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

Reactions of Gaseous Ions. VI. Hydride Ion Transfer Reactions

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Secondary ions of mass one unit less than those of the parent ions have been observed in C_2H_6, C_3H_8, n-C_4H_{10}, iso-C_4H_{10} neo-C_5H_{12}, neo-C_6H_{14} and mixtures of these compounds with CH_4. By means of appearance potential measurements it has been established that the reaction occurring in neopentane is a hydride ion transfer to the allyl ion, and it is inferred that the secondary ions observed from the other compounds are also formed by means of hydride ion transfer reactions. Approximate calculations of the reaction cross-sections are made, and the values obtained range from 264 Å.^{2} for ethane to 7 Å.^{2} for neohexane. No explanation can be advanced for the variation in the reaction cross-sections. It is tentatively postulated that the hydride ion transfer reaction is non-specific, *i.e.*, that it may be expected to occur with many different kinds of ions and many different kinds of molecules.

In this paper we report the results of our studies of gas phase hydride ion transfer reactions in several paraffin hydrocarbons. The reactions are observed to occur in the ionization chamber of a mass spectrometer. The hydrocarbons investigated were ethane, propane, n-butane, isobutane, neopentane and neohexane (2,2-dimethylbutane), both in the pure state and in mixtures with methane.

Experimental

The experiments were made in a Westinghouse Type LV mass spectrometer using techniques previously described.[1,2] The pertinent conditions in the ionization chamber were: electron current = 2.0 microamp.; ion repeller = 2.6 v., which corresponds to an ionization chamber field strength of 5.71 v./cm.; ion accelerating voltage = 600 v.; ionization chamber temperature = *ca.* 260°. Magnetic scanning was used. Pressures in the gas handling reservoir were measured with a mercury manometer. Phillips Research Grade hydrocarbons were condensed in liquid nitrogen and distilled, taking a center cut for the measurements. Appearance potential measurements were made using the vanishing current technique.

Results

Pure Compounds.—Secondary ions of mass one unit lower than the molecular weight of the compound studied have been observed in all the systems investigated. The phenomenon is most obvious and was first observed in neopentane because of the fact that the primary ions from neopentane containing five carbon atoms have a negligibly small intensity and consequently do not obscure any secondary ions which may be formed in this mass region. A plot of the ratio of the mass 71 intensity to the sum of the intensities of mass 71 and 41 against the neopentane pressure in the reservoir is given in Fig. 1. The increase observed in the ratio indicates very strongly that a secondary reaction is occurring. We think that the linearity to be observed over an appreciable pressure range is fortuitous and results from the cancellation of the upward curvature generally observed when ion current is plotted against reservoir pressure (as distinguished from ionization chamber concentration) and the downward curvature to be expected from differential scattering of ions of appreciably disparate masses. The latter factor is probably the cause of the low current ratio values observed at the three highest pressures. It might be mentioned that because of the divergence of the electron beam we have not been successful in determining the ionization chamber concentrations in our Westinghouse mass spectrometer, and all results in this paper are reported in terms of reservoir pressure.

To help with the identification of the reaction(s) producing the mass 71 secondary ion, we measured its appearance potential and the appearance potentials of the major primary ions from neopentane. The results are given in Table I.[3] The secondary ion appearance potential is for practical purposes identical with that of the mass 41 ion and the lower mass 15 appearance potential. However, the intensity of the mass 15 ions having the lower appearance potential is very small, and these ions could not give rise to observable secondary ions. Thus we conclude that the mass 41 ion constitutes a reactant ion, and the reaction occurring must almost certainly be

$$C_3H_5^+ + \text{neo-}C_5H_{12} \longrightarrow C_5H_{11}^+ + C_3H_6 \qquad (1)$$

Any reaction not involving the formation of propylene would be strongly endothermic and would not occur. The reaction as written may be considered to be a hydride ion transfer reaction.

