compound, one would predict that both π-donation and σ-withdrawal should activate attack at F atoms, thus lowering the efficiency of the transfer reaction.

On the other hand, when one starts with the deuterated halobenzene ions as reactants with neutral D_2O (Table III), the trends in reactivity for the chemical species described above are reversed: o-$C_6H_4F_2D^+$ and p-$C_6H_4F_2D^+$ undergo efficient H/D transfer reactions, while m-$C_6H_4F_2D^+$ reacts with an efficiency of only 0.03. This would suggest that proton (deuterons) associated with a halogen atom are more readily transferred than are $H^+(D^+)$ species on the ring. However, in these reactions, the occurrence of successive exchange steps analogous to those written in eq 1, demonstrates that rearrangement of the H^+/D^+ species within the ion does occur.

Absolute Heats of Formation for Gas-Phase Cations

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Abstract: The relationship between $\Delta H_f{}^\circ{}_{298}(A^+)$ and the appearance energy for the process $AB + h\nu \rightarrow A^+ + B + e^-$ is examined. A general-purpose expression is derived and applied to the measurement of absolute 298 K enthalpies of formation for some simple alkyl cations. If a stationary electron convention is adopted for $\Delta H_f{}^\circ{}_{298}(A^+)$, the following values are obtained: $CH_3^+ = 261.3 \pm 0.4$ kcal mol^{-1}; $C_2H_5^+ = 216.0 \pm 0.5$ kcal mol^{-1}; s-$C_3H_7^+ = 191.8 \pm 0.4$ kcal mol^{-1}; t-$C_4H_9^+ \lesssim 166.2 \pm 0.8$ kcal mol^{-1}. Absolute proton affinities are calculated for ethylene, propene, and isobutene. From a consideration of other studies, a value of 34.4 ± 0.7 kcal mol^{-1} is recommended for the methyl radical heat of formation.

The precise determination of heats of formation for cations in the gas phase has assumed considerable importance in recent years. With the development of experimental techniques for the measurement of equilibrium constants associated with proton-transfer reactions among positive ions, extensive networks of relative gas-phase basicities and proton affinities have been compiled.[1] The assignment of absolute proton affinities relies on the use of suitable reference standards which are usually derived from heats of formation for positive ions. However, these are still not firmly established, with uncertainties in appearance energies, ionization energies, and supplementary thermochemical data giving rise to values over ranges of several kilocalories per mole.[2] A recent study of proton-transfer reactions involving alkyl ions and alkenes[3] has produced a set of relative ionic heats of formation which may assist in their absolute determination.

The most precise ionic heats of formation have been obtained from variable-temperature photoionization experiments.[4] These can lead to reliable 0 K values, provided that the auxiliary thermochemical data at 0 K is available or can be estimated; in most cases this is the major source of uncertainty in $\Delta H_f{}^\circ{}_0$ (ion). Extrapolation of data from experiments performed at temperatures very much above room temperature is of limited application because of possible thermal decomposition effects; there is also the likelihood of errors being introduced as a result of extrapolation over a large temperature range.[5] The best technique is to perform low-temperature experiments, although these are not always practicable due to problems with sample condensation and reduced sample pressure. It would thus be useful if a method could be developed to enable ionic heats of formation to be accurately estimated from room-temperature photoionization measurements.

In this paper we examine the relationship between $\Delta H_f{}^\circ{}_{298}(A^+)$ and the appearance energy (AE) for the general process

$$AB + h\nu \rightarrow A^+ + B + e^- \qquad (1)$$

with particular application to the enthalpies of formation, at 298 K, for some simple alkyl cations.

Experimental Section

The computer-controlled photoionization mass spectrometer employed in this study has been described in detail elsewhere.[6] The source of photons used was the hydrogen many-line spectrum, and the band-pass of the monochromator in the present experiments was 1.25 Å. The absolute energy scale was calibrated with known atomic emission lines and found to be accurate to better than ±0.005 eV. All compounds used were commerical samples of research grade which showed no impurities of significance in their mass spectra. The measurements were carried out with sample pressures in the range 10^{-6}–10^{-5} torr.

Results and Discussion

Convention for Cationic Heats of Formation. In order to obtain absolute heats of formation for positive ions in the gas phase, it is necessary to adopt a standard state convention for the electron ejected in the ionization process. This can be readily demonstrated by considering the standard gas-phase heat of formation for a proton, $\Delta H_f{}^\circ(H^+)$, which refers to the enthalpy change for the reaction

$${}^1/{}_2H_2(g) \rightarrow H^+(g) + e^-(g)$$

At 0 K, the heat of reaction is the adiabatic ionization energy (IE) and corresponds to the formation of a proton and an electron with zero translational energy, i.e., at rest. For the reaction at a temperature T, it is possible to consider $\Delta H_f{}^\circ{}_T$ with reference to the production of either a proton and an electron, each with ${}^3/{}_2RT$

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[1] See, for example: (a) Aue, D. H.; Bowers, M. T. In "Gas-Phase Ion Chemistry"; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 2. (b) Wolf, J. F.; Staley, R. H.; Koppel, I.; Taagepera, M.; McIver, R. T., Jr.; Beauchamp, J. L.; Taft, R. W. *J. Am. Chem. Soc.* **1977**, *99*, 5417-5429. (c) Yamdagni, R.; Kebarle, P. *Ibid.* **1976**, *98*, 1320-1324.

[2] Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data Suppl. 1* **1977**, *6*.

[3] Lias, S. G.; Shold, D. M.; Ausloos, P. *J. Am. Chem. Soc.* **1980**, *102*, 2540-2548.

[4] See, for example: (a) McCulloh, K. E. *Int. J. Mass Spectrom. Ion Phys.* **1976**, *21*, 333-342. (b) McCulloh, K. E.; Dibeler, V. H. *J. Chem. Phys.* **1976**, *64*, 4445-4450. (c) Chupka, W. A. *Ibid.* **1968**, *48*, 2337-2341.

