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Supplementary Material Available: Tables of total and relative energies, zero-point vibrational energies, thermochemical corrections, and 6-31G* optimized structures in the form of "archive entries" (7 pages). Ordering information is given on any current masthead page.

Ionized Methyl Formate ($CH_3OCHO^{\cdot+}$) and Its Distonic Isomer ($^{\cdot}CH_2OC^+HOH$)

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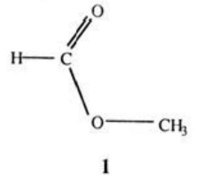
Contribution from the Research School of Chemistry, Australian National University, Canberra, A.C.T. 2601, Australia. *Received July 30, 1991*

Abstract: Ab initio molecular orbital calculations have been carried out for ionized methyl formate ($CH_3OCHO^{\cdot+}$) and its distonic isomer ($^{\cdot}CH_2OC^+HOH$). The ground state of ionized methyl formate is $^2A'$ (σ) and the lowest energy structure has COCO syn and a staggered methyl group (**2a**). The $^2A''$ (π) state (**3**) lies 74 kJ mol^{-1} above the $^2A'$ state (**2a**); its preferred conformation also has COCO syn but in this case the methyl group is eclipsed. The two structures of the distonic isomer (**4**) of lowest energy are both asymmetric but may be described approximately as COCO syn and OCOH anti (**4a**) and COCO anti and OCOH syn (**4b**); **4a** lies 62 kJ mol^{-1} *lower* in energy than **2a**. Rearrangement of **2a** to **4** requires 41 kJ mol^{-1}. Vertical ionization of methyl formate produces an ion lying 35 kJ mol^{-1} above **2a**; consequently, rearrangement to the distonic ion **4** only requires a further 6 kJ mol^{-1}. The calculations thus predict that ionization of methyl formate initially produces the σ state of the methyl formate radical cation (**2a**) which may rearrange with a small barrier to the distonic isomer **4**.

Introduction

In recent years, electron spin resonance (ESR) spectroscopy in conjunction with matrix isolation techniques has provided an attractive method for the investigation of organic radical cations.[2] Irradiation at low temperature of dilute solutions of neutral substrates having ionization energies smaller than that of the solvent (typically a freon such as trichlorofluoromethane) gives the corresponding cations. The resulting spectral data can yield valuable information on the molecular and electronic structures of the radical cations, which is not readily attainable from other experimental procedures. Complications can arise, however, because of complexation with the solvent matrix or because of unimolecular rearrangement of the species under examination.[3] A case in point involves ionization of matrix-isolated methyl formate (**1**), the simplest ester, for which agreement has yet to be reached as to the nature of the observed ions.



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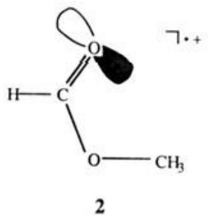

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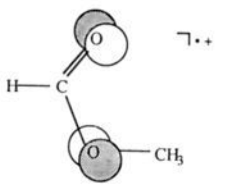
In 1983, Sevilla[4] and Symons[5] and co-workers independently reported that the methyl formate radical cation (**2**) in trichlorofluoromethane forms a stable σ^* complex with a solvent molecule at 77 K and that the complex decomposes on annealing at 140 K, yielding an isolated π-type cation **3**. Evidence in support of **3** was provided by INDO calculations of the spin density.[4]



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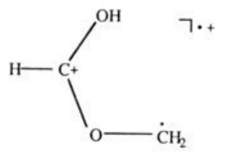
In a subsequent paper, Iwasaki and co-workers[6] also proposed that the primary radical cation has the π structure (**3**) but argued that it is produced directly from the σ radical (**2**) at 4 K without the intervention of a σ^* complex with the matrix. In addition, these authors argued, on the basis of proton hyperfine coupling constants, that **3** readily converts into the carbon-centered radical ion **4** via a McLafferty-type rearrangement upon warming from 4 K to 77 K.



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There has been vigorous discussion[7] of the reasons for the differing interpretations of the experimental data. The most recent

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[1] Present address: Department of Chemistry, University of Leuven, Celestijnenlaan 200-F,B-3001-Leuven-Heverlee, Belgium.

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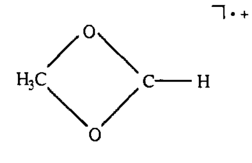
studies[8,9] appear to support the view that the species detected following ionization of methyl formate at 77 K is the σ^* complex and that this rearranges to **4** (rather than forming the π cation **3** as originally proposed) on warming. There does not seem to be agreement as to whether the uncomplexed methyl formate cation prefers a π structure (**3**) (favored by Iwasaki et al.[6]) or a σ structure (**2**) (favored by Symons et al.[10]).

