results of this study showed that only the chloro derivatives followed Mechanism III-a and that the bromo derivatives followed Mechanism III-a and that the bromo derivatives followed Mechanism III-b. This will be discussed in more detail later. The bromo derivatives have been classified under a special case of III instead of Mechanism II for three reasons: (1) the activation energies for dissociative electron attachment to the bromo aromatic derivatives were lower than those for the aliphatic bromides for the same change in internal energy,¹⁷ (2) two negative ion potential energy curves are involved as in the case of Mechanism III-a, and (3) an intermediate negative molecular ion forming prior to dissociation has been confirmed for both bromo and chloro aromatic derivatives by the electron beam experiment discussed earlier. However, the expected temperature dependence for Mechanism III-b is the same as that for Mechanism II (Figure 8).

The experimental data for 3'- and 4'-chloroacetophenone is Figure 2 show a unique temperature dependence involving three different phenomena. This has been discussed earlier in relation to the temperature dependence expected for Mechanism III-a. The existence of the positive slope at intermediate temperatures definitely establishes the thermal electron attachment mechanism as III-a. These two compounds are the only ones that have been investigated which have shown all three temperature dependent regions discussed earlier. These regions correspond to K acquiring the expressions given in Equations 17, 18, and 21.

Since the experimental data for 3'- and 4'-chloroacetophenone show either very short or non-existent linear regions, the leastsquares adjustment may not be very reliable. Equation 15 was programmed in Fortran IV and ln $\mathrm{KT}^{3/2}$ values were calculated to fit the experimental data. The calculated curves are shown by the solid lines through the experimental data in Figure 2. The parameters used in calculating these curves are compared to the leastsquares parameters in Table VIII.

TABLE VIII

LEAST SQUARES PARAMETERS VERSUS ADJUSTED PARAMETERS FOR

| 3'- AND 4'- CHL | OROACEIOPHENONE |
|-----------------|-----------------|
|-----------------|-----------------|

| Compound | Adjusted ^a Intercept | Least- Squares Intercept | Adjusted ^a EA,kcal | Least- Squares EA,kcal | Adjusted ^a E*,kcal | Least- Squares E*,kcal |
|--------------------------------|------------------------------------|--------------------------------|----------------------------------|------------------------------|----------------------------------|------------------------------|
| 3'-Chloro- | - 35.80 | 35.46±.61 | | | 4.60 | 4.00±.60 |
| aceto- phenone ^C | 14.30 | 14.79±.11 ^b | 13.50 | 13.45±.13 ^b | - | - |
| 4'-Chloro- | - | | | | | |
| phenone ^d | 36.00 | 37.94±.66 | - | - | 4.80 | 6.57±.66 |
| | 14.30 | 14.80±.11 ^b | 13.00 | 13.07±.12 ^b | - | - |

^aAdjusted by Equation 15.

^bCommon intercept least squares used.

^CEquation 15 used with intercept and slope of 32.28 and 0.0, respectively, for low temperature region shown in Figure 2.

^dEquation 15 used with intercept and slope of 32.05 and 0.0, respectively, for low temperature region shown in Figure 2.

The experimental data for 1-chloronapthalene in Figure 3 show two slopes corresponding to the dissociative, Equation 21, and nondissociative, Equation 17, regions discussed earlier for Mechanism III-a. Although the low temperature region, Equation 18, was not observed, the positive slope in Figure 3 definitely establishes the mechanism as III-a.

The experimental data for chlorobenzene and o-chlorotoluene in Figure 2 show a change in slope at low temperatures; however, this change in slope does not arise from a limiting case of Equation 14. This type of behavior has also been reported for several aliphatic halides¹⁷ and always occurs when ln $KT^{3/2}$ is 18 - 19. Several possible explanations for this behavior have been reported.¹⁷

For all the other halogen derivatives studied, only a negative slope in the ln $KT^{3/2}$ versus 1/T plots was observed. The classification of these compounds to either Mechanism III-a or b will be discussed later. When a positive slope in the ln $KT^{3/2}$ versus 1/T plot is not observed, Mechanism III-a and III-b cannot be differentiated by thermal electron attachment studies alone.

C. Correlation of Thermal Electron Attachment and Electron Beam Studies

of Dissociative Electron Attachment to the Aromatic Halogen Derivatives

Representative potential energy curves and the various energy relationships for dissociative electron attachment by Mechanism III are shown in Figures 14 and 15. If the dissociation process is assumed to affect only the carbon-halogen bond, the potential energy

curves can be represented in two dimensions by Equations 22, 34, and 37, where B now refers to the halogen atom and A refers to the remaining aromatic portion of the molecule. This will allow some quantitative comparison to be made between electron beam and thermal electron attachment studies. This two dimensional approximation is not strictly correct since the benzene negative molecular ion is distorted from its neutral configuration³⁰ and this distortion would also be expected to occur in the substituted benzenes. The amplitude of this distortion has been determined to be only 0.25 $Å^{30}$. The significance of the two negative ion potential energy curves has been discussed earlier. The necessary equations to calculate the potential energy curves, the relative cross section distributions, and the activation energies were also given earlier.

When the vertical energies of maximum cross section measured by electron beam studies were not known, k_A was calculated from the molecular electron affinities by Equation 38. For all cases, k_B for the dissociative negative ion curve, Equation 34, was calculated from Equation 33. The relative capture cross section distributions were calculated from Equation 29. The activation energies for dissociative thermal electron attachment were calculated from Equation 39 or 40, depending on whether the dissociative process follows Mechanism III-a or III-b. Table IX given the parameters used in making the above calculations. All the bond dissociation energies refer to a carbon-halogen bond. EA_B refers to the electron affinity

| TABLE | ΙX |
|-------|-------|
| | ± / ` |

PARAMETERS USED TO CALCULATE POTENTIAL ENERGY CURVES AND RELATIVE CROSS SECTION DISTRIBUTIONS

| Compound | D _{AB} kcal/ mole | D _{AB} g kcal/ mole | β, Å-1 | r _o , ^a A | EA _A kcal/ mole | EA _B , ^b kcal/ mole | κ _Α | . k _B | α, h Å-2 |
|----------------------------|----------------------------------|------------------------------------|-----------|------------------------------------|----------------------------------|---|----------------|------------------|-------------|
| Chlorobenzene | 87. ^C | 88. | 1.455 | 1.70 | 50.9d | 83.16 | .587 | .097 | 214. |
| o-Dichloroben- zene | 87. ^e | 88. | 1.455 | 1.70 | 55.0 ^e | 83.16 | .630 | .097 | 214. |
| o-Chlorotoluene | 87. ^e | 88. | 1.455 | 1.70 | 50.9e | 83.16 | .555 | .097 | 214. |
| 3'-Chloroaceto- phenone | 87. ^e | 88. | 1.455 | 1.70 | 60.0 ^e | 83.16 | .678 | .097 | 214. |
| 4'-Chloroaceto- phenone | 87. ^e | 88. | 1.455 | 1.70 | 60.0 ^e | 83.16 | .674 | .097 | 214. |
| l-Chloronaphtha- lene | 87. ^e | 88. | 1.455 | 1.70 | 45. e | 83.16 | .742 | .097 | 214. |
| Bromobenzene | 70.9 ^f | 71.8 | 1.486 | 1.86 | 50.9 ^d | 77.55 | .497 | .150 | 211. |
| o-Bromotoluene | 70.9 ^e | 71.8 | 1.486 | 1.86 | 50.9 ^e | 77.55 | .479 | .150 | 211. |
| l-Bromonaphtha- lene | 70.9 ^f | 71.8 | 1.486 | 1.86 | 45. e | 77.55 | .645 | .150 | 211. |
| Iodobenzene | 57. ^f | 57.7 | 1.426 | 2.05 | 50.9 ^d | 70.63 | | .232 | 194. |

FOR THE AROMATIC HALOGEN DERIVATIVES

FOOTNOTES TO TABLE IX

^a<u>Tables of Interatomic Distances and Configuration in Molecules and Ions</u>, Special Publication 18, The Chemical Society, London, 1965.

^DR. S. Berry and C. W. Riesmann, J. Chem. Phys., <u>38</u>, 1540 (1963).

^CS. W. Benson, <u>Foundations of Chemical Kinetics</u>, McGraw-Hill, New York, 1960.

^dA. F. Gaines and F. M. Page, Trans. Faraday Soc., <u>59</u>, 1266 (1963).

^eEstimated (see text).

^fM. Szwarc and D. Williams, J. Chem. Phys., <u>20</u>, 1170 (1952).

^gStretching frequencies for C-Cl, C-Br, and C-I were used as 700, 600, 500 cm⁻¹, respectively.

^hForce constants for C-Br, C-Cl, and C-I from E. A. Molelywn-Hughes, <u>Physical Chemistry</u>, Pergamon Press, Oxford, 1964. of the halogen atom and EA_A refers to the electron affinity of the aromatic radical. Table X compares the activation energies calculated from Equation 39 or 40 with the experimental values. Table X also includes calculated molecular electron affinities and vertical energies of maximum cross section. \vec{E}^* could only be calculated for Mechanism III-b.

Since the two cases for Mechanism III could not be distinguished unless a positive slope was observed in the ln $KT^{3/2}$ versus 1/Tplot, classification of the aromatic halogen derivatives was made by use of the calculated potential energy curves when necessary.

