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Effect of Methyl Substitution on the Thermochemistry of Ketene

Christiane Aubry and John L. Holmes*

Department of Chemistry, University of Ottawa, 10 Marie-Curie, Ottawa, Ontario K1N 6N5, Canada

Johan K. Terlouw

Department of Chemistry, McMaster University, 1280 Main Street West, Hamilton, Ontario L8S 4M1, Canada

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The heats of formation of ketene, methylketene, and dimethylketene have been measured by energy-selected electron-induced dissociation of phenyl acetate, propanoate, and isobutyrate, respectively. The values are $\Delta_f H°[CH_2{=}C{=}O] = -54 \pm 5$ kJ mol^{-1}, $\Delta_f H°[CH_3CH{=}C{=}O] = -95 \pm 5$ kJ mol^{-1}, and $\Delta_f H°[(CH_3)_2C{=}C{=}O] = -137 \pm 5$ kJ mol^{-1}. For ketene, the new result was in excellent agreement with literature data and recent high-level ab initio calculations. The values for the methyl-substituted analogues differed significantly from those obtained by the recent calculations. The heats of formation of ionized methyl- and dimethylketene were also measured to be 765 and 683 ± 5 kJ mol^{-1}, respectively. These experimental results show that the effect of methyl substitution in neutral ketene decreases the heat of formation by ca. 40 kJ mol^{-1} per methyl group, which is in keeping with the effect of methyl substitution in structurally related systems.

Introduction

There has been only one accurate measurement reported for the heat of formation ($\Delta_f H°$) of a compound containing the ketene function [C=C=O], namely ketene itself, $CH_2{=}C{=}O$. The $\Delta_f H°$ value, -47.7 ± 2.5 kJ mol^{-1}, is listed in the selected thermochemical data source book of Pedley, Naylor, and Kirby.[1] The method used to determine $\Delta_f H°[CH_2CO(g)]$ was not combustion to CO_2 and H_2O, but a measurement of the heat of solution of ketene in aqueous sodium hydroxide.[2] The result has not been challenged by later experiments or by recent state-of-the art theoretical calculations,[3] thus giving confidence in the 1971 result. The data compilation of Lias *et al.*[4] also contain $\Delta_f H°$ values for methylketene, $CH_3CH{=}C{=}O$, and dimethylketene, $(CH_3)_2C{=}C{=}O$, of −105 and −134 kJ mol^{-1}, respectively. These however are not experimentally based values, and moreover the latter value was quoted as −155 kJ mol^{-1} in the original estimate,[5] where it reflected an additivity term of about −50 kJ mol^{-1} per methyl group. Other thermochemical data available for $CH_2{=}C{=}O$, $CH_3CH{=}C{=}O$, and $(CH_3)_2C{=}C{=}O$ include the ionization energy (IE) values experimentally determined by Bock[6] and reported as 9.64, 8.95, and 8.45 eV, respectively.

Recently, McKee and Radom,[7] using ab initio molecular orbital theory calculations at the G2 level, reported $\Delta_f H°_{298}$ values for $CH_3CH{=}C{=}O$ and $CH_3CH{=}C{=}O^{\bullet+}$ of −65.1 and 797.0 kJ mol^{-1}, respectively, and an adiabatic IE for methylketene of 8.93 eV. This IE value is in excellent agreement with that reported by Bock[6] (8.95 eV). However, an earlier unpublished value of 765 ± 4 kJ mol^{-1} was obtained in our laboratory for $\Delta_f H°[CH_3CH{=}C{=}O^{\bullet+}]$ from the measured appearance energy (AE) of the ion in the following reaction:

$$CH_3CH_2COCH_2OH \rightarrow CH_3CH{=}C{=}O^{\bullet+} + CH_3OH \qquad AE = 9.88 \pm 0.05\ \text{eV} \quad (1)$$

a result which is not in good agreement with the above calculations. Support for the estimated $\Delta_f H°[CH_3CH{=}C{=}O]$ came from a late 1996 experimental value,[8] −97 kJ mol^{-1}, a result based on the measurement of the proton affinity, 842 ± 3 kJ mol^{-1}, and using $\Delta_f H°[CH_3CH_2CO^+] = 591 \pm 2.3$ kJ mol^{-1}.[9]

