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

The Energy Dependence for Reaction Cross Sections of Ion-molecule Reactions of Cyclopropane in the Mass Spectrometer[1]

BY ROSWELL F. POTTIE, ANDRÉE J. LORQUET AND WILLIAM H. HAMILL

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Appearance potentials of the important primary ions, and of 14 secondary ions, have been measured for cyclopropane. The dependence of secondary ion reaction cross sections upon ion velocity show discontinuities which can be described by analytical expressions allowing for head-on collisions and upper energy limits of secondary ion stability.

Introduction

Recent work in this Laboratory[2] has shown, for certain ion-molecule reactions involving neopentane, that the familiar inverse dependence of reaction cross section upon ion velocity should not apply under certain conditions. Reactions of many hydrocarbon ions with cyclopropane have proven to be particularly suitable to study these effects.

Experimental

Material.—Cyclopropane was introduced into a sample bulb and degassed several times before use.

Apparatus.—The preliminary measurements were performed with a CEC model 21-103A mass spectrometer, which is described elsewhere.[2] For the experiments reported here, the normal amplifying and recording systems of the mass spectrometer were replaced by a Cary Vibrating Reed Electrometer Model 30, modified for critical damping, and a Sargent Recorder Model MR.

TABLE I

APPEARANCE POTENTIALS OF PRIMARY AND SECONDARY IONS FROM CYCLOPROPANE

m/e	Rel. intensity[a]	Linear extrap., e.v.	Van. cur. (value used), e.v.
42^+	100.0	10.2	10.2
41^+	91.9	12.2	12.0
40^+	30.0	12.7	12.4
39^+	74.4	15.4(16.6)[b]	14.4
38^+	14.7	21.7	16.4
37^+	10.9	24.4	19.4
27^+	31.6	15.4	13.6
26^+	12.8	17.3(19.7; 21.6)[b]	14.6
15^+	3.8	19.6	17.0
14^+	6.1	21.8	18.8
13^+	1.9	25.9	23.3
50^+	20.4	22.8(24.9)[b]	17.5
51^+	49.0	19.7(21.4; 24.2)[b]	19.0
52^+	38.3	18.6(19.7; 22.7)[b]	17.2 or 14.2
53^+	78.9	15.0(15.6)[b]	14.5
54^+	24.9	12.4	12.3
55^+	100.0	11.7	11.6
56^+	61.8	10.2	10.2
65^+	5.6	17.4	15.1
66^+	3.7	15.7(16.5)[b]	14.7 or 14.5
67^+	15.8	12.4	11.8
69^+	4.8	10.2	10.1
77^+	6.4	15.7(17.1)[b]	14.7
79^+	3.2	15.7	13.9
81^+	2.8	12.3	. .

[a] At an electric field 4 v.cm.$^{-1}$ and an ionizing voltage 70 v. [b] These values refer to higher breaks in the ionization efficiency curve.

Results

The appearance potentials of all significant primary ions from cyclopropane have been determined and are reproduced in Table I together with the relative abundances of the same ions.

TABLE II

ION-MOLECULE REACTION OF CYCLOPROPANE

Reaction	ΔH (kcal./mole) reaction	$Q \times 10^{16}$ (cm.^{2}) at 2.8 v./cm.	$Q \times 10^{16}$ (cm.^{2}) at 12 v./cm.
$C_3H_3^+ + C_3H_6 \longrightarrow C_4H_5^+ + C_2H_4$	−18.5 or −1.5	58	20
$C_3H_4^+ + C_3H_6 \longrightarrow C_4H_6^+ + C_2H_4$	−53.5	48	12.5
$C_3H_5^+ + C_3H_6 \longrightarrow C_4H_7^+ + C_2H_4$	−36.5	75	17.9
$C_3H_6^+ + C_3H_6 \longrightarrow C_4H_8^+ + C_2H_4$	−31.5	45	10.7
$C_3H_3^+ + C_3H_6 \longrightarrow C_5H_5^+ + CH_4$	−91	3.1	1.2
$C_3H_3^+ + C_3H_6 \longrightarrow C_5H_6^+ + CH_3$	−36	2.4	0.8
$C_3H_5^+ + C_3H_6 \longrightarrow C_5H_7^+ + CH_4$	−54	9.3	2.5
$C_3H_6^+ + C_3H_6 \longrightarrow C_5H_9^+ + CH_3$	−24	2.6	0.7
$C_3H_3^+ + C_3H_6 \longrightarrow C_6H_5^+ + 2H_2$	0	7.0	2.1
$C_3H_5^+ + C_3H_6 \longrightarrow C_6H_9^+ + H_2$	. . .[b]	2.6	0.6
$C_3H_3^+ + C_3H_6 \longrightarrow C_6H_7^+ + H_2$	−64	4.3[a]	1.0[a]
$C_3H_2^+ + C_3H_6 \longrightarrow C_4H_4^+ + C_2H_4$ or $C_2H_2^+ + C_3H_6 \longrightarrow C_4H_4^+ + CH_4$	−37.5 −81 or −45	117 135	53.5 64.4
$C_3H^+ + C_3H_6 \longrightarrow C_4H_3^+ + C_2H_4$	−73	178	98
$C_3H_2^+ + C_3H_6 \longrightarrow C_4H_2^+ + C_2H_6$	−34	107	49

