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Effects of Relative Velocity upon Gaseous Ion–Molecule Reactions; Charge Transfer to the Neopentane Molecule[1]

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The dependence of ion–molecule reaction cross section upon relative velocity g is not adequately described for ion-induced dipole forces by expressions previously used, which are presumed valid for point particles. Introducing an energy-independent component in the microscopic cross section σ leads to discontinuity in the functional dependence of σ upon ion velocity and in the macroscopic cross section Q upon the kinetic energy E_e of the ions at the exit slit. Charge transfer from various ions to *neo*-C_5H_{12} to give $C_5H_{12}^+$ appears to be energy-limited, for which $Q \propto E_e^{-1}$ is predicted and observed.

Introduction

In order to understand radiation chemistry in terms of ionic processes it is necessary to consider, among others, the phenomenon of charge transfer. A recently reported example[2] is

$$C_2H_2^+ + C_6H_6 \longrightarrow C_2H_2 + C_6H_6^+$$

which accounts for the previously observed retarding effect of benzene on the alpha-induced polymerization of acetylene.[3] The same study[2] also indicates that charge transfer may not occur when an efficient ion–molecule reaction also is allowed.

The present study was undertaken with neopentane as the common electron donor in various binary mixtures in a conventional mass spectrometer. This choice of donor molecule was dictated by the impossibility of detecting an increment in the ion current of the molecular (unfragmented) ion when it also was produced, even in fairly low abundance, by electron impact. The ion $C_5H_{12}^+$ from neopentane has a relative abundance of only *ca.* 0.01%, and even small contributions from bimolecular processes can be detected efficiently.

Incidental to the study of neopentane in various mixtures for evidence of charge transfer, it was observed that the yield of $C_5H_{11}^+$ ions (0.04%) also was enhanced by bimolecular processes. This effect also has been observed by Field and Lampe.[4]

Experimental

Measurements were made in a CEC 21–103A mass spectrometer with a model 31–402 ion source. The repeller potential was manually adjusted using dry cells and step-potentiometers adjustable by 0.1 v. increments over the range 0–24 v. The ionizing voltage was continuously adjustable over the range 5–73 v. and in steps of 0.1 v. over the range 5–28 v. Electron current was 10 μ-amp. The distance from the center of the electron beam, which is 0.018 cm. thick, to the exit slit is 0.130 cm. and to the repeller plates is 0.120 cm. The electron energy therefore is increased by one-half the applied repeller voltages.

The leak consists of two fine holes in a thin gold foil, and observation shows gas flow to be effusive within the range of pressures used. Pumping of gas from the source also is effusive and the ratio of pressures between the reservoir and the source is constant and independent of the gas used. By calibration,[5] the concentration of gas in the ion source is 1.58×10^{10} mol./cc. per micron of reservoir pressure.

Results

The dependence upon ion repeller field of the cross section Q of the reaction

$$Ar^+ + H_2 \longrightarrow ArH^+ + H$$

was measured on the Notre Dame instrument to allow comparison with published results. We find, in terms of the equation $Q = 2\,\sigma_L/E^{1/2} + \sigma_k$ that $\sigma_L = 67 \times 10^{-16}$ cm.^{2} ev.$^{1/2}$ and $\sigma_k = 11 \times 10^{-16}$ cm.^{2} From our graph of the data of Stevenson and Schissler,[5] who used a Westinghouse Type LV, $\pi/2$-sector analyzer mass spectrometer, we obtain $\sigma_L = 71 \times 10^{-16}$ cm.^{2} ev.$^{1/2}$ and $\sigma_k = 13 \times 10^{-16}$ cm.^{2} The theoretical value of σ_L is 70×10^{-16} ev.$^{1/2}$ for a reaction probability of unity.

Pressure Dependence.—A necessary condition for ion-molecule reactions is a second order pressure dependence for the secondary ion, whereas a primary ion exhibits first order pressure dependence. We have found that at fairly low repeller field strength this is not the case. Thus, for CD_4^+ and CD_5^+ ions by first and second order processes in CD_4, and at 4 v. cm.$^{-1}$, the order is 0.88 and 1.66, respectively. At 8 and 40 v. cm.$^{-1}$, however, the expected integral order dependences actually were observed. Measurements of cross sections on instruments of the type used in this work often are not dependable at less than 10 v. cm.$^{-1}$ repeller field strength.

