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The Dissociation of $C_2H_2D_2$ by Electron Impact

J. DELFOSSE* AND JOHN A. HIPPLE, JR.**
Palmer Physical Laboratory, Princeton University, Princeton, New Jersey

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The dissociation of $C_2H_2D_2$ by electron impact has been investigated. In order to obtain a consistent interpretation of the distribution of intensities of the different ions produced, it is necessary to assume that there is a selective process favoring the splitting of the $C-H$ bond over the splitting of $C-D$. The probability p introduced to take this effect into account has been calculated. From that value of p, an estimate of the intensity of the ion C_2HD has been made, which agrees with the measured one. In addition to that, it has been shown that the formation of CH_2 in C_2H_4 is a splitting of the double bond between the carbons alone, and that in the formation of H_2^+ in C_2H_4, the hydrogen atoms come from the same radical.

THE mass spectrometer has been used recently to a considerable extent to study the manner in which polyatomic molecules are dissociated by a single electron impact. This study has revealed many interesting facts, and in numerous instances it has been possible to correlate the results obtained with thermochemical data. In all this work, although the resultant charged fragments are readily identified, there is no means of telling how the bonds are broken when there are several atoms of the same kind in a molecule as, for example, in the hydrocarbons. The authors have been fortunate in obtaining a pure sample of di-deutero-ethylene, *cis* and *trans*, prepared by Jungers of the University of Louvain.[1] From the study of the Raman spectra, it was known that the sample was practically pure cis- and transdeutero-ethylene—the amount of asymmetric form present being less than 1.0 percent. A mass-spectrometer analysis of this gas was made[2] and the results compared with those obtained in C_2H_4 by Kusch, Hustrulid and Tate.[3] In this comparison, some striking differences were noted. An analysis of these differences leads to a better insight into the manner in which the ethylene molecule is dissociated.

The discussion in this paper is concerned with the relative intensities of the product ions, rather than their appearance potentials. The analysis was made with a mass spectrometer previously described in the literature.[4] To show how intensities measured on this instrument check with those of K, H and T, the analysis of C_2H_4 has been repeated and the results are given in Table I along with those of K, H and T. The results obtained in different runs with the same apparatus show considerably better agreement than would be indicated by the table where two different instruments are compared.

In Table II is shown the distribution of intensities obtained with $C_2H_2D_2$.

If we assume that the ions containing the same number of carbon and hydrogen atoms are equally probable, we can write:

$$\text{(a)}\ (C_2HD_2)=(C_2H_2D);\quad \text{(b)}\ (C_2H_2)=(C_2D_2);\quad \text{(c)}\ (C_2H)=(C_2D),$$

where the expression (C_2X_n) represents the intensity of the ion C_2X_n on the scale used in the table. But then, the relations (a) and (c) together with the data of Table II give:

$$(C_2D_2)=35-34=1;\quad (C_2H_2)=11-2.7=8.3;$$

and the relation (b) is not satisfied. Evidently, the assumption that it is equally as probable to

TABLE I. *Relative intensities of ions produced in C_2H_4 by 75-volt electrons. Comparison of our results with those of Kusch, Hustrulid and Tate.*

ION	K, H, T	AUTHORS	ION	K, H, T	AUTHORS
C_2H_4	100	100	CH_3	0.6	0.5
C_2H_3	57.2	60	CH_2	5.2	4.8
C_2H_2	51.3	57	CH	2.5	2.65
C_3H	8.8	9.6	C	1.7	1.4
C_2	2.7	3.1			

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* C. R. B. Fellow.

** Now at Westinghouse Research Laboratories, East Pittsburgh, Pennsylvania.

[1] DeHemptinne, Jungers and Delfosse, J. Chem. Phys. **6**, 319–324 (1938).

[2] Delfosse and Hipple, Phys. Rev. **53**, 683 (*A*) (1938).

[3] Kusch, Hustrulid and Tate, Phys. Rev. **52**, 843 (1937).

