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Methylcarbyne Radical [$CH_3C(\tilde{X}^2A''; \tilde{a}^4A_2)$] and the Chemiionization Reaction: $CH_3C + O \rightarrow CH_3CO^+ + e^-$

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The heat of formation of the methylcarbyne radical (CH_3C) is calculated using various ab initio approaches. The most accurate value, at the CCSD(T)/6-311G(3df,3pd)//MP2/6-311G(3df,3pd) level of theory, is derived as $\Delta H_f^{298}[CH_3C(\tilde{X}^2A'')] = 122 \pm 1$ kcal mol^{-1}; in addition $\Delta H_f^{298}[CH_3C(\tilde{a}^4A_2)]$ is calculated as 152 ± 2 kcal mol^{-1}. The $\tilde{a}^4A_2-\tilde{X}^2A''$ excitation energy is derived as 1.3 ± 0.1 eV [29 ± 2 kcal mol^{-1}]. For both electronic states, the equilibrium geometry and harmonic vibrational frequencies are calculated. The use of the Gaussian-2 (G2) theoretical model to calculate the maximum electron kinetic energy from chemiionization reactions is explored. In particular, the $CH_3C + O \rightarrow CH_3CO^+ + e^-$ and $CH + O \rightarrow HCO^+ + e^-$ chemiionization reactions at 298 K are considered for the doublet and quartet states of the hydrocarbon radical. These calculations lead to a maximum electron kinetic energy of 1.04 and 2.46 eV for the former reaction, and 0.22 and 1.05 eV for the latter reaction, where the first number in each case refers to the ground doublet state of the reacting radical and the second refers to the lowest quartet. It is concluded that the G2 method is adequate for determining the thermodynamics of chemiionization reactions involving species in their ground electronic states; however, a higher level of theory is required for excited states.

I. Introduction

The methylcarbyne (ethylidyne) radical, CH_3C, is a fundamental organic radical, in the same family as the ubiquitous CH radical, yet very little information is known about it. In particular, the heat of formation is not well established. Vinckier et al. have estimated[1] the heat of formation as 130 kcal mol^{-1} from ΔH_f^{298}(CH) and group additivity rules; on the other hand, in a paper by Dyke et al.,[2] $\Delta H_f^{298}(CH_3C)$ was estimated as (119.5 ± 1.5) kcal mol^{-1}, by using the heat of formation of the vinyl radical,[3] together with the theoretically derived vinyl−CH_3C isomerization energy,[4] on the doublet surface. Clearly, therefore, there is a need for a reliable determination of $\Delta H_f^{298}(CH_3C)$.

CH_3C has been implicated in chemiionization reactions by Hou and Bayes,[5] who observed CH_3CO^+ ions after reaction of the photolysis products of 1,1,1-tribromoethane at 193 nm with O atoms. They inferred the presence of the CH_3C radical, formed directly from the photolysis. Dyke et al.[2] also observed CH_3CO^+ ions in an effusive crossed-beam reaction, where 2-butyne (dimethylacetylene) reacted with O atoms; a similar observation had been reported by Vinckier et al.,[1] previously. All three of these papers concluded that the CH_3CO^+ ions were being formed from the following chemiionization reaction:

$$CH_3C + O \rightarrow CH_3CO^+ + e^- \qquad (1)$$

In ref 2, the energy distribution of the electrons formed in the chemiionization reaction (a chemielectron spectrum) was measured, and when combined with known or estimated enthalpies of formation of CH_3C, O and CH_3CO^+, it was concluded that the $\tilde{a}^4A_2$ state of CH_3C was also present in the O/2-butyne reaction mixture. Hou and Bayes[5] also concluded that the quartet state of CH_3C was present, on the basis of ab initio calculations by Nielsen et al.[4] and the observed kinetic behavior.

It should be noted that reaction 1 is the analogue of the well-known chemiionization reaction that is thought to be responsible for the nascent ions in hydrocarbon oxidation:[6]

$$CH + O \rightarrow HCO^+ + e^- \qquad (2)$$

In low-pressure systems, the $X^2\Pi$ and $a^4\Sigma^-$ states of CH have been shown to be involved.[7] This reaction is thought to occur in flames with these and higher electronic states of CH.[8] The energy release in this reaction was also studied in the present work because some of the features in the chemielectron spectra recorded from an effusive crossed-beam reaction between O and C_2H_2 were assigned[9] as arising from reaction 2, with both the $X^2\Pi$ and the $a^4\Sigma^-$ states of CH reacting.

