on a time scale of $<2 \times 10^{-12}$ s. This means that although the position of the proton may fluctuate, the time scale for such events will be short in comparison to the average lifetime of an ion cluster. Hence, on the reaction time scale of approximately 1×10^{-6} s the distribution of proton positions will appear highly averaged and maximized at the configuration of lowest potential energy. The experimental results support this view. If on the reaction time scale the proton moved a significant distance from either the methanol or ethanol molecules in $\{ROH{\cdot}(H_2O)_m\}H^+$ clusters, the decrease in the strength of the ion–induced dipole interaction would be sufficient for loss of ROH to occur, and this is not observed.

The picture in $\{(ROH)_n{\cdot}H_2O\}H^+$ clusters will be slightly different. If proton transfer throughout the entire ROH network were significant then it might be expected that the alcohol molecules, with their high polarizabilities, would always be preferentially bound to the cluster irrespective of it's size. However, the fact that this type of ion cluster does reach a size where long-range interactions between the proton and the alcohol molecules become important must mean that in the configuration of lowest potential energy some alcohol molecules reside a relatively long distance from the proton site. This introduces the possibility that a subset of alcohol molecules within ion clusters of this type form a stable structure containing the proton, with the remaining ROH molecules situated at the perimeter. Unfortunately, the results in Figures 4 and 5 do not indicate whether such a structure is present and if so how many ROH molecules it contains. It may be possible to investigate this problem further by studying reaction 13 for larger values of n than those given in Figure 7. The reactions involving loss of CH_3OH may then act as a probe as to features of the cluster core. If the size of this central structure can be determined then it will be possible to assign a symmetry number to processes like reaction 7 in the text.

In clusters where the nucleus is an alkali metal ion the thermodynamic data indicate the presence of a well-defined coordination shell for the attachement of species like NH_3.[22-24] Behavior similar to that found in the present work is observed when the enthalpies of clustering for H_2O and NH_3 ($\mu = 1.48$ D, $\alpha_P = 2.26$ Å^3) are compared. The bond energy for the attachment of a single NH_3 is greater than that for H_2O; but beyond the fourth cluster molecule H_2O is more strongly bound. However, the results in Figures 4 and 5 suggest that at least 9 and quite possibly 10 alcohol molecules are preferentially bound to a proton. That such relatively large numbers are involved could be the result of two factors: (1) the alcohols both have larger polarizabilities than NH_3; and (2) if a fixed number of alcohol molecules form a stable core in association with the proton, then by virtue of the large surface area it could present to the solvent molecules the core would have a high coordination number for the first and subsequent solvation shells. In order to provide a detailed analysis of the behavior of these large ion clusters it may be necessary to take into account not only ion–molecule interactions but also solvent molecule–solvent molecule interactions for those species sited a relatively long distance from the central ion.

Registry No. Proton, 12586-59-3; methanol, 67-56-1; ethanol, 64-17-5.

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Heat of Formation for Acetyl Cation in the Gas Phase

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Abstract: The ionization energies and CH_3CO^+ appearance energies have been measured by photoionization mass spectrometry for a series of substituted methyl ketones. When the *stationary* electron convention for cationic heats of formation is used, a value of 657.0 ± 1.5 kJ mol^{-1} is obtained for $\Delta H_f{}^\circ{}_{298}(CH_3CO^+)$ which leads to an absolute proton affinity for ketene of 825.4 ± 3.2 kJ mol^{-1}. Previous acetyl cation heats of formation obtained from photoionization data are shown to be in error because of an incorrect method of calculation. From the results for acetic anhydride an upper limit of ≤ -227 kJ mol^{-1} can be placed on the heat of formation for the acetoxy radical. With few exceptions there is little evidence to suggest any significant excess energy at the decomposition threshold. It is shown that translational energy measurements made at energies greater than threshold cannot be applied in a straightforward manner as thermochemical corrections for the experimental CH_3CO^+ appearance energies.

