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REACTIONS OF IONS WITH MOLECULES IN THE GAS PHASE

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Abstract—Existing knowledge concerning the gas phase reactions of ions with molecules is summarized in terms of the identification of the reactions, the rate constants of the reactions, and the energetic properties of the ions observed to be formed and of those inferred as intermediates.

INTRODUCTION

IN the last few years considerable attention has been given to a newly recognized type of chemical reaction, namely, gas-phase reaction between ions and molecules. Although it has been recognized for a long time that such reactions were possibly of considerable importance in many gas-phase processes such as radiation chemistry, electric discharges, flames, etc., little or no detailed knowledge of the reactions existed. The constant improvement in mass spectrometric instrumentation and technique, while permitting the compilation of a large amount of useful information concerning the properties of isolated gaseous ions,[1] caused a neglect of the study of the reactions that take place upon collision of the ions with molecules. Secondary reactions between ions and molecules were observed by early workers in mass spectrometry[2] but were treated, for the most part, as nuisances due to experimental difficulties. The existence of such reactions also was recognized theoretically many years ago, as evidenced by the calculations on the rate of formation of H_3^+ in ionized hydrogen, by Eyring *et al.*[3] However, it was not until about 1952 that papers directly concerned with the experimental study of these secondary reactions began to appear in the literature. Such mass spectrometric investigations are of considerable general interest to chemists because they afford the opportunity of obtaining information not only on the energetics and unimolecular decomposition reactions of isolated ions but also on the bimolecular reactions of the ions with normal molecules. It goes without saying that such information is of value to persons working with systems in which ions are involved, a classification which includes those interested in both physical and organic chemistry.

Gaseous ions are high-energy transient entities and it is therefore not surprising that all direct observations of their reactions (both unimolecular and bimolecular) have been made in instruments designed to separate and detect such electrically charged molecular species, namely, in mass spectrometers. In the last few years indirect evidence of reactions between gaseous ions and molecules has come from radiation chemistry studies while similar information concerning ion-molecule interaction in condensed phases has long been available in the framework of the

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[1] F. H. Field and J. L. Franklin, *Electron Impact Phenomena and the Properties of Gaseous Ions*. Academic Press, New York (1957).
[2] H. D. Smyth, *Rev. Mod. Phys.* 3, 347 (1931).
[3] H. Eyring, J. O. Hirschfelder and H. S. Taylor, *J. Chem. Phys.* 4, 479 (1936).

carbonium ion theory of organic chemical reactions. In this paper, however, we shall be concerned primarily with reactions that have been directly observed and shall mention sources of indirect evidence only in passing. As a further restriction in subject matter, we discuss only those reactions in which the ion kinetic energy is below about 5 eV. This excludes many studies of charge exchange, dissociative charge exchange, and collision-induced ion dissociations, which in a strict sense, are also ion-molecule reactions.

Experimental Techniques

In the usual ionization chamber of a mass spectrometer ions, formed by electron impact, are impelled out of the chamber by a small applied electric field. Under conventional analytical conditions the pressure in the ionization chamber is so low (10^{-5} to 10^{-6} mm) that a primary ion has no opportunity to collide with a molecule during its brief residence time (10^{-6} to 10^{-7} sec) in the chamber. Thus under these conditions one sees no secondary reactions, but rather only the primary mass spectrum, consisting of the parent ion and the various fragment ions characteristic of the breakdown pattern of the molecule. However, if the pressure in the ionization chamber is raised sufficiently the fraction of primary ions that suffers collisions with molecules during the average residence time becomes appreciable; often the result of these collisions is a chemical reaction which produces a new or secondary ion and an electrically neutral entity.

The criteria used to decide if an ion, that appears in a "high pressure" mass spectrum but not in the corresponding "low pressure" spectrum, is formed by a bimolecular gas phase reaction are twofold.[4,5] Firstly, the intensity of a secondary ion will increase with the square of the pressure whereas a primary ion intensity, including, of course, that of primary ions due to impurities, will increase with the first power of the pressure. Obviously, the ratio of the intensity of a secondary ion to that of a primary ion will increase as the first power of the pressure. Such behavior for the CH_5^+ and $C_2H_5^+$ secondary ions in methane is shown in Fig. 1.[4] The slight curvature exhibited by the data pertaining to the $C_2H_5^+$ ion is due to differential scattering in the analyser of the mass spectrometer; it is not a phenomenon that occurs in the ionization chamber (the reaction vessel in these studies) and is, therefore, of no consequence to this discussion. The second criterion is based upon an empirical fact;[4] it has been observed that the behavior of ions formed in a gas phase collision with variation in the electric field strength in the ionization chamber is different from ions formed by electron impact in the electron beam. This difference in behavior enables one to make a differentiation between secondary ions formed by a gas phase collision, and secondary ions formed by electron impact subsequent to some other process such as pyrolysis on the electron-emitting filament. This phenomenon is not understood but probably results from the secondary ions being formed in a different region of the ionization chamber than the primary ions.

Once having established a secondary ion to be due to a bimolecular gas phase collision, it is, of course, desirable to ascertain the chemical reaction that is involved. It is generally assumed that the electrically neutral species taking part in the reaction is one of the molecules introduced into the mass spectrometer. The identity of the

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

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

ionic reactant is usually established by measurement of the ionizing electron energy at which the secondary ion first appears in the spectrum (appearance potential). The primary ion whose appearance potential most closely corresponds to that of the secondary ion is considered to be the ionic reactant,[4,5,7] provided that the reaction then visualized is not endothermic by more than one or two kcal/mole. This requirement of endothermicity is easily seen; in general, secondary ion abundances are quite small and, if we assume any reasonable collision cross-section, an exponential term involving significant activation energy ($E_{act} \geqslant \Delta H_R$) would so decrease the probability of occurrence of a reactive collision that we could not detect a reaction. For further details of reaction identification the original papers should be consulted.[4–7]

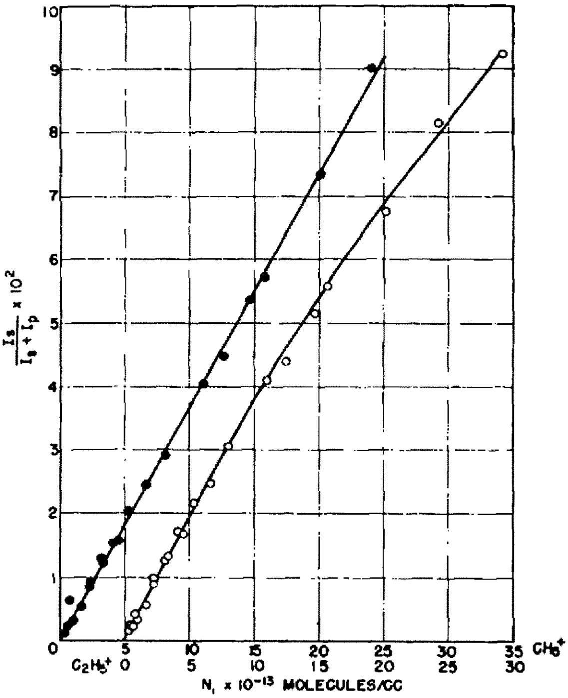

FIG. 1. Typical curves of current ratios against ion chamber concentration.