One problem that arises in calculating the maximum energy of the chemielectrons emerging from chemiionization reactions such as reactions 1 and 2 is that the energies of the species on both sides of the equation are needed. In chemielectron spectroscopy, one important parameter is the high kinetic energy onset, HKEO (the highest kinetic energy of electrons), since this gives a measure of the maximum energy available from the reaction. In some ways it is analogous to the adiabatic

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ionization energy (AIE) in photoelectron spectroscopy. (Note that the AIE may not always be observed in an experiment, owing to poor Franck−Condon factors; in a similar way, the HKEO may not correspond to the maximum excess energy from a chemiionization reaction.) It will be argued below that enthalpy should also not be used to calculate the energy release in a chemiionization reaction; what should be used is the internal energy *U* (more discussion on this is presented below). The internal energy *U* is not something that is usually available (although the difference between ΔU and ΔH is quite small at reasonable temperatures for $A + B \rightarrow AB^+ + e^-$; specifically, at 298 K, since $\Delta n = -1$, the difference between ΔU and ΔH is ∼0.6 kcal mol^{-1}). Taking into account these considerations, it would be useful to be able to calculate directly the internal energy change using ab initio techniques, since then one is not reliant on experimental heats of formation, where sometimes accurate values are not available, particularly for excited states. The Gaussian-2 (G2) method[10] has proven itself to be fairly robust in many circumstances, and so this method was tested to see if it was able to predict the maximum energy of chemielectrons, without having to rely on heats of formation of the individual species involved or whether these are calculated or derived from experiment.

Thus, the aims of the present paper are (i) to calculate an accurate heat of formation for the CH_3C radical for both the $\tilde{X}^2A''$ and the $\tilde{a}^4A_2$ states, which are so far unavailable and (ii) to calculate the internal energy change of the chemiionization reactions 1 and 2.

Previous Work on CH_3C. Experimentally, apart from the chemiionization studies mentioned above, there appears to be no other information on the isolated CH_3C radical; there is, however, some information from surface studies. CH_3C is generally thought to form by the rearrangement of adsorbed ethylene on a variety of surfaces, and can also be formed from the reaction of acetylene with coadsorbed hydrogen (see the very recent ref 11 and other references quoted therein). Reference 11 has examined the vibrational spectrum of CH_3C [adsorbed on Ni(111)] in some detail, and this work will be referred to below. The C−C bond length of adsorbed CH_3C has been deduced by NMR,[12] dynamical LEED,[13] and shape resonances,[14] giving a value of 1.45−1.50 Å.

There are two theoretical studies, to the authors' knowledge. The first is by Kalcher and Sax,[15] who deduced a C_s structure at the ROHF/DZ+d level of theory, presumably for the doublet state, with a C−C bond length of 1.481 Å; they also reported the C−C stretching frequency (at the same level of theory) as 1084 cm^{-1}. The second study was by Nielsen et al.,[4] who optimized the geometry of both the doublet and the quartet states of CH_3C at the Hartree−Fock and CISD level. For the $\tilde{X}^2A''$ state, the C−C bond length was calculated to be 1.464 Å at the Hartree−Fock level (but it is not mentioned whether ROHF or UHF wave functions were employed) using a TZ2P basis set and 1.456 Å at the CISD level with the same basis set. The geometry of the doublet state was of C_s symmetry, whereas that of the quartet state was C_{3v}. Vibrational frequencies at the Hartree−Fock level were also reported.

In the present work, the equilibrium geometry and vibrational frequencies of the CH_3C radical are calculated at the MP2/6-31G* and MP2/6-311G(3df,3pd) levels for both electronic states. The heat of formation is then calculated at the CCSD(T)/6-311G(3df,3pd)//MP2/6-311G(3df,3pd) level of theory and compared to that calculated using the Gaussian-2 (G2) method.[10]

II. Computational Details

The calculations in the present work were performed using Gaussian94.[16] For CH_3C, geometry optimizations were started at the geometries reported in ref 4 and analytic gradient methods were used, employing UHF wave functions. (In all cases $\langle S^2 \rangle$ was less than 0.78 for the doublet state and less than 3.76 for the quartet state, implying that spin contamination was small for these species.) CCSD(T) single-point calculations were performed at the MP2/6-311G(3df,3pd) optimized geometries. For all CCSD(T) and the MP2 calculations outside of the G2 method, the frozen core approximation was employed.

