

# JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Registered in U. S. Patent Office. © Copyright, 1963, by the American Chemical Society

VOLUME 85, NUMBER 2

FEBRUARY 7, 1963

## PHYSICAL AND INORGANIC CHEMISTRY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE RADIATION LABORATORY OF THE UNIVERSITY OF NOTRE DAME, NOTRE DAME, INDIANA]

### Velocity Dependence of Ion-Molecule Reaction Cross Sections in a Mass Spectrometer<sup>1</sup>

BY DON A. KUBOSE AND WILLIAM H. HAMILL

RECEIVED JULY 10, 1962

The cross sections  $Q$  of ion-molecule reactions have been studied in a mass spectrometer as a function of primary ion energy  $E_0$ . Reactions are of the type  $X^+ + RH \rightarrow XH^+ + R$ , where  $R$  is a non-polar molecule. The results show that  $Q$  is not proportional to  $E_0^{-1/2}$  over the range. At large  $E_0$ ,  $Q$  is linear in  $E_0^{-1}$  beyond a well defined transitional energy. The results cannot, in either energy interval, be described in terms of point particles. Allowing for head-on collision cross sections, taken to be energy independent, leads to expressions of the type  $Q = aE_0^{-1/2} + b$  for small  $E_0$  and  $Q = cE_0^{-1} + d$  for large  $E_0$ . The results are well described by these equations.

#### Introduction

The dependence of ion-molecule reaction cross sections,  $Q$ , on the ion energy,  $E_0$ , has been the subject of several recent publications from this laboratory.<sup>2-4</sup> These reports have pointed out that there is a transitional energy,  $E_t$ , above which long range forces are not controlling and only head-on collisions can occur. This consideration has led to expressions for  $Q = f(E_0)$  that describe the experimental results more adequately than those obtained from previous treatments.<sup>5,6</sup>

The dependence of  $Q$  on  $E_0$  is given by the expressions

$$Q_1 = 2P_L\sigma_L/E_0^{1/2} + \sigma_K(P_K - P_L); E < E_t \quad (1)$$

$$Q_2 = P_L\sigma_L E_t^{1/2}/E_0 + P_K\sigma_K; E > E_t \quad (2)$$

$$E_t^{1/2} = \sigma_L/\sigma_K \quad (3)$$

where

$$\sigma_L = e(2\alpha(m_1 + m_2)/m_2)^{1/2} \quad (4)$$

and  $\alpha$  is the molecular polarizability,  $m_1$  the mass of the ion and  $m_2$  the mass of the molecule.  $\sigma_K$  represents the hard sphere collision cross section and the  $P$ -factors are reaction efficiencies, taken to be energy independent but depending upon the type of collision. Long range forces lead to spiralling collisions and the relative translational energy of the ion-molecule pair appears mostly as rotational energy in the activated complex. For head-on collisions, the relative translational energy is present largely as vibrational energy in the complex. It is plausible that  $P_L \neq P_K$ . The assumed energy independence of  $P_L$  and  $P_K$  is based on convenience and, lacking information, on necessity. Fortunately, it receives a *posteriori* support.

These equations predict that the functional dependence of  $Q$  on  $E_0$  changes from  $E_0^{-1/2}$  below  $E_t$  to  $E_0^{-1}$  above  $E_t$ , as observed. Stevenson and Schissler<sup>7</sup>

take a different view to explain the deviation of  $Q$  from the  $E_0^{-1/2}$  dependence. They suggest that the reaction efficiency,  $P_L$ , is energy dependent. If this were the case it would be difficult to explain why  $P_L$  varies with  $E_0$  in the same manner for all reactions studied in this work.

Results for ion-molecule reactions in neopentane mixtures,<sup>2</sup> cyclopropane,<sup>2</sup> alkyl halides and benzene mixtures<sup>4</sup> have been interpreted in terms of equations 1 and 2. Reactions of the type  $X^+ + RH \rightarrow XH^+ + R$  have been re-examined in the same context and are reported here.