CHLOROBENZENE: The vertical energy of maximum cross section for dissociative electron attachment to chlorobenzene is .86 ev.¹¹ k_A and k_B were calculated to be .587 and .097, respectively. The potential energy curves are shown in Figure 19. From these potential energy curves, chlorobenzene has been assigned to Mechanism III-a. The activation energy calculated from Equation 39 was 9.76 kcal which compares favorably to the experimental value of 9.25 ± .28 kcal. \overline{E}^* was not calculated from equation 41 for chlorobenzene since the vibrational spacing for the negative molecular ion was not known. Assuming $v_{0, AB}^{-}$ to be zero, the molecular electron affinity calculated from Equation 38 was -6.83 kcal.

The distribution of relative cross sections as a function of electron energy calculated from Equation 29 is compared with the experimental distribution in Figure 19. The fit of the two distributions is quite

TABLE X

CALCULATED ACTIVATION ENERGIES, VERTICAL ELECTRON ENERGIES, AND MOLECULAR ELECTRON AFFINITIES[†]

| COMPOUND . | E* ^C kcal/mole | E _{v,max} kcal/mole | EA _{AB} , kcal/mole |
|---------------------|------------------------------|---|---------------------------------|
| Chlorobenzene | 9.76 (9.25±.6 | 6) **(19.82) ^b | -6.83 |
| o-Chlorotoluene | 11.10 (10.26±1 | .19) **(25.36) ^b | -10.00 |
| o-Dichlorobenzene | 7.46 (6.91±.2 | 9) ^a **(8.30) ^b | 2.16 |
| 3'-Chloroacetopheno | one 5.84 (4.60) | | **(13.45±.13) |
| 4'-Chloroacetophenc | one 5.52 (4.80) | | **(13.07±.12) |
| 1-Chloronapthalene | 8.04 (9.87±. | 29) ^a | **(6.3 9±.08) |
| Bromobenzene | 5.53 (5.91±. | 33) ^a **(19.36) ^b | - 2.27 |
| o-Bromotoluene | 6.44 (6.31±. | 34) **(21.90) ^b | - 3.49 |
| l-Bromonaphthalene | .10 (1.74±. | 43) ^a 5.00 | |
| Iodobenzene | 1.20 (1.55±. | 32) ^a 17.27 | |

[†]Experimental values are in parentheses.

^aR. Tung, M.S. Thesis, University of Houston, 1965.

- ^bL. G. Christophorou, R. N. Compton, G. S. Hurst, and P. W. Reinhardt, J. Chem. Phys., <u>45</u>, 536 (1966).
- ^CThe E* values are larger than the E* values, generally around 1 kcal. Since E* could not be calculated for all the derivatives, only the E* values are compared to the experimental values. The E* values for the chloro derivatives may be smaller than calculated due to the "non-crossing" rule (see text).

^dCalculated from Equation 38 assuming $v_{0,AB}$ - to be zero.

** adjusted to experimental values.

FIGURE 19

POTENTIAL ENERGY CURVES FOR THERMAL ELECTRON ATTACHMENT, TO CHLOROBENZENE (----) AND o-CHLOROTOLUENE (----)

Potential energy curves given by $Ar \cdot + Cl \cdot + e^{-}$ and $Ar \cdot + Cl^{-}$ are common to both derivatives. $Ar = C_6H_5$ and $CH_3C_6H_4$ for chlorobenzene and o-chlorotoluene, respectively.

0 represents experimental points for relative cross section (arbitary units) distribution as a function of electron energy.



good at low electron energies, but deviates at higher electron energies. This deviation partly arises from the fact that the negative ion potential energy function does not approach infinity as r approaches zero.

The results of the comparison between thermal electron attachment and electron beam measurements for dissociative electron attachment to chlorobenzene appear to be quite good. This represents the best case of comparison for the aromatic chloro derivatives since all the necessary parameters were known: bond dissociation energy (87 kcal),³¹ electron affinity for the chlorine atom (83.16 kcal),³² and the electron affinity for the phenyl radical (50.9 kcal).³³ In the other chloro derivatives, an estimate for at least one of these parameters was necessary.

o-CHLOROTOLUENE, o-DICHLOROBENZENE: The vertical energies of maximum cross section obtained by the swarm-beam technique¹¹ were 1.1 and .36 ev, respectively. In both cases, the vertical energies of maximum cross section were used to calculate k_A . k_A was calculated to be .630 and .555 for o-dichlorobenzene and o-chlorotoluene, respectively. The potential energy curves are shown in Figures 19 and 20 for o-chlorotoluene and o-dichlorobenzene, respectively. From these potential energy curves, both derivatives have been assigned to Mechanism III-a. The activation energies for o-dichlorobenzene and o-chlorobenzene and o-chlorotoluene to the experimental values of 6.91 \pm .29 and 10.26 \pm .63 kcal.

FIGURE 20 POTENTIAL ENERGY CURVES FOR THERMAL ELECTRON ATTACHMENT TO o-DICHLOROBENZENE

 $Ar = C1C_6H_4$

 $\boldsymbol{\Theta}$ represents experimental points for relative cross section distribution as a function of electron energy.



For both derivatives, the bond dissociation energies were assumed to be the same as that for chlorobenzene. Support for using the same bond dissociation energy has been presented in an earlier publication,⁵ where the bond dissociation energy for bromobenzene was compared to the bond dissociation energies for some substituted bromobenzenes. The electron affinity for the tolyl radical was taken to be the same as the value for the phenyl radical, 50.9 kcal. The electron affinity for the chlorophenyl radical was determined by adjusting the value to give an activation energy reasonable to the experimental value. The value used was 55 kcal. It has been reported that substitution in the phenyl nucleus makes little difference to the electron affinity of the radical, 2,5-dichlorophenyl, benzoquinonyl, and napthyl radicals all having electron affinities similar to that for phenyl.³⁴

The experimental and calculated relative cross section distributions for o-chlorotoluene and o-dichlorobenzene are shown in Figures 19 and 20, respectively. The calculated cross section distribution for o-dichlorobenzene predicts the onset of dissociation to occur at a higher electron energy than is observed by electron beam studies. The shapes of the calculated cross sections agree favorably with the experimental results.

3'- and 4'-CHLOROACETOPHENONE, 1-CHLORONAPTHALENE: Swarm-beam data were not available for these derivatives, but both the activation energies for dissociation and the molecular electron affinities have been determined. k_A in each case was calculated from Equation 38. The potential energy curves are shown in Figure 21 for 3'-chloroaceto-

FIGURE 21

POTENTIAL ENERGY CURVES FOR THERMAL ELECTRON ATTACHMENT TO 3'-CHLOROACETOPHENONE (A) AND 1-CHLORONAPTHALENE (B)

Ar = $CH_3COC_6H_4$ and $C_{10}H_7$ for 3'-chloroacetphenone and 1-chloronapthalene, respectively



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phenone and 1-chloronapthalene. The potential energy curves for 4'-chloroacetophenone are not shown, but are quite similar to those of 3'-chloroacetophenone. From the potential energy curves, these derivatives were assigned to Mechanism III-a. This is in agreement with the experimental classification from thermal electron attachment measurements discussed earlier. The calculated activation energies are given in Table X.

The bond dissociation energies were assumed to be 87 kcal for each of these derivatives. The electron affinities for napthyl and $CH_3COC_6H_4$ radicals were adjusted to give reasonable agreement between the calculated and experimental activation energies. The values used were 45 and 60 kcal, respectively. The napthyl radical has been shown to have a lower electron affinity than does the phenyl radical in solution.³⁵ If this is also the case in the gas phase, then a value of 45 kcal for the napthyl radical does not seem unreasonable. No calculated capture cross sections were included since there were no experimental data for comparison.

BROMOBENZENE: By the swarm-beam technique, the vertical energy of maximum cross section was determined to be .84 ev.¹¹ k_A and k_B were calculated to be .497 and .150, respectively. The potential energy curves are shown in Figure 22. Bromobenzene has been assigned to Mechanism III-b on the basis of these curves. The activation energy calculated from Equation 40 was 5.53 kcal compared to the

FIGURE 22

POTENTIAL ENERGY CURVES FOR THERMAL ELECTRON ATTACHMENT TO BROMOBENZENE (-----) AND o-BROMOTOLUENE (----)

Potential energy curves given by $Ar \cdot + Br \cdot + e^{-}$ and $Ar \cdot + Br^{-}$ are common to both derivatives. $Ar = C_6H_5$ and $CH_3C_6H_4$ for bromobenzene and o-bromotoluene, respectively.

0 represents experimental points for relative cross section (arbitrary units) distribution as a function of electron energy.



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experimental value of 5.91 \pm .33 kcal. The actual activation energy, \overline{E}^* , calculated from Equation 41 was 7.01 kcal. Assuming $v_{0,AB}^-$ to be zero, the molecular electron affinity calculated from Equation 38 was -2.27 kcal.

The distribution of relative cross sections calculated from Equation 29 is shown in Figure 22 along with the experimental distribution from swarm-beam studies.¹¹ The fit is quite good but not as satisfactory as that for chlorobenzene. The deviations at higher electron energies are larger than those for chlorobenzene.