TABLE I

APPEARANCE POTENTIALS OF IONS FROM NEOPENTANE

Mass	Ion	*A* (e.v.)	Type of ion
71	$C_5H_{11}^+$	13.15 ± 0.18	Secondary
57	$C_4H_9^+$	10.83 ± 0.07	Primary
41	$C_3H_5^+$	13.13 ± 0.05	Primary
39	$C_3H_3^+$	17.08 ± 0.22	Primary
29	$C_2H_5^+$	13.81 ± 0.09	Primary
27	$C_2H_3^+$	17.93 ± 0.09	Primary
15	CH_3^+	13.14 ± 0.14, 20.1 ± 0.2	Primary

Unfortunately, the heat of the reaction cannot be calculated exactly because of uncertainties concerning the structures and energies of both the reactant and product ion. If the reaction proceeds without rearrangement, the primary neopentyl ion is formed, but the energies of ions with primary structures are not known. If one assumes that rearrangement to t-pentyl ion occurs and if one takes the values of 220 and 152 kcal./mole which have been tabulated[4] for $\Delta H_f(C_3H_5^+)$ and ΔH-(t-$C_5H_{11}^+$), respectively, one calculates a value of

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

[2] F. W. Lampe, F. H. Field and J. L. Franklin, *ibid.*, **79**, 6132 (1957).

[3] A discussion of the primary ion values will be given in a forthcoming publication.

[4] F. H. Field and J. L. Franklin, "Electron Impact Phenomena and the Properties of Gaseous Ions," Academic Press, New York, N. Y., 1957.

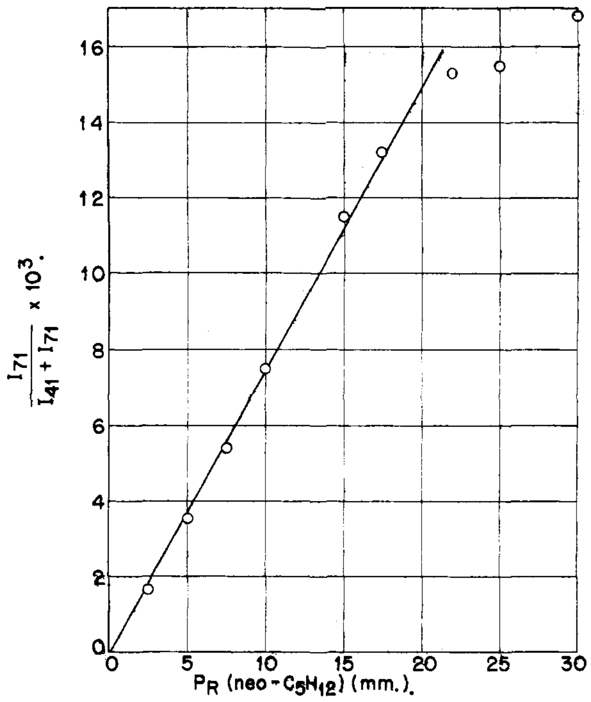

Fig. 1.—Hydride ion transfer in neopentane.

—23 kcal./mole for the heat of reaction, and the reaction is allowed on energetic grounds. Without taking the space here to go into details, we should mention that partially as a result of our measurement of the neopentane appearance potentials, we think it possible that the tabulated value of $\Delta H_f(t\text{-}C_5H_{11}^+)$ may be too low. If this is true, the heat of the hydride ion transfer reaction may be barely exothermic even with the assumption that rearrangement to the tertiary structure occurs, and the reaction in the absence of rearrangement will be energetically prohibited. However, the occurrence of rearrangement would be in keeping with the known structural mobility of ions, and we think that a hydride ion transfer reaction in neopentane is energetically allowed.

From the appearance potential measurements it may be considered as established that $C_3H_5^+$ ion undergoes the hydride ion transfer reaction with neopentane, but it is not established that other primary ions from neopentane with higher appearance potentials cannot undergo the reaction. The onset of the production of pentyl ions by reactions with such ions would result only in discontinuities in the pentyl ion ionization efficiency curve, and under the prevailing experimental conditions these would be undetectable. Indeed, in view of the simple nature of the reaction, we intuitively expect that it will occur with all ions containing an unoccupied valence orbital, provided that the energetics are favorable.

In this regard, it is of interest that since the appearance potential of the *t*-butyl ion from neopentane is appreciably lower (10.85 v.) than the secondary pentyl ion appearance potential (13.13 v.), *t*-butyl ion does not undergo the hydride ion transfer reaction with neopentane. The *t*-butyl ion is the most abundant ion in the neopentane mass spectrum, so the lack of reaction cannot be attributed to insufficient intensity. The most probable explanation is that the reaction is endothermic. From the tabulated[4] values of the heats of formation of $t\text{-}C_4H_9^+$ and $t\text{-}C_5H_{11}^+$, one calculates that the reaction is 6 kcal./mole exothermic, but we have already mentioned that we suspect the latter heat of formation with being low, and the use of a revised value based on our experimental appearance potentials leads to the result that the transfer reaction is 3 kcal./mole endothermic. An endothermicity of this magnitude would be quite sufficient to prevent the observation of the reaction in a mass spectrometer.

