1260 *J. Phys. Chem. A* **1997,** *101,* 1260−1266

UV-Induced Rotamerization and Vibrational Spectra of the Conformers of Cyanomethyl Formate: Matrix Isolation Infrared and ab Initio Studies

M. Dahlqvist*

Department of Organic Chemistry, University of Turku, FIN-20500, Turku, Finland

M. Hotokka

Department of Physical Chemistry, Åbo Akademi, FIN-20500, Turku, Finland

M. Räsänen

Laboratory of Physical Chemistry, P.O. Box 55, University of Helsinki, FIN-00014, Helsinki, Finland

Received: July 24, 1996; In Final Form: October 4, 1996⊗

Ab initio RHF and MP2 calculations with the standard 6-31G* and 6-311G** basis sets were carried out on cyanomethyl formate ($HCOOCH_2CN$). The calculations indicated two stable conformers (*Z,ap* and *Z,sc*) for this molecule. However, the energy difference between the conformers varied at different levels of theory. The calculations with the 6-311G** basis set and correlated wave functions indicated equal energy for these conformers, whereas all the other calculations slightly preferred the *Z,ap* conformer (by 0.2−2.1 kJ mol^{-1}). The existence of the *Z,ap* and *Z,sc* conformers of cyanomethyl formate was confirmed by matrix isolation infrared studies in argon. Immediately after deposition the spectrum showed two peaks both in carbonyl and asymmetric C−O−C stretching regions. The behavior of these pairs of infrared peaks upon UV irradiation and the comparison with the results obtained for related esters strongly indicate that these doublets are caused by two different conformers. It was observed that the *Z,ap* and *Z,sc* conformers can be surmounted thermally in an argon matrix. This is consistent with the calculated values of 2.6 kJ mol^{-1} (MP2/6-31G*) or 3.7 kJ mol^{-1} (RHF/6-31G*) for the potential energy barrier of this process. A conformer interconversion process, proceeding from both the *Z,ap* and *Z,sc* to the *E,sc* conformer, was induced by UV irradiation at 248 nm. The *E,sc* conformer is the main product of isomerization. This was established by ab initio calculations and by analysis of the spectral changes in the (C═O) and (C−O−C) stretching regions. Upon prolonged irradiation at the same wavelength, the *E,sc* conformer decomposed to stable products including a hydrogen-bonded (1:1) complex of CO and cyanomethanol. (CO_2 production was also observed. However, its counterpart could not be identified, presumably due to further decomposition.)

Introduction

In matrixes at low temperatures (10−60 K) thermal, Boltzmann type conformational equilibrium tends to favor the population of only the state corresponding to the lowest energy conformer, unless the conformational energy differences are small (a few hundred J mol^{-1}). If the potential energy barriers are low (at 20 K lower than 6 kJ mol^{-1}), they can be surmounted thermally in matrixes. If the barriers are higher, the higher energy conformers can be "trapped" at these low temperatures. Thus, otherwise inaccessible higher energy conformers can be observed as products of photoprocesses in matrixes, provided the energy barriers for photoprocesses are not too high and barriers for thermal processes not too low.[1] Usually infrared-induced processes proceed without decomposition of the sample, whereas UV-induced processes tend to produce both higher-energy conformers and decomposition products.

Although a number of compounds have been investigated in low-temperature matrixes, only a few studies concerning the formic acid esters have been reported. Owing to the small size of the acyl group, these esters play an interesting role in conformational studies of esters. It has been reported that some formates with bulky alkyl groups can give rise to rotational isomers as a result of internal rotation around the C(O)-O bond. *tert*-Butyl formate is a classical example, for which both the *Z* and *E* conformers have been observed under normal conditions.[2] (For the ester conformers, the same notation is used in this paper as previously for other alkyl-substituted formates.[3] See Figure 1.) It is probable that the existence of the *E* conformation is generally possible for other esters only when the molecular structure is determined by ring formation (lactones).[4]

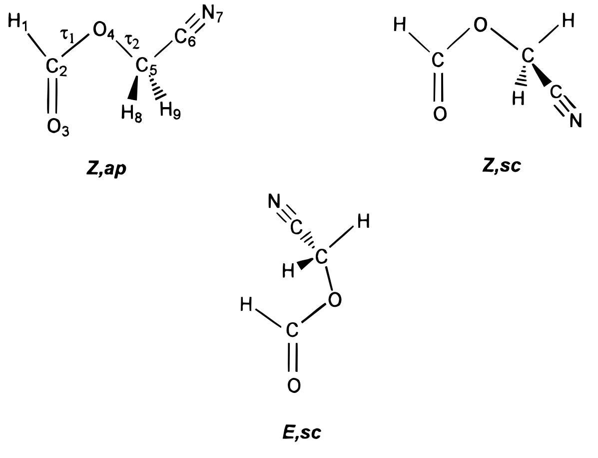

Figure 1. Conformers of cyanomethyl formate. Atom numbering and the axes of internal rotation (τ_1 and τ_2) are depicted for the *Z,ap* conformer.

Some years ago Müller et al.[5] observed that irradiation at 248 nm led to photorotamerization of methyl formate from *Z*

⊗ Abstract published in *Advance ACS Abstracts,* January 1, 1997.

