Table XVI. Heats of Formation (298 K) from Atom Equivalents[a]

species	HF/3-21G	HF/6-31G*	MP2/6-31G* //HF/3-21G	exptl[b]
CH_4	-18.7	-17.0	-18.1	-17.9
CH_3F	-53.8	-54.2	-54.6	-55.9
CH_2F_2	-104.4	-106.5	-106.3	-107.4
CHF_3	-166.6	-168.5	-166.7	-166.4
CF_4	-233.0	-231.1	-224.9	-222.0
CH_3Cl	-26.2	-21.2	-20.7	-19.65
CH_2Cl_2	-28.0	-22.9	-24.4	-22.47
$CHCl_3$	-27.0	-21.0	-25.6	-24.64
CCl_4	-25.4	-14.9	-22.8	-24.6
CH_2FCl	-62.4	-62.2	-61.8	-62.6
CHF_2Cl	-111.2	-114.7	-112.9	-113.7
$CHFCl_2$	-64.1	-65.4	-67.2	-67.7
CF_3Cl	-168.6	-172.7	-170.0	-169.1
CF_2Cl_2	-112.0	-116.5	-117.3	-117.75
$CFCl_3$	-63.9	-63.8	-68.1	-69.5
CH_3	22.6	29.8	35.0	34.8
CH_2F	-15.7	-9.7	-6.1	-7.8
CHF_2	-57.1	-56.6	-56.8	-59.2
CF_3	-106.4	-110.7	-113.5	-113.2
CH_2Cl	16.8	23.0	28.6	30.55
$CHCl_2$	23.7	23.1	23.3	25.7
CCl_3	30.2	24.9	17.9	18.75
CHFCl	-12.6	-14.0	-13.3	
CF_2Cl	-53.4	-61.2	-65.1	-64.3
$CFCl_2$	-7.0	-15.5	-21.0	-23.0

[a] Values are in kcal/mol. [b] Values from Table I corrected to 298 K.

simultaneously determined. Since C–$(H)_3$(R) is used for the carbon in methane[89] and $^\bullet$C–$(H)_2$(R) is chosen to represent the carbon in CH_3, these data are not sufficient to uniquely determine the atom equivalents. Any constant can be added to the H–(C), F–(C), and Cl–(C) values as long as four times this constant is subtracted from all carbon atom equivalents. To circumvent this problem, the MP2/6-31G*//HF/3-21G energy of ethane[90] and its heat of formation[89] are added to the set of equations used to determine the atom equivalents.

The resulting HF/3-21G, HF/6-31G*, and MP2/6-31G*//HF/3-21G heats of formation at 298 K are compared with experiment in Table XVI. For example, the theoretical heat of formation of CH_2FCl is obtained by taking the ab initio energy and subtracting C–$(H)_2(R)_2$, H–(C) twice, F–(C), and Cl–(C). Multiplying the result by 627.509 converts the heat of formation (298 K) from hartrees to kcal/mol. The average absolute errors between theory and experiment for these compounds are 5.6 kcal/mol at HF/3-21G, 3.5 kcal/mol at HF/6-31G*, and 1.2 kcal/mol at MP2/6-31G*//HF/3-21G. The excellent agreement between experiment and the MP2/6-31G*//HF/3-21G values is due to both the improved theoretical energy caused by adding electron correlation and the fact that only these data (and C_2H_6 to remove the additive constant) are used to determine the atom equivalents. It is interesting to note that the results in Tables XIII and XVI show that all theoretical heats of formation of CF_4 are significantly below experiment. Increasing the basis set and adding electron correlation decrease the error, but the MP2/6-31G*//HF/3-21G result in Table XVI is still too low by 2.9 kcal/mol. Since the experimental error bars are quite small for this compound (Table I), it appears to be necessary to go beyond the MP2 level to obtain an accurate heat of formation.

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On the Mechanism of $(C,H_3,O)^\bullet$ Loss from Ionized Methyl Acetate. An ab Initio Molecular Orbital Study

Nikolaus Heinrich,[†] Jochen Schmidt,[†] Helmut Schwarz,*[†] and Yitzhak Apeloig[‡]

Contribution from the Institut für Organische Chemie der Technischen Universität, D-1000 Berlin 12, FRG, and the Department of Chemistry, Technion-Israel Institute of Technology, Haifa 32000, Israel. *Received July 24, 1986*

Abstract: Ab initio molecular orbital calculations executed at the MP2/6-31G(d)//3-21G level of theory and corrected for zero-point energies were used to provide insight into the gas-phase chemistry of ionized methyl acetate (**1**) and to resolve opposing interpretations of the experimental findings. The minimal energy requirement path has been located, and it is suggested that the experimentally observed dissociation of $CH_3CO_2CH_3^{\bullet+}$ (**1**) $\rightarrow$ $CH_3CO^+/CH_2OH^\bullet$ follows a multistep isomerization/dissociation pattern. In the first step, **1** isomerizes to the distonic ion $CH_3C(OH)OCH_2^{\bullet+}$ (**6**), which further rearranges to the hydrogen-bridged radical ion/dipole complex $CH_3CO\cdots H\cdots OCH_2^{\bullet+}$ (**8**). The latter, probably in its first excited state $^2(A'')$, is the direct precursor to the observed fragments CH_3CO^+ + $CH_2OH^\bullet$. The theoretical analysis provides a coherent description of the gas-phase ion chemistry of metastable **1**, which could not be achieved by the analysis of experimental data only. Semiempirical methods, like MNDO and MINDO/3, are less suited to describe the potential energy surface of ionized methyl acetate.

There is now ample experimental evidence that the $C_2H_3O^+$ ions generated from metastably dissociating molecular ions of methyl acetate (**1**) have the acetyl structure **2**.[1] The structure of the neutral fragment generated, the (C,H_3,O) radical, formed together with **2** in the dissociation of **1** (Scheme I) is, however, under dispute. The straightforward possibility is that the $(C,H_3,O)^\bullet$ radical is a methoxy radical, $CH_3O^\bullet$ (**3**). However, this suggestion has been revised recently[2a–e] by the claim that the

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* To whom correspondence should be addressed.
[†] Institut für Organische Chemie der Technischen Universität.
[‡] Israel Institute of Technology.