The ion **4** belongs to the general class of *distonic*[11] radical cations, whose structures and stabilities in the gas phase have recently received extensive attention.[12] Such species contain formally separated charge and radical centers and do not generally have stable neutral counterparts. Therefore, they can normally only be prepared via rearrangement and/or fragmentation processes. In the present case, **4** is formed through intramolecular 1,4-hydrogen transfer from the methyl group to the carbonyl oxygen in **2**.



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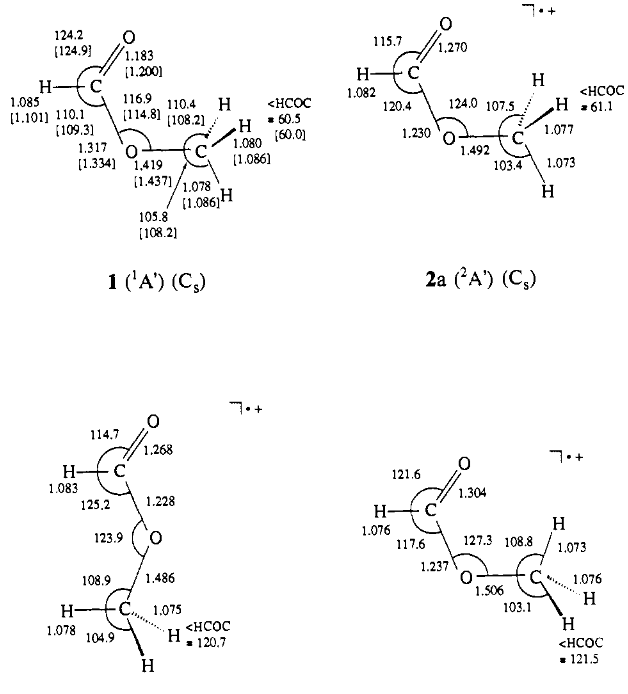
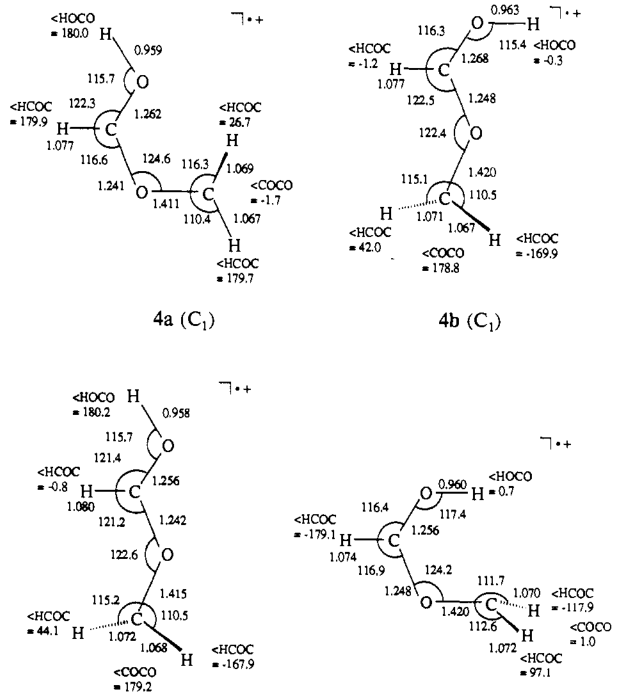
The nature of ionized methyl formate in the gas phase has also been studied theoretically and experimentally.[13-22] It was suggested on the basis of CNDO calculations[13] that the cation has a bridged-structure (**5**) featuring a pentavalent carbon bearing a positive charge. However, a subsequent ^{18}O-labeling experiment found no evidence for structure **5**.[14] A number of $C_2H_4O_2^{\bullet+}$ isomers were considered in collisional activation[15,16] and (low energy) energy-resolved mass spectrometry (ERMS)[17] experiments, but surprisingly the distonic species **4**, prominent in the matrix studies, was not one of them. However, evidence for the existence of the distonic ion has been produced in more recent neutralization-reionization[19,20] and collisional activation[21] mass spectrometry experiments on methyl formate radical cation, and in the metastable dissociation of propyl formate radical cation.[22]



1 (^{1}A') (C$_s$) **2a** (^{2}A') (C$_s$)

2b (^{2}A') (C$_s$) **3** (^{2}A'') (C$_s$)

Figure 1. HF/6-31G* optimized geometries for neutral (**1**) and ionized (**2a, 2b, 3**) methyl formate. Experimental values for **1** are given in square brackets. The methyl group in **1** was assumed to be symmetrical with its symmetry axis aligned along the C–O bond in the experimental analysis.[29]



4a (C$_1$) **4b** (C$_1$)

4c (C$_1$) **4d** (C$_1$)

Figure 2. HF/6-31G* optimized geometries for the various isomers of the distonic radical cation (**4**).

