# G2 Theory and Experiment in Concert: Enthalpy of Formation of $CH_3O{-}C{=}O^+$ and Its Isomers Revisited[†]

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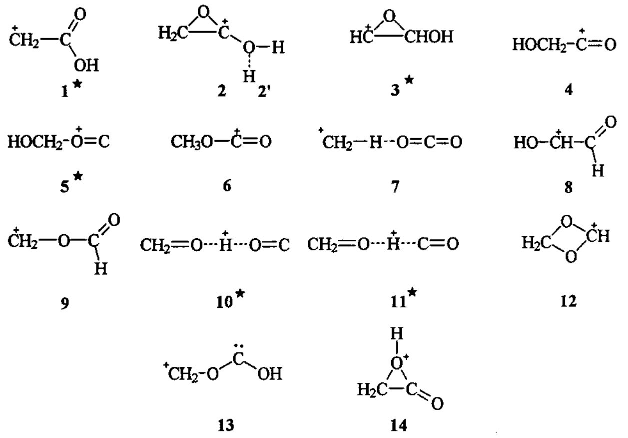
Ab initio molecular orbital calculations at the Gaussian-2 level of theory on a set of isodesmic, atomization, and substitution type reactions have been used to deduce the enthalpy of formation of the methoxycarbonyl ion as $\Delta H_f^{298}[CH_3O{-}C{=}O^+] = 130 \pm 2$ kcal/mol. From the G2 computed ionization energy ($IE_a = 7.32$ eV) and $\Delta H_f^{298}$ ($-40$ kcal/mol) of the parent radical $CH_3O{-}C^{\bullet}{=}O$, we arrive at 129 kcal/mol for its ionic counterpart. Combining these theoretical findings with a reevaluation of existing experimental data (appearance energy measurements) yields $129 \pm 2$ kcal/mol as our recommended value for $\Delta H_f^{298}[CH_3O{-}C{=}O^+]$, a large upward revision of the current literature value of 120 kcal/mol. By use of the new value as the anchor point, G2 derived $\Delta H_f^{298}$ values for the isomers $H_2C{-}O{-}C(H)OH^+$, $HOCH_2{-}C{=}O^+$, $^+CH_2{-}H{\cdots}O{=}C{=}O$, $^+CH(OH)\text{-}C({=}O)H$, $^+CH_2{-}O{-}C({=}O)H$, $CH_2{-}O{-}C(H){-}O^+$, and $^+CH_2O{-}\ddot{C}{-}OH$ have been calculated as 147, 131, 157, 144, 144, 140, and 177 kcal/mol, respectively.

## Introduction

The field of gas-phase ion chemistry has sparked the interest of physical chemists for a great many years. The determination of thermochemical quantities (such as enthalpy of formation $\Delta H_f$) of isomeric ions has been performed almost since the inception of computational chemistry. Computational thermochemistry has now reached a point where composite theoretical methods such as G2 and CBS-Q can often reproduce $\Delta H_f$ of systems containing up to 10 heavy atoms to chemical accuracy, ±1−2 kcal/mol.[1] The structural assignment of gas-phase ions via mass spectrometric experiments also has a long history, and its development has been greatly aided by the availability of such thermochemical information.[2] Indeed, this interplay between theory and experiment has had so much success that this partnership is becoming the norm. This paper uses this powerful combination with the emphasis on the computational aspects in a study of the methoxycarbonyl ion, (*m*/*z* 59) $CH_3OC{=}O^+$. This key fragment ion in the mass spectra of many methyl esters is of current interest because of its methyl cation donor ability and its role in aromatic substitution reactions in the gas phase.[3]

More than 10 years ago, the structure and stability of the $CH_3OC{=}O^+$ ion, $\mathbf{6}^+$, and 11 of its isomers (see structures **1**−**11** in Scheme 1) were investigated with the fruitful combination of (tandem) mass spectrometry and ab initio MO calculations.[4] (Ions marked with an asterisk were computationally considered in ref 4 but not in this study.) The relative energies of the various isomers were calculated using a coupled electron pair approximation procedure (CEPA/6-31G*//6-31G*), which yielded $\Delta H_f^{298}[\mathbf{6}^+] = 120 \pm 1$ kcal/mol using the experimentally determined $\Delta H_f$ of the isomeric hydroxyoxiranyl cation, $\mathbf{2}^+$, as the anchor point.

**SCHEME 1**



In that study, results of appearance energy (AE) measurements on nine selected precursor molecules were also reported with the aim of obtaining an accurate experimental value for $\Delta H_f$($\mathbf{6}^+$). However, the resulting value, 131 ± 4 kcal/mol, was deemed to be too high because of competitive shifts in the measurements. In support of this, shortly after this work appeared, McMahon and co-workers[5] reported the methyl cation affinity (MCA) of carbon dioxide as 49.5 kcal/mol, and this translates

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[†] This paper is dedicated to the memory of Dr. F. P. Lossing.