One of the predominant fragment ions observed in the mass spectra of oxygenated organic compounds is the acetyl ion. Despite the wealth of information available for this gas-phase cation there is still considerable uncertainty surrounding its 298 K enthalpy of formation. The recommended value of Rosenstock et al.[1] is 630 kJ mol^{-1}, which is based on a photoionization value for the appearance energy (AE) of CH_3CO^+ from acetone,[2] corrected for 10.5 kJ mol^{-1} translational energy of decomposition.[3] Other cited photoionization values vary between 648 and 667 kJ mol^{-1}.[1]

In a recent paper[4] we discussed the relationship between photoionization AE measurements and absolute gas-phase heats of formation. It was shown that for the general process

$$AB + h\nu \rightarrow A^+ + B + e^-$$

the standard cationic heat of formation at temperature T could be given by

$$\Delta H_f{}^\circ{}_T(A^+) = AE_T - \Delta H_f{}^\circ{}_T(B) + \Delta H_f{}^\circ{}_T(AB) + \Delta H_{corr} \qquad (1)$$

where AE_T is the experimental appearance energy based on a threshold linear extrapolation of the photoion yield curve and ΔH_{corr} is given by

$$\Delta H_{corr} = \int_0^T Cp(A^+)\,dT + \int_0^T Cp(B)\,dT - \tfrac{5}{2}RT \qquad (2)$$

The ΔH_{corr} term in eq 1 was not included in the calculated 298 K heats of formation obtained by Rosenstock et al,[1] which will result in a range of underestimated values. It should be noted

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[‡] Division of Chemical Physics, CSIRO, Clayton, Victoria 3168.

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

(2) (a) Murad, E.; Inghram, M. G. *J. Chem. Phys.* **1964**, *40*, 3263–3275. (b) Murad, E.; Inghram, M. G. *Ibid.* **1964**, *41*, 404–409.

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0002-7863/82/1504-5318$01.25/0

that eq 1 assumes the *stationary* electron convention for cationic heats of formation (i.e., $\int_0^T Cp(e^-)\, dT = 0$).[5]

Several workers have measured the proton affinity (PA) of ketene and calculated from it a heat of formation for CH_3CO^+.[6–10] In all cases the PA values are not absolute, being based on the PA for isobutene which is in turn derived from the heat of formation for the *tert*-butyl cation; this still has not been firmly established.[11] and its use as a PA reference standard is to be discouraged. The present study was undertaken in an attempt to precisely measure the absolute heat of formation for the acetyl cation and hence provide a reliable reference point for the many extensive networks of relative proton affinities.

Experimental Section

The photoionization efficiency curves obtained in this study were measured with a microcomputer-controlled photoionization mass spectrometer that has been described in detail elsewhere.[12] The hydrogen pseudocontinuum was used as the photon source with the band pass of the monochromator set at 0.125 nm for the present experiments. All compounds were of research grade purity and showed no impurities of significance in their mass spectra. The experiments were performed at ambient temperature (296 K) with sample pressures in the range 10^{-3}–10^{-4} Pa.

The He I photoelectron spectra were obtained with a computer-controlled spectrometer based on a 150° double-hemispherical analyzer.[13] Acetylene and hydrogen bromide were used as electron-energy calibrants and the resolution was measured at 30 meV for argon.

Results and Discussion

The compounds selected for this study were substituted methyl ketones capable of producing the acetyl cation via a simple bond cleavage. In all cases this was the lowest-energy fragmentation process so that any kinetic or competitive effects should be minimal. The possibility of a reverse activation energy cannot be ignored.[14] Haney and Franklin[3] measured translational energies of decomposition for several acetyl compounds and, from an empirical relationship, obtained excess energy values which they used to correct the calculated heats of formation for the acetyl cation. However, the translational energies used in their calculations were obtained from an extrapolation of measurements made at elevated internal energies and may not accurately reflect the excess energy at fragmentation threshold. If there is any reverse activation energy involved with the processes studied in this work it should not be the same for different precursor molecules with a resultant spread of values for the calculated CH_3CO^+ heats of formation.

The mass spectra of the acetyl halides are all characterized by an intense peak at m/z 43. However, like the *tert*-butyl halides,[15] the chloro- and bromo-substituted compounds showed no molecular ion, with only a very weak peak being observed for acetyl iodide. Photoelectron spectra were measured for acetyl chloride and acetyl bromide and found to have first-band ionization onsets identical with the photon energies at which m/z 43 fragment ions first appeared; the adiabatic ionization energies were estimated from the photoelectron spectra as 10.78 and 10.24 eV, respectively, in good agreement with measurements given by previous workers.[16] We were unable to obtain a satisfactory photoelectron spectrum from acetyl iodide but it is assumed that the adiabatic ionization energy (IE) will be close to the CH_3CO^+ AE of 9.28 eV. As a result, the CH_3CO^+ heats of formation calculated from the appearance energies of these compounds will represent upper limits to the true value.