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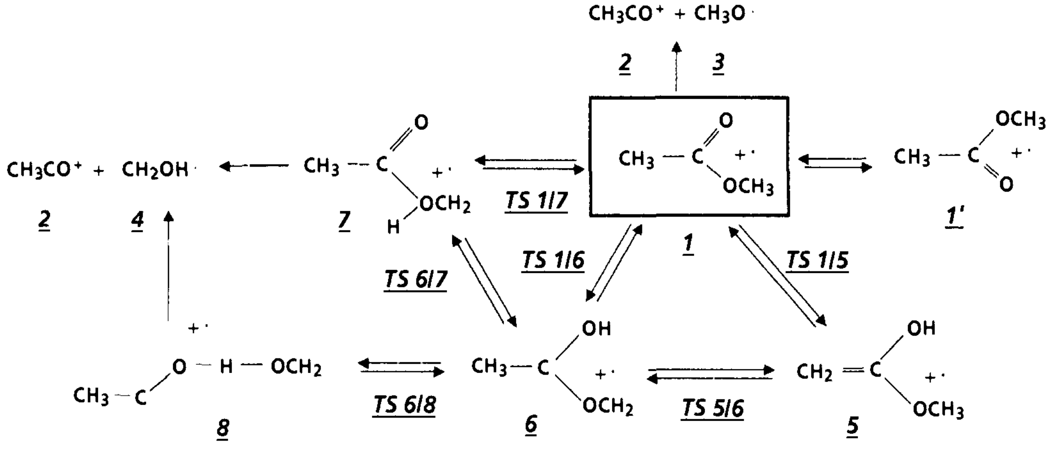
0002-7863/87/1509-1317$01.50/0

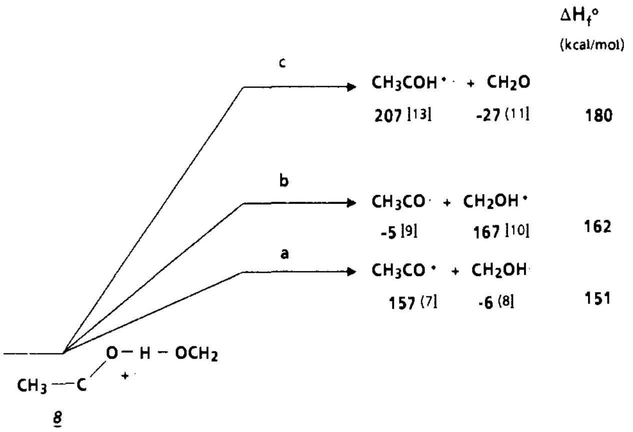
Scheme I



experimental facts are more consistent with the formation of a hydroxymethyl radical, $CH_2OH^{\bullet}$ (**4**). We cannot discuss here the experimental evidence in detail. It may suffice to state that in spite of the variety of experimental techniques (including collisional activation studies, kinetic energy release, thermochemical measurements, the study of labeled isotopomers, and different precursors that generate isomers of **1**) which were used to unravel the identity of the (C,H_3,O) radical, the situation remains clouded. In particular, McLafferty and his co-workers argued,[1d,3] that the neutral $(C,H_3,O)^{\bullet}$ fragment generated is the methoxy radical **3**, about 20% of which isomerizes to **4**. In a very recent paper[2f] Holmes and Terlouw modify their original view (exclusive generation of $CH_2OH^{\bullet}$) and concede that the $(C,H_3,O)^{\bullet}$ neutral formed from **1** is a mixture of both $CH_3O^{\bullet}$ and $CH_2OH^{\bullet}$, which are formed in competition. Moreover, the mechanistic details by which **1** may rearrange prior to dissociation, to produce reactive intermediates which can fall apart to **2** and **4** (or according to McLafferty **3**), are the subject of current controversies.

Extensive labeling experiments[1b,d2e,4] on methyl acetate and its enol (**5**) have led to the proposal that the distonic ion[5] $CH_3C(OH)OCH_2^{\bullet+}$ (**6**) is the key intermediate which accounts for the extensive, but imcomplete, loss of positional identity of the hydrogen/deuterium atoms labeled isotopomers. While equilibration of the oxygen atoms in **1** via migration of the ester methyl group (**1** ⇄ **1'**) could be excluded,[4] and isomerization of **1** to the distonic ion **7** could also be ruled out[2e] on the basis of a combination of ^{18}O labeling and collisional activation, agreement could not be reached on the following points: (i) Which step is rate-determining (RDS) in the isomerization **1** ⇄ **5** (Scheme I)? (ii) Which species serve as the immediate precursors for the generation of CH_3CO^+ and the (C,H_3,O) radical? (iii) Last but not least, is the cogeneration of $CH_3O^{\bullet}$ and $CH_2OH^{\bullet}$ reflected in comparable activation energies? While $CH_3O^{\bullet}$ could be formed in an entropically favored direct α-cleavage process $\mathbf{1} \rightarrow \mathbf{2} + CH_3O^{\bullet}$, it is obvious that for structural reasons neither **1** nor **5** can serve as immediate precursors for the generation of **2** and $CH_2OH^{\bullet}$. Similarly, Wesdemiotis et al.[1d] ruled out, on experimental grounds, the involvement of ionized hydroxyacetone ($CH_3COCH_2OH^{\bullet+}$) in the gas-phase chemistry of **1**. Furthermore, the tempting suggestion that **6** (or **1**) might rearrange to [7], which can easily

Scheme II



generate the two products **2** and **4**, was rejected on the ground that ionized $CH_3C^{18}OOCH_3$ (i) did not eliminate ^{18}O-labeled hydroxymethyl radical. (ii) Collision-induced loss of CH_2 from the same precursor gave exclusively $CH_3C(O)^{18}OH^{\bullet+}$.[2e]