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into a low value, 118 ± 3 kcal/mol, for the methoxycarbonyl cation's heat of formation.

However, adopting the 120 kcal/mol value for $\Delta H_f[CH_3OC{=}O^+]$ makes it difficult to understand some aspects of the gas-phase ion chemistry of low-energy (metastable) methyl pyruvate and methyl acetate radical cations. Using simple thermochemical arguments, we would expect the metastable ion (MI) spectrum of ionized methylpyruvate, $CH_3COCOOCH_3^{\bullet+}$, to display signals at both *m/z* 43 and *m/z* 59 for its competing dissociations into $CH_3C{=}O^+$ (*m/z* 43) + $CH_3OC{=}O^\bullet$ and $CH_3OC{=}O^+$ (*m/z* 59) + $CH_3C{=}O^\bullet$ because both sets of products have the same energy ($\sum\Delta H_f^{298}$[products] = 116 and 117 kcal/mol, respectively).[6] A similar situation is obtained for ionized methyl acetate, $CH_3COOCH_3^{\bullet+}$, where dissociation into $CH_3C{=}O^+ + CH_3O^\bullet$ and $CH_3OC{=}O^+ + CH_3^\bullet$ is also calculated to be competitive ($\sum\Delta H_f^{298}$[products] = 160 and 155 kcal/mol, respectively).[6] Nevertheless, an *m/z* 59 signal is absent in either MI spectrum. On the other hand, these observations are readily understood if $\Delta H_f[CH_3OC{=}O^+]$ were several kcal/mol higher, i.e., in line with the results derived from the direct AE measurements mentioned above.

This prompted us to reinvestigate this ion's enthalpy of formation by performing a G2 computational study on the series of reactions depicted in Scheme 2.

SCHEME 2

$$CH_3OC{=}O^+ \rightarrow C^+ + C + 2O + 3H \quad (1)$$

$$CH_3OC{=}O^+ \rightarrow CH_3C{=}O^+ + O \quad (2)$$

$$CH_3OC{=}O^+ \rightarrow CH_3^+ + CO_2 \quad (3)$$

$$CH_3OC{=}O^+ + CO \rightarrow CH_3C{=}O^+ + CO_2 \quad (4)$$

$$CH_3OC{=}O^+ + H_2O \rightarrow CH_3OH_2^+ + CO_2 \quad (5)$$

$$CH_3OC{=}O^+ + HCOOH \rightarrow HOC{=}O^+ + CH_3OCH{=}O \quad (6)$$

$$CH_3OC{=}O^+ + CH_3OH \rightarrow CH_2OH^+ + CH_3OCH{=}O \quad (7)$$

$$CH_3OC{=}O^+ + CH_3CH{=}O \rightarrow CH_3C{=}O^+ + CH_3OCH{=}O \quad (8)$$

$$CH_3OC{=}O^+ + CH_2{=}O \rightarrow HOC{=}O^+ + CH_3CH{=}O \quad (9)$$

$$CH_3OC{=}O^+ + N_2 \rightarrow CH_3N_2^+ + CO_2 \quad (10)$$

Currently many schemes are used to derive heat of formation values for ions and neutrals from ab initio calculations.[7] Most popular and accurate are (i) the atomization procedure, where the ab initio atomization energy of the species is related to the experimental heats of formation of the constituent atoms, and (ii) the use of isodesmic substitution reactions, which combines the species of unknown $\Delta H_f$ with components of well-established $\Delta H_f$ (typically at 298 K). The reaction energy is theoretically determined, and the sought-after $\Delta H_f$ calculated.

In this study, we have used these procedures (see reactions 1 and 6−8 in Scheme 2) to determine the heat of formation of the methoxycarbonyl ion. The isodesmic reactions 6−8 involving the ion were designed along the lines of the bond separation scheme developed by Curtiss et al. for neutral species.[7] In addition, we have examined selected dissociation and non-isodesmic substitution reactions (reactions 2−5, 9, and 10) for which reliable experimental heat of formation data are available.

We have also used the G2 methodology to obtain an expectedly more reliable energy for the $CH_3OC{=}O^+$ ion and its key isomers vis-à-vis the hydroxyoxiranyl cation, **2**$^+$, which was used as the anchor point in the determination of $\Delta H_f(\mathbf{6}^+)$ in the previous CEPA ab initio study.[4]

**TABLE 1: $\Delta H_f^0$ [$CH_3OC{=}O^+$] Values (kcal/mol) Calculated by the G2 Method on the Basis of Reactions 1−10 in Scheme 2**

| reaction | G2 (0 K) expt[a] | G2 (0 K) theory[b] |
|---|---|---|
| 1 | 132.2 | 132.2 |
| 2 | 131.3 | 132.2 |
| 3 | 133.9 | 132.2 |
| 4 | 132.1 | 132.2 |
| 5 | 133.3 | 131.3 |
| 6 | 134.5 | 132.2 |
| 7 | 133.9 | 130.5 |
| 8 | 133.5 | 132.2 |
| 9 | 132.0 | 132.2 |
| 10 | 129.3 | 131.7 |
| average | 132.6 ± 1.6 | 131.9 ± 0.6 |

[a] Using the G2 $\Delta H_{reaction}$ and experimental $\Delta H_f^0$. [b] Using the G2 $\Delta H_{reaction}$ and theoretical $\Delta H_f^0$.

