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Acetylketene: Conformational Isomerism and Photochemistry. Matrix Isolation Infrared and Ab Initio Studies

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The *s-Z* and *s-E* conformers of acetylketene (**5**) were generated by flash vacuum pyrolysis (FVP) and matrix photolysis of precursors **1–4**. Both conformers were characterized by low-temperature IR spectroscopy in argon, xenon, and nitrogen matrices. The observed frequencies and intensities are in excellent agrement with ab initio calculations at the MP2/6-31G* level. UV irradiation of *s-Z*/*s-E*-**5** in nitrogen or xenon matrices allows the clean interconversion of conformers. Prolonged UV irradiation resulted in decarbonylation and formation of methylketene (**7**). However, the photolysis of argon matrix isolated **5** produced a new set of bands in the IR spectrum very close to the *s-Z*/*s-E* absorptions. Annealing of the matrix to 35 K removed these bands. This unusual phenomenon was shown to be due to a photochemically induced matrix site effect. Consistent with experimental observations, high-level calculations (QCISD(T)/6-311+G(2d,p)+ZPVE) predict that the *s-Z* and *s-E* conformers have virtually identical energies.

Introduction

α-Oxo ketenes (acylketenes) are of considerable current interest not only because of their use as intermediates in organic synthesis,[1] but also as the subject of recent kinetic,[2] mechanistic,[2,3] spectroscopic,[2a–d,3a,4] and computational[2e,f,5] studies. In some cases UV spectroscopy in connection with flash photolysis studies has been employed to observe these reactive ketenes directly;[2c,d] however, the method of choice for the characterization of this type of molecules has been matrix isolation IR spectroscopy.[2a,b,4a–f,i,j] In the latter experiments the ketenes are usually generated by pyrolysis[2a,b,4a–f] or matrix photolysis[4a,b,e,f,i,j] of suitable precursors, allowing in some cases the simultaneous observation of individual conformers due to the high resolution achieved under such conditions.[2a,4a–c,i] In agreement with ab initio[5] and semiempirical[5a] calculations open-chain α-oxo ketenes can normally exist as *s-Z* and *s-E* conformers. If substituted by bulky substituents, the *s-E* conformer predominates;[5a] steric hindrance also enhances the stability of these ketenes dramatically.[4c,d]

The first definitive IR spectroscopic observation of acetylketene (**5**), one of the simplest α-oxo ketenes, was published in 1989 by Clemens and Witzeman[2a] who generated acetylketene by pyrolysis of dioxinone **1** followed by trapping in an argon matrix. These authors observed two IR bands for acetylketene which they tentatively assigned to different conformers.[2a] In 1991 Freiermuth and Wentrup[4a] reported their investigtion of the pyrolysis of **1** and assigned the ketene and carbonyl frequencies for *s-Z* and *s-E*-acetylketene (**5**).[4a] Recent independent ab initio calculations by Janoschek et al.[5a] and Birney[5b] on acetylketene (**5**) support these assignments and predict the *s-Z* and *s-E* conformers to be almost equal in energy, with a slight preference for the *s-Z* conformer.[5a,b] On photolysis of acetylketene in an argon matrix, Freiermuth and Wentrup[4a] observed the formation of a new set of strong ketene bands which were ascribed to new conformers or sites.[4a]

The present study aims to clarify the matrix photochemistry of acetylketene. Herein we report a detailed IR characterization of both *s-Z* and *s-E*-acetylketene generated by flash vacuum pyrolysis (FVP) and matrix photolysis of four different precursors (**1–4**). We also show that both forms can be interconverted by UV-induced rotamerization in nitrogen and xenon matrices. The previously described photolysis experiments in argon matrices[4a] were reexamined, and the results can now be interpreted in terms of an unusual matrix site effect. Ab initio calculations were performed to resolve the energetics and geometries of **5** in the ground and excited states and to aid the interpretation of IR spectra.

Experimental and Computational Details

Dioxinone **1** was purchased from Aldrich Chemical Co and vacuum distilled before use. Precursors **2**,[6] **3**,[7] and **4**[8] were prepared as described.[6–8]

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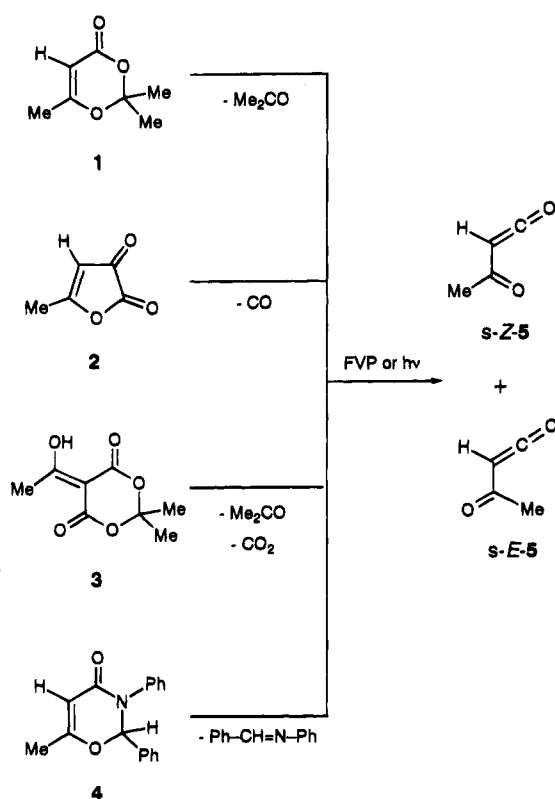
IR spectroscopy was performed using a Perkin Elmer 1720-X FTIR spectrometer typically accumulating 16 scans. The resolution used was 1 cm^{-1} in the spectral range 750–4000 cm^{-1}. Samples were deposited on a BaF$_2$ window cooled by a Leybold–Heraeus (LH) Model ROK 10–300 closed cycle helium cryostat. The temperature of the refrigerator flange was measured using a carbon resistor and an HR-1 digital controller from LH. Spectra were recorded at 14 K unless stated otherwise. The FVP apparatus employed a 100 mm length (8 mm i.d.) quartz tube wrapped with Kantal wire and fitted with a thermocouple in housings flanged directly to the LH cryostat. During deposition an operating pressure of 10^{-5} mbar or lower was maintained. Similar arrangements were used for the direct deposition of precursors. For matrix isolation, samples were sublimed (at −20 °C for **1**, 0 °C for **2**, 30 °C for **3**, 70 °C for **4**) and codeposited with the matrix gas (flow ca. 5 mmol h^{-1}) in ca. 40–60 min, thus ensuring a high M/S ratio to avoid aggregation. Matrix gases were of ultrahigh purity (Ar and N$_2$: 99.999% CIG; Xe 99.999% Spectra Gases). UV irradiation of the matrices was carried out with a 1000 W Hanovia high pressure Xe–Hg lamp with a 150 mm water- and interference filters (Schott) or a monochromator (Schoeffel GM252). For irradiation at 254 nm, a 350 W low pressure Hg lamp (Gräntzel, Karlsruhe) was used.