[a] At mass 79 there is an impurity and the cross section of that reaction is smaller than the indicated value. [b] No data are available for the heats of formation of one of the ions. [c] In the calculation of ΔH reaction, the value for ΔH_f (C_3H^+) was based on $A(C_3H^+)$ = 19.4 ev. from Table I.[3] If the value $A(C_3H^+)$ = 15.0 e.v. (from ref. 2) is used, then ΔH reaction = + 29 kcal.

All appearance potentials A have been referred to the ion m/e = 42 on the basis: A ($C_3H_6^+$) = 10.2 e.v.[3] These values were determined using both the vanishing current method of Warren[4] and the linear extrapolation method. For all ions which exhibited a second order pressure dependence, the corresponding results are also summarized in Table I. The primary ion-secondary ion correlations are listed in Table II. The first eleven reactions seem well established, with one exception. There is good agreement between the values of appearance potentials of primary and secondary ions; these reactions are not endothermic and the values of their cross sections are compatible with the ion-induced dipole force law. In the case of secondary ions at m/e 50, 51 and 52, the tentative assignments must be presumed dubious because of the large cross sections. The dependence of reaction cross section upon ion energy E has been examined for ten of these

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[1] Supported in part under USAEC contract AT(11-1)-38.

[2] N. Boelrijk and W. H. Hamill, *J. Am. Chem. Soc.*, in press (1960).

[3] F. H. Field, *J. Chem. Phys.*, **20**, 1734 (1952).

[4] J. W. Warren, *Nature*, **165**, 811 (1950).

TABLE III

SUMMARY OF RESULTS AND COMPARISON OF OBSERVED WITH PREDICTED PARAMETERS

Primary and corresponding secondary ions	$E_{t, \text{obsd.}}$, e.v.	$E_{c, \text{obsd.}}$, e.v.	$P_L\sigma_L$, Å.² e.v.$^{1/2}$	$P_L\sigma_K$, Å.²	$P_K\sigma_K$, Å.²	Slope of the middle segment Obsd.	Slope of the middle segment Pred.	Slope of the segment at high energy Obsd.	Slope of the segment at high energy Pred.	σ_L calcd., Å.² e.v.$^{1/2}$	σ_K obsd.[a] Å.²
$56^+/42^+$	0.4	1.4	33.9	70.5	1.5	14.7	14.5	16.4	16.6	57.5	91.3
$55^+/41^+$	.45	2.5	54.1	110.0	3	23.4	23.0	32.2	30.5	57.1	85.2
$54^+/40^+$	.5	1.6	29.4	52.5	2	16.2	15.5	19.9	18.7	56.8	80.0
$53^+/39^+$	.5	2.0	27.5	41.5	8	18.8	18.2	35.4	34.2	56.3	79.3
$69^+/42^+$	.6	1.75	1.38	2.2	0.15	0.80	0.83	1.04	1.09	57.5	73.7
$67^+/41^+$	.6	1.3	4.62	7.1	.7	2.92	2.95	3.86	3.86	57.1	73.2
$81^+/41^+$	.4	1.4	3.0	7.7	.2	0.70	0.70	1.00	0.98	57.1	90.6
$77^+/39^+$	.45	1.75	5.1	10.7	.65	2.15	1.97	3.15	3.11	56.3	84.0
$65^+/39^+$	.48	1.8	1.46	2.55	.7	0.83	0.83	1.84	2.09	56.3	80.4
$66^+/39^+$	.45	1.4	1.18	1.85	.28	0.80	0.74	1.23	1.13	56.3	84.0

[a] The calculated σ_K from van der Waals radii is estimated at 51 Å.² in all cases. [b] σ_L calcd. is calculated from equation 2.

secondary ions and representative results for two of them appear in Figs. 1 and 2.

