CH_3 + isooctane $\longrightarrow$ CH_4 + isooctyl radical k_1

CH_3 + olefin $\longrightarrow$ olefin·CH_3 k_2

k_1 is a constant at constant temperature, while k_2 depends on the nature of the investigated olefin. Thus k_2/k_1 measures the relative rate of addition of methyl radicals.

Table I lists the obtained values (each an average of 4–10 experiments) of k_2/k_1. The plots of log (k_2/k_1) against the reciprocals of temperature give excellent straight lines from which the following values for the activation energies $E_2 - E_1$ and temperature independent factors A_2/A_1 were obtained.

Ethylene $E_2 - E_1 = -0.6$ kcal./mole $A_2/A_1 = 13.0$

Tetrafluoroethylene $E_2 - E_1 = -2.8$ kcal./mole $A_2/A_1 = 5.3$

The reactivity of tetrachloroethylene is too low to determine the activation energy with any reasonable accuracy.

We conclude that the reactivity of tetrafluoroethylene is approximately ten times greater than that of ethylene, while tetrachloroethylene is unreactive. The higher reactivity of tetrafluoroethylene is shown to result from the lower activation energy of the addition reaction (as compared with ethylene), while the A_2/A_1 factor is lower for the reaction involving tetrafluoroethylene than that for ethylene. The methyl affinity of ethylene is comparable to that of vinylacetate, is approximately 80 times greater than that of benzene and $^1/_{25}$ as large as that of styrene.

TABLE I

Compound	T, °C.	k_2/k_1
Ethylene	54.7	37.3 ± 0.6
Ethylene	64.9	34.1 ± 2.2
Ethylene	74.8	34.6 ± 0.6
Ethylene	85.2	35.5 ± 1.5
Tetrafluoroethylene	54.7	400 ± 7
Tetrafluoroethylene	64.9	342 ± 14
Tetrafluoroethylene	74.8	307 ± 8
Tetrafluoroethylene	85.2	273 ± 8
Tetrachloroethylene	64.9	<0.3

The course of the addition of a radical to an aromatic or olefinic compound was discussed previously.[1,2,3,5] It was pointed out that the transition state is determined by the crossing of the repulsion and attraction curves. The former represents an interaction between the "normal," non-excited molecule and the radical, and the latter shows an interaction between the excited molecule (say in its triplet state or an "electron localized" state) and the radical (see Fig. 1). The repulsion curve results probably from the coulombic force acting between the negative cloud of π electrons of the olefinic or aromatic compound and the negative cloud of the p electron of the approaching radical. If so, electron withdrawing groups should weaken the repulsion and flatten the repulsion curve (A in Fig. 1) while electron donating groups should strengthen the repulsion and make the curve steeper (C in Fig. 1). Hence, the activation energy of the addition process should decrease in the first case and increase in the second, this in turn increasing the methyl affinity in the former case and decreasing it in the latter. Such changes in the methyl affinities were observed in studies of reactions of substituted quinones.[6] However, studies of methyl affinities of ethylene and tetrafluoroethylene show clearly that this effect is indeed due to a decrease in the activation energy of the process.

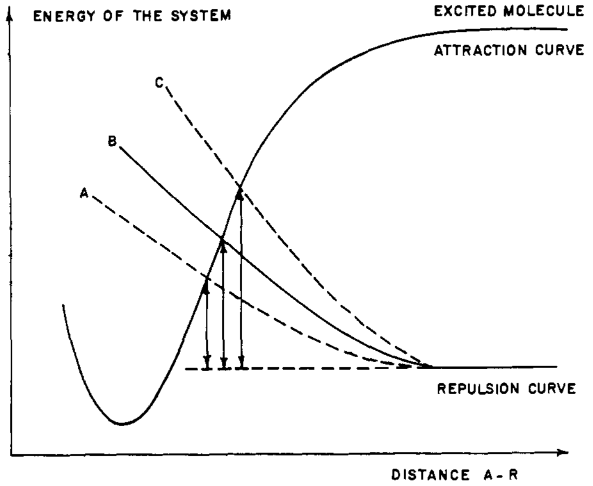

Fig. 1.