Most recently, Scott and Radom[3] published a paper on the effect of methyl substitution in ketene extending their earlier calculations to ketene and dimethylketene and reviewing the previously reported $\Delta_f H°$ value for methylketene. The calculated values were $\Delta_f H°[CH_2{=}C{=}O] = -52$ kJ mol^{-1}; $\Delta_f H°[CH_3CH{=}C{=}O] = -68$ kJ mol^{-1}, and $\Delta_f H°[(CH_3)_2C{=}C{=}O] = -92$ kJ mol^{-1}. The remarkably small change in the calculated $\Delta_f H°$ in going from ketene to methylketene, from −52 to −68 kJ mol^{-1}, and methylketene to dimethylketene, from −68 to −92 kJ mol^{-1} (smaller than that for any other methyl substitution, as discussed in the following section), aroused our interest in trying to measure the $\Delta_f H°$ of $CH_3CH{=}C{=}O$ and $(CH_3)_2C{=}C{=}O$ and in obtaining a new experimental value for $\Delta_f H°[CH_2{=}C{=}O]$.

The method chosen was one which we have used to advantage in other studies[10] to determine a neutral $\Delta_f H°$ by measuring the AE of a fragment ion of established $\Delta_f H°$ value with which the neutral of interest is cogenerated. To determine the $\Delta_f H°$ of neutral ketene, methylketene, and dimethylketene, the AE of ionized phenol in the reactions

$$R_1R_2CHCO_2C_6H_5 \rightarrow R_1R_2C{=}C{=}O + C_6H_5OH^{\bullet+} \quad (2)$$

where R_1 and R_2 are either CH_3 or H, were measured.

Experimental Section

The electron monochromator and mass spectrometer used for these measurements and the operation of the instrument have been described in detail elsewhere.[11] The AE of the phenol ion was determined by detecting the threshold for an ion current at the appropriate mass, *m*/*z* 94, as the energy of the electrons was increased in 0.02 eV steps. The energy scale was calibrated against the IE of H_2O. The apparatus and sample inlet operated at room temperature. The $\Delta_f H°$ of ionized phenol is accurately

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* Corresponding author. e-mail: jholmes@oreo.uottawa.ca.

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TABLE 1: Effect of Methyl Substitution in Ethene, Allene, and Formaldehyde[a]

species	IE	ΔIE	$\Delta_f H°$	$\Delta\Delta_f H°$
CH_2CH_2	10.51		52.2	
CH_3CHCH_2	9.73	−0.78	20.2	−32.0
$(CH_3)_2CCH_2$	9.24	−0.49	−16.9	−37.1
CH_2CCH_2	9.69		190.6	
CH_3CHCCH_2	9.03	−0.66	162.3	−28.3
H_2CO	10.87		−108.7	
CH_3CHO	10.23	−0.64	−165.8	−57.1
$(CH_3)_2CCO$	9.71	−0.52	−217.2	−51.4

[a] All values are from ref 4; IE are in eV and $\Delta_f H°$ in kJ mol^{-1}.

TABLE 2: AE for $C_6H_5OH^{•+}$ and Derived $\Delta_f H°$ for $CH_2{=}C{=}O$, $CH_3CH{=}C{=}O$, and $(CH_3)_2C{=}C{=}O$ (AE in eV and $\Delta_f H°$ in kJ mol^{-1})

precursors	$\Delta_f H°$[esters]	AE[$C_6H_5OH^{•+}$] (±0.05)	$\Delta_f H°$[ketenes] (±5)
$CH_3CO_2C_6H_5$	−279.7[4]	9.83	−54 (−47.7)[a] (−52.2)[b]
$CH_3CH_2CO_2C_6H_5$	−297[12]	9.58	−95 (−105)[c] (−65.1)[b] (−68)[b] (−84)[d] (−97)[e]
$(CH_3)_2CHCO_2C_6H_5$	−331[12]	9.50	−137 (−155)[c] (−92)[b]

[a] Experimental, ref 2. [b] Ab initio calculations, refs 3 and 7. [c] Estimated, ref 5. [d] Estimated, ref 9. [e] From PA[CH_3CHCO], ref 8.