It is impossible to reconcile our appearance potentials for primary ions at *m/e* 26, 37, 38 with those reported by Field.[3] The corresponding ionization efficiency curves have abnormally long tails, rendering precise evaluation difficult or impossible. The assignment of primary 26-, 37-, and 38-ions to the secondary 50-, 51- and 52-ions depended both upon correspondence of appearance potentials and of the shapes of the ionization efficiency curves. The discussion of the phenomena illustrated which follows does not depend upon the uncertainties of assignments in Table II.

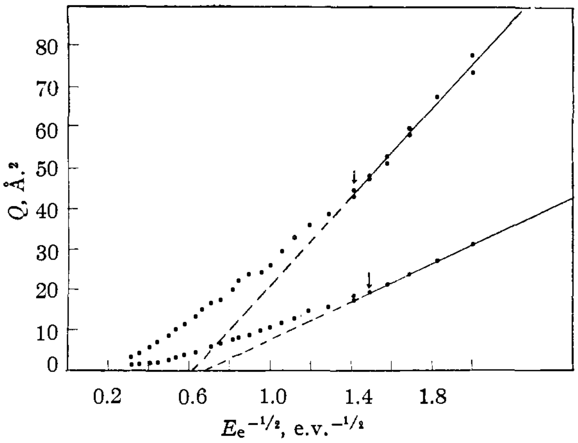

Fig. 1.—Reaction cross section as a function of $E_e^{1/2}$ for the secondary ions $C_4H_5^+$ (upper) and $C_5H_6^+$ (lower), for which the Q-scale is one-tenth that of the first. The arrows designate estimated E_t.

Discussion

Other measurements have indicated the advantages of describing the microscopic reaction cross section $\sigma(E)$ by the equation[2]

$$\sigma(E) = P_L(\sigma_L E^{-1/2} - \sigma_K) + P_K\sigma_K \quad (1)$$

where

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

in terms of ion energy E, ion mass m_1, molecular mass m_2, molecular polarizability α, collision cross section σ_K and reaction efficiencies P_L and P_K. That is, we modify the point particle description of Gioumousis and Stevenson[5] by including billiard-ball collisions. The phenomenological cross section Q at low ion energy, *viz.* $E < (\sigma_L/\sigma_K)^2$, follows by integrating equation 1 over the range $E = 0$ to $E = E_e$

$$Q = 2P_L\sigma_L E_e^{-1/2} + \sigma_K(P_L - P_K) \quad (3)$$

where E_e is the ion energy at the exit slit. The upper linear segments of the curves in Fig. 1 illustrate this dependence.

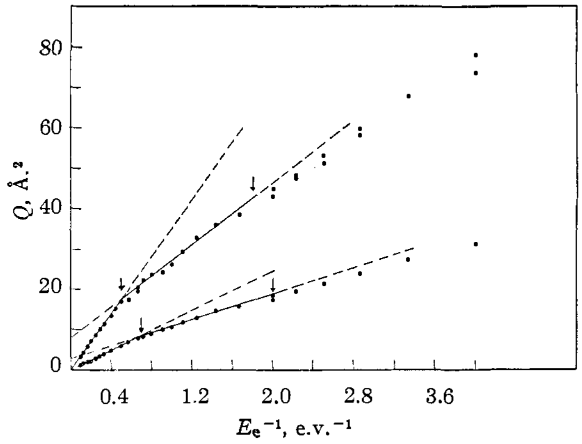

Fig. 2.—Reaction cross sections as a function E_e^{-1} for $C_4H_5^+$ (upper) and $C_5H_6^+$ (lower). Arrows designate E_t and E_c.

Departure from equation 3 occurs for $E_e > (\sigma_L/\sigma_K)^2$. The transitional energy E_t is indicated by arrows in Fig. 1 and for the succeeding energy interval one obtains

$$Q = [2P_L\sigma_L E_t^{1/2} - P_L\sigma_K E_t]E_e^{-1} + P_K\sigma_K \quad (4)$$

as the integral of equation 1. The linear segments between arrows in Fig. 2 correspond to this description. At sufficiently high primary ion energy E_c we must expect that the secondary ion either becomes unstable or cannot form and

$$Q = [2P_L\sigma_L E_t^{1/2} - P_L\sigma_K E_t + P_K\sigma_K E_c]E_e^{-1} \quad (5)$$

The high energy components of Fig. 2 pass through the origin and can be accounted for by equation 5.