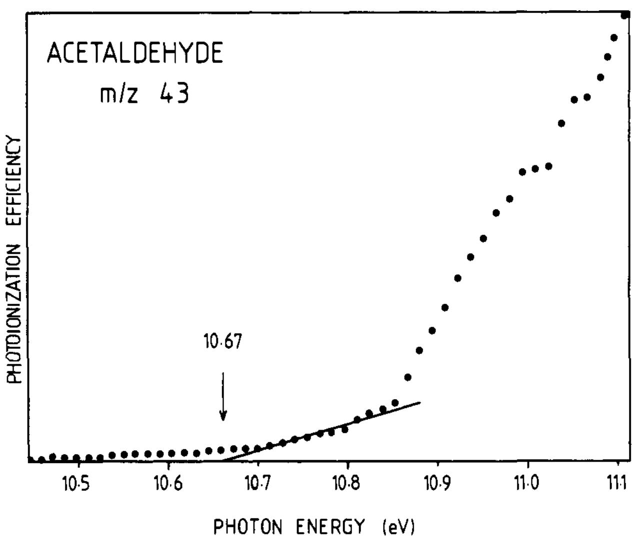

Figure 1. Threshold photoionization efficiency curve for CH_3CO^+ fragment ions produced from acetaldehyde.

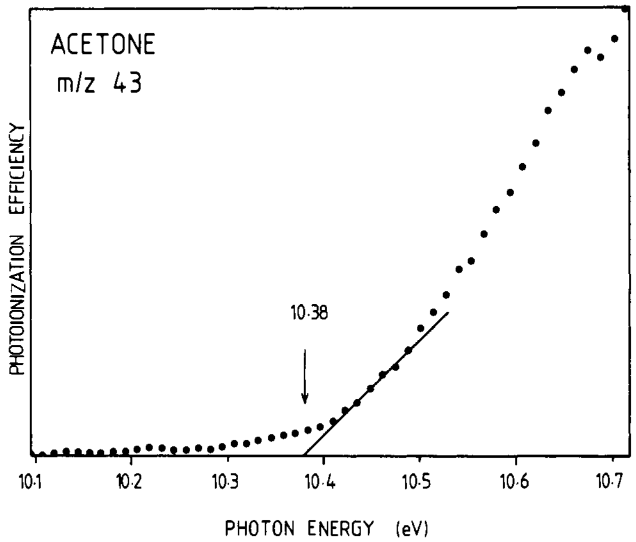

Figure 2. Threshold photoionization efficiency curve for CH_3CO^+ fragment ions produced from acetone.

The only other acetyl compound which readily forms CH_3CO^+ by loss of a monatomic neutral fragment is acetaldehyde. Previous photoionization studies[17] have obtained appearance energies of 10.90 and 10.82 eV, which are not in good agreement. This is probably due to the very low ion abundance in the threshold region as has been suggested by Staley et al.[17b] Our experimental photoionization efficiency (PIE) curve (Figure 1) was obtained after an extended data acquisition period (50 h) in order to more clearly identify the AE. A linear extrapolation of the steeply rising section of the curve in the region of 10.9 eV leads to an AE of

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(5) For a discussion of this see ref 4. See also: Ausloos, P., Ed. "Kinetics of Ion-Molecule Reactions"; Plenum Press: New York, 1979. Rosenstock, H. M. "Standard States in Gas Phase Ion Thermochemistry"; NATO Advanced Study Institute Series B (Physics); Vol. 40, pp 246–249.

(6) Ausloos, P.; Lias, S. G. *Chem. Phys. Lett.* **1977**, *51*, 53–56.

(7) Vogt, J.; Williamson, A. D.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1978**, *100*, 3478–3483.

(8) Davidson, W. R.; Lau, Y. K.; Kebarle, P. *Can. J. Chem.* **1978**, *56*, 1016–1019.

(9) Debrou, G. B.; Fulford, J. E.; Lewars, E. G.; March, R. E. *Int. J. Mass Spectrom. Ion Phys.* **1978**, *26*, 345–352.

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(11) See, for example: (a) Table 7 of ref 10. (b) Houle, F. A.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1979**, *101*, 4067–4074. (c) Reference 4.

(12) (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.

(13) Willett, G. D. Ph.D. Thesis, La Trobe University, 1977.

(14) See, for example: (a) Franklin, J. L. In "Gas-Phase Ion Chemistry", Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 1. (b) Beynon, J. H.; Eilbert, J. R. *Ibid.*, Vol. 2.

(15) McLoughlin, R. G.; Traeger, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 5791–5792.

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(16) Chadwick, D.; Katrib, A. *J. Electron Spectrosc. Relat. Phenom.* **1974**, *3*, 39–52.