Standard ab initio molecular orbital calculations[9] were carried out with the GAUSSIAN 92[10] series of programs. Geometry optimizations were performed with the standard polarized split-valence 6-31G* basis set[9] at the Hartree–Fock (HF) and second-order Møller-Plesset perturbation (MP2) levels.[9] Harmonic vibrational frequencies and infrared intensities were predicted at these levels using analytical second derivatives. The directly calculated HF and MP2 frequencies were scaled by 0.8929 and 0.9427, respectively, to account for the overestimation of vibrational frequencies at these levels of theory.[11] For the same reason the calculated zero point vibrational energies (ZPVEs) were scaled by a factor of 0.9135.[11] Improved relative energies were obtained through quadratic configuration interaction with singles, doubles, and augmented triples [QCISD(T)][12] calculations with the larger 6-311+G(2d,p)[9] basis set, based on the MP2(full)/6-31G* optimized geometries. This level of theory is evaluated with the use of the additivity approximation,

$$\Delta E(\text{QCISD(T)/6-311+G(2d,p)}) = \Delta E(\text{QCISD(T)/6-31G*}) -$$
$$\Delta E(\text{MP2/6-31G*}) + \Delta E(\text{MP2/6-311+G(2d,p)}) \quad (1)$$

Our best relative energies discussed below correspond to QCISD(T)/6-311+G(2d,p) values with zero-point vibrational contributions. Unless otherwise noted, these are the values referred to in the text. The frozen-core approximation was employed for all single-point correlated calculations. The vertical transition energies of acetylketene (**5**) and furan-2,3-dione (**2**) were calculated via the configuration interaction with singles (CIS) method[13] using the 6-311+G** basis set,[9] based on the MP2/6-31G* geometry. Several excited states of acetylketene were fully optimized and vibrational frequencies determined numerically at the CIS/6-31G* level of theory.

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Scheme 1

Results

A. s-Z and s-E-Acetylketene by FVP of 1–4. For the present spectroscopic study we have chosen four different thermal and photochemical precursors (**1–4**) to acetylketene (Scheme 1). Apart from the previously employed[2a,4a] 1,3-dioxin-4-one **1** ("diketene–acetone adduct"), 5-acetyl-2,2-dimethyl-1,3-dioxin-4,6-dione (acetyl Meldrum's acid, **3**) and 2,3-diphenyl-6-methyl-2,3-dihydro-4*H*-1,3-oxazin-4-one (**4**) were used, as these systems can be expected[7,8] to undergo efficient cleavage into **5** and acetone/CO$_2$, or benzylideneaniline, respectively. Furan-2,3-diones such as **2** constitute another clean source of α-oxo ketenes.[4d,e,h] These five-membered diones have the advantage that the only byproduct of their fragmentation is CO, which does not interfere with the carbonyl and fingerprint regions of the IR spectrum, in contrast to the situation when acetone (from **1** and **3**) or benzylideneaniline (from **4**) are the byproducts. However, the CO absorptions are very close to the ketene bands of acetylketene (vide infra) and thus make the identification of these bands troublesome. It was therefore necessary to consider all four precursors for a reliable IR identification of s-Z- and s-E-acetylketene.[14]

The FVP of **1–4** was studied in the temperature range from 300–800 °C with product isolation in an argon matrix at 14 K and monitoring by FTIR spectroscopy. All four precursors produced nearly identical spectra of acetylketene, in addition to bands due to acetone (from **1**), CO (from **2**), acetone/CO$_2$ (from **3**), and benzylideneaniline (from **4**). It has been reported[7] that solution thermolysis of **3** gave not only acetylketene (**5**) but also carboxyacetylketene, which was trapped with imines (Scheme 2). However, we found no spectroscopic evidence for carboxyacetylketene, even at the lowest practical pyrolysis temperature (ca. 250 °C).

