white solid. The solid, recrystallized from hexane, gave 2.0 g. (87%) of white crystals, m.p. 93–96° (reported[20] m.p. 96.5).

Other amidates (Table II) were made in the same manner except that in the case of di-*n*-butyl N-methylphosphoramidate anhydrous methylamine was passed directly into an ethereal solution of the chloridate and in the case of bis-(2-chloroethyl) N-phenylphosphoramidate the precipitated mixture of amidate and aniline hydrochloride was separated by washing out the latter with water.

Reaction of Sulfuryl Chloride with Triethyl Phosphite in Styrene.—Sulfuryl chloride (5.4 g., 0.04 mole) was added dropwise over a 15-minute period to a stirred solution of 6.65 g. (0.04 mole) of triethyl phosphite in 31.2 g. (0.3 mole) of freshly distilled styrene maintained at 0° in an atmosphere of dry nitrogen. The clear colorless mixture was then allowed to come to room temperature and stirred for two hours. During this time sulfur dioxide formed was swept out of the system by a stream of anhydrous nitrogen and passed through a known amount of standard iodine solution; 93% of the theoretical amount of sulfur dioxide was accounted for.

After diluting the mixture with 100 ml. of ethyl ether, an excess of dilute sodium hydroxide (125 ml. of a 5% solution) was added dropwise with cooling over a 30-minute period and the suspension was then stirred at room temperature for 30 minutes; the ether and aqueous layers were separated. The basic aqueous layer was extracted twice with 25-ml. portions of ethyl ether, the combined ether extracts were washed with three 25-ml. portions of water, and then dried over anhydrous sodium sulfate. The dry ether solution was concentrated under reduced pressure and the residual liquid was flash-distilled *in vacuo* yielding 25.0 g. (0.25 mole, 83.3% recovery) of styrene boiling at 47–50° (20 mm.). The residue, 4.28 g., was taken up in benzene; addition of an equal volume of methanol to the resulting clear solution gave 0.2 g. of a white amorphous solid in which phosphorus was absent and which appeared to be polystyrene. The filtrate was concentrated under reduced pressure and the residual oil was distilled, yielding a fraction boiling at 30–36° (0.04 mm.), and leaving approximately 2 g. of residue. The distillate gave a positive test for phosphorus and also for unsaturation but its identity could not be positively established.

Acknowledgments.—We wish to express our appreciation to R. W. Cogley for carrying out some of the experimental work.

LANCASTER, PENNA.

[CONTRIBUTION FROM THE REFINING RESEARCH AND DEVELOPMENT DIVISION, HUMBLE OIL AND REFINING CO.]

Cross Sections for Ionization by Electrons

BY F. W. LAMPE, J. L. FRANKLIN AND F. H. FIELD

RECEIVED MARCH 30, 1957

Cross sections for ionization by 75 v. electrons have been measured for 35 substances using the ion source of a CEC model 21-620 mass spectrometer. Values at variance with those reported by other workers are obtained, and as a consequence reservations concerning the validity of a proposed method of calculating ionization cross sections are expressed. It is found that the measured ionization cross sections are linearly related to polarizability, and a theoretical rationalization of this relationship is given.

Introduction

Total cross sections for ionization by electron impact of a wide variety of substances were reported recently by Otvos and Stevenson[1] (O. and S.). In addition, these authors assert that the atomic ionization cross sections of the elements are proportional to the number of valence electrons weighted by the mean square radii of these electrons as calculated using hydrogenic wave functions. Furthermore, they assert that the ionization cross section of a molecule can be obtained by adding the ionization cross sections of the constituent atoms.

Partially as a consequence of studies concerning ion–molecule reactions taking place in mass spectrometer ionization chambers, we have had occasion to measure total ionization cross sections by electron impact. We wish to report here our values since some of them disagree with those of O. and S., and this disagreement causes us to think that the proposed calculation of atomic ionization cross sections and postulate of additivity of atomic ionization cross sections are not so generally valid as O. and S. imply.

Experimental

In general, the method consisted of measuring the saturation ion-current collected on the ion-repeller of a CEC model 21-620, cycloidal focusing mass spectrometer when the repeller was biased negatively (5 volts) with respect to the ionization chamber. The ion-current was measured with a Keithley electrometer. The electron accelerating voltage was about 75 volts; the electron current was 10.0/μamp.; and the path length of the ionizing electrons was 0.56_3 cm.