#### Experimental

The instrument used for all the measurements was a CEC 21-103A mass spectrometer equipped with a model 31-402 ion source. Modification of the ionizing voltage and repeller voltage circuits to facilitate ion-molecule measurements are described elsewhere.<sup>2</sup> Ion currents were measured with an Applied Physics model-30 vibrating reed electrometer and a Sargent model-MR chart recorder. The range of sensitivity attainable with this combination is  $10^{-7}$  to  $10^{-13}$  ampere.<sup>3</sup>

Gases of normal isotopic composition used in this study were obtained from Matheson Co. and were purified as needed by standard techniques. Deuterium was obtained from the Stuart Oxygen Co. and methane- $d_4$  from Merck Sharp and Dohme of Canada: *n*-butane- $d_{10}$  was prepared by catalytic exchange between *n*-C<sub>4</sub>H<sub>10</sub> and D<sub>2</sub>. Hydrogen cyanide was prepared from phosphoric acid and potassium cyanide.

All cross sections were measured under the following source conditions: ion accelerating voltage, 500 v.; electron energy, 70 v.; electron current, 10.5 microamperes; total pressure in the three liter reservoir bulb, 570 microns, which corresponds to  $1.2 \times 10^{13}$  molecules/cm.<sup>3</sup> in the ion source.

#### Results and Discussion

Before presenting the actual experimental results it is instructive to examine a "synthetic" reaction with regard to plots of  $Q$  against  $E_0^{-1/2}$  and  $E_0^{-1}$ . Such a reaction has been constructed using equations 1 and 2 with  $\sigma_L = 50 \times 10^{-16}$  cm.<sup>2</sup> ev.<sup>1/2</sup>,  $E_t = 1.0$  ev.,  $\sigma_K = 35.4 \times 10^{-16}$  cm.<sup>2</sup> and  $P_L = P_K = 1$  and ap-

(1) This article is based upon a thesis submitted by Don A. Kubose in partial fulfillment of the requirements for the Ph.D. degree in the University of Notre Dame, June 1962. This work was supported in part under U.S.A.E.C. contract AT(11-1)-38.

(2) N. Boelrijk and W. H. Hamill, *J. Am. Chem. Soc.*, **84**, 730 (1962).

(3) R. F. Pottier, A. J. Lorquet and W. H. Hamill, *ibid.*, **84**, 529 (1962).

(4) L. P. Theard and W. H. Hamill, *ibid.*, **84**, 1134 (1962).

(5) G. Gioumousis and D. P. Stevenson, *J. Chem. Phys.*, **29**, 294 (1958).

(6) F. H. Field, J. L. Franklin and F. W. Lampe, *J. Am. Chem. Soc.*, **79**, 2419 (1957).

(7) D. P. Stevenson and D. O. Schissler, "The Chemical and Biological Action of Radiations," Vol. V, M. Haissinsky, Ed., Academic Press, New York, N. Y., 1961, pp. 249-251.

(8) Detailed descriptions of the instrument modifications and of the techniques used for measuring appearance potentials, source pressure, reaction cross sections and other related measurements are given in "Notes on Techniques for Studying Ion-Molecule Reactions" by T. F. Moran and D. A. Kubose which is available at no cost from W. H. Hamill.

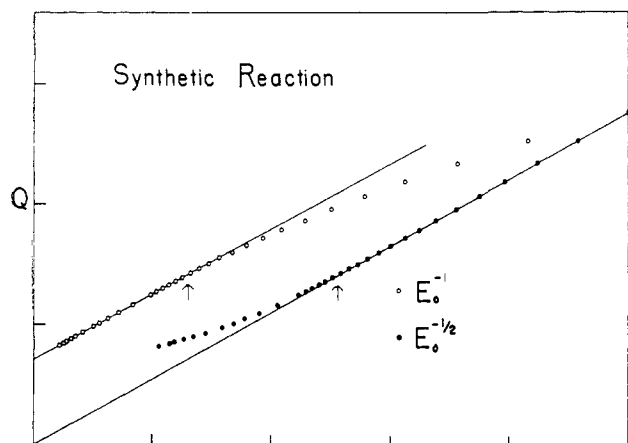
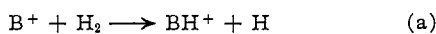


Fig. 1.—Plot of  $Q$  against  $E_0^{-1/2}$  and  $E_0^{-1}$  for a synthetic reaction. Range of  $E_0$  is 0.5 to 11.5 ev. The arrows indicate  $E_t$ .