Neopentane.—An examination of many substances for evidence of charge transfer in appropriate mixtures resulted in choosing neopentane because of its particularly small 72-ion abundance. Incidental to this study we found, as did Field and Lampe,[4] evidence for secondary 71-ion formation from neopentane. Such parent-mass-minus-one secondary ions are of common occurrence, both by unimolecular decomposition and by "hydride ion" transfer.

In the present work it was observed that the 71-ion current increased as the 1.66 power of the pressure of neopentane, both at 12 and at 40 v. cm.$^{-1}$ This suggests a combination of primary and secondary processes. The i_{71}-ion current may be referred arbitrarily to the primary i_{65}-ion current, as a matter of convenience, since they are of the same magnitude. For later reference we note that $i_{65}/i_{57} = 0.0354\%$. It is to be expected then that $i_{71} = a'\,p_1 + b'\,p_1^2$ and $i_{65} = a''\,p_1$ where p_1 is the pressure of neopentane. It was found that $i_{71}/i_{65} = 0.63 + 1.03 \times 10^{-2}\,p_1$ at a repeller field 12 v. cm.$^{-1}$ and $i_{71}/i_{65} = 0.58 + 3.91 \times 10^{-3} p_1$ at 40 v. cm.$^{-1}$, expressing p in microns reservoir pressure.

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[2] P. S. Rudolph and C. E. Melton, *J. Chem. Phys.*, **32**, 586 (1960).

[3] S. C. Lind and P. S. Rudolph, *ibid.*, **26**, 1768 (1957).

[4] F. H. Field and F. W. Lampe, *J. Am. Chem. Soc.*, **80**, 5587 (1958).

[5] D. P. Stevenson and D. O. Schissler, *J. Chem. Phys.*, **29**, 282 (1958).

In neopentane mixtures it may be expected that $i_{71} = a'p_1 + b'\,p_1^2 + c'\,p_1\,p_2$, where p_2 is the pressure of additive. The ratio i_{71}/i_{65} should be linear in p_2. Ethane, propane and carbon disulfide give such results. Keeping $p_1 = 105$ microns and E_e, the ion energy at the exit slit, at 1.8 ev., the results for added ethane are described by the equation

$$i_{71}/i_{65} = 1.51 + 3.8 \times 10^{-3}\,p_2$$

and for added propane by

$$i_{71}/i_{65} = 1.55 + 3.4 \times 10^{-3}\,p_2$$

In mixtures with carbon disulfide it was not possible to refer i_{71} to i_{65} because of interference. The results for these mixtures at $E_e = 1.56$ ev. and 418 microns constant total pressure may be expressed by

$$i_{71}/p_1 = 0.42 + 2.1 \times 10^{-3}\,p_1$$

Since the parameters of this equation are not derivable from those for pure neopentane by a common factor, it appears that an ion from carbon disulfide (shown to be CS_2^+) also induces the formation of $C_5H_{11}^+$.

TABLE I

EFFECTS OF ADDITIVES UPON 71- AND 72-ION ABUNDANCES RELATIVE TO THE PRIMARY 65-ION AT E_e = 0.4 e.v.

Additive (*M*)	$\Delta \frac{i_{71}}{i_{65}}$	$\Delta \frac{i_{72}}{i_{65}}$	$\Delta \frac{i_{72}{}^b}{i_{65} i_{M^+}}$	*I* (*M*)
He	0.0	0.0		24.58
D_2	.0	.0		15.44
N_2	.5	.0		15.56
NH_3	.0	.0		10.23
CO_2	− .3	.0		13.79
CD_4	2.7	.0		13.26
C_2H_2	0.0	.0		11.41
C_2H_4	1.7[a]	.10	0.16	10.51
C_2H_6	2.7	.21	.23	11.65
C_2D_6	2.8	.28	.27	11.65
C_3H_6	3.7	.0		9.7
c-C_3H_6	4.8	.0		10.09
C_3H_8	10.6[a]	.18		11.21
i-C_4H_8	7.1	.0		9.35
1-C_4H_8	4.5	.0		9.72
n-C_4H_{10}	4.8	.1		10.8
n-C_4D_{10}	4.8	.1		10.8
CH_3Cl	2.0	.0		11.22
CH_3Br	3.4	.26	.26	10.54
CH_3I	1.1	.0		9.54
C_2H_5Cl	2.5	.03	.064	10.97
C_2H_5Br	4.5	.45	.65	10.29
C_2H_5I	5.9	.0		9.33
CH_3OH	1.9	.0		10.85
Pyridine	1.9	.0		9.8
CS_2	−0.2	2.40	1.3	10.08