S1089-5639(96)02242-6 CCC: $14.00

to *E* conformation. As a result of this study the infrared spectra and vibrational assignments for the unstable *E* conformation of methyl formate and its deuterium derivatives have been reported in detail. Furthermore, it was observed that due to a too low barrier of thermal processes, the unstable *E* conformation decomposes in a consecutive photolysis step by three different routes, leading to a hydrogen-bonded (1:1) complex between CO and methanol, for example.

After the above-mentioned study we reported the UV-induced conformer interconversion process for chloromethyl formate ($HCOOCH_2Cl$) in a cryogenic argon matrix.[6] In this study we have showed that the only stable conformation (*Z,sc*) of chloromethyl formate interconverts to the unstable *E,sc* conformation on irradiation in a narrow wavelength region between 255 and 275 nm. In a further paper we have reported the results obtained by irradiation of chloromethyl formate and vinyl formate at shorter wavelengths.[7] Decomposition of the sample enabled us to measure and analyze in detail the matrix infrared spectra of two novel substituted methanols, chloromethanol and vinyl alcohol.

The preparation and investigation of cyanomethyl formate ($HCOOCH_2CN$) continue our interest in this type of molecules and their photoprocesses. Cyanomethyl formate is interesting in the following respects:

(i) No previous spectroscopic or other physicochemical studies of this particular molecule are known to the authors.

(ii) It is the cyano analogue of ethyl and propargyl formates for which the conformers *Z,ap* and *Z,sc* have been observed under normal conditions by vibrational spectroscopy[8,9] and, on the other hand, the cyano analogue for chloromethyl formate which exists only in the *Z,sc* conformation.[6,10]

(iii) If the photoprocess proceeds as in the case of chloromethyl and vinylformates,[7] one would expect cyanomethanol to be one of the decomposition products. This would confirm the concept that formic acid esters, as precursors, allow for the production of alcohols, which have the same alkoxy groups as their precursors.

(iv) In our laboratory one of the authors has used cyanoalkyl esters as starting materials in the studies of enzymatic acyl-transfer reactions.[11] Thus, their physicochemical properties are also of interest.

For comparative purposes, we have carried out ab initio calculations at different levels of theory aiming to study structural parameters and relative energies of possible conformers, heights of the barriers to internal rotations, vibrational spectra, and assignments of the normal modes of cyanomethyl formate.

Experimental Section

Cyanomethyl formate was prepared in the usual way from cyanomethanol (glycolic acid nitrile, $CNCH_2OH$, Fluka AG) and formic acid (HCOOH, Merck, Uvasol). The final distillation was performed with a Perkin-Elmer 251 auto annular still and the fraction boiling at 70−71 °C/19 mmHg (n_d^{20} 1.4072) was collected. The purity of the product was established by gas chromatography.

The matrixes were prepared by spraying a 1:500 mixture of cyanomethyl formate and Ar onto a CsI window at 15 K. The spectra were run on a Nicolet 60 SX FTIR-spectrometer, typically at 0.5 cm^{-1} resolution. Irradiation was performed by a KrF (248 nm) excimer laser (ELI-76, Estonian Academy of Sciences), the 10 ns pulse energies at the sample (diameter 20 mm) being ~10 mJ.

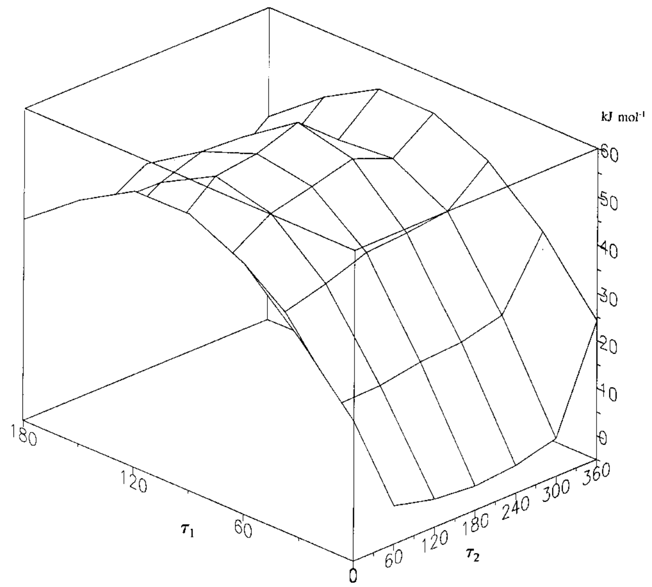

Figure 2. Ab initio RHF/3-21G calculated potential energy surface for cyanomethyl formate.

Results and Discussion

Ab Initio Calculations. The ab initio calculations were performed mainly by the GAMESS software package.[12] The initial potential energy surface (PES) map was produced at the restricted Hartree−Fock level of theory (RHF/3-21G).[13] This economical method is quite sufficient for rough mapping of the conformational space of organic molecules. The minima and saddle points were reoptimized at the RHF/6-31G* level.[14] The vibrational zero-point energies and the correlated energies were calculated using the 6-31G* basis set at the RHF geometry. The correlation energies were calculated using the second-order Møller−Plesset perturbation theory (MP2).[15] The basis set superposition error was estimated using the 6-311G** basis set.[16] The error turned out to be almost the same for both *Z,ap* and *Z,sc* conformers and was therefore omitted. The vibrational analysis at the three minima is based on analytical Cartesian force constant matrixes calculated at the RHF/6-311G** level at a carefully reoptimized geometry by Gaussian-92.[17] To allow for comparison with experimental results, the calculated wavenumbers were scaled by factors 0.91 and 0.88 in the regions of 4000−2800 and 2800−0 cm^{-1}, respectively. A separate program was used for the calculation of the potential energy distributions (PED) in terms of symmetry coordinates.[7,18]