To calculate the heat of formation of CH_3C, it is necessary to consider an appropriate reaction where all but the species of interest have well-established heats of formation; then, the heat of reaction may be calculated using ab initio methods, and the unknown heat of formation may then be deduced. Some workers have used atomization energies as a means to calculate heats of formation;[17,18] however, this does not allow for the greatest cancellation of errors, which arise because of differential correlation energy and basis set incompleteness for the different species involved. To obtain the most reliable value, it is desirable to choose a reaction that is isogyric and isodesmic. The reactions selected in the present work were

$$CH_3C(\tilde{X}^2A'') + CH_4 \rightarrow CH(X^2\Pi) + C_2H_6 \qquad (3)$$

and

$$CH_3C(\tilde{X}^2A'') + H_2 \rightarrow CH(X^2\Pi) + CH_4 \qquad (4)$$

Reaction 3 is both isogyric and isodesmic, assuming the character of the C−C bond is approximately the same in CH_3C and C_2H_6. Reaction 4 is isogyric; it is not, however, isodesmic. Reactions 3 and 4 have the benefit that CH and CH_3C are members of the same family of radicals and that the heats of formation of H_2, CH, CH_4 and C_2H_6 are all well established. One of the main reasons for choosing isogyric and isodesmic reactions is to try to ensure the greatest cancellation of errors; as will be seen below, all methods used to calculate the heat of formation of CH_3C give almost identical results, suggesting that these errors are almost completely canceled or are small. Therefore, we are confident that this route to the heat of formation of CH_3C should be reliable.

For each species in reactions 3 and 4, the corresponding energies at the relevant levels of theory needed to be calculated (obviously including optimized geometries and vibrational frequencies). For both reactions 3 and 4, the standard G2 method was employed. For reaction 4, the heat of reaction was also calculated using the CCSD(T) single-point energies, together with a correction for zero-point energy and thermal effects taken from the MP2/6-311G(3df,3pd) calculation. Once the enthalpy change of reactions 3 and 4 had been calculated, the heat of formation of CH_3C could be calculated using the well-established values for the other species.

Since there is the possibility of the lowest quartet state also being involved in the chemiionization reaction, the following reactions also had to be considered in order to calculate the corresponding heat of formation:

$$CH_3C(\tilde{a}^4A_2) + CH_4 \rightarrow CH(a^4\Sigma^-) + C_2H_6 \qquad (5)$$

$$CH_3C(\tilde{a}^4A_2) + H_2 \rightarrow CH(a^4\Sigma^-) + CH_4 \qquad (6)$$

For this, the heat of formation of $CH(a^4\Sigma^-)$ was needed. This

TABLE 1: Calculated Equilibrium Geometry for $CH_3C(\tilde{X}^2A'')$-C_s Symmetry[a]

parameter	MP2/6-31G*	MP2/6-311G(3df,3pd)
R_{CC}	1.461	1.457
R_{CH1}	1.109	1.104
R_{CH2}	1.098	1.092
θ_{H1CC}	99.0	98.9
θ_{H2CC}	115.7	115.4
θ_{H2CH1}	106.9	106.9
θ_{H2CH3}	111.1	111.8

[a] Bond lengths in Å, bond angles in degrees.

TABLE 2: Calculated Equilibrium Geometry for $CH_3C(\tilde{a}^4A_2)$-C_{3v} Symmetry[a]

parameter	MP2/6-31G*	MP2/6-311G(3df,3pd)
R_{CC}	1.496	1.492
R_{CH}	1.095	1.089
θ_{HCC}	110.5	110.4
θ_{HCH}	108.5	108.6

[a] Bond lengths in Å, bond angles in degrees.

was calculated by adding the experimental T_0 value (5985 ± 65 cm^{-1})[19] to the heat of formation of $CH(X^2\Pi)$ (note that the difference in the thermal corrections for the vibrational, rotational, and translational energies between the $CH(X^2\Pi)$ and $CH(a^4\Sigma^-)$ states was negligible). This yielded a heat of formation for $CH(a^4\Sigma^-)$ of 159.6 ± 0.5 kcal mol^{-1}.