The comparison between thermal electron attachment and electron beam measurements for bromobenzene is quite good. This represents the best comparison for the bromo derivatives since all the necessary parameters were known (see Table X).

o-BROMOTOLUENE, 1-BROMONAPTHALENE: Only o-bromotoluene has been studied by the swarm-beam technique,¹¹ having a vertical energy of maximum cross section of .95 ev. k_A was calculated from Equation 25 and found to be .479 for o-bromotoluene. The molecular electron affinity for 1-bromonapthalene was estimated to be 4 kcal. This value is between that for napthalene (3.02 kcal) and 1-chloronapthalene (6.39 kcal). k_A was calculated from Equation 38 to be .645 using this electron affinity estimate for 1-bromonapthalene. The electron affinity used for the tolyl and napthyl radicals were 50.9 and 45 kcal, respectively. The potential energy curves for o-bromotoluene and 1-bromonapthalene are shown in Figures 22 and 23, respectively.

FIGURE 23 POTENTIAL ENERGY CURVES FOR THERMAL ELECTRON ATTACHMENT TO 1-BROMONAPTHALENE

Ar = $C_{10}H_7$. Calculated relative cross section distribution as a function of electron energy also shown.



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From these curves, both derivatives have been assigned to Mechanism III-b. The activation energies calculated from Equation 40 were 6.55 and .10 kcal for o-bromotoluene and 1-bromonapthalene, respectively, compared to the experimental values of 6.31 \pm .34 and 1.74 \pm .43. The E* values calculated from Equation 41 were 7.79 and 1.24 kcal.

The calculated cross section distributions for o-bromotoluene and l-bromonapthalene are also shown in Figures 22 and 23, respectively. There was no experimental distribution available for l-bromonapthalene.

IODDBENZENE: The electron beam data for iodobenzene show two peaks with maxima at 0.0 and .38 ev.¹¹ The electron energy scale was not adjusted by the swarm-beam technique. Iodobenzene was the only aromatic halogen derivative which fit the relationship given in Equation 32 for the aliphatic halides. This leads to the interpretation that iodobenzene follows Mechanism II, i.e., the dissociative negative ion curve is the lower in energy of the two negative ion curves involved in Mechanism III. k_B was calculated to be .232 from Equation 33. This would give a calculated vertical energy of maximum cross section of .75 ev, which could possibly correspond to the second peak observed by electron beam studies.¹¹ The potential energy curves and the calculated cross section distribution are shown in Figure 24.

The experimental difference ion current obtained by beam measurements¹¹ was displaced so that the second peak maximum would correspond to the calculated value of .75 ev. Further interpretation will be needed to explain the two maxima observed by electron beam studies.

FIGURE 24

POTENTIAL ENERGY CURVES FOR THERMAL ELECTRON ATTACHMENT TO IODOBENZENE

 $Ar = C_6 H_5.$

0 represents experimental points for relative cross section distribution as a function fo electron energy.



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GENERAL: Although in some cases the electron affinity for the aromatic radical was estimated, it does not appear to introduce large errors in the calculated activation energies. For instance, a variation of ± 10 kcal for the electron affinity of the chlorophenyl radical changes the calculated activation energy for 0-dichlorobenzene by ± 2 kcal.

For the bromo derivatives, the activation energies calculated from Equation 40 tend to be lower than the experimental values. As stated earlier, the activation energies calculated from Equations 39 and 40 should be lower than the experimental values. However, in the chloro derivatives the trend is for the activation energies calculated from Equation 39 to be higher than the experimental values. If the "non-crossing" rule applies, the calculated values for the chloro derivatives would be lower than those shown in Table X, while the calculated activation energies for the bromo derivatives would not be greatly affected. If the potential energy curves are assumed to give calculated activation energies consistently lower than the experimental values for both the chloro and bromo derivatives, then the fact that the values calculated from Equation 39 are higher could be evidence that the "non-crossing" rule is applicable to the two negative ion curves involved in Mechanism III.

Potential energy curves for o-bromofluorobenzene and m-bromobenzotrifluoride were not constructed since the electron affinities

nor the vertical energies of maximum cross section have been determined. However, the results in Figure 3 appear to be consistent with Mechanism III-b.

D. <u>Thermal Electron Attachment Studies to Some Carbonyl and Nitro</u> Derivatives

During the course of this study, thermal electron attachment to four carbonyl derivatives was investigated. The results of these studies are shown in Figure 4. Biacetyl and l-acetonapthone show the proper temperature dependence for Mechanism I. Biacetyl shows a slight negative slope at low temperatures in Figure 4 corresponding to E_1^* . The temperature dependencies for diacetyl benzene and pthalaldehyde in Figure 4 show only a single negative slope, corresponding to Et of Mechanism I. The assignment to Mechanism I was made since benzaldehyde and acetophenone followed Mechanism I.¹⁵ Based on the electron affinities for benzaldehyde and acetophenone,¹⁵ the molecular electron affinities for these two compounds should be sufficiently large. An activation energy for nondissociative electron attachment has been reported for some carbonyl derivatives in which the carbonyl group was forced out of plane with the benzene ring due to steric factors.¹⁶ This does not appear to be the case here. The negative molecular ions for diacetyl benzene and pthalaldehyde have been shown to exist as cis- and trans-isomers.³⁶ In the thermal electron attachment studies, both isomers are probably formed. Further work will be needed to explain the activation energies for electron attachment to these two compounds.

Nitromethane was also investigated by the pulse sampling technique. Since the bond dissociation energy for (CH₃-NO₂) is 53.6 kcal²⁹ compared to 83.0 kcal for the electron affinity of the NO₂ radical³⁷, it would not follow Mechanism IV. The data in Figure 4 definitely shows a positive slope; however, the intercept for this positive slope is 8.5. The lowest observed intercept for this region has been 11.88. ³⁸ Evidently this positive slope is due to an impurity on the order of 1 part per 1,000. Nitromethane has been assigned to Mechanism II, since E* is greater than the change in internal energy. This is in agreement with what would be expected.

VII. CONCLUSIONS

CONCLUSIONS

A. Thermal Electron Attachment to Organic Acetates - Mechanism IV

In conclusion, the agreement between the activation energy for dissociation and the change in internal energy for the process strongly supports Mechanism IV which involves the formation of an intermediate negative molecular ion but does not follow a dissociative potential energy curve. The activation energy is thus the difference in the bond dissociation energy and the electron affinity of the radical (D_{AB} -EA_A), permitting the evaluation of either of these two quantities providing the other is known. This technique of determining electron affinities of radicals or bond dissociation energies is limited however. With the present electron capture cell, the quantity (D_{AB} -EA_A) must be on the order of 16 kcal or less. To apply this technique, one must be able to exclude the possibility that the dissociative mechanism is II. As seen for benzyl acetate, ethylacetate, ethyl trifluoroacetate, and acetic anhydride, E^{*}₁ was less than E*; but, this may not always be the case.

B. <u>Thermal Electron Attachment to the Aromatic Halogen Derivatives</u> -Mechanism III

The correlation between thermal electron attachment and electron beam studies of dissociative electron attachment to the aromatic halogen derivatives appears to be quite good. In all cases, except iodobenzene, where the vertical energies of maximum cross section were known, the calculated activation energies were within 1 kcal of the experimental values. There is also good agreement between the calculated and experimental cross section distributions. For the compounds studied, it can be seen that the two methods of studying electron attachment processes are quite complementary and enable a more complete understanding of the electron attachment process.

In a previous publication,⁵ it was implied that all aromatic halogen derivatives undergoing dissociative thermal electron attachment did so according to Mechanism III-a. However, from the results of this study using the empirical negative ion function, the bromo derivatives followed Mechanism III-b. Case (b) of Mechanism 1II would not reveal a temperature dependence corresponding to the formation of a negative molecular ion as does case (a). This has been shown for 1-bromonapthalene⁵ and 1-chloronapthalene. 1-Bromonapthalene showed only a single negative slope in the ln $\mathrm{KT}^{3/2}$ plot. Ideally, one should be able to differentiate Mechanism III-a and b from the type of temperature dependence observed; but, this is not always possible. The present electron capture cell is limited in temperature range by the flowing point of teflon at high temperatures and the volatility of the compound studied at low temperatures. Thus, it becomes necessary to distinguish the two cases of Mechanism III by using the empirical negative ion potential energy function.

Although the bromo and chloro derivatives studied followed Mechanism III-b and III-a, respectively, this should not be generalized

to apply for all bromo and chloro derivatives. The particular case of Mechanism III that an aromatic halogen derivative will follow, depends upon the relative magnitudes of the bond dissociation energy, the molecular electron affinity, and the electron affinity for the aromatic radical.

SUMMARY STATEMENT

The work concerning Mechanism IV and the organic acetates has been accepted for publication.³⁹ Portions of the work concerning the aromatic halogen derivatives and the temperature dependencies for the various mechanisms will appear in a review article.⁴⁰

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VIII. APPENDIX

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APPENDIX A

CALCULATION OF 1nKT^{3/2} FROM THERMAL ELECTRON ATTACHMENT DATA

The responses of the electron capture cell and the analog computer are given below.



The electron capture cell response is studied as a function of temperature. The following measurements are made on each electron capture peak:

1. B = b (see figure above) - referred to as span

2. H = h (see figure above) - converted areas in arbitrary units

3. T = temperature of the electron capture cell, °K

4. S = sample size injected, μ l

The other data needed are:

M = concentration of compound in grams/ml

MW = molecular weight of compound

 $T0 = room temperature, ^{\circ}K$

- BO = b or span when no gas chromatographic column is connected to the electron capture cell and the cell is at room temperature, arbitrary units
- FR = flow rate of argon-ten percent methane through the electron
 capture cell, ml/min

CS = chart speed of recorder, in./min

N = number of data points

A typical example of the measurements made are given in Table I of Appendix A. The data was then used in computer program I to calculate ln $KT^{3/2}$ and 1/T. K in the program is the electron capture coefficient and RT is 1/T. LN in the program is ln $KT^{3/2}$. A plot of ln $KT^{3/2}$ versus 1/T was then made (see Figure 3).