[5] McCulloh and Dibeler[4b] propose that the difference between their 0 K appearance energy for the formation of CH_3^+ from methane and that of Chupka[4c] is due to the different temperature ranges over which the data were extrapolated.

[6] (a) Traeger, J. C.; McLoughlin, R. G. *Int. J. Mass Spectrom. Ion Phys.* **1978**, *27*, 319-333. (b) McLoughlin, R. G. Ph.D. Thesis, La Trobe University, 1980.

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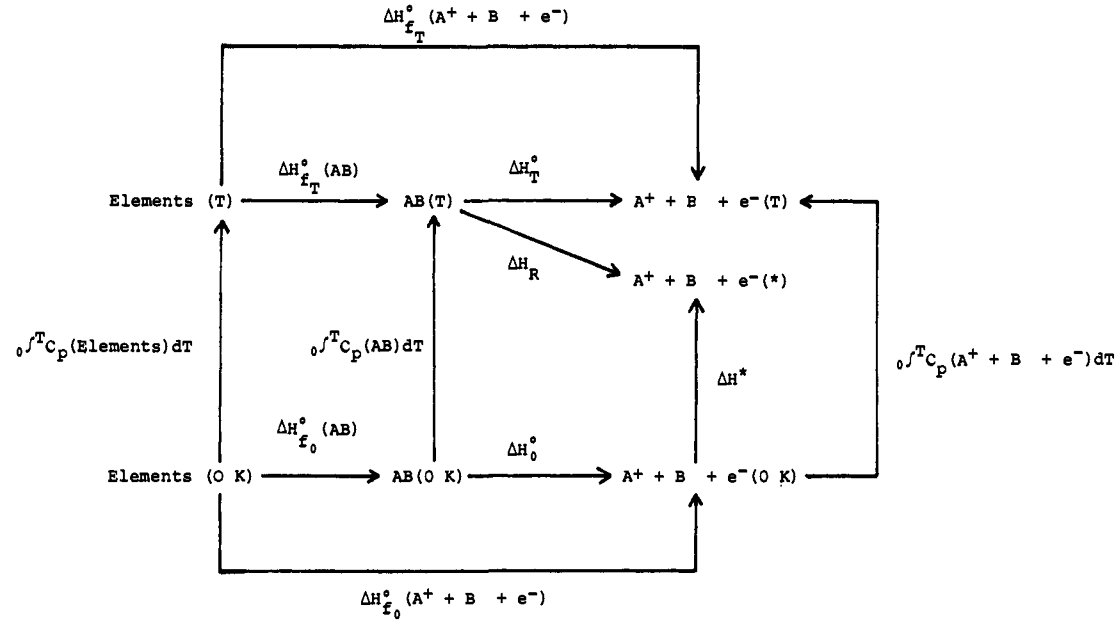

Figure 1. Thermochemical cycle relevant to the unimolecular decomposition of ions.

translational energy (thermal electron), or a proton with $^3/_2RT$ translational energy and an electron with zero kinetic energy (stationary electron). At 298 K there will be a difference of 1.48 kcal mol^{-1} [7] between the two differently defined heats of formation.

Most workers have tended to follow the stationary electron convention, as is used in the extensive compilation of gaseous ion energetics by Rosenstock et al.[2] However, the thermal electron convention for ionic heats of formation has been adopted by Stull and Prophet in the widely used JANAF thermochemical tables[8] and is also followed by Aue and Bowers[1a] in their recent tables of carbocation thermodynamic data at 298 K.

Until there is agreement as to which convention should be followed, it is necessary to clearly specify whether a thermal electron or a stationary electron has been used in the derivation of gas-phase cationic heats of formation. The stationary electron convention has been used throughout the course of this work.

Thermochemical Aspects of Photoionization Appearance Energies. Consider the generalized process 1 for which the potential barrier to the reverse reaction is assumed to be zero. Constraints on the reaction (unimolecular decomposition) require that the initial translational momentum of the center of mass (CM) and the angular momentum about the CM of the precursor molecule plus photon be conserved during the reaction. In addition, the total energy of the photon and the precursor molecule must be conserved. From a consideration of these factors it is possible to construct a thermochemical cycle relevant to the dissociation of ions following photoionization (Figure 1).

If the unimolecular decomposition is sufficiently rapid that there is no kinetic shift effect, then the observed appearance energy (AE_T(exptl)) corresponds to the adiabatic appearance energy (AE_T(ad)), which represents the minimum energy to form $A^+ + B + e^-$ from AB at temperature T. The products of this process ($A^+ + B + e^-$) are not formed at any well-defined equilibrium thermodynamic temperature because the reaction occurs in isolation (unimolecular decomposition). Rather, they are formed with 0 K translational energy (with respect to the CM), with essentially 0 K internal energy (apart from the small residual rotational energy associated with conservation of angular momentum about the CM), and with a CM translational energy equivalent to that of the precursor molecule (AB) at the temperature (T). For this reason the products of reaction are considered to be formed at a "quasi-temperature", labeled with an asterisk in Figure 1.

As noted above, at threshold, the fragmentation products are formed with zero translational energy with respect to their CM and as such cannot do any work of expansion. Thus

$$\mathrm{AE}_T(\mathrm{exptl}) = \Delta H_\mathrm{R} \qquad \text{(I)}$$

where ΔH_R is the enthalpy difference between $A^+ + B + e^-$ (*) and AB(T).