The potential energy surface calculated at the RHF/3-21G level of approximation is shown in Figure 2. The figure clearly indicates that the most important conformations are those with $\tau_1 = 0°$ (*Z* conformations) and that those with $\tau_1 = 180°$ (*E* conformations) correspond to local minima. Cross sections of the PES at these two torsional angles, calculated at the RHF/6-31G* level, are shown in Figure 3. The energies of the minima and saddle points are given in Table 1. The geometries at the minima are reported in Table 2.

Cyanomethyl formate has two minimum energy conformations, the *Z,ap* and *Z,sc* forms (Figure 1). Our calculations with the 6-311G** basis set and correlated wave functions show that these two minima have the same energy. This means that both conformations are equally populated at all temperatures. According to the Hartree−Fock calculations with the same basis set, the *Z,ap* is the most stable conformation, *Z,sc* being 2.1 kJ mol^{-1} less favorable. The barrier between the conformers is low, only 2.6 kJ mol^{-1} (MP2) or 3.7 kJ mol^{-1} (RHF), suggesting

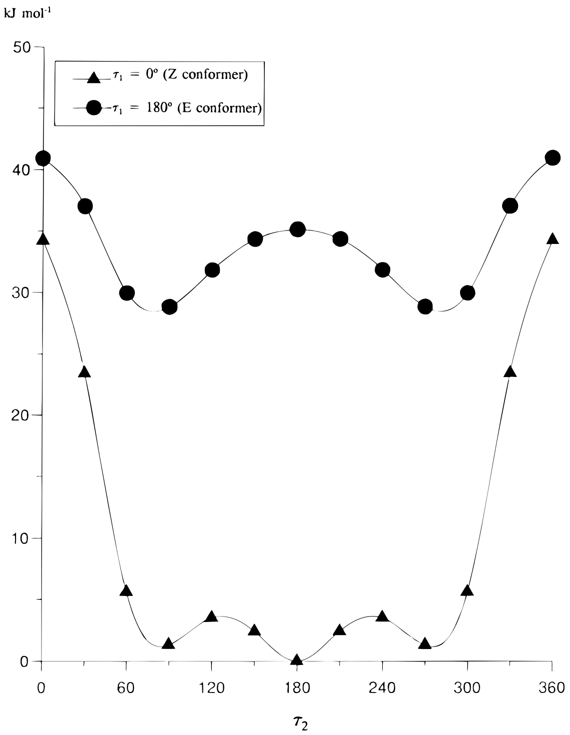

Figure 3. Ab initio RHF/6-31G* calculated cross-sections of the potential energy surface of cyanomethyl formate at torsional angles τ_1 and τ_2.

TABLE 1: Energies (kJ mol^{-1}) of Cyanomethyl Formate at the Minima and Saddle Points (sp) of the Potential Energy Surface[a]

	conformation					
level	*Z,ap*	*Z,sc*	*E,sc*	*Z,ac*(sp)	*E,ap*(sp)	*Z*−*E*(sp)
HF/6-31G*	0	1.1	28.3	3.7	41.9	51.9
HF/6-311G**	0	2.1	28.6			
Corr/6-31G*	0	0.2	27.6	2.6	48.8	53.9
Corr/6-311G**	0	0.0	25.2			

[a] The reported energies have been calculated using 6-31G* and 6-311G** basis set and are relative to the most stable conformation. The corrected energies include an MP2 correlation correction and the zero-point energy.

TABLE 2: Ab Initio RHF/6-31G* Geometries for Conformers *Z,ap*, *Z,sc*, and *E,sc* of Cyanomethyl Formate[a]

	conformer		
internal coordinates	*Z,ap*	*Z,sc*	*E,sc*
$C{=}O$	118	118	117
C_2O_4	133	133	134
O_4C_5	141	141	140
CC	147	148	148
CN	113	113	113
$O{=}C{-}O$	125	125	122
COC	116	117	118
OCC	107	111	112
$H_1C_2O_4C_5$ (τ_1)	0	0	180
$C_2O_4C_5C_6$ (τ_2)	180	83	78

[a] The bond lengths are given in picometers and the angles in degrees.

thermal equilibrium between these species even at the matrix temperatures used.[1]

The value for the dihedral angle $C_2O_4C_5C_6$ of the *Z,sc* conformer was calculated to be 83° (Table 2). This value is almost the same as calculated previously for chloromethyl formate (86°)[6] and fluoromethyl formate (84°).[19]

The *E,sc* conformation also corresponds to a local minimum on the conformational PES, but it lies 25.2 kJ mol^{-1} (MP2/6-311G** + ZPE) above the stable conformations and can be neglected under normal conditions. For comparison, it can be mentioned that the values of 23.3 (MP2/6-31G** + ZPE) and 21.4 kJ mol^{-1} (HF/4-31G*) have been reported for the *E* conformation of methyl formate[20] and the *E,sc* conformation of chloromethyl formate,[6] respectively. The experimental value for the *E* conformation of methyl formate is 19.9 ± 0.8 kJ mol^{-1}.[21]