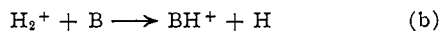
pears in Fig. 1.  $P_K$  and  $P_L$  will not always be unity for actual cases, but different values of  $P_K$  and  $P_L$  will only shift the curves along the ordinate. Arrows indicate the position of  $E_t$  on the energy scale. It is evident that  $E_t$  cannot be determined accurately by direct observation.  $E_t$  can be determined analytically, however, from the ratio of the slopes of curves described by equations 1 and 2. An actual representative set of results which can be compared with the synthetic case appears in Fig. 2. For this reaction  $P_K$  is zero. The qualitative similarity of these curves is evident.

There are several tests of the treatment. First, values of  $P_L\sigma_L$  obtained from the slope of  $Q$  against  $E_0^{-1/2}$  can be compared to the value of  $\sigma_L$  using equation 4. These values, which appear in Table I, are acceptable provided  $\sigma_{L, \text{calcd.}} \geq \sigma_{L, \text{obsd.}}$  since  $P_L \leq 1$  but its value cannot be predicted.

The high values of  $P_L\sigma_L$  for mixtures of light and heavy hydrogen with nitrogen, carbon monoxide and argon can be explained by the following consideration. Hutchison, *et al.*,<sup>9</sup> and Giese and Maier<sup>10</sup> have pointed out that in some systems the secondary ion can arise from the reaction going both by



and also by



Consider the following: in general

$$i_s = i_p N l_0 E_0^{-1} \int_0^{E_0} \sigma(E) dE \quad (5)$$

$$i_s / (i_p N l_0) = Q = E_0^{-1} \int_0^{E_0} \sigma(E) dE \quad (6)$$

where  $i_s$  is the secondary ion current,  $i_p$  the primary ion current,  $N$  the concentration of molecules in the ion source and  $l_0$  the distance from the electron beam to the exit slit of the ion source. Also

$$i_s = i_{s,a} + i_{s,b}$$

where  $i_s$  is the total measured ion current of  $BH^+$ . Substituting and rearranging

$$i_s / (i_p N l_0) = E_0^{-1} \int_0^{E_0} \sigma_a(E) dE + i_{p,b} N_a / (i_{p,a} N_b) E_0^{-1} \int_0^{E_0} \sigma_b(E) dE \quad (8)$$

Using equation 6 and  $i_p = kN$

$$Q_a' = Q_a + (k_b/k_a) Q_b \quad (9)$$

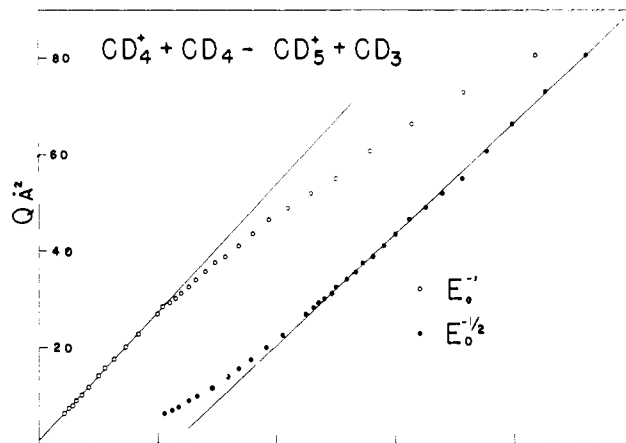


Fig. 2.—Plot of  $Q$  against  $E_0^{-1/2}$  and  $E_0^{-1}$  for the reaction  $CD_4^+ + CD_4 \rightarrow CD_5^+ + CD_3$ . Range of  $E_0$  is 0.5 to 11.5 ev.