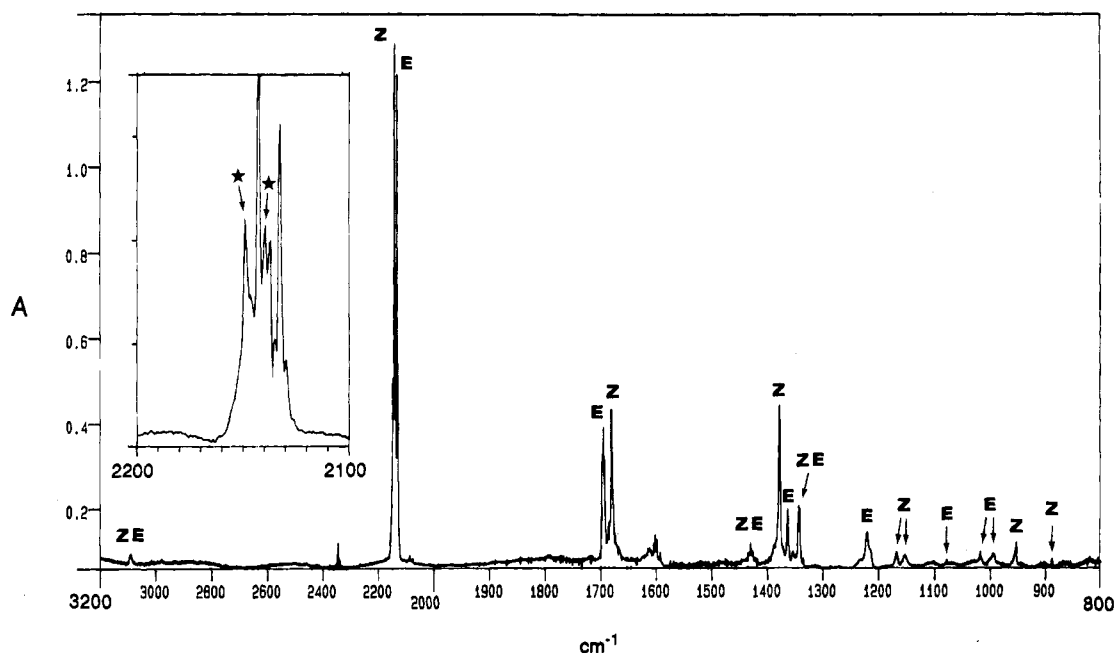Both acetylketene conformers were formed by FVP from all four precursors (**1–4**) and readily identified by

Figure 1. FTIR spectrum (Ar, 14 K) of *s-Z/s-E*-acetylketene (**5**) produced by FVP (400 °C, 10^{-5} mbar) of **2**. Assignments based on *E/Z* isomerization experiments (see Figures 4c and 5) and ab initio calculations (for exact values and discussion of individual bands, see Table 1). Weak bands at 2345 and ca. 1600 cm^{-1} are due to CO_2 and H_2O, respectively. The inset shows the expanded ketene region (2200–2100 cm^{-1}): Bands due to CO (★) are observed at 2149 and 2139 cm^{-1}. The shoulder at 2147 cm^{-1} is due to the minor *s-Z* ketene absorption.

Scheme 2
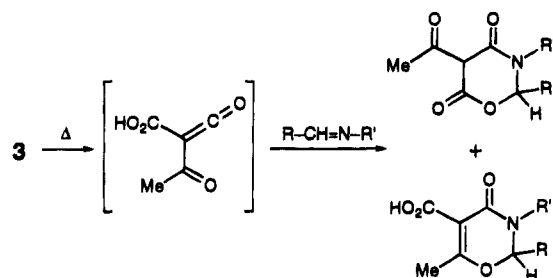
their ketene and carbonyl frequencies.[4a] The ratio of *s-Z* to *s-E* conformer remained virtually unchanged on variation of the pyrolysis temperature (300–800 °C). This implies that a (nearly) 1:1 ratio is present, and hence that the two conformers have almost identical energies (see Section B). The FVP of furandione **2** at 400 °C produced a clean spectrum of the *s-Z* and *s-E* conformers of acetylketene (Figure 1). Apart from the major ketene absorptions at 2143 (*s-Z*) and 2133 cm^{-1} (*s-E*), bands due

to CO (2149, 2139 cm^{-1}),[15] and the minor ketene bands (2148, and 2137 cm^{-1})[4a] were also present in the ketene region (see inset, Figure 1). Figure 2a–c shows the partial IR spectra (ketene region) of *s-Z* and *s-E*-acetylketene generated from **1**, **3**, and **4**. Here the interpretation is not complicated by absorptions due to CO, and this type of precursor (especially **1**) was used for most of the following studies on the *E/Z* isomerization. The minor ketene bands, however, are always present, and their intensities are subject to considerable change (Figure 2). It must be emphasized that these fluctuations in intensities are *not* dependent on the precursor employed or the pyrolysis temperature, but rather on the argon/solute (M/S) ratio *and* the deposition rate, which makes it difficult to exactly reproduce these intensities on going from one precursor to the other (Figure 2a–c). Figures 2, parts d and e, show spectra obtained under "extreme" conditions, i.e. at low M/S ratio with fast deposition (Figure 2d), and high M/S ratio with slow deposition (Figure 2e), respectively. These splittings are evidently due to a matrix site effect[16] and seem to be more pronounced for the *s-E* conformer. Annealing experiments support these findings (see section C). Accordingly, the bands due to CO[15] (from **2**, see Figure 1) and CO_2[17] (from **3**) are also split by a matrix site effect.

In order to obtain a more complete assignment not only of the ketene and carbonyl IR absorptions but also of other bands in the IR spectrum of **5**, ab initio calculations of the IR frequencies of both conformers were carried