The hydrogen-bridged molecule/radical ion pair **8** ($CH_3CO \cdots H \cdots OCH_2^{\bullet+}$) was not seriously considered previously as a potential intermediate in the isomerization/dissociation pattern of **1**. This is surprising in light of the following observations: (i) There is an increasing number of examples clearly demonstrating that ion/dipole complexes play a decisive role in unimolecular chemistry.[6] (ii) Dissociation of **8** to CH_3CO^+ and

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Table I. Total Energies (in hartrees) and Zero-Point Vibrational Energies, ZPE (in kcal/mol), of $C_3H_6O_2^{•+}$ Ions (Equilibrium and Transition Structures) and Some Dissociation Products[a]

	3-21G//3-21G		6-31G(d)//3-21G		MP2/6-31G(d)//3-21G		ZPE
species	E_{101}	E_{rel}	E_{101}	E_{rel}	E_{101}	E_{rel}	(3-21G)[b]
1	−265.039 73	(0.0)	−266.521 59	(0.0)	−267.199 28	(0.0)	52.3
5	−265.053 13	(8.4)	−266.535 06	(−8.5)	−267.230 24	(−19.4)	52.3
6 (syn)	−265.041 45	(−1.1)	−266.520 19	(0.9)	−267.217 93	(−11.7)	51.6
6 (anti)	−265.036 89	(1.8)	−266.517 22	(2.7)	−267.215 96	(−10.5)	51.5
7	−265.018 06	(13.6)	−266.480 08	(26.1)	−267.192 25	(4.4)	50.9
8	−265.014 10	(16.1)	−266.490 47	(19.6)	−267.195 47	(2.4)	49.4
TS **1/5**	−264.948 98	(57.0)	−266.431 99	(56.3)	−267.147 55	(32.5)	49.1
TS **1/6**	−264.973 56	(41.6)	−266.458 04	(39.9)	−267.175 99	(14.6)	49.4
TS **1/7**	−264.931 95	(67.7)	−266.409 73	(70.3)	−267.123 53	(47.6)	47.2
TS **6/5**	−264.977 73	(39.0)	−266.459 12	(39.3)	−267.171 52	(17.4)	49.6
TS **6/7**	−264.955 94	(52.7)	−266.421 67	(62.8)	−267.146 11	(33.4)	48.8
TS **6/8**	−264.983 71	(35.2)	−266.471 22	(31.7)	−267.168 62	(19.3)	50.1
2	−151.201 31		−152.058 38		−152.475 68		26.9
3	−113.791 95		−114.418 45		−114.684 07		22.3
4	−113.773 82		−114.407 12		−114.695 24		21.8

[a] Values in parentheses are relative energies in kcal/mol. [b] Scaled by a factor of 0.89.

$CH_2OH^•$ is structurally feasible, and thermochemically it is the most favored pathway (Scheme II).

It was suggested[2e] that extensive ab initio calculations at a sufficiently high level of theory would be required to establish the detailed reaction mechanism for the fragmentation of **1** and to resolve the existing discrepancies and disputes. Previous theoretical studies on a related problem, i.e., the gas-phase chemistry of the $C_2H_4O^{•+}$ isomers,[14] have convincingly demonstrated that a detailed description of the isomerization/dissociation pathways could be obtained by ab initio calculations, provided that a split-valence basis set is employed for geometry optimizations and that the final energy comparisons include the effects of polarization functions and of correlation energy. Fulfilling these requirements, the agreement between the theoretically predicted and the experimentally obtained data was excellent.[14a,b,15] In many cases, semiempirical molecular orbital (MO) methods were less suitable for this purpose, and they may, at best, provide a qualitative description.[14c] We have therefore undertaken an extensive ab initio study of the ionized methyl acetate problem.

Table II. Relative Energies (in kcal/mol) Derived from Table I, Heats of Formation (in kcal/mol) Calculated by MNDO and MINDO/3, and Experimentally Determined Energies

	MP2/ 6-31G(dd)// 3-21G +	E_{rel}			
species	ZPVE	MNDO	MINDO/3[a]	exptl[b]	
1	0.0	0	0	0	
5	−19.4	−36	−29	−23.9	[1b, 28]
6 (syn)	−12.2	−38		−8.1	[2e]
6 (anti)	−11.3	−36	−37	−8.1	[2e]
7	3.0	−11	−7	−7.8	[2d]
8	−0.5				
TS **1/5**	29.3	45	14		
TS **1/6**	11.7	30	21		
TS **1/7**	42.5	47	15		
TS **6/5**	14.7	3	0		
TS **6/7**	29.9	35	29		
TS **6/8**	17.0				
2 + 3	21.7	15	22	22.7	[1b, 7, 27]
2 + 4	14.2	−16	−4	12.2	[1b, 7, 8]

[a] Taken from ref 25. [b] Brackets indicate references.

Results and Discussion

Standard ab initio MO calculations have been carried out by using the GAUSSIAN 82 series of programs.[16] Optimized geometries, harmonic frequencies, and zero-point vibrational energies (ZPE) were calculated with the split-valence 3-21G basis set.[17] The force constant matrices for all stationary points of the potential energy hypersurface were calculated and checked to have the correct number of negative eigenvalues (0 for equilibrium and 1 for transition structures). The vibrational frequencies obtained were scaled by a factor of 0.89[18] before the zero-point vibrational energy was calculated in order to correct for the fact that at the HF level the normal frequencies are overestimated by approximately 10%. Single-point calculations at the 3-21G geometries were performed with the more flexible 6-31G(d) basis set,[19] which includes a set of polarization functions on all non-hydrogen atoms. (The notations 6-31G(d) and 6-31G(d,p) are identical with Pople's notation 6-31G* and 6-31G**. We prefer, however, the former as they are more informative.) To further improve the reliability of the calculations, electron correlation was included by using the Møller–Plesset perturbation theory up to second order (MP2).[20] The level of theory described above and used throughout in the paper for energy comparisons is referred to as MP2/6-31G(d)//3-21G + ZPE. For open-shell systems the UHF level has been used.[21] The results are presented in Tables I and II. The 3-21G optimized geometries of some structures, which are relevant in the present context, are given in Chart I. Bond lengths are given in angstroms and bond angles in degrees. For comparison we have also performed semiempirical calculations using modified versions of Dewar's MNDO[22] and MINDO/3[23] programs, which