For the chemiionization reactions 1 and 2, the G2 method was employed to calculate the excess energy available from the reaction, which appears as the kinetic energy of the chemielectron.

III. Results and Discussion

Geometry. The calculated equilibrium geometries for $CH_3C(\tilde{X}^2A'')$ at the MP2/6-31G* level (from the G2 calculations) and MP2/6-311G(3df,3pd) level are shown in Table 1, with that for the $CH_3C(\tilde{a}^4A_2)$ state being shown in Table 2. As may be seen, the $\tilde{X}^2A''$ state is of C_s symmetry, whereas the $\tilde{a}^4A_2$ state is of C_{3v} symmetry. These conclusions are the same as those reached by Schaefer and co-workers[4] and also by Kalcher and Sax,[15] presumably for the ground state. The values of the geometric parameters are very similar to those of ref 4, but the C−C bond lengths here are a little shorter than those calculated in ref 15 for the $\tilde{X}$ state. The C−C bond length is also in line with the experimental values obtained from surface studies mentioned above, bearing in mind that these will be affected by the adsorption process. The good agreement between the previous values and those calculated here with the two basis sets suggests that the true geometry will be close to that calculated.

Vibrational Frequencies. The calculated harmonic vibrational frequencies for the two states of CH_3C are presented in Tables 3 and 4. As noted in the Introduction, there are no gas-phase vibrational frequencies for CH_3C available, but there are values for the doublet state from both ab initio studies and surface studies. The available values are summarized in Table 3, together with the values calculated in the present work. As may be seen, considering that the CH_3C may be significantly perturbed by the Ni(111) surface on which it was absorbed, the agreement between the surface HREELS features and the present calculations for the doublet state is good. The correspondence with the previous calculations at the Hartree−Fock level is reasonable for both the doublet and quartet state, although it is to be noted that some values increase and some values decrease when correlation energy is included, suggesting that a global scaling factor of vibrational frequencies is not wholly appropriate; in particular, it is noteworthy that there is a change in the ordering of the two lowest frequency vibrations on going from the MP2/6-31G* to the MP2/6-311G(3df,3pd) level for the doublet state (unfortunately, in ref 4, no symmetry assignments were given for comparison with those here) and between the Hartree−Fock and the MP2 level for the quartet state. Again, the generally reasonable agreement between the two sets of calculations here and the previous ones suggests that the true values should not be too far removed from the MP2/6-311G(3df,3pd) ones, although anharmonicity may play a significant role. From the values in Tables 3 and 4, we can conclude that calculations of at least MP2/6-311G(3df,3pd) quality are needed in order to obtain the correct ordering of the lowest frequencies (cf. the HREELS assignment of the symmetric CH wag vibration).

Heat of Formation of the CH_3C Radical. At the G2 level, the ΔH_{298} heat of reaction for reaction 3 was calculated to be 18.2 kcal mol^{-1}. This could be combined with the known heats of formation in Table 5 to yield a ΔH_f^{298} value of 122.0 kcal mol^{-1} for $CH_3C(\tilde{X}^2A'')$. The ΔH^{298} heat of reaction for reaction 4 was calculated at the G2 level to be 2.7 kcal mol^{-1}, which, when combined with the well-established heats of formation (Table 5), led to a calculated $\Delta H_f^{298}[CH_3C(\tilde{X}^2A'')]$ of 122.0 kcal mol^{-1}. G2 heats of formation should be accurate to a couple of kcal mol^{-1}, which would yield a value of $\Delta H_f^{298} = 122 \pm 2$ kcal mol^{-1}. A more accurate approach than the G2 method is to perform CCSD(T)/6-311G(3df,3pd) single-point energy calculations at the MP2/6-311G(3df,3pd) geometry; this was done for reaction 4 and led to $\Delta H_f^{298} = 122.3$ kcal mol^{-1}. The close agreement between this high level of theory and the G2 method, which employs some empirical corrections, gives added credence to both sets of values and suggests that a final value of $\Delta H_f^{298}[CH_3C(\tilde{X}^2A'')] = 122 \pm 1$ kcal mol^{-1} should be reliable. Note that when the G2 atomization route is used, as in refs 17 and 18, a value of 122 kcal mol^{-1} is also obtained, suggesting cancellation of errors.