Secondary ions with mass one unit less than that of the molecule-ion (M) also have been observed with ethane, propane, *n*-butane, isobutane and neohexane (2,2-dimethylbutane). The mass spectrometer reservoir pressure (P_R) was varied from about 2 to 30 mm., and over this range the plots of I_{M-1}/I_M *vs.* P_R are generally linear at the lower pressures with a gentle upward curvature at the higher pressures. The initial slopes are listed in Table II. A typical plot of I_{M-1}/I_M *vs.* P_R is given (for ethane) in Fig. 2.

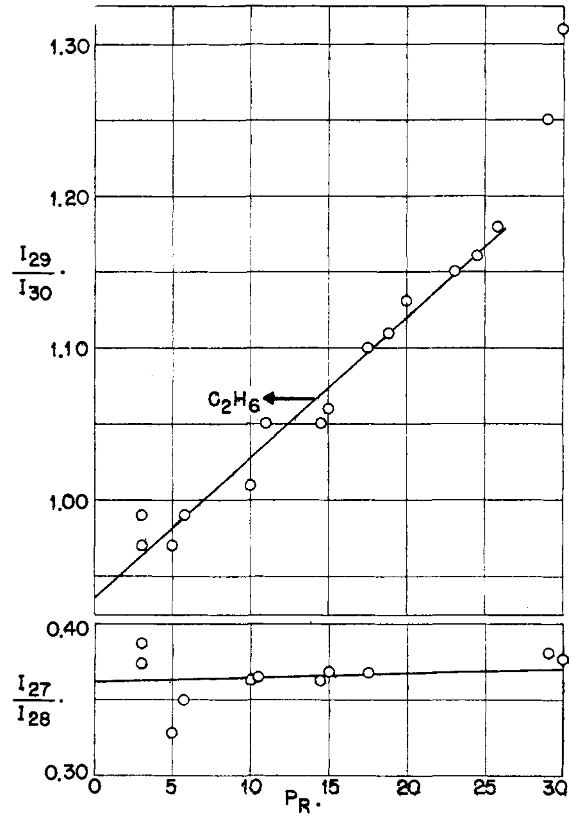

Fig. 2.—Hydride ion transfer in ethane (upper plot) and differential scattering in ethane (lower plot).

For the compounds other than neopentane and neohexane the primary ion mass spectra contain appreciable intensities of the ions of mass $M - 1$, and the change in the ratios I_{M-1}/I_M as the pressure is varied is small (see, for example, Fig. 2). Consequently, it is necessary to be somewhat cautious in attributing the observed increases in

TABLE II

INITIAL SLOPES OF PLOTS OF I_{M-1}/I_M *vs.* RESERVOIR PRESSURE P_R

Compound	Mass	Slope (mm.$^{-1}$)
C_2H_6	30	8.45×10^{-3}
C_3H_8	44	1.01×10^{-2}
n-C_4H_{10}	58	1.25×10^{-2}
i-C_4H_{10}	58	5.03×10^{-2}
neo-C_5H_{12}	72	7.47×10^{-4}[a]
neo-C_6H_{14}	86	1.14

[a] Slope for plot of I_{71}/I_{41} *vs.* P_R.

I_{M-1}/I_M to the occurrence of a secondary reaction until possible experimental artifacts are considered. Probably the most serious of these is differential scattering of ions of different masses.