There are means to test the treatment. On the arbitrary basis of van der Waals radii for propylene, we estimate a value of the collision cross section σ_K. This may be compared with the value of σ_K from $E_t = (\sigma_L/\sigma_K)^2$ using the observed

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

value for E_t and the calculated value for σ_L. It is also possible, using the preceding equations, to predict the slope of the middle segment and of the segment at high energy (Fig. 1) from values of the parameters obtained from the observed value for the intercept of the middle segment (Fig. 1) and for the intercept and the slope of the segment at low energy (Fig. 2); these predicted slopes may be compared to those observed. The calculated and observed values for the ten ion-molecule reactions studied are summarized in Table III. The values for the slopes agree very well, while the observed cross section [$\sigma_{K,\ \text{obsd.}} = 82 \pm 9\text{Å.}^2$] is higher than the one estimated [$\sigma_{K.\ \text{calcd.}} = 51\text{Å.}^2$]. This disagreement is not very significant since the estimated value is highly arbitrary. It is significant that $\sigma_{K.\ \text{obsd}}$ is practically constant, as required for a common molecule and very similar primary ions, although values of Q vary greatly.

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The Free Radical, High Pressure Polymerization of Ethylenes. The Effects of Initiator Concentration, Monomer Concentration and Pressure on the Polymerization Rate[1]

BY ROBERT O. SYMCOX[2] AND PAUL EHRLICH

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The polymerization of ethylene, initiated by di-*t*-butyl peroxide, was studied in the presence of propane at 129° and at 750 to 2500 atm. The reaction is $^1/_2$ order over a more than 100 fold variation in initiator concentration and between first and second order in monomer. The logarithm of the polymerization rate and of the over-all rate constant are proportional to the pressure as in the polymerization of styrene. The pressure coefficient of the rate is smaller than that reported in other studies with ethylene. The difference is attributed to the fact that the present study was carried out under homogeneous conditions and that special care was taken to exclude oxygen. The application of the transition state theory to nonideal supercritical systems is discussed, and it is concluded that, to a first approximation, it should be possible to interpret the pressure coefficient of the polymerization rate in terms of a volume of activation which is found to equal −20 to −23 cc./mole. Using literature data for the rate of initiator decomposition, values of $k_p/k_t^{1/2}$ are found to be higher, but within about an order of magnitude of those reported near atmospheric pressure.

Introduction

There is general agreement that our understanding of the kinetics of the free radical high pressure polymerization of ethylene is rudimentary; indeed, kinetic data on gas phase reactions of non-ideal gases at high pressures are scarce. Consequently, no theory for the interpretation of the kinetics of such reactions has been firmly established. There has been some question, for instance, whether the transition state theory, as ordinarily employed to interpret the effect of pressure[3,4] on liquid phase polymerizations[5,6] can be extended to ethylene in a straightforward manner.[7]

It was the purpose of this work to study the free radical initiated polymerization of ethylene at pressures up to several thousand atmospheres and under conditions where a kinetic analysis could be attempted. In particular, it was desired to obtain values of the rate constants for propagation and termination ($k_p/k_t^{1/2}$) valid in the high pressure region and to determine and interpret the effect of pressure on this ratio.

A previous study carried out in this laboratory[8] had demonstrated that traces of oxygen, in the parts per million range, could affect strongly and sometimes dominate the kinetics, in particular the pressure coefficient of the polymerization rate. The initiating mechanism by oxygen was shown to be of the branching chain type and therefore complex and not describable by a single rate constant. In addition, evidence has accumulated recently that nonideality renders the monomer, although a gas, a solvent for the polymer, but that the mutual miscibility of the two components depends strongly on the pressure.[9] In order to determine the effect of pressure on the rate constants under conditions where a generalization of the results to gaseous systems at high pressures might be permissible, it seemed therefore necessary to meet at least the two following conditions: initiation of the polymerization at known and reproducible rates where co-initiation by oxygen was negligible and operation under single-phase conditions. This was apparently accomplished by initiating with di-*t*-butyl peroxide under rigid control of oxygen at a temperature where the initiation rate of the latter was not excessive and by addition of propane, a better solvent for polyethylene than its monomer.[9]

Experimental

Reactor and Preparation of Reaction Mixture.—The reactor design, principle of carrying out the rate measurements, and method of filling with ethylene and propane were essentially as described for pure ethylene[8,10]. The pres-

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(1) Presented in part at the 139th Meeting of the American Chemical Society, St. Louis, Missouri, March 1961.

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(3) M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, **31**, 857 (1935).

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(9) P. Ehrlich and E. B. Graham, *ibid.*, **45**, 246 (1960).

(10) P. Ehrlich, J. D. Cotman, Jr., and W. F. Yates, *ibid.*, **24**, 283 (1957).