$$\log K_{\mathrm{T}/1} = 0.02409(10^3/T)^3 - 0.1874(10^3/T)^2 + 1.096(10^3/T) - 1.081\ (\pm 0.011)$$

The former equation covers the temperature range from 251 to 883°K; the latter, from 251 to 724°K. Thermodynamic properties derived therefrom are presented in Table II.

Benson[3] discusses the sources and reliability of the thermodynamic data in the API tables and points out that the entropy values for 1-butene are least reliably known. This is the result of estimations used in assignment of low-frequency vibrations upon which the thermodynamic calculations were based. The good agreement of all authors for the 1-trans isomerization should allow more accurate assignment of these frequencies and permit extension of reliable calculations to lower temperatures.

Because of the agreement among the data of different investigators for the 1-ene to trans isomerization, it is worthwhile making a quantitative estimate of the absolute entropy of 1-butene to replace the value used in compiling the API data. To be completely objective, the curve including the data of all authors should be used. When this is done, the value of ΔS at 298.16°K is -3.60 eu. Using the API value for *trans*-2-butene of 70.86, we find the value for $S°_{298}$ for 1-butene to be 74.46 eu. The accuracy of this number is determined by the error in $S°_{298}$ for *trans*-2-butene.

In the case of the cis–trans isomerization, the values of $\Delta H°$ and $\Delta S°$ in Table II are within the limits of error of the API data at all temperatures.

For all the equilibrium constants presented in Table I, it was assumed the gases behave ideally. This assumption was checked for 250°K using the second virial coefficient data of Roper quoted by Dymond and Smith.[11] The ratio of fugacity coefficients for the cis–trans as well as for 1-ene–trans isomerization is 0.998. Application of these refinements is not justified by the experimental error in the equilibrium constants.

Conclusion

Recent work questioning the validity of the API data for the 2-butenes has not been substantiated. The most reliable data for equilibrium constants provide thermodynamic properties in agreement with the API values up to 900°K, and the present work extends them down to 250°K. On the other hand, the original API value for the standard entropy of 1-butene at 298.16°K is definitely erroneous. The old value of 73.04 eu should be replaced by 74.46 eu with an error determined by the accuracy of the absolute entropy of *trans*-2-butene.

Acknowledgment. The gas chromatograph used in this work was a gift of the Richardson Company; the platinum resistance thermometer and Mueller Bridge used for temperature calibration were purchased with financial assistance from the Research Corporation. We are grateful to Drs. Akimoto, Sprung, and Pitts for permission to use their data prior to publication.

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Heats of Formation of Protonated Cyclopropane, Methylcyclopropane, and Ethane

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Abstract: Equilibrium constants have been measured for proton transfer reactions between protonated methanol or protonated formic acid with propylene, *trans*-2-butene, cyclopropane, methylcyclopropane, and ethane. The single ion source of a mass spectrometer was used as reactor. From the free energies of reaction and assuming negligible entropy change, proton affinities have been determined for the above compounds assuming $\Delta H_f(i\text{-}C_3H_7^+)$ to be 191.7 kcal/mol. Heats of formation of the various protonated ions calculated from these values show that protonated cyclopropane and methylcyclopropane have heats of formation different from that of the propyl or butyl ions showing that the ring structure for these ions is maintained. The heat of formation of $C_2H_7^+$ is about 0.2 kcal/mol less than that of $C_2H_5^+$. This is in accord with the postulated instability of $C_2H_7^+$.

This research has been directed toward establishing thermodynamic properties of certain interesting hydrocarbon positive ions for which no suitable values have yet been determined. Several investigators have postulated protonated cyclopropane or methylcyclopropane as intermediate in the solvolysis of norbornyl derivatives,[1] in the addition of acids,[2–4] acetyl chloride,[5] and bromine[6] to cyclopropane, and in the reaction of cyclopropanecarboxylic acids.[7] Recently, Ausloos, *et*

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al.,[8,9] found that, under irradiation, the addition of ammonia to *n*-butane gave cyclopropane and suggested that $C_3H_7^+$ in the reaction

$$C_3H_7^+ + NH_3 \longrightarrow c\text{-}C_3H_6 + NH_4^+ \qquad (1)$$

was the protonated cyclopropane. In an earlier paper, Grubb and Meyerson[10] suggested, on the basis of appearance potentials and isotope distributions, that the $C_3H_7^+$ and $C_4H_9^+$ ions in certain mass spectra might be protonated cyclopropane or methylcyclopropane rather that the corresponding carbonium ion.