If any of the equilibrium thermodynamic quantities in Figure 1 are to be calculated from AE measurements recorded at $T \neq 0$ K, then ΔH^* (the enthalpy difference between $A^+ + B + e^-$ (*) and $A^+ + B + e^-$ (0 K)) must be estimated with reasonable accuracy. Chupka[9] has shown that if an extrapolation of a linear post-threshold region can be used to determine AE_T(exptl), then

$$\mathrm{A}E_0(\mathrm{exptl}) = \mathrm{AE}_T(\mathrm{exptl}) + \bar{E}_\mathrm{i} \qquad \text{(II)}$$

where $\bar{E}_\mathrm{i}$ is the average internal thermal energy (of AB(T)) effective in dissociation. From Figure 1

$$\Delta H^\circ_0 = \int_0^T C_\mathrm{p}(\mathrm{AB})\,\mathrm{d}T + \Delta H_\mathrm{R} - \Delta H^* \qquad \text{(III)}$$

and for fragmentation at threshold, where $\Delta H^\circ_0 = \mathrm{AE}_0$(exptl) and $\Delta H_\mathrm{R} = \mathrm{AE}_T$(exptl)

$$\mathrm{AE}_0(\mathrm{exptl}) = \int_0^T C_\mathrm{p}(\mathrm{AB})\,\mathrm{d}T + \mathrm{AE}_T(\mathrm{exptl}) - \Delta H^* \qquad \text{(IV)}$$

By substitution of eq II in eq IV it follows that

$$\Delta H^* = \int_0^T C_\mathrm{p}(\mathrm{AB})\,\mathrm{d}T - \bar{E}_\mathrm{i} \qquad \text{(V)}$$

Conservation of angular momentum about the CM requires that some of the initial internal thermal energy of rotation and vibration of AB(T) be ineffective in causing dissociation. However, experiments[4] indicate that the amount of energy is small and that to a good approximation all rotational and vibrational energy associated with the precursor molecule is effective in dissociation. Moreover, calculation of the heights of the rotational barriers for dissociations of the ions considered here (following the method of Chupka[4c]) indicates that they are insignificant. In those cases where fragmentation involves the separation of an ion and a neutral fragment with a permanent dipole, no rotational barrier is formed.[10] On this basis

$$\bar{E}_\mathrm{i} = \int_0^T C_{\mathrm{p}_\mathrm{rot}}(\mathrm{AB})\,\mathrm{d}T + \int_0^T C_{\mathrm{p}_\mathrm{vib}}(\mathrm{AB})\,\mathrm{d}T \qquad \text{(VI)}$$

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(7) $H^\circ_{298} - H^\circ_0 = 1.48$ kcal mol^{-1} for an unexcited monatomic gas.

(8) Stull, D. R.; Prophet, H. *Natl. Stand. Ref. Data Ser. (U.S., Natl. Bur. Stand.)* **1971**, *No. 37*.

(9) Chupka, W. A. *J. Chem. Phys.* **1971**, *54*, 1936–1947.

(10) Herzberg, G. "Spectra of Diatomic Molecules"; Van Nostrand-Reinhold: New York, 1950; pp 378–381.

and by substitution of eq VI in eq V

$$\Delta H^* = \int_0^T C_{p_{\mathrm{trans}}}(\mathrm{AB})\,\mathrm{d}T \simeq {}^5\!/_2 RT \qquad \text{(VII)}$$

From Figure 1 and $\Delta H_R = \mathrm{AE}_T(\mathrm{exptl})$ it follows that

$$\mathrm{AE}_T(\mathrm{exptl}) = \Delta H_f{}^{\circ}{}_T(\mathrm{A}^+ + \mathrm{B} + \mathrm{e}^-) - \Delta H_f{}^{\circ}{}_T(\mathrm{AB}) - \int_0^T C_p(\mathrm{A}^+ + \mathrm{B} + \mathrm{e}^-)\,\mathrm{d}T + \Delta H^* \qquad \text{(VIII)}$$

Adopting the stationary electron convention (i.e., $\int_0^T C_p(\mathrm{e}^-)\,\mathrm{d}T = 0$) and expanding and rearranging eq VIII

$$\Delta H_f{}^{\circ}{}_T(\mathrm{A}^+) = \mathrm{AE}_T(\mathrm{exptl}) - \Delta H_f{}^{\circ}{}_T(\mathrm{B}) + \Delta H_f{}^{\circ}{}_T(\mathrm{AB}) + \int_0^T C_p(\mathrm{A}^+)\,\mathrm{d}T + \int_0^T C_p(\mathrm{B})\,\mathrm{d}T - \Delta H^* \qquad \text{(IX)}$$

At $T = 0$ K, eq IX simplifies to the equation[11] which is normally used to derive ionic heats of formation from ion AE's.

In order to test the general applicability of eq IX, we calculated values for $\Delta H_f{}^{\circ}{}_{298}(\mathrm{OH}^+)$ and $\Delta H_f{}^{\circ}{}_{298}(\mathrm{NH_2}^+)$ from a linear extrapolation of the 298 K fragment photoion yield (PIY) curves for H_2O and NH_3, respectively.[4a] These two ions were chosen because their 0 K heats of formation, which have been accurately measured by variable low-temperature mass spectrometry,[4a] could be readily corrected to 298 K for comparison purposes. If the values of $\mathrm{AE}_{298}(\mathrm{OH}^+)$ = 686 Å (18.07 eV) and $\mathrm{AE}_{298}(\mathrm{NH_2}^+)$ = 788 Å (15.73 eV) are substituted into eq IX, together with the appropriate supplementary thermochemical data (Table I), values of $\Delta H_f{}^{\circ}{}_{298}(\mathrm{OH}^+)$ = 308.9 kcal mol^{-1} and $\Delta H_f{}^{\circ}{}_{298}(\mathrm{NH_2}^+)$ = 302.0 kcal mol^{-1} are obtained. These figures are in excellent agreement with the corresponding values of 309.0 and 302.0 kcal mol^{-1} obtained by correcting the 0 K heats of formation ($\Delta H_f{}^{\circ}{}_0(\mathrm{OH}^+)$ = 309.0 kcal mol^{-1} and $\Delta H_f{}^{\circ}{}_0(\mathrm{NH_2}^+)$ = 302.7 kcal mol^{-1})[4a] to 298 K.