(17) (a) Krässig, V. R.; Reinke, D.; Baumgärtel, H. *Ber. Bunsenges. Phys. Chem.* **1974**, *78*, 425–436. (b) Staley, R. H.; Wieting, R. D.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1977**, *99*, 5964–5972.

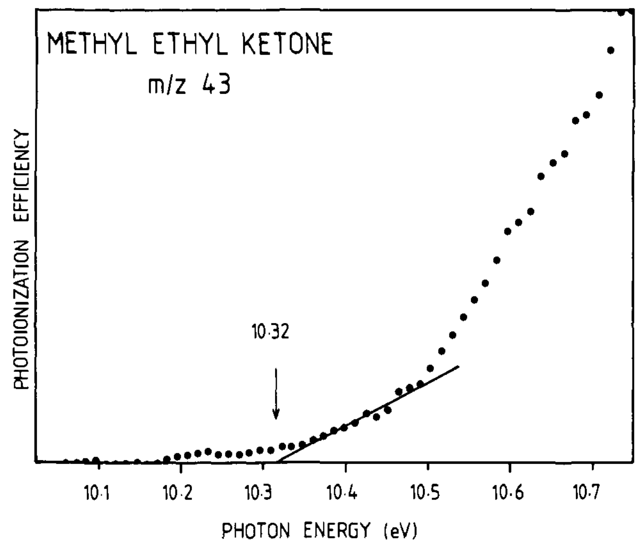

Figure 3. Threshold photoionization efficiency curve for CH_3CO^+ fragment ions produced from methyl ethyl ketone.

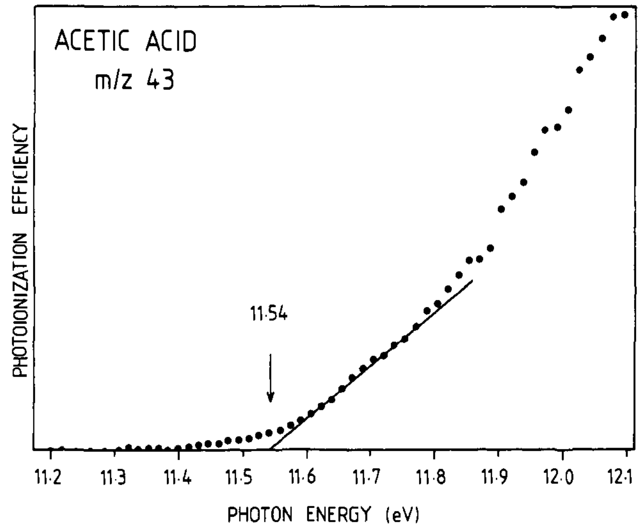

Figure 4. Threshold photoionization efficiency curve for CH_3CO^+ fragment ions produced from acetic acid.

10.81 eV, in close agreement with the measurement given by Staley et al.[17b] However, this results in a low-intensity tail of approximately 0.3 eV which cannot be correlated with the hot-band strucure to be expected from photoionization of thermally excited acetaldehyde molecules.[18] We consider that the indicated value of 10.67 eV shown in Figure 1 is more representative of the AE although it is possible that this could still be too high due to a "kinetic-shift" effect.[19]

PIE curves for acetone and methyl ethyl ketone are shown in Figures 2 and 3. Like acetaldehyde the CH_3CO^+ ion count rate was very low in the threshold region so that extensive signal averaging was required to obtain reliable measurements. As a consequence of these relatively slow fragmentation processes both curves exhibit considerable curvature which increases the uncertainity associated with the extrapolated appearance energies. However, the quoted values of 10.38 and 10.32 eV are in good agreement with previous photoionization measurements.[2,17b] The PIE for CH_3CO^+ from *n*-propyl methyl ketone was measured but a long low-intensity tail precluded any definite AE assignment, even after a prolonged data acquisition period; an upper limit of 10.3 eV could be estimated from the curve.