$Q_a'$  is the cross section plotted using the measured  $i_s$  and taking  $B^+$  as the nominal reactant ion. For a given ion energy equation 9 can be written

$$\sigma'_{L,a} = \sigma_{L,a} + (k_b/k_a) \sigma_{L,b} \quad (10)$$

For the case that  $P_L$  is unity for reactions a and b the ratio  $\sigma_{L,b}/\sigma_{L,a}$  can be obtained from theory

$$\sigma_{L,b}/\sigma_{L,a} = (m_a \alpha_b / m_b \alpha_a)^{1/2} \quad (11)$$

where  $m_a$  and  $m_b$  are the masses of the neutral molecules and  $\alpha_a$  and  $\alpha_b$  their respective polarizabilities. Calling this ratio  $\beta$

$$\sigma'_{L,a} = (1 + k_b/k_a \beta) \sigma_{L,a} \quad (12)$$

In Table II calculated values of  $\sigma'_{L,a}$  from equation 12 are compared with observed values. The agreement is satisfactory.

TABLE I  
COMPARISON OF  $\sigma_{L, \text{calcd.}}$  AND  $\sigma_{L, \text{obsd.}}$

Ion	Molecule	Sec. ion	$\sigma_{L, \text{calcd.}}$ , $\text{\AA}^2 \text{ ev.}^{1/2}$	$P_L \sigma_{L, \text{obsd.}}$ , $\text{\AA}^2 \text{ ev.}^{1/2}$
D <sub>2</sub>	H <sub>2</sub>	D <sub>2</sub> H	26	31.7
O <sub>2</sub> *	H <sub>2</sub>	O <sub>2</sub> H	61.6	25
O <sub>2</sub> *	D <sub>2</sub>	O <sub>2</sub> D	45	14.6
H <sub>2</sub> O	D <sub>2</sub>	H <sub>2</sub> OD	35	28
D <sub>2</sub> O	H <sub>2</sub>	D <sub>2</sub> OH	47.4	45
H <sub>2</sub> O	<i>n</i> -D <sub>4</sub> D <sub>10</sub>	H <sub>2</sub> OD	55	56.5
CD <sub>4</sub>	CD <sub>4</sub>	CD <sub>5</sub>	38	42
CD <sub>3</sub>	CD <sub>4</sub>	C <sub>2</sub> D <sub>5</sub>	37	40
N <sub>2</sub>	H <sub>2</sub>	N <sub>2</sub> H	58	84
N <sub>2</sub>	D <sub>2</sub>	N <sub>2</sub> D	42	66.5
CO	H <sub>2</sub>	COH	58	75
CO	D <sub>2</sub>	COD	42	57
CO <sub>2</sub>	H <sub>2</sub>	CO <sub>2</sub> H	71.6	50.5
CO <sub>2</sub>	D <sub>2</sub>	CO <sub>2</sub> D	51.8	36
A	H <sub>2</sub>	AH	68.5	76
A	D <sub>2</sub>	AD	49.6	60.5
HCN	D <sub>2</sub>	HCND	41.6	48.6
D <sub>2</sub>	D <sub>2</sub>	D <sub>3</sub>	21.2	21.5
H <sub>2</sub>	H <sub>2</sub>	H <sub>3</sub>	21.1	23.5

TABLE II  
COMPARISON OF CORRECTED  $\sigma_{L, \text{obsd.}}$  AND  $\sigma_{L, \text{calcd.}}$

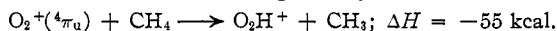
System	Sec. ion	$\sigma'_{L, \text{calcd.}}$ , $\text{\AA}^2 \text{ ev.}^{1/2}$	$\sigma_{L, \text{obsd.}}$ , $\text{\AA}^2 \text{ ev.}^{1/2}$
N <sub>2</sub> -H <sub>2</sub>	N <sub>2</sub> H	71	84
CO-H <sub>2</sub>	COH	71	75
A-H <sub>2</sub>	AH	77	76
N <sub>2</sub> -D <sub>2</sub>	N <sub>2</sub> D	53	66
CO-D <sub>2</sub>	COD	53	57
A-D <sub>2</sub>	AD	58	60