From the above it is evident that the concept of the protonated cyclopropane has been of considerable importance in interpreting several reaction mechanisms. However, a direct observation of this ion has never definitely been accomplished. The present study is an attempt to obtain unequivocal evidence for its existence by determining the proton affinity of cyclopropane in an equilibrium proton transfer reaction and to ascertain whether the heat of formation of the ion so formed differs significantly from that of iso- or *n*-propyl.

Protonated ethane, $C_2H_7^+$, has been observed by Field, *et al.*,[11] and by Munson and Field[12] in high-pressure mass spectrometric studies of methane containing small amounts of ethane and by Munson, *et al.*,[13] in high pressure studies of ethane alone. The latter found the appearance potential of $C_2H_7^+$ from ethane to be 12.7 eV, corresponding to the appearance potential of $C_2H_5^+$. However, $\Delta H_f(C_2H_7^+)$, calculated on the assumption that $C_2H_5^+$ is the precursor, is unreasonably low, and the authors concluded that an excited ethane ion probably was the precursor of $C_2H_7^+$. If so, the heat of formation of $C_2H_7^+$ would be approximately 228 kcal/mol. Recently, Harrison[14] has shown that CD_5^+ will react with ethane to give $C_2H_6D^+$ and has measured the rate of the reaction. Thus, the proton (or deuteron) affinity of ethane is somewhat greater than that of methane. However, no reliable value for $PA(C_2H_6)$ or $\Delta H_f(C_2H_7^+)$ has been previously determined except by the approximate method of bracketing employed by Munson and Field.[12] In an effort to determine $\Delta H_f(C_2H_7^+)$, we have attempted to determine the equilibrium constant for the reaction

$$CH_5^+ + C_2H_6 \longrightarrow C_2H_7^+ + CH_4 \qquad (2)$$

Experimental Section

A quadrupole mass filter equipped with a high-pressure ion source was employed in this investigation. The instrument has been previously described.[15]

In order to determine the equilibrium constant for a proton transfer reaction in our instrument, it is necessary to employ a reaction of small free energy. Since these reactions will involve little or no entropy change, the heat of reaction will also be small. For the ethane study we employed CH_5^+ as mentioned above; for the cyclopropane, methylcyclopropane, and *trans*-2-butene studies we employed the protonated ions of methanol, $CH_3OH_2^+$, and of formic acid, $HC(OH)_2^+$. In addition, the isopropyl ion from propylene was employed to redetermine the proton affinities of formic acid and methanol.

In each of the experiments, the proton donor was present in the source in high intensity as a result of its conjugate base being present at elevated pressures (0.2–0.6 Torr). The proton acceptor was then added in small increments until the equilibrium constant was achieved. This method has been successfully employed in previous investigations in this laboratory.[16]

The methanol and formic acid employed in these studies were common reagent grade. The methane, ethane, and cyclopropane were research grade gases obtained from Matheson Chemical Co. Propylene and *trans*-2-butene were research grade gases from Phillips Petroleum Co., and methylcyclopropane was research grade obtained from K & K Laboratories.

Results

Methanol and Formic Acid. The heat of formation of isopropyl ion is given by Franklin, *et al.*,[17] as 190 kcal/mol from which we compute the proton affinity of propylene to be 181 kcal/mol. Subsequently, Lossing and Semeluk[18] determined the ionization potential of isopropyl ion to be 7.55 ± 0.05 eV. When this is combined with the preferred value of $\Delta H_f(i\text{-}C_3H_7)$ of 17.6 ± 1 kcal/mol,[19] we find $\Delta H_f(i\text{-}C_3H_7^+)$ and $PA(C_3H_6)$ to be 191.7 ± 2.1 and 179.2 ± 2.1 kcal/mol, respectively. In computing the proton affinity of propylene we have assumed $\Delta H_f(C_3H_6)$ to be 4.88 kcal/mol and to involve only negligible error. We consider these later values to be the most accurate available and have referred the thermodynamic properties determined in this paper (except for $\Delta H_f(C_2H_7^+)$) to the isopropyl ion as standard.