TABLE I

EXPERIMENTAL DATA

o-Dichlorobenzene N = 15 M = 1.305×10^{-4} gm/ml, MW = 147.01, AF = 4.03×10^{-3} in/mm, CS = .5 in/min, FR = 150 ml/min, BO = 200 mm, TO = 300° K

| <u>T, °K</u> | <u>S, µ</u>] | B, mm | H, mm |
|--------------|---------------|-------|------------------|
| 480 | 2 | 143 | 169 |
| 476 | 2 | 145 | 155 |
| 467 | 2 | 145 | 134 [.] |
| 459 | 2 | 145 | 114 |
| 444 | 2 | 145 | 72 |
| 439 | 2 | 145 | 69 |
| 428 | 3 | 145 | 96 |
| 419 | 3 | 145 | 79 |
| 410 | 4 | 145 | 93 |
| 401 | 4 | 145 | 78 |
| 389 | 4 | 146 | 62 |
| 372 | 4 | 146 | 47 |
| 348 | 4 | 146 | 30 |
| 325 | 6 | 146 | 32 |
| 306 | 8 | 146 | 23 |

\$ COMPILE MAD, EXECUTE





INPUT DATA

N=15, TC=300, BC=200, MW=147.01, M=1.3048E-4, AF=4.032E-3, CS=.5, FR=150,

T(1) = 480, 476, 467, 459, 444, 439, 428, 419, 410, 401, 389, 372, 348, 325, 306,

S(1)=2,2,2,2,2,2,3,3,4,4,4,4,4,6,8,

H(1)=169,155,134,114,72,69,96,79,93,78,62,47,30,32,28,

PROGRAM LANGUAGE:

MAD

PROGRAM I: CALCULATION OF InKT^{3/2} AND 1/T FROM EXPERIMENTAL DATA (CONTINUED)

OUTPUT DATA

| | LN(1) | | 28.627987, | RT(1) = | = | 2.083333E-03, | K(1) | = | 2.577005E (| ся́ |
|---|--------|-----|-------------|------------|---|---------------|-------|-----|-------------|------------|
| | LN(2) | = | 28.506704, | RT(2) = | = | 2.1008408-03, | K(2) | = | 2.311501E (| 68 |
| | LN(3) | - | 28.313397, | RT(3) = | = | 2.141328E-03, | K(3) | = | 1.960546E | 08 |
| | LN(4) | = | 28.108558, | RT(4) = | = | 2.178649E-03, | К(4) | = | 1.639355E (| 08 |
| | LN(5) | | 27.565962', | RT(5) = | = | 2.252252E-03, | K(5) | = | 1.001546E (| 8 0 |
| | LN(6) | = | 27.495089, | RT(6) = | = | 2.277904E-03, | К(С) | = | 9.490062E | 07 |
| | LN(7) | = | 27.356425, | RT(7) = | = | 2.336449E-03, | K(7) | = | 8.581815E (| 07 |
| | LN(8) | # | 27.108394, | RT(8) = | = | 2.386635E-03, | К(8) | = | 6.913616E (| 0 7 |
| | LN(9) | = | 26.929579, | RT(9) = | = | 2.4390242-03, | K(9) | = ' | 5.972996E (| 07 |
| | LN(10) | = . | 26.698199, | RT(10) = | = | 2.4937662-03, | к(10) | = | 4.899643E (| 07 |
| : | LN(11) | = | 26.385797, | . RT(11) = | z | 2.570694E-03, | K(11) | = | 3.752164E (| 07 |
| | LN(12) | = | 25.997096, | RT(12) = | = | 2.688172E-03, | K(12) | = | 2.720078E (| 07 |
| | LN(13) | = | 25.381418, | RT(13) = | : | 2.8735632-03, | K(13) | = | 1.624206E (| ∩ 7 |
| | LN(14) | = | 24.869548, | RT(14) = | = | 3.076923E-03, | K(14) | = | 1.078655E (| 07 |
| | LN(15) | = | 24.297734, | RT(15) = | = | 3.267074E-03, | K(15) | = | 6.664845E (| 06 |

APPENDIX B

LEAST-SQUARES ADJUSTMENT OF THE In KT^{3/2} VERSUS 1/T PLOTS

The calculated ln $KT^{3/2}$ and l/T values were then used in computer program II to obtain a least-squares adjustment.

A weighted least-squares fit of the data was done according to the procedure published earlier.¹ An error of ten percent was assigned to the electron capture coefficient, K. An error of .5 degrees in the temperature was used. This program can also be used to do a least-squares adjustment with a common intercept.²

The least-squares program gives the intercept and the slope times R along with their errors. The errors are then modified by the external error. By subtracting the errors obtained from the program from $\ln KT^{3/2}$ the least-squares (L.S.) $\ln KT^{3/2}$ values are obtained.

From the least-squares adjustment to the slope, either the electron affinity or a quantity related to the activation energy for dissociation or electron attachment is obtained by multiplying the slope by R. If the slope is negative, the activation energy for dissociation or electron attachment can be obtained by subtracting 3/2 RT from the (slope XR). T is an average of the temperatures studied. If the slope is positive, multiplication of the slope by R gives the electron affinity.

The nomenclature for computer program II is:

N = number of data points

SLOPE = initial estimate of the slope

AOINT = intial estimate of the intercept

AOAVE = common intercept, 14.79

SWAO = weighting factor for common intercept, 75.81

The above data and the calculated ln $KT^{3/2}$ and 1/T values comprise the input data. AOAVE and SWAO were determined previously.² When a least-squares adjustment without a common intercept is done, AOAVE and SWAO are equal to zero.

BO = slope X R

AO = least-squares intercept

TR = 1/T

DELTA(Y) = corrections to original ln $KT^{3/2}$ values

SIGYE = external errors

The sample program is for o-dichlorobenzene. The ln $KT^{3/2}$ values were given in Appendix A.

С C DIMENSION LNKT(50), TR(50), NAME(5), 1SY0(50),Y(50),F(50),PFY(50),PFX(50),PFA(50),PFB(50),CL(50),X(50), 2SIGY2(50),SIGX2(50),WY(50),WX(50) REAL LNKT R=1.987 50 READ(5,100,END=60) NANAME, SLOPE, ADINT, ADAVE, SWAD 100 FORMAT(12,5A4,4F10.0) WRITE(6,190) NAME 190 FORMAT(1H1,25X,63HWEIGHTED LEAST SQUARES CALCULATION OF LNKT3/2 VS 1. TR+10**3 FOR ,5A4) IF (AJAVE . EQ. 0. . AND . SWAD . EQ. 0.) GO TO 120 WRITE(6,13C) ADAVE 130 FORMAT(//,40X,25HWITH A FIXED INTERCEPT AT,F6.2) 120 WRITE(6,180) SLOPE, AOINT 180 FORMAT(//,20X,56HTHE INITIAL VALUES OF THE PARAMETERS ARE: SLOPE (180/R) =, F6.2, 2X, 20 HAND INTERCEPT (A0) =, F6.2) READ(5,110) (LNKT(I), TR(I), I=1,N) 110 FORMAT(2F20.0) B0≠SL5PE+R A8=A9INT M=O 205 SPFAA=0. SPFAB=C. SPFB8=0. SPFA0=0. SPFB0=0. $SY\theta(M)=0$. D8 210 I=1,N Y(I) = LNKT(I)X(I) = TR(I)SIGY2(I)=0+1+5+625E=07*X(I)**2 SIGX2(I)=2.50E=07*X(I)**4

* FORTRAN PROGRAM FOR A WEIGHTED LEAST SQUARES FIT OF LNKT3/2 VS. TR*10**3 *

ERROR IN K ASSIGNED 10% AND ERROR IN T ASSIGNED 0.5 DEGREES

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PROGRAM LANGUAGE: FORTRAN IV -