For the quartet state, a similar approach via reaction 5 yielded $\Delta H_f^{298}[CH_3C(\tilde{a}^4A_2)] = 152.5$ kcal mol^{-1} at the G2 level of theory. A similar approach using reaction 6 also gave a ΔH_f^{298} value of 152.5 kcal mol^{-1}. At the CCSD(T)/6-311G(3df,3pd)//MP2/6-311G(3df,3pd) level of theory, a value of 152.7 kcal mol^{-1} is obtained using reaction 6. Consequently, we feel confident in quoting $\Delta H_f^{298}[CH_3C(\tilde{a}^4A_2)] = 152 \pm 2$ kcal mol^{-1}, where the major sources of error are in the calculation of the electronic energy difference using the ab initio techniques and in the experimental heats of formation (Table 5). The atomization route yields a G2 value of 154.4 kcal mol^{-1}, which is slightly higher than the values obtained via the other two routes, probably owing to the different requirements for the basis set and correlation energy between the atoms and $CH_3C(\tilde{a}^4A_2)$.

In addition, by using the internal energies at 0 K, it is possible to calculate the T_0 value for the $CH_3C(\tilde{a}^4A_2) \leftrightarrow CH_3C(\tilde{X}^2A'')$ process. At the G2 level, this yields 32.8 kcal mol^{-1} (1.42 eV), and 29.3 kcal mol^{-1} (1.27 eV) at the CCSD(T)/6-311G(3df,3pd)//MP2/6-311G(3df,3pd) level, with a correction for zero-point vibrational energy taken from the MP2/6-311G(3df,3pd) calculations. The latter value compares very well with the value of $T_e = 27.1$ kcal mol^{-1} obtained by Nielssen et al.,[4] calculated at the CISD+Q/ANO//CISD/TZ2P level of theory; correction for zero-point energy should increase this value by ~1 kcal mol^{-1}, leading to a value of $T_0 =$ ca. 28 kcal mol^{-1}. We show below that for CH the G2 method overestimates the T_0 value by 2−3 kcal mol^{-1}, and consequently, we believe that the G2

TABLE 3: Vibrational Frequencies for $CH_3C(\tilde{X}^2A'')$ in cm^{-1} [e]

mode	previous ab initio	MP2/6-31G*	MP2/6-311G (3df,3pd)	surface studies[c]	approximate description[d]
ω_1	716[a]	729.6 (a′)	799.3 (a″)		asym CH wag
ω_2	879[a]	861.7 (a″)	970.3 (a′)	1025 ± 5	sym CH wag
ω_3	1113[a] (1084)[b]	1119.0 (a′)	1192.3 (a′)	1129 ± 4	C−C stretch
ω_4	1464[a]	1387.0 (a′)	1334.8 (a′)	1336 ± 3	sym CH_3 scissor
ω_5	1489[a]	1415.0 (a″)	1351.4 (a″)	1410 ± 8	asym CH_3 scissor
ω_6	1588[a]	1518.9 (a′)	1471.5 (a′)		asym CH_3 bend
ω_7	3094[a]	3016.6 (a′)	3013.6 (a′)	2883 ± 3	sym CH_3 stretch
ω_8	3176[a]	3109.9 (a′)	3085.5 (a′)		asym CH_3 stretch
ω_9	3215[a]	3150.5 (a″)	3127.9 (a″)	2940 ± 8	asym CH_2 stretch

[a] From ref 4. Calculations performed at the Hartree−Fock level using a TZ2P basis set. Note that no assignment of the vibrational frequencies was given therein; the order here is purely numerical. [b] From ref 15. [c] From ref 11. HREELS study of CH_3C adsorbed onto Ni(111). [d] Some of the modes have mixed character. The description here is approximate. Note that in ref 11 assignments have been given; these correlate with those given here. [e] The symmetry of the vibration is given in parentheses. (All reported vibrational frequencies are unscaled.)