Finally, the previously reported appearance energy (AE) data on the methoxycarbonyl cation were combined, where appropriate, with recently revised $\Delta H_f$ values for the neutral species. The resulting experimental $\Delta H_f(\mathbf{6}^+)$ was compared with the theoretical findings and the number obtained from the reevaluated methyl cation affinity of $CO_2$.

## Theoretical Method

Standard ab initio MO calculations were performed with the Gaussian 94 series of programs.[8] The G2 method approximates an energy at the QCISD(T)/6-311+G(3df,2p) level of theory based on MP2/6-31G(d) optimized geometries, incorporating scaled HF/6-31G(d) zero-point energies and an empirical higher level correction.[1] The G2 method was performed on all ions and molecules shown in Schemes 1 and 2, and the results of these calculations are summarized in Tables 1 and 2. Table 1 presents the G2 calculated $\Delta H_f$ for the $CH_3OC{=}O^+$ ion, **6**$^+$, based on reactions 1−10, whereas Table 2 gives the calculated (G2/atomization method) and experimental enthalpies of formation for the ionic and neutral components of reactions 1−10. For most of the species examined in this study the available experimental enthalpy of formation refers to 298 K. These values were converted to 0 K using a correction term $\Delta H_T$ in Table 2, based on standard thermodynamic formulas and scaled vibrational frequencies.[1]

Table 3 presents $\Delta H_f(\mathbf{6}^+)$ values derived from experiment (appearance energy measurements) and will be discussed in section 2 of "Results and Discussion". The relative energies, G2 total energies, and derived $\Delta H_f$ values of selected $C_2H_3O_2^+$ isomers are presented in Table 4. Figure 1 presents the optimized geometries of the methoxycarbonyl cation and the various isomers. When not explicitly referenced, the experimental $\Delta H_f$ values have been taken from ref 6.

Apart from atomization and isodesmic reactions, Scheme 2 also lists some other reactions. These had to be chosen carefully to avoid significant systematic errors: for instance, if the reaction $CH_3^+ + CO \rightarrow CH_3C{=}O^+$ were chosen to calculate $\Delta H_f[CH_3C{=}O^+]$, then from $\Delta H_{rxn}$(G2,0K) = 74 kcal/mol, $\Delta H_f^0$ [CO] = −27 kcal/mol, and $\Delta H_f^0$ [$CH_3^+$] = 262 kcal/mol, one obtains $\Delta H_f^0[CH_3C{=}O^+]$ = 161 kcal/mol. This value compares poorly with the expected 157 kcal/mol derived from the well-established experimental $\Delta H_f^{298}$ value and the $\Delta H_T$ correction mentioned above (see Table 2). Such errors stem from differences between the G2 calculated and experimental $\Delta H_f$ values of the various components of a given reaction. For the

**TABLE 2: G2 Calculated and Experimental Enthalpies of Formation (kcal/mol) for the Species in Scheme 2**

| species | $\Delta H_f^0$ G2 | $\Delta H_f^{298}$ G2 | $\Delta H_f^0$ expt[d] | $\Delta H_f^{298}$ expt | $\Delta H_T$[a] calculate | $\Delta H_T$[b] expt | $\Delta 298$[c] G2 expt |
|---|---|---|---|---|---|---|---|
| $CO_2$ | −96.67 | −96.80 | −93.96 | −94.05 | −0.16 | −0.09 | 2.8 |
| $H_2O$ | −57.39 | −58.10 | −57.10 | −57.80 | −0.72 | −0.7 | 0.3 |
| HCOOH | −90.78 | −92.50 | −88.8 | −90.5 | −1.73 | | 2.0 |
| $CH_3OC(H){=}O$ | −85.68 | −88.67 | −82.0 | −85.0 | −3.01 | | 3.7 |
| $CH_3OH$ | −46.79 | −49.46 | −45.6 | −48.2 | −2.68 | −2.6 | 1.3 |
| $CH_3C(H){=}O$ | −38.49 | −41.09 | −37.0 | −39.6 | −2.62 | −2.6 | 1.5 |
| CO | −29.04 | −28.60 | −27.20 | −26.42 | 0.42 | 0.78 | 2.2 |
| $CH_2{=}O$ | −27.06 | −28.31 | −25.0 | −26.0 | −1.25 | −1.0 | 2.3 |
| $CH_3CO^+$ | 159.92 | 158.74 | 157 | 156 | −1.18 | | −2.7 |
| $CH_3^+$ | 263.02 | 261.76 | 262.0 | 261.3 | −1.26 | −0.7 | −0.5 |
| $CH_2OH^+$ | 169.62 | 167.50 | 170 | 168 | −2.12 | | 0.5 |
| $HOC{=}O^+$ | 142.60 | 141.96 | 143 | 142 | −0.63 | | −1.0 |
| $CH_3OC{=}O^+$ | 132.20 | 129.79 | | | −2.41 | | |
| $HC{=}O^+$ | 197.74 | 197.38 | 197.7 | 197.3 | −0.36 | | −0.1 |
| $CH_3OH_2^+$ | 141.26 | 138.67 | 139 | 136 | −2.59 | | −2.7 |
| $CH_3N_2^+$ | 222.81 | 223.45 | 218 | 217 | −1.42 | | −4.4 |
| $N_2$ | 1.19 | 1.21 | 0 | 0 | 0.02 | | −1.2 |