Table I. Equilibrium Constant for the Reaction $CH_3C^+HCH_3 + CH_3OH \rightleftarrows CH_3CH{=}CH_2 + CH_3OH_2^+$ [a]

CH_3OH pressure, μ	$I(CH_3OH_2^+)/I(i\text{-}C_3H_7^+)$	K_{eq}
29	0.590	3.26
41	0.755	2.95
54	1.048	3.11
67	1.175	2.81
85	1.415	2.66
122	2.17	2.85
155	3.15	3.24
178	3.74	3.36
		Av 3.03 ± 0.21

[a] Propylene pressure 160 μ. Ion intensities corrected for carbon-13 isotope contribution.

In Table I the results of the measurements of the equilibrium constant for the reaction

$$i\text{-}C_3H_7^+ + CH_3OH \rightleftarrows CH_3CH{=}CH_2 + CH_3OH_2^+ \qquad (3)$$

are given with an average value of 3.03 ± 0.21. Taking the source temperature to be 340°K, we compute ΔG to be -0.76 ± 0.05 kcal/mol. The intrinsic entropy change occurring in a proton transfer reaction such as (3) may reasonably be taken as zero. However, account must be taken of the reaction path degeneracies. In (3) this would be 6 in the forward and 2 in the re-

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verse direction, giving a ratio for the reaction of 3. Deducting $RT \ln 3$ from $-\Delta G$ gives the estimated heat of reaction to be −0.01 kcal/mol. With this and heats of formation given in Table VIII, the proton affinity of methanol and $\Delta H_f(CH_3OH_2^+)$ are computed to be 179.0 ± 2.2 and 139.0 kcal/mol, respectively. This result is, within the error limits, in fair agreement with Haney and Franklin's[20] value of 182 ± 3 kcal/mol and is, in our opinion, considerably more accurate.

In a similar fashion, mixtures of propylene and formic acid were studied, and values determined for the equilibrium constant for the reaction

$$HC(OH)_2^+ + CH_3CH{=}CH_2 \rightleftharpoons HCOOH + i\text{-}C_3H_7^+ \quad (4)$$

are given in Table II leading to an average value of the equilibrium constant of 2.06 ± 0.04 and ΔG of reaction of −0.49 ± 0.02 kcal/mol. Assuming the intrinsic entropy of reaction to be negligible, and correcting for reaction path degeneracies, yields PA(HCOOH) = 178.0 ± 2.12 kcal/mol and $\Delta H_f(HCOOH_2^+)$ = 97.5 kcal/mol. Haney and Franklin,[20] employing a different method, found PA(HCOOH) to be 179 ± 3 kcal/mol.

Table II. Equilibrium Constant for the Reaction $HCOOH_2^+ + CH_3CH{=}CH_2 \rightleftharpoons HCOOH + CH_3C^+HCH_3$ [a]

$CH_3CH{=}CH_2$ pressure, μ	$I(i\text{-}C_3H_7^+)/I(HCOOH_2^+)$	K_{eq}
37	0.664	2.15
64	1.068	2.00
78	1.350	2.08
92	1.545	2.01
110	1.875	2.04
138	2.39	2.08
178	3.00	2.02
203	3.52	2.08
		Av 2.06 ± 0.04

[a] Formic acid pressure 120 μ. Ion intensities corrected for carbon-13 isotope contribution.

Cyclopropane. In order to study the proton affinity of cyclopropane, we have chosen methanol and formic acid as our reagents and have proceeded in the same manner as above but employing the values for proton affinities of the two reagents determined in the preceding section. Tables III and IV give equilibrium constants determined for the reactions

$$CH_3OH_2^+ + c\text{-}C_3H_6 \rightleftharpoons CH_3OH + C_3H_7^+ \quad (5)$$

$$HC(OH)_2^+ + c\text{-}C_3H_6 \rightleftharpoons HCOOH + C_3H_7^+ \quad (6)$$

Table III. Equilibrium Constant for the Reaction $CH_3OH_2^+ + c\text{-}C_3H_6 \rightleftharpoons CH_3OH + c\text{-}C_3H_7^+$ [a]

$c\text{-}C_3H_6$ pressure, μ	$I(C_3H_7^+)/I(CH_3OH_2^+)$	K_{eq}
210	0.655	0.557[b]
165	0.439	0.439
184	0.525	0.471
214	0.587	0.452
220	0.613	0.460
252	0.840	0.550
313	0.873	0.461
		Av 0.484 ± 0.039

[a] Methanol pressure 165 μ. Ion intensities corrected for carbon-13 isotope contribution. [b] $p(CH_3OH)$ = 178 μ.