known,[4] and the $\Delta_f H°$ values for the neutral precursor esters can be estimated with confidence using Benson's additivity scheme.[12] Compounds not commercially available were synthesized by standard procedures and purified before use such that phenol was undetectable in the esters by GC/MS. Normal, metastable ion (MI), collision-induced dissociation (CID), and collision-induced dissociative ionization (CIDI) mass spectra were recorded using a modified VG ZAB-2F mass spectrometer.[13]

Results and Discussion

Effect of Methyl Substitution in Analogous Systems. Molecules structurally related to ketene can be used to estimate the effect of methyl substitution on both the IE and $\Delta_f H°$. Such molecules include ethene and allene (where the methyl substitution is at a double bond) and formaldehyde (where the methyl substitution is on carbonyl). Table 1 gives the IE and $\Delta_f H°$ of these species and those for their methyl- and dimethyl-substituted analogues.

The decrease in IE following the first and second methyl substitution in ethene, allene, and formaldehyde is of the order of 0.7 and 0.5 eV, respectively. The differences between Bock's[6] IE for $CH_2{=}C{=}O$ and $CH_3CH{=}C{=}O$ and for $CH_3CH{=}C{=}O$ and $(CH_3)_2C{=}C{=}O$ are −0.69 and −0.59 eV, respectively (Table 1), consistent with the effect in analogous systems and suggesting that the experimental and calculated IE are correct.

For ethene and allene and other species such as propene, benzene, and toluene, methyl substitution lowers $\Delta_f H°$ by 33 ± 5 kJ mol^{-1}, with no significant difference between the π-electron systems. On the other hand, methyl substitution in formaldehyde and other carbonyl-containing compounds (ketones, acids, and esters) has a much larger effect of ca. −54 kJ mol^{-1}. The latter was chosen by Deming and Wulff,[5] e.g., $-48 \rightarrow -102 \rightarrow -156$ kJ mol^{-1}. The theoretically calculated energy changes,[3] $CH_2{=}C{=}O$ to $CH_3CH{=}C{=}O$ and $CH_3CH{=}C{=}O$ to $(CH_3)_2C{=}C{=}O$, of only −16 and −24 kJ mol^{-1}, respectively, appear to be anomalous for methyl substitution.

Mass Spectrometry of Phenyl Esters. Before discussing the present thermochemical results, the mass spectrometry experiments should first be described. The three phenyl esters each show a relatively intense molecular ion in their normal electron impact mass spectra. The metastable ion (MI) mass spectra of the acetate and propanoate contain only *m*/*z* 94, whereas the MI mass spectrum of isobutyrate contains m/z 70, $(CH_3)_2C{=}C{=}O^{•+}$ (100%), and only a very weak *m*/*z* 94 peak (1%). The kinetic energy releases calculated from the half-height widths of these Gaussian fragment ion peaks in the MI mass spectra, were 7, 9, 10, and 18 meV, respectively. The kinetic energy releases associated with these four processes are all small, and so corrections for kinetic shift can confidently be disregarded.[10] Finally, the collision-induced dissociation (CID) mass spectra of the *m*/*z* 94 ions, $C_6H_6O^{•+}$, produced in the dissociation of the esters were identical with that of ionized phenol,[14] thus leaving no doubt as to the fragment ions' structure. It should be noted that phenyl esters which contain *no* H atom α to the CO group generate only very small *m*/*z* 94 ions in their normal mass spectra.[15] The H transferred to the ester oxygen in the present experiments thus is taken to originate from the α position.

$\Delta_f H°$ of $CH_2{=}C{=}O$, $CH_3CH{=}C{=}O$, and $(CH_3)_2C{=}C{=}O$. Table 2 shows the results of the AE measurements, together with the derived $\Delta_f H°$ values for the ketenes, using the well-established $\Delta_f H°$ [$C_6H_5OH^{•+}$] of 722 kJ mol^{-1}.[4]