Alkyl Ion Heats of Formation. (A) CH_3^+. PIY curves have been measured for CH_3^+ from both methyl iodide and methyl bromide (Figure 2). The relatively sharp onsets indicate rapid fragmentation processes with no apparent kinetic shift, the small amount of tailing in the threshold region being consistent with the extent of expected hot-band structure. There should be negligible reverse activation energies as Eland and co-workers[12] have shown that, from a photoion–photoelectron coincidence study, the kinetic energy release at threshold is essentially zero for the fragmentation of $CH_3I^{+\cdot}$ and $CH_3Br^{+\cdot}$ to give CH_3^+. In both cases molecular ions are observed with IE's significantly lower than the corresponding fragment ion AE.

The AE for CH_3^+ from methyl bromide obtained in the present work (12.77 ± 0.01 eV) is in excellent agreement with the photoionization value of 12.77 eV determined by Krauss, Walker, and Dibeler.[13] Similarly, the AE for CH_3^+ from methyl iodide (12.18 ± 0.01 eV) is in good agreement with the value of 12.22 eV reported by Lossing and Semeluk.[14] Using eq IX and the supplementary thermochemical data provided in Table II, we calculate a value of $\Delta H_f{}^{\circ}{}_{298}(\mathrm{CH_3}^+)$ = 261.3 ± 0.4 kcal mol^{-1}. If the 0 K heat of formation for CH_3^+, derived from photoionization studies of methane,[4b] is corrected to 298 K, a value of 261.8 kcal mol^{-1} is obtained, in good agreement with the present values. (A value of 261.8 kcal mol^{-1} is also obtained if a 298 K appearance energy of 868 Å (14.28 eV) for CH_3^+ from methane[4b] is used in conjunction with eq IX and the supplementary thermochemical data from the Table I).

Table I. Supplementary Thermochemical Data

(1) $H^{\circ}{}_{298} - H^{\circ}{}_0$ Values for Selected Ions, Molecules, and Radicals in the Gas Phase[a]

M	$H^{\circ}{}_{298} - H^{\circ}{}_0$, kcal mol^{-1}	comments
C(s)	0.25	ref 8
H_2	2.02	ref 8
O_2	2.08	ref 8
N_2	2.07	ref 8
CH_4	2.40	ref 8
H_2O	2.37	ref 8
NH_3	2.40	ref 8
C_2H_4	2.51	ref 8
monatomic gas	1.48	ref 8
CH_3	2.49	ref 8
C_2H_5	2.96	calcd vib frequencies from ref 30; out-of-plane deformation (404 cm^{-1}) from ref 34; torsion considered as free rotor[35]
s-C_3H_7	3.83	calcd vib frequencies from ref 30; out-of-plane deformation (369 cm^{-1}) from ref 36; torsion treated as hindered internal rotation with 1.98-kcal mol^{-1} barrier[37]
t-C_4H_9	4.30	calcd vib frequencies from ref 30; out-of-plane deformation (350 cm^{-1}) from ref 38; torsion considered as free rotor[35]
OH^+	2.06	ref 8
NH_2^+	2.37	assumed to be same as NH_2[8]
CH_3^+	2.38	vib frequencies as for CH_3 except out-of-plane deformation = 1380 cm^{-1} [39]
$C_2H_5^+$	2.74	because of the uncertain structure of this ion[17] a value midway between C_2H_5 and C_2H_4 has been chosen
s-$C_3H_7^+$	3.69	calcd vib frequencies from ref 40
t-$C_4H_9^+$	4.11	calcd vib frequencies from ref 41

(2) Selected Gas-Phase Enthalpies of Formation at 298 K (kcal mol^{-1}) from ref 27

NH_3	−11.0	CH_4	−17.8
H_2O	−57.8	C_3H_8	−25.0

(3) Conversion Factors Used in This Work

1 kcal mol^{-1} = 4.184 kJ mol^{-1}
1 eV = 8065.73 cm^{-1} = 23.061 kcal mol^{-1}

[a] Calculations are based on equations from ref 8.

Table II. Thermochemistry for the Gas-Phase Reaction $RX + h\nu \rightarrow R^+ + X + e^-$

		$\Delta H_f{}^{\circ}{}_{298}$, kcal mol^{-1}		
RX	AE_{298}, eV	RX[a]	X[b]	R+[c]
CH_3Br	12.77 ± 0.01	−8.9 ± 0.2	26.74	261.2 ± 0.4
CH_3I	12.18 ± 0.01	3.7 ± 0.2	25.52	261.4 ± 0.4
C_2H_5H	12.40 ± 0.03	−20.08 ± 0.05	52.10	216.5 ± 0.7
C_2H_5Cl	11.67 ± 0.02	−26.8 ± 0.1	28.99	216.1 ± 0.6
C_2H_5Br	11.06 ± 0.01	−14.9 ± 0.2	26.74	216.2 ± 0.4
C_2H_5I	10.44 ± 0.01	−2.2 ± 0.2	25.52	215.8 ± 0.4
s-C_3H_7Cl	10.92 ± 0.01[d]	−34.7 ± 0.1	28.99	191.8 ± 0.3
s-C_3H_7Br	10.33 ± 0.01[d]	−23.5 ± 0.2	26.74	191.7 ± 0.4
s-C_3H_7I	9.70 ± 0.01[d]	−9.9 ± 0.4	25.52	192.0 ± 0.6

[a] Reference 27. [b] Reference 28. [c] Calculated by using eq IX and supplementary thermochemical data from Table I. [d] Reference 29.