In an attempt to resolve some of the uncertainties noted above, we have carried out relevant ab initio molecular orbital calculations, examining the ionization of methyl formate and the subsequent rearrangement of the primary ion. Our calculations

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Table I. Calculated Total Energies (Hartrees) and Zero-Point Vibrational Energies (ZPVE, kJ mol^{-1}) for HF/6-31G* Optimized Structures

	HF/6-31G*	$\langle S^2 \rangle$	MP2/6-31G**	MP2/6-311G**	MP4/6-31G**	ZPVE
1	−227.789 42	0.00	−228.424 70	−228.526 13	−228.471 76	177.4
$\mathbf{1}^{+}_{v,\sigma}$	−227.436 11	0.76	−228.018 23	−228.117 82	−228.074 39	177.4
$\mathbf{1}^{+}_{v,\pi}$	−227.409 52	0.98	−227.980 09	−228.079 18	−228.041 35	177.4
2a	−227.456 45	0.76	−228.034 09	−228.131 72	−228.089 80	173.1
2b	−227.455 05	0.76	−228.031 80	−228.129 81	−228.087 32	172.7
3	−227.425 96	0.87	−227.997 60	−228.093 77	−228.055 87	169.9
4a	−227.463 28	0.77	−228.063 88	−228.163 16	−228.111 93	170.4
4b	−227.462 84	0.76	−228.061 84	−228.161 34	−228.109 91	169.9
4c	−227.457 97	0.76	−228.057 82	−228.157 59	−228.105 88	169.6
4d	−227.458 36	0.76	−228.057 81	−228.156 59	−228.105 98	170.7
6 (TS: **2b** → **2a**)	−227.434 86	0.76	−228.008 13	−228.105 63	−228.064 19	168.6
7a (TS: **4d** → **4a**)	−227.440 32	0.77	−228.039 63	−228.138 26	−228.088 02	163.7
7b (TS: **4d** → **4b**)	−227.438 95	0.76	−228.035 41	−228.132 52	−228.083 76	168.1
7c (TS: **4c** → **4a**)	−227.436 41	0.76	−228.033 17	−228.135 52	−228.081 50	167.7
7d (TS: **4c** → **4b**)	−227.437 09	0.77	−228.036 05	−228.135 09	−228.084 47	162.0
8 (TS: **2** → **4**)	−227.396 58	0.80	−228.014 40	−228.114 64	−228.066 79	160.1

predict that the initially formed ion is the σ-radical cation (**2**) which can readily rearrange to the distonic ion **4**.

Method and Results

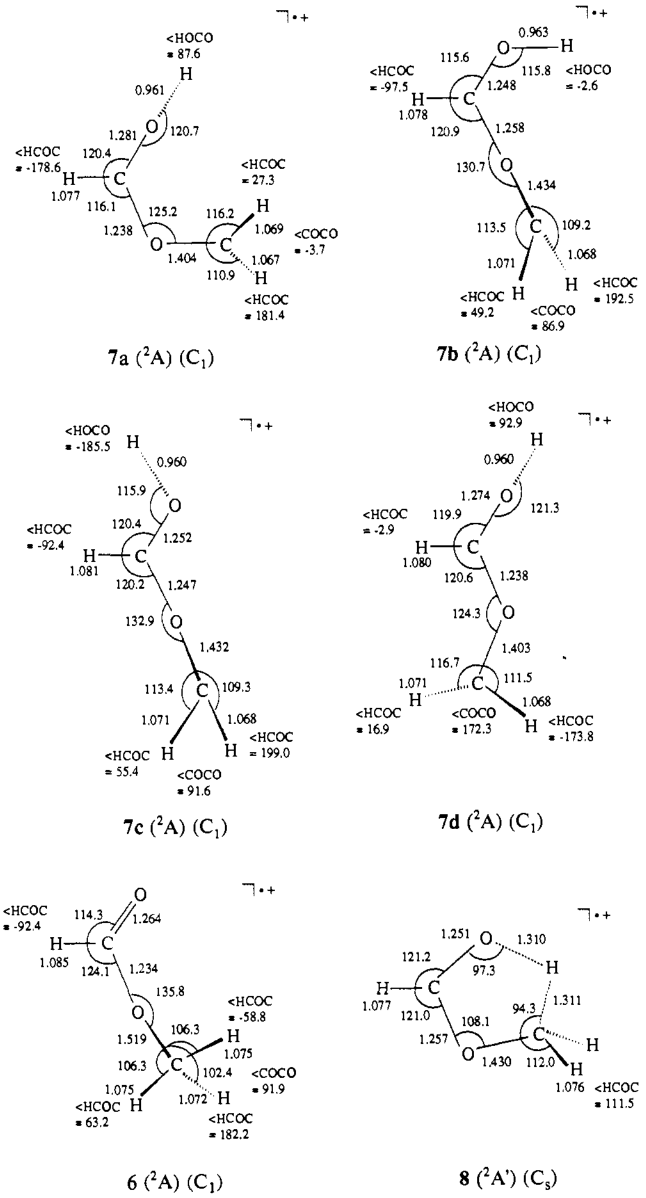
Standard ab initio molecular orbital calculations[23] were carried out with modified versions of the GAUSSIAN82,[24] GAUSSIAN88,[25] and GAUSSIAN90[26] systems of programs. Optimized geometries were obtained initially for a variety of conformations of ionized methyl formate (**2**, **3**) and its distonic isomer (**4**) at the HF/3-21G level using gradient techniques in order to identify the structures of most interest and relevance. For all the structures reported in the present paper, improved geometries were obtained at the HF/6-31G* level. Harmonic vibrational frequencies were also calculated at the HF/6-31G* level in order to characterize stationary points as minima (representing equilibrium structures) or first-order saddle point (representing transition structures) and, after scaling by 0.9, to estimate zero-point vibrational contributions to relative energies.