At very low pressures in the reservoir the gas flow both in and out of the ionization chamber is effusive. In such a pressure region, the concentration of all gases in the ionization chamber will be the same for a given reservoir pressure and a plot of ion-current *versus* reservoir pressure will be linear, with the slope proportional to the total ionization cross section of the gas. Absolute total ionization cross sections are obtained from the slopes by comparison with the known absolute values of total ionization cross sections for argon and neon for 75 volt electrons as summarized by Massey and Burhop.[2]

At higher pressures in the reservoir mass flow into the ionization chamber begins to become important and, since there is still effusive flow out of the chamber, the ionization chamber pressure becomes proportional to a higher power of the reservoir pressure. The observed result is an upward curvature of the plot of ion-current *versus* reservoir pressure. A typical plot of ion-current *versus* reservoir pressure is shown in Fig. 1. The initial slope, shown by the dotted line, is used to determine the relative ionization cross section.

Results and Discussion

Table I gives our results and the results of previous workers. The cross-sections given in column III were calculated from the slopes of the ion current *vs.* pressure plots (column II) by taking the absolute total ionization cross section for argon to be $3.5_2 \times 10^{-16}$ cm.^{2} as given by Massey and Burhop.[2] Values for other gases summarized by Massey and Burhop[3] are given in column IV. Columns V and

---

[1] J. W. Otvos and D. P. Stevenson, THIS JOURNAL, **78**, 546 (1956).

[2] H. S. W. Massey and E. H. S. Burhop, "Electronic and Ionic Impact Phenomena," Oxford University Press, London, 1952, p. 38.

[3] Reference 2, p. 265.

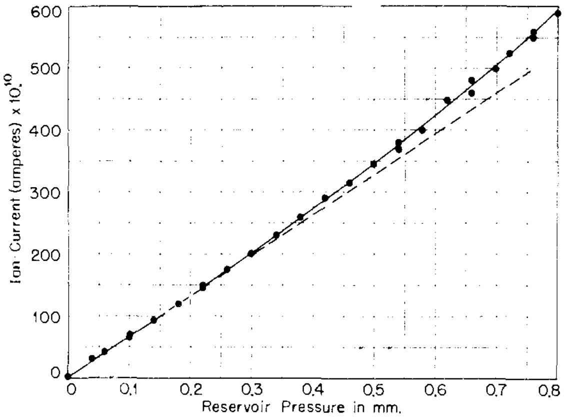

Fig. 1.—Ion-current *vs.* reservoir pressure for cyclopentane.

VI contain experimental and theoretical cross-section values recalculated from the paper of O. and S.[4] The original values given by O. and S. are relative quantities based on an assigned value of 10.9 units for the cross section of argon, and as such they are not directly comparable with our values. The experimental values in cm.² listed in column V were obtained by multiplying the O. and S. values by $3.52 \times 10^{-16}/10.9$. The recalculation of the O. and S. theoretical values will be considered later.

From Table I it may be seen that our values agree with those of Massey and Burhop to within 10% except for H_2 and C_2H_2 (our values higher by 20 and 17%, respectively). The agreement between our values and the experimental values of O. and S. is generally poor, and for the hydrocarbons our values are usually at least 50% higher. We should mention, however, that for the hydrocarbons both our values and those of O. and S. are individually internally consistent, and if the intercomparison between the two sets of values is made at one of the hydrocarbons rather than at argon, a large area of agreement is observed, with serious disagreement occurring only for the inorganic substances. Nevertheless, for several reasons we think the intercomparison at argon to be the more desirable.

Otvos and Stevenson propose a method of theoretical calculation of ionization cross sections based on the postulates that (1) atomic ionization cross sections are proportional to the number of valence shell electrons in an atom weighted by the mean square radii of these electrons, and (2) molecular ionization cross sections can be obtained by a simple summation of the cross sections of the constituent atoms. With this method O. and S. have calculated values for the substances they studied experimentally, and an inspection of their paper will show that for most substances the agreement between the calculated and experimental values is very good. On the basis of this agreement, O. and S. are led to claim that with their method ionization cross sections can be calculated to a good approximation and thus that the postulates on which the method is based are valid.