A quantitative interpretation of the results, in terms of the usual kinetic quantities (specific reaction rate or reaction cross-sections), requires a knowledge of the gas concentration in the ionization chamber. This quantity is usually determined as a function of the more easily measured mass spectrometer reservoir pressure of the gas.[4,5,8] In this method the ionization cross-section of the gas under investigation is determined by comparison of the total positive ion-current produced in it to that produced in a gas of known total ionization cross-section under identical conditions and in the limit of zero pressure. With the total ionization cross-section of a gas known, measurement of the total ionization produced in it permits calculation of the ionization chamber concentration as a function of the manometrically measured

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[6] V. L. Tal'roze and A. K. Lyubimova, *Dokl. Akad. Nauk SSSR* **86**, 909 (1952).
[7] V. L. Tal'roze and E. L. Frankevich, *Dokl. Akad. Nauk SSSR* **111**, 376 (1956).
[8] D. P. Stevenson and D. O. Schissler, *J. Chem. Phys.* **23**, 1353 (1955).

reservoir pressure. As a result of such measurements many ionization cross-sections for 75 eV are now recorded in the literature.[9,10]

Kinetics of Ion-Molecule Reactions

A. *Theory*

To convert the mass spectrometer ion-currents and measured ionization chamber concentrations for a given reaction into kinetic quantities, it is necessary to choose a model for the reaction. We consider[4] the reaction of a primary ion with a neutral molecule to consist of the formation of a transition-state ion which decomposes unimolecularly to various product ions and neutral entities. That is,

$$\mathrm{P}^+ + \mathrm{M} \xrightarrow{k_1} \mathrm{PM}^+ \tag{1}$$

$$\mathrm{PM}^+ \xrightarrow{k_{s_j}} \mathrm{S}_j^+ + F_j \tag{2}$$

where there may be a set of the above reactions for each primary ion that undergoes reaction with molecules. If the time of decomposition of PM^+ is short compared with ionic residence times (that is, if $k_{s_j} \gg 10^6$–10^7 sec^{-1}) then we can write for the number of ions S_j formed

$$n_{s_j} = \frac{k_{s_j}}{\sum k_{s_j}} n_{\mathrm{PM}} \, . \tag{3}$$

The number of ions, PM, formed is

$$n_{\mathrm{PM}} = f\Omega[M]n^\circ_p \tag{4}$$

where n°_p = the number of primary ions formed
f = collision efficiency for formation of PM^+
Ω = total number of collisions made by a single primary ion with neutral molecules at unit concentration
$[M]$ = concentration of neutral molecules.

Combining (3) and (4) and introducing τ_p, the residence time of the primary ion in the ionization chamber, we get

$$\frac{n_{s_j}}{n^\circ_p} = \frac{k_{s_j}}{\sum\limits_j k_{s_j}} \frac{f\Omega}{\tau_p} [M]\tau_p \, . \tag{5}$$

If the ratio of the number of secondary ions to the number of precursor primary ions is small (a condition always fulfilled), the quantity $(f\Omega)/(\tau_p)$ is the time-average rate of effective collisions, at unit concentrations, for PM^+ formation; this is, of course, the bimolecular rate constant k_1. Furthermore, $n^\circ_p = n_p + \sum\limits_j n_{s_j}$, where n_p is the number of primary ions collected. Making the further assumption that the collection efficiencies of all ions are equal, (5) becomes

$$\frac{I_{s_j}}{I_p + \sum\limits_j I_{s_j}} = \frac{k_{s_j}}{\sum\limits_j k_{s_j}} k_1[M]\tau_p \tag{6}$$

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[9] J. W. Otvos and D. P. Stevenson, *J. Amer. Chem. Soc.* **78**, 546 (1956).
[10] F. W. Lampe, J. L. Franklin and F. H. Field, *J. Amer. Chem. Soc.* **79**, 6129 (1957).

where the I's are the observed ion-currents. k_1 is easily evaluated from (6) by the additional relationship:

$$\frac{I_{s_j}}{\sum\limits_j I_{s_j}} = \frac{k_{s_j}}{\Sigma k_{s_j}}. \tag{7}$$

Another often-used way of expressing the rate is by means of the reaction cross-section. It is easily shown that the quantity Ω, defined earlier, is equal to the product of the collision cross-section, Q_c, and the distance, x, that the primary ions travel from the time that they are formed in the electron beam to the time that they pass out of the ionization chamber. That is

$$f\Omega = fQ_c x. \tag{8}$$

Comparison of (5), (6), and (8) shows immediately that

$$k_1 = fQ_c \frac{x}{\tau_p}. \tag{9}$$

Assuming the primary ions to be formed, on the average, with zero velocity component in the degree of freedom corresponding to the direction of the electric field, the primary ion residence time is, from the laws of motion,

$$\tau_p = \left(\frac{2m_i d}{eE}\right)^{\frac{1}{2}} \tag{10}$$

where d is the distance between the center of the electron beam and the ion-exit slit, m_i is the mass of the ion, E is the electric field strength, and e is the electronic charge. Although x, the distance traveled by a primary ion in its path through the ionization chamber, is a function of E and becomes equal to d only in the limit of infinite field strength, at all practical field strengths employed it may be replaced by d with little error. Then combining (9) and (10) we get

$$k_1 = \left(\frac{eEd}{2m_i}\right)^{\frac{1}{2}} fQ_c \tag{11}$$

a result identical to that obtained from a much more elaborate derivation.[11]

Eyring *et al.*[3] have shown that for absolute reaction rate theory the interaction between a molecule and an ion is adequately represented by an inverse fourth power attractive potential. For this type of interaction the *collision* cross-section is inversely proportional to the square root of the initial kinetic energy of the collision partners.[4,11,12] Strictly speaking, the initial kinetic energy will be an additive function of the thermal energies of both ion and molecule and the kinetic energy due to the acceleration of the ion by the electric field. However, at the field strengths generally employed in ion-molecule reaction studies, the thermal energy contribution is negligibly small and the collision cross-section should vary inversely with the square root of the electric field strength. That is,

$$Q_c \propto \left(\frac{1}{E}\right)^{\frac{1}{2}}. \tag{12}$$

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

[12] M. A. Eliason, D. E. Stogryn and J. O. Hirschfelder, *Proc. Natl. Acad. Sci.* **42**, 546 (1956).