[a] Measured at $E_e = 0.25$ ev. [b] $i_M{}^+$ is the current of the molecular ion of additive except for C_2H_6, C_2D_6 when it refers to $C_2H_4^+$, $C_2D_4^+$.

The 72-ion current for neopentane, as received, was not altered by gas chromatographic purification of the material. Neither does this current arise from a secondary reaction, since 22 measurements of i_{72}/i_{65} (corrected for the isotopic component from i_{71}) at various p_1 and repeller fields showed no significant variation. The results of tests with many additives are reported in Table I. No ion with ionization potential *I* greater than 11 ev. enhanced i_{72}. Propane is an apparent exception, but for this and all other hydrocarbons tested there is a fairly good correlation between $\Delta\, i_{72}/i_{65}$ and i_{28}. The largest effect observed for any additive was produced by carbon disulfide.

Secondary Ion Current–Repeller Dependence.—Carbon disulfide increases i_{71} rather less than i_{72}, but the dependence of i_{71} upon E_e is unlike that for any other additive; the results for carbon disulfide and for ethane-d_6 are compared in Table II.

TABLE II

EFFECT OF REPELLER FIELD

Added subs.	*Ee*	0.42	1.04	1.56	2.60	5.20
CS_2	$\Delta i_{72}/i_{65}$	2.40	0.99	0.67	0.38	0.18
CS_2	$\Delta i_{71}/i_{65}$	−0.20	.50	.40	.26	.18
C_2D_6	$\Delta i_{72}/i_{65}$	0.282	.138	.085	.064	.029
C_2D_6	$\Delta i_{71}/i_{65}$	3.10	1.31	.95	.59	.35

The dependence of the 71-ion current upon E_e, the terminal ion energy, relative to the 65-ion current, is reported in Table III for pure neopentane and for several mixtures. The parameters *M* and *C* refer to the empirical equations $i_{71}/i_{65} = C + ME_e^{-1/2}$, etc., as indicated.

TABLE III

DEPENDENCE OF SECONDARY-TO-PRIMARY ION CURRENTS UPON REPELLER FIELD STRENGTH

Additive	Reservoir *p*, microns	Range E_e, e.v.	*C*	*M*
None	418	1.3– 5.2	−0.97	7.36[c]
None	217	1.9– 5.2	− .52	4.18[c]
None	217	1.6– 8.3	.09	3.41[a,c]
None	217	5.2–12.5	.75	4.4[a,e]
C_2H_6	209 + 209	1.3– 5.2	− .85	5.65[c]
C_2H_6	105 + 313	1.6– 6.2	− .35	4.14[c]
C_2H_6	105 + 313	5.0–12.5	.61	4.44[e]
C_2D_6	209 + 209	1.0– 5.2	− .47	1.79[d]
C_2D_6	209 + 209	1.0– 5.2	− .36	1.57[d]
C_2D_6	209 + 209	1.0– 5.2	.0	0.14[b,f]
C_2D_6	209 + 209	1.0– 5.2	.0	0.15[b,f]
n-C_3H_6	209 + 209	1.0– 5.2	− .78	3.13[d]
C_3H_8	209 + 209	1.6– 4.3	−1.28	7.77[c]
CH_3Cl	209 + 209	1.0– 5.2	−0.25	1.37[d]
CS_2	209 + 209	1.0– 5.2	−0.02	1.06[b,f]

[a] The accelerating voltage was 1500 v. for this series and 600 v. for all others. This may account for the discrepancy between the intercepts for this and the preceding series in the plot *vs.* $E_e^{-1/2}$. [b] Corrected for isotopic contributions from $C_5H_{11}^+$. [c] Parameters refer to $i_{71}/i_{65} = C + ME_e^{-1/2}$. [d] Parameters refer to $\Delta i_{71}/i_{65} = C + ME_e^{-1/2}$. [e] Parameters refer to $i_{71}/i_{65} = C + ME_e^{-1}$. [f] Parameters refer to $\Delta i_{72}/i_{65} = C + ME_e^{-1}$.