TABLE I

TOTAL IONIZATION CROSS SECTIONS FOR 75 V. ELECTRONS

		$Q_i \times 10^{16}$, cm.²			
I Substance	II $\lambda \times 10^{10}$, amps. mm.$^{-1}$	III This work	IV Massey and Burhop	V O. and S. (exptl.)	VI O. and S. (calcd.)
A	134	(3.52)	3.52	(3.52)	5.45
He	14.6	0.386	0.322	0.291	0.347
Ne	23.4	0.615	0.622	0.562	0.875
Kr	193	5.18		5.39	8.70
Xe	272	7.31			12.1
H_2	45.9	1.21	1.01	0.872	1.00
N_2	109	2.88	2.74	2.64	3.84
O_2	93.6	2.51	2.70	2.28	3.29
H_2O	112	2.96			3.08
CO	113	2.99	2.99	2.66	3.73
CO_2	163	4.31		3.46	5.37
NO	115	3.04	3.08		3.57
NH_3	134	3.54			3.42
H_2S	243	6.42		4.23	7.40
HCl	178	4.70		3.68	6.40
CH_4	176	4.65		2.84	4.08
C_2H_2	224	5.92	4.98		5.16
C_2H_4	252	6.66		4.17	6.16
C_2H_6	316	8.35		4.91	7.15
C_3H_6	368	9.73		6.20	9.24
Cyclo-C_3H_6	408	10.8			9.24
C_3H_8	420	11.1		6.85	10.2
i-C_4H_8	488	12.9		8.37	12.3
i-C_4H_{10}	545	14.4			13.3
n-C_4H_{10}	532	14.1		8.91	13.3
i-C_5H_{10}	664	17.5		10.1	15.4
Cyclo-C_5H_{10}	654	17.3			15.4
n-C_5H_{12}	703	18.6		11.1	16.4
i-C_5H_{12}	682	18.0			16.4
neo-C_5H_{12}	643	16.9			16.4
C_6H_6	639	16.9		10.8	15.5
Cyclo-C_6H_{12}	894	23.6		11.5	18.5
n-C_6H_{14}	845	22.3		12.8	19.5
CH_3Cl	357	9.44		5.26	9.48
C_2H_5Cl	456	12.1			12.6

We wished to compare the O. and S. calculated values with our experimental values, but since O. and S. express their calculated values in the same relative units used for their experimental values, a conversion of the calculated values to our units of cm.² was required. In essence the conversion involves the choice of a base for the relative quantities. Many choices are possible, and we think it best to base the values on hydrogen atom. Taking 1.01×10^{-16} cm.² from Massey and Burhop as the correct ionization cross section for H_2 and assuming the postulate of additivity of atomic cross sections, the cross section for H atom is to a satisfactory approximation 0.50×10^{-16} cm.². Since in the relative calculated atomic cross sections tabulated by O. and S. (O. and S., Table II) the H atom is given a value of 1.00, calculated atomic cross sections in cm.² can be obtained from the O. and S. values simply by dividing by 2×10^{16} cm.$^{-2}$. When this is done and the additivity postulate applied, the values given in Table I, column VI are obtained.

By comparing columns III, V and VI of Table I it may be seen that for the inorganic substances there is generally poor agreement between the cal-

---

(4) Simple average of the values obtained by different experimental methods.

culated values and both sets of experimental values, and for the hydrocarbons the calculated values agree moderately well with our experimental values but disagree with the O. and S. experimental values.

Thus we are faced with the apparently paradoxical situation that a seemingly trivial change in the base for the calculated values brings about a drastic change in the agreement with two sets of differing experimental values. Because of this paradox we have examined the seeming agreement between the O. and S. calculated and experimental values more closely, and we have come to the opinion that it is the consequence of compensating errors. Let us examine the calculated atomic cross sections. In Table II we list the ratios of the calculated and experimental cross sections of the rare gases, nitrogen atom and oxygen atom to the cross section of H_2. The experimental values are the averages of the available values from O. and S., Massey and Burhop, and our work. The experimental values for O and N are calculated from the values for O_2 and N_2 assuming additivity of atomic cross sections. The same assumption is made in obtaining the calculated value for H_2. It is clear from the table that the calculated values do not agree well with the experimental values when the elements being compared differ appreciably in atomic number. The more or less equal deviations found for O, N and Ne, on the one hand, and for A, Kr and Xe on the other lead one to think that under certain circumstances relative calculated values might be approximately correct, but on the whole these data do not support the unqualified contention of O. and S. that their calculation gives atomic ionization cross sections to a good approximation. More specifically for the problem at hand, there can be no question that relative to argon the calculated hydrogen cross-section is erroneously low.

TABLE II

RATIOS OF CALCULATED AND EXPERIMENTAL IONIZATION CROSS SECTIONS

X_1/X_2	$Q_i(X_1)/Q_i(X_2)$ Exptl. (aver.)	$Q_i(X_1)/Q_i(X_2)$ Calcd. (O. and S.)	Difference, % (calcd. − exptl.)
He/H_2	0.330	0.347	5.2
Ne/H_2	0.602	0.875	45
A/H_2	3.42	5.45	59
Kr/H_2	5.14	8.70	73
Xe/H_2	7.09	12.1	70
N/H_2	1.34	1.92	43
O/H_2	1.25	1.65	32
CH_4/A	0.807,[a] 1.32[b]	0.749	7.2,[a] −43[b]

[a] O. and S. [b] This work.