There is very good agreement between our value for $\Delta_f H°$[$CH_2{=}C{=}O$] and the previous experimentally[2] determined $\Delta_f H°$. The new experimental values for $\Delta_f H°$[$CH_3CH{=}C{=}O$] and $\Delta_f H°$[$(CH_3)_2C{=}C{=}O$], however, do not agree with Radom's[3] calculated values and are somewhat more positive than the estimated values.[5] The difference between the experimental and estimated $\Delta_f H°$ is even greater for the $\Delta_f H°$[$(CH_3)_2C{=}C{=}O$], suggesting that the carbonyl additivity term selected by Deming and Wulff,[5] for methyl substitution at carbonyl, is too large. From our experimental results, the additivity term reflecting the effect of methyl substitution on the ketene function is ca. −40 kJ mol^{-1} per methyl group as opposed to −16 and −24 kJ mol^{-1} for the first and second substitution predicted by the calculations[3] and −50 kJ mol^{-1} chosen by Deming and Wulff.[5] Consequently, according to our results, methyl substitution in ketene is more stabilizing than in carbon−carbon π-systems but less stabilizing than on carbonyl groups. It is possible that the AE values for precursor molecules of this size may be subject to appreciable kinetic shift effects. That this is unlikely is shown by the result for ketene itself, where all the experiments and theory are in excellent agreement. Kinetic shifts would necessarily lead to higher (i.e., more positive) *apparent* $\Delta_f H°$ values for the ketenes, and thus this effect would only *increase* the discrepancy between theory and experiment. The likelihood that the neutral species accompanying the phenol ion are isomers of methyl- and dimethylketene can be disregarded on mass spectrometric grounds. The CIDI mass spectrum of phenyl propanoate is markedly different from the CID of acrolein (the only other C_3H_4O species having a negative $\Delta_f H°$); the former shows major peaks at *m*/*z* 41 and *m*/*z* 28, no *m*/*z* 29, while the latter has an intense *m*/*z* 29 and only a weak *m*/*z* 41. Three C_4H_6O isomers have negative $\Delta_f H°$. However, the CID (and normal) mass spectra of methyl vinyl ketone, but-2-en-al, and 2-methylpropenal contain major peaks absent in the mass spectra (normal, CID, and CIDI) of the $(CH_3)_2C{=}C{=}O$. The ketone's spectra are dominated by *m*/*z* 55, and the aldehydes display *m*/*z* 29. The ketene has no *m*/*z* 29 and a weak *m*/*z* 55, and the spectra contain an intense *m*/*z* 42 ion, which, as shown elsewhere,[16] is ionized dimethylcarbene.

TABLE 3: AE and Derived $\Delta_f H°$ for $CH_3CH{=}C{=}O^{•+}$ and $(CH_3)_2C{=}C{=}O^{•+}$ (AE in eV and $\Delta_f H°$ in kJ mol^{-1})

precursors	$\Delta_f H°$[precursors][12]	AE (±0.05)	$\Delta_f H°$[ketenes$^{•+}$] (±5)
$CH_3CH_2COCH_2OH$	−389	9.88	765 (771)[a] (796.1)[b] (778.4)[c]
$CH_3CH_2CO_2C_6H_5$	−297	≤10.36[a]	≤798
$(CH_3)_2CHCO_2C_6H_5$	−331	9.52	683 (685)[a] (725.6)[b] (684.6)[d]

[a] Calculated from IE and $\Delta_f H°[CH_3CHCO]$ and $[(CH_3)_2CCO]$, ref 4. [b] Ab initio caculation, refs 3 and 7. [c] Experimental, ref 21. [d] Estimated, using effect of methyl substitution in CH_3CHCO, ref 22. [e] Not a metastable process.

The IE of $CH_2{=}C{=}O$, $CH_3CH{=}C{=}O$, and $(CH_3)_2C{=}C{=}O$, 9.58, 8.92, and 8.43 eV, respectively, calculated by Scott and Radom[3] are all in excellent agreement with those published by Bock.[6] However, the calculated $\Delta_f H°$ of the two methyl-substituted ketenes are far from the experimentally determined values. Although the authors acknowledge the unusual effect of methyl substitution in ketene predicted from their calculations, no physicochemical explanations are provided to rationalize this result. However, the authors[3] do note that for both methylketene and dimethylketene the calculated C=C bond lengths are somewhat longer than the experimental values and that the calculated $C{-}C_d$ bond lengths are somewhat shorter than the experimental values. It is only in these two cases that significant discrepancies between the calculated and experimental $\Delta_f H°$ values are observed. For ketene, the calculated geometry is in very good agreement with the experimental geometry, and the close fit of all the $\Delta_f H°$ values suggests that, in the case of methylketene and dimethylketene, the calculated geometries may be the source of the discrepancies. It has been shown for sulfine,[17] $CH_2{=}S{=}O$, that when the geometry optimization did not accurately reproduce the experimental structure, significant discrepancies where observed between the calculated and experimental $\Delta_f H°$.