Comparison of (11) and (12) indicates that if the efficiency or probability factor of the reaction, f, is independent of reactant energy, the rate constant, k_1, is independent of electric field strength.

B. *Results*

Equations (6) and (9) indicate that if one plots the observed ion-current ratio versus the gas concentration a straight line having a slope equal to

$$\frac{k_{s_i}}{\sum_j k_{s_j}} fQ_c x$$

is obtained. Such plots for the reactions

$$CH_4^+ + CH_4 \rightarrow CH_5^+ + CH_3 \qquad (R1)$$

$$CH_3^+ + CH_4 \rightarrow C_2H_5^+ + H_2 \qquad (R2)$$

are shown in Fig. 1. As mentioned earlier the curvature in the plot for the $C_2H_5^+$ is a result of differential scattering[4] and is of no consequence in this discussion; in cases where differential scattering occurs the initial slope is used to determine rate quantities. For reactant ions which produce only one product ion, such as in (R1) and (R2), $k_{s_i}/\sum_j k_{s_j}$ is unity and fQ_c is obtained directly (taking $x = d$). Otherwise (7) must be used to evaluate $k_{s_i}/\sum_j k_{s_j}$. To express the results in terms of specific reaction rate (11) is used.

For a certain class of reactions (usually reactions involving H_2 or H_2^+) that obeys (12) specific reaction rates can be determined at constant concentration by study of the variation of ion-current ratio with electric field strength.[5,13] Generally, however, (12) is not obeyed[4,13,16] with the consequence that k_1 is a function of electric field strength, decreasing with increasing field. A semi-empirical attempt to rationalize the effect of electric field for those cases in which (12) is not obeyed has been made,[4] primarily to obtain an extrapolation function; however, no really satisfactory explanation has yet been advanced.

A further interesting kinetic question concerns the nature of the transition state ion. Is it better represented as a charged system of two molecular species, each of which retains its identity, held together by polarization forces, for example in the case of (R1) by

$$(CH_4 \ldots \overset{+}{.} \ldots CH_4)$$

or is it better represented by a charged molecular system in which intimate mixing has occurred, that is, by $(C_2H_8)^+$?

Experiments with deuterated compounds suggest that both types of transition state ion exist. For the system CH_4—CD_4, Wagner *et al.*[17] have measured the relative abundances of CD_5^+, CD_4H^+, $CH_3D_2^+$, and CH_5^+ and have shown quite conclusively that no intimate mixing of hydrogen and deuterium occurs. Thus for this system the transition state ion is better represented by the first type of complex, that of individual molecular species physically bound together.

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[13] D. P. Stevenson, *J. Phys. Chem.* **61**, 1453 (1957).

[16] F. W. Lampe, F. H. Field and J. L. Franklin, *J. Amer. Chem. Soc.* **79**, 6132 (1957).

[17] C. D. Wagner, P. A. Wadsworth and D. P. Stevenson, *J. Chem. Phys.* **28**, 517 (1958).

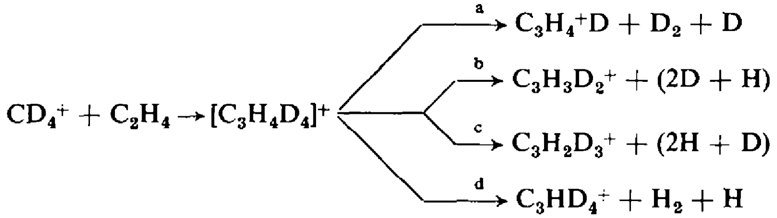
On the other hand, for systems in which the stoichiometry of the transition state corresponds to a stable ionic structure and in which much more atomic rearrangement occurs on reaction, the intimately mixed complex seems to be the appropriate model. The evidence for this is twofold: firstly, the agreement of the "secondary mass spectra" due to the reactions

$$C_2H_4^+ + C_2H_4 \rightarrow [C_4H_8]^+ \rightarrow \text{fragmentation} \tag{R3}$$

$$C_2H_2^+ + C_2H_4 \rightarrow [C_4H_6]^+ \rightarrow \text{fragmentation} \tag{R4}$$

$$C_2H_2^+ + C_2H_2 \rightarrow [C_4H_4]^+ \rightarrow \text{fragmentation} \tag{R5}$$

with the primary mass spectra of C_4H_8, C_4H_6, and C_4H_4 compounds is evidence of a chemically bound intermediate structure;[4,15] secondly, the relative abundances of the deuterated $C_3H_5^+$ ionic products in the reaction[18]



$$CD_4^+ + C_2H_4 \rightarrow [C_3H_4D_4]^+ \left\{ \begin{array}{l} \xrightarrow{a} C_3H_4^+D + D_2 + D \\ \xrightarrow{b} C_3H_3D_2^+ + (2D + H) \\ \xrightarrow{c} C_3H_2D_3^+ + (2H + D) \\ \xrightarrow{d} C_3HD_4^+ + H_2 + H \end{array} \right. \tag{R6}$$

are a : b : c : d = 1 : 4 : 4 : 1. Completely equivalent hydrogen atoms in the complex would lead to 1 : 6 : 6 : 1. Thus in (R6) also it appears as if intimate mixing does occur and that the transition-state-ion is better represented by a chemically bound charged entity.

In the following sections of this paper we have tabulated the ion-molecule reactions observed to date. The reaction cross-sections reported are, in general, those obtained in our laboratory at a field strength of 10 V/cm. In the case of values reported by other workers[13,14] we have tabulated the cross-sections as reported for those reactions not obeying (12) and have converted the reported rate constants for those reactions obeying (12) to reaction cross-sections at 10 V/cm by means of equation (11). In comparing rate constants and cross-sections of ion-molecule reactions and in utilizing them in interpretations of similar reactions carried out in more conventional reaction vessels, it should be kept in mind that the reported values, in general, refer to an electric field strength and may be dependent upon field strength.

Ion-Molecule Reactions Observed

A. *Reactions involving neutral atom and positive atomic ion transfer*

This type of reaction includes those first observed by early workers in mass spectrometry and often results in a type of molecular species both new and interesting from a structural point of view, namely, the protonated molecular structures long postulated as intermediates in organic chemistry. In Table 1 we present the reactions known to date, along with the type of transfer involved, the reaction cross-section reported, and the observers. In cases in which more than one reaction cross-section

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[14] D. O. Schissler and D. P. Stevenson, *J. Chem. Phys.* **24**, 926 (1956).

[15] F. H. Field, J. L. Franklin and F. W. Lampe, *J. Amer. Chem. Soc.* **79**, 2665 (1957).

[18] This Laboratory, Unpublished results.