Appearance Potentials.—Appearance potentials were measured relative to xenon, at 0.7 to 0.8 repeller voltage. The results appear in Table IV.

TABLE IV

APPEARANCE POTENTIALS OF NEOPENTANE, ALONE AND IN MIXTURES

Additive:	None	CS_2	C_2H_6	C_2H_4
$C_5H_{11}^+$	12.5		11.8	10.7
$C_5H_{12}^+$	12.4	10.1	12.1	10.6

The appreciable primary 71-ion current made it impossible to establish the primary ion from neopentane responsible for the second order contribution to i_{71}/i_{65}. Field and Lampe[4] have reported on the basis of appearance potential measurements, that the 41-ion was responsible. They emphasized that such "hydride ion" reactions are probably rather general, and the present results support this view for neopentane.

The appearance potentials of CS_2^+, CS^+, S^+ and C^+ from CS_2 are 10.10, 14.8, 14.1 and 25.1, respectively.[6] The charge transfer process in mixtures with carbon disulfide is considered to be

$$CS_2^+ + C_5H_{12} \longrightarrow CS_2 + C_5H_{12}^+$$

The only appearance potentials below 13.5 ev. for ethane and ethylene are: $C_2H_6^+$, 11.65; $C_2H_5^+$, 12.84; $C_2H_4^+$, 12.09 from ethane and[7,8] $C_2H_4^+$, 10.51 from ethylene.[9]

The indicated reactions in mixtures with ethylene are

$$C_2H_4^+ + C_5H_{12} \longrightarrow C_5H_{12}^+ + C_2H_4 \qquad (A)$$

$$C_2H_4^+ + C_5H_{12} \longrightarrow C_2H_5 + C_5H_{11}^+ \qquad (B)$$

A second break in the ionization efficiency curve of $C_5H_{11}^+$ for the neopentane–ethylene mixture was observed at 13.0 ev. This may be attributed to a reaction of $C_3H_5^+$ from neopentane itself. The reported appearance potential for the primary 41-ion[10] is 13.13 ev.

In mixtures with ethane it is difficult to assign the primary ions with assurance but the best agreement is found for the processes

$$C_2H_6^+ + C_5H_{12} \longrightarrow C_5H_{11}^+ + C_2H_6 + H \qquad (C)$$

$$C_2H_6^+ + C_5H_{12} \longrightarrow C_5H_{11}^+ + C_2H_5 + H_2 \qquad (D)$$

The reactions A and B probably also take place in these mixtures.

Discussion

Ion-induced dipole forces lead to energy-dependent collision cross sections[11,12]

$$\sigma(E) = \pi b_0^2 = 2\pi(e^2\alpha/\mu g^2)^{1/2} \qquad (1)$$

where α, μ and g are the electric polarizability of the molecule, the reduced mass and the relative velocity of the collision pair. As an adequate approximation the molecule may be considered to be at rest and the energy E of the ion of mass m_1 taken as $E = {}^1/_2 m_1 g^2$. The current of secondary ions i_s formed from i_p primary ions over a path d_0 at a concentration of N molecules/cc. is expressible in terms of the phenomenological cross section Q

$$Q = i_s/i_p N d_0 \qquad (2)$$

Since we also have

$$Q = E_e^{-1}\int_0^{E_e} \sigma(E)\mathrm{d}E \qquad (3)$$

it follows that

$$Q = 2\pi e(2m_1\alpha/\mu E_e)^{1/2} = 2\sigma_1 E_e^{-1/2} \qquad (4)$$

where E_e is the ion energy at the exit slit and σ_L represents the collected constants or the value of $\sigma(E)$ at one ev. This equation has been used to describe the results of several ion-molecule reactions.[5,12] There are, however, many more reactions which depart considerably from the predicted linear dependence of Q upon $E_e^{-1/2}$, in particular reactions of hydrocarbons for which[13] Q varies as E_e^{-1}.