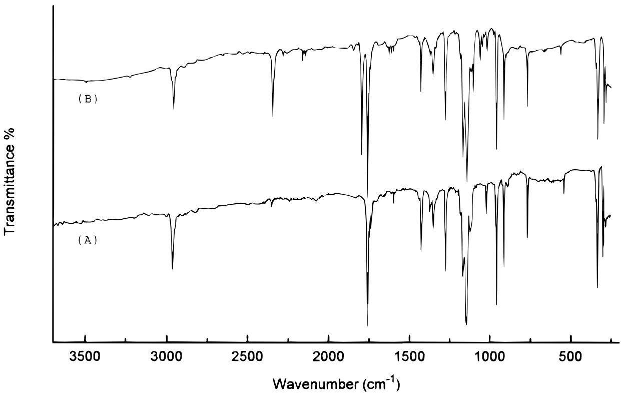

Figure 4. Argon matrix spectra of cyanomethyl formate at 15 K: (A) recorded immediately after deposition; (B) after ~4000 pulses at 248 nm.

The barrier to internal rotation from the *Z,ap* to the *E,sc* conformation is calculated to be 53.9 kJ mol^{-1} (MP2/6-31G* + ZPE), which corresponds to 4500 cm^{-1}. This value is large enough to prevent infrared-induced photorotamerization as confirmed experimentally in this work. On the other hand, the value of 29 kJ mol^{-1} for the height of the reverse barrier (process *E,sc*→*Z,ap*) suggests that the *E,sc* conformer should be thermally stable at temperatures below 60 K.[1]

It is interesting to note that the calculated *Z,ap*→*E,sc* barrier of cyanomethyl formate is close to the value of 56.2 kJ mol^{-1} (MP2/6-31G* + ZPE) calculated for *Z*→*E* barrier of methyl formate[20] but significantly greater than that of 45 kJ mol^{-1} (HF/4-31G*) calculated for the *Z,sc*→*E,sc* barrier of chloromethyl formate.[6] It was observed experimentally that chloromethyl formate photorotamerizes as a result of lower energy UV irradiation than methyl and cyanomethyl formates, in accordance with the calculated values.

Cyanomethyl formate behaves in accordance with the "*trans*-angle rule" proposed originally for alcohols and amines and extended later to other compounds, too.[22] As can be seen from Table 2, the angle OCC for the *Z,ap* conformer of cyanomethyl formate is 4° smaller than that of the *Z,sc* conformer. This is in accordance with the "*trans*-angle rule", which can be generalized as follows: if in a nonlinear bonding sequence XCYZ (Y = O or N) the bond XC is *trans* to the bond YZ, the angle XCY is 3−7° smaller than in other conformations of molecule.

The Conformers after Deposition. The infrared spectrum of cyanomethyl formate in an argon matrix, recorded immediately after deposition at 2 cm^{-1} resolution, is shown in Figure 4A. Spectrum B in the same figure was recorded after UV irradiation at 248 nm. It can be seen that the irradiation has induced both photorotamerization and decomposition of the sample. Parts of expanded spectra, recorded at 0.5 cm^{-1} resolution and showing the most important changes upon the UV irradiation at 248 nm are presented in Figure 5.

As can be seen from Figure 5A the spectrum recorded immediately after deposition shows two carbonyl (1763 and 1760 cm^{-1}) and two asymmetric C−O−C stretching peaks (1163 and 1138 cm^{-1}). Because our ab initio calculated values

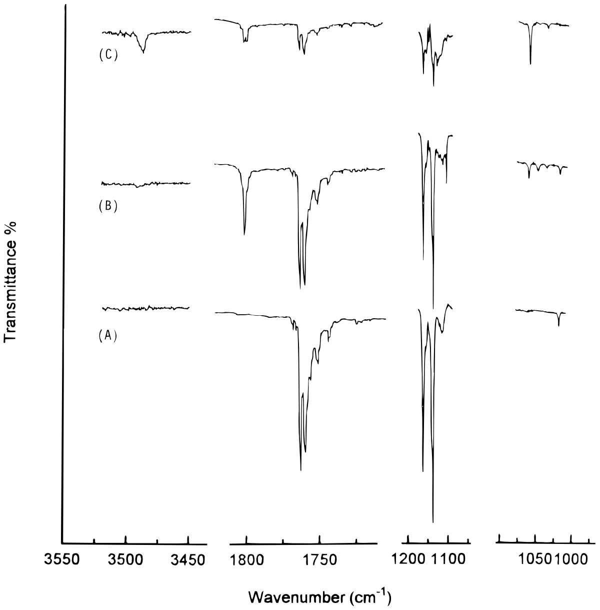

Figure 5. Parts of the expanded spectra (recorded at 0.5 cm^{-1} resolution), showing the most important changes of cyanomethyl formate upon UV irradiation at 248 nm: (A) recorded immediately after deposition, (B) after ~4000 pulses, and (C) after ~20000 pulses.

for vibrational frequencies of the carbonyl and asymmetric C−O−C stretching peaks of the *Z,ap* and *Z,sc* conformers of cyanomethyl formate agree well with the values observed in the argon matrix spectrum, these doublets can be attributed to the presence of these two conformers.