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(10) Obtained from $\Delta H_f°(CH_2O)^{11}$ $\Delta H_f°(H^+)$,[11] and PA(CH_2O) = 170.3 kcal/mol.[12]

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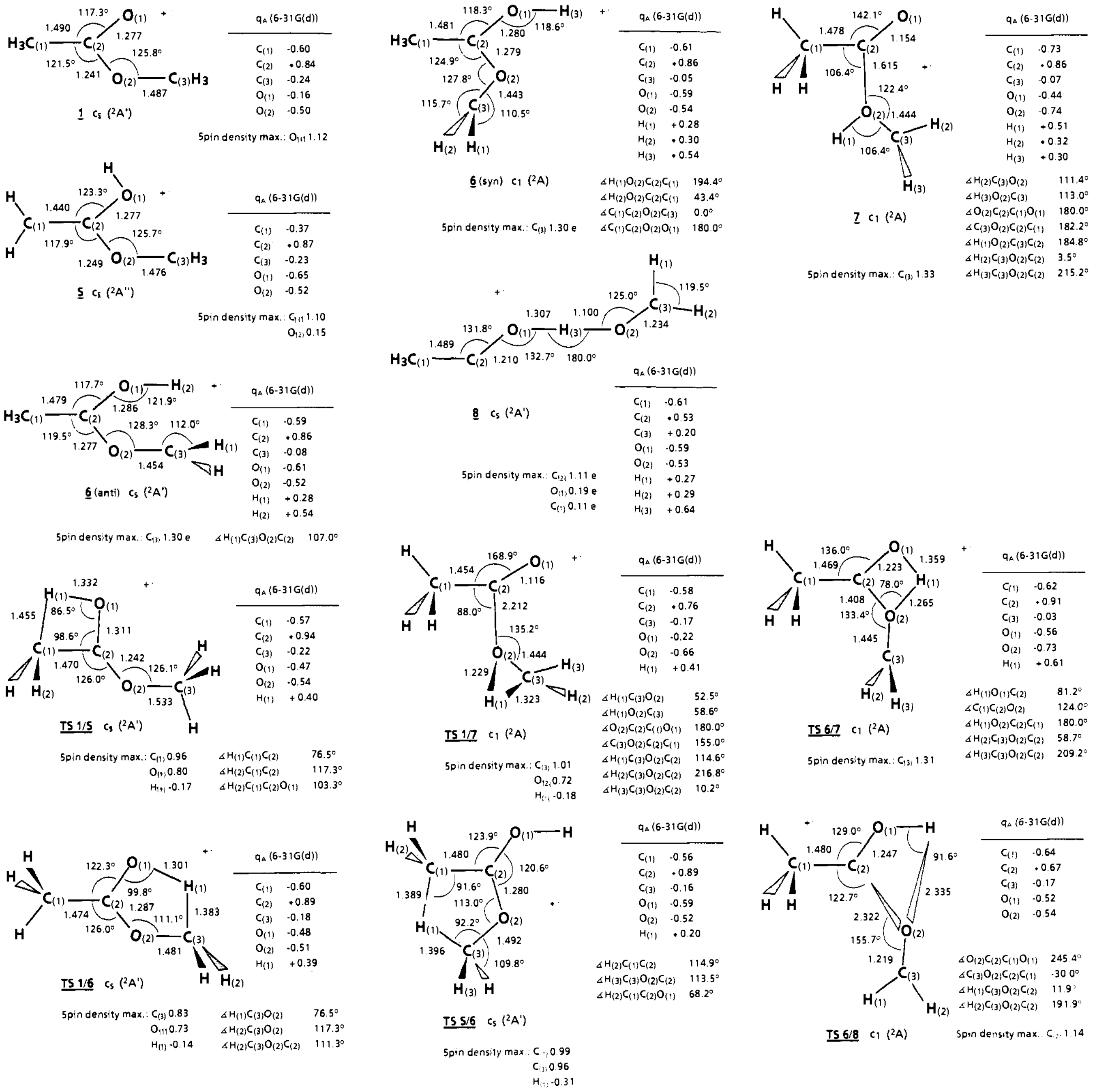
Chart I



1 c_s ($^2A'$)

	q_A (6-31G(d))
$C_{(1)}$	-0.60
$C_{(2)}$	+0.84
$C_{(3)}$	-0.24
$O_{(1)}$	-0.16
$O_{(2)}$	-0.50

Spin density max.: $O_{(1)}$ 1.12

5 c_s ($^2A''$)

	q_A (6-31G(d))
$C_{(1)}$	-0.37
$C_{(2)}$	+0.87
$C_{(3)}$	-0.23
$O_{(1)}$	-0.65
$O_{(2)}$	-0.52

Spin density max.: $C_{(1)}$ 1.10
$O_{(2)}$ 0.15

6 (anti) c_s ($^2A'$)

	q_A (6-31G(d))
$C_{(1)}$	-0.59
$C_{(2)}$	+0.86
$C_{(3)}$	-0.08
$O_{(1)}$	-0.61
$O_{(2)}$	-0.52
$H_{(1)}$	+0.28
$H_{(2)}$	+0.54

Spin density max.: $C_{(3)}$ 1.30 e

∡$H_{(1)}C_{(3)}O_{(2)}C_{(2)}$ 107.0°

TS 1/5 c_s ($^2A'$)

	q_A (6-31G(d))
$C_{(1)}$	-0.57
$C_{(2)}$	+0.94
$C_{(3)}$	-0.22
$O_{(1)}$	-0.47
$O_{(2)}$	-0.54
$H_{(1)}$	+0.40