Since the adiabatic ionization energy, IE(ad), for methyl radical is well characterized at 9.843 ± 0.001 eV,[15] it should be possible to determine $\Delta H_f{}^{\circ}{}_{298}(\mathrm{CH_3})$. In this situation care must be taken with the manipulation of thermodynamic quantities. As noted by Lias and Ausloos,[16] for a given molecule, A

$$\mathrm{IE(ad)} = \Delta H_f{}^{\circ}{}_0(\mathrm{A}^+) - \Delta H_f{}^{\circ}{}_0(\mathrm{A}) \qquad \text{(X)}$$

which is equal to the heat of ionization, defined as

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(11) Boyd, R. K.; Beynon, J. H. *Int. J. Mass Spectrom. Ion Phys.* **1977**, *23*, 163–188.

(12) Eland, J. H. D.; Frey, R.; Kuestler, A.; Schulte, H.; Brehm, B. *Int. J. Mass Spectrom. Ion Phys.* **1976**, *22*, 155–170.

(13) Krauss, M.; Walker, J. A.; Dibeler, V. H. *J. Res. Natl. Bur. Stand., Sect. A* **1968**, *72*, 281–293.

(14) Lossing, F. P.; Semeluk, G. P. *Can. J. Chem.* **1970**, *48*, 955–965.

(15) Herzberg, G. *Proc. R. Soc. London, Ser. A* **1961**, *262*, 291–317.

(16) Lias, S. G.; Ausloos, P. *J. Am. Chem. Soc.* **1978**, *100*, 6027–6034.

$$\Delta H°_T(\text{ionization}) = \Delta H_f°_T(\text{A}^+) - \Delta H_f°_T(\text{A}) \qquad \text{(XI)}$$

only in the event that the integrated heat capacities of the ion and neutral species are identical. In general

$$\Delta H°_T(\text{ionization}) = \text{IE(ad)} + \int_0^T C_p(\text{A}^+)\, \text{d}T - \int_0^T C_p(\text{A})\, \text{d}T \qquad \text{(XII)}$$

The heat of formation for CH_3 at 298 K may be obtained by combining eq XI and XII:

$$\Delta H_f°_{298}(\text{CH}_3) = \Delta H_f°_{298}(\text{CH}_3^+) - \text{IE(ad)} + \int_0^{298} C_p(\text{CH}_3)\, \text{d}T - \int_0^{298} C_p(\text{CH}_3^+)\, \text{d}T \qquad \text{(XIII)}$$

When $\Delta H_f°_{298}(CH_3)$ is determined in this manner, with use of the supplementary information from Table I, a value of 34.4 ± 0.4 kcal mol^{-1} is obtained. Any error in the difference between the two integrated heat capacities in eq XIII is predicted to be small since the vibrational frequencies in both CH_3 and CH_3^+ are relatively high (with respect to kT), the main difference being due to the change in the out-of-plane bending frequency.[17]

The present value compares favorably with earlier kinetic data (33.9 kcal mol^{-1})[18] and more recent determinations, on the basis of the photoionization studies of McCulloh and Dibeler (34.9 kcal mol^{-1})[19] and Chupka (34.8 kcal mol^{-1})[8] and VLPP studies by Benson and co-workers (34.9 and 35.1 kcal mol^{-1}).[20] Shaw[21] has recently proposed that the currently accepted heat of formation for methyl radical of 34.9 kcal mol^{-1} is too high and that it should be reduced to 33.7 kcal mol^{-1} to be consistent with an extrapolation of rate constant data for hydrogen abstraction from methane; the present results support a lowering of the CH_3 heat of formation, although not by 1.2 kcal mol^{-1}.

Making an unambiguous choice between the various values for $\Delta H_f°_{298}(CH_3)$ is not straightforward. Values based on the photoionization studies of Chupka[4c] and McCulloh and Dibeler[4b] have a higher precision than the present results but are based on measurements for only one system. Although there is a possibility that excess energy is released to the fragments at threshold, this has been discounted by McCulloh and Dibeler[4b] following the metastable ion decomposition measurements of Solka et al.[22] Stockbauer[23] has concluded from his experiments that there is indeed only a small kinetic energy release; his upper estimate of 30 meV (0.7 kcal mol^{-1}) is, however, consistent with the observed discrepancy between the methane and methyl halide data. The results of the present work are based on two systems ($CH_3I \rightarrow CH_3^+ + I + e^-$ and $CH_3Br \rightarrow CH_3^+ + Br + e^-$) for which there is also good evidence[12] of negligible excess energy of the products at threshold. Moreover, the likelihood of both systems having errors which fortuitously lead to the same value for the methyl radical heat of formation is minimal. On the basis of available evidence it is recommended that $\Delta H_f°_{298}(CH_3)$ = 34.4 ± 0.7 kcal mol^{-1}.

(B) $C_2H_5^+$. The PIY curves of $C_2H_5^+$ from several precursor molecules have been measured and are shown in Figure 3; the thermochemistry is summarized in Table II. As noted for the fragmentation of the methyl halides, it is expected that there will be no observable kinetic shift for ethyl iodide and ethyl bromide. For ethyl chloride and ethane, some slight kinetic effect may be observed due to the presence of a lower energy fragmentation process leading to formation of $C_2H_4^{+}\cdot$; this appears to be the case for ethane. A more important influence on the threshold PIY curves for these two molecules is the contribution of the $^{13}CCH_4^{+}\cdot$ ion peak; the curves for ethane and ethyl chloride (Figure 3) have been analytically corrected for this contribution.[6b] Because of the possibility that slight distortions of the PIY curves may have been introduced in the process of analytical correction, more significance should be given to the $C_2H_5^+$ heat of formation derived from ethyl bromide and ethyl iodide.