Table IV. Equilibrium Constant for the Reaction $HCOOH_2^+ + c\text{-}C_3H_6 \rightleftharpoons HCOOH + c\text{-}C_3H_7^+$ [a]

$c\text{-}C_3H_6$ pressure, μ	$I(C_3H_7^+)/I(HCOOH_2^+)$	K_{eq}
33	0.775	3.94
42	0.870	3.48
52	1.047	3.38
65	1.480	3.82
82	1.625	3.33
94	2.090	3.76
110	2.18	3.33
124	2.92	3.96
197	4.37	3.73
253	5.71	3.79
		Av 3.65 ± 0.22

[a] Formic acid pressure 168 μ. Ion intensities corrected for carbon-13 isotope contribution.

The equilibrium constants determined were 0.48 ± 0.04 and 3.65 ± 0.22 for reactions 5 and 6, respectively. Treating the entropy of reaction as before and assuming the reaction path symmetry of the $c\text{-}C_3H_7^+$ ion to be 3, we compute the heats of formation of protonated cyclopropane to be 199.9 ± 2.2 and 199.6 ± 2.2 kcal/mol, respectively, from reactions 5 and 6. Averaging the two values gives the heat of formation of protonated cyclopropane as 199.8 ± 2.2 kcal/mol. The corresponding values for the proton affinity of cyclopropane are 178.8 and 179.1 kcal/mol with an average proton affinity of 179.0 kcal/mol.

Although the proton affinity of cyclopropane is thus quite close to that of propylene, the heat of formation of the protonated cyclopropane ion is distinctly different from that of either propyl ion and, indeed, falls approximately halfway between them. It is thus established that the protonated cyclopropane ion is a different entity from the two propyl ions as has been postulated by several scientists and discussed above.

It may be argued that the $C_3H_7^+$ ion detected in these studies is in fact a propyl ion. However, if this were the case, considerably different results would be expected. For example, if we take the reaction

$$CH_3OH_2^+ + c\text{-}C_3H_6 \longrightarrow CH_3OH + i\text{-}C_3H_7^+ \quad (7)$$

the heat of reaction would be some 4 kcal/mol, and in addition there would be an entropy increase of about 10 eu so that the free energy of reaction would be about 7–8 kcal/mol. This free energy is too great for the reaction to attain equilibrium at the conditions in our instrument. Further, it would have been quite possible to employ a proton donor such as dimethyl ether or acetone to achieve protonation of the cyclopropane. Obviously, with methanol the equilibrium constant is quite small, and it would be very certain that a less vigorous protonating agent would have given no detectable proton transfer. Thus, we are confident that the $C_3H_7^+$ ion obtained with cyclopropane in these experiments is not propyl but is indeed the protonated cyclopropane.

A large number of theoretical treatments of protonated cyclopropane have been reported in the literature

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[20] M. A. Haney and J. L. Franklin, *J. Phys. Chem.*, 73, 4328 (1969).

but we will not attempt to summarize them here. It is appropriate, however, to mention two theoretical recent studies of the $C_3H_7^+$ and $C_4H_9^+$ ions. Bodor and Dewar[21] employed a MINDO/2 treatment and obtained excellent agreement of their calculated values of propyl ions with experimental values. They found, however, that the heat of formation of the edge-protonated cyclopropane is slightly (4 kcal/mol) more stable than *i*-$C_3H_7^+$. This disagrees with our results by some 12–13 kcal/mol and, further, disagrees with the order of stabilities of the $C_3H_7^+$ ions obtained experimentally.

Radom, *et al.*,[22] have also made theoretical calculations of the relative energies of various configurations of $C_3H_7^+$. They found *n*-propyl and corner-protonated cyclopropane to be of very similar energy and to be some 17 kcal/mol higher in energy than isopropyl. Edge- and face-protonated cyclopropanes were found to be 27 and 139 kcal/mol more energetic than isopropyl. The calculated results for corner-protonated cyclopropane are in directional agreement with our experimental results, but the calculated energy is about 9 kcal/mol greater than the experimental value. Further, the close agreement of the calculated energies of protonated cyclopropane and *n*-propyl is in serious disagreement with experiment.