Using magnetic scanning of the mass spectrum as was the case in this work, the ion accelerating voltage remains constant for all ions, and according to an approximate treatment[1] of scattering in a mass spectrometer, the scattering cross-sections for all of the ions in the mass spectrum of a compound should be identical. Actually, we find that different ions are scattered by somewhat different amounts, although the magnitude of the differential scattering found with magnetic scanning is smaller than that found with ion voltage scanning. From an investigation of the intensities of several ions in the propane mass spectrum with propane pressure, we find the following relative scattering cross-sections: CH_3^+ ($M = 15$), $\sigma_s = 1.00$; $C_2H_5^+$ ($M = 29$), $\sigma_s = 1.12$; $C_3H_5^+$ ($M = 41$), $\sigma_s = 1.27$; $C_3H_8^+$ ($M = 44$), $\sigma_s = 1.37$. From a plot of $\Delta\sigma_s$ against ΔM we can obtain a value of $\Delta\sigma_s$ for a mass difference of one mass unit, and when this value is used in a differential scattering calculation, we obtain the result that the value of I_{M-1}/I_M at a reservoir pressure of 20 mm. will be as a result of differential scattering only 0.2% higher than the value of the ratio at reservoir pressures approaching zero. Included in Fig. 2 is a plot of I_{27}/I_{28} from ethane, and it may be seen that indeed the differential scattering is trivially small. Of course, in these scattering considerations we assume that ion–molecule reactions which will affect the intensities are absent for those ions used to establish the magnitude of the ion scattering. Obviously the possibility exists that for some ions the occurrence of unknown ion–molecule reactions may render this assumption incorrect, and consequently we investigated the variation of the ratios of several propane ion intensities as a function of added argon pressure. When the propane pressure was maintained constant at 2.5 mm. and the argon pressure was varied from 0 to 23.5 mm., I_{43}/I_{44} changed only from 0.956 to 1.000. Taking everything into account, we are firmly of the opinion that the increases of I_{M-1}/I_M observed in the compounds studied are the result of ion–molecule reactions rather than differential scattering or other trivial causes.

For the compounds studied other than neopentane we have no experimental information concerning the reactions producing the observed secondary ions. For the compounds other than neopentane and neohexane the presence of appreciable abundances of primary ions of mass $M - 1$ appears to make the measurement of the appearance potentials of the relatively low intensity secondary ions of mass $M - 1$ a hopeless task. For neohexane the intensity of the primary mass 85 ion is small enough so that this difficulty can be overcome, but the appearance potentials of the major primary ions from neohexane are not known. While these difficulties are unfortunate, we do know the identities of the neutral reactant and the product ion, and from energetic considerations we can impose some limits upon the possible ionic reactants and neutral products. From tabulated data[4] and taking into account ions with relative intensities of about 10% and greater, we calculate the heats of hydride ion transfer reactions $R^+ + MH \rightarrow M^+ + RH$ of the several primary fragment ions with the parent molecule. Endothermic reactions are rejected as not allowed in the mass spectrometer. For those which are allowed we calculate the heats of reactions involving various modes of decomposition of RH. Endothermic reactions are again rejected. These mass spectrometer reactions are non-equilibrum processes, which require that the distribution of the energy between the several products of a reaction must be taken into account. Since we do know how to predict this distribution exactly, the best we can say is that RH decomposition reactions which are exothermic can occur. The allowed reactant ions are listed in Table III. When further decomposition of RH is allowed the decomposition products are given in parentheses following the formula for the reactant ion. The over-all exothermicities for the allowed RH decomposition reactions are small, and because of the energy distribution problem we are inclined to think that in actuality the RH molecules do not decompose.

TABLE III

ALLOWED REACTANT IONS

Compound	Reactant ions
C_2H_6	CH_3^+, $C_2H_3^+$
C_3H_8	CH_3^+, $C_2H_3^+$ $(C_2H_2 + H_2)$, $C_2H_4^+$, $C_2H_5^+$ $(C_2H_4 + H_2)$, $C_3H_3^+$, $C_3H_5^+$
n-C_4H_{10}	$C_2H_3^+$ $(C_2H_2 + H_2)$, $C_2H_4^+$, $C_2H_5^+(C_2H_4 + H_2)$, $C_3H_3^+$, $C_3H_5^+$, $C_3H_6^+$, $C_3H_7^+$
i-C_4H_{10}	$C_2H_3^+$ $(C_2H_2 + H_2)$, $C_3H_3^+$, $C_3H_5^+$, $C_3H_6^+$, $C_3H_7^+$
neo-C_5H_{12}	$C_2H_3^+$ $(C_2H_2 + H_2)$, $C_2H_5^+$ $(C_2H_4 + H_2)$, $C_3H_3^+$, $C_3H_5^+$
neo-C_6H_{14}	$C_2H_3^+$ $(C_2H_2 + H_2)$, $C_2H_5^+$ $(C_2H_4 + H_2)$, $C_3H_3^+$, $C_3H_5^+$, $C_3H_7^+$, $C_4H_8^+$, $C_4H_9^+$. $C_5H_{11}^+$

We now consider the quantitative treatment of the data. To accomplish this we assume that for each compound the corresponding ions listed in Table III will react, and, in addition, that all ions in the primary mass spectra with relative intensities less than 10% also react. The latter assumption is reasonable since it is oftentimes the case that low intensity is the consequence of high ion energy.