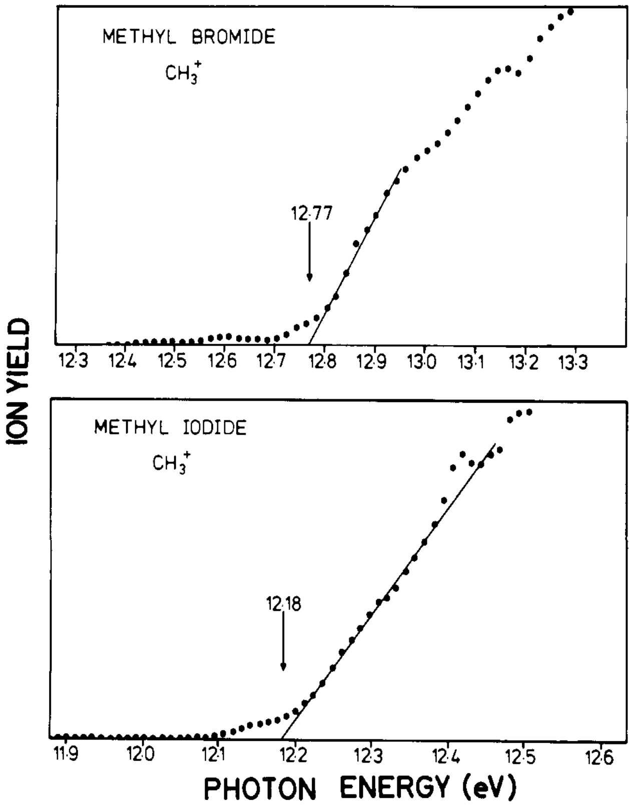

Figure 2. Threshold photoion yield curves for CH_3^+ fragment ions produced from methyl bromide and methyl iodide.

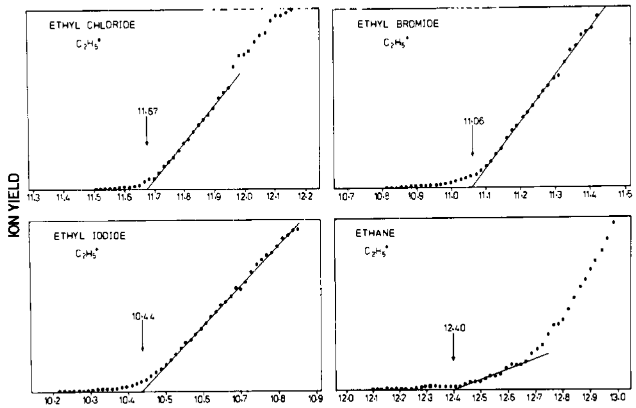

Figure 3. Threshold photoion yield curves for $C_2H_5^+$ fragment ions produced from ethane and the ethyl halides.

In all cases molecular ions are observed with significantly lower ionization energies than the corresponding fragment ion appearance energies. The kinetic energy release for the fragmentation of $C_2H_5I^{+}\cdot$ to $C_2H_5^+$ has been reported by Baer[24] to approach zero at the dissociation onset. No kinetic energy release measurements are available for formation of $C_2H_5^+$ from the other precursors studied here, but it may be inferred that they have similar kinetic energy releases at threshold if the calculated $C_2H_5^+$

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[17] Houle, F. A.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1979**, *101*, 4067–4074.

[18] Gac, N. A.; Golden, D. M.; Benson, S. W. *J. Am. Chem. Soc.* **1969**, *91*, 3091–3093.

[19] Obtained by correcting $\Delta H_f°_0(CH_3)$ = 35.7 kcal mol^{-1} [4b] to 298 K.[8]

[20] (a) Baghal-Vayjooee, M. H.; Colussi, A. J.; Benson, S. W. *J. Am. Chem. Soc.* **1978**, *100*, 3214–3215. (b) Baghal-Vayjooee, M. H.; Colussi, A. J.; Benson, S. W. *Int. J. Chem. Kinet.* **1979**, *11*, 147–154.

[21] Shaw, R. *J. Phys. Chem. Ref. Data* **1978**, *7*, 1179–1190.

[22] Solka, B. H.; Beynon, J. H.; Cooks, R. G. *J. Phys. Chem.* **1975**, *79*, 859–862.

[23] Stockbauer, R. *Int. J. Mass Spectrom. Ion Phys.* **1977**, *25*, 401–410.

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heats of formation correspond to a common value.

The appearance energy for formation of $C_2H_5^+$ from ethyl iodide obtained in this work (10.44 ± 0.01 eV) is in excellent agreement with the photoionization values obtained by Baer[24] (10.42 eV) and Akopyan et al.[25] (10.42 ± 0.05 eV). The $C_2H_5^+$ AE for ethyl chloride measured here (11.67 ± 0.02 eV) also agrees with the onset quoted by Akopyan et al.[25] of 11.65 ± 0.03 eV; however, the AE we have obtained for ethyl bromide (11.06 ± 0.01 eV) is considerably higher than their value of 10.92 ± 0.05 eV. The present AE's have been obtained from a linear extrapolation of the PIY curves in the threshold region whereas Akopyan et al. have taken the actual onset of the PIY curve as the AE. A "vanishing current" technique will always lead to lower values because of contributions from the ionization and subsequent fragmentation of thermally excited precursor molecules (hot bands).[9] This thermal structure is particularly pronounced for ethyl bromide (Figure 3) which accounts for the 0.14-eV difference between the two sets of photoionization data.