Spin density max.: $C_{(1)}$ 0.96
$O_{(1)}$ 0.80
$H_{(1)}$ -0.17

∡$H_{(1)}C_{(1)}C_{(2)}$ 76.5°
∡$H_{(2)}C_{(1)}C_{(2)}$ 117.3°
∡$H_{(2)}C_{(1)}C_{(2)}O_{(1)}$ 103.3°

TS 1/6 c_s ($^2A'$)

	q_A (6-31G(d))
$C_{(1)}$	-0.60
$C_{(2)}$	+0.89
$C_{(3)}$	-0.18
$O_{(1)}$	-0.48
$O_{(2)}$	-0.51
$H_{(1)}$	+0.39

Spin density max.: $C_{(3)}$ 0.83
$O_{(1)}$ 0.73
$H_{(1)}$ -0.14

∡$H_{(1)}C_{(3)}O_{(2)}$ 76.5°
∡$H_{(2)}C_{(3)}O_{(2)}$ 117.3°
∡$H_{(2)}C_{(3)}O_{(2)}C_{(2)}$ 111.3°

6 (syn) c_1 (^2A)

	q_A (6-31G(d))
$C_{(1)}$	-0.61
$C_{(2)}$	+0.86
$C_{(3)}$	-0.05
$O_{(1)}$	-0.59
$O_{(2)}$	-0.54
$H_{(1)}$	+0.28
$H_{(2)}$	+0.30
$H_{(3)}$	+0.54

Spin density max.: $C_{(3)}$ 1.30 e

∡$H_{(1)}O_{(2)}C_{(2)}C_{(1)}$ 194.4°
∡$H_{(2)}O_{(2)}C_{(2)}C_{(1)}$ 43.4°
∡$C_{(1)}C_{(2)}O_{(2)}C_{(3)}$ 0.0°
∡$C_{(1)}C_{(2)}O_{(2)}O_{(1)}$ 180.0°

8 c_s ($^2A'$)

	q_A (6-31G(d))
$C_{(1)}$	-0.61
$C_{(2)}$	+0.53
$C_{(3)}$	+0.20
$O_{(1)}$	-0.59
$O_{(2)}$	-0.53
$H_{(1)}$	+0.27
$H_{(2)}$	+0.29
$H_{(3)}$	+0.64

Spin density max.: $C_{(2)}$ 1.11 e
$O_{(1)}$ 0.19 e
C[illegible] 0.11 e

TS 1/7 c_1 (^2A)

	q_A (6-31G(d))
$C_{(1)}$	-0.58
$C_{(2)}$	+0.76
$C_{(3)}$	-0.17
$O_{(1)}$	-0.22
$O_{(2)}$	-0.66
$H_{(1)}$	+0.41

Spin density max.: $C_{(3)}$ 1.01
$O_{(2)}$ 0.72
H[illegible] -0.18

∡$H_{(1)}C_{(3)}O_{(2)}$ 52.5°
∡$H_{(1)}O_{(2)}C_{(3)}$ 58.6°
∡$O_{(2)}C_{(2)}C_{(1)}O_{(1)}$ 180.0°
∡$C_{(3)}O_{(2)}C_{(2)}C_{(1)}$ 155.0°
∡$H_{(1)}C_{(3)}O_{(2)}C_{(2)}$ 114.6°
∡$H_{(2)}C_{(3)}O_{(2)}C_{(2)}$ 216.8°
∡$H_{(3)}C_{(3)}O_{(2)}C_{(2)}$ 10.2°

TS 5/6 c_s ($^2A'$)

	q_A (6-31G(d))
$C_{(1)}$	-0.56
$C_{(2)}$	+0.89
$C_{(3)}$	-0.16
$O_{(1)}$	-0.59
$O_{(2)}$	-0.52
$H_{(1)}$	+0.20

∡$H_{(2)}C_{(1)}C_{(2)}$ 114.9°
∡$H_{(3)}C_{(3)}O_{(2)}C_{(2)}$ 113.5°
∡$H_{(2)}C_{(1)}C_{(2)}O_{(1)}$ 68.2°

Spin density max.: C[illegible] 0.99
$C_{(3)}$ 0.96
H[illegible] -0.31

7 c_1 (^2A)

	q_A (6-31G(d))
$C_{(1)}$	-0.73
$C_{(2)}$	+0.86
$C_{(3)}$	-0.07
$O_{(1)}$	-0.44
$O_{(2)}$	-0.74
$H_{(1)}$	+0.51
$H_{(2)}$	+0.32
$H_{(3)}$	+0.30

∡$H_{(2)}C_{(3)}O_{(2)}$ 111.4°
∡$H_{(3)}O_{(2)}C_{(3)}$ 113.0°
∡$O_{(2)}C_{(2)}C_{(1)}O_{(1)}$ 180.0°
∡$C_{(3)}O_{(2)}C_{(2)}C_{(1)}$ 182.2°
∡$H_{(1)}O_{(2)}C_{(3)}C_{(2)}$ 184.8°
∡$H_{(2)}C_{(3)}O_{(2)}C_{(2)}$ 3.5°
∡$H_{(3)}C_{(3)}O_{(2)}C_{(2)}$ 215.2°

Spin density max.: $C_{(3)}$ 1.33

TS 6/7 c_1 (^2A)

	q_A (6-31G(d))
$C_{(1)}$	-0.62
$C_{(2)}$	+0.91
$C_{(3)}$	-0.03
$O_{(1)}$	-0.56
$O_{(2)}$	-0.73
$H_{(1)}$	+0.61

∡$H_{(1)}O_{(1)}C_{(2)}$ 81.2°
∡$C_{(1)}C_{(2)}O_{(2)}$ 124.0°
∡$H_{(1)}O_{(2)}C_{(2)}C_{(1)}$ 180.0°
∡$H_{(2)}C_{(3)}O_{(2)}C_{(2)}$ 58.7°
∡$H_{(3)}C_{(3)}O_{(2)}C_{(2)}$ 209.2°