(14) (a) Another precursor of **5** is 1-diazobutane-2,3-dione (**6**), which under pyrolysis conditions has been inferred[14b] to undergo Wolff rearrangement to yield **5**. Work from this laboratory indicates that FVP of **6** at 440 °C provides the usual *Z/E* mixture of **5** (spectrum identical to Figure 4a), whereas photolysis (λ > 265 nm) in argon matrix initially generates the *E* form predominantly (together with a smaller amount of the *Z* and/or "photo"-*Z* form). Prolonged photolysis causes partial conversion to the *Z* form (after 50 min, λ > 265 nm, the spectrum is very similar to that shown in Figure 6b). Ab initio calculations (MP2/6-31G*) indicate that the *E-Z* form of **6** shown is more stable than the *Z-Z* form by 33 kJ mol^{-1}. Thus, the preferred formation of *s-E*-**5** in the matrix is in accord with a concerted in-plane Wolff rearrangement of *E-Z*-**6**: Leung-Toung, R.; Wong, M. W.; Wentrup, C. Unpublished results. (b) Biesiada, K. A.; Shevlin, P. B. *J. Org. Chem.* **1984**, *49*, 1151.
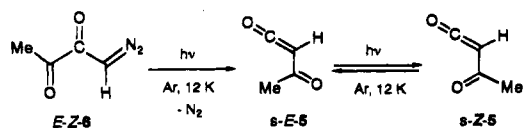
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(17) For matrix effects on CO_2 bands, see Irvine, M. J.; Mathieson, J. G.; Pullin, D. E. *Aust. J. Chem.* **1982**, *35*, 1971.
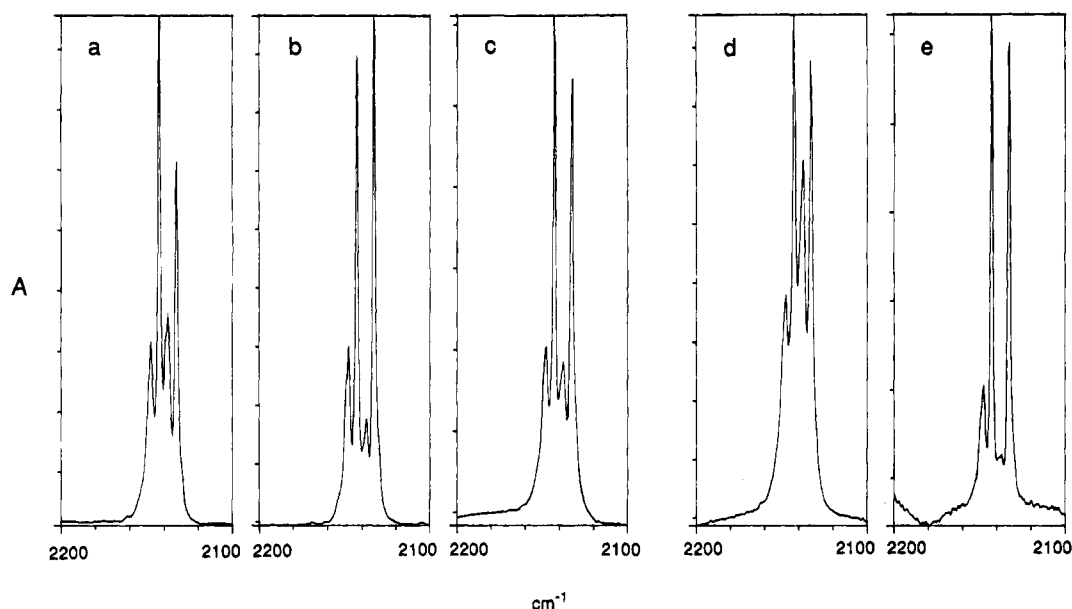
Figure 2. Partial FTIR spectra (Ar, 14 K) of s-Z/s-E-acetylketene (**5**) produced by FVP of precursors **1–4**: (a) from **1** at 400 °C; (b) from **3** at 400 °C; (c) from **4** at 600 °C; (d) from **3** at 400 °C with low argon/solute ratio (10 min deposition time); and (e) from **4** at 600 °C with high argon/solute ratio (45 min deposition time). Bands due to s-Z-**5** at 2143 and 2148 cm^{-1}; bands due to s-E-**5** at 2133 and 2137 cm^{-1}. For discussion, see text. A full spectrum corresponding to Figure 2b is given in the supplementary material.

Table 1. Calculated and Experimental Infrared Spectra of s-Z- and s-E-Acetylketene^{a,b}

	s-Z-acetylketene					s-E-acetylketene		
mode		HF/6-31G* ^{c}	MP2/6-31G* ^{c}	expt^d	mode		HF/6-31G* ^{c}	MP2/6-31G* ^{c}	expt^d
ν_1	A'	3049 (8)	3098 (12)	3095	ν_1	A'	3043 (15)	3092 (22)	3084
ν_2	A'	2974 (12)	3048 (5)		ν_2	A'	2975 (9)	3052 (3)	
ν_3	A''	2920 (17)	3008 (6)		ν_3	A''	2917 (15)	3005 (5)	
ν_4	A'	2868 (6)	2929 (2)		ν_4	A'	2866 (6)	2928 (2)	
ν_5	A'	2133 (1195)	2107 (604)	2143	ν_5	A'	2119 (1127)	2096 (583)	2133
ν_6	A'	1751 (265)	1652 (124)	1681	ν_6	A'	1771 (536)	1660 (235)	1698
ν_7	A''	1447 (8)	1449 (10) }	1434–1421^e	ν_7	A''	1451 (10)	1453 (13) }	1434–1421^e
ν_8	A'	1440 (14)	1445 (13) }		ν_8	A'	1440 (4)	1444 (8) }	
ν_9	A'	1397 (250)	1377 (252)	1379	ν_9	A'	1387 (49)	1363 (55)	1365
ν_{10}	A'	1361 (125)	1342 (81)	1345	ν_{10}	A'	1350 (75)	1315 (106)	1343
ν_{11}	A'	1158 (81)	1152 (57)	1169^f	ν_{11}	A'	1209 (179)	1208 (120)	1221^g
ν_{12}	A'	1092 (5)	1078 (0)		ν_{12}	A'	1084 (6)	1063 (7)	1081
ν_{13}	A''	1031 (11)	1011 (5)	1015	ν_{13}	A''	1028 (10)	1008 (6)	1021
ν_{14}	A'	948 (34)	942 (28)	956	ν_{14}	A'	997 (38)	982 (32)	997
ν_{15}	A'	890 (12)	878 (9)	889	ν_{15}	A'	779 (2)	786 (1)	
ν_{16}	A'	628 (99)	620 (19)		ν_{16}	A''	647 (80)	604 (41)	
ν_{17}	A''	637 (25)	574 (35)		ν_{17}	A'	610 (6)	589 (8)	
ν_{18}	A''	563 (0)	533 (3)		ν_{18}	A''	561 (22)	519 (15)	
ν_{19}	A''	519 (16)	491 (37)		ν_{19}	A'	482 (6)	475 (13)	
ν_{20}	A'	472 (15)	450 (5)		ν_{20}	A''	484 (21)	468 (18)	
ν_{21}	A'	343 (4)	340 (3)		ν_{21}	A'	378 (4)	371 (2)	
ν_{22}	A'	138 (2)	131 (1)		ν_{22}	A'	139 (8)	133 (5)	133 (5)
ν_{23}	A''	104 (0)	110 (0)		ν_{23}	A'	116 (6)	114 (2)	
ν_{24}	A''	87 (0)	84 (0)		ν_{24}	A''	58 (2)	60 (3)	