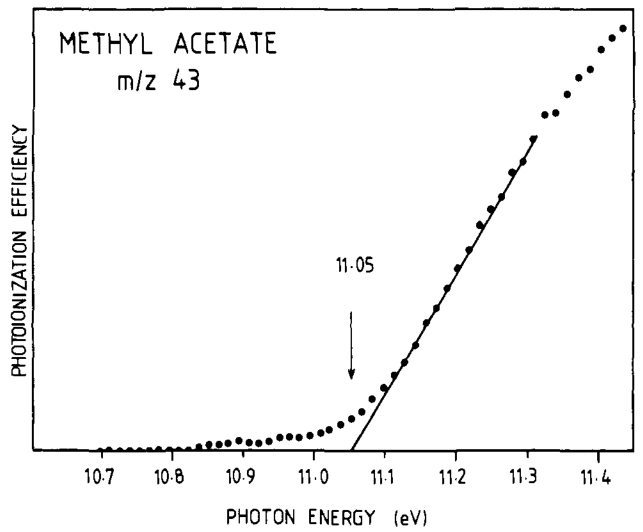

Figure 5. Threshold photoionization efficiency curve for CH_3CO^+ fragment ions produced from methyl acetate.

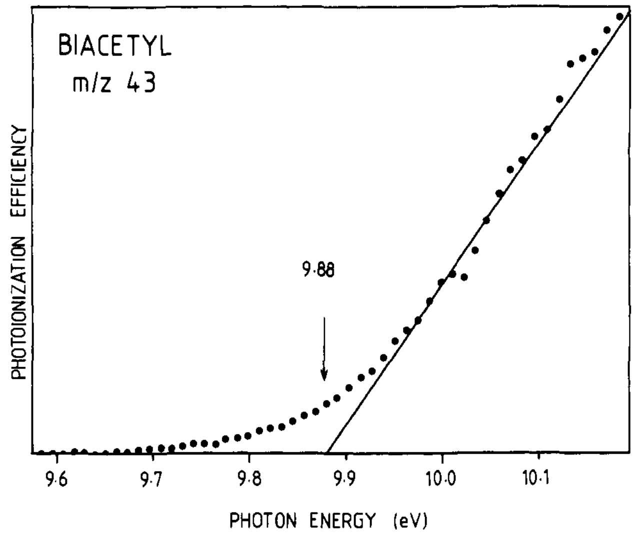

Figure 6. Threshold photoionization efficiency curve for CH_3CO^+ fragment ions produced from biacetyl.

Unlike the alkyl-substituted methyl ketones the CH_3CO^+ PIE curves for acetic acid, methyl acetate, and biacetyl (Figures 4–6) all have very sharp onsets with no apparent kinetic shift. The photoion count rate for biacetyl in the threshold region was greater than that for the other compounds studied here with the result that the observed hot-band structure is more pronounced; there was no evidence to suggest that the prethreshold tail could be ascribed to a kinetic-shift effect. Our measured AE for loss of OH from acetic acid (11.54 eV) is in excellent agreement with the electron-impact value obtained by Lossing.[20] However, the corresponding value for loss of CH_3O from methyl acetate (10.94 eV)[21] is considerably lower than the present photoionization result of 11.05 eV; no ready explanation can be given for this discrepancy. The measured CH_3CO^+ AE for biacetyl is identical with a previous photoionization measurement of 9.88 eV.[2b]

The only other acetyl compound studied here was acetic anhydride. No molecular ion was observed in the mass spectrum so that the measured CH_3CO^+ AE of 10.14 eV (Figure 7) may represent a pseudoionization energy. This is supported by a recent photoelectron spectrum of acetic anhydride[22] which shows a

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(18) All appearance energies measured in this work have been obtained from linear extrapolations which yield hot-band structure consistent with that observed for the relevant molecular ion.

(19) For a discussion of this see, for example: Gordon, S. M.; Reid, N. W. *Int. J. Mass Spectrom. Ion Phys.* **1975**, *18*, 379–391.

(20) Holmes, J. L.; Lossing, F. P. *J. Am. Chem. Soc.* **1980**, *102*, 3732–3735.

(21) Holmes, J. L.; Lossing, F. P. *Org. Mass Spectrom.* **1979**, *14*, 512–513.

(22) Bock, H.; Hirabayashi, T.; Mohmand, S. *Chem. Ber.* **1981**, *114*, 2595–2608.