Re-examination of Previous Work.—In the derivation of equation 4 by Gioumousis and Stevenson[12] the most serious restriction imposed is that the gas kinetic collision cross section σ_K shall be small compared to πb_0^2. "Thus the analysis is most likely to be valid for some such reaction as that between a noble gas ion and hydrogen, or hydrogen with hydrogen."[12] On the other hand, if the preceding description is to be consistent with short range repulsive forces, it is to be expected that as the relative energy of the collision partners increases the Q of equation 4 becomes eclipsed by a nearly energy-independent cross section, σ_K, whose value should approximate the gas kinetic collision cross section.

Some of the relevant parameters are listed herewith in Table V for a few reactions.

TABLE V

COMPARISON OF σ_L AND σ_K

Ion	Molecule	$\alpha \times 10^{24}$ cc.	$\frac{m_1 + m_2}{m_2}$	$\sigma_L \times 10^{16}$ ev.$^{1/2}$ cm.^{2}	$\sigma_K \times 10^{16}$ cm.^{2}	$(\sigma_L/\sigma_K)^2$
$H_2^+(D_2^+)$	$H_2(D_2)$	0.78	2	21	21	1.0
Ar^+	H_2	.79	21	69	24	8.2
Kr^+	H_2	.79	43	97	26	14.0
H_2^+	Kr	2.48	1.0	33	26	1.6
CH_4^+	CH_4	2.6	2	38	33	1.4
$C_2H_4^+$	C_2H_4	4.26	2	49	40	1.5
O_2^+	D_2	0.79	9	45	24	6.6
D_2^+	O_2	1.60	1.1	22	24	0.8

Values of σ_K are based on van der Waals radii. The last column lists values of the particular ion energy E_t at which $\sigma_L/E_e^{1/2} = \sigma_K$. It is

$$E_t = (\sigma_L/\sigma_K)^2 = 2\pi^2 e^2\alpha(m_1 + m_2)/m_2\sigma_K^2 \qquad (5)$$

It appears that equation 4 is inadequate to describe Q(E) for many reactions, even at relatively low ion energy, and also for reactants as small as H_2^+ and H_2. Let us represent the *reaction cross section* by

$$\sigma(E) = [\sigma_l/E^{1/2} - \sigma_0] + \sigma_k \qquad (6)$$

The term in square brackets represents the effective area for glancing collisions; σ_0 and σ_k correspond to head-on collisions. In the language of collision theory, each sigma involves the product of an area and an efficiency factor. Tentatively we may identify σ_l with $P_L\sigma_L$ and σ_0 with $P_L\sigma_K$ where σ_K is a gas kinetic collision cross section. Similarly, σ_k becomes $P_K\sigma_K$; the reaction probability factors P_L and P_K need not be equal, so that σ_0 and σ_k may be quite different and either may well be zero. For lack of information σ_0 and σ_k are taken to be independent of energy. The equation is valid for $0 < E < E_t$ for which the term in

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[6] H. D. Smyth and J. P. Blewett, *Phys. Rev.*, **46**, 276 (1934).

[7] D. P. Stevenson and J. A. Hipple, *J. Am. Chem. Soc.*, **64**, 1588 (1942).

[8] K. Watanabe, *J. Chem. Phys.*, **26**, 542 (1957).

[9] W. C. Price and W. T. Tutte, *Proc. Roy. Soc.* (*London*), **A174**, 207 (1940).

[10] F. W. Lampe and F. H. Field, *J. Am. Chem. Soc.*, **81**, 3238 (1959).

[11] P. Langevin, *Ann. chim. phys.*, **5**, 245 (1905).

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

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

brackets equals or exceeds zero. For $E > E_t$ we assume

$$\sigma(E) = \sigma_k \quad (7)$$

Integration over the low energy range gives

$$Q = E_e^{-1}\int_0^{E_e}\sigma(E)\mathrm{d}E = 2\sigma_1E_e^{-1/2} + \sigma_{k0};\ E_e < E_t \quad (8)$$

where $\sigma_{k0} = \sigma_k - \sigma_0$. At higher energy

$$Q = E_e^{-1}\int_0^{E_t}\sigma(E)\mathrm{d}E + E_e^{-1}\int_0^{E_e}\sigma(E)\mathrm{d}E = E_e^{-1}[2\sigma_1E_t^{1/2} - \sigma_0E_t] + \sigma_k = E_e^{-1}\Sigma + \sigma_k \quad (9)$$