$\Delta_f H°$ of $CH_3CH{=}C{=}O^{•+}$ and $(CH_3)_2C{=}C{=}O^{•+}$. From the available thermochemical data, i.e., Bock's IE[6] and the experimentally determined neutral $\Delta_f H°$, it is possible to calculate the $\Delta_f H°$ of the corresponding ionized ketenes using the following equation:

$$\Delta_f H°[\text{ketene}^{•+}] = \text{IE}[\text{ketene}] + \Delta_f H°[\text{ketene}] \tag{3}$$

Note that the $\Delta_f H°$ of the ionized ketenes may also be obtained independently from an AE measurement. In order for the determined thermochemical quantities to be consistent, the $\Delta_f H°$ obtained via these two independent routes *must be* equal; i.e., $\Delta_f H°$ values for the ketene ions derived from IE and AE measurements must be the same. Table 3 shows the results of the AE measurements together with the derived $\Delta_f H°$ values for the ionized ketenes, using the well-established $\Delta_f H°[C_6H_5OH]$ and $\Delta_f H°[CH_3OH]$ of −96.3[4] and −201.6 kJ mol^{-1},[4] respectively. The $\Delta_f H°[CH_3CH{=}C{=}O^{•+}]$ derived from the AE of this ion generated from the corresponding phenyl ester can only be taken as an upper limit since the process is not the fragmentation of lowest energy requirement, and so the contribution of a competitive shift cannot be ignored. If Bock's[6] IE values are combined with our $\Delta_f H°$ values for the neutral ketenes, the expected values for $\Delta_f H°[CH_3CH{=}C{=}O^{•+}]$ and $\Delta_f H°[(CH_3)_2C{=}C{=}O^{•+}]$ are 771 and 685 kJ mol^{-1}, respectively. These predicted values are in excellent agreement with the *independently* measured experimental values (765 and 683 kJ mol^{-1}) and demonstrate that the present results are *self-consistent*.

TABLE 4: Sum of the $\Delta_f H°$ of $(CH_3)_2C{=}C{=}O^{•+}$ and $(CH_3)_2C{=}C{=}O$ ($\Delta_f H°$ and $\sum\Delta_f H°$ in kJ mol^{-1})

source	$\Delta_f H°[(CH_3)_2C{=}C{=}O]$	$\Delta_f H°[(CH_3)_2C{=}C{=}O^{•+}]$	$\sum\Delta_f H°$
experimental (this work)	−137	683	546
AE *m*/*z* 70 from TMCBD			≤608 (600)[18]
calculations[3]	−95	725.6	631

Dissociation of 2,2,4,4-Tetramethyl-1,3-cyclobutanedione. To further support our experimental data, another precursor molecule, namely 2,2,4,4-tetramethyl-1,3-cyclobutanedione (TMCBD), was used to obtain the sum of the $\Delta_f H°$ of $(CH_3)_2C{=}C{=}O$ and $(CH_3)_2C{=}C{=}O^{•+}$. Following electron impact, TMCBD, a dimer of dimethylketene, undergoes a retro-Diels−Alder type reaction to produce ionized and neutral $(CH_3)_2C{=}C{=}O$. From the AE for $(CH_3)_2C{=}C{=}O^{•+}$ the value of the sum of the products $\Delta_f H°$ may be calculated from

$$\text{AE}[(CH_3)_2C{=}C{=}O^{•+}] + \Delta_f H°[\text{TMCBD}] = \Delta_f H°[(CH_3)_2C{=}C{=}O^{•+}] + \Delta_f H°[(CH_3)_2C{=}C{=}O] \tag{4}$$

This quantity can then be compared to the values obtained by our measurements and by Radom's calculations. The $\text{AE}[(CH_3)_2C{=}C{=}O^{•+}]$ was measured to be 9.5 ± 0.1 eV, in excellent agreement with the value measured independently, using photoionization mass spectrometry, by Traeger ($\text{AE}[(CH_3)_2C{=}C{=}O^{•+}] = 9.41$ eV[18]).