Table II also contains the cross section ratios for argon and methane, which can be taken as representative of all the hydrocarbons studied. A considerable discrepancy exists between the O. and S. experimental ratio and ours, and if our value be taken as correct, we may say that the O. and S. experimental cross section for methane (and the hydrocarbons in general) relative to argon is erroneously low by about 40%. This error will cancel to a considerable extent the erroneously high calculated cross section of argon relative to hydrogen and produce the seeming good agreement found by O. and S. Since this good agreement is indeed false, it does not militate against our experimental values.

It is of interest now to examine the postulate of the additivity of atomic ionization cross sections. In Table III we give cross sections for O, N, C and Cl calculated by means of the additivity postulate from our experimental cross sections for various molecules. To obtain these values a cross section of 0.50×10^{-16} cm.^{2} was assumed for H atom. Also included in Table III are the theoretically calculated cross sections for the various atoms. The tabulated values do not show the constancy to be expected if the cross sections were additive, except when compounds of a very similar type are considered. Thus the additivity concept does apply to the hydrocarbons, for the atomic carbon cross sections calculated from the 18 hydrocarbons studied in this work exhibited an average deviation from average of only 6% and a maximum–minimum spread of 0.75×10^{-16} cm.^{2} or 30%. Similarly, CO and CO_2 have the same atomic carbon cross section. However, we are forced to the conclusion that our data do not support an unqualified postulate of atomic cross section additivity.

TABLE III

ATOMIC IONIZATION CROSS SECTIONS (CM.^{2} × 10^{16}) FROM ADDITIVITY RULE

Compound	Q_i(O)	Compound	Q_i(C)
Calcd.	1.65	Calcd.	2.08
O_2	1.26	C_nH_m[b]	2.47 ± 0.16
H_2O	0.98	CO	1.73[a]
		CO_2	1.79[a]
	Q_i(N)		Q_i(Cl)
Calcd.	1.92	Calcd.	5.90
N_2	1.44	HCl	4.20
NH_3	0.83	CH_3Cl	5.47[c]
NO	1.78[a]	C_2H_5Cl	4.66[c]

[a] Taking $Q_i(O) = 1.26$. [b] Represents the 18 hydrocarbons studied. [c] Taking $Q_i(C) = 2.47$.

Attention also should be directed to the lack of agreement between the experimental and calculated cross sections given in Table III. In this regard, it must be remembered that the theoretical calculation of atomic cross sections involves the assumption that the additivity concept is valid for the calculation of the H atom cross section from that of H_2. The lack of agreement between theoretically calculated and experimental values discussed in the preceding paragraphs may be caused by failure of the additivity concept.

It is probably possible to calculate approximate cross sections for organic molecules using the additivity postulate, particularly if the cross sections of the carbon and hydrogen in the molecule might be expected to constitute a major portion of the total cross section. In making such calculations we would be inclined to use wherever possible experimental atomic cross sections such as those given in Table III.

By chance we plotted our experimental ionization cross sections against the polarizabilities of the various substances as taken from Landolt-

Börnstein,[5] and we find that a linear relationship exists between these quantities, as is shown in Fig. 2. This relationship can be rationalized theoretically as follows. From Slater[6] we write for the static polarizability of an atom

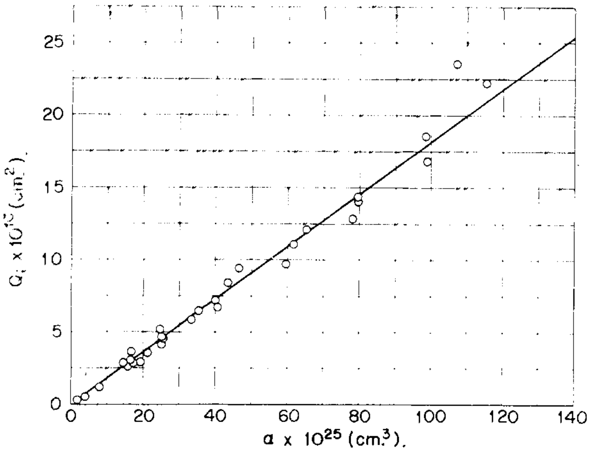

Fig. 2.—Total ionization cross section *vs.* polarizability.