For the reactions under consideration we write

$$n_M \sum_i k_i \tau_i n_{pi} = n_{M-1} \qquad (2)$$

where

n_M = concn. of reactant molecules
k_i = rate constant for the ith reacting primary ion
τ_i = residence time for the ith reacting primary ion
n_{pi} = concn. of the ith reacting primary ion
n_{M-1} = concn. of the secondary ion (mass = $M - 1$)

or, converting to ion currents

$$n_M \sum_i k_i \tau_i I_{pi} = I_{M-1} \tag{3}$$

Since we do not know exactly what primary ions are involved in forming the secondary ion, we are forced to use as an approximation some kind of average or effective rate constant $\bar{k}$ and residence time $\bar{\tau}$, *i.e.*

$$n_M \bar{k}\,\bar{\tau} \sum_i I_{pi} = I_{M-1} \tag{4}$$

or

$$\bar{k}\bar{\tau} n_M = I_{M-1}/\sum_i I_{pi} \tag{5}$$

As a good approximation at low pressures the ionization chamber concentration n_M is proportional to the reservoir pressure P_R

$$n_M = aP_R \tag{6}$$

The intensity of the molecule–ion can be used as a measure of the summed intensities of the reacting primary ions

$$I_M = b \sum_i I_{pi} \tag{7}$$

For neopentane the mass 41 ions is used as a measure of the primary ions, and (7) is written as

$$I_{41} = b' \sum_i I_{pi} \tag{7a}$$

Substituting (6) and (7), (5) becomes

$$I_{M-1}/I_M = \frac{a\bar{k}\bar{\tau}}{b} P_R \tag{8}$$

or

$$I_{M-1}/I_M = \lambda P_R \tag{9}$$

where

$$\lambda = a\bar{k}\,\bar{\tau}/b \tag{10}$$

The quantity b (or b') is obtained from the mass spectrum of the compound under investigation and λ is obtained from a plot of I_{M-1}/I_M *vs.* P_R. In this way relative values of $\overline{ak\tau}$ are obtained.

To convert these relative values to absolute values, comparison is made with the a $k\tau$ for a reaction proceeding at a known rate. We have chosen $CH_4^+ + CH_4 \rightarrow CH_5^+ + CH_3$, and for this reaction we write

$$k\tau(CH_4)(CH_4^+) = (CH_5^+) \tag{11}$$

$$(CH_4) = a'P_R \tag{12}$$

$$I_{17s}/(I_{17s} + I_{16}) \cong I_{17s}/I_{16} = a'k\,\tau\,P_R \tag{13}$$

where I_{17s} is the secondary ion portion of the observed mass 17 ion current. Measurements in our Westinghouse mass spectrometer at an ionization chamber field strength of 5.71 v./cm. gave the result that the slope of the plot of I_{17S}/I_{16} *vs.* P_R is 11.0 × 10^{-4} mm.$^{-1}$, *i.e.*

$$\lambda = a'k\,\tau = 11.0 \times 10^{-4} \text{ mm.}^{-1} \tag{14}$$

However, $k\tau = f\sigma Q'$ ($f\sigma$ = reaction cross-section and Q' = a constant defined in ref. 1), and from ref. 1, at a field strength of 5.71 volt/cm. $f\sigma$ = 68 Å.^{2}, from which $a'Q' = 1.62 \times 10^{-5}$ mm.$^{-1}$. For the low pressure region where ion current increases more or less linearly with pressure, as a good approximation the value of a may be taken as constant from one compound to another, that is, $a' = a$; and (10) may be written as

$$\bar{k}\bar{\tau}/Q' = (f\sigma)_{eff} = b\lambda/1.62 \times 10^{-5} \tag{15}$$

where $(f\sigma)_{eff}$ is the effective reaction cross-section for the set of hydride ion transfer reactions occurring.

Values of $(f\sigma)_{eff}$ calculated from (15) are given in column 2 of Table IV. The necessary values of λ where taken from Table II, and those of b were calculated from the mass spectra using all energetically allowed ions with relative intensities greater than 1% of that of the most intense ion. Of course, the parent ion and the ion with mass one unit less than the parent ion are not included in the calculation.