For the system O<sub>2</sub>-H<sub>2</sub>(D<sub>2</sub>), the reactant ion is taken to be O<sub>2</sub><sup>+</sup> in its first excited state. Since not all O<sub>2</sub><sup>+</sup>

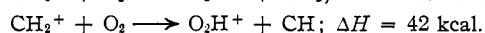
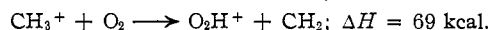
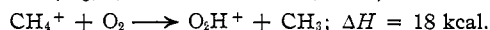
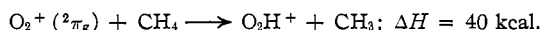
(9) D. Hutchison, A. Kuppermann and L. Pobe, presented at ASTM Committee E-14 on Mass Spectrometry, Chicago, Illinois, June, 1961.

(10) C. F. Giese and W. B. Maier, II, *J. Chem. Phys.*, **35**, 1913 (1961).

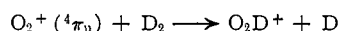
are excited,  $P_L\sigma_{L,obsd.}$  will be less than  $\sigma_{L,calcd.}$  Earlier work assigns  $H_2^+$  as the reactant ion.<sup>11,12</sup> Although the appearance potentials of  $O_2H^+$  and  $H_2^+$  coincide, the first excited state of  $O_2^+$  also matches<sup>13</sup> and is therefore allowed. The formation of  $O_2H^+$  in a mixture of oxygen and methane requires excited  $O_2^+$  for the reaction to be energetically allowed.<sup>14</sup>



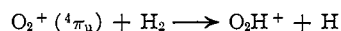
The following reactions are endothermic and are presumed not to occur.



Another fact which strongly supports the choice of  $O_2^{+*}$  is that  $E_t$  is observed graphically, and is in the measurable range of  $E_0$ , for



but not for



Replacing  $H_2$  by  $D_2$  as the *molecule* will lower the value of  $E_t$  by about a factor of two but is expected to have little effect if  $H_2^+$  and  $D_2^+$  are involved. This is evident on inspecting equations 3 and 4.

This feature of being unable to observe graphically a discontinuity associated with  $E_t$  also applies to mixtures of light and heavy hydrogen with argon, nitrogen or carbon monoxide. According to equation 3 the combination of large  $\sigma_L$  and small  $\sigma_K$  dictates a large  $E_t$ . Values of  $Q$  for the  $N_2 + H_2$  and  $N_2 + D_2$  systems were re-examined at higher  $E_0$  by using additional batteries in the repeller voltage circuit.  $E_t$  was then observed for both mixtures. The calculated ratio  $E_{t,H_2}/E_{t,D_2}$  from equations 3 and 4 is 1.88; the observed ratio is 2.1.

Another test of our description is to compare  $\sigma_K$  obtained from

(11) D. P. Stevenson and D. O. Schissler, *J. Chem. Phys.*, **29**, 282 (1957).

(12) P. Dong and M. Cottin, *J. chim. phys.*, **57**, 557 (1960).

(13) D. C. Frost and C. A. McDowell, *J. Am. Chem. Soc.*, **80**, 6183 (1958).

(14) Values of  $\Delta H_f$  are taken from F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press, Inc., New York, N. Y., 1957.

$$\sigma_K = \sigma_L/E_t^{1/2} \quad (13)$$

with values calculated from van der Waals equation,  $\sigma_{vdw}$ , gas viscosity,  $\sigma_{gv}$ , and molar refraction,  $\sigma_{mr}$ . These comparisons appear in Table III. The values of  $\sigma_K$  are very plausible and in fact appear to reflect the differences between the molecules more faithfully than do the other  $\sigma$ 's.