Methylcyclopropane and *trans*-2-Butene. It would be expected that methylcyclopropane and 2-butene would have similar proton affinities and that these would be rather close to those of cyclopropane and propylene. Proton-exchange reactions of methylcyclopropane and *trans*-2-butene with protonated methanol gave very satisfactory values for the equilibrium constant.

$$CH_3OH_2^+ + CH_3\text{-c-}C_3H_6 \rightleftharpoons CH_3OH + CH_3\text{-c-}C_3H_7^+ \quad (8)$$

$$CH_3OH_2^+ + \textit{trans}\text{-2-}C_4H_8 \rightleftharpoons CH_3OH + CH_3\overset{+}{C}H\text{-}C_2H_5 \quad (9)$$

The equilibrium constants in Tables V and VI give values of the free energies for (8) and (9) of −0.72 ± 0.03 and −1.1 ± 0.03 kcal/mol, respectively. Taking $\Delta H_f(CH_3OH_2^+)$ as determined above, we compute $\Delta H_f(CH_3\text{-c-}C_3H_7^+)$, assuming a reaction path symmetry of 3, and $\Delta H_f(\textit{sec}\text{-}C_4H_9^+)$ to be respectively 192.4 ± 2.2 and 183.2 ± 2.2 kcal/mol. These correspond respectively to proton affinities of 180.0 ± 2.2 and 180.1 ± 2.2 kcal/mol. Our value for $\Delta H_f(\textit{sec}\text{-}C_4H_9^+)$ agrees quite well with Lossing and Semeluk's[18] value of 183 kcal/mol for this ion. We are convinced that $\Delta H_f(\textit{sec}\text{-}C_4H_9^+)$ is close to 183 kcal/mol and that the preferred value of 192 kcal/mol given by Franklin, *et al.*,[17] is seriously in error. Thus, we find the heat of formation of protonated methylcyclopropane to be some 10 kcal/mol greater than that of *sec*-$C_4H_9^+$. Further, it is distinctly different from Lossing and Semeluk's[18] heats of formation of 167, 199, and 201 kcal/mol respectively for the *tert*-, iso- and *n*-butyl ions. Thus, we conclude the protonated methylcyclopropane ion to be different from any of the butyl ions and may be presumed to have a different structure which probably retains the cyclopropane ring configuration.

Table V. Equilibrium Constant for the Reaction $CH_3OH_2^+ + CH_3\text{-c-}C_3H_6 \rightleftharpoons CH_3OH + CH_3\text{-c-}C_3H_7^+$ [a]

$CH_3\text{-c-}C_3H_6$ pressure, μ	$I(C_4H_9^+)/I(CH_3OH_2^+)$	K_{eq}
66	1.535	2.84
88	2.20	3.06
137	3.30	2.94
160	3.61	2.75
181	3.95	2.68
190	4.21	2.71
198	4.33	2.66
211	5.04	2.91
229	5.75	3.06
		Av 2.85 ± 0.13

[a] Methanol pressure 122 μ. Ion intensities corrected for carbon-13 isotope contribution.

Table VI. Equilibrium Constant for the Reaction $CH_3OH_2^+ + \textit{trans}\text{-}CH_3CH{=}CHCH_3 \rightleftharpoons CH_3OH + CH_3C^+HCH_2CH_3$ [a]

trans-$CH_3CH{=}CHCH_3$ pressure, μ	$I(C_4H_9^+)/I(CH_3OH_2^+)$	K_{eq}
25	1.231	5.22[b]
32	1.630	5.41[b]
85	4.48	5.16
103	5.33	5.07
124	6.19	4.90
162	7.60	4.60
217	11.1	5.01
239	12.36	5.07
285	13.10	4.52
		Av 5.00 ± 0.22

[a] Methanol pressure 98 μ. Ion intensities corrected for carbon-13 isotope contribution. [b] Methanol pressure 106 μ.