Table I. Thermochemistry for the Gas-Phase Reaction $CH_3COX + h\nu \rightarrow CH_3CO^+ + X + e^-$

				$\Delta H_f{}^\circ{}_{298}$		
X	IE^a	AE^a	$\Delta H_{corr}{}^{b,c}$	CH_3COX^d	X	$CH_3CO^{+\,e}$
H	10.22	10.67	11.7	−165.8	218.0^f	657.4
CH_3	9.70	10.38	15.9	−217.2	143.9^g	656.3
C_2H_5	9.52	10.32	18.0	−240.8	116.3^h	656.6
OH	10.63	11.54	14.6	−432.1	39.3^i	656.7
CH_3O	10.25	11.05	17.1	−410.0	15.9^j	657.4
CH_3CO	9.30	9.88	18.0	−327.1	−15.0^k	659.2
CH_3COO	^{l}	10.14	19.2	−567.3	−207.9^m	638.2
Cl	10.78	10.78	11.7	−242.8	121.3^f	687.7
Br	10.24	10.24	11.7	−190.4	111.9^f	697.4
I	^{l}	9.28	11.7	−126.1	106.8^f	674.2

^{a} eV. ^{b} kJ mol^{-1}. ^{c} Reference 23. ^{d} Reference 26. ^{e} Calculated by using eq 1 and 1 eV = 96.487 kJ mol^{-1}. ^{f} Reference 27. ^{g} Reference 4. ^{h} Reference 28. ^{i} Reference 24. ^{j} Reference 29. ^{k} Reference 30. ^{l} See Results and Discussion. ^{m} Reference 31.

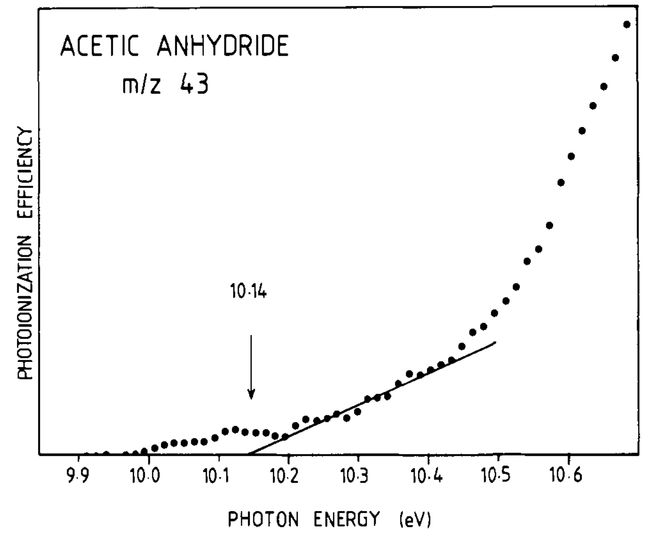

Figure 7. Threshold photoionization efficiency curve for CH_3CO^+ fragment ions produced from acetic anhydride.

first-band ionization onset in the region of 10.15 eV. Like the acetyl halides, any calculated CH_3CO^+ heat of formation will represent an upper limit.

The CH_3COX ionization energies and CH_3CO^+ appearance energies measured in this work are summarized in Table I together with the CH_3CO^+ heats of formation obtained from eq 1 and the supplementary thermochemical data used in these calculations. The heats of formation for all precursor molecules have been obtained from the Sussex N.P.L compilation of Pedley and Rylance.[26] As no similar single source exists for radical heats of formation we have adopted the most recent literature values where possible; some small corrections have been made in order to maintain self-consistency with other thermochemical data used. The ΔH_{corr} values in Table I have been obtained from statistical mechanical calculations as described by Stull and Prophet.[24] Where no experimental vibrational frequencies are available we have made an estimation based on the observed frequencies for analogous RH molecules.[25]

The calculated $\Delta H_f{}^\circ{}_{298}(CH_3CO^+)$ values for all compounds with a CH_3CO^+ AE greater than the corresponding molecular IE are in excellent agreement, yielding an average of 657.3 ± 1.0 kJ mol^{-1}. The only value at variance is that for biacetyl, which if excluded results in an average of 656.9 ± 0.5 kJ mol^{-1}. The error associated with the heat of formation for the acetyl radical is quoted as ±3 kJ mol^{-1}; an increase of only 2 kJ mol^{-1} is needed to bring the data for biacetyl into agreement with the data for other precursor molecules studied here. From a consideration of this and the error associated with the $H^\circ{}_{298} - H^\circ{}_0$ value for the acetyl cation (11.7 ± 1.0 kJ mol^{-1}), we recommend that $\Delta H_f{}^\circ{}_{298}(CH_3CO^+) = 657.0 \pm 1.5$ kJ mol^{-1}.

The acetyl halides all give calculated acetyl cation heats of formation considerably in excess of the above average. This is to be expected as the fragmentation processes, which occur subsequent to initial ionization of the neutral precursor, all have thermochemical thresholds below the respective ionization energies. The results for acetic anhydride are somewhat different in that the calculated heat of formation is 19 kJ mol^{-1} *lower* than the average. This is despite the fact that the observed AE corresponds to a pseudo-IE, implying an even lower thermochemical threshold. As the threshold shape of the PIE curve is inconsistent with an ion-pair process, the only feasible explanation for this anomaly is that the acetoxy radical heat of formation used in the calculations[31] is too high. Because of the unknown excess energy at the decomposition threshold we can only place an upper limit of ≤−227 kJ mol^{-1} on $\Delta H_f{}^\circ{}_{298}(CH_3COO)$.