[4] Bleakney and Hipple, Phys. Rev. **53**, 521 (1938).

TABLE II. *Relative intensities of ions produced in* $C_2H_2D_2$ *by 75-volt electrons.*

ION	MASS	INT.	ION	MASS	INT.
$C_2H_2D_2$	30	100	C_2	24	2.7
C_2HD_2	29	34	CHD	15	4.8
C_2H_2D, C_2D_2	28	35	CD	14	2.15
C_2HD	27	32.5	CH	13	1.08
C_2H_2, C_2D	26	11	C	12	1.65
C_2H	25	2.7			

knock off a hydrogen as a deuterium atom is not justified.

The solution to the problem appears to be indicated by the lower mass region. At mass 13, there is a peak which can be attributed only to CH. The peak at mass 14 could conceivably be attributed to CD or CH_2. However, in view of the structure of this molecule, it would appear to be more likely to form CD than CH_2. The absence of a corresponding CD_2 peak is a confirmation of this view. It, therefore, seems legitimate to attribute all of mass 14 to CD. Now it is interesting to note that the intensity of mass 14 is twice that of mass 13 (within the experimental error). That is to say:

$$(CD)/(CH) = 2.15/1.08 = 2.$$

This indicates that in the breakup of the parent molecule, it is twice as probable for the carbon atom to retain a deuterium atom as it is for it to retain a hydrogen atom when there is a choice.

It is now of interest to investigate whether the distribution of intensities in the upper mass region can be explained on the same basis. It is immediately evident that the difficulties mentioned earlier will be helped considerably by again assuming that the relative probability is the same as in the lower region. However, it is possible to use the intensity distribution to determine the relative probability. Let the probability of forming an ion by removing a deuterium and a hydrogen atom be p and 1, respectively. Then from Table II, the following relations are obtained:

$$\begin{aligned}
&(1)\ (C_2HD_2) = 34,\\
&(2)\ (C_2H_2D) + (C_2D_2) = 35,\\
&(3)\ (C_2H_2) + (C_2D) = 11,\\
&(4)\ (C_2H) = 2.7,\\
&(5)\ p(C_2HD_2) = (C_2H_2D),\\
&(6)\ p^2(C_2D_2) = (C_2H_2),\\
&(7)\ p(C_2D) = (C_2H),
\end{aligned}$$

which gives for p the value $p = 0.33$, and for the intensities of the different ions, the following values:

$$\begin{aligned}
&(C_2HD_2) = 34, && (C_2H_2) = 2.6,\\
&(C_2H_2D) = 11, && (C_2H) = 2.7,\\
&(C_2D_2) = 24, && (C_2D) = 8.2.
\end{aligned}$$

Furthermore, from these data an estimate of the intensity (C_2HD) can be made. Although the formation of C_2HD is four times as probable as that of C_2D_2, the factor p has to be taken into account in correcting for the intrinsic probabilities of D and H, which gives

$$(C_2HD) = 4p(C_2D_2) \quad \text{or} \quad (C_2HD) = 32,$$

in good agreement with the experimental value given in Table II. Finally, it is interesting to compare the relative abundances of the ions C_2H_n in C_2H_4 with the sum of the relative abundances of the corresponding ions in $C_2H_2D_2$.

TABLE III. *Comparison of relative abundances of corresponding ions in* C_2H_4 *and* $C_2H_2D_2$.

(C_2H_4)	100	$(C_2H_2D_2)$	100
(C_2H_3)	60	$(C_2H_2D)+(C_2HD_2)$	45
(C_2H_2)	57	$(C_2H_2)+(C_2D_2)+(C_2HD)$	59
(C_2H)	9.6	$(C_2H)+(C_2D)$	10.9
(C_2)	3.1	(C_2)	2.7
(CH_2)	4.8	(CHD)	4.8
(CH)	2.65	(CH)+(CD)	3.22
(C)	1.4	(C)	1.65

This table shows that except for C_2H_3, the relative abundances are nearly the same in both C_2H_4 and $C_2H_2D_2$.