TABLE 1. NEUTRAL ATOM AND POSITIVE ATOMIC ION TRANSFER REACTIONS

Reaction	Entity transferred	$fQ_c \times 10^{16}$ cm^2	Reference
$H_2^+ + H_2 \rightarrow H_3^+ + H$	?	27·4[a]	3
$D_2^+ + D_2 \rightarrow D_3^+ + D$	?	26·8	8, 13
$H_2^+ + C_2H_6 \rightarrow H_3^+ + C_2H_5$	H.	—	19
$Ne^+ + H_2 \rightarrow NeH^+ + H$	H.	14·1	14
$A^+ + H_2 \rightarrow AH^+ + H$	H.	111	8, 13
$A^+ + HD \rightarrow AD^+ + H$	D.	46·3	8, 13
$A^+ + HD \rightarrow AH^+ + D$	H.	40·5	8, 13
$A^+ + D_2 \rightarrow AD^+ + D$	D.	82·1	8, 13
$Kr^+ + H_2 \rightarrow KrH^+ + H$	H.	42·5	13, 14
$Kr^+ + D_2 \rightarrow KrD^+ + D$	D.	29·8	14
$CH_4^+ + CH_4 \rightarrow CH_5^+ + CH_3$	?	61·0	4, 6, 20
$CD_4^+ + CD_4 \rightarrow CD_5^+ + CD_3$	?	63·4, 57·2	8, 17, 21
$(CD_4 + CH_4)^+ \rightarrow CH_4D^+ + CH_3$	?	73	21, 22
$(CH_4 + H_2)^+ \rightarrow CH_5^+ + H$	?	<0·2	19, 34
$CD_4^+ + C_2H_6 \rightarrow CD_4H^+ + C_2H_5$	H.	8·1	21, 22
$CH_4^+ + C_3H_6 \rightarrow CH_5^+ + C_3H_5$	H.	—	19
$CD_4^+ + C_3H_8 \rightarrow CD_4H^+ + C_3H_7$	H.	4	21, 22
$CD_4^+ + i\text{-}C_4H_{10} \rightarrow CD_4H^+ + C_4H_9$	H.	3	21, 22
$CD_4^+ + CH_3Cl \rightarrow CD_4H^+ + CH_2Cl$	H.	3	21, 22
$CD_4^+ + NH_3 \rightarrow CD_4H^+ + NH_2$	H.	6·4	21, 22
$CD_4^+ + H_2S \rightarrow CD_4H^+ + HS$	H.	12	21, 22
$(CH_4 + HCl)^+ \rightarrow CH_5^+ + Cl$	?	33[b]	21
$(CD_4 + HCl)^+ \rightarrow CD_4H^+ + Cl$	?	41[b]	21, 22
$C_2H_3^+ + C_2H_4 \rightarrow C_2H_5^+ + C_2H_2$	H^+	32, 359[c]	4, 13, 14
$C_3H_8^+ + C_2H_4 \rightarrow C_2H_5^+ + C_3H_7$	H^+	—	23
$C_3H_6^+ + C_3H_6 \rightarrow C_3H_7^+ + C_3H_5$	?	—	6, 14
$i\text{-}C_4H_8^+ + i\text{-}C_4H_8 \rightarrow t\text{-}C_4H_9^+ + C_4H_7$	?	—	6
$N_2^{+*} + N_2 \rightarrow N_3^+ + N$	?	—	24, 25
$N_2^+ + D_2 \rightarrow N_2D^+ + D$	D.	86·3	13, 14
$NH_3^+ + NH_3 \rightarrow NH_4^+ + NH_2$	?	—	18, 26
$O_2^+ + H_2 \rightarrow H_2O^+ + O$	O^+	—	27
$H_2O^+ + H_2O \rightarrow H_3O^+ + OH$	?	95·0	6, 7, 16
$D_2O^+ + D_2O \rightarrow D_3O^+ + OD$	?	102	16
$D_2O^+ + H_2 \rightarrow HD_2O^+ + H$	H	63·0	16
$(H_2O + CH_4)^+ \rightarrow H_3O^+ + CH_3$	?	180	6, 16
$(D_2O + CH_4)^+ \rightarrow HD_2O^+ + CH_3$	?	148	16
$H_2O^+ + C_2H_2 \rightarrow H_3O^+ + C_2H$	?	—	7
$C_2H_6^+ + D_2O \rightarrow HD_2O^+ + C_2H_5$	H^+	440	16
$D_2O^+ + \text{cyclo } C_3H_6 \rightarrow HD_2O^+ + C_3H_5$	H.	40	16
$H_2O^+ + C_3H_8 \rightarrow H_3O^+ + C_3H_7$	H.	—	7
$C_3H_8^+ + H_2O \rightarrow H_3O^+ + C_3H_7$	H^+	—	7

TABLE 1 (*continued*)

Reaction	Entity transferred	$fQ_0 \times 10^{16}$ cm^2	Reference
$C_3H_8^+ + D_2O \rightarrow HD_2O^+ + C_3H_7$	H^+	440	16
$D_2O^+ + n\text{-}C_4H_{10} \rightarrow HD_2O^+ + C_4H_9$	H.	96	16
$H_2O^+ + NH_3 \rightarrow H_3O^+ + NH_2$	H.	—	7
$H_2O^+ + H_2S \rightarrow H_3O^+ + HS$	H.	—	7
$H_2S^+ + H_2O \rightarrow H_3O^+ + HS$	H^+	—	7
$H_2^+ + O_2 \rightarrow HO_2^+ + H$	H^+	126	13, 14
$D_2^+ + O_2 \rightarrow DO_2^+ + D$	D^+	88	13, 14
$CO^+ + D_2 \rightarrow CDO^+ + D$	D.	72·5	14
$CH_3OH^+ + CH_3OH \rightarrow CH_3OH_2^+ + CH_3O$	?	583	13, 14
$CH_3OH^+ + H_2O \rightarrow CH_3OH_2^+ + OH$	H.	—	23
$C_2H_5OH^+ + H_2O \rightarrow C_2H_5OH_2^+ + OH$	H.	—	23
$(CO_2 + H_2)^+ \rightarrow HCO_2^+ + H$	?	—	29
$H_2O^+ + CO_2 \rightarrow HCO_2^+ + OH$	H^+	—	29
$O^+ + N_2 \rightarrow NO^+ + N$	N.	2000[e]	30
$HCl^+ + HCl \rightarrow H_2Cl^+ + Cl$	?	24, 48	14, 21
$(HCl + CH_4)^+ \rightarrow H_2Cl^+ + CH_3$	?	129[f]	21
$(HCl + CD_4)^+ \rightarrow HDCl^+ + CD_3$	?	109[f]	21
$CH_3Cl^+ + CH_3Cl \rightarrow CH_4Cl^+ + CH_2Cl$	?	—	18
$HBr^+ + HBr \rightarrow H_2Br^+ + Br$	?	39	14
$H_2S^+ + H_2S \rightarrow H_3S^+ + HS$	?	31	21, 22
$H_2S^+ + CD_4 \rightarrow H_2DS^+ + CD_3$	D.	14	21, 22

[a] Theoretical calculation of k_1 combined with equation (11).
[b] Calculated on the assumption that CH_4^+ (or CD_4^+) is the ionic reactant.
[c] Probably at about 8 V/cm.
[d] Calculated on the assumption that H_2O^+ (or D_2O^+) is the ionic reactant.
[e] Very uncertain.
[f] Calculated on the assumption that HCl^+ is the ionic reactant.