The HF/6-31G*-optimized structures for methyl formate (**1**) and various conformations and electronic states of ionized methyl formate (**2**, **3**) are shown in Figure 1. Figure 2 displays the optimized structures for different conformations of the distonic ion **4**. Geometrical parameters for the transition structure (**6**) for rotation about the C–O(CH$_3$) bond in **2**, the transition structures (**7**) linking the various isomers of the distonic ion **4**, and the transition structure (**8**) for rearrangement of **2** to **4** are presented in Figure 3.

Improved energies were obtained through calculations at the HF/6-31G* optimized geometries with a larger basis set (6-311G**) and with incorporation of electron correlation using Møller–Plesset perturbation theory (MP2, MP4). With the aid of the additivity approximation:[27]

$$\Delta E(\text{MP4/6-311G**}) \approx \Delta E(\text{MP4/6-31G**}) + \Delta E(\text{MP2/6-311G**}) - \Delta E(\text{MP2/6-31G**}) \quad (1)$$

these calculations yielded relative energies corresponding to MP4/6-311G**//HF/6-31G* values, corrected for zero-point vibration. Calculated total and relative energies at these levels



7a (^{2}A) (C$_1$) **7b** (^{2}A) (C$_1$)

7c (^{2}A) (C$_1$) **7d** (^{2}A) (C$_1$)

6 (^{2}A) (C$_1$) **8** (^{2}A′) (C$_s$)

Figure 3. HF/6-31G* optimized geometries for the transition structures (**7a–d**) linking the various distonic minima (**4a–d**), the transition structure (**6**) for rotation about the C–O(CH$_3$) bond in **2**, and the transition structure (**8**) separating ionized methyl formate (**2a**) and the distonic isomer (**4a**).

are presented in Tables I and II, respectively.

For the more important structures, still further calculations were carried out at the HF/6-31G* optimized geometries using the

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Table II. Calculated Relative Energies (kJ mol^{-1}) for HF/6-31G* Optimized Structures[a]

	HF/6-31G*	MP2/6-31G**	MP2/6-311G**	MP4/6-31G**	MP4/6-311G**[b]	MP4/6-311G**[c]
1	−874	−1026	−1036	−1003	−1013	−1009
$\mathbf{1}^+_{v,\sigma}$	53	42	36	40	34	38
$\mathbf{1}^+_{v,\pi}$	123	142	138	127	123	127
2a	0	0	0	0	0	0
2b	4	6	5	7	6	6
3	80	96	100	89	93	90
4a	−18	−78	−83	−58	−63	−65
4b	−17	−73	−78	−53	−58	−61
4c	−4	−62	−68	−42	−48	−51
4d	−50	−62	−65	−42	−45	−47
6 (TS: **2b** → **2a**)	57	68	68	67	67	63
7a (TS: **4d** → **4a**)	42	−14	−17	5	2	−6
7b (TS: **4d** → **4b**)	46	−3	−7	16	12	7
7c (TS: **4c** → **4a**)	53	2	−2	22	18	13
7d (TS: **4c** → **4b**)	51	−5	−9	14	10	0
8 (TS: **2** → **4**)	157	52	45	60	53	41

[a] Calculated using total energies from Table I. [b] MP4/6-311G** values calculated using the additivity approximation of eq 1. [c] MP4/6-311G** values together with zero-point vibrational corrections.