[a] From scaled vibrational frequencies. See text. [b] $\Delta H_f^{298}$(expt) − $\Delta H_f^0$(expt). [c] $\Delta 298 = \Delta H_f^{298}$(expt) − $\Delta H_f^{298}$(theory). [d] Experimental values used when available, otherwise derived from $\Delta H_f^{298}$(expt) using $\Delta H_T$ (calc).

**TABLE 3: $\Delta H_f^{298}[CH_3OC{=}O^+]$ Values Derived from Appearance Energy Measurements[a]**

| precursor molecule (M) | $\Delta H_f$(M) kcal/mol | AE m/z 59 (±0.05 eV) | neutral product and $\Delta H_f$ values kcal/mol | | $\Delta H_f(CH_3OCO^+)$ kcal/mol |
|---|---|---|---|---|---|
| $(CH_3O)_2CO$ | −137[b] | 11.50 | $CH_3O^\bullet$ ($CH_2OH^\bullet$) | 4.1 (−4.0[e]) | 124 (132) |
| $BrCH_2COOCH_3$ | −89 | 11.16 | $CH_2Br^\bullet$ | 42.0 | 126 |
| $ClCH_2COOCH_3$ | −99 | 11.10 | $CH_2Cl^\bullet$ | 28.3 | 129 |
| $ClCOOCH_3$ | −104 | 11.24 | $Cl^\bullet$ | 29.0 | 126 |
| $CH_3COOCH_3$ | −98.0 | 11.32 | $CH_3^\bullet$ | 35.0 | 128 |
| cy-$C_3H_5COOCH_3$ | −72.4 | 10.56 | $CH_2CHCH_2^\bullet$ | 40.9 | 130 |
| | | | cy-$CH_2CHCH_2^\bullet$ | 39.5 | 132 |
| $CH_3CH_2COOCH_3$ | −103.8 | 11.42 | $CH_3CH_2^\bullet$ | 29.4 | 130 |
| $HOCH_2COOCH_3$ | −133 | 11.38 | $CH_2OH^\bullet$ | −4.0[e] | 133 |
| $FCH_2COOCH_3$ | −139[c] | 11.16[d] | $FCH_2^\bullet$ | −8[f] | 126 |

[a] Unless indicated otherwise, data are obtained from ref 4. [b] Reference 9. [c] Estimate, based on G2 $\Delta H_f^{298}[FCH_2COOH] = -144$ kcal/mol, adding 5.3 kcal/mol for $CH_3$ substitution (methyl substitution effect based on $\Delta H_f[CH_3COOCH_3] - \Delta H_f[CH_3COOH] = 5.3$ kcal/mol[6a]). [d] Reference 10. [e] Reference 11. [f] Reference 12.

**TABLE 4: G2 Total Energies (hartrees), Relative Energies $E_{rel}$ (kcal/mol), and $\Delta H_f$ Values for Selected $C_2H_3O_2^+$ Isomers Based on the Recommended $\Delta H_f^{298}[CH_3OC{=}O^+]$ ($6^+$) = 129 kcal/mol**

| ion | G2 (0 K) | G2 (298 K) | $E_{rel}$ (0 K) | $E_{rel}$ (298 K) | $E_{rel}$ (CEPA)[a] | $\Delta H_f^0$ [b] | $\Delta H_f^{298}$ [b] |
|---|---|---|---|---|---|---|---|
| $\mathbf{2}^+$ | −227.771 41 | −227.767 52 | 18.8 | 18.1 | 20.5 | 150 | 147 |
| $\mathbf{2'}^+$ | −227.769 79 | −227.765 94 | 19.8 | 19.1 | | 151 | 148 |
| $\mathbf{4}^+$ | −227.798 54 | −227.793 91 | 1.7 | 1.6 | 3.6 | 133 | 131 |
| $\mathbf{6}^+$ | −227.801 31 | −227.796 39 | 0.0 | 0.0 | 0.0 | 131 | 129 |
| $\mathbf{7}^+$ | −227.758 59 | −227.751 73 | 26.8 | 28.0 | 27.2 | 158 | 157 |
| $\mathbf{8}^+$ | −227.776 80 | −227.772 63 | 15.4 | 14.9 | 11.3 | 146 | 144 |
| $\mathbf{9}^+$ | −227.777 83 | −227.773 08 | 14.3 | 14.6 | 9.4 | 145 | 144 |
| $\mathbf{12}^+$ | −227.782 24 | −227.778 71 | 12.0 | 11.1 | | 143 | 140 |
| $\mathbf{13}^+$ | −227.724 40 | −227.719 81 | 48.3 | 48.1 | | 179 | 177 |