TABLE 4: Vibrational Frequencies for $CH_3C(\tilde{a}^4A_2)$ in cm^{-1} [b]

mode	previous ab initio[a]	MP2/6-31G*	MP2/6-311G (3df,3pd)	approximate description
ω_1	1081 (a_1)	1066.8 (e)	1036.5 (e)	CCH bend
ω_2	1108 (e)	1082.4 (a_1)	1057.5 (a_1)	CC stretch
ω_3	1512 (a_1)	1443.1 (a_1)	1391.7 (a_1)	umbrella
ω_4	1601 (e)	1536.7 (e)	1488.8 (e)	scissors
ω_5	3172 (a_1)	3088.7 (a_1)	3053.9 (a_1)	sym stretch
ω_6	3237 (e)	3179.9 (e)	3145.3 (e)	asym stretch

[a] From ref 4. Calculations performed at the Hartree−Fock level using a TZ2P basis set. No symmetry assignments are given in ref 4, but the degeneracy of the vibrations is noted, and the symmetry label may be deduced from this. [b] The symmetry of the vibration is given in parentheses. (All vibrational frequencies reported are unscaled.)

TABLE 5: Calculated and Experimental Thermodynamic Quantities[a]

species	$H_{CCSD(T)//MP2}$ [ZPVE]	H_{G2} [ZPVE]	ΔH_f^{298} (expt)
O		−74.979 670	59.6 ± 0.0[b]
CH_3CO^+		−152.676 557 [27.00]	157.0 ± 0.4[c]
HCO^+		−113.397 685 [10.14]	197.3 ± 0.6[d]
$CH(X^2\Pi)$	−38.398 711 [4.26]	−38.409 285 [3.90]	142.5 ± 0.3[e]
$CH(a^4\Sigma^-)$	−38.373 091 [4.62]	−38.378 404 [4.36]	159.6 ± 0.5[f]
$CH_3C(\tilde{X}^2A'')$	−77.632 440 [23.37]	−77.657 654 [21.69]	
$CH_3C(\tilde{a}^4A_2)$	−77.585 771 [24.08]	−77.605 452 [22.77]	
H_2	−1.158 904 [6.45]	−1.163 053 [5.93]	0.0[g]
CH_4	−40.388 799 [28.49]	−40.407 076 [26.77]	−17.8 ± 0.1[b]
C_2H_6		−79.626 400 [44.69]	−20.1 ± 0.1[b]

[a] Calculated enthalpies (1 atm pressure and 298 K) are given in E_h; zero-point vibrational energies (ZPVE) and experimental ΔH_f^{298} values are given in kcal mol^{-1}. Note that the MP2/6-311G(3df,3pd) ZPVE is unscaled, whereas by convention, the G2 ZPVE values arise from scaled HF/6-31G* values. [b] From ref 21. [c] From ref 22. [d] From ref 23. [e] From ref 24. [f] See text. [g] By definition.

value here is too high, and so the CCSD(T) value is the more reliable. We quote a value based on these calculations of $T_0 = (29 \pm 2)$ kcal mol^{-1} [(1.3 ± 0.1) eV].

Chemiionization Reactions. There are a number of types of chemiionization reactions, but the one under consideration here is the associative ionization reaction

$$A + B \rightarrow AB^+ + e^- \tag{7}$$

For this to occur, there must be energy available from the reaction to allow the chemielectron to be emitted. In an idealized case, the internal energies of both A and B would be well defined (i.e., A and B have been prepared in selected rovibronic levels) so that if AB^+ is formed in its ground rovibronic state, then there is no ambiguity in evaluating the maximum energy release of the chemiionization reaction from ab initio calculations (except for the translational term that is rather small: at 298 K $E_{trans} = 0.88$ kcal mol^{-1}). If AB^+ is not formed in its ground vibronic state and if the chemielectron spectrum is well-enough resolved, then it will be possible to identify the energy levels excited. If, however, the resolution of the chemielectron spectrum is poor, then the interpretation becomes more difficult.

In practice, of course, the reactant energies are not well-defined, and consequently, the product cations will have a range of internal excitation (as a result of the initial distribution of the reactant molecules' internal energy and as a result of the dynamics of the chemiionization reaction). In this case, the HKEO may not be simple to interpret; for example, there may be small contributions to the chemielectron spectrum from excited reactant molecules in the tail of the Boltzmann distributions. In the experiments reported in refs 2 and 9, effusive beams were used, and so there will be a Boltzmann spread of all types of energy. Since also the CH and CH_3C were formed from chemical reactions, they may have also been additionally internally excited. Thus, there will be limitations on how well the calculated maximum energy release will match the experimental HKEO, especially when one considers the possible effects of experimental sensitivity. It has been shown, however, that the HKEO can give information regarding the thermodynamics of chemiionization reactions.[2,9,20]