Table III. Calculated Total Energies (Hartrees) and Higher Level Relative Energies (kJ mol^{-1})[a]

	total energy		relative energy		
	MP2/6-31G*	QCISD(T)/6-31G*	QCISD(T)/6-31G*	QCISD(T)/ 6-311G**[b]	QCISD(T)/6-311G**[c]
1	−228.392 98	−228.435 92	−988	−1000	−996
$\mathbf{1}^+_{v,\sigma}$	−227.987 98	−228.045 55	37	31	35
$\mathbf{1}^+_{v,\pi}$	−227.950 07	−228.023 07	93	89	93
2a	−228.004 02	−228.059 53	0	0	0
3	−227.967 56	−228.030 65	73	77	74
4a	−228.029 82	−228.076 65	−45	−60	−62
4d	−228.024 15	−228.070 41	−29	−41	−43
7a (TS: **4d** →**4a**)	−228.005 27	−228.053 09	17	−3	−11
8 (TS: **2** → **4**)	−228.980 69	−228.033 11	69	53	41

[a] HF/6-31G* optimized structures. [b] QCISD(T)/6-311G** values calculated using the additivity approximation of eq 2. [c] QCISD(T)/6-311G** values together with zero-point vibrational corrections.

Table IV. Calculated Thermodynamic and Kinetic Parameters for the Gas-Phase Conversion of Ionized Methyl Formate (**2a**) to Its Distonic Isomer (**4a**)

	298 K	140 K
ΔH (kJ mol^{-1})[a]	−62.1	−62.5
ΔS (J K^{-1} mol^{-1})[b]	−3.5	−5.0
ΔG (kJ mol^{-1})[c]	−61.1	−61.8
$\Delta H^‡$ (kJ mol^{-1})[a]	38.7	40.3
$\Delta S^‡$ (J K^{-1} mol^{-1})[b]	−19.8	−12.0
$\Delta G^‡$ (kJ mol^{-1})[c]	44.6	42.0
E_a (kJ mol^{-1})[d]	41.2	41.5
S (s^{-1})[e]	1.6×10^{12}	1.9×10^{12}
k (mol s^{-1})[f]	9.8×10^4	6.4×10^{-4}
κ[g]	7.2	28.9
k^* (mol s^{-1})[h]	7.0×10^5	1.9×10^{-2}

[a] Calculated using relative energies from Table III and theoretically derived temperature corrections. [b] Calculated using (scaled by 0.9) HF/6-31G* frequencies. [c] $\Delta G = \Delta H - T\Delta S$. [d] $E_a = \Delta H^‡ + RT$. [e] $A = (k_BT/h)e^{(\Delta S^‡/R)}$. [f] $k = Ae^{(-Ea/RT)}$. [g] κ is the tunneling correction, as estimated using the Wigner procedure (ref 32): $\kappa = 1 + u^2/24$ where $u = h\nu_i^‡/k_BT$ and $\nu_i^‡$ is the imaginary frequency at the saddle point (2799i cm^{-1}). [h] κ^* is the rate constant including the tunneling correction: $k^* = \kappa k$.

quadratic configuration interaction (QCISD(T)) procedure.[28] Our best relative energies in this paper correspond to QCISD(T)/6-311G**//HF/6-31G* values, corrected for zero-point vibrational energies, in this case evaluated using the additivity approximation:

$$\Delta E(\text{QCISD(T)/6-311G**}) \approx \Delta E(\text{QCISD(T)/6-31G*}) + \Delta E(\text{MP2/6-311G**}) - \Delta E(\text{MP2/6-31G*}) \quad (2)$$

Unless otherwise noted, energies in the text refer to this level. Relevant total and relative energies are presented in Table III.

Figure 4 gives a schematic energy profile showing the energetic relationship between the species involved in the ionization of methyl formate (**1**), and the subsequent rearrangement of ionized methyl formate (**2**) to its distonic isomer (**4**). Finally, additional thermodynamic and kinetic characteristics of the rearrangement of **2** to **4** are summarized in Table IV.

In all cases, the frozen-core approximation has been employed and the spin-unrestricted formalism (UHF, UMP) has been used for open-shell species. Values of $\langle S^2 \rangle$, tabulated in Table I and typically around 0.77, indicate that spin contamination is not important for most of the structures investigated in the present study. In those cases where spin contamination is significant, use of the quadratic configuration procedure is particularly relevant. Throughout this paper, bond lengths are given in angstroms and bond angles in degrees. Structural parameters in the figures are HF/6-31G*-optimized values.