TABLE IV

REACTION CROSS-SECTIONS FOR HYDRIDE ION TRANSFER REACTIONS

Compound	$(f\sigma)_{eff}$, Å.^{2}	Compound	$(f\sigma)_{eff}$, Å.^{2}	$k \times 10^9$, cc./molecule sec.
C_2H_6	264	$C_2H_6 + CH_4$	171	3.8
C_3H_8	66	$C_3H_8 + CH_4$	107	2.4
n-C_4H_{10}	32	n-$C_4H_{10} + CH_4$	60	1.3
i-C_4H_{10}	34	i-$C_4H_{10} + CH_4$	101	2.2
neo-C_5H_{12}	14	neo-$C_5H_{12} + CH_4$	12	0.27
neo-C_6H_{14}	7	neo-$C_6H_{14} + CH_4$	16	0.35

Mixtures with Methane.—To investigate the hydride ion transfer reaction further, the compounds were studied in mixtures with methane. Since the number of kinds of fragment ions from methane which can undergo the transfer reaction is less than the number formed from the pure compounds studied, the indeterminateness concerning the reactions occurring is smaller in the mixture studies. For practical purposes one can consider the reactions to involve the CH_3^+ and CH_2^+ ions only, for these constitute 74 and 14%, respectively, of the fragment ions formed from methane. Both these ions have sufficient energy to undergo the hydride ion transfer reaction, and with CH_2^+ the neutral products formed in the reactions with all the compounds except ethane are energetically capable of decomposition.

The mixtures were made with varying pressures (0–25 mm.) of methane and constant (within the limits of experimental control) pressures (2–5 mm.) of the other reactant. Adequate time (experimentally determined to be 20–30 min.) was allowed for complete mixing of the components.

It is found that the value of I_{M-1}/I_M (M refers to the compound other than methane) varies with the methane pressure, and this is taken as evidence for the occurrence of hydride ion transfer reaction(s) involving the ion(s) formed from methane. As will be shown below, a plot of $(1/P_R(M))I_{M-1}/I_M$ *vs.* $P_R(CH_4)$ should be essentially linear, and as an example such a plot for the system i-C_4H_{10}–CH_4 is given in Fig. 3. The initial slopes of these plots for the several systems studied are given in

Table V. For ethane I_{29} was corrected for contributions from the reaction $CH_3^+ + CH_4 \rightarrow C_2H_5^+ + H_2$.

TABLE V

INITIAL SLOPES OF PLOTS OF I_{M-1}/I_M *vs.* METHANE RESERVOIR PRESSURE, $P_R(CH_4)$

System	$P_R(M)$ (mm.)	M	Slope (mm.$^{-2}$)
C_2H_6–CH_4	2.5	30	1.10×10^{-3}
C_3H_8–CH_4	2.5	44	1.81×10^{-3}
n-C_4H_{10}–CH_4	2.5	58	1.80×10^{-3}
i-C_4H_{10}–CH_4	2.5	58	1.07×10^{-2}
neo-C_5H_{12}–CH_4	5.1	72	3.33×10^{-5}[a]
neo-C_6H_{14}–CH_4	2.8	86	1.12×10^{-1}

[a] Slope for plot I_{71}/I_{41} *vs.* $P_R(CH_4)$.

The quantitative analysis of these data is rendered more complicated than that for the pure substances because ions both from CH_4 and from the substance under investigation can undergo the hydride ion transfer reaction. We are presently concerned only with the former reactions. Using the method and notation given above, we write

$$n_M \sum_i k_i \tau_i n_{pi} + n_M \sum_j k_j \tau_j n_{pj} = n_{M-1} \qquad (16)$$

where the index j refers to ions from CH_4 and the index i refers to ions from the other component of the mixture.

Converting to ion currents, writing average values of k and τ, and rearranging

$$\bar{k}_M \bar{\tau}_M + \bar{k}_{CH_4} \bar{\tau}_{CH_4} \sum_i I_i / \sum_j I_j = I_{M-1}/n_M \sum_j I_j \qquad (17)$$

In this notation $\overline{k_{CH_4}}$ and $\overline{\tau_{CH_4}}$ represent the effective values of the quantities referring to the ions formed from CH_4, and analogously for $\overline{k_M}$ and $\overline{\tau_M}$.