[19] E. L. Frankevich and V. L. Tal'roze, *Dokl. Akad. Nauk SSSR* **119**, 1174 (1958).
[20] G. G. Meisels, W. H. Hamill and R. R. Williams, Jr., *J. Chem. Phys.* **25**, 790 (1956).
[21] F. H. Field and F. W. Lampe, *J. Amer. Chem. Soc.* **80**, 5583 (1958).
[22] F. W. Lampe and F. H. Field, *J. Amer. Chem. Soc.* **79**, 4244 (1957).
[23] V. L. Tal'roze and E. L. Frankevich, *J. Amer. Chem. Soc.* **80**, 2344 (1958).
[24] M. Saporoschenko, *Phys. Rev.* **111**, 1550 (1958).
[25] G. Junk and H. J. Svec, *J. Amer. Chem. Soc.* **80**, 2908 (1958).
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[27] D. A. Hutchinson, Paper presented at *Amer. Chem. Soc. Meeting*, Minneapolis, Minnesota, Sept. (1955).
[28] M. M. Mann, A. Hustrulid and J. T. Tate, *Phys. Rev.* **58**, 340 (1940).
[29] J. J. Mitchell, R. H. Perkins and F. F. Coleman, *J. Chem. Phys.* **16**, 835 (1948).
[30] R. F. Potter, *J. Chem. Phys.* **23**, 2462 (1955).
[34] F. W. Lampe and F. H. Field, *J. Amer. Chem. Soc.* **81**, 3238 (1959).

have been reported, we tabulate all available values. For cases in which reactants are written as $(A + B)^+$ we do not know which of the species is the ionic reactant.

Although the theory of the rates of ion-molecule reactions gives order-of-magnitude agreement with observation, the deviations in rate from one reaction to another are not, in general, accounted for by the theory.

It is perhaps of interest to point out that the cross-sections of those reactions in Table 1 that are known to involve the transfer of a proton are usually an order of magnitude larger than those involving the transfer of a hydrogen atom. Again, this fact is not explainable by the present theory of ion-molecule reaction rates.

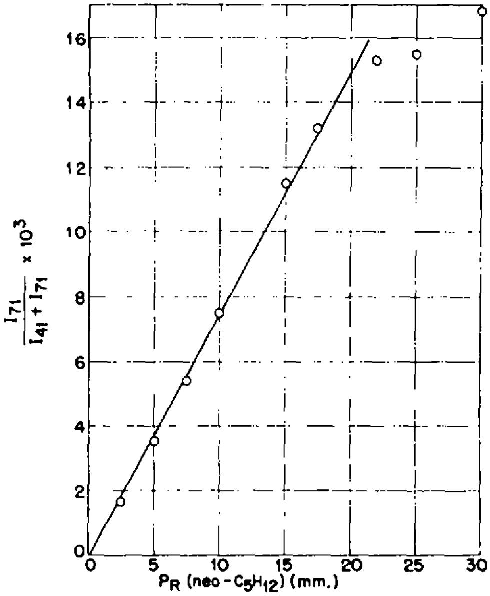

FIG. 2. Hydride ion transfer in neopentane.

B. *Hydride ion transfer reactions*

Reactions involving the transfer of a hydride ion have been postulated for many years[31,32] and are considered to be of much importance in many processes such as alkylation, isomerization and cationic polymerization. Prior to their detection in the gas phase,[33] however, there had never been, to our knowledge, direct observation of the elementary reactions.

Recognition of the fact that hydride ion transfer reactions were occurring in the gas phase was due to the observation that in many paraffinic compounds the "high pressure" mass spectra show secondary ions of mass one unit lower than the molecular weight of the parent compound. The phenomenon is most obvious (and was here first observed) in neopentane because in this system the primary ions containing five carbon atoms have a negligible intensity; hence any secondary ions formed in this mass region will not be obscured. In Fig. 2[33] we show a plot of the ratio of the mass

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[31] P. D. Bartlett, F. E. Condon and A. Schneider, *J. Amer. Chem. Soc.* **66**, 1531 (1944).
[32] F. C. Whitmore, *J. Amer. Chem. Soc.* **54**, 3274 (1932).
[33] F. H. Field and F. W. Lampe, *J. Amer. Chem. Soc.* **80**, 5587 (1958).

71 intensity to the sum of the intensities of the mass 71 and mass 41 ions against the neopentane pressure. The rise of this ratio shows without doubt that $C_5H_{11}^+$ is a secondary ion. The appearance potential of the $C_5H_{11}^+$ ion is identical to the appearance potential of the $C_3H_5^+$ primary ion from neopentane[34] and it may be concluded that $C_3H_5^+$ is a reactant ion. Any reaction between $C_3H_5^+$ ion and neopentane to form the $C_5H_{11}^+$ ion that does not involve the formation of propylene would be strongly endothermic and hence not observable by mass spectrometric technique. Therefore, the reaction occurring must be

$$C_3H_5^+ + \text{neo}C_5H_{12} \rightarrow C_5H_{11}^+ + C_3H_6 \tag{R7}$$

which is obviously a hydride ion transfer reaction.

Although appearance potential measurements establish $C_3H_5^+$ as a reactant ion they do not rule out the possibility that other ions of higher appearance potentials may also be reactant ions. In view of its simple nature it seems likely that the reaction will occur with all ions having an unoccupied valence orbital, provided that it is not energetically prohibited. In this respect it is of interest to point out that appearance potential measurements do rule out the occurrence of the reaction

$$\text{t-}C_4H_9^+ + \text{neo}C_5H_{12} \rightarrow \text{iso}C_4H_{10} + C_5H_{11}^+. \tag{R8}$$

Since the lack of occurrence of (R8) cannot be due to intensity limitations ($\text{t-}C_4H_9^+$ is the major primary ion) it may be limited energetically; an endothermicity of 2 kcal/mole would certainly preclude its observation. Taking the most reliable value of $\Delta H_+(\text{t-}C_4H_9^+)$ to be 178 kcal/mole[34,46] would then lead to $\Delta H_f(C_5H_{11}^+) \geqslant 168$ kcal/mole.