TABLE III

VALUES OF  $E_t$  AND  $\sigma_K$ 

Ion	Molecule	$E_t^{1/2}$ , ev. <sup>1/2</sup>	$\sigma_{K,obsd.}$ , Å. <sup>2</sup>	$\sigma_{Kgv}$ , Å. <sup>2</sup>	$\sigma_{Kvdw}$ , Å. <sup>2</sup>	$\sigma_{Kmr}$ , Å. <sup>2</sup>
D <sub>2</sub>	D <sub>2</sub>	2.64	8	18.3	24	10.8
H <sub>2</sub>	H <sub>2</sub>	2.60	8.1	18.3	24	10.8
D <sub>2</sub>	H <sub>2</sub>	2.42	10.7	18.3	24	10.8
H <sub>2</sub> O	D <sub>2</sub>	1.57	22.2	18.8	25	13.3
D <sub>2</sub> O	H <sub>2</sub>	2.76	17.2	18.8	25	13.3
H <sub>2</sub> O	n-C <sub>4</sub> D <sub>10</sub>	2.00	27.5	34.8	44	31.6
CD <sub>4</sub>	CD <sub>4</sub>	1.65	23	31.4	33	24.2
CD <sub>3</sub>	CD <sub>4</sub>	1.75	21.2	31.4	33	24.2

Values of  $P_L$  obtained from the comparison of  $\sigma_{L,calcd.}$  and  $P_L\sigma_{L,obsd.}$  are unity for most of the reactions studied. Values of  $P_K$ , however, are not reliable due to the cumulative errors in determining  $E_t$ , slopes and intercepts. The reproducibility of replicate measurements is indicated in Table IV for the hydrogen self reaction.

TABLE IV

REPRODUCIBILITY OF REPLICATE MEASUREMENTS FOR THE HYDROGEN SELF REACTION

Slope of $Q$ vs. $E_0^{-1}$ , Å. <sup>2</sup> ev. <sup>-1</sup>	Intercept of $Q$ vs. $E_0^{-1}$ , Å. <sup>2</sup>
65.5	5
64.1	5
65.6	10
60.5	11

Unpublished work of Dr. T. F. Moran<sup>15</sup> in this laboratory with molecules possessing permanent dipole moments have indicated a "locking-in" effect which greatly enhances the observed cross section. The present results do not indicate analogous "locking-in" of the ion on a particular orientation of the induced dipole of the molecule.

(15) T. F. Moran, Ph.D. Thesis, University of Notre Dame, 1962.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, LOS ANGELES STATE COLLEGE, LOS ANGELES, CALIF.]

## The Effect of Certain Variables on the Ultrasonic Cleavage of Phenol and of Pyridine<sup>1</sup>

BY DOUGLAS L. CURRELL, GEORGE WILHEIM AND SZABOLCS NAGY

RECEIVED JULY 23, 1962

The effect of pH and dissolved gases on the ultrasonic reaction of aqueous solutions of phenol and of pyridine to produce acetylene has been investigated. Phenol in alkaline solution and pyridine in acid solution are essentially unaffected by ultrasonic waves. The rate of production of acetylene is dependent upon the ratio of specific heats of the dissolved gases. The rate of the ultrasonic cleavage of the pyridine ring was shown to be independent of the surface tension of the reaction solution. The significance of these results is discussed in terms of possible mechanisms for the chemical effect of ultrasonic waves.

### Introduction

Current theories as to the mechanism by which ultrasonic waves bring about chemical change<sup>2</sup> involve the phenomenon of cavitation, *i.e.*, the formation of bubbles in a liquid system subjected to an intense

ultrasonic beam. When the applied ultrasonic beam is of an intensity insufficient to produce cavitation, no chemical change is observed. Further, it appears the presence of a dissolved gas whose function is to furnish nuclei is necessary for the occurrence of cavitation.

From experiments on the effect of dissolved gases on the ultrasonic reaction, Griffing<sup>3</sup> has proposed that

(1) Presented at the Pacific Southwest Regional Meeting of the American Chemical Society, Los Angeles, Calif., December, 1960. This research was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research.

(2) For leading references *cf.* A. Weissler, *J. Am. Chem. Soc.*, **81**, 1077 (1959).

(3) V. Griffing, *J. Chem. Phys.*, **20**, 939 (1952); M. E. Fitzgerald, V. Griffing and J. Sullivan, *ibid.*, **25**, 926 (1956).