The relative PA for ketene has been measured by several workers.[6-10] However, because of the uncertainties associated with the PA's of reference compounds the absolute PA is still in doubt; both NH_3 and isobutene have been used as standards. To make a comparison with the present results we have adopted a common reference PA of 822 kJ mol^{-1} for isobutene[32] which places PA(NH_3) = 863 kJ mol^{-1};[34] all quoted literature values have been adjusted to this reference.

Ausloos and Lias[6] obtained a value of 824 ± 4 kJ mol^{-1} for PA(ketene) which was subsequently redetermined as 835 ± 5 kJ mol^{-1}.[10] The measured values of both Beauchamp et al.[7] (837 ± 8 kJ mol^{-1}) and Kebarle et al.[8] (833 ± 6 kJ mol^{-1}) are in agreement with those of Lias.[10] March and co-workers[9] used quadrupole ion storage mass spectrometry to obtain a value of 813 ± 8 kJ mol^{-1} which was later revised to 814 ± 8 kJ mol^{-1}[35] following a reevaluation of symmetry effects. If we use our experimental value of $\Delta H_f{}^\circ{}_{298}(CH_3CO^+) = 657$ kJ mol^{-1} with $\Delta H_f{}^\circ{}_{298}$(ketene) = −47.7 ± 1.7 kJ mol^{-1}[26,36] and assume the *stationary* electron convention, i.e., $\Delta H_f{}^\circ{}_{298}(H^+) = 1530.1$ kJ

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(23) $H^\circ{}_{298} - H^\circ{}_0$ values from ref 4 or calculated with equations from ref 24; radical vibrational frequencies were estimated from data in ref 25.

(24) Stull, D. R.; Prophet, H. *Natl. Stand. Ref. Data Ser.* (*U.S., Natl. Bur. Stand.*) **1971**, *37*.

(25) Shimanouchi, T. *Natl. Stand. Ref. Data Ser.* (U.S., *Natl. Bur. Stand.*) **1972**, *39*.

(26) Pedley, J. B.; Rylance, J. "Sussex-N.P.L. Computer Analysed Thermochemical Data: Organic and Organometallic Compounds"; University of Sussex, 1977.

(27) CODATA recommended values: *J. Chem. Thermodyn.* **1976**, *8*, 603–605.

(28) Value from Castelhano et al. (Castelhano, A. L.; Marriott, P. R.; Griller, D. *J. Am. Chem. Soc.* **1981**, *103*, 4262–4263) corrected for $\Delta H_f{}^\circ$(ethyl iodide) = −9.0 kJ mol^{-1}.[26]

(29) Batt, L.; McCulloch, R. D. *Int. J. Chem. Kinet.* **1976**, *8*, 491–500.

(30) Value from Watkins and Word (Watkins, K. W.; Word, W. W. *Int. J. Chem. Kinet.* **1974**, *6*, 855–873) corrected for $\Delta H_f{}^\circ(CH_3) = 144$ kJ mol^{-1}.[4]

(31) Benson, S. W.; O'Neal, H. E. *Natl. Stand. Ref. Data Ser.* (*U.S., Natl. Bur. Stand.*) **1970**, *21*.

(32) Obtained by adjusting the results of Houle and Beauchamp[11b] for the recently determined value of $\Delta H_f{}^\circ{}_{298}(t\text{-}C_4H_9) = 43.9$ kJ mol^{-1}.[33]

(33) (a) Canosa, C. E.; Marshall, R. M. *Int. J. Chem. Kinet.* **1981**, *13*, 303–316. (b) Pacansky, J.; Chang, J. S. *J. Chem. Phys.* **1981**, *74*, 5539–5546.

(34) The difference between PA(NH_3) and PA(isobutene) is 41 kJ mol^{-1}.[10]

(35) Armitage, M. A.; Higgins, M. J.; Lewars, E. G.; March, R. E. *J. Am. Chem. Soc.* **1980**, *102*, 5064–5068.