It was shown[6] that the substitution of *all* the reacting positions by bulky chlorine atoms hinders the addition reaction (steric hindrance). This is observed also in the case of tetrachloroethylene. The difference in the behavior of small fluorine atoms and bulky chlorine atoms is spectacular.

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(5) M. Szwarc, *J. Chem. Phys.*, **23**, 204 (1955).

(6) A. Rembaum and M. Szwarc, THIS JOURNAL, **77**, 4468 (1955).

GAS PHASE IONIC REACTIONS. METHANE AND ETHYLENE

Sir:

We have measured rate constants and reaction cross sections for ionic reactions occurring in methane and ethylene in the ion source of a mass spectrometer. Recently Stevenson and Schissler[1] have reported similar measurements. A portion of our results is given in Table I. The rates depend upon the electric field strength in the mass spectrometer ionization chamber (*i.e.*, on the ion velocity), and the values given in the table are for a field strength of 10 v./cm. Table II shows a typical variation of the reaction rate constants and cross sections with field strength.

These constants and cross sections refer to exceedingly fast reactions. By way of comparison, the collision cross sections for methane and ethylene are[2] 12.3 × 10^{-16} cm.^{2} and 17.1 × 10^{-16} cm.^{2}, respectively. Such very fast reactions will obviously be of importance in any process wherein ions are likely to be formed as, for example, in radiation chemistry processes. It is of interest, then, to at-

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(1) D. P. Stevenson and D. P. Schissler, *J. Chem. Phys.*, **23**, 1353 (1955); D. O. Schissler and D. P. Stevenson, *ibid.*, **24**, 926 (1956).

(2) Landolt-Börnstein, "Zahlenwerte und Functionen," 6 Auflage, Atom- und Molekularphysik, 1 Teil, Springer Verlag, Berlin, 1950, p. 370.

tempt to come to a better theoretical understanding of these reactions. We have used an approach similar to that introduced by Eyring, Hirschfelder, and Taylor,[3] assuming the reaction cross section to be determined by the distance at which the centrifugal force tending to separate the ion and the molecule is exactly counterbalanced by the polarization force between the ion and the molecule. The rotational energy arises from the translational energy of the ion and the molecule, and the rotation is treated classically. We obtain

$$\sigma = \frac{e\pi\sqrt{2\alpha}}{\sqrt{6kT + \frac{eVd_0}{2} + \left(\frac{\beta kTeVd_0}{2}\right)^{1/2}}} \qquad (1)$$

where

σ = reaction cross section
e = electronic charge
α = polarizability of molecule
V = ionization chamber field strength
d_0 = distance from electron beam to ion exit slit

Cross sections at 10 v./cm. calculated from Equation 1 are tabulated in Table I, and the values for reaction 2 as a function of field strength are shown in Table II. The agreement is quite satisfactory. While there are some detailed differences between the theoretical and experimental values, we believe that the theoretical treatment is essentially valid and that the dominant factor in determining the cross sections for ion-molecule reactions is the polarization interaction.

TABLE I

Reaction	$k \times 10^{10}$ cm.^{3}/molecule sec.	$\sigma \times 10^{16}$, cm.^{2} at V = 10 v./cm. Experimental	Theoretical
$CH_4^+ + CH_4 \rightarrow CH_5^+ + CH_3$	5.8	39	34
$CH_3^+ + CH_4 \rightarrow C_2H_5^+ + H_2$	5.6	39	34
$C_2H_3^+ + C_2H_4 \rightarrow C_2H_5^+ + C_2H_2$	2.3[a]		
$C_2H_2^+ + C_2H_4 \rightarrow C_3H_3^+ + CH_3$	2.1		
$C_2H_2^+ + C_2H_4 \rightarrow C_4H_5^+ + H$	1.3		
$C_2H_2^+ + C_2H_4 \rightarrow [C_4H_6^+]$	3.4	30	43
$C_2H_4^+ + C_2H_4 \rightarrow C_3H_5^+ + CH_3$	3.9		
$C_2H_4^+ + C_2H_4 \rightarrow C_4H_7^+ + H$	0.4		
$C_2H_4^+ + C_2H_4 \rightarrow [C_4H_8^+]$	4.3	41	43
$C_2^+ + C_2H_4 \rightarrow C_4H_2^+ + H_2$	9.2	81	43
$C_2H^+ + C_2H_4 \rightarrow C_4H_3^+ + H_2$	3.3	29	43

[a] Value quite uncertain.