^{a} Frequencies in cm^{-1}. ^{b} Intensity values (in km mol^{-1}) are in parentheses. ^{c} Scaled by 0.8929 and 0.9427 for the HF/6-31G* and MP2/6-31G* frequencies, respectively. ^{d} Recorded in Ar matrix. Assignments based on Figure 1 and additional spectra reproduced in the supplementary material. Distinction between s-Z and s-E form was made on the basis of Figures 4, 5, and 7. ^{e} Several bands in this region; individual conformers were not assigned. ^{f} A band at 1155 cm^{-1} is probably associated with this band (matrix splitting). ^{g} Previously assigned to the s-Z conformer.[5b]

out and compared with the experimental values (Table 1). The distinction between individual bands being due to either the s-Z or the s-E conformer (in particular in the fingerprint region) is facilitated by difference spectra obtained from E/Z interconversion (vide infra, see Figures 4c and 5). Independently of our work, calculated IR frequencies for **5** at the RHF/6-31G* level of theory were recently reported,[5b] together with a partial assignment of our previously published[4a] experimental frequencies. Due to the experimental data we now have at hand, we are able to observe and assign most of the IR bands

that have significant intensities and are within the spectral range of our experiments (4000–750 cm^{-1}) for both conformers.

Frequencies were calculated both at the HF/6-31G* and the MP2/6-31G* levels of theory. The changes in frequency and intensity on going from HF to the correlated level (MP2) are generally small. The calculated HF and MP2 frequencies were scaled by 0.8929 and 0.9427, respectively.[11] These "universal" scale factors are generally appropriate for all the raw theoretical frequencies. In general, there is an excellent agreement between
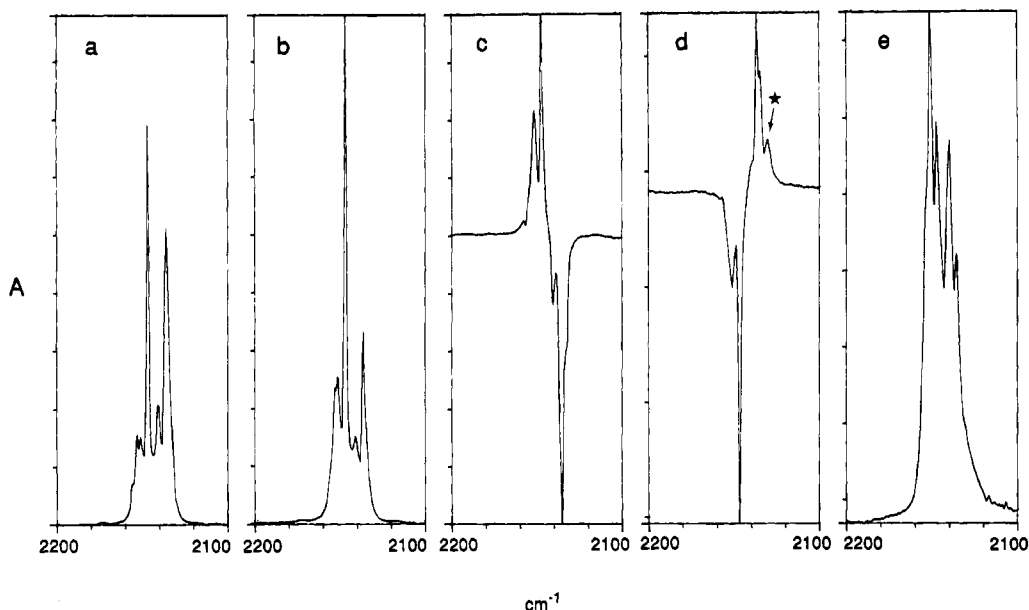
Figure 3. Optimized geometries (MP/2-31G*) of s-Z and s-E-acetylketenes (bond lengths (Å) and bond angles (deg)).

the observed and calculated (scaled) frequencies (Table 1). The mean absolute error of the HF and MP2 scaled frequencies are 21 and 16 cm^{-1}, respectively. The predicted intensities are also in good qualitative agreement with the observed spectra. Note that the MP2 theory provides a better prediction for the carbonyl stretching vibrations of the acetyl ketenes. The prediction of ketene stretching frequencies can be improved by comparing calculated MP2/6-31G* and experimental values for several molecules containing the C=C=O functional group (Table S1 in the supplementary material). The calculated C=C=O stretching frequencies are consistently higher than the experimental values by 4%, thus suggesting a scaling factor of 0.960, instead of the "universal" value of 0.9427,[11] may provide an improved prediction of the C=C=O vibrational frequencies. Indeed, by applying this special scaling factor (0.960) to the directly calculated MP2/6-31G* values, our best theoretical estimates of $\nu_{C=C=O}$ for s-Z and s-E-acetylketene are 2145 and 2134 cm^{-1}, respectively, in excellent agreement with the experimental values (2143 and 2133 cm^{-1}, respectively). It is important to note that *quantitative* interpretations of IR spectra derived from matrix isolated species (e.g. for **5**)[5b] have to be treated with some reservations, considering the manifold and unpredictable matrix effects[16] (vide supra) that can obscure the true intensities of particular IR absorptions.