Protonated Ethane. Since deuteron transfer from CD_5^+ to ethane had been observed,[14] we have attempted to achieve equilibrium in reaction 2 by employing a source pressure of 384 μ of methane and adding ethane at various pressures up to about 300 μ. The data given in Table VII are not as precise as we would have liked but clearly indicate that equilibrium in reaction 2 has been reached. It is perhaps of interest that the relative concentrations of the protonated ethane at these elevated pressures (about 6% of the total ionization

Table VII. Equilibrium Constant for the Reaction $CH_5^+ + C_2H_6 \rightleftharpoons CH_4 + C_2H_7^+$ [a]

C_2H_6 pressure, μ	$I(C_2H_7^+)/I(CH_5^+)$	K_{eq}
101	1.395	5.28[b]
120	1.450	4.65
175	1.980	4.35
211	2.680	4.88
241	3.210	5.11
268	3.190	4.57
280	4.090	5.60
291	3.85	5.08
		Av 4.94 ± 0.33

[a] Methane pressure 384 μ. Ion intensities corrected for carbon-13 isotope contribution. [b] Methane pressure 382 μ.

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(21) N. Bodor and M. J. S. Dewar, *J. Amer. Chem. Soc.*, **93**, 6685 (1971).

(22) L. Radom, J. A. Pople, V. Buss, and P. v. R. Schleyer, *ibid.*, **93**, 1813 (1971).

Table VIII. Heats of Formation Employed in This Study[a]

	ΔH_f, kcal/mol		ΔH_f, kcal/mol
H^+	366	CH_4	−17.88
CH_4^+	274	C_2H_6	−20.24
CH_5^+	222.1	$CH_3CH{=}CH_2$	4.88
$C_2H_5^+$	219	c-C_3H_6	12.74
i-$C_3H_7^+$	191.7	*trans*-$CH_3CH{=}CHCH_3$	−2.67
n-$C_3H_7^+$	208	CH_3-c-C_3H_5	6.4
		CH_3OH	−47.96
		HCOOH	−90.48

[a] All values were taken from ref 17 except those for the propyl ions which were taken from ref 18.

for 200 eV electrons) are comparable to that observed by Harrison.[14]

From the equilibrium constant given in Table VII, we compute the free energy of reaction 10 to be −1.09 ± 0.05 kcal/mol. Again assuming the intrinsic entropy change to be zero and correcting for reaction path degeneracies, we compute $\Delta H_f(C_2H_7^+)$ to be 218.8 ± 1.05 kcal/mol, which is some 3 kcal/mol less than $\Delta H_f(CH_5^+)$ of 222.1 kcal/mol deduced from the paper of Munson and Field[12] with correction for later thermochemical values of the ions involved.[17] The corresponding value for the proton affinity of C_2H_6 is 127.0 ± 1.05 kcal/mol and is thus only about 1 kcal/mol greater than that of methane.

The heat of formation of $C_2H_5^+$ is 219 kcal/mol and, since $\Delta H_f(C_2H_7^+)$ is 218.8 kcal/mol, reaction 10 is

$$C_2H_7^+ \longrightarrow C_2H_5^+ + H_2 \qquad (10)$$

essentially athermal if reactants and products are in the ground state. However, reaction 10 involves an increase in entropy of about 25 eu so that it would have a favorable free energy of about 8 kcal/mol. The fact that $C_2H_7^+$ is observed in reasonable concentrations in these and other experiments suggests that reaction 10 has an activation energy of at least a few kilocalories/mole. Thus, it is not surprising that previous investigators found relatively small intensities of $C_2H_7^+$ or that the $C_2H_7^+$ ion formed as an intermediate in the reaction of methyl ion with methane has never been successfully stabilized by collision. The reaction would be some 23 kcal/mol exothermic and it is seldom possible to remove such a large amount of energy by collision.

Table IX. Proton Affinities and Heats of Formation (in kcal/mol) Determined in This Study

Molecule (M)	PA(M)	$\Delta H_f(MH^+)$
Propylene	179.2 ± 2.1	191.7
Methanol	179.0 ± 2.15	139.0
Formic acid	178.0 ± 2.12	97.5
Cyclopropane	179.0 ± 2.6	199.8
trans-2-Butene	180.1 ± 2.18	183.2
Methylcyclopropane	180.0 ± 2.18	192.4
Ethane	127.0 ± 1.05	218.8

Table VIII gives all of the heats of formation employed in this study.

Summary

We have shown that equilibrium can be attained in certain proton transfer reactions of small free energy by employing the single ion source of a mass spectrometer as reactor. From the equilibrium constants measured, free energies of reactions, proton affinities, and heats of formation of several ions have been computed. Table IX summarizes the thermodynamic properties determined in this study.

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