$$\alpha = \frac{2}{h} \sum_{a} \frac{|M_{ao}|^2}{\nu_{ao}^8} \qquad (1)$$

where $|M_{ao}|$ is the aoth element of the dipole moment matrix and ν_{ao} is the frequency corresponding to the transition between the states o (ground state) and a. An approximate expression for atomic ionization cross sections is[7]

$$Q^{i}_{nl} = \frac{2\pi e^4}{mv^2} \frac{c_{nl}}{|E_{nl}|} Z_{nl} \log \left(\frac{2mv^2}{C_{nl}}\right) \qquad (2a)$$

$$c_{nl} = (Z^2_{eff}/n^2a_0^2) \int |X_{nl,K}|^2 dK \qquad (2b)$$

where the integration in equation 2b is carried out over the appropriate portion of the ionization continuum. The matrix element $|X_{nl,K}|$ will be proportional to the corresponding dipole moment matrix element $|M_{nl,K}|$, and to the extent that the variation in $\Sigma_a(M_{ao}^2/\nu_{ao})$ parallels that in $c_{nl}/|E_{nl}|$ in going from one atom to another, a linear relationship between polarizability and cross section should be observed. We expect that analogous expressions apply to molecules.

The empirical equation for the line in Fig. 2 is $Q_i = (1.80 \times 10^8)\alpha$ where Q_i is in cm.^{2} and α in cm.^{3}. The average deviation of the experimental cross sections plotted in Fig. 2 (30 compounds) from those calculated from the above equation is 8%. Thus this equation offers a means of estimating the cross section of a substance if its polarizability is known. Unlike the situation with the additivity concept, our data indicate that no restriction of similarity of compound type need be placed on this correlation.

Acknowledgment.—We wish to express our appreciation to Mr. B. L. Clark for carrying out the experimental work reported in this paper.

(5) Landolt-Börnstein, "Zahlenwerte und Functionen," 6 Auflage, "Atom und Molecularphysik," 3 Teil, Springer-Verlag, Berlin, 1950, pp. 510–517.

(6) J. C. Slater, "Quantum Theory of Matter," McGraw-Hill Book Co., Inc., New York, N. Y., 1951, pp. 388–396.

(7) N. F. Mott and H. S. W. Massey, "The Theory of Atomic Collisions," Oxford University Press, London, 1949, p. 247.

BAYTOWN, TEXAS

[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT DIVISION, HUMBLE OIL AND REFINING COMPANY]

Reactions of Gaseous Ions. IV. Water

BY F. W. LAMPE, F. H. FIELD AND J. L. FRANKLIN

RECEIVED MAY 27, 1957

The gas phase reactions of H_2O and D_2O with H_2O, D_2O, CH_4 and H_2 have been investigated and the specific reaction rates and cross sections measured. Relative cross sections of the reactions of D_2O with C_2H_6, C_3H_8, cyclo-C_3H_6, and *n*-C_4H_{10} have been measured. The ionic reactants in the ethane and propane systems are $C_2H_6^+$ and $C_3H_8^+$, respectively; water ion is the ionic reactant in all other systems (ionic reactant in the methane systems not known). The reaction cross sections are compared with those predicted from the polarizability theory of ion–molecule reactions, and it is concluded that the theory does not account satisfactorily for the values observed. The significance of the experimental results to the radiation chemistry of water is discussed.

Introduction

As a continuation of investigations[1,2] into the reactions of gaseous ions, we report in this paper the results of detailed studies of ionic reactions of water with water, hydrogen and methane. Also, we present the results of briefer studies of the reactions and relative rates involved in the formation of gaseous hydronium ion from water and water, hydrogen, methane, ethane, propane, cyclopropane and *n*-butane.

The possibility that the formation of H_3O^+ in the ionization chamber of a mass spectrometer was due to a secondary process was first recognized by Mann, Hustrulid and Tate.[3] Tal'roze and Lyubimova[4] reported the H_3O^+ ion to be formed by the reaction between the water molecule-ion and water and methane, but they presented no quantitative results such as specific reaction rates or reaction cross sections. In recent work directed toward obtaining the proton affinity of water, Tal'roze and Frankevich[5] have studied the formation of H_3O^+ in water and in mixtures of water and NH_3, H_2S, C_2H_2 and C_3H_8. No rate data are given.

(1) F. H. Field, J. L. Franklin and F. W. Lampe, THIS JOURNAL, **79**, 2419 (1957).

(2) F. H. Field, J. L. Franklin and F. W. Lampe, *ibid.*, **79**, 2665 (1957).

(3) M. M. Mann, A. Hustrulid and J. T. Tate, *Phys. Rev.*, **58**, 340 (1940).

(4) V. L. Tal'roze and A. K. Lyubimova, *Doklady Akad. Nauk S.S.S.R.*, **86**, 909 (1952).

(5) V. L. Tal'roze and E. L. Frankevich, *ibid.*, **111**, 376 (1956).