(36) Nuttall, R. L.; Laufer, A. H.; Kilday, M. V. *J. Chem. Thermodyn.* **1971**, *3*, 167–174.

mol^{-1},[1] we calculate PA(ketene) = 825.4 ± 3.2 kJ mol.$^{-1}$ This is in excellent agreement with the original result of Ausloos and Lias[6] and lies in the middle of the range of values cited above. Any correction for excess energy at threshold based on the data of Haney and Franklin[3] results in a PA for ketene which is too high by more than 70 kJ mol^{-1}. We do not believe that translational-energy measurements made at energies significantly greater than threshold can be applied in a straightforward manner as thermochemical corrections for experimental appearance energies.

Conclusion

The general application of eq 1 for calculating 298 K cationic heats of formation from AE measurements has extended previous work[4,37] to include unimolecular decompositions in which the neutral fragment is not a monatomic species. The range of values for $\Delta H_f°_{298}(CH_3CO^+)$ obtained from photoionization data[1] has been shown to be due to a neglect of the necessary enthalpy corrections (ΔH_{corr}) and in some cases to an overestimation of the AE because of kinetic-shift effects. Except for the acetyl halides and acetic anhydride, there is no evidence to suggest any significant excess energy at the decomposition threshold for the acetyl compounds studied here. When the *stationary* electron convention for cationic heats of formation is used, the recommended value for $\Delta H_f°_{298}(CH_3CO^+)$ is 657.0 ± 1.5 kJ mol^{-1} which leads to PA(ketene) = 825.4 ± 3.2 kJ mol.$^{-1}$ An upper limit of ≤ -227 kJ mol^{-1} can be placed on the heat of formation for the acetoxy radical.

Acknowledgment. We are pleased to acknowledge the financial support of the Australian Research Grants Committee and the assistance of Dr. J. B. Peel with the photoelectron spectroscopic measurements.

Registry No. Acetyl cation, 15762-07-9; acetaldehyde, 7507-0; acetone, 67-64-1; methyl ethyl ketone, 78-93-3; acetic acid, 64-19-7; methyl acetate, 79-20-9; biacetyl, 431-03-8; acetic anhydride, 108-24-7.

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(37) Traeger, J. C. *Org. Mass Spectrom.* **1981** *16*, 193–194.

Electrochemistry of Perfluorotetracyclobuta-1,3,5,7-cyclooctatetraene, a Powerful Neutral Organic Oxidant

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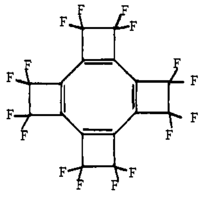
Abstract: The electrochemistry of perfluorotetracyclobuta-1,3,5,7-cyclooctatetraene (**1**) (a flat cyclooctatetraene) shows two reversible one-electron reductions at 0.79 and 0.14 V vs. SCE. The apparent electron-transfer rate constant for the first reduction is 0.07 ± 0.02 cm/s. The first reduction potential of **1** is more than 2.3 V positive of cyclooctatetraene (COT), and the apparent rate constant is more than an order of magnitude higher. It is suggested that the larger electron transfer rate constant for **1** compared with COT is due to the lower molecular reorganization energy required to reach the transition state for electron transfer. The unusually positive reduction potential of **1** is probably due at least in part to the 16 fluorine atoms.

We report our findings on the electrochemistry of perfluorotetracyclobuta-1,3,5,7-cyclooctatetraene,[1] **1**, which is one of the most powerful neutral organic oxidants known, reducing at positive 0.79 V vs. SCE.



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Our initial interest in the electrochemistry of **1** was prompted because it is a flat cyclooctatetraene[2] (COT), and comparison of its electrochemistry with tub-shaped COT[3] and other COT derivatives of various conformations[4] could provide insight into the structural changes occurring prior to electron transfer. The COT molecule has been an important species for electrochemical studies because electron transfer awaits COT ring flattening to afford the planar anion radical.[3,4] Experimental data[3,4] suggest the activation energy for ring flattening is manifested by the slow electron transfer rate constant in support of Marcus' theory.[5] It was therefore anticipated that electron transfer to **1** would be faster than to COT, since **1** is already flat. We have confirmed this expectation by fundamental harmonic ac voltammetry measurements.[6]

Experimental Section

Chemicals. Baker HPLC grade acetonitrile was passed through a column of activated alumina (550 °C, ≥15 h; MCB chromatography grade) immediately before use. All electrochemical cell components, syringes, volumetric flasks, and electrolytes were dried in a vacuum oven at 120 °C for at least 8 h before use. Tetrabutylammonium hexafluorophosphate was dried for 24 h in a vacuum oven at 120 °C and

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