The next point is what type of computed thermodynamic quantity should be used to compare to the experimental HKEO: internal energy *U*, enthalpy *H*, or free energy *G*. If one considers an isolated system where the reactants collide and produce the product ion plus an electron, then it seems clear that the internal energy change ΔU should be used as a measure of the maximum kinetic energy of the electron, since no ensemble of molecules exists (and so pressure is undefined) and no work is being done on the surroundings (and hence the *pV* term is zero). Bearing in mind the above discussion, we have calculated ΔU^{298} as an estimate of the HKEO, where implicitly this assumes that A, B, and AB^+ are thermalized at 298 K. We note that the difference between ΔU^0 and ΔU^{298} consists of three terms: translational, rotational, and vibrational. The first two terms can be treated classically and amount to 2−2.5 kcal mol^{-1} for associative ionizations, such as reaction 7; the vibrational contribution is usually smaller. How much of this thermal energy can be converted to excess chemielectron kinetic energy will depend on the dynamics of the reaction; however, we note that the vibrational contributions could be determined (as vibrational structure) if the resolution of the chemielectron spectrum were good enough. Note also that if an activation energy barrier exists, then the amount of energy emerging from the reaction may be more than anticipated, since only the reactants with energies greater than the barrier will react, in the main; these reacting species will have a higher-than-average kinetic energy, owing to the high-energy tail in the Boltzmann distribution at a particular temperature.

Chemiionization Reaction 2. By use of internal energies, the maximum amount of energy that the chemielectron can carry away from reaction 2 may be calculated from G2 internal energies at 298 K. For the reaction involving the $CH(X^2\Pi)$ state the calculated ΔU^{298} is -0.22 eV, and for the $CH(a^4\Sigma^-)$ state, it is -1.05 eV. The latter value is in good correspondence with the highest HKEO observed in ref 9, (1.10 ± 0.10) eV; however, there was some uncertainty as to the assignment of this spectrum, since this HKEO was only observed when the acetylene was in excess (but HCO^+ was the predominant chemiion under all circumstances). Under conditions where $CH(a^4\Sigma^-)$ was quenched, and so only $CH(X^2\Pi)$ was reacting, and when oxygen atoms were in excess, it was found that the chemielectron spectrum consisted of a single feature with a maximum at 0.06 eV and a HKEO of (0.25 ± 0.10) eV, which was assigned to the $CH(X^2\Pi) + O \rightarrow HCO^+ + e^-$ reaction. This latter value is in very good agreement with the calculated maximum energy available to the chemielectron in reaction 2 when $CH(X^2\Pi)$ is one of the reactants and is also in good agreement with the value of (0.21 ± 0.04) eV obtained using experimental enthalpies of formation (Table 5). Thus, these results suggest that the maximum kinetic energy of a chemielectron can be calculated to within ± 0.05 eV using G2 internal energies, at least for the ground state.

For the $a^4\Sigma^-$ state, the experimental enthalpies of formation may also be used to derive the maximum kinetic energy of chemielectrons emerging from the corresponding chemiionization reaction; this gives a value of (0.95 ± 0.05) eV. This value differs from that calculated using the G2 method (1.05 eV) by 0.10 eV; this difference is mainly associated with the electronic energy difference between the $a^4\Sigma^-$ state and the $X^2\Pi$ state. The calculated difference is 0.84 eV, compared to the experimental separation $T_0 = (0.742 \pm 0.008)$ eV.[19] At the CCSD(T)/6-311G(3df,3pd)//MP2/6-311G(3df,3pd) level of theory, the energy difference is calculated as 0.70 eV, with the zero-point energy being taken from the MP2/6-311G(3df,3pd) calculations; clearly, this is in very good agreement with the experimental value. This suggests that for excited states, the G2 method is inadequate but that the CCSD(T)//MP2 method should be reliable.