Secondary ions of mass one unit less than the parent molecule also have been observed in ethane, propane, n-butane, isobutane, and neohexane. However, for these compounds no experimental information concerning the details of the reactions is available because of the presence of appreciable quantities of primary ions having masses one unit less than the parent molecule. The identities of the neutral reactant and product ion are known, though, and coupled with energetic considerations permit the assignment of some limits upon the possible ionic reactants and neutral products. In Table 2[33] we show the possible hydride ion transfer reactions that account for the observations. The list of possible ionic reactants was arrived at by assuming that only exothermic reactions of primary ions having abundances of 10 per cent or greater need be considered. It should be recognized that in some instances sufficient energy will be available for further decomposition of the neutral product.

Studies of hydride ion transfer reactions have also been made with the same pure compounds admixed with methane.[33] Since the only ions from methane which can undergo the reaction are the CH_2^+ and CH_3^+ ions, there is less uncertainty concerning the reactions involved in removing a hydride ion from the parent molecule. These systems are also listed in Table 2 and a typical plot for the $\text{i-}C_4H_{10}$—CH_4 mixtures is shown in Fig. 3.

Values of reaction cross-section listed in Table 2 were obtained by assuming the reactant ions to be those primary ions of more than 10 per cent relative intensity

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[46] F. P. Lossing, P. Kebarle and J. B. Desousa, Paper presented at the Institute of Petroleum Hydrocarbon Research Group and A.S.T.M. Committee E-14 Joint Conference on *Mass Spectrometry*, London, September (1958).

TABLE 2. HYDRIDE ION TRANSFER REACTIONS

System	Allowed reactant ions	Reaction cross-section (A^2)
C_2H_6	CH_3^+, $C_2H_3^+$	264
C_3H_8	CH_3^+, $C_2H_3^+$, $C_2H_4^+$, $C_2H_5^+$, $C_3H_3^+$, $C_3H_5^+$	66
n-C_4H_{10}	$C_2H_3^+$, $C_2H_4^+$, $C_2H_5^+$, $C_3H_3^+$, $C_3H_5^+$, $C_3H_6^+$, $C_3H_7^+$	32
i-C_4H_{10}	$C_2H_3^+$, $C_3H_3^+$, $C_3H_5^+$, $C_3H_6^+$, $C_3H_7^+$	34
neo-C_5H_{12}	$C_2H_3^+$, $C_2H_5^+$, $C_3H_3^+$, $C_3H_5^+$	14
neo-C_6H_{14}	$C_2H_3^+$, $C_2H_5^+$, $C_3H_3^+$, $C_3H_5^+$, $C_3H_7^+$, $C_4H_8^+$, $C_4H_9^+$, $C_5H_{11}^+$	7
C_2H_6–CH_4	CH_3^+, CH_2^+	171
C_3H_8–CH_4	CH_3^+, CH_2^+	107
n-C_4H_{10}–CH_4	CH_3^+, CH_2^+	60
i-C_4H_{10}–CH_4	CH_3^+, CH_2^+	101
neo-C_5H_{12}–CH_4	CH_3^+, CH_2^+	12
neo-C_6H_{14}–CH_4	CH_3^+, CH_2^+	16

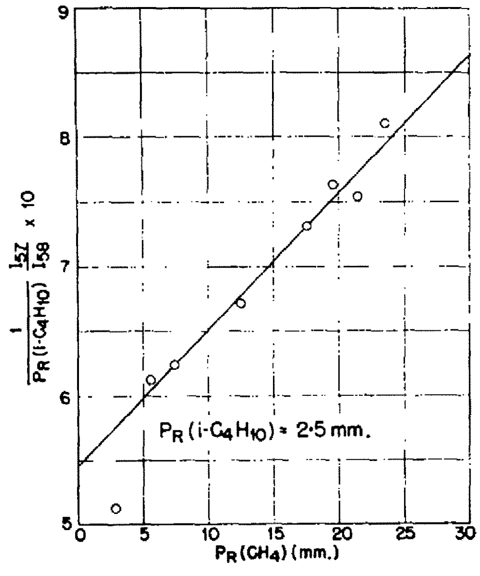

FIG. 3. Hydride ion transfer in i-C_4H_{10}—CH_4.

which are energetically capable of reaction, for the case of the pure compounds, and CH_2^+ and CH_3^+ for the methane mixtures. Slopes of ion-current ratios versus pressure plots (Figs. 2 and 3) were then compared to slopes observed for (R1), for the calculation of reaction cross-sections. The cross-sections so calculated depend strongly upon the correctness of the assumption of which ions are reactants. Consequently, the agreement between the values found for the pure compounds and methane mixtures, while certainly not exact, may be considered as satisfactory. In both sets of values there is a trend of decreasing reaction cross-section with increasing molecular weight. We have no explanation for this trend which is in the direction opposite to that expected.

In a sense the reactions observed by Meisels *et al.*,[20,35] viz.

$$A^+ + CH_4 \rightarrow CH_3^+ + H + A \tag{R9}$$

$$Kr^+ + CH_4 \rightarrow CH_3^+ + H + Kr \tag{R10}$$

$$Kr^+ + C_2H_6 \rightarrow C_2H_5^+ + H + Kr \tag{R11}$$

$$Xe^+ + C_3H_8 \rightarrow C_3H_7^+ + H + Xe \tag{R12}$$

could be considered as hydride ion transfers resulting in an unstable molecule which immediately dissociates. However, there may be some question about (R10) since if it occurs without any excess energy in Kr^+ it is the first endothermic reaction observed ($\Delta H = +7$ kcal/mole). Moreover, since the parent peaks in the methane, ethane, and propane spectra for the systems indicated in (R10)–(R12) also increase with rare gas pressure,[35] these reactions are best considered as dissociative charge transfer processes.

C. *Condensation type reactions*

Under this heading we group all those reactions that involve considerably more molecular rearrangement than the simple transfer of an atom or atomic ion. In all reactions of this class, observed to date, carbon–carbon or carbon–sulfur bond formation occurs; hence the use of the term condensation. The reactions reported along with their specific reaction rates are shown in Table 3.

In addition to the reactions listed in Table 3, Levy and Skahan[40] have found secondary ions in *cis*-2-butene, the most prominent of which were the $C_5H_7^+$ and $C_5H_9^+$ ions. As has proven to be generally true, they found no dimer ions ($C_8H_{16}^+$) but did observe ion masses up to 105.

Many of the reactions shown in Table 3 are of an unexpected and even surprising nature. Knowledge of the existence of such reactions is proving of considerable aid in radiation chemistry mechanism studies because such unusual reactions would never be postulated on an a priori basis. Of course, their importance in other reaction systems depends upon whether or not the reactant ions are formed.

D. *Negative ion reactions*

As is true in studies of the properties of isolated ions in the gas phase and organic chemical reactions in condensed phases, much more is known about bimolecular positive ion reactions than the corresponding negative ion reactions. To the authors' knowledge there have been only two negative ion-molecule reactions observed to date (other than collision induced dissociations at high ion energies), namely,

$$H^- + H_2O \rightarrow OH^- + H_2. \tag{R13}$$[41]

and

$$HCOO^- + N_2 \rightarrow CN^- + (HNO_2?) \tag{R14}$$[42]

Reaction (R13) is probably most easily visualized as the transfer of a proton from the water to the hydride ion.