If the preceding considerations are valid, the dependence of Q upon E_e for the reaction

$$D_2^+ + D_2 \longrightarrow D_3^+ + D$$

should obey equations 8 and 9, rather than 4. The results of Stevenson and Schissler,[5] for this and other reactions, appear in Fig. 1, all expressed in terms of Q *vs.* $E_e^{-1/2}$. The cross section for ArH^+ obeys equation 8 rather than 4, while that for D_3^+ and DO_2^+ indicate departure from equation 8 at fairly low E_e. Since we attribute greater precision to these measurements than did the observers, further consideration is desirable.

There is a necessary relationship between the parameters of equations 8 and 9 for the particular functional dependence of Q upon E which we have postulated Considering that insufficient data are available to establish empirically the correctness of the postulated functions by graphing, we may take the concordance of the observed and calculated slopes as a limited test of the adequacy of equations 8 and 9 to describe the facts. The results of this comparison appear in Table VI. Values of E_t, σ_1 and Σ are all in fair agreement with theory. The present data do not permit a critical test of the alternative descriptions. Other work[14–16] provides further evidence of the effects implied in equations 6–10.

TABLE VI

	$E_t{}^a$, e.v.	$\sigma_k{}^a$	$\sigma_{k0}{}^a$	σ_1,^{a} obsd.	σ_1,^{b} calcd.	Σ, obsd.	Σ,^{c} calcd.
$D_2^+ + D_2 \rightarrow$							
$D_3^+ + D$	1.7	6	11	17	21	50	42
$D_2^+ + O_2 \rightarrow$							
$DO_2^+ + D$	1.5	0	9	16	22	62	44

[a] From Fig. 2. [b] By eq. 4, identifying σ_L and σ_1. [c] Assuming $\sigma_0 = 0$ and $\sigma_1E_t^{1/2} = \sigma_L^2/\sigma_K$.

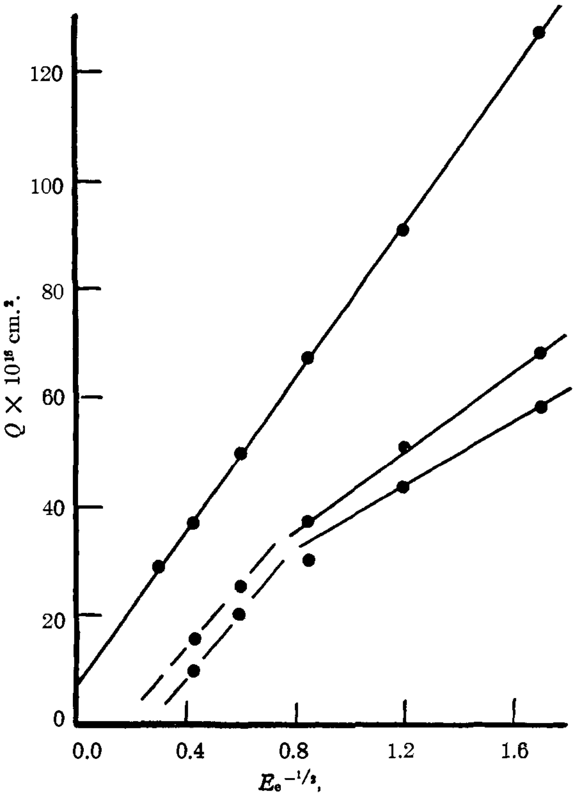

Fig. 1.—Ion-molecule reaction cross section Q as function of ion energy from the work of Stevenson and Schissler.[5] From top to bottom, curves refer to ArH^+, D_3^+ and DO_2^+.