The AE for the corresponding process in ethane obtained here (12.40 ± 0.03 eV) is at variance with that obtained from the photoionization measurements of Chupka and Berkowitz[26] (12.59 ± 0.08 eV). However, Chupka and Berkowitz report the observation of two processes in the threshold region for $C_2H_5^+$ formation

$$C_2H_6 + h\nu \rightarrow C_2H_5^+ + H^- \quad AE(0\ K) = 12.00 \pm 0.05\ eV \quad (i)$$

$$C_2H_6 + h\nu \rightarrow C_2H_5^+ + H + e^- \quad AE(0\ K) = 12.65 \pm 0.08\ eV \quad (ii)$$

yet in their breakdown curves for ethane (ref 26, Figure 14) the $C_2H_5^+$ curve shows a distinct change in gradient at 12.40 eV. This is interpreted here to mean that AE(298 K) for process ii above is 12.40 eV and not 12.59 eV. Also, the assignment of the low intensity tail solely to an ion-pair process is questionable. Similar features observed by Chupka[4c] in the PIY curves for CH_3^+ from methane and assigned to ion-pair processes have not been verified by other workers.[4b]

The onset of the low-intensity tail does coincide very closely with the onset of $C_2H_4^{+\cdot}$ formation, and Chupka and Berkowitz[26] have not reported applying any correction for the $^{13}CCH_4^{+\cdot}$ peak. Hence, it may well be that the low-intensity tail is due to interference from the $^{13}CCH_4^{+\cdot}$ ion. The PIY curve of Chupka and Berkowitz is found to bear a striking resemblance to the $C_2H_5^+$ PIY curve obtained from ethane in the present work prior to correction for the $^{13}CCH_4^{+\cdot}$ contribution.[6b] In any event, an AE(298 K) of 12.40 eV leads to a heat of formation for $C_2H_5^+$ which is in excellent agreement with the other values calculated here (Table II).

From the results for the ethyl halides (Table II) it is proposed that $\Delta H_f{}^\circ{}_{298}(C_2H_5^+) = 216.0 \pm 0.5$ kcal mol^{-1}, which is in good agreement with the recent value of Baer.[24] As discussed by Baer, this implies that the adiabatic ionization energy for the C_2H_5 radical has not been observed.[14,17] Assuming the stationary electron convention, $\Delta H_f{}^\circ{}_{298}(H^+) = 365.7$ kcal mol^{-1},[2] and using $\Delta H_f{}^\circ{}_{298}(C_2H_4) = 12.5 \pm 0.3$ kcal mol^{-1},[27] we calculate PA(C_2H_4) = 162.3 ± 0.8 kcal mol^{-1}.

(C) s-$C_3H_7^+$ and t-$C_4H_9^+$. From a photoionization study of the propyl halides[29] a value of 188 kcal mol^{-1} was proposed for the heat of formation of s-$C_3H_7^+$. This does not represent $\Delta H_f{}^\circ{}_{298}$ because no correction was made for the ion enthalpy. When the experimental $C_3H_7^+$ appearance energies[29] are combined with the relevant thermochemical data (Table II), an average value of 191.8 ± 0.4 kcal mol^{-1} is obtained. This compares favorably with the value of 190.8 kcal mol^{-1}, derived by Baer[24] from photoionization data for 2-iodopropane, and 192.5 kcal mol^{-1}, calculated from a 298 K appearance energy (11.53 eV)[26] for $C_3H_7^+$ from propane and supplementary data from Table I; it is in excellent agreement with an electron-impact value of 191.7 kcal mol^{-1}.[14] However, there is a discrepancy of 4.5 kcal mol^{-1} with the heat of formation (187.3 kcal mol^{-1}) obtained by Houle and Beauchamp[17] from a PES study of the isopropyl radical. This can only be resolved if the adiabatic ionization energy or the radical heat of formation (or both) are increased. Given that the upper limit to $\Delta H_f(s\text{-}C_3H_7)$ is 21.0 kcal mol^{-1},[30] it would seem, from the results presented here, that the adiabatic ionization energy for the radical is >7.36 eV.

The heat of formation for *tert*-butyl cation has been calculated to be 162.9 kcal mol^{-1} from a PES study of the *tert*-butyl radical.[17] This was shown to be in good agreement with a value of 162.1 kcal mol^{-1} derived from a photoionization appearance energy measurement for isobutane.[31] A recalculation of $\Delta H_f{}^\circ{}_{298}((CH_3)_3C^+)$ using eq IX leads to a value of 166.2 ± 0.8 kcal mol^{-1}. In view of the curvature in the threshold region of the PIY curve[31] this must be regarded as an upper limit; some of the curvature may be attributed to the effects of a "competitive shift" since the thermochemical threshold[2] for the rearrangement process involving loss of CH_4 is ~3.5 kcal mol^{-1} lower than the threshold for $(CH_3)_3C^+$ formation.[32]

The recent work of Lias and co-workers[3] has attempted to establish a scale of relative heats of formation for alkyl ions. Of particular interest is the heat of formation for t-$C_4H_9^+$ which is calculated to be 22.4 kcal mol^{-1} less than that for s-$C_3H_7^+$. This would imply that, based on the present value of 191.8 kcal mol^{-1} for $\Delta H_f{}^\circ{}_{298}(s\text{-}C_3H_7^+)$, the heat of formation for t-$C_4H_9^+$ should be 169.4 kcal mol^{-1} which is considerably higher than our estimated upper limit of 166.2 kcal mol^{-1}; further experimental work will be required to resolve this discrepancy. Lias et al.[3] also observed that the free radical heats of formation derived from their results, although internally consistent, were lower than the corresponding literature values by 2–4 kcal mol^{-1} (based on 164.2 kcal mol^{-1} for $\Delta H_f(t\text{-}C_4H_9^+)$). This suggests that the absolute 298 K heat of formation for *tert*-butyl cation is not significantly less than our proposed upper limit of 166.2 kcal mol^{-1} and that PA(i-C_4H_8) $\gtrsim$ 195.5 ± 0.9 kcal mol^{-1}; the calculated PA for propene is 178.7 ± 0.5 kcal mol^{-1}.[33]

Conclusion

The present work has shown that it is possible to calculate absolute 298 K heats of formation for ions directly from photoionization appearance energy measurements at room temperature, provided that the convention adopted for the electron ejected in the ionization–fragmentation process is specified. Based on the *stationary* electron convention for cationic heats of formation, a general-purpose equation has been derived and applied to a number of ion-fragmentation processes in which the unimolecular decomposition following photoionization is not subject to any appreciable reverse activation energy or kinetic shift, and the neutral fragment is a monatomic species. Apart from these restrictions, the main problem associated with the widespread application of the method is the lack of suitable auxiliary data for calculating relevant values of $H^\circ_{298} - H^\circ_0$.