[a] Reference 4. [b] Recommended values ± 2 kcal/mol; see text.

components of the reactions that we have selected, the differences are listed as $\Delta^{298}$ in the final column of Table 2. To minimize the overall error, we have chosen reactions $CH_3OC{=}O^+ + A \rightarrow B + C$, where A, B, and C are species with established experimental $\Delta H_f$ and where the errors in the G2 calculation of $\Delta H_f$ compensate, i.e., $\Delta A^{298} \cong \Delta B^{298} + \Delta C.^{298}$

## Results and Discussion

**1. $\Delta H_f[CH_3O{-}C{=}O^+]$ Derived from G2 Calculations on the Reactions Depicted in Scheme 2.** In Table 1 we present the results of the G2 calculations of $\Delta H_f(\mathbf{6}^+)$ on reactions 1−10. We have performed two different comparisons with two different sets of independent references. The first set of $\Delta H_f$ reference compounds uses experimental values for all the molecules and carbocations in reactions 1−10; the results of these calculations are presented in the first column of Table 1. The second set of reference values is a "pure G2" set where the independent references are the heats of formation of the atoms only; that is, the enthalpies of formation used are calculated with the G2 atomization method. Hence, these values are more self-consistent and have a lower standard deviation. Combining these results, we obtain $\Delta H_f^{298}(\mathbf{6}^+) = 130 \pm 2$ kcal/mol, which includes a −2.4 kcal/mol temperature correction (see Table 2). Reactions 3 and 10 refer to methyl cation affinities, and this point will be discussed in section 4.

The agreement between the two approaches is satisfactory, but the resulting $\Delta H_f^{298}(\mathbf{6}^+)$ value is 10 kcal/mol higher than the current literature value. However, our reevaluation of the experimental AE data (see section 2) also points to a much higher value, 129 kcal/mol. It is known that the G2 atomization procedure sometimes fails to reproduce $\Delta H_f$ of C=O containing molecules with chemical accuracy.[7] Thus, one may argue that