Apart from their vibrational frequencies, the geometries for s-Z- and s-E-acetylketene were calculated at the MP2/6-31G* level to provide a more definitive theoretical estimate of the molecular structures of **5** (Figure 3).

B. UV-Induced Rotamerization of Acetylketene Conformers.

Previous experiments[4a] aimed at the photochemical interconversion of the argon matrix isolated acetylketene conformers led to the production of a *new* set of ketene bands, whose nature is discussed in section C. In order to avoid this phenomenon, we have tried to employ other host gases, viz. xenon and nitrogen, in our studies. In order to simplify the discussion, these results are presented first. When a mixture of s-Z- and s-E-acetylketene (produced by FVP of **1**) was isolated in a N$_2$ matrix, an IR spectrum (Figure 4a) similar to the one in Figure 2a was obtained, except that all frequencies were shifted ca. 4–5 cm^{-1} to higher wavenumbers (Table 2). Photolysis of this mixture at 313 nm (monochromator) for 2 h resulted in partial $E \rightarrow Z$ conversion, clearly demonstrated by the difference spectrum (Figure 4c). After this time a photostationary state was reached and no further changes took place on prolonged irradiation

Table 2. Ketene and Carbonyl Frequencies (cm^{-1}) of s-Z- and s-E-Acetylketene in Different Matrix Environments

matrix (14 K)	s-Z-5		s-E-5	
	$\nu_{C=C=O}$	$\nu_{C=O}$	$\nu_{C=C=O}$	$\nu_{C=O}$
Ar	2143 s 2148 m	1681	2133 s 2137 m	1698
N$_2$	2147 s 2151 m 2153 m 2156 w	1682	2136 s 2141 m	1692
Xe[a]	2137 s 2143 w 2145 w	1679	2128 s 2126 s	1689

[a] Spectra reproduced in the supplementary material.

at 313 nm. Similar results were achieved by irradiation with interference filters ($\lambda > 310$ nm, or $\lambda > 295$ nm). The Z/E ratio increased from roughly 1:1 to ca. 4:1 after irradiation at 313 nm for 2 h as estimated from the intensity changes of the ketene absorptions in Figure 4a,b. Similar changes were also found in the carbonyl and fingerprint regions of the difference spectrum, thus allowing an unequivocal distinction of bands due to either the s-Z or the s-E conformer (Figure 5). Irradiation of the ca. 4:1 Z/E mixture of **5** with broad-band UV light (1000 W high pressure Xe-Hg lamp) for 5 min transformed part of the s-Z isomer back to the s-E form with concomitant formation of a small amount of methylketene (**7**) (Figure 4d). It is well known that α-oxo ketenes under intense UV irradiation decarbonylate to oxocarbenes which then undergo Wolff rearrangement to form substituted ketenes.[4b,e,i] After 2 h of broad-band irradiation, all signals due to s-Z- and s-E-acetylketene disappeared from the spectrum with only the methylketene absorption at 2130 cm^{-1} and CO (2140 cm^{-1}) remaining. For the purpose of comparison, an IR spectrum of methylketene was generated by FVP of propionic anhydride[18a] at 650 °C with product isolation in a nitrogen matrix at 14 K. This experiment confirmed that the band observed at 2130 cm^{-1} is indeed due to methylketene (**7**). This band appears at 2125 cm^{-1} in Ar matrix.[4a] Authentic methylketene (2125 cm^{-1}, Ar, 12 K) was also produced by photolysis (broad-band, 5 min) of Ar matrix isolated diazoacetone (itself absorbing at 2110 and 2115 cm^{-1}).[18b]

Analogous $E \rightarrow Z$ conversion in **5** was also observed by irradiation of xenon matrix isolated s-Z/s-E-acetylketene at 313 nm. Ketene and carbonyl stretching frequencies observed in the three matrix hosts are given in Table 2.

The wavelength dependent rotamerization of α-oxo ketenes is not without precedent: a similar behavior was observed for formylketene isolated in an *argon* matrix.[4i]

Our calculations, at significantly higher level of theory than those previously reported for acetylketene,[5a,b] suggest that the s-Z and s-E forms of acetylketene are almost identical in energy, with 0.1 kJ mol^{-1} (ΔE) in favor of the s-E form (Table 3). Calculated entropies (S) of the s-Z and s-E forms are 313.6 and 315.9 cal mol^{-1} K^{-1}, respectively, derived from the MP2/6-31G* frequencies. Using the equation $\Delta G = \Delta H - T\Delta S$, the estimated E/Z free energy differences ($\Delta\Delta G$) at 300 and 800 °C are 1.4 and 1.9 kJ mol^{-1}, respectively, in favor of the s-Z form. This calculated result is consistent with the fact that the Z/E ratio obtained by FVP shows little temperature dependence (i.e. the FVP spectra reflect a nearly 1:1 ratio

(18) (a) Baxter, G. J.; Brown, R. F. C.; Eastwood, F. W.; Harrington, K. J. *Aust. J. Chem.* **1977**, *30*, 459. (b) Leung-Toung, R.; Wentrup, C. Unpublished results.