Chemiionization Reaction 1. If the G2 energies at 298 K are used, then the maximum energy available to a chemielectron emerging from reaction 1 may be calculated as $\Delta U = 1.04$ eV when the $\tilde{X}^2A''$ state of CH_3C reacts and $\Delta U = 2.46$ eV when the $\tilde{a}^4A_2$ state reacts. From the above, for the $\tilde{X}^2A''$ state, it is to be expected that the G2 values should be accurate to within ± 0.05 eV; however, for the quartet state, the error is probably larger (ca. 0.2 eV) owing to the inaccuracy in the calculation of the electronic energy difference between the quartet and the doublet state. By looking at the doublet–quartet separation at the G2 and CCSD(T)//MP2 level, it may be seen that the T_0 value at the G2 level is higher by 0.15 eV; the CCSD(T)//MP2 value is expected to be the more reliable, since it uses a larger basis set and a more complete treatment of electron correlation energy.

The CH_3C radical is expected to be formed in oxidation reactions of hydrocarbons.[1,2,5] However, it has been shown by Schaefer and co-workers[4] that the ground state only has a small barrier ($\sim$9 kcal mol^{-1}) to isomerization to the vinyl radical. Consequently, and as argued in refs 2 and 5, the $\tilde{X}^2A''$ state is not expected to be present in sufficient concentrations to be seen. The quartet state, on the other hand, has a much larger barrier to isomerization ($\sim$57 kcal mol^{-1}), and so the CH_3CO^+ ions observed in refs 1, 2, and 5 may arise from reaction 1 involving the $\tilde{a}^4A_2$ state of CH_3C. The chemielectron spectrum under fuel-rich conditions, presented in ref 2, showed two features, one with a maximum at 0.06 eV and the other with a maximum at 0.27 eV. The high-kinetic-energy onset (HKEO) of the chemielectron spectrum represents an estimate of the maximum internal energy change of the chemiionization reaction giving rise to the chemielectrons. This was measured to be (1.3 ± 0.3) eV. Since this was higher than the calculated enthalpy of reaction 1 involving the $\tilde{X}^2A''$ state (ref 2), it was concluded that the $\tilde{a}^4A_2$ state must be present. The calculated enthalpy of reaction 1 in ref 2 was (0.93 ± 0.02) eV. The value is a little lower than the values calculated here, since $\Delta H_f^{298}(CH_3C)$ was estimated as (119.5 ± 1.5) kcal mol^{-1} therein. The value obtained here, $\Delta H_f^{298}[CH_3C(\tilde{X}^2A'')] = 122 \pm 1$ kcal mol^{-1}, ought to be more reliable than that estimate and certainly more accurate than the estimate of 130 kcal mol^{-1} from ref 1.

It is clear that the calculated heat of the chemiionization reaction involving either doublet or quartet CH_3C is consistent with the observed HKEO from the chemielectron study;[2] however, in those studies HKEOs greater than 1.1 eV were seen. This could be due to three possibilities. First, a reaction scheme such as that suggested in ref 2 could produce $CH_3C(\tilde{X}^2A'')$ with some internal excitation, which could lead to added excess energy. Second the quartet state could be involved, with the true HKEO not seen owing to poor intensity (the chemielectron spectrum in ref 2 has a very shallow onset). Or third, there is an activation energy barrier, and so only the reactants, such as $CH_3C(\tilde{X}^2A'')$, with energies in the tail-end of the Boltzmann distribution give rise to the chemielectrons. The favored interpretation in ref 2 that it is the quartet state that is reacting—a conclusion consistent with the deductions of ref 5—is not inconsistent with the calculated maximum electron kinetic energy here; however, the other possibilities cannot be discounted. Nevertheless, it is clear that the reactants must have excess energy, whether this be translational, rotational, vibrational, or electronic.

V. Conclusions

An accurate heat of formation of CH_3C has been calculated, giving a value $\Delta H_f^{298}[CH_3C(\tilde{X}^2A'')] = 122 \pm 1$ kcal mol^{-1}; the analogous value for the quartet state is $\Delta H_f^{298}[CH_3C(\tilde{a}^4A_2)] = 152 \pm 2$ kcal mol^{-1}. The energy available to chemielectrons emerging from the $CH_3C + O \rightarrow CH_3CO^+ + e^-$ and $CH + O \rightarrow HCO^+ + e^-$ chemiionization reactions has been calculated, and the results were found to be consistent with experiment and also with estimates based on enthalpies of formation. Consequently we conclude that the use of G2 internal energies is a relatively inexpensive way of obtaining information on the viability or otherwise of suggested chemiionization reactions involving ground-state reactants and can minimize the necessity of having enthalpies of formation of all of the species involved, for which reliable values may not always be available. For excited electronic states, higher levels of theory may be required.

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