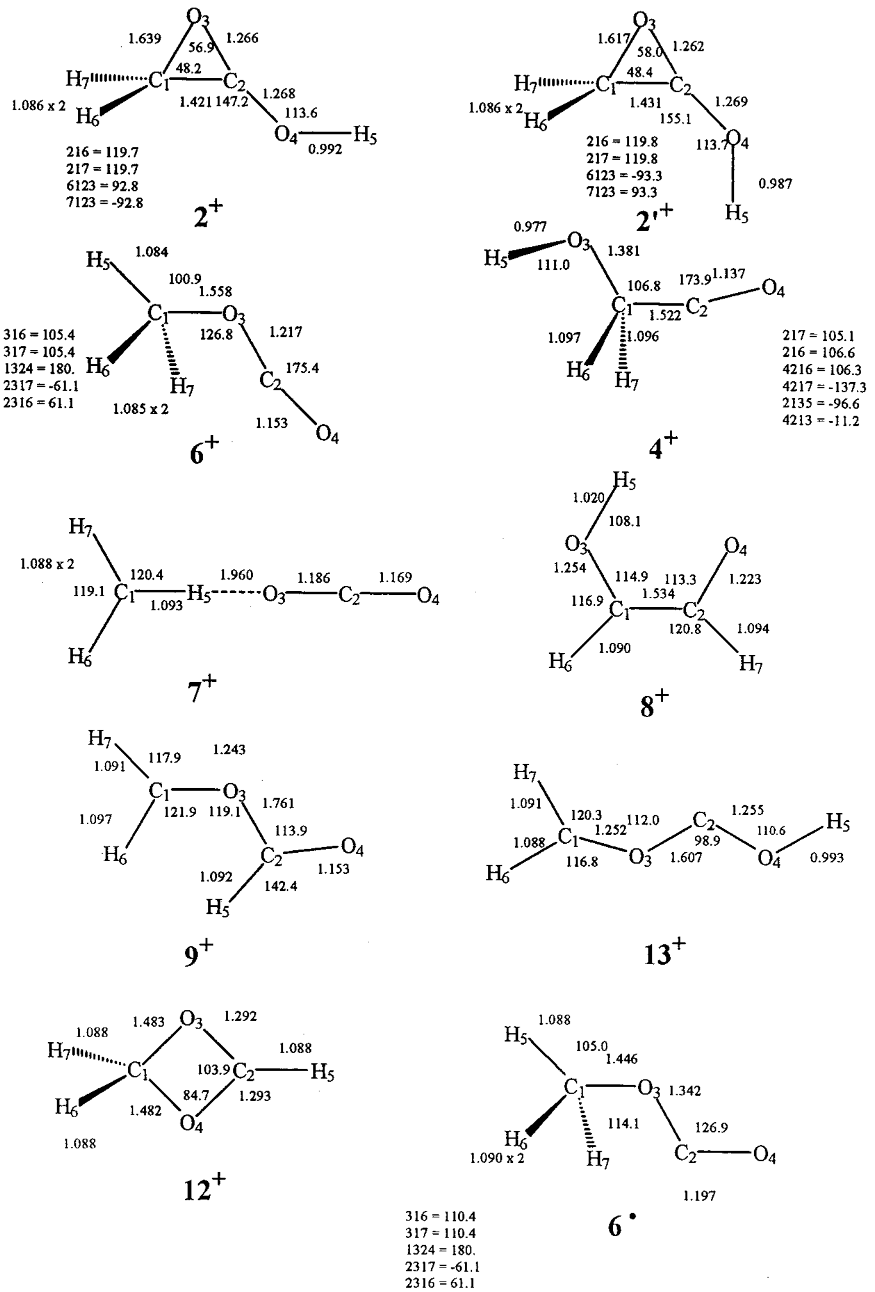

**Figure 1.** MP2(full)/6-31G(d) optimized geometries of selected $C_2H_3O_2^+$ isomers. Bond lengths are in angstroms and bond angles in degrees.

the value derived from reaction **1** could be in error by several kcal/mol. However, the excellent agreement with the numbers derived from the isodesmic substitution reactions (where errors in the description of certain bonds are expected to cancel) and the consistency with the data for the other reactions clearly lend credence to the derived value.

Two further approaches based on theory support the above value. First, we derived $\Delta H_f(\mathbf{6}^+)$ from G2 calculations of the heat of formation and ionization energy of the methoxycarbonyl radical, $\mathbf{6}^\bullet$, whose optimized geometry is presented in Figure 1. The heat of formation was calculated as $\Delta H_f^{298}(\mathbf{6}^\bullet) = -40.1$ kcal/mol using the atomization procedure, in excellent agreement with the experimental value.[6b] The IE obtained from G2 calculations at 0 K is 7.32 eV (169 kcal/mol), and this yields $\Delta H_f^{298}(\mathbf{6}^+) = 129$ kcal/mol.

Second, we calculated the G2 and G2MP2 energy difference between ionized methyl acetate and its direct bond cleavage dissociation products $CH_3OC{=}O^+$ and $CH_3^\bullet$. The result, 25.4 and 24.9 kcal/mol, combined with experimental $\Delta H_f^{298}$ values for the ionized ester (139 kcal/mol[6a]) and the methyl radical (35.0 kcal/mol[6a]), yields $\Delta H_f^{298}(\mathbf{6}^+) = 129$ and 128 kcal/mol, respectively. The resulting value is the same as that derived from the appearance energy measurement tabulated in Table 3, and this indicates that this reaction does not suffer from a competitive shift.

**2. $\Delta H_f[CH_3O-C{=}O^+]$ Derived from Direct AE Measurements**. Table 3 reproduces the previously published[4] AE measurements and combines these with the partially revised thermochemical data on the precursor molecules and neutral reaction products required to derive $\Delta H_f^{298}(\mathbf{6}^+)$. One precursor molecule from the original study, methyl pyruvate, is not listed because the generation of $\mathbf{6}^+$ therefrom is not a simple direct bond cleavage reaction.[4] Instead, we have included an as yet unpublished AE measurement on methyl fluoroacetate as the last entry in the table. The derived enthalpy of formation of ion $\mathbf{6}^+$ for the reactions listed in the table range from 124 to

133 kcal/mol, with an average value of 129 kcal/mol. The average value (and also the range) is smaller than that previously reported. Nevertheless, it is still 9 kcal/mol higher than the preferred value in ref 4 but in excellent agreement with the G2 result proposed above. This agreement indicates that very little, if any, competitive shift is present in the AE measurements. Hence, a value of 129 ± 2 kcal/mol becomes our preferred value for $\Delta H_f[CH_3OC{=}O^+]$.

**3. $\Delta H_f[CH_3O-C{=}O^+]$ Derived from the G2 Calculated Energy Difference with Other Isomers**. Another established procedure to derive an ion's heat of formation involves the calculation of its relative energy vis-à-vis that of an isomeric reference ion whose enthalpy of formation is experimentally well established. This procedure was followed in ref 4, that is, $\Delta H_f^{298}(\mathbf{6}^+)$ was derived from the computed energy difference with the ionic isomer $\mathbf{2}^+$ whose $\Delta H_f^{298}$ was experimentally determined, from an AE measurement on the loss of iodine from iodoacetic acid, as 141 ± 1 kcal/mol. This procedure yielded the 120 kcal/mol value that we now question. The discrepancy with the newly proposed value could a priori originate from an inaccuracy in either (i) the computationally derived energy difference or (ii) the heat of formation of the anchor point, or (iii) the structure assigned to the anchor point ion is incorrect. In this section we address these three questions.