Figure 4. Partial FTIR spectra (N_2, 14 K) of s-Z/s-E-acetylketene (**5**) produced by FVP (400 °C, 10^{-5} mbar) of **1**. (a) After deposition; (b) after irradiation at 313 nm for 2 h; (c) difference spectrum (b minus a) (s-Z-**5** top, s-E-**5** bottom); (d) difference spectrum after further irradiation with broad-band UV light for 5 min (s-Z-**5** bottom, s-E-**5** top); the band at 2130 cm^{-1} (★) is due to **7**. (e): s-Z/s-E-**5** produced by photolysis (N_2, 14 K) of **1** at 254 nm for 2 h. For exact values see Table 2.
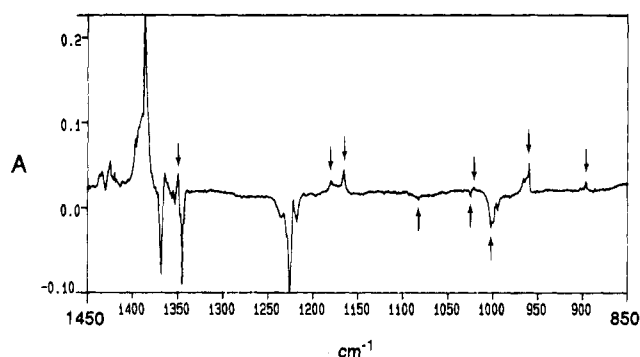
Figure 5. Fingerprint region (1450–850 cm^{-1}) of the IR difference spectrum corresponding to Figure 4c (N_2, 14 K). s-Z-**5** (top): 1386, 1349, 1180, 1167, 1021, 961, 897 cm^{-1}; s-E **5** (bottom): 1369, 1345, 1226, 1083, 1025, 1001 cm^{-1}. Weak absorptions highlighted (↓). The true intensity of the band at 1349 cm^{-1} (s-Z) might be obscured due to the near coincidence with the band at 1345 cm^{-1} (s-E). No attempts were made to assign the 1450–1400 region of the spectrum. The bands for the =C—H stretch appear at 3100 (s-Z, top) and 3088 cm^{-1} (s-E, bottom) (not shown).

Table 3. Calculated Total Energies (hartrees) and Zero-Point Vibrational Energies (ZPVE, kJ mol^{-1}) of Acetylketene and Related Species

| species | total energy[a] | | | ZPVE[b] |
	MP2/ 6-31G*	QCISD(T)/ 6-31G*	MP2/ 6-311+G(2d,p)	
s-Z-**5**	−304.35499	−304.41482	−304.58720	200.6
s-E-**5**	−304.35350	−304.41395	−304.58650	200.2
8	−304.31950	−304.37777	−304.55913	204.2
5 E/Z TS	−304.33693	−304.39869	−304.56968	198.4
1,3-H shift TS	−304.26909	−304.32490	−304.50750	187.4
2	−417.39644	−417.47256	−417.70474	237.1
CO	−113.02121	−113.03900	−113.10040	14.6

[a] Based on MP2(full)/6-31G* geometry. [b] HF/6-31G* values.

of s-Z-**5** and s-E-**5**). Interconversion of the two conformers is predicted to have an energy barrier of 39 kJ mol^{-1} (Table 3). This relatively high rotamerization barrier prevents easy equilibration of acetylketene conformers

in low-temperature matrices. Experimental studies indicate[19] that conformers with barriers higher then ca. 6 kJ mol^{-1} can be trapped at 20 K, while annealing to 35–40 K leads to the loss of the less stable conformers for molecules with barriers of less than ca. 12 kJ mol^{-1}.[19] Annealing of an acetylketene mixture enriched in s-Z (ca. 4:1) at 60 K (xenon matrix) did not lead to a detectable change in the s-Z/s-E ratio.

These results prompted us to reinvestigate the matrix photolysis of the dioxinone precursor **1**. Irradiation of **1** in a nitrogen matrix at 254 nm first produced s-Z-acetylketene together with only a small amount of the s-E isomer. Further irradiation increased the amount of the s-E isomer until a photostationary state was reached after 2 h (Figure 4e). Interestingly, here the population of matrix sites was reversed as compared to thermally produced acetylketene (Figure 4a). This effect might be due to a different orientation or site adopted by the dioxinone precursor in the nitrogen lattice before irradiation, or to acetone being generated and trapped in the same matrix cavity as **5** on photolysis.

None of the above photolysis experiments in nitrogen or xenon matrices gave any evidence for the formation of *new* bands in the IR spectra apart from the methylketene absorption formed on prolonged broad-band photolysis. This is in marked contrast to the photolysis experiments in argon described below.

C. Photolysis Studies on Acetylketene in Argon Matrices. Photolysis of the argon matrix isolated mixture of s-Z and s-E-acetylketene (Figure 6a; cf. section A), at 313 nm (monochromator) for 2 h, resulted in the formation of new bands in the ketene region of the IR spectrum at 2156, 2154, 2149, and 2130 cm^{-1} (Figure 6b,c), together with a new band in the carbonyl region at 1687 cm^{-1} and a strong absorption at 1385 cm^{-1}. Prolonged photolysis at 313, 366, or 254 nm produced no further changes in the IR spectrum. Annealing of the matrix to ca. 35 K (2 min) caused the complete loss of all
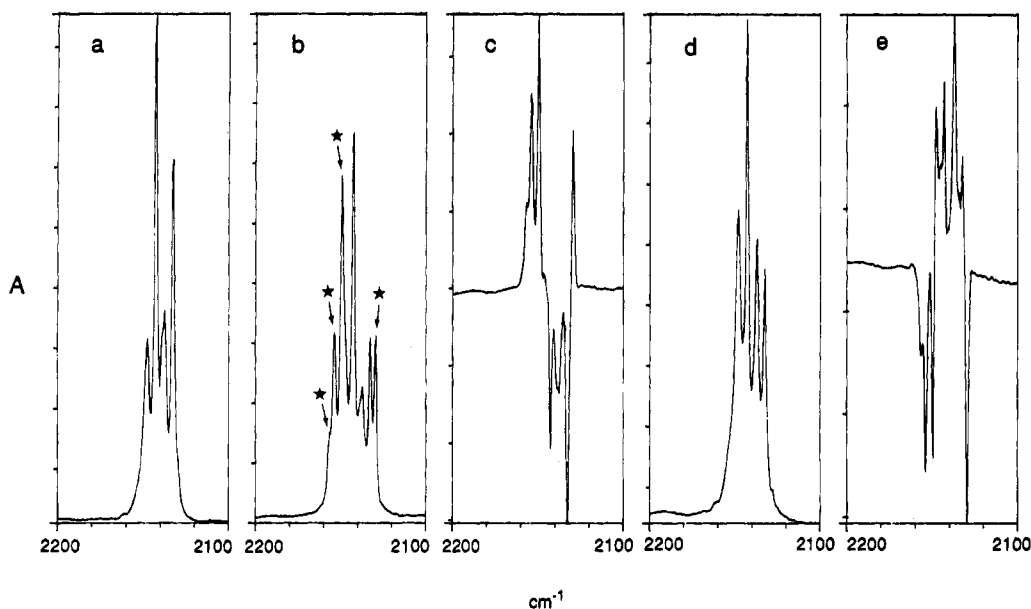
(19) Barnes, A. J. *J. Mol. Struct.* **1984**, *113*, 161.