Spin density max.: $C_{(3)}$ 1.31

TS 6/8 c_1 (^2A)

	q_A (6-31G(d))
$C_{(1)}$	-0.64
$C_{(2)}$	+0.67
$C_{(3)}$	-0.17
$O_{(1)}$	-0.52
$O_{(2)}$	-0.54

∡$O_{(2)}C_{(2)}C_{(1)}O_{(1)}$ 245.4°
∡$C_{(3)}O_{(2)}C_{(2)}C_{(1)}$ -30.0°
∡$H_{(1)}C_{(3)}O_{(2)}C_{(2)}$ 11.9°
∡$H_{(2)}C_{(3)}O_{(2)}C_{(2)}$ 191.9°

Spin density max.: C[illegible] 1.14

include routines for locating and characterizing transition structures by employing the McIver/Komornicki procedure.[24] In a recent paper Caballol et al.[25] reported related MINDO/3 results on the chemistry of **1**. Although the authors took into account kinetic aspects by using RRKM theory, the *potential energy surface* used is *inadequate* because of the fact that semiempirical methods provide, at best, only a qualitative insight into the energetic requirements of the chemistry of open-shell ions of interest here.

Stable $C_3H_6O_2^{\bullet+}$ Isomers. At the MP2/6-31G(d)//3-21G + ZPE level several minima were located on the $C_3H_6O_2^{\bullet+}$ energy surface, among which **1**, **5**, **6**, **7**, and **8** are of interest in the present context. The data given in Table II clearly show that the semiempirical methods are not suitable for analyzing the problem at hand. Neither the relative stabilities nor the energetics of the dissociation processes match the experimentally established sequences. For example, according to both MINDO/3 and MNDO, dissociation of $CH_3CO_2CH_3^{\bullet+}$ to CH_3CO^+ and $HOCH_2^{\bullet}$ is predicted to be *exothermic*, while the well-established experimental numbers give an *endothermicity* of 12.2 kcal/mol. Similarly, MNDO predicts that **5** and **6** are comparable in energy, and according to MINDO/3 the global minimum corresponds to **6**, in contrast with experimental findings (see below). The ab initio data are in much better agreement with the experimental findings (see below) than are the MNDO and MINDO/3 calculations. Thus, the latter will not be discussed further.

In general, there is good agreement between the computational results at the MP2/6-31G(d)//3-21G + ZPE level and the ex-

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perimental data (both shown in Table II). Thus, the calculated endothermicities of the dissociation processes of **1** to give either $CH_3CO^+/CH_3O^•$ or $CH_3CO^+/CH_2OH^•$ are in nearly perfect agreement with experiment (i.e., 21.7 vs. 22.7 and 14.2 vs. 12.2 kcal/mol, respectively). The experimental/theoretical agreement for the relative stabilities of the ions is also reasonable. Computationally, the order of ion stabilities is **5** > **6** > **1** > **7** compared to the experimental sequence of **5** > **6** > **7** > **1**. Thus, theory and experiment agree that the ionized enol form **5** is the global minimum and the next higher minimum is the distonic ion **6**. Experimentally, **5** is more stable than ionized methyl acetate (**1**) by 23.9 kcal/mol, in reasonable agreement with the theoretical value of 19.4 kcal/mol. According to the most reliable experimental measurements,[2e] **6** is by 8.1 kcal/mol more stable than **1** compared to 7.2 kcal/mol theoretically. The only major discrepancy between theory and experiment is regarding the second distonic ion **7**. Experimentally, **7** and **6** are estimated to be of comparable stability, but this is based on additivity schemes and assumptions which are questionable.[2d] According to the calculations, **7** is by 15.2 kcal/mol less stable than **6**, and on this basis we recommend a redetermination of the heat of formation of **7**. Finally, the experimental heat of formation of **8** is not known, and the calculations suggest that its stability is comparable to that of **1**.

The general good agreement between theory and experiment lends support to the theoretical predictions for other species for which experimental data are not available and also to the conclusions drawn below regarding the energetics of various pathways and processes.

A brief discussion of selected properties of **6**, **7**, and **8** is appropriate. The distonic ion **6**, which was generated and characterized for the first time by Wesdemiotis et al.,[1d] exists in two conformations syn and anti with regard to the C–C–O–C skeleton. The anti conformer is predicted to be by 0.9 kcal/mol more stable than the syn conformer. **6** can be viewed as a covalent rather than an electrostatic complex of ionized hydroxy(methyl)carbene ($CH_3COH^{•+}$)[29] interacting with formaldehyde, CH_2O. The positive charge is located mainly at the CH_3COH unit, while the spin is localized at the formaldehyde carbon. This theoretical description is in line with recent ESR studies on **6**[31] and its lower homologue, i.e., $HC(OH)OCH_2^{•+}$.[30]

The distonic ion **7** is calculated to have charge and spin distributions as in $CH_3CO^+\cdots CH_2OH^•$. This electronic structure makes this species an ideal candidate for generating $CH_3CO^+/CH_2OH^•$. However, as demonstrated below, the formation of **7** involves high activation energies; so although it is attractive, intermediate **7** can be ruled out as the immediate precursor to $CH_3CO^+/CH_2OH^•$.

Species **8**, a proton-bound dimer of CH_2O and $CH_3CO^•$, is calculated to be slightly more stable (by 0.5 kcal/mol) than ionized methyl acetate (**1**). As in the neutral analogues,[32] this stability can be attributed to dipole/dipole interactions. Other examples of hydrogen-bound complexes of open-shell ions are known (see, for example, ref 6o,p, which give a detailed account on ethylene$^{•+}$/H_2O, ethylene$^{•+}$/CH_3OH, and ketene$^{•+}$/water complexes). **8** might be viewed as a proton solvated by neutral formaldehyde and an acylium radical. However, the Mulliken population analysis suggests that **8** is better described as CH_2OH^+ complexed via hydrogen bonding with a CH_3CO radical. For example, nearly all the positive charge of **8** is concentrated in the CH_2OH^+ unit, and most of the spin resides on the CH_3CO substructure. Also, the $O_{(1)}$–H bond length of 1.307 Å is substantially longer than the $O_{(2)}$–H bond (1.100 Å). We note the unusual O–H–O bond angle of 180°.