When $\sigma(E) > 0$ at low values of E_e and $\sigma(E) = 0$ above a critical limit, then for measurements in the interval above this limit the expression QE_e = const. must apply. Thus, it already has been found that $Q \propto E_e^{-1}$ for the formation of the persistent collision complex.[17] In such instances one expects the complex to be rather unstable and the rate of decomposition to increase rapidly with increasing ion energy. With fixed collection time in a mass spectrometer, this would be expressed by a limiting, critical energy E_c beyond which $\sigma(E)$ rapidly approaches zero. If, for simplicity, this limit is treated as a discontinuity, then equation 9 also should apply to this case. The data for charge transfer to the 72-ion in neopentane are of this type and all the facts strongly suggest that $C_5H_{12}^+$ is very unstable. We conclude that it is susceptible to unimolecular decomposition following charge transfer when a critical ion–molecule relative velocity has been exceeded. We obtain from the preceding equations for ion-induced dipoles, at fairly low energy

$$Q = E_e^{-1}\int_0^{E_c}\sigma(E)\mathrm{d}E + E_e^{-1}\int_{E_c}^{E_e}\sigma(E)\mathrm{d}E = (2\sigma_1E_c^{-1/2} - \sigma_0E_c)/E_e;\ E_c < E_t \quad (10)$$

It is evident that the relation

$$QE_e = \text{constant} \quad (11)$$

will apply regardless of the force law.

Charge Exchange.—The qualitative dependence of $\Delta i_{72}/i_{65}$ upon the ionization potential of the added gas is evident. Concerning fragment ions we can, of course, eliminate at once all for which the difference of ionization potentials is endothermic (*e.g.*, $C_2H_3^+$, $C_2H_5^+$ and $C_3H_7^+$). Comparison of results for C_2H_4 and C_2H_6 and their ion abundances strongly indicates $C_2H_4^+$ as the effective primary ion. This is supported by the results with added *n*-C_4H_{10} and *n*-C_4D_{10} but not by those with *i*-C_4H_8 and 1-C_5H_8. The disagreement may arise from differences in structure of the $C_2H_4^+$-ions.

The possibility that the increased 72-ion current in mixtures is due to reaction rather than simple charge exchange was tested with C_2D_6 and with C_4D_{10}, for which the sum of all ion currents

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[14] L. P. Theard and W. H. Hamill, *J. Am. Chem. Soc.*, in press.

[15] R. F. Pottie, A. J. Lorquet and W. H. Hamill, *ibid.*, **84**, 529 (1962).

[16] Don Kubose, Andrée Lorquet and Thomas Moran, this Laboratory.

[17] R. F. Pottie and W. H. Hamill, *J. Phys. Chem.*, **63**, 877 (1959).

from m/e = 73 to 78 was 0.14 i_{72} and 0.52 i_{72} respectively. For comparison, in mixtures with C_2H_6 and C_4H_{10} the values were 0.23 i_{72} and 0.45 i_{72}. Also, such a hypothesis would not explain the dependence of Q upon E_e^{-1}.

TABLE VII

ENERGY DEPENDENCE FOR REACTION CROSS SECTIONS

Primary ion	Secondary ion	$\sigma_1 \times 10^{16}$ cm.² e.v.$^{1/2}$	$\sigma_0 \times 10^{16}$, cm.²	$QE_e \times 10^{16}$ cm.² e.v.
CS_2^+	$C_5H_{12}^+ + C_5H_{11}^+$	5.3	3.1	
$C_3H_5^{+a}$	$C_5H_{11}^+$	30	15	
$C_2H_4^{+b}$	$C_5H_{11}^+$	7	4	
$C_2D_4^{+c}$	$C_5H_{12}^+$			1.5
$C_2H_4^+ + C_3H_6^{+d}$	C_5H_{12}			1.5
$C_2H_4^{+e}$	$C_5H_{12}^+$			1.0
CS_2^+	$C_5H_{12}^+$			5.3

[a] For pure neopentane or added propylene. [b] Combined average for $C_2H_4^+$ and $C_2D_4^+$ from runs with C_2H_6 or with C_2D_6. [c] From C_2D_6. [d] Combined average for $C_2H_4^+$ and $C_3H_6^+$ from C_3H_8, assuming equal efficiencies. [e] From C_2H_6.