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F(I) = Y(I) = (B \Theta / R) * X(I) = A \Theta
     PFY(I)=1.0
     PFX(I) = BR/R
     PFA(I) = 1.0
     PFB(I) = -X(I)/R
     WY(I) = 1 \cdot 0 / SIGY2(I)
     WX(I) = 1 \cdot 0 / SIGX2(I)
     CL(I) = PFX(I) * *2/WX(I) + PFY(I) * *2/WY(I)
     SPFAA=SPFAA+PFA(I)**2/CL(I)
     SPFAB=SPFAB+(PFA(I)*PFB(I))/CI(I)
     SPFBB=SPFBB+PFB(I)**2/CL(I)
     SPFBP=SPFBP+(PFB(I)*F(I))/CL(I)
     SPFAG = SPFAO + (PFA(I) + F(I)) / CL(I).
     SYO(M) = SYO(M) + F(I) * * 2/CL(I)
 210 CONTINUE
     SPFAA=SPFAA+SWA0
     SPFA0=SPFA0=SWA0*(A0AVE=A0)
     AA=SPFAA*SPFBB+SPFAB**2
     DA=(SPFA0*SPFBB*SPFB0*SPFAB)/AA
     DB=(SPFB0*SPFAA-SPFA0*SPFAB)/AA
    . A0=A0-DA
     B0=B0-DB
     IN=M+1
     WRITE(6,300) IN, B0, A0
 300 FORMAT(//,35X,21HAPPROXIMATION NUMBER ,12,5X,4HB0 =,F10+6,5X,4HA0
    1 = F_{10.6}
     IF(M.LT.1) G0 T0 220
     AN=N-2
     G8 T0 225
 220 M=1
     G8 18 205
225 IF((ABS(SY0(M)-SY9(M+1)))+LE+(AN/100+)) G0 T0 230
     IF(M+GE+20) G0 T0 235
     M=M+1
     G8 T8 205
 235 WRITE(6,310)
 310 FORMAT(//,10X,56HLEAST SQUARES CALCULATION NOT CONVERGING SOMEBODY
    1 \text{ GOOFED}
     G0 T0 50
230 SA02=SPFBB/AA
```

SB82=SPFAA/AA SA9 SORT (ABS(SA02)) SB0=SORT(ABS(SB02)) SIGYE2=SYG(M)/AN SIGYE=SQRT(ABS(SIGYE2)) SLOPE=BO/R SSLAP=SB0/R WRITE(6,320) 320 FORMAT(////30X,41HRESULTS OF LEAST SQUARES CALCULATION ARE:) WRITE(6,330) SLOPE, SSLOP, A0, SA0 330 FORMAT(//,20X,14HSLOPE (BO/R) =,F10.6,1X,2H+=,F10.6,10X,16HINTERCE 1PT (A0) =, F10.6, 1X, 2H+-, F10.6) WRITE(6,370) B9,SB0 370 FORMAT(//,30X,4HB0 =,F10.6,1X,2H+=,F10.6,2X,12H(KCAL./MOLE)) WRITE(6,340) SIGYE2, SIGYE 340 FORMAT(//,25X,28HEXTERNAL ERRORS SIGYE2 =, F10, 6, 10X, 7HSIGYE =, 1F10.6WRITE(6,350) 350. FORMAT(////20X/10HDELTA (Y) /20X/11HLNKT3/2 (Y)/20X/12HTR+10++3 (X 1)) D8 240 I=1,N $DY=Y(I)=((B\theta/R)*X(I)+A\theta)$ WRITE(6,360) DY,Y(I),X(I) 360 FORMAT(//,20X,F10.6,20X,F10.6,20X,F10.6) 240 CONTINUE GO TO 50 60 STOP END

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Corrections to $\ln KT^{3/2}$

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Input Data

| DELTA (Y) | LNKT3/2 (Y) | TR*10**3 (x) |
|-------------------|------------------------------|-----------------|
| 0•130280 | 28+627991 | : 2•082999 |
| 0.087814 | 28,506989 | 2.101000 |
| 0•068344 | 28•312988 | 2:141000 |
| 0:030136 | 28 · 108994 03 2 € 079 | 2.179000 |
| -0.194351 | 27.565994 | 2.222000 |
| •0+151917 | 27.494995 | 2.278000 |
| - 0∗037857 | 27.355988 | 2:335999 |
| -0.063339 | 27.107986 | 2•386999 |
| -0.014450 | 26 • 925993 | 2,438999 |
| -0.010834 | 26 • 697998 | 2 • 4 3 2 9 9 9 |
| 0:017471 | 26.385986 | 2.570999 |
| 0.138962 | 25 • 996994 | 2.688000 |
| | 15 . 35 0 | • |

PROGRAM II CONTINUED

PROGRAM II CONTINUED

RESULTS OF LEAST-SQUARES

WEIGHTED LEAST SQUARES CALCULATION OF LNKT3/2 VS. TR+10++3 FOR DICHLOROBENZENE

THE INITIAL VALUES OF THE PARAMETERS ARE: SLOPE (BO/R) = =9.00 AND INTERCEPT (A0) = 37.90

APPROXIMATION NUMBER 1 BO = -8,670134 AO = 37,586380

APPROXIMATION NUMBER 2 BO = -8.669496 AO = 37.586075

APPROXIMATION NUMBER 3 60 = -8,669510 A0 = 37,586090

RESULTS OF LEAST SQUARES CALCULATION ARE:

SLOPE (80/R) = =4:363116 += 0:495056 INTERCEPT (A0) = 37:586090 += 1:156555

B0 = -8.669510 +- 0.983676 (KCAL./MOLE)

EXTERNAL ERRORS SIGYE2 = 0.116337 SIGYE = 0.341082



The input data for Equation 15 is in the form shown above. The nomenclature used in the computer program is:

$$A = \ln \left(\frac{A_{1}A_{2}}{k_{D}A_{-1}}\right)$$

$$B = R \times \text{slope} = -(E_{2} + E_{1} - E_{-1})$$

$$C = \ln \left(\frac{k_{L}}{k_{D}} - \frac{A_{1}}{A_{-1}}\right)$$

$$D = R \times \text{slope} = -(E_{1} - E_{-1})$$

$$E = \ln \left(\frac{A_{1}}{k_{D}}\right)$$

$$F = R \times \text{slope} = -E_{-1}$$

$$KD = k_{D} = 2400 \text{ sec}^{-1}, \text{ determined previously}^{3}$$

$$T1 = \text{high temperature limit, }^{K}$$

$$T2 = \text{low temperature limit}$$

 E_1 , E_2 and E_{-1} are the activation energies defined in the text,

with the pre-exponential term, i.e., $E_1^* = E_1 - 3/2 R\overline{T}$.

An additional quantity, $\ln (A_1/A_{-1})$, was needed to get the input data in a form that could be used to make the calculations. This quantity has been evaluated from fundamental constants⁴ and found to be equal to 12.5.

The computer program calculated 1/T and $\ln KT^{3/2}$ values. A plot is then made of $\ln KT^{3/2}$ versus 1/T. The example included here is for plot 5 in Figure 5.

C C EF=E1 FORWARD ER=E=1 REVERSE 00000 AF=A1 FORWARD AR=A=1 REVERSE AF/KD=TT=EXP(E) KT IS K TIMES T TO 3/2 POWER T2 IS SMALLEST TEMP K . T1 IS LARGEST TEMP K 101 FORMAT(5F12.3) 102 FORMAT(1H1,5X,9F12.3) 103 FORMAT(20X, E12.5, 20X, F15.5) PROGRAM LANGUAGE: FORTRAN IV REAL LNKT, KD, KL, KT, K 1 READ (5, 101) A, B, C, D, E, F, T1, T2, KD WRITE(6,102) A, C, E, B, D, F, T1, T2, KD R=1.987 EF==F ER=D=F E2=D+B $X = C = 12 \cdot 5 + AL \theta G (KD)$ KL = EXP(X)TT=EXP(E) Y=E=12:5+AL0G(KD) AR=EXP(Y) Z=A=12*5+ALOG(KD)A2=EXP(Z) DT=1:/T2 1 DELT=1 ./T1 Η 16 IF (DELT .GT. DT) G0 T0 17 XX=(=EF/R)*DELT YY=(=E2/R)*DELT ZZ=(=ER/R)*DELT KT=(TT*EXP(XX))*(A2*EXP(YY)*KL)/(AR*EXP(ZZ)+A2*EXP(YY)*KL) LNKT=ALBG(KT) WRITE(6,103) DELT, LNKT DELT=DELT+5.0E=05 G0 T0 16 17 G8 T8 1 END

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PROGRAM III: CALCULATION OF ln _{KT}3/2 FROM EQUATION

5

| PROGRAM | III | CONTINUED | |
|---------|-----|-----------|--|

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| А | C | Input E | Data B | D |
|--------|---|------------|-----------|--|
| 31•700 | 14•30(| 31.700 | -14000•0 | 00 <u>1</u> 0940.000 |
| | | | 70 | . KD |
| | F | 11 | 12 | KU . |
| -600 | 00.000 | 700.000 | 200.000 | 2400.000 |
| | , | Output | Data | |
| • | 1/T | | | Ln KT ^{3/2} |
| | 14286E+02 14785E+02 15286E+02 15785E+02 16285E+02 16285E+02 17285E+02 18785E+02 19285E+02 20285E+02 21285E+02 21285E+02 21285E+02 2285E+02 2285E+02 | | | 22.95844 23.09889 23.29005 23.51094 23.74593 23.98373 24.21568 24.43398 24.63083 24.79819 24.92859 25.01640 25.05927 25.05927 25.05876 25.01988 24.94954 24.85495 |

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| PROGRAM III | CONTINUED | Qutput data | |
|-------------|-----------------|-------------|----------------|
| | 1/T | · · | $\ln KT^{3/2}$ |
| | ., | | |
| | · | | |
| | 0+227858+02 | | 24.74258 |
| | 0 • 23285E • 02 | | 24+61765 |
| | 0+23785E+02 | | 24•48404 |
| | 0+24285E+02 | | 24 • 34 457 |
| | 0.247855.02 | | 24.20117 |
| | 0+252835+02 | , | 24•05519 |
| | 0+257835+02 | | 23•90747 |
| | 0+262851+02 | | 23.75864 |
| | C+26783F+02 | | 23.60905 |
| | 0.272856.02 | | 23•45898 - |
| | 0.277855-02 | | 23:30859 |
| | 0+282831+02 | | 23•15800 |
| | 0•28785E*02 | | 23.00729 |
| | 0.53582L-05 | | 22+85648 |
| | 0.29785E.02 | | 22.70560 |
| | 0.302851-02 | | 22.55469 |
| | 0.307855+02 | | 22+40375 |
| | 0+312835+02 | | 22+25281 |
| | 0.317855-02 | | 22.10184 |
| | 0+3228 \$E+02 | | 21.95087 |
| | 0+327830+02 | | 21.79990 |
| | 0.3355.05 | | 21.64893 |
| | C•3378 5F *02 | | 21.49796 |
| | 0+3428>/*02 | | . 21•34697 |
| | 0+34/855+02 | | 21 • 19598 |
| | 0.325835.02 | | 21 • 04 501 |
| | 0+35/8 st =02 | | 20,89403 |
| | 0+3628 + + 02 | | 20 • / 4304 |
| | 0.367831.02 | | 20,59207 |
| | 0.3728 31 02 | | 20.44110 |
| | C+3//8 >2=02 | • | 20.29010 |
| | 0+38785tm02 | | |
| | Q+38/831-92 | | 13,38014 |
| | 0.3958.16.05 | | 17+83/17 |
| | 0•3978 st = 02 | | 19+68620 |

APPENDIX D CALCULATION OF POTENTIAL ENERGY CURVES

The potential energy curves are calculated from equations 22 and 23. A computer program for Equation 23 allows the potential energy curves to be calculated. To obtain the potential energy curve for the neutral molecule, equation 22, k is set equal to one and EA_A or B is set equal to zero. The necessary parameters to do these calculations are given in the text. The computer program prints out potential energy, kcal, versus internuclear distance, Å.

A sample calculation is shown for hydrogen, Figure 9. The nomenclature used in the program is:

$$D = D_{AB}^{\circ}, \text{ kcal}$$

$$B = \beta, \text{ }^{A-1}$$

$$RE = r_{o}, \text{ }^{A}$$

$$EA = EA_{A \text{ or } B, \text{ kcal}}$$

$$K = k$$

$$E = \text{ potential energy, kcal}$$

$$R = \text{ internuclear distance, }^{A}$$

PROGRAM IV: COMPUTER PROGRAM FOR POTENTIAL ENERGY CURVES

PROGRAM LANGUAGE: FORTRAN IV - H

MORSE PUTENTIAL ENERGY FUNCTION CALCULATION OF ENERGY VS INTERNUCLEAR DISTANCE REAL K 101 FORMAT(5F12+6) 102 FORMAT(1H1,5F12.6) 103 FORMAT (20X, 2815.5) 1 READ(5,101) D, B, RE, EA, K WRITE (6, 102) D.B.RE, EA.K R=C • 4 IF (R.GT.5.) GE TO 9 R=R++1 E=-2.*K+0*EXP(-6*(R-RE))+D ARITE(6,103) R.E GH TH 4 9 GO TO 1 END

PROGRAM IV CONTINUED

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| D | В | RE | EA | К |
|---|--|---|--------------------|------------------------|
| 109+475996 | 1.929999 | -741500 | 0+000000 | 1.000000 |
| ulli (Mini de Sindia di Sinda ang Katagaran | 0.1 | 100008 - +00 | 0.547152+03 | |
| | 0 * 6 | 210005+00 | 0.26265E+03 | |
| | 0.3 | 300005£∓00 | | |
| Internuclear d | listance. 0-4 | +004JE+00 | -0.14171E+02 | Potential |
| | 0.5 | 50000E+00 T | -0.70833E+02 | Fnergy. |
| | Α Οιά | 00+300008 | -0.98684E+02 | kcal |
| | 0,7 | 20005+00 | -C.10872E+03 | |
| | | 30010E+00 | -0.10823E+03 | |
| | 0 • S | 90000E+00 | -0.101832+03 | |
| | 0 • 1 | 00005+01 | -0.92585E+02 | |
| | Ú - 1 | 10005+01 | -C-32173E+02 | |
| · | 0.1 | | -0.71723C+02 | |
| ************************************** | 0 • 1 | 130002411 | +0+61835F+02 | • • • |
| | 0.1 | 40005401 | -0-52817E+02 | |
| | | 50005401 50005401 | -0.447946402 | |
| | 0 • 1 | (00000 <u>0</u> -01 | -0.37780F+02 | |
| — | | 170000407 <u>1</u> | -0.317256402 | and an and a |
| | 0.1 | 10105401 | -0.245/35-02 | |
| | ······································ | | -0.221555402 | |
| | 093 C. 2 | 200000401 20000401 | -0+221002402 | |
| tan akanantetaga - Appendista versikat anda di siya akapa nyak-appendingkon sepakatangkan sepak | | | | |
| | U+C | 200105-01 200105-01 | -C 10704E+02 | |
| | | - C G G G G G G G G G G G G G G G G G G | -0+12/200+02. | |
| • | Us a | | *U*10049E+02 | |
| ······· | V: A | こまでいたに マント | | |
| | | | -0.72203E+01 | |
| | <u>5</u> ec | 10 Juli + JI | 、そしもなジオオシビキジ上。 | |
| • | U # 0 | ことしてに 手に手 | | |
| | Q•s | | | · ~ |
| | Q • 2 | 00002+01 | -J.33/10E+01 | <u>ا</u> |
| | ÿ:3 | 30000E+01 | -0+278322+01 | |
| | 0,3 | 1000E+01 | -0.229732+01 | |
| | Q • 3 | 20002401 | -0.18955E+01_ | الم المراجع المراجع ال |
| | Q • 3 | 33000E+01 | -C.15643E+01 | |
| | Q•3 | 14000E+01 _ | •0·129095401 | * |
| | 0.3 | 15 D D T = 1 | -C.1C64454C1 | |

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PROGRAM IV CONTINUED

| Intern | uçlear distance | Potential energy, kcal |
|---------------------------------------|-------------------|------------------------------------|
| ۰. ۰۰. | A 0+360.0E+01 | -0.37810E+00 |
| | 0,37000E+01 | -0.72423E+00 |
| | 0,38000E+01 | -0.59729E+00 J. N |
| | 0+39000E+01 | -0.45258E+00 |
| | <u> </u> | -0.40620E+00 (|
| | 0.410005+01 | -0+33496E+00 / 1, 17 |
| | 0.480,0E+Q1 | -0.276212+00 |
| | 0+43000E+01 | +0+22775E+001 |
| | 0,440005+01 | |
| | 0.400002+01 | |
| | | |
| | | |
| | | |
| | | -0 500077.01 # ³ |
| | | |
| D | B RE | |
| 109.479996 | 1.929999 0.741800 | 17.229993 0.497000 |
| | | C.90973E+03 |
| | 0.20000E+00 | 0.55856F+03 |
| | 0+30000F+00 | 0.32937E+03 |
| • • • • • • • • • • • • • • • • • • • | 0,40007+00 | 0.18144E+03 A |
| | 0,5000000+00 | 0.87353E+02 |
| | 0+60000E+00 | 0.287492+02 |
| | 0,700005+00 | +0+66873E+01 |
| | 0.+300002+00 | -0.271448+02 |
| | 0+900005+00 | -0.380555+02 |
| | .0.1000E+01 | +0+43003E+02 |
| • | G,11000E+01 | -0+44331E+02 |
| 1 | 0+120005+01 | -0.43556E+02 |
| | <u> </u> | =0.41645E+02 |
| | 0-140005+01 | -0.32205E+02 |
| | <u> </u> | -0+36604E+02· |
| | 0:16000E+01 | -0.340692+02 |
| | 0+17050E+01 | -0.316952+02 |
| | 0+13000E+01 | -0+295592+02 |
| | <u> </u> | -0-27672E+02 |
| | 0.200000000 | -0.26031E+02 |
| | | • |

J
| Internuclear distance, Å | Potential energy, kcal |
|--------------------------|-------------------------------------|
| 0.210.07+ | 01 -0+24620F+02 |
| 0,220,0E+ | 01 -0.23417E+02 |
| 0,230:05+ | 01 +0.223936+02 |
| +30006+ | 01 -0+215402+02 |
| 0+250005+ | 01 +0+20821E+02 · |
| 0.26000E+ | 01 -0+262132+02 |
| 0,270005+ | 01 -0.19717E+02 |
| 0,230005+ | 01 -0.19290E+02 |
| D+29000E+ | 01 -0.18952E+02 |
| 0,30000000 | 01 -0.18664E+02 |
| 0.310005+ | 010.18426E+02 |
| C.38000E+ | 01 -C.18228E+02 |
| 0.330008+ | 01+0+18065E+02 |
| 0,34000E+ | 01 -0.179292+02 |
| 0,35000E+ | 01 -0.178132+02 |
| 0,300002+ | 01 -0.17726E+02 |
| 0,37000E+ | 01 -0+17649E+02 |
| 0-380005+ | 01 -0+17586E+02 |
| 0-30000E+ | 01C.17535E+02 |
| 0.40000E+ | 01 -0.17492E+02 |
| 0+41000E+ | 010+17456E+02 |
| 0.400000+ | 01 -0.17427E+02 |
| 0.430002+ | 01 -0-17403E+02 |
| 0,440005+ | 01 -C.17383E+02 - |
| 0:45000E+ | 01 -0.17367E+02 |
| 0:46000E+ | 01 -0.17353E+02 / /// 51/ |
| 0·470\02+ | 01 -0.17342E+02 N |
| 0+48000E+ | 01 +0+17333E+02 / 2/ ^N . |
| 0.43000E+ | 01=0+17326E+02 / T(SAN - SA |
| 0+50000000 | 01 -0.17319E+02 |
| 0,51000E+ | 01 -0.17314E+02, J NUT. |

APPENDIX E

CALCULATION OF RELATIVE CROSS SECTION DISTRIBUTIONS

The distributions of relative cross sections as a function of electron energy were calculated from Equation 29. A computer program was used to make these calculations. The calculated relative cross sections, $P(E_v)$, are divided by the value of $P(E_v)$ at $(r-r_o)$, equal to zero to have all the values near one or less. This is only a matter of convenience. The calculations only involve the first two vibrational levels for the molecule. The second vibrational level, n = 1, is modified by e^{-hv_o}/RT , the Boltzmann factor. The contributions from the n = 1level are added to the n = 0 level values for the relative cross sections. All the necessary parameters have been described in the text.

The nomenclature of the program is:

$$B = \beta, A^{-1}$$

$$D = D_{AB}^{\circ}, kcal$$

$$EA = EA_{A \text{ or } B}$$

$$C = 1/2 hv_{o}, kcal$$

$$F = RT, kcal = .592 kcal at 25^{\circ}C$$

$$K = k$$

$$ALPHA = ^{\alpha}, A^{-2}$$

$$EV = E_{v}$$

$$SI2 = P(E_{v})$$

$$X = (r-r_{o})$$

The computer program calculates X, EV, and SI2. The relative cross sections are then plotted versus the electron energy (energy for the vertical process). Figure 9 has an example of this plot.

PROGRAM V: COMPUTER PROGRAM FOR RELATIVE CROSS SECTION DISTRIBUTIONS

PROGRAM LANGUAGE: FORTRAN IV - H