Rearrangement and Dissociation Pathways of Ionized Methyl Acetate (1). There are several pathways connecting ionized methyl acetate (**1**) with its isomers **5**, **6**, **7**, and **8**, of which the most feasible are indicated in Scheme I. The central questions to be answered are as follows: (i) What are the minimal energy requirement paths (MERP) connecting these species? (ii) Which intermediate serves as the immediate precursor for generating $CH_3CO^+/CH_2OH^•$? It is obvious that the size of the molecules in question is prohibitive for a calculation of *all* theoretical possible pathways. Therefore, we confine ourselves to a consideration of those which are, from a chemical point of view, the most feasible ones.

Let us first consider the possibility that $CH_3CO_2CH_3^{•+}$ (**1**) dissociates directly via an α-cleavage to $CH_3CO^+/OCH_3^•$. Inspection of the calculated C–O ester bond length of **1** indicates that the process **1** → **2** + $CH_3O^•$ should indeed be less favored than that for an ordinary C–O single bond. The C–O ester bond of **1** (1.241 Å) is close to a C–O double bond and is in fact shorter than the C–O carbonyl "double" bond of **1** (1.277 Å), thus making α-cleavage relatively difficult. Dissociation of **1** to $CH_3CO^+/CH_3O^•$ is calculated to be a continuously endothermic process with an endothermicity of 21.7 kcal/mol, which is in very satisfying agreement with a value of 22.7 kcal/mol based on the experimental[1b,7,27] heats of foramtion of **1**, **2**, and **3**. As the formation of $CH_3O^•$ from **1** would be entropically favored over that of $CH_2OH^•$, the fact that both neutrals are formed in competition from **1**[2f] requires that the formation of $CH_2OH^•$ must be favored *energetically. Thus, the 21.7–22.7 kcal/mol range sets an upper limit for the internal energy of **1**.* Ions **1** having an internal energy *above* this value are very likely to fall apart to CH_3CO^+ and $CH_3O^•$, while those with lower energy content will form, in competition, $CH_3O^•$ *and* $CH_2OH^•$. The experiments rule out (see above) the direct rearrangement of **1** to either **5** or **7**. Theory is fully in line with these facts. The calculated energies of the transition structures TS **1**/**5** and TS **1**/**7** are indeed higher (29.3 and 42.5 kcal/mol, respectively) than the 21 kcal/mol limit. Our first conclusion is therefore that processes **1** → **5** and **1** → **7** must not any longer be considered as essential for the chemistry of ionized methyl acetate (**1**).

On the other hand, the barrier for rearranging **1** to the distonic ion **6** (via TS **1**/**6**) is calculated to be 11.7 kcal/mol, substantially smaller than the above defined limit of 21.7 kcal/mol and lower in energy than all other transition states considered in the present context. So according to the calculations the first step is the rearrangement of **1** and **6**. What is the fate of **6**? Isomerization **6** → **7**, via TS **6**/**7** that requires 42.1 kcal/mol (i.e., 29.9 kcal/mol above **1**), also exceeds the 21 kcal/mol upper limit, and this process can therefore be excluded. Similarly, direct dissociation of **6** to $CH_3COH^{•+}$ and CH_2O (which might appear feasible according to the charge and spin distributions of **6**, see above) can be ruled out as the two products have a combined energy of 35.2 kcal/mol above **1**, again well above the 21 kcal/mol limit. Substantially less energy, i.e., 26.9 kcal/mol (14.7 kcal/mol above *1*), is required to isomerize **6** to the enol form **5** via TS **6**/**5**. Thus, according to the calculations in the overall keto/enol tautomerization **1** ⇄ **6** ⇄ **5**, the step **6** → **5** is rate-determining. Experimentally, Burgers et al.[2e] concluded that step **1** → **6** is rate-determining. As the calculated energy difference between the two processes is very small, this discrepancy is not alarming. Support for the calculated small energy difference between these two pathways comes from recent ESR experiments[31] showing that in the condensed phase **1** isomerizes to **6** but not further to **5**. In the gas phase, the processes **1** ⇄ **6** ⇄ **5** account for both the observed hydrogen scrambling and the loss of CH_3OH to generate ionized ketene.[1b,d] The latter process will be analyzed theoretically in a forthcoming paper.[34] The rearrangement of **6** to complex **8** via TS **6**/**8** requires 29.2 kcal/mol, placing it 17.0 kcal/mol above **1**, only little more energy than is required for the process **6** → **5** (26.9 kcal/mol). Note, however, that this energy is still smaller than the upper limit value of 21.7 kcal/mol above the energy of

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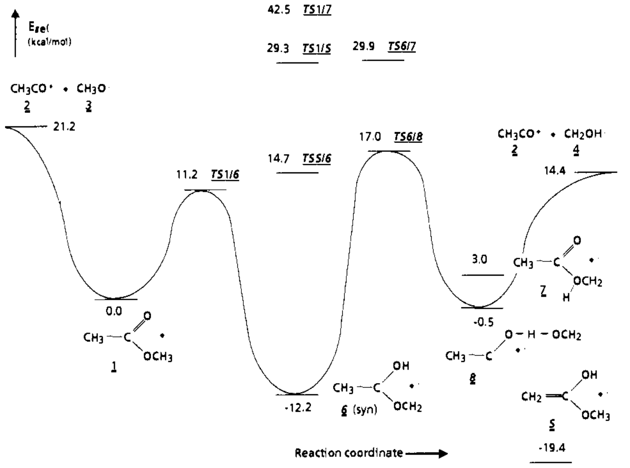

Figure 1. Minimal energy requirement for isomerization/dissociation processes of ionized methyl acetate (**1**) (MP2/6-31G(d)//3-21G + ZPE).