Discussion

Neutral Methyl Formate (1). The preferred conformation of methyl formate is well established[29] to have COCO syn and a staggered methyl group. We note here only that our HF/6-31G* optimized geometrical parameters are in reasonable agreement with experimental values (**1**, Figure 1).

The highest occupied molecular orbital (HOMO) of methyl formate (13a′) has σ symmetry and is largely a lone-pair-type orbital on the carbonyl oxygen. The next highest occupied orbital (3a″) has π symmetry and is largely a nonbonding combination of p_π orbitals on the two oxygen atoms. The calculated energy separation between the 13a′ and 3a″ orbitals is 16.1 kJ mol^{-1} (HF/6-311G**). Because of the closeness of these two orbitals, it might be expected that the two ions produced by removal of an electron from either orbital will have similar energies.

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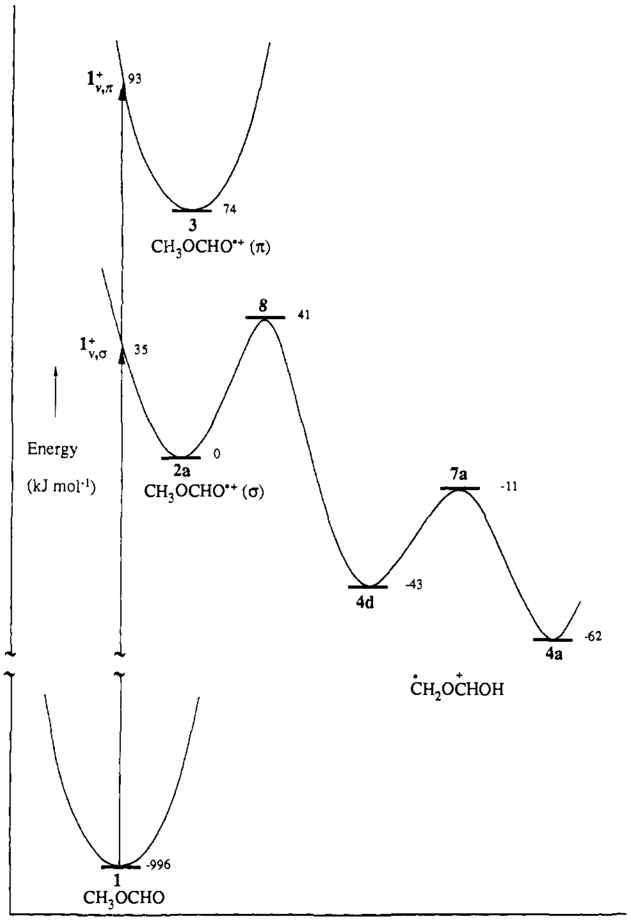

Figure 4. Schematic potential energy profile (QCISD(T)/6-311G**//HF/6-31G* plus zero-point vibrational corrections) describing ionization of methyl formate (**1**) and the subsequent rearrangement of ionized methyl formate (**2a**) to distonic isomers (**4d** and **4a**).

Methyl Formate Radical Cation: The σ Ground State (2). Our calculations predict that the ground state of the methyl formate radical cation is the $^2A'$ (σ) state, arising formally from removal of an electron from the 13a′ HOMO of neutral methyl formate (**1**). We note that the resulting singly occupied molecular orbital (SOMO) in the radical cation (**2**) has large coefficients not only on the oxygen atom of the carbonyl group but also on the oxygen and carbon atoms of the CH_3O group.

As in the neutral parent, **2** can exist in configurations with COCO syn and anti and with staggered and eclipsed conformations of the methyl group. We only show here those structures (**2a** and **2b**, Figure 1) which are minima on the ground-state energy surface. These may be described as COCO syn, methyl-staggered (**2a**) and COCO anti, methyl-eclipsed (**2b**). The alternative COCO syn, methyl-eclipsed and COCO anti, methyl-staggered conformations have a single calculated imaginary frequency and represent transition structures for internal rotation. The corresponding barriers to methyl rotation amount to 0.6 and 1.8 kJ mol^{-1} (HF/3-21G) in **2a** and **2b**, respectively. The COCO syn form **2a** is found to be more stable by 6 kJ mol^{-1} (MP4/6-311G**) than the anti form **2b**, but a barrier of 57 kJ mol^{-1} (via transition structure **6**, MP4/6-311G**) separates **2b** from **2a**. The preferred conformation in **2** is the same as that in the neutral counterpart (**1**). Comparison of the calculated structures for **1** and **2a** shows that the effect of ionization is substantial. The terminal C–O bond is stretched and the central C–O bond compressed in **2a** compared with **1**, in both cases by nearly 0.1 Å. The changes in bond angles are also appreciable (up to 10°).