```
С
      CALCULATION OF DISTRIBUTIONS
С
      C IS 1/2 HV
С
      Y IS HV
C
      KT IS REPRESENTED BY C
      REAL K
  200 FORMAT(1HO, 27H DISTRIBUTION FOR N=0 LEVEL)
 201 FERMAT (30X, 3F15.5)
  202 FORMAT(1HO, 27H DISTRIBUTION FOR N=1 LEVEL)
203 FORMAT(7F10+5)
  204 FORMAT(1H1,30X,7F10.5)
    1 READ (5,203) B, D, EA, C, F, K, ALPHA
      WRITE(6,204) B.D.EA,C.F.K.ALPHA
      WRITE(6,200)
      XX = 1 \cdot / (B \cdot 2 \cdot D \cdot (1 \cdot - K))
      X=0
  10 IF(X .GT. .25) G0 T0 15
      EV= =2 ** K*D*EXP(=3*X)+D*EXP(=2 ** B*X)+D=EA=C
      SI2= EXP(-ALPHA*X**2)/(2**B*D*EXP(+B*X)*(EXP(+B*X)*K)*XX)
      WRITE(6,201) X, EV, SI2
      x=X+*01
      G0 T6 10
  15 X=0
  16 IF(X +LT+ ++25) G9 T8 20
      EV= +2,*K*D*EXP(+B*X)+D*CXP(+2,*B*X)+D+EA+C
      SIS= EXP(-ALPHA+X++2)/(2++B+D+EXP(-B+X)+(EXP(-B+X)+K)+XX)
      WRITE(6,201) X, EV, SI2
      x=X-+01
      G9 T8 16
```