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Since $\bar{E}_i$ for large polyatomic molecules can be quite large, it is important that consideration be given to the effect that the method of determining AE_T(exptl) has on $\Delta H_f{}^{\circ}{}_T$(ion). If AE_T(exptl) is determined by any method other than that based on an extrapolation of a linear post-threshold region, the relationship between AE_T(exptl), AE_0(exptl), and $\bar{E}_i$ must be reestablished and the appropriate modifications made to eq IX. Work is underway in our laboratory to assess the difficulties associated with the application of the above method to larger systems, particularly fragmentations involving the loss of a diatomic or polyatomic neutral species.

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Calculation of the Nuclear Spin–Spin Coupling Constants. 3. σ- and π-Electron Contributions in Some Simple Unsaturated Hydrocarbons

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Abstract: The sum-over-states calculations of the nuclear spin–spin coupling constants by Nakatsuji's formula, including doubly excitated configurations, have reproduced exact finite perturbation results. in addition, a new method of separation of the coupling constants into σ- and π-electron contributions has been proposed. It has been shown that π-electron coupling constants alternate in sign with the number of bonds while their magnitudes are approximately independent of the number of bonds.

Introduction

In papers 1[1] and 2[2] of this series, we showed that the finite perturbation (FP) method is superior to the sum-over-states (SOS) one in the calculation of the nuclear spin–spin coupling constants. This is because FP calculations show a clear convergence to experimental values as the size of the basis set is increased. On the other hand, the SOS calculations show divergence even if the singly excited triplet configuration interaction calculation (we denote as SOS1) is invoked.[3] Ditchfield et al.[4] studied the relation between the SOS and FP methods and pointed out that the FP theory corresponds to introducing doubly excited states in a restricted way (see the following section). We thus conjectured that the doubly excited states introduced into the FP calculation brought about the convergent trend. However, no proof of this could be presented directly in our previous papers. It would therefore seem important to confirm whether the SOS calculations with double excitations (we denote as SOS2) can reproduce the FP results, and this we do in this paper. Moreover, the SOS2 method makes it possible to estimate the π contribution to the nuclear spin–spin coupling constant, which is quite difficult in the FP method. Thus we will show the separation of the nuclear spin–spin coupling constant into the sum of the σ and π-contributions.

Method

Nakatsuji[5] showed that eq 50 of his paper is the best expression of the second-order SOS perturbation energy based on the Hartree–Fock (HF) wave function. From this expression for the second-order perturbation energy, we can write the SOS2 formula for the nuclear spin–spin coupling constants, $J_{NN'}$ (in Hz), in the INDO level as follows (in SI units):

$$J_{NN'} = -\frac{64}{9}\mu_B{}^2 h\left(\frac{\mu_0}{4\pi}\right)^2 \gamma_N\gamma_{N'}S_N(0)^2 S_{N'}(0)^2 \times \sum_n \sum_{ij}^{\substack{\sigma\\ \mathrm{occ}}} \sum_{ab}^{\substack{\sigma\\ \mathrm{unocc}}} T_n{}^{-1} V_{i\to a,n} V_{j\to b,n} C_{Ni} C_{Na} C_{N'b} C_{N'j} \quad (1)$$

where T_n is the nth eigenvalue of the **H** matrix defined below. $V_{i\to a,n}$ is the coefficient of the triplet excitation i → a in the nth eigenvector of **H**. μ_0 is the magnetic permeability in vacuo. The other notations are the same as in eq 3.2 in the review by Kowalewski.[6] The matrix **H** is defined as follows:

$$\mathbf{H}_{i\to a,j\to b} = \langle {}^3\Psi_{i\to a}|\mathbf{H}_0|{}^3\Psi_{j\to b}\rangle + \langle {}^1\Psi_0|\mathbf{H}_0|\Psi_{i\to a,j\to b}\rangle - \delta_{ij}\delta_{ab}\langle {}^1\Psi_0|\mathbf{H}_0|{}^1\Psi_0\rangle \quad (2)$$

where $\mathbf{H}_0$ is the unperturbed Hamiltonian and ${}^1\Psi_0$ is the ground-state wave function approximated by the single determinant composed of doubly occupied SCF MO's. The triplet states ${}^3\Psi_{i\to a}$ are formed by promoting one electron from an occupied MO, ψ_i, to an unoccupied one, ψ_a. $\Psi_{i\to a,j\to b}$ are the doubly excited wave functions which are not the eigenfunctions of the total electronic spin operator $\hat{S}^2$. They are written explicitly as $\Psi_{i\to a,j\to b} = \|\ldots iajb(\alpha\beta\alpha\beta + \alpha\beta\beta\alpha + \beta\alpha\alpha\beta + \beta\alpha\beta\alpha)/2\ldots\|$ in standard notation.

Using the SCF MO energies ϵ_i associated with ψ_i and the molecular integrals of electron repulsion, we can rewrite the matrix elements of **H** as

$$\mathbf{H}_{i\to a,j\to b} = \delta_{ij}\delta_{ab}(\epsilon_a - \epsilon_i) - [ij|ab] - [ib|ja]$$

where $[ij|ab] = \int \psi_i(1)\psi_j(1)r_{12}{}^{-1}\psi_a(2)\psi_b(2)\, d\tau_1 d\tau_2$. The real symmetric matrix **H** is diagonalized to give the diagonal matrix **T** by the orthogonal matrix **V** whose nth column vector gives the coefficients $V_{i\to a,n}$ in eq 1. Thus $HV = VT$.

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