The combined current, $\Delta i_{72} + \Delta i_{71}$, should be a measure of the primary process **F**, provided decomposition does not proceed beyond $C_5H_{11}^+$. In fact equation 8 describes the results very well on this basis, and it would be expected that the primary process F obey such an energy dependence.

$$CS_2^+ + C_5H_{12} \longrightarrow CS_2 + C_5H_{12}^+ \qquad (F)$$

$$C_5H_{12}^+ \longrightarrow C_5H_{11}^+ + H \qquad (G)$$

The results appear in Table VII. On the other hand, the net Δi_{72} obeys equation 11. Considering all the evidence, we conclude that Δi_{72} also obeys the particular law, 10. If one accepts this interpretation, the critical energy for the decomposition reaction G can be obtained from the measured values of the parameters in equations 8 and 10 if we assume that $\sigma_k = 0$. We have $QE_e = 2\sigma_1 E_c^{1/2} - \sigma_0 E_c = 5.3 \times 10^{-16}$ cm.² e.v. and $2\sigma_1 = 10.6 \times 10^{-16}$ cm.² e.v.$^{1/2}$; $-\sigma_{k0} = \sigma_0 = 3.1 \times 10^{-16}$ cm.² One obtains E_c = 0.39 ev. for $C_5H_{12}^+$. Finally, using the same parameters we find $E_t = (5.3/1.3)^2 = 2.9$ ev. for $C_5H_{11}^+$ and $C_5H_{12}^+$ combined which places an approximate upper limit on the range of validity of the measurements suitable for testing the preceding equation.

The preceding data in Table VI also support the crude description by collision theory mentioned above, *viz.* $\sigma_1/\sigma_0 = \sigma_L/\sigma_K$, assuming that reaction P-factors cancel. For the first three entries in Table VII we find ratios of 1.7, 2.0 and 1.8. The corresponding calculated ratios of σ_L/σ_K are 1.5, 1.1 and 1.0.

Neopentane.—It appears that no single ionic species is responsible for the enhanced 71-ion formation, either in mixtures or in neopentane alone. Comparison of the results in Table I with the mass spectral patterns suggests that CH_3^+, $C_2H_5^+$ and $C_2H_4^+$ are effective. The parameters σ_1 and σ_0 for the more efficient reactions appear in Table VII. It is significant that every additive which enhances i_{72} also enhances i_{71}, while the converse appears not to hold. This suggests that, in addition to the mechanism previously proposed by Lampe and Field,[10] there is also a spontaneous decomposition following charge transfer. The effect is most pronounced for carbon disulfide for which we postulate, as suggested by the data of Table II, the consecutive reactions F and G.

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The Ultraviolet Spectra of N-Phenyl-substituted Cyclic Imines[1]

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The ultraviolet spectra of *N*-phenyl-substituted cyclic imines ranging in ring size from 3 to 6 have been examined. From comparisons of the ultraviolet spectra, base strengths and molar refractions it can be concluded that the resonance energy due to phenyl ring-nitrogen interaction increases as the ring size of the imine is varied in the order 3 < 6 < 4 < 5. Comparison of the spectra of these imines with that of N,N-dimethylaniline (I) indicates that the configuration about nitrogen in I and the great majority of aromatic amines approaches the pyramidal configuration much more closely than the trigonal configuration and that π–sp³-conjugation between a phenyl ring and an amine nitrogen is as effective as π–π-conjugation in lowering the energy of the system. The effects of polar and hydrogen-bonding solvents on the spectra of the amines studied are discussed.

Introduction

Wepster[2] has pointed out that the stereochemistry of nitrogen in aromatic amines is complicated, among other reasons, because the optimum configuration is a compromise between the intrinsic tendency of trivalent nitrogen to be pyramidal and the expected tendency in conjugated systems to assume the trigonal configuration in order to maximize the resonance interaction with the benzene ring. Thus, the lone pair of electrons on the nitrogen atom in an aromatic amine may have *sp*³-character, *p*-character or some intermediate character, depending upon how the various factors affecting the potential energy of the molecule vary with the valency angles about nitrogen. For example, in aromatic amines in which rotation about the aromatic carbon–nitrogen bond can occur, the valency angles of nitrogen would be expected to increase toward 120° as the "angle of twist" ϕ[3] approaches 0°, provided that the resonance energy

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[2] B. M. Wepster, *Rec. trav. chim.*, **72**, 661 (1953).

[3] The angle of twist ϕ is defined by the plane through the aromatic carbon–nitrogen bond perpendicular to the benzene ring and the plane through the aromatic carbon–nitrogen bond and the axis of symmetry of the lone pair of the nitrogen atom.