```
20 WRITE(6,202)
   BD= 2.*ALPHA*EXP(-2.*C/F)
   x=0
22 IF(X +GT+ +25) G8 T8 25
   EV= =2.*K*D*EXP(=B*X)+D*EXP(=2.*B*X)+D=EA=3.*C
   SI2= BD+X++2*EXP(-ALPHA+X++2)/(2++B+D+EXP(-B+X)+(EXP(-B+X)-K)+XX)
   WRITE(6,201) X, EV, SI2
. X=X++01
   GO T9 22
25 X=0
26 IF(X +LT+ -+25) G0 T0 30
   EV= -2.*K*D*EXP(=B*X)+D*EXP(=2.*B*X)+D=EA=3.*C
   SI2= BD*X**2*EXP(=ALPHA*X**2)/(2**B*D*EXP(=B*X)*(EXP(=B*X)-K)*XX)
   WRITE (6,201) X, EV, SI2
   X=X-,01
   GO TO 26 .
30 GO TO 1
  END
```

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| | | | Ir | nput Data | | | |
|---|--------|-----------|--|--|---|--|--|
| | В | D | EA | C | F | K | ALPHA |
| 1 | •93000 | 109.48000 | 17-28999 | 6:29000 | 0:59000 | 0+49700 | . 65 : 39000 |
| | | • - | · | | •• _ Output d | ata | |
| | | | ······································ | Х | EV | | SI2 |
| | | | | D - 00000E + 00 - 10000E + 01 - 20000E + 01 - 3000E + 01 - 40000E + 01 - 40000E + 01 - 60000E + 01 - 70000E + 01 - 70000E + 00 - 10000E + 00 - 10000E + 00 - 12000E + 00 - 22000E + 00 - 2200E + 00 - 200E + | 0.86557 0.24492 0.22544 0.80707 0.76979 0.77352 0.77352 0.75823 0.75823 0.75823 0.75823 0.75823 0.75823 0.75823 0.75823 0.75823 0.75823 0.75823 0.75823 0.7595 0.6241 0.62515 0.62515 0.62515 0.62515 0.62515 0.62515 0.62515 0.62515 0.62515 0.62515 | File File | <pre>*10000E+01 *10529E+01 *10949E+01 *11249E+01 *11446E+01 *11446E+01 *11337E+01 *10731E+01 *10731E+01 *10256E+00 *0444E+00 *0444E+00 *0444E+00 *0444E+00 *0444E+00 *0444E+00 *041313E+00 *041313E+00 *1315E+00 *1313E+00 *1315E+00</pre> |
| | | | | J+24000E+00 J+25000E+00 J+00000E+00 | 0+60773 0+60440 0+86557 | E+02 0 E+02 0 | •13981E+00 •11381E+00 •10000E+01 |

| | Х | EV | SI2 | |
|---|---------------------|----------------|---------------------------------------|----|
| | -0.10000F-01 | 0.88745E+02 | 0.93815E+00. | _ |
| | -0.20000E-01 | 0.91061E+02 | 0+86929E+00 | - |
| | <u>-0-30000E-01</u> | 0.93511E+02 | 0 • 79553E+00 | |
| | -0,40000E-01 | 0.961C1E+02 | C#719C2E+00 | |
| | 0-5UCOCE-01 | _ 0+98×39E+02_ | 0+64181E+00 | |
| • | -0+60000E-01 | 0•10173E+03 | 0.56575E+CO | |
| | 0.7UCOCE-01 | 0.10478E+03 | 0+49250E+00 | |
| | -0.80000E-01 | 0.10300E+03 | 0+42337E+00 | |
| | 90000E-01 | 0•11139E+03 | 0:35938E+00 | |
| | ~0.10000E+00 | 0•11496E+03 | 0•30125E+00 | |
| | -0.11000E+00_ | 0.11873E+03 | 0#24934E+00 | |
| | -0.12600E+00 | 0+12270E+03 | 0+20379E+00 | |
| | -0.13000g+00 | 0.12687E+03 | 0+164452+00 | |
| • | -0.14000E+00 | 0+13126E+03 | 0+13104E+00 | |
| | | 0.13588E+03 | 0.10310E+00 | |
| | -C-16000E+00 | 0.14073E+03 | 0+80085E=01 | |
| | -0.17000E+00_ | 0+14584E+03 | 0.614228-01 | |
| | -C.180005+00 | 0.151202+03 | 0:46512E-01 | |
| | -0.19000E+00_ | 0.15683E+03 | 0+34774E=01 | |
| | -0-2000CE+00 | 0.16274E+03 | 0•25668E+01 | |
| · | 0.21000E+00 | 0•16894E+03_ | C+18706E-01 | |
| | -0+55000E+00 | 0.17545E+03 | 0•13459E-01 | |
| | <u> </u> | 0•18228E+03 | | |
| | -0-24000E+00 | 0•18944E+03 | 0:67046E-02 | |
| | -U-25000E+00 | 0.19695E+03 | 0•46419E=02 | |
| DISTRIBUTION FOR N≈1 LEVEL | | | | |
| an an a the second s | C.OCCOVE+00 | 0.73977E+02 | | |
| | C * 1 COGCE = 01 | 0.71312E+02 | 0,75662E-11 | |
| | 0.20000E-01 | 0+69964E+02 | '0.31475E-10 | |
| | C-30000E-01 | 0.68127E+02 · | '0+72753E-10 | |
| | 0+400005-01 | 0.66399E+02 | 0.13126E-09 | |
| | 0.50000E-01 | 0.64772E+02 | _ 0:20563E=09 | |
| · · · · | 0+600002-01 | 0.632432+02 | 0+29331E=09 | |
| | 0.7000CE-01 | 0+61607E+02 | 0.300/3E-09 | |
| | 0.30000E-01 | 0.604615+02 | 0.49357E-09 | |
| | 0.90000E-01 | Ç¥59199E+02- ' | ~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~ | |
| | 0.10000E+00 | | 0+69619E-09 | ·. |

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| Х | EV | | SI2 |
|------------------|--------------|-----------------------------|--------------------------------------|
| 0.11000E+00 | 0.56916 | E+U2 J-O | 78646E-09 |
| 0.12000E+00 | 0.658876 | E+02\\; 0 | 86379E-09 |
| 6 • 1 3000E+00 | 0.549231 | E+02 | 92498E-09 1 |
| 0.140002+004 | 0.54037 | E+02 - 1 04 | 96787E-09 V |
| 0,15000E+00'. | 0.53210 | L+02 - 0 | 99140E-09 |
| 0.13000E+00 ** | 0+524444 | E+02 👾 0- | 99558E-09 |
| 0.17000E+00 - 1 | 6.51736 | 2+02 · 0 | 98148E-09 |
| 0.12000E+00 | 0.51084 | E+02` _0+ | 95094E=09 |
| 0+19000E+00 | 0:504841 | E+02 10 | 90648E-09 / |
| 0.20000E+00, ··· | 0+49935 | E+02 ^{[1} //////01 | •85100E-09, / |
| 0+21000E+00 Å* . | 0.494331 | 10+02-12-0 | 78756E-09 |
| 0.55000E+00 ¥ | 0+48977 | E+0S.⊴}0+ | 71920E-09 |
| 0+23000E+00 📢 | 0.485646 | E+05 ,01 | 64875E-C9 |
| 0.240005400 | .0•481931 | E+02 0 | 57871E-09 |
| 0+35000E+00 | 0+478601 | E+020; | 51116E-09 |
| 0.000066+00 | 0.73977 | 5+02 0i | 00000E+00. |
| -0.10000E-01 | 0.76165 | E+02 0- | 67419E-11 |
| -0-20006E-01 | 0.78481 | E+02 0 | 24988E-10 |
| -0.33000UE-01 | 0+80931 | E+02 0 | 51453E-10 |
| -0.40000E-01 | 0.83521 | E+02+: 0+ | •82675E-10 : |
| -0.5000E-01 | 0.86259 | E+02 ··· 0 | 11531E=09 |
| -0+60CCOE-01 | C•89149 | -+02 0 | 14637E-09 |
| =0.70000E=01 | 0.92199 | 2+02 0 | 17342E-09 |
| | 0.95417 | 2+02 0 | 194/2E=09 |
| =0.90000E=01 | 0+95809 | +02 01 | 20920E=09 |
| +0.10000E+00 | 0+102338 | ±+03 0+ | 216498#09 |
| | 0.100100 | | 210021-09 |
| | 0 11/20 | E+03 0 | 100705-00 |
| •0•13000E+00 | 0.114291 | 2+03 0 | 199736-09 |
| +0.14000E+00 | 0+11668 | E+03 0 | 1849/E=U9 |
| | 0.123301 | | 16670E=09 |
| | 0.12204 | 1403 Ur 1403 Or | 107575-00 |
| | 0.100401 | ロサレタ U1 に足のつ 「「」」つ | 1000000000 |
| | 0 1 1 1 0000 | EFUB U' | |
| | 0.15014 | 1403 U | ▼ 20214E=10 、 7つ786E=10 ^ ~ ~ ~ ~ |
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APPENDIX F

CALCULATION OF THE AVERAGE ACTIVATION ENERGY

The calculation of the average activation energy, E^* , was done by evaluating equation 41. The integrals were evaluated by the trapezoid rule. D, B, and K have the same meaning as they did for the potential energy curve program. C is equal to $1/2 hv_0$ and EAA is the electron affinity of the appropriate radical. ALPHA is α defined in the text.

The example presented here is the calculation of E* for bromobenzene.

PROGRAM LANGUAGE: FORTRAN IV - H