The first question is dealt with in Table 4, which lists the CEPA relative energies from ref 4 and compares these with the G2 results. It appears that the G2 energy difference between ions $\mathbf{6}^+$ and $\mathbf{2}^+$ is somewhat lower than the original CEPA value, but the derived $\Delta H_f^{298}(\mathbf{6}^+) = 123$ kcal/mol still falls short of the recommended value by 6 kcal/mol.

In this context, we verified that ion $\mathbf{2}^+$'s rotamer, $\mathbf{2'}^+$, is a species of higher energy and also that its ring-opened isomer $\mathbf{1}^+$ remained a saddle point on the potential energy surface (see ref 4) when electron correlation was included in the geometry optimizations.

As for the second question, we will first consider an alternative anchor point, viz., the $C_2H_3O_2^+$ ion generated by loss of $CH_3^\bullet$ from ionized ethyl formate, $CH_3CH_2O-C({=}O)H^{\bullet+}$. Ion $\mathbf{9}^+$ in Scheme 1, $^+CH_2O-C({=}O)H$, has been proposed to be the product ion structure. Its appearance energy from the ester, AE = 11.60 ± 0.16 (268 ± 4 kcal/mol), was determined using the sophisticated threshold photoelectron photoion coincidence (TPEPICO) technique.[13] Using $\Delta H_f^{298}[CH_3CH_2O-C({=}O)H] = -93.5$ kcal/mol,[4] we then arrive at $\Delta H_f^{298}(\mathbf{9}^+) = 139 \pm 4$ kcal/mol, not inconsistent with the 144 ± 2 kcal/mol proposed in Table 4. However, when it is postulated that the $CH_3^\bullet$ loss from the ester does not yield ion $\mathbf{9}^+$ (by direct bond cleavage) but rather its ring-closed isomer $\mathbf{12}^+$ (via anchimeric assistance), the agreement becomes much better: $\Delta H_f^{298}(\mathbf{12}^+)$ as proposed in Table 4 is 140 ± 2 kcal/mol. Unfortunately, this proposal cannot be substantiated, since the reported CID spectrum (ref 4) is clearly compatible with either of the proposed ion structures.

As far as the original experimental anchor point is concerned, we note that $\Delta H_f(\mathbf{2}^+) = 141 \pm 1$ kcal/mol is based on AE(*m/z* 59) = 10.86 ± 0.05 eV, $\Delta H_f[I^\bullet] = 25.5$ kcal/mol,[6] and $\Delta H_f[ICH_2COOH] = -84 \pm 1$ kcal/mol.[4] The latter heat of formation may be less certain than originally proposed and could be revised to $-83.2 \pm 2.5$ kcal/mol,[14] but this does not substantially reduce the discrepancy noted above.

The discrepancy would disappear if the ions generated by loss of $I^\bullet$ from $ICH_2COOH^{\bullet+}$ would not have structure $\mathbf{2}^+$ but rather that of an isomeric ion of slightly lower energy, such as ions $\mathbf{8}^+$, $\mathbf{9}^+$, or $\mathbf{12}^+$ in Scheme 1 **(**see Table 4). However, there is little evidence that the original assignment of the ion structure is incorrect. In the previous study, the collision-induced dissociation (CID) mass spectrum of *source*-generated ions was analyzed and, on the basis of the observed dissociation reactions structure $\mathbf{2}^+$, was assigned to the ions. We have repeated this measurement, found an identical spectrum, and agree with this assignment. Nevertheless, it is not inconceivable that the *low-energy* product ions have a different structure (see ref 15 for a classical example involving $CH_3-S^+{=}O$ vs $CH_2{=}S{=}OH^+$). Since it is these low-energy species that are sampled in the AE experiment, we have obtained a CID spectrum of the metastably generated *m/z* 59 ions from $ICH_2COOH^{\bullet+}$. The resulting spectrum (see Figure 2) is essentially the same as that of the source-generated ions (obtained at the same translational energy), and this leaves little doubt that the original assignment was correct.

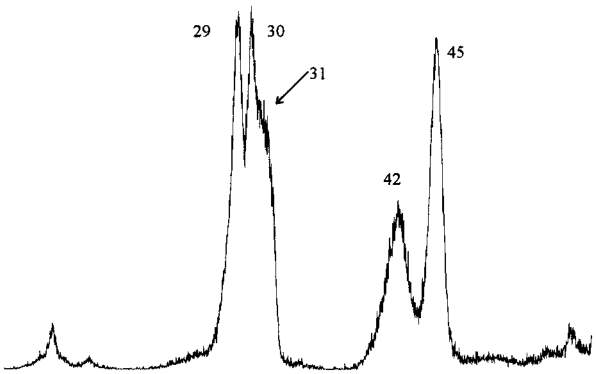

**Figure 2.** CID (3ffr, $O_2$) mass spectrum of the $C_2H_3O_2^+$ ions generated from low-energy (metastable) iodoacetic acid ions.