From the calculated energies for **1** and **2a**, an adiabatic ionization energy (IE_a) of 10.3 eV is obtained for methyl formate. The vertical ionization energy (IE_v) can also be evaluated as the difference in energy of **1** and the ion resulting from vertical ionization to the $^2A'$ state (denoted $1^+_{v,\sigma}$). The calculated IE_v of 10.7 eV compares favorably with the experimental value of 11.0 eV.[30]

Methyl Formate Radical Cation: The π Excited State (3). As mentioned above, the highest occupied π orbital (3a″) in neutral methyl formate (**1**) lies quite close in energy to the σ HOMO (13a′). The $^2A'$ and $^2A''$ states of the ion are therefore expected to lie close together in energy. Indeed, ionized methyl formate was originally assigned as a π electronic state (**3**).[4-6] Our calculations indicate, however, that the $^2A''$ state (**3**) lies 74 kJ mol^{-1} above **2a**. The calculated vertical ionization energy to the $^2A''$ state (corresponding to formation of the structure denoted as $1^+_{v,\pi}$) is 11.3 eV, which compares well with the experimental photoelectron value of 11.6 eV.[30] The calculated difference between the $^2A'$ and $^2A''$ ionization energies is 0.6 eV which may be compared with the experimental separation between the first two bands in the photoelectron spectrum of 0.6 eV.[30]

As in **2a**, the SOMO (3a″) in **3** also possesses large coefficients on atoms of the CH_3O group. One interesting feature of the preferred conformation of **3** is that, in contrast to the situation in **2a** ($^2A'$), it contains an eclipsed methyl group. The relevant staggered conformation is calculated to have one imaginary frequency. The barrier to internal rotation in the $^2A''$ state, as in $^2A'$, is quite small (3.6 kJ mol^{-1}, HF/3-21G).

The Distonic Radical Cation (4). Conformational possibilities for this ion arise from the combination of (i) COCO syn and anti orientations with respect to the C–O(CH_2) bond; (ii) OCOH syn and anti orientations with respect to the C–O(H) bond; and (iii) different configurations of the CH_2 group including planar, symmetrical pyramidal (C_s) and asymmetrical pyramidal (C_1). We have examined a large number of these combinations at the HF/3-21G level and, on the basis of the results so obtained, have selected four equilibrium structures (**4a–d**) for examination at higher levels.

The four equilibrium structures of the distonic species (**4**) are ordered in energy as follows: **4a** (0 kJ mol^{-1}, MP4/6-311G**) < **4b** (1) < **4c** (11) < **4d** (15) with the COCO syn, OCOH anti conformation **4a** being the most stable closely followed by the COCO anti, OCOH syn conformation **4b**. It is interesting to note that all these conformations of the distonic ion are calculated to be of *lower* energy than the conventional isomers (**2a** and **2b**). The energy difference between the most stable distonic species **4a** and the most stable methyl formate cation **2a** amounts to 62 kJ mol^{-1} (Table III) in favor of the former.

All four structures (**4a–d**) have an essentially planar COCOH skeleton. Nonplanarity is largely introduced through the pyramidal disposition of the the bonds of the terminal CH_2 group. In all cases, arrangement of the CH_2 group in either planar or symmetrical–pyramidal (C_s) orientations leads to geometries exhibiting one imaginary frequency at the HF/6-31G* level. These structures presumably represent transition structures for inversion and rotation, respectively, of the CH_2 group.

In contrast to structures **4a–c**, **4d** has the terminal methylene group almost perpendicular to the COCOH plane. Perhaps this arrangement in **4d** may be attributed to stabilization by O—H···C bonding. Alternatively, the all-planar arrangement may be destabilized by steric repulsion between the hydroxyl hydrogen and one of the hydrogen atoms of the CH_2 group, and this would be minimized by rotation about the O–CH_2 bond. The barrier to rotation about the O–CH_2 bond amounts to 7.1 kJ mol^{-1} (HF/3-21G). The structure calculated at the HF/6-31G* level for **4d** is asymmetric, the two methylene hydrogen atoms being very slightly nonequivalent. The closely related symmetrical (C_s) structure, although a minimum at the HF/3-21G level, has one small imaginary frequency at HF/6-31G*. At the MP2/6-311G**//HF/6-31G* level, however, the C_s structure lies less than 0.1 kJ mol^{-1} above **4d**.

According to the Mulliken population analysis, the positive charge in **4** is shared by the central carbon and hydrogen atoms

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(30) Cannington, P. H.; Ham, N. S. *J. Electron Spectrosc. Relat. Phenom.* **1985**, *36*, 203.

while the spin density of the unpaired electron is located almost exclusively on the terminal carbon. It is directed essentially perpendicular to the COCO plane in **4a–c** but within the COCO plane of **4d**.