However, the MI mass spectrum of ionized TMCBD *does not* contain *m*/*z* 70, $(CH_3)_2C{=}C{=}O^{•+}$, but *m*/*z* 84 ($C_6H_{12}^{•+}$), indicating that the process leading to the production of ionized and neutral $(CH_3)_2C{=}C{=}O$ is not the lowest energy dissociation channel. Consequently, the measured AE will set an *upper limit* to the sum of the products $\Delta_f H°$. The CID mass spectrum of the ion at *m*/*z* 70 was characteristic of $(CH_3)_2C{=}C{=}O^{•+}$ and so was the collision-induced dissociative ionization (CIDI) mass spectrum of the neutral cogenerated, thus leaving no doubt as to the ion and neutral structures. The AE of the metastable peak for the loss of two CO (*m*/*z* 84) from ionized TMCBD was measured by a comparative method[19] as was the IE of the molecule. These were 9.4 and 9.3 ± 0.1 eV, respectively. The absence of *m*/*z* 70 in the MI mass spectrum very likely results from a facile ring opening of the molecular ion to give a distonic ion having a significantly lower $\Delta_f H°$. It is this species which produces the metastable ion characteristics (production of *m*/*z* 84) described above. If ring opening is facile, the AE for *m*/*z* 70 may even be limited by the IE of TMCBD, reducing the $\Delta_f H°$ sum by a further ca. 20 kJ mol^{-1}. The sum of the products $\Delta_f H°$ obtained from the AE measurement (using $\Delta_f H°[\text{TMCBD}] = -308$ kJ mol^{-1} [4]) as well as from the study of the phenyl isobutyrate and the calculations[3] are presented in Table 4. The sum of the products $\Delta_f H°$ obtained from this measurement, which must be taken as an upper limit, is higher than the value from our experimental data but lower than the calculated data.[3] This clearly indicates that the calculated $\Delta_f H°[(CH_3)_2C{=}C{=}O]$ is too positive, thus increasing the sum of the products $\Delta_f H°$.

Vinyl Substitution in Ketene. The $\Delta_f H°$ for $CH_2{=}CH{-}CH{=}C{=}O$ has been measured from the $\Delta_f H°$ for the radical cation, 812 ± 4 kJ mol^{-1}, and IE for vinyl ketene, 8.32 ± 0.05 eV,[20] $\Delta_f H°[CH_2{=}CHCH{=}C{=}O] = 9 \pm 4$ kJ mol^{-1}. In terms of vinyl substitution, the experimental $\Delta\Delta_f H°$ from ketene is +60 ± 3 kJ mol^{-1}. This change in $\Delta_f H°$ lies closer to the effect of vinyl substitution at olefin ($\Delta\Delta_f H° = 60 \pm 2$ kJ mol^{-1})[1] than at carbonyl ($\Delta\Delta_f H° = +41$ kJ mol^{-1}).[1] Thus, this substituted ketene is not atypical in its $\Delta_f H°$ value, a result which lends further support for the experimentally derived values for the methyl-substituted ketenes.

Conclusions

The $\Delta_f H°$ of $CH_2{=}C{=}O$, $CH_3CH{=}C{=}O$, and $(CH_3)_2C{=}C{=}O$ have been determined to be −54, −95, and −137 kJ mol^{-1}, respectively. From these measurements, it has been demonstrated that methyl substitution in ketene decreases the $\Delta_f H°$ of the methyl-substituted species by ca. 40 kJ mol^{-1}, which is in keeping with the effect of methyl substitution in structurally related systems. In addition, the $\Delta_f H°$ of $CH_3CH{=}C{=}O^{\bullet +}$ and $(CH_3)_2C{=}C{=}O^{\bullet +}$ have been determined to be 765 and 683 kJ mol^{-1}, respectively, with an estimated error of ±5 kJ mol^{-1}. These values are in excellent agreement with the values calculated using the $\Delta_f H°$ of the neutrals and their corresponding IE. In view of these observations, it is suggested that there may exist a computational problem associated with the geometry optimization for the methyl-substituted ketenes which in turn leads to erroneous values of $\Delta_f H°$. However, alternative experimental sources for these ions and neutrals are being actively sought.

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