To reinforce this conclusion, we also verified that the isomeric ions $\mathbf{13}^+$ and $\mathbf{14}^+$ could be eliminated as potential product ions generated in the loss of $I^\bullet$ from $ICH_2COOH^{\bullet+}$. The carbene type ion $\mathbf{13}^+$ represents the C−C ring-opened form of ion $\mathbf{2}^+$, but not unexpectedly, this isomer lies very high in energy at 177 kcal/mol (Table 4). The carbonyl protonated acetolactone ion $\mathbf{14}^+$ plays no role in this dissociation either; upon geometry optimization it collapses to the hydroxyacetylium ion, $\mathbf{4}^+$, whose CID spectrum is entirely different from that assigned to ion $\mathbf{2}^+$.

Thus, combining G2 relative energies with ion $\mathbf{2}^+$ as the anchor point yields $\Delta H_f(\mathbf{6}^+) = 124 \pm 3$ kcal/mol, whereas ion $\mathbf{9}^+/\mathbf{12}^+$ as the anchor point gives $\Delta H_f(\mathbf{6}^+) = 125/129 \pm 4$ kcal/mol. The numbers resulting from this approach are somewhat lower than the recommended value, but their uncertainties are such that consistency is still maintained.

**4. Methyl Cation Affinity of Carbon Dioxide**. Finally, one more important experimental finding remains to be addressed, i.e., the heat of formation of $CH_3OC{=}O^+$ derived from the methyl cation affinity (MCA) of $CO_2$, defined as the negative enthalpy change for the reaction $CH_3^+ + CO_2 \rightarrow CH_3OC{=}O^+$. As stated in the "Introduction", the literature value, 49.5 ± 3 kcal/mol,[5] supports the originally proposed low enthalpy value for ion $\mathbf{6}^+$. In sharp contrast, a much lower value, 38.3 ± 2.0 kcal/mol, follows from our G2 calculations on reaction **3** in Scheme 2 (see Table 1/column 3) using $\Delta H_f^{298}(\mathbf{6}^+) = 129$ kcal/mol in combination with experimental enthalpy data for $CO_2$ and $CH_3^+$. In 1994 the MCA of $N_2$ was reevaluated[16] using high-pressure mass spectrometry based experiments and G2 theory, and this transforms the MCA ($CO_2$) reported in ref 5 to 46.2 and 44.7 kcal/mol, respectively.[17] From these values one derives $\Delta H_f^{298}(\mathbf{6}^+) = 121-123$ kcal/mol, some 7 kcal/mol below our recommended value. Considering the evidence presented in sections 1−3, we feel that a reexamination of the experimentally determined MCA of $CO_2$ would appear appropriate.

## Concluding Remarks

Evidence has been presented that the enthalpy of formation of the methoxycarbonyl cation, **6**$^+$, and some of its key isomers should be revised. The revision is based on (i) a G2 study of a series of different reactions producing $\Delta H_f^{298}(\mathbf{6}^+) = 130 \pm 2$ kcal/mol, (ii) the AE of $CH_3OC{=}O^+$ from 10 different precursor molecules, yielding an average value of 129 kcal/mol, and (iii) G2 calculated energy differences with two isomeric ions used as the anchor point. We recommend $\Delta H_f^{298}[CH_3OC{=}O^+] = 129 \pm 2$ kcal/mol. By use of this value as the anchor point, G2 derived $\Delta H_f^{298}$ values for the isomers $H_2\overline{C{-}O{-}C}(H)OH^+$ (**2**$^+$), $HOCH_2{-}C{=}O^+$ (**4**$^+$), $^+CH_2{-}H{\cdots}O{=}C{=}O$ (**7**$^+$), $^+CH(OH){-}C({=}O)H$ (**8**$^+$), $^+CH_2{-}O{-}C({=}O)H$ (**9**$^+$), $\overline{CH_2{-}O{-}C(H){-}O}^+$ (**12**$^+$), and $^+CH_2O{-}\ddot{C}{-}OH$ (**13**$^+$) have been calculated as 147, 131, 157, 144, 144, 140, and 177 kcal/mol, respectively.

The revised heat of formation of the methoxycarbonyl cation also provides a rationale for the absence of these ions in the MI spectra of ionized methyl pyruvate and methyl acetate.

Finally, we note that our revised $CH_3{-}O{-}C^+{=}O$ enthalpy value leads to a 13 kcal/mol stabilization brought about by methyl substitution in $H{-}O{-}C^+{=}O$ ($\Delta H_f^{298} = 142$ kcal/mol[18]). This stabilization energy is virtually identical with that established by the late Dr. Lossing[19] for the analogous substitution on the noncharge-bearing O atom in $H{-}O{-}CH_2^+$.

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