Because **4d** is likely to be the initial product resulting from the 1,4-hydrogen migration in **2a**, it is worthwhile to examine its isomerization to the lower energy conformations. Structures **7a** and **7b** (Figure 3) represent the transition structures for the rotations around C–O(H) (yielding **4a**) and C–O(CH_2) (yielding **4b**) bonds, respectively. The calculated barrier heights for both processes are sizable (41 kJ mol^{-1} via **7a** and 54 kJ mol^{-1} via **7b**, MP4/6-311G**). This is consistent with the fact that both these CO bond lengths in **4** lie in the range 1.24–1.27 Å, reflecting partial-double-bond character (Figure 2). Structures **7c** and **7d** represent the transition structures for rotation about the C–O-(CH_2) bond of structure **4a** and the C–O(H) bond of structure **4b** which both lead to structure **4c**. The barriers for the processes **4c** → **4a** and **4c** → **4b** are 64 and 51 kJ mol^{-1} (MP4/6-311G**), respectively.

Unimolecular Rearrangement of Ionized Methyl Formate (2a) to Its Distonic Isomer (4a). Having established that the distonic radical cation (**4**) lies lower in energy than the methyl formate radical cation (**2**), we now examine the interconversion of **2** and **4** by means of an intramolecular hydrogen transfer. The corresponding transition structure **8** (Figure 3) has a methyl-eclipsed conformation implying rotation of the CH_3 group during the rearrangement process. The barrier height for the reaction decreases substantially with the inclusion of electron correlation. Our best estimate for the barrier height (Table III) is 41 kJ mol^{-1}. The corresponding calculated exothermicity is 62 kJ mol^{-1}. The calculated activation entropy ($\Delta S^{\ddagger} = -19.8$ J mol^{-1} K^{-1}, Table IV)[31] is surprisingly large for a unimolecular reaction, implying an appreciable entropic contribution to the free energy of activation ($\Delta G^{\ddagger} = 44.6$ kJ mol^{-1} at 298 K). The tunnelling correction to the reaction rate, estimated using the Wigner approximation,[32] is substantial (28.9 at 140 K). This is consistent with the markedly higher observed[8] stability (with respect to rearrangement) of the σ^* complex in the case of $CD_3OCHO^{\bullet+}$ compared with $CH_3OCHO^{\bullet+}$. Our calculated energies (Table III, Figure 4) suggest that the methyl formate radical in its σ ground state (**2a**) should be observable in a matrix at low temperature (4 K). It should be pointed out, however, that the energy of vertically ionized methyl formate ($\mathbf{1}^{+}_{v,\sigma}$) lies very close to that of transition structure **8**, so that transformation of $\mathbf{1}^{+}_{v,\sigma}$ to **4d** requires substantially less energy (6 kJ mol^{-1}) than does transformation of **2a**. Our calculations do not provide any information regarding the likelihood of complexation of **2a** with the freon matrix.

In summary, our calculated results provide theoretical support for the view that the ion observed at higher temperatures (e.g., 140 K) in the matrix experiments[3-9] is the distonic ion **4**. Our results suggest that the ion produced at lower temperatures is the σ ground state of ionized methyl formate (**2a**) (which at intermediate temperatures might form a complex with the matrix) rather than the π state **3**. The distonic ion (**4**) is likely to be produced along with ionized methyl formate in the mass spectroscopic studies, as proposed also to account for the rearrangement–fragmentation processes in ionized methyl acetate.[33]

Concluding Remarks

In this paper, we have presented a detailed theoretical study of the structures and stabilities of ionized methyl formate (**2, 3**) and its distonic isomer (**4**). Our calculations predict that the initially formed ion has a σ ground state ($^2A'$, **2a**). The electronically excited π state ($^2A''$, **3**) lies 74 kJ mol^{-1} higher in energy. The methyl formate ion (**2a**) is, however, less stable than the *distonic* species **4a** (by 62 kJ mol^{-1}) and rearranges to the latter with an energy barrier of about 41 kJ mol^{-1}. The activation entropy is negative and appreciable (~ -20 J mol^{-1} K^{-1}). Overall, these data predict that the primary methyl formate ion (**2a**) can exist as a discrete species at very low temperature but converts to the more stable distonic isomer (**4**) upon warming. The possibility of complexation between the σ ion **2a** and matrix molecules (CF_3Cl) cannot be excluded.

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Registry No. 1, 107-31-3; **2**, 82188-89-4; **4**, 91024-59-8.

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[32] See, for example: Glasstone, S.; Laidler, K. J.; Eyring, H. *The Theory of Rate Processes*; McGraw-Hill: New York, 1941.

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