Figure 6. Partial FTIR spectra (Ar, 14 K) of s-Z/s-E-acetylketene produced by FVP (400 °C, 10^{-5} mbar) of **1**. (a) After deposition; (b) after irradiation at 313 nm for 2 h (new bands marked with ★); (c) difference spectrum (b minus a) (the minor ketene absorption at 2148 cm^{-1} is not seen due to near coincidence with the new band formed at 2149 cm^{-1}); (d) after annealing to 35 K (2 min); spectrum recorded after recooling to 14 K; (e) difference spectrum (d minus b). For discussion, see text.

the bands produced by irradiation (Figure 6d,e). Careful monitoring of the annealing process in the 30-35 K temperature range revealed that the band at 2130 cm^{-1} disappeared first, with concomitant formation of the minor s-E band at 2137 cm^{-1}. By comparison of the IR spectra in Figure 6d and 6a it becomes evident that the "net" result of this photolytic process (after annealing) is an increase in the intensities of the minor ketene bands for both conformers, rather than a major change in the E/Z ratio. In fact, annealing of an *unphotolyzed s-Z/s-E*-acetylketene mixture to ca. 35 K (2 min) also caused an increase in the intensities of these minor absorptions. This may reflect an aggregation site effect or the population of more than one type of cage within the argon lattice ("multiple trapping sites").[16]

Irradiation of dioxinone **1** (Ar, 14 K) at 254 nm for 15 min produced only the bands due to s-Z-acetylketene plus the high frequency part of the photolytically generated absorptions ("photo-Z" form)[4a]. Bands due to the s-E isomer and the band at 2130 cm^{-1} ("photo-E" form)[4a] were formed only on further irradiation at 313 and 366 nm. This demonstrates the apparent association of the high frequency bands with the s-Z conformer, and of the low frequency bands with the s-E conformer. From the estimated total intensities of these absorptions in Figure 6b,c ("photo-Z" versus "photo-E" forms) it is evident that the formation of the photo-Z form is dominant.

Interestingly, photolysis of 5-methylfuran-2,3-dione (**2**) at 366 nm for 4 h (Ar, 14 K) furnished exclusively the photo-Z form (Figure 7), which on further photolysis (366 nm, 2 h) was partially converted to the (normal) s-E isomer. The bright yellow dione **2** could also be photolyzed at 435 nm but the reaction was considerable slower and could not be carried to completion. Broad-band photolysis of **2** on the other hand was complete in 5 min. All of the frequencies ascribed to the photo-Z form in Figure 7 are in close proximity to the frequencies of the normal s-Z conformer (Figure 1), shifted ca. 3−8 cm^{-1} to higher wavenumbers. This lends further confidence to the assignment of bands due to the s-Z conformer (Table

1). On annealing to ca. 35 K (2 min) the photo-Z form was completely converted to the normal s-Z conformer, as expected.

Discussion

It appears that the matrix photochemistry of acetylketene is strongly dependent on the matrix environment, i.e. the host gas. Whereas UV irradiation of thermally or photochemically produced acetylketene in nitrogen or xenon matrices allows clean E/Z interconversion, the analogous experiment in an argon matrix causes the apparent formation of new "photo" forms. In order to rationalize this photochemical effect we have considered a number of possible explanations that will be discussed below.

Maier et al. reported that prolonged irradiation (313 nm, 19 h) of formylketene in an argon matrix at 10 K produces (hydroxymethylene)ketene via a 1,3-hydrogen shift.[4i] This was supported by the observation of new sets of bands in the IR (3526, 2128, and 1692 cm^{-1}) and UV spectra.[4i] It is conceivable that such a 1,3-H shift could also take place in acetylketene (from the s-E but not the s-Z form) producing [hydroxy(methyl)methylene]ketene (**8**) (Scheme 3). However, the similarity of IR bands for the "photo-Z" and s-Z forms, both in frequency and intensity (see Figures 1 and 7), makes it very unlikely that the "photo-Z" form is actually a different structural isomer of acetylketene (the absence of an OH absorption is particularly noteworthy, although the inevitable presence of traces of water makes examination of this region less rigorous). We also find that the matrix UV spectrum (Ar 14 K, λ_{max} 220 nm) of s-Z/s-E-acetylketene remains virtually unchanged upon irradiation at 313 nm.[20] Furthermore it cannot easily be rationalized why such a 1,3-shift would occur in argon but not in nitrogen or xenon matrices. For similar reasons we also do not consider the hypothetical enolization of the acetyl group as a possibility. Our conclusion is further supported by ab initio calculations on the IR spectrum (MP2/6-31G*) of the methyleneketene **8** and the activation barrier for the