We may write

$$\frac{\sum_i I_i}{\sum_j I_j} = \frac{Q_{CH_4}}{Q_M} \times \frac{g_{CH_4}}{g_M} \times \frac{P_R(CH_4)}{P_R(M)} \qquad (18)$$

where

Q_{CH_4} and Q_M = total ionization cross-sections for CH_4 and M

$P_R(CH_4)$ and $P_R(M)$ = reservoir pressures for CH_4 and M

g_{CH_4} and g_M = fraction of reacting ions in mass spectra of CH_4 and M

In writing (18) it is assumed that the same proportionality factor between P_R and ionization chamber concentration exists for CH_4 and M.

We also need the relations

$$\sum_j I_j = b_M I_M \qquad (19)$$

$$n_M = a\, P_R(M) \qquad (20)$$

Substituting (18), (19) and (20) into (17) and rearranging slightly

$$\overline{k_M}\ \overline{\tau_M}\ ab_M + \overline{k_{CH_4}}\ \overline{\tau_{CH_4}}\ a \frac{b_M Q_{CH_4} P_R(CH_4)}{g_M Q_M P_R(M)}\, g_{CH_4} = \frac{1}{P_R(M)} \frac{I_{M-1}}{I_M} \qquad (21)$$

But

$$\frac{b_M}{g_M} = \frac{\sum_j I_j/I_M}{\sum I_j/\Sigma I(M)} = \frac{\Sigma I(M)}{I_M} \qquad (22)$$

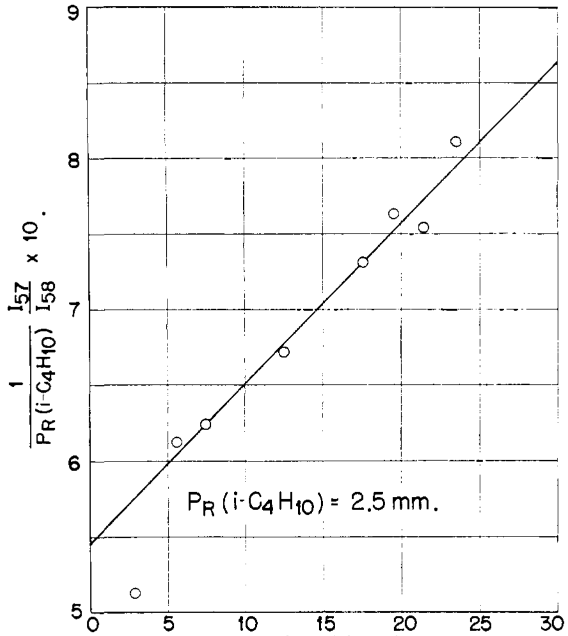

Fig. 3.—Hydride ion transfer in *i*-C_4H_{10}–CH_4.

where $\Sigma I(M)$ is the sum of the intensities of all the ions formed from the compound M. I_M, on the other hand, is the intensity of the molecule–ion from the molecule M.

A plot of $(1/P_R(M))I_{M-1}/I_M$ against $P_R(CH_4)$ should be a straight line from the slope of which $\overline{k_{CH_4}}\ \overline{\tau_{CH}}$ can be calculated. As before taking $aQ' = 1.62 \times 10^{-5}$, we have finally

$$\frac{k_{CH_4}\ \tau_{CH_4}}{Q'} = (f\sigma)_{eff} = \frac{\lambda}{1.62 \times 10^{-5}} \times \frac{Q_M}{Q_{CH_4}} \times \frac{I_M}{\Sigma I(M)} \times \frac{P_R(M)}{g_{CH_4}} \qquad (23)$$

Values of $(f\sigma)_{eff}$ obtained in this work are given in column 4 of Table IV. Values of λ were taken from Table V. Ionization cross-sections were taken from previous work in this Laboratory.[5] Values of $I_M/\Sigma I(M)$ and of g_{CH_4} were calculated from the appropriate mass spectra. Bimolecular reaction rate constants were calculated from these cross-sections by means of the relationship $k = f\sigma Q'/\tau$, calculating Q' and τ from equations 7b and 17 of ref. 1. The rate constants are given in column 5 of Table IV.