This assignment is confirmed by comparing these doublets and their behavior upon UV irradiation with the results obtained for related esters[8,9] and from ab initio calculations.

According to our ab initio calculations with the 6-311G** basis set and correlated wave functions the conformers *Z,ap* and *Z,sc* of cyanomethyl formate have equal energies. This causes the Boltzmann type conformational equilibrium to lead to equal population of both conformers even in the low-temperature argon matrix. Consequently the appearance of the conformer sensitive carbonyl and ester peaks as doublets can be taken as evidence that two different conformers cause the peaks.

Because the calculated energy barriers between the *Z,ap* and *Z,sc* conformers are in the range 2.6−3.7 kJ mol^{-1} (see Table 1) the conformers can be surmounted thermally in the matrix. This leads us to expect that the relative intensities of the conformer doublets should not change upon UV irradiation. As can be seen from Figure 5, both of the doublets behave accordingly. No attempts were made to evaluate the possible small energy difference between these species.

As mentioned in the Introduction, ethyl and propargyl formates (analogues for cyanomethyl formate) exist in *Z,ap* and *Z,sc* conformers under normal conditions.[8,9] It was shown by crystallization of the sample that the appearance of the asymmetric C−O−C stretching vibration as a doublet is in both cases indicative of the presence of the above-mentioned conformers. However, the carbonyl stretching vibrations of these compounds were observed to appear as singlets. (It must be mentioned at this stage that despite many attempts we were not able to crystallize liquid cyanomethyl formate.)

The calculated vibrational frequencies of cyanomethyl formate suggest that the higher and lower frequency carbonyl stretching peaks represent *Z,sc* and *Z,ap*, and the corresponding asymmetric stretching peaks *Z,ap* and *Z,sc* conformers, respectively (see Table 4). This means that the asymmetric C−O−C stretching peaks behave in a fashion similar to those of ethyl and propargyl formates. We have every reason to assume that the carbonyl stretching bands behave similarly in all these three esters even though only the singlet bands were observed in the case of ethyl and propargyl formates. This assumption is based on the fact that for cyanomethyl formate the wavenumber difference in argon matrix between the two carbonyl peaks is only 3 cm^{-1}. Because the spectra of ethyl and propargyl formates have been recorded in gas, liquid, and crystalline solid phases, it is evident that the wavenumber difference is too small to allow for the resolution of the conformer bands in these phases.

TABLE 3: Local-Symmetry Coordinates for Cyanomethyl Formate

symmetry coordinates	description
$S_1 = r_1$	ν(CN)
$S_2 = r_2$	ν(C−C)
$S_3 = r_3$	$\nu(O_4-C_5)$
$S_4 = r_4$	$\nu(C_2-O_4)$
$S_5 = r_5$	$\nu(CH_1)$
$S_6 = r_6$	ν(C=O)
$S_7 = (1/\sqrt{2})(r_7 + r_8)$	$\nu(CH_2)_{symm}$
$S_8 = (1/\sqrt{6})(2\alpha_1 - \alpha_2 - \alpha_3)$	δ(O=C−O)
$S_9 = (1/\sqrt{2})(\alpha_2 - \alpha_3)$	$\delta(CH_1)$
$S_{10} = \alpha_4$	δ(C−O−C)
$S_{11} = (1/\sqrt{30})(5\alpha_5 - \alpha_6 - \alpha_7 - \alpha_8 - \alpha_9 - \alpha_{10})$	δ(O−C−C)
$S_{12} = (1/2)(\alpha_6 + \alpha_7 - \alpha_8 - \alpha_9)$	wag (CH_2)
$S_{13} = (1/2\sqrt{5})(4\alpha_{10} - \alpha_6 - \alpha_7 - \alpha_8 - \alpha_9)$	sciss (CH_2)
$S_{14} = (1/\sqrt{2})(r_7 - r_8)$	$\nu(CH_2)_{asymm}$
$S_{15} = (1/2)(\alpha_6 - \alpha_7 - \alpha_8 + \alpha_9)$	twist (CH_2)
$S_{16} = (1/2)(\alpha_6 - \alpha_7 + \alpha_8 - \alpha_9)$	rock (CH_2)
$S_{17} = \gamma_1$	$\gamma(CH_1)$
$S_{18} = \gamma_2$	γ(C−CN)
$S_{19} = \delta$	δ(C−CN)
$S_{20} = \tau_1$	$\tau(C_2-O_4)$
$S_{21} = \tau_2$	$\tau(O_4-C_5)$

Assigning the other peaks of cyanomethyl formate to the *Z,ap* and *Z,sc* conformers is difficult. This is mainly due to the fact that absorption bands may coincide or the intensities of the peaks are too weak to allow definite identification. Only three pairs of infrared peaks, appearing in the spectrum immediately after deposition and losing their intensities with equal rates upon UV irradiation of the sample, can be identified to the *Z,ap* and *Z,sc* conformer doublets. These peaks and their assignments (see Table 4) are as follows: 1453 (*Z,ap*) and 1431 (*Z,sc*) scissor (CH_2), 1276 (*Z,ap*) and 1281 (*Z,sc*) twist (CH_2), and 910 (*Z,ap*) and 890 cm^{-1} (*Z,sc*) (C−C) stretching vibration.