1. In the rearrangement of **6** to **8**, formaldehyde migrates intramolecularly in the electrostatic field of ionized hydroxy(methyl)carbene, and the rearrangement occurs *well below* the energy of the separated units, i.e., $CH_3COH^{•+}$ and CH_2O. Analysis of the pertinent geometrical data shows that the $C_{(2)}$–$O_{(2)}$ and the $H_{(3)}$–$O_{(2)}$ distances are of comparable length (2.33 and 2.32 Å, respectively).

The thermochemical data in Scheme II clearly show that once **8** is generated then the dissociation of lowest energy leads to $CH_3CO^+/CH_2OH^•$. The calculations predict that the enthalpy of dissociation of **8** → CH_3CO^+ + $CH_2OH^•$ is 14.7 kcal/mol.

The seemingly one-step process **8** → CH_3CO^+ + $CH_2OH^•$ is, however, more complex than anticipated. Starting with the electronic ground state of **8** (i.e., $^2A'$), a continuous lengthening of the $CH_3CO\cdots HOCH_2^{•+}$ bond results in a charge distribution opposite to that observed experimentally, e.g., $CH_3CO^•/CH_2OH^+$. This "symmetry allowed" dissociation is, however, a costly process requiring at least 11 kcal/mol more than the formation of $CH_3CO_+/CH_2OH^•$ (Scheme II and Figure 2). The dissociation leading to the correct products can, however, occur in the first excited state ($^2A''$) of **8**, which has the correct charge distribution and is "symmetry correlated" with the products $CH_3CO^+/HOCH_2^•$. The $^2A''$ state of **8** lies roughly 20 kcal/mol (HF-3-21G//3-21G) above the $^2A'$ state. This value is still below the limiting value of 21.7 kcal/mol. Although a detailed analysis of the dissociation of **8** → $CH_3CO^+/CH_2OH^•$, which requires extensive configuration interaction calculations, is for the time being inpractical due to the size of the system, it is conceivable that this process involves an avoided crossing between the $^2A''$ and $^2A'$ states as indicated in Figure 2, and it therefore requires less energy than the $^2A'$–$^2A''$ excitation energy, placing this dissociation process below the 21 kcal/mol limit.

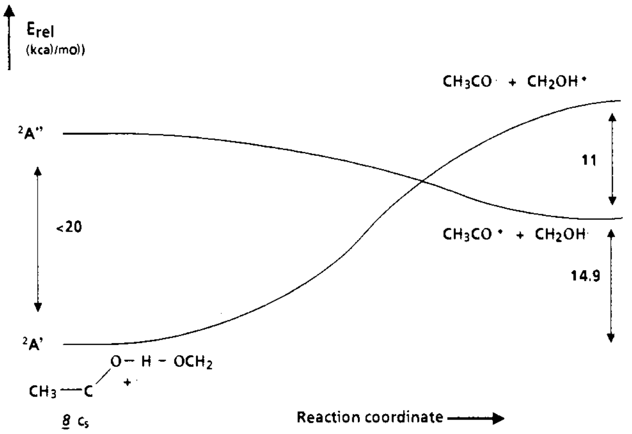

Figure 2. Dissociation of ground-state ($^2A'$) and first-excited-state ($^2A''$) ions **8** to products.

In conclusion, the present analysis provides, for the first time, a detailed coherent description of the gas-phase chemistry of metastable ionized methyl acetate (**1**). Due to the complexity of the system it is not practical to investigate the entire potential energy surface, and we cannot therefore exclude the possibility (although we believe this to be unlikely) that we have overlooked an important reaction path. With this cautionary remark in mind we conclude that the lowest energy path for the dissociation of **1** to CH_3CO^+ and $CH_2OH^•$ is the one shown in Figure 1. It involves the isomerization of **1** to the distonic ion **6** followed by an isomerization of **6** to the ion/dipole complex **8**. This intermediate, presumably from its first excited electronic state, dissociates to yield the observed products $CH_3CO^+/CH_2OH^•$.[34] Obviously, precursor ions **1** having greater internal energies may react via other, e.g., entropically favored, processes (like α-cleavage of **1** to give directly $CH_3CO^+/CH_3O^•$).

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(34) The possibility that the radicals $CH_3O^•$ (**3**)/$CH_2OH^•$ (**4**) generated from **1** might interconvert has also been considered. **3** is at our best level of theory 6.8 kcal/mol less stable than **4**; the experimentally determined difference is slightly larger (10.5 kcal/mol).[8] The barrier for rearrangement **3** → **4** has been determined to 35.6 kcal/mol at the SDQMBPT/DZP//6-31G(d,p) level of theory by Adams, G. F.; Bartlett, R. J.; Purvis, G. D. *Chem. Phys. Lett.* **1982**, *87*, 311. Also see: (a) Saebø, S.; Radom, L.; Schaefer, H. F. *J. Chem. Phys.* **1983**, *78*, 845. (b) Colwell, S. M. *Mol. Phys.* **1984**, *51*, 1217. (c) Solgadi, D.; Flament, J. P. *Chem. Phys.* **1985**, *98*, 387. For experimental evidence that the reaction **3** → **4** does *not* occur, see: (d) Gutman, D.; Sanders, N.; Nutler, J. E. *J. Phys. Chem.* **1982**, *86*, 66. (e) Dulcey, C. S.; Hudgens, J. W. *J. Phys. Chem.* **1983**, *87*, 2296. Dulcey, C. S.; Hudgens, J. W. *J. Chem. Phys.* **1986**, *84*, 5262. (f) For recent experimental evidence that gaseous $CH_3O^•$ and $CH_2OH^•$ do *not* interconvert, see ref 2f.