```
REAL K
      DIMENSION X(51), EA(51), PSI2(51), PEA(51), EPEA(51), Y(51)
  100 FURMAT(6F12.5)
200 FORMAT(1H1,20X,6F12.5)
 201 FORMAT(1HC,20X,25H X .VS. ACTIVATION ENERGY)
  202 FURMAT(40X,2F15.5)
  203 FORMAT(1H1,20X,29H X .VS. PSI2(X) FOR N=O LEVEL)
  204 FORMAT(1H1,20X,29H X .VS. PSI2(X) FOR N=1 LEVEL)
  205 FORMAT(1H1,20X,29H X .VS. PSI2(X) FOR N=2 LEVEL)
  206 FURMAT(1H0,25X,29H AVERAGE ACTIVATION ENERGY = F10.5) .
     D IS BOND ENERGY + 1/2 HV
С
    B IS BETA FUR MORSE POTENTIAL
С
   ALPHA IS BEFA FOR VIBRATIONAL ENERGY WAVE FUNCTION
С
 K IS MODIFICATION TO MURSE (CALCULATED FROM EV)
EAA IS EA OF A
С
С
  C IS 1/2 HV
EA IS ACTIVATION ENERGY AT X
EBAR IS AVERAGE ACTIVATION ENERGY
С
С
С
    PSI2 IS PROUABILITY (X)
C
   PEA=PSI2 TIMES ENERGY DISTRIBUTION
С
С
    EPEA IS EA TIMES PEA AT X
C
     INTEGRATION BY TRAPEZOID RULE
   1 READ(5,100) D,B,ALPHA,K,C,EAA
      WRITE(6,200) D,B,ALPHA,K,C,EAA
     X(1)=-.25
     DØ 5 I=1, 50
     X(I+1) = X(I) + .01
    5 CONTINUE
      DO 10 I=1, 51
      EA(I) = -2.*K*D*EXP(-B*X(I))+D*EXP(-2.*B*X(I))+D-EAA-C
   10 CONTINUE
```

```
WRIFE(6,201)
    D0 12 I = 1,51
    WRITE(6,202) X(I), EA(I)
 12 CONTINUE
    AB=SQRT(ALPHA/3.1416)
    DØ 15 I=1, 51
    PSI2(I)=AB*EXP(-ALPHA*X(I)**2)
    IF (EA(I)) 16, 14, 14
 14 PEA(I) = PSI2(I) + EXP(-EA(I)/.592)
    EPEA(I) = EA(I) * PEA(I)
 15 CONTINUE
 16 SUMP=0.
    D0 20 I=1, 50
    IF (EA(1+1)) 21,19,19
 19 SUMP = SUMP + .5 * (PEA(I) + PEA(I+1)) * ABS(EA(I) - EA(I+1))
 20 CONTINUE
21 SUME=0.
    DØ 25 I=1,50
    IF(EA(I+1)) 26,24,24
 24 SUME=SUME+.5*(EPEA(I)+EPEA(I+1))*ABS(EA(I)-EA(I+1))
 25 CONTINUE
 26 EBAR=0.
    WRITE(6,203)
    DØ 28 I=1,51
    WRITE(6,202) X(I), PSI2(I)
 28 CONTINUE
    DØ 30 I=1,51
    PSI2(I)=0.
    PEA(I)=0.
    EPEA(I)=0.
 30 CONTINUE
    BB=2.*C
    D0 35 I=1,51
    PSI2(I)=2.*AB*ALPHA*X(I)**2*EXP(-ALPHA*X(I)**2)
     IF(EA(I)-6B) 35,34,34
 34 PEA(I) = PSI2(I) * EXP(-EA(I)/.592)
    EPEA(I) = EA(I) * PEA(I)
 35 CONTINUE
    DØ 40 J=1,50
    IF(EA(I+1)-68) 40,39,39
```

```
39 SUMP=SUMP+.5*(PEA(I)+PEA(I+1))*ABS(EA(I)-EA(I+1))
40 CONTINUE
   00 45 I=1.50
   IF(EA(I+1)-BB) 45.44.44
44 SUME=SUME+.5*(EPEA(I)+EPEA(I+1))*ABS(EA(I)-EA(I+1))
45 CONTINUE
   WRITE(6,204)
   UC 48 I=1.51
   WRITE(6,202) X(I), PSI2(I)
48 CONTINUE
   DØ 50 I=1,51
   PSI2(I)=0.
   PEA(I)=0.
   EPEA(I)=0.
50 CONTINUE
  CC=2.*88
   DØ 55 · I=1,51
   Y(1)=4.*ALPHA*X(1)**2-2.
   PSI2(I) = AB * Y(I) * * 2 * EXP(-ALPHA * X(I) * * 2)/8.
  IF(EA(I)-CC) 55,54,54
54 PEA(I) = PSI2(I)*EXP(-EA(I)/.592)
   EPEA(I) = EA(I) * PEA(I)
55 CONTINUE
   UØ 60 I=1,50
   IF(EA(I+1)-CC) 60,59,59
59 SUMP=SUMP+.5*(PEA(I)+PEA(I+1))*ABS(EA(I)-EA(I+1))
60 CONTINUE
   D0.65 I=1,50
   IF(EA(I+1)-CC) 65,64,64
64 SUME=SUME+.5*(EPEA(I)+EPEA(I+1))*ABS(EA(I)-EA(I+1))
65 CONTINUE
  EDAR=EBAR+SUME/SUMP
   WRITE(6,205)
   D0 68 I=1,51
   WRITE(6,202) X(I), PSI2(I)
68 CONTINUE
   WRITE(6,206) EBAR
   GØ TØ 1
   END
```

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Input Data

| D | В | ALPHA | К | C | EAA |
|----------|--------|-----------|---------|---------|----------|
| 71.80000 | 1.4860 | 211.00000 | 0.49700 | 0.90000 | 50.90000 |

Output Data

AVERAGE ACTIVATION ENERGY = 7.01059

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|----|--|
| 2. | E. Chen, Ph.D. Dissertation, University of Houston (1966). |
| 3. | W. E.Wentworth, E. Chen and J. E. Lovelock, J. Phys. Chem., <u>70</u> , 445 (1966). |
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