TABLE II

Field strength (volts/cm.)	$k_2 \times 10^{10}$	σ_2(obs.) $\times 10^{16}$	σ_2(calcd.) $\times 10^{16}$
2	3.0	31	46
6	4.9	38	39
8	5.3	39	36
10	5.6	39	34
20	5.6	30	28
40	4.6	18	22
60	3.4	11	18
100	2.2	5	15

The rate constants or cross sections for thermal speed ions, which are of particular interest, may be obtained from Equation 1 for $V = 0$ and the equation $k = \sigma\bar{\xi}$ where $\bar{\xi}$ is the average relative velocity of the components of the reaction. Evaluating $\bar{\xi}$ in the usual way gives

$$k = e\pi\alpha^{1/2}\left(\frac{3m_\beta + m_\alpha}{3m_\beta\, m_\alpha{}^{1/2}}\right) \qquad (2)$$

where m_α and m_β are the masses of the faster and slower components respectively. The rate constant expression developed by Eyring, Hirschfelder, and Taylor[3] is

$$k = 2\pi Ke\alpha^{1/2}\left(\frac{m_\alpha + m_\beta}{m_\alpha m_\beta}\right)^{1/2} \qquad (3)$$

This differs from Equation 2 by only a factor of two. Rate constants and cross sections for thermal reactions calculated from Equations 2 and 3 are given in Table III.

TABLE III

Reaction	σ calcd. $\times 10^{16}$, cm.^{2}	k thermal $\times 10^{10}$, cm.^{3}/molecule sec. From Eq. 2	From Eq. 3
$CH_4^+ + CH_4 \rightarrow CH_5^+ + CH_3$	58	6.2	11.2
$CH_3^+ + CH_4 \rightarrow C_2H_5^+ + H_2$	58	6.3	11.4
$C_2H_4^+ + C_2H_4 \rightarrow [C_4H_8^+]$	73	5.9	12.8
$C_2H_2^+ + C_2H_4 \rightarrow [C_4H_6^+]$	73	6.1	13.0
$C_2H^+ + C_2H_4 \rightarrow C_4H_3^+ + H_2$	73	6.1	13.1
$C_2^+ + C_2H_4 \rightarrow C_4H_2^+ + H_2$	73	6.2	13.3

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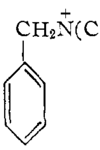
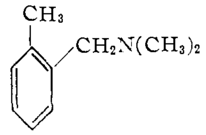
ALICYCLIC AMINE FROM REARRANGEMENT OF 2,4,6-TRIMETHYLBENZYLTRIMETHYLAMMONIUM ION AND ITS RECONVERSION TO AROMATIC SYSTEM[1]

Sir:

It has been shown previously[2] that, whereas the benzyltrimethylammonium ion (I) undergoes the *ortho* substitution rearrangement to form tertiary amine II on treatment with sodium amide followed by acid, the 2,4,6-trimethylbenzyltrimethylammonium ion (III), in which the *ortho* positions are blocked, is converted to isodurene (IV) under similar conditions.



I



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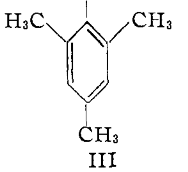
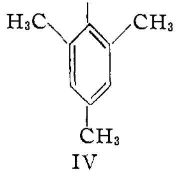


III



IV

A further study has now revealed that the latter reaction undergoes the first phase of the *ortho* substitution rearrangement to form alicyclic amine (V)

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[3] H. Eyring, J. O. Hirschfelder and H. S. Taylor, *J. Chem. Phys.*, **4**, 479 (1936). See also Glasstone, Laidler and Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, pp. 220 ff.

[1] Supported in part by the National Science Foundation.

[2] S. W. Kantor and C. R. Hauser, THIS JOURNAL, **73**, 4122 (1951).