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[35] G. G. Meisels, W. H. Hamill and R. R. Williams, Jr., *J. Phys. Chem.* **61**, 1456 (1957).

[40] E. J. Levy and D. J. Skahan, Paper presented at Meeting of A.S.T.M. Committee E-14 on *Mass Spectrometry*, New Orleans, Louisiana, June (1958).

[41] E. E. Muschlitz, *J. Appl. Phys.* **28**, 1414 (1957).

[42] C. E. Melton and Gus A. Ropp, *J. Amer. Chem. Soc.* **80**, 5573 (1958).

TABLE 3. CONDENSATION TYPE REACTIONS

Reaction	$fQ_c \times 10^{16}$ cm^2	Reference
$CH_3^+ + CH_4 \rightarrow C_2H_5^+ + H_2$	58, 165[a]	4, 13, 14, 20, 35
$CD_3^+ + CD_4 \rightarrow C_2D_5^+ + D_2$	161[a]	13, 14, 18
$CH^+ + C_2H_2 \rightarrow C_3H^+ + H_2$	39	15
$CH^+ + C_2H_2 \rightarrow C_3H_2^+ + H$	19	15
$C_2H_2^+ + C_2H_4 \rightarrow C_3H_3^+ + CH_3$	22, 24[a]	4,14
$C_2H_4^+ + C_2H_4 \rightarrow C_3H_5^+ + CH_3$	43, 112[a]	4, 13, 14
$C_2H_3^+ + C_2H_6 \rightarrow C_3H_5^+ + CH_4$	78[a]	14
$CH_4^+ + C_2H_4 \rightarrow C_3H_6^+ + H_2 + H$	—	18
$CD_4^+ + C_2H_4 \rightarrow C_3H_4D^+ + D_2 + D$	—	18
$CD_4^+ + C_2H_4 \rightarrow C_3H_3D_2^+ + (2D + H)$	—	18
$CD_4^+ + C_2H_4 \rightarrow C_3H_2D_3^+ + (2H + D)$	—	18
$CD_4^+ + C_2H_4 \rightarrow C_3HD_4^+ + H_2 + H$	—	18
$C_2^+ + C_2H_2 \rightarrow C_4H^+ + H$	68	15
$C_2H_2^+ + C_2H_2 \rightarrow C_4H_2^+ + H_2$	35	15
$C_2^+ + C_2H_4 \rightarrow C_4H_2^+ + H_2$	89	4
$C_2H_2^+ + C_2H_2 \rightarrow C_4H_3^+ + H$	42	15
$C_2H^+ + C_2H_4 \rightarrow C_4H_3^+ + H_2$	34	4
$C_2H_2^+ + C_2H_4 \rightarrow C_4H_5^+ + H$	14	4
$C_2H_4^+ + C_2H_4 \rightarrow C_4H_7^+ + H$	4	4
$C_3H_5^+ + C_3H_6 \rightarrow C_4H_7^+ + C_2H_4$	140[a]	13, 14
$C_3H_6^+ + C_3H_6 \rightarrow C_4H_8^+ + C_2H_4$	74[a]	13, 14
$C_3H_2^+ + C_4H_6 \rightarrow C_5H_5^+ + C_2H_3$	—	39
$C_4H_6^+ + C_4H_6 \rightarrow C_5H_6^+ + C_3H_6$	—	39
$C_4H_6^+ + C_4H_6 \rightarrow C_5H_7^+ + C_3H_5$	—	39
$C_4H_2^+ + C_4H_6 \rightarrow C_6H_4^+ + C_2H_4$	—	39
$C_4H_4^+ + C_4H_6 \rightarrow C_6H_5^+ + C_2H_5$	—	39
$C_4H_6^+ + C_4H_6 \rightarrow C_6H_6^+ + C_2H_6$	—	39
$C_4H_6^+ + C_4H_6 \rightarrow C_6H_7^+ + C_2H_5$	—	39
$C_4H_6^+ + C_4H_6 \rightarrow C_6H_8^+ + C_2H_4$	—	39
$\begin{matrix} C_3H_3^+ \\ \text{or} \\ C_4H_5^+ \end{matrix} + C_4H_6 \rightarrow C_7H_7^+ + \begin{matrix} H_2 \\ \text{or} \\ CH_4 \end{matrix}$	— —	39
$\begin{matrix} C_3H_3^+ \\ \text{or} \\ C_4H_5^+ \end{matrix} + C_4H_6 \rightarrow C_7H_8^+ + \begin{matrix} H \\ \text{or} \\ CH_3 \end{matrix}$	—	39
$C_4H_6^+ + C_4H_6 \rightarrow C_7H_9^+ + CH_3$	—	39
$CH_3^+ + H_2S \rightarrow CHS^+ + 2H_2$	{16}	21
$CH_4^+ + H_2S \rightarrow CHS^+ + 2H_2 + H$		21
$CH_3^+ + H_2S \rightarrow CH_3S^+ + H_2$	{52}	21
$CH_4^+ + H_2S \rightarrow CH_3S^+ + H_2 + H$		21

[a] Probably at about 8 V/cm.

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[36] F. W. Lampe, *J. Amer. Chem. Soc.* 79, 1055 (1957).

[37] F. W. Lampe, *Rad. Res.* **10**, 691 (1959).

[38] R. H. Schuler, *J. Chem. Phys.* 26, 425 (1957).

[39] R. Barker, R. R. Williams, Jr. and W. H. Hamill, Paper presented at Meeting of A.S.T.M. Committee E-14 on *Mass Spectrometry*, New Orleans, Louisiana, June (1958).

The reaction cross-section for (R13) was found to be 3×10^{-17} cm^2 which corresponds to a rate constant comparable to those observed in positive ion-molecule reaction studies.