The Photoprocess Producing the *E,sc* Conformer. As can be seen from Figures 4B and 5B,C, UV irradiation induces changes in the spectrum of cyanomethyl formate. The peaks of *Z,ap* and *Z,sc* conformers diminish and new peaks grow. Even though the number of the peaks increasing in intensity in the spectra of cyanomethyl formate was found to be smaller than in the case of methyl and chloromethyl formates,[5,6] the photoprocess proceeds in a straightforward manner.

As can be seen from Table 1, in addition to the *Z,ap* and *Z,sc* conformers, the *E,sc* conformer of cyanomethyl formate also corresponds to a local minimum at 25.2 kJ mol^{-1} above the energy of the stable *Z* conformers. Because the ab initio calculated value of 29 kJ mol^{-1} to the process *E,sc*→*Z,ap* allows trapping of the *E,sc* conformer, it is reasonable to expect that UV irradiation of the sample should produce this conformer. The three increasing peaks, which can be related to the conformer sensitive ν(C=O) and asymmetric and symmetric ν(C−O−C) vibrations, offer good evidence in support of this conclusion.

The new carbonyl peak emerging at 1801 cm^{-1} is a strong indication of the fact that irradiation leads to the *E,sc* conformation. This conclusion is based on the facts that the ab initio

TABLE 4: Observed (Ar Matrix) and ab Initio RHF/6-311G Calculated Wavenumbers ($\mathrm{cm^{-1}}$) for Conformers *Z,ap*, *Z,sc*, and *E,sc* of Cyanomethyl Formate**

Z,ap			*Z,sc*			*E,sc*			
exp	calc[a]	PED[b]	exp	calc[a]	PED[b]	exp	calc[a]	PED[b]	assignm
3020[c]	2995	100(14)	3020[c]	3020	99(14)		2994	96(14)	$\nu(\mathrm{CH_2})_{\mathrm{as}}$
2969	2977	98(5)	2969	2979	96(5)		2898	97(5)	$\nu(\mathrm{CH_1})$
2963	2950	99(7)	2963	2969	97(7)		2947	94(7)	$\nu(\mathrm{CH_2})_{\mathrm{sy}}$
2258	2304	91(1), 9(2)	2258	2297	92(1), 8(2)		2295	92(1), 8(2)	ν(CN)
1760	1757	85(6), 6(4), 6(9)	1763	1766	85(6), 6(4), 6(9)	1801	1808	87(6), 6(9)	ν(C=O)
1453	1429	96(13)	1431	1414	97(13)		1429	90(13), 6(9)	$\delta(\mathrm{CH_2})$
1374	1354	86(12), 7(2)	1374	1356	75(12), 14(9)		1346	84(12), 7(9), 5(2)	w($\mathrm{CH_2}$)
1358	1340	93(9)	1358	1342	78(9), 17(12)		1378	81(9), 9(13), 6(12)	$\delta(\mathrm{CH_1})$
1276	1221	97(15)	1281	1260	85(15), 8(4)		1263	80(15), 12(4)	tw($\mathrm{CH_2}$)
1163	1185	58(4), 24(3), 14(8)	1138	1162	45(4), 29(3), 14(8)	1106	1135	40(4), 46(3), 6(15)	$\nu(\mathrm{COC})_{\mathrm{as}}$
1021	1039	100(17)	1021	1038	99(17)	1040	1030	97(17)	$\gamma(\mathrm{CH_1})$
962	987	89(16), 5(18)		1016	66(16), 10(10),6(3), 6(15)	974	950	58(16), 20(4), 11(8), 6(3)	$\rho(\mathrm{CH_2})$
958	969	60(3), 18(4), 10(11), 5(10)		935	55(3), 17(4), 12(2), 6(16), 5(8)	1052	1055	27(3), 22(16), 15(8), 13(4), 10(10), 9(15)	$\nu(\mathrm{COC})_{\mathrm{sy}}$
910	923	54(2), 13(10), 13(11), 8(8), 5(12), 5(1)	890	862	59(2), 22(11), 5(1), 5(3)		856	69(2), 18(11), 6(1)	ν(C−C)
764	742	56(8), 22(2), 8(10), 8(3)	764	740	50(8), 20(10), 13(4), 12(16)	664	666	37(8), 23(11), 8(18), 7(10), 7(2), 6(4), 5(3)	δ(O=C−O)
558	521	46(19), 30(11), 7(2), 6(4), 5(3)	558	558	28(19), 36(11), 16(2), 6(3), 5(8)		506	20(11), 8(19), 25(8), 15(18), 13(3), 10(2)	δ(C−CN) δ(O−C−C)
335	364	81(18), 10(16), 5(15)	335	359	70(18), 13(16), 5(21)		352	22(18), 52(19), 13(16) 7(21)	γ(C−CN) δ(C−CN)
299	298	96(20)	294	310	64(20), 27(19), 5(11)		109	80(20), 11(11)	$\tau(\mathrm{C_2{-}O_4})$
279	260	44(10), 20(19), 17(8), 10(11), 5(2)		296	63(10), 18(8), 14(18)		325	74(10), 15(8), 6(18)	δ(COC)
193[d]	158	38(11), 34(19), 24(10)	193[d]	173	44(11), 39(19), 13(20)		234	29(11), 20(19), 21(20), 25(18)	δ(C−CN) δ(O−C−C)
99[d]	48	78(21), 20(20)	99[d]	50	82(21), 9(10)		64	82(21), 7(18)	$\tau(\mathrm{O_4{-}C_5})$