From the preceding remarks, it is evident that with the introduction of a constant, p, a consistent interpretation of the intensity distribution is obtained. Whether the probability p is 0.5 or 0.3 or some intermediate value (or not the same in the upper mass region as in the lower one) this evidence does show that there is a selective process favoring the splitting of the C–H bond over the splitting of C–D.

Another remark has to be made with regard to Table III. The fact that the relative abundance of the ions CH_2 in C_2H_4, and CHD in $C_2H_2D_2$ is the same, together with the absence of any ion CD_2 is evidence that the formation of CH_2 from C_2H_4 by electron impact is a splitting of the double bond between the carbons alone. The study of molecular hydrogen ions produced from the ethylene $C_2H_2D_2$ is also of interest. It is possible to tell whether the molecular hydrogen ions formed come from two atoms belonging to the same radical, or whether all the combinations of hydrogen atoms are possible. In the first case the ratio DD/HD would be 0, and in the second case it would be $\frac{1}{4}$. Using first a hot tungsten filament as electron source, the ratio obtained was $\frac{1}{4}$. But because of a possible thermal decomposition of the ethylene against the filament, the same experiment was repeated with an oxide coated filament, and gave the result 1/15. The comparison between the two results shows clearly that in the first experiment the most important role was played by the molecular hydrogen ion coming from thermodissociation. With the oxide coated filament, this effect is far less important. In view of this, we can assume the true ratio to be less than 1/15. This is strongly in favor of the first assumption mentioned before.

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An Atomic Distribution Function for Liquid Sodium

C. N. Wall*
North Central College, Naperville, Illinois

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An atomic distribution function for liquid sodium is developed. A simple liquid model of the quasi-solid type is assumed in which each atom is trapped by its immediate neighbors in a small spherical cell within which it is free to move about. The resulting distribution function contains three parameters which are evaluated by fitting the function to the experimental distribution curves for liquid sodium given by Trimble and Gingrich. An approximate value of the free volume of the liquid as a function of the absolute temperature is obtained. By means of the free energy equation the entropies and latent heats of fusion and vaporization for liquid sodium are calculated and compared with the observed values.

Introduction

In a recent article, Trimble and Gingrich[1] have given atomic distribution curves for liquid sodium at temperatures of 100°C and 400°C. These curves, which are derived by an analysis of the x-ray diffraction patterns of the liquid,[2] give the radial atomic configuration in the liquid. Presumably they should yield important information about the liquid state of sodium.

For a profitable use of atomic or molecular distribution curves, it is of considerable value to represent them by an analytical function. Prins[3] has proposed a series of error functions for the general liquid distribution function. This representation is based upon a "smeared out" model of the corresponding crystalline solid. Bernal[4] has generalized the treatment to some extent. For the case of monatomic or quasi-monatomic liquids, assumed to possess molecular homogeneity,[5] he has shown that the distribution function of a liquid can be derived from a knowledge of its intermolecular potential function. Unfortunately this potential function is not known in many cases, or, if known, is expressed in a form so complex as to destroy its utility.

The purpose of this paper is to develop a distribution function for liquid sodium somewhat different in form from that proposed by Prins. A direct consequence of this development is the determination of the so-called free volume of liquid sodium.

Free Energy Equation and Free Volume

The concept of free volume has been very fruitful in the study of liquids and gases. Guggen-

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* On leave of absence at M. I. T. during 1937–38.

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[2] Zernike and Prins, Zeits. f. Physik **41**, 184 (1927).

[3] Prins, Physica **3**, 147 (1936).

[4] Bernal, Trans. Faraday Soc. **33**, 27 (1937); also, Kirkwood, J. Chem. Phys. **3**, 300 (1935).

[5] All interior molecules of the liquid have statistically equivalent molecular environments.