Ion Energetics

As mentioned earlier the observance of a secondary ion enables one to conclude, within an error of one or two kcal/mole, that for the reaction involved in its formation, $\Delta H \leq O$. If the reaction producing the secondary ion can be established and if the standard heats of formation of reactants and neutral product(s) are known, upper limits to the heats of formation of the product ions may be calculated by the use of Hess's Law of constant heat summation. That is,

$$\Delta H_f(\text{product ion}) \leq \Sigma\Delta H_f(\text{reactants}) - \Sigma\Delta H_f(\text{neutral products}). \qquad (13)$$

Contrary to one point of view,[23] however, this requirement that $\Delta H \leq O$ is a necessary but is not a sufficient condition for the observation of a given reaction. Thus the failure to detect a given reaction does not permit one to conclude without qualification that the reaction is endothermic. There may be other factors involved which result in failure to observe a given reaction. One possibility is the occurrence of a more probable competitive reaction; an example of this is provided by the finding of Meisels *et al.*[20,35] that A^+ undergoes a dissociative charge transfer reaction with methane rather than the hydrogen atom abstraction reaction which would be energetically equivalent to the established formation of AH^+ in argon–hydrogen mixtures.[8] Another possibility and one which may account for the failure to observe $C_2H_7{}^+$ and $C_3H_9{}^+$ ions in ethane–hydrogen and propane–hydrogen mixtures,[23] respectively, is that of the very rapid further decomposition of a highly energetic product ion formed in a very exothermic reaction. An extreme example of this alternative is the complete failure so far to detect the dimer ion formed by the association of the reactants. Lower limits to the heats of formation of product ions, derived from the assumption that a given reaction is endothermic because it is not observed, are therefore to be regarded with reservation. In Table 4 we present limits to the heats of formation of ions, for which, for the most part, no energetic values from independent methods are available. For the most part the upper limits are derived from the reactions known to take place which we have tabulated in Tables 1 and 3. The ΔH_f limits for the protonated paraffins other than methane are based on the reasonable assumption that in the hydride ion transfer reactions observed in methane mixtures, $CH_3{}^+$ is a reactant ion. The transition state ion in this case must be of the formula $C_nH^+_{2n+3}$ and in order for reaction to be observable its heat of formation must be lower than the sum of the heats of formation of the reactants. The values for $CH_3SH_2{}^+$, $CH_4SH_2{}^+$, $C_6H_{11}{}^+$, $C_6H_{12}{}^+$, and $C_8H_{17}{}^+$ were derived in a similar way.

Many of the ions shown in Table 4 have the structure of stable and often saturated molecules to which a proton has been added and it is of interest to express the energetics of such important and unusual species as proton affinities of the original molecule.[6–8,19,23] Since the proton affinity of a molecule, M, is defined as the negative of the enthalpy change of the reaction

$$M + H^+ \rightarrow MH^+ \qquad (R15)$$

it follows that

$$P.A.(M) = \Delta H_f(H^+) + \Delta H_f(M) - \Delta H_f(MH^+). \qquad (14)$$

TABLE 4. STANDARD HEATS OF FORMATION OF GASEOUS IONS

Ion	ΔH_f in kcal/mole	
	Ion-molecule reactions	Independent method
NeH^+	< 445	None
AH^+	< 312	None
KrH^+	< 271	None
H_3^+	$286^a < \Delta H_f < 304$	311[43]
CH_5^+	$218^a < \Delta H_f < 233$	None
$C_2H_7^+$	< 244	None
$C_3H_9^+$	< 242	None
$C_4H_{11}^+$	< 237	None
$C_5H_5^+$	< 309	226[1]
$C_5H_6^+$	< 261	231[1]
$C_5H_7^+$	< 233	226[1]
$C_5H_{13}^+$	< 232	None
$C_6H_4^+$	< 366	329[1]
$C_6H_7^+$	$201^a < \Delta H_f < 241$	None
$C_6H_8^+$	< 254	None
$C_6H_{11}^+$	< 230	None
$C_6H_{12}^+$	< 236	197–211[1]
$C_6H_{15}^+$	< 222	None
$C_7H_7^+$	< 330	215–244[1]
$C_7H_8^+$	< 281	215[1]
$C_7H_9^+$	< 235	None
$C_7H_{17}^+$	< 218	None
$C_8H_{17}^+$	< 190	None
N_3^+	< 398	388[44]
N_2H^+	< 307	278[44]
NH_4^+	< 180	154[45]
HO_2^+	< 304	271[1]
H_3O^+	$136^a < \Delta H_f < 140$	None
CHO^+	< 245	203[1]
$CH_3OH_2^+$	$134^a < \Delta H_f < 140$	None
$C_2H_5OH_2^+$	$107^a < \Delta H_f < 124$	None
HCO_2^+	< 156	140–195[1]
H_2Cl^+	< 225	None
H_2Br^+	< 226	None
H_3S^+	< 187	None
$CH_3SH_2^+$	< 257	None
$CH_4SH_2^+$	< 280	None

[a] Lower limit obtained by assumption that a reaction was endothermic because it was not observed. This is to be accepted with reservation.

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[43] R. S. Baker, J. C. Giddings and H. Eyring, *J. Chem. Phys.* **23**, 344 (1955).

[44] J. L. Franklin, V. H. Dibeler, R. M. Reese and M. Kraus, *J. Amer. Chem. Soc.* **80**, 298 (1958).

[45] F. D. Rosini, D. D. Wagman, W. H. Evans, Samuel Levine, and I. Jaffe, *Selected Values of Chemical Thermodynamic Properties*. N.B.S. Circular 500 (1952).

TABLE 5. PROTON AFFINITIES OF MOLECULES IN GAS PHASE

Molecule	Proton affinity (kcal/mole)		Independent method
	Lower limit	Upper limit	
Ne	−80	—	—
A	43	—	—
Kr	94	—	—
H_2	61	79[a]	—
CH_4	114	129[a]	—
C_2H_6	101	—	—
C_3H_8	98	—	—
C_4H_{10}	98	—	—
cyclo-C_5H_6	164	—	—
C_5H_{12}	98	—	—
C_6H_6	144	—	—
cyclo-C_6H_{10}	132	—	—
C_6H_{14}	103	—	—
C_7H_8	142	—	—
C_7H_{16}	102	—	—
C_8H_{16}	155	—	—
N_2	58	—	—
NH_3	174	—	200[45]
O_2	61	—	—
H_2O	167	171[a]	—
CO	94	—	136[1]
CH_3OH	177	183[a]	—
C_2H_5OH	185	202[a]	—
CO_2	115	—	76–131[1]
HCl	120	—	—
HBr	130	—	—
H_2S	175	—	—
CH_3SH	105	—	—

[a] Upper limit obtained by assumption that a reaction was endothermic because it was not observed. This is to be accepted with reservation.

The data in Table 4 which represent upper and lower limits to $\Delta H_f(MH^+)$ can be used in (14) to calculate lower and upper limits, respectively, of the affinity of the original molecule, M, for the proton. In Table 5 we show proton affinity limits for those stable molecules whose protonated forms, MH^+, appear in Table 4. The reservation concerning the lower limits to the standard heats of formation of the ions applies to the upper limits of molecular proton affinities.

As expected the proton affinities of unsaturated molecules and of molecules containing unshared electron pairs are quite high (usually greater than 140 kcal/mole) and considerably higher than those of the saturated molecules. Nevertheless the proton affinities of the saturated molecules are surprisingly high. The protonation of saturated molecules is now being recognized as important in the radiation chemistry of gases and it may well be that such protonation plays a larger part than generally considered in chemical reactions in condensed phases that proceed by ionic mechanisms.