The agreement of the cross-sections for pure compounds with those of the methane mixtures is obviously not exact, but the values are of the same order of magnitude. In both series of values the same trend of decreasing cross-section with increasing molecular weight is to be observed, even granting that the methane mixture values show some irregularities. We are of the opinion that the two sets of values are mutually supporting. Since the reactant ions in the mixtures with methane are known with only a relatively small degree of uncertainty, the agreement between the two sets of cross-section values indicates that our assumption that a variety of ions serve as reactants

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[5] F. W. Lampe, J. L. Franklin and F. H. Field, THIS JOURNAL, **79**, 6129 (1957).

in the pure compounds is not grossly in error. Pure compound cross-sections calculated on the assumption that only a single ion reacts do not agree with the mixture values as well as the values given in Table IV.

In somewhat the same regard, we might point out that the compounds and systems reported in this paper constitute all of our investigations in this area except for an investigation of pure methane, and in all but pure methane the hydride transfer reaction has been observed. This indicates to us that the reaction is one of considerable generality with respect to both ions and neutral molecules. We attribute our failure to observe reaction in methane to experimental difficulties involving the small reactant ion intensity and the fact that CH_3^+ and CH_4^+ serve as reactants in other ion-molecule reactions.

The observed decrease in reaction cross-section with increasing molecular weight is interesting and puzzling. As the molecular weight increases the polarizability increases, and theoretically[1,6] the reaction cross-section should increase with the square root of the polarizability. Furthermore, with increasing molecular weight the number of available hydrogens per hydrocarbon molecule increases, and the carbon–hydrogen bond dissociation energies in the molecules should decrease somewhat. One would expect both of these factors to contribute to an increase in reaction cross-section with increasing molecular weight.

We have considered the possibility that the observed decrease in cross-section may be the result of the rapid decomposition of the product ion of mass $M - 1$ into product ions of lower molecular weight, which would generally not be detected in our experiments. However, while for the two heaviest molecules one cannot completely exclude this possibility, it can be excluded on the basis of energetics for the lighter molecules. Thus no decompositions of $C_2H_5^+$ ion from ethane are energetically possible. In propane the reactions of $C_2H_3^+$ and $C_2H_5^+$ with C_3H_8 will produce $C_3H_7^+$ containing enough energy to decompose to $C_3H_5^+$ if it be assumed that the neutral molecule formed in the hydride ion transfer reaction carries away none of the heat of reaction. However, if one makes a more reasonable assumption concerning the distribution of the heat of reaction, the decomposition to $C_3H_5^+$ becomes energetically impossible. In accordance with this view, an inspection of the mass 41 intensities in propane shows no evidence of the growth to be expected if appreciable amounts of secondary $C_3H_5^+$ ions were being formed. Thus we certainly cannot attribute the fact that the hydride ion transfer reaction cross-section in propane is only 25% that in ethahe to decomposition of the $C_3H_7^+$ ion. Similar, although less unequivocal, considerations apply to the other molecules studied. We are forced to the admission that we do not at all understand the observed decrease in the reaction cross-sections.

Discussion

Hydride ion transfer reactions have been postulated for many years and are considered to be of much importance in many processes, but to our knowledge these are the first observations of the elementary reactions and the first measurements of their rates. These rates are of the same large order of magnitude as those found for other gas phase ionic reactions, and thus hydride ion transfer can be expected to occur readily in any system containing ions. We think that our results coupled with chemical intuition support the tentative postulate that the hydride ion transfer reaction is a general phenomenon which will occur with many ions and many molecules. It is certain that these results will have to be considered in possible mechanisms for gaseous radiation chemistry systems, and it may be that the occurrence of these reactions make the systems simpler than has previously been thought. Because of these reactions the number of types of ions present in the radiation plasma may be diminished, which could simplify the over-all reaction mechanism. Similar considerations might apply to certain catalytic systems.

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[CONTRIBUTION FROM THE NUCLEAR PHYSICS GROUP OF THE ECOLE NORMALE SUPÉRIEURE]

The Szilard–Chalmers Effect in Solid Ethyl Bromide

BY MIRIAM MILMAN

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The contribution of diffusion dependent reactions following radiative neutron capture by the bromine atom in solid ethyl bromide, has been investigated. The scavenger effect of elementary bromine and 1,2-dibromoethylene, as well as the influence of irradiation temperature and crystalline structure were examined. It was found that the high yield of radioactive organic species is due to a great enhancement of "hot" processes, the "diffusion controlled" reactions having a smaller relative importance than in the case of the neutron irradiation of liquid ethyl bromide.

Introduction

Previous work on the nuclear activation of halogen atoms in liquid organic media[1a] has shown that the reactions of the tagged atom occur in two stages. In the first, the recoiling atom loses

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