[a] Calculated wavenumbers are scaled by a factors of 0.91 and 0.88 in the regions 4000−2800 and 2800−0 $\mathrm{cm^{-1}}$, respectively. [b] PED contributions smaller than 5% have been omitted. [c] Liquid phase value. [d] Raman value (liquid).

calculated value for this peak is 1808 $\mathrm{cm^{-1}}$ and that the shift of the carbonyl peak of the *E* conformer to higher wavenumbers has been observed previously in the case of methyl and chloromethyl formates.[5,6] The blue-shifts for methyl, chloromethyl, and cyanomethyl formates are 32, 36, and 38 $\mathrm{cm^{-1}}$, respectively.

Another emerging peak upon UV irradiation was found at 1106 $\mathrm{cm^{-1}}$ and can be assigned to the asymmetric C−O−C stretching vibration of the *E,sc* conformation. For comparison, it can be mentioned that in methyl and chloromethyl formates the corresponding peak appears at 1099 and 1091 $\mathrm{cm^{-1}}$, respectively. Thus, all the formic acid esters studied so far in low-temperature matrixes show the asymmetric ν(C−O−C) peak of the *E* conformation at lower wavenumbers than that of the corresponding *Z* conformation. The red-shifts are 106 and 29 $\mathrm{cm^{-1}}$ for methyl and chloromethyl formates and 32 and 57 $\mathrm{cm^{-1}}$ for the *Z,ap* and *Z,sc* conformers of cyanomethyl formate, respectively. On the basis of these values, it can be concluded that the red-shift of the asymmetric ν(C−O−C) peak of the *E* conformation decreases upon substitution of the alkyl group of formic acid esters.

These results, obtained for the three esters mentioned above, show further that substitution of the alkyl groups decreases the intensities of the asymmetric ν(C−O−C) peaks. In the case of methyl formate[5] the intensity of this peak is very strong, whereas chloro[6] and cyanomethyl formates show medium and weak asymmetric ν(C−O−C) peaks, respectively. Without doubt the differences in the intensities are due to mode mixing. In the case of methyl formate the potential energy distribution (PED) of the asymmetric ν(C−O−C) peak consists of three symmetry coordinates, whereas in the case of chloro and cyanomethyl formates this coordinate is mixed also with other coordinates to a much larger extent. As a result of such mixing, the intensity of this peak decreases because mixing distributes the intrinsinc intensity of this peak over several infrared bands. Additional work to determine the magnitudes of the shifts and intensities of the asymmetric ν(C−O−C) peaks of formic acid esters is, however, needed to explain the substituent effects.

According to ab initio calculations and experimental results obtained for methyl[5] and chloromethyl formate[6] the symmetric ν(C−O−C) peak of the *E,sc* conformation should appear at much higher wavenumbers than that of the *Z* conformers. The experimentally observed blue-shifts for methyl and chloromethyl formates are 96 and 112 $\mathrm{cm^{-1}}$, respectively. For cyanomethyl formate, a peak, increasing in intensity at a rate approximately equal to the carbonyl stretching and asymmetric ν(C−O−C) peaks, can be observed at 1052 $\mathrm{cm^{-1}}$. We assign this peak to the symmetric ν(C−O−C) vibration of the *E,sc* conformation, in agreement with the ab initio calculated value of 1055 $\mathrm{cm^{-1}}$. Consequently, the blue-shift of the symmetric ν(C−O−C) peak is 94 $\mathrm{cm^{-1}}$ when going from the *Z* to the *E,sc* conformation.

The other peaks of cyanomethyl formate, emerging upon UV irradiation and assigned to vibrations of the *E,sc* conformation, are as follow: $\gamma(\mathrm{CH_1})$ at 1040 $\mathrm{cm^{-1}}$, $\rho(\mathrm{CH_2})$ at 974 $\mathrm{cm^{-1}}$, and δ(O=C−O) at 664 $\mathrm{cm^{-1}}$ (see Table 4). It can be observed that the δ(O=C−O) peak shows a red-shift of 100 $\mathrm{cm^{-1}}$ when going from the *Z* to the *E,sc* conformer. This is close to the red-shift value of 132 $\mathrm{cm^{-1}}$, observed for methyl formate.[5] Unfortunately the value of this shift for chloromethyl formate is speculative, because the spectrum of this compound is very complex in this spectral region.[6]

Photodecomposition of the Sample. It can be seen from Figures 4 and 5 that after the photochemical steady state between the conformers *Z,ap*, *Z,sc*, and *E,sc* was reached, some new peaks grew at approximately equal rates in the spectra. This phenomenon indicates that prolonged irradiation leads to decomposition of the sample. The main product in this photoprocess is a hydrogen-bonded (1:1) complex of carbon monoxide (CO) and cyanomethanol ($\mathrm{CNCH_2OH}$).

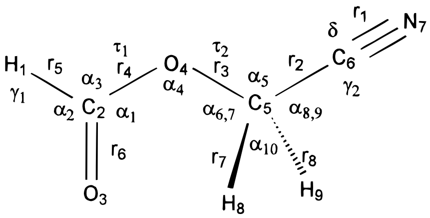

Figure 6. Internal coordinates of cyanomethyl formate (*Z,ap* conformation).

Both CO_2 and CO absorption bands grow during irradiation. The intensity of the asymmetric $\nu(CO_2)$ stretching peak is about 10 times larger than that of ν(CO), suggesting roughly equal yield for complexes containing CO_2 and CO.[23] The complexing species with CO_2 would be acetonitrile. However, no indication of its presence was found, indicating that it is further decomposed on irradiation at 248 nm in solid Ar.

The most intense new peak is located at 1065 cm^{-1}, which is a typical value for the CO stretching vibration of alcohols. Three other significant emerging peaks were found at 3493, 2281, and 376 cm^{-1} and can be assigned to OH stretching, CN stretching, and OH torsional vibrations of cyanomethanol, respectively.

The stretching absorption of carbon monoxide was observed to appear at 2160 cm^{-1}. Thus, there is a blue-shift of 20 cm^{-1} compared to the free CO value when CO forms a complex with cyanomethanol. This is quite a typical shift for CO during complexation. Only an insignificant amount of absorption was recorded at the free CO stretching region. This suggests that cyanomethanol is stable on irradiation at 248 nm and also that the kinetic energy of the fragments during primary photodissociation is insufficient for cage exit. On the basis of our previous experiments, we suggest that the primary process breaks the C_2O_4 bond, forming a short-lived HCO radical. This then donates a H atom to the other fragment yielding cyanomethanol.

Vibrational Assignment. Cyanomethyl formate has 21 normal modes of vibration. Owing to the C_s symmetry of the *Z,ap* and C_1 symmetry of the *Z,sc*, and *E,sc* conformers, all the vibrations are infrared active. The assignments of the normal modes are based on the calculated frequencies and potentential energy distributions (PED). The internal coordinates, used in these calculations are given in Figure 6, and the symmetry coordinates in Table 3. The observed and scaled RHF/6-311G** frequencies as well as the PEDs for the conformers *Z,ap*, *Z,sc*, and *E,sc* of cyanomethyl formate are given in Table 4.

Due to the straightforward assignment of most of the peaks of cyanomethyl formate (only 7 normal modes of 21 do not fulfill the general rule that not less than 66% of the potential energy should be associated with a single internal coordinate to warrant classification as a localized group frequency), the discussion is restricted into cases where additional information was obtained from spectra of related compounds or spectra recorded by other techniques.

In the studies on the infrared spectra of esters with molecular formula $YCOOCH_2X$ (where Y = D, Cl, and CCl_3 and X = Cl, CCl_3, and CN), we have observed that the asymmetric $\nu(CH_2)$ vibration is always invisible in the matrix and vapor phase spectra but appears in the liquid phase with moderate intensity. From the studies of the spectra of solutions with different dielectric strengths, it became evident that the intensity of this band increases with the polarity of the solvent. In the spectra, recorded from polar solutions, it is the most intense band in the 3000 cm^{-1} region. On the basis of these facts, the observed frequency for asymmetric $\nu(CH_2)$, given in Table 4, is taken from the liquid-phase spectrum.

The other very weak absorption in the argon matrix spectrum is assigned to ν(CN). Contrary to the results obtained, for example, for methyl cyanoacetate,[24] this peak is very weak in other phases, too. In the Raman spectrum, recorded from the liquid-phase sample by the authors, the ν(CN) peak appears with strong intensity at 2258 cm^{-1}. On the basis of this value, the very weak matrix infrared peak at 2258 cm^{-1} was assigned to ν(CN).

The calculations of the PEDs for low-frequency skeletal bending modes of cyanomethyl formate indicated in some cases a considerable mode mixing between these vibrations. Especially the δ(O−C−C), δ(C−CN), and γ(C−CN) vibrations are so delocalized that it would be arbitrary to assign them to any group frequency.

Conclusion

The present study of matrix-infrared spectroscopy and ab initio molecular orbital calculations has clarified the existence of the conformers and the assignment of their vibrational spectra as well as the UV-induced photorotamerization and decomposition of cyanomethyl formate. Both theoretical calculations and experimental findings suggest that cyanomethyl formate has two low-energy conformers (*Z,ap* and *Z,sc*), which can be surmounted thermally in a low-temperature argon matrix. Consistent with ab initio calculations, the UV-induced photorotamerization at 248 nm produces the *E,sc* conformation. This process becomes predominant after a photochemical steady state between the three conformers, *Z,ap*, *Z,sc*, and *E,sc*, has been reached. During prolonged irradiation at 248 nm the *E,sc* conformer decomposes to 1:1 complex of cyanomethanol and carbon monoxide or to CO_2 and acetonitrile (the latter of which seems to disappear during photolysis). This experimental finding is consistent with the concept that formic acid ester precursors allow the production of alcohols, which contain the same alkoxy groups as the precursors. Comparison of the results of three different formic acid esters, studied in low-temperature argon matrixes, indicates that the shifts of the most characteristic infrared peaks of the *E* conformers behave similarly. Compared to the corresponding peaks of the *Z* conformers the asymmetric ν(C−O−C) peaks of the *E* conformers are at lower wavenumbers (red-shift), whereas the ν(C=O) and symmetric ν(C−O−C) peaks appear at higher wavenumbers (blue-shift). Additional work is needed to explain the effects of the alkyl substituents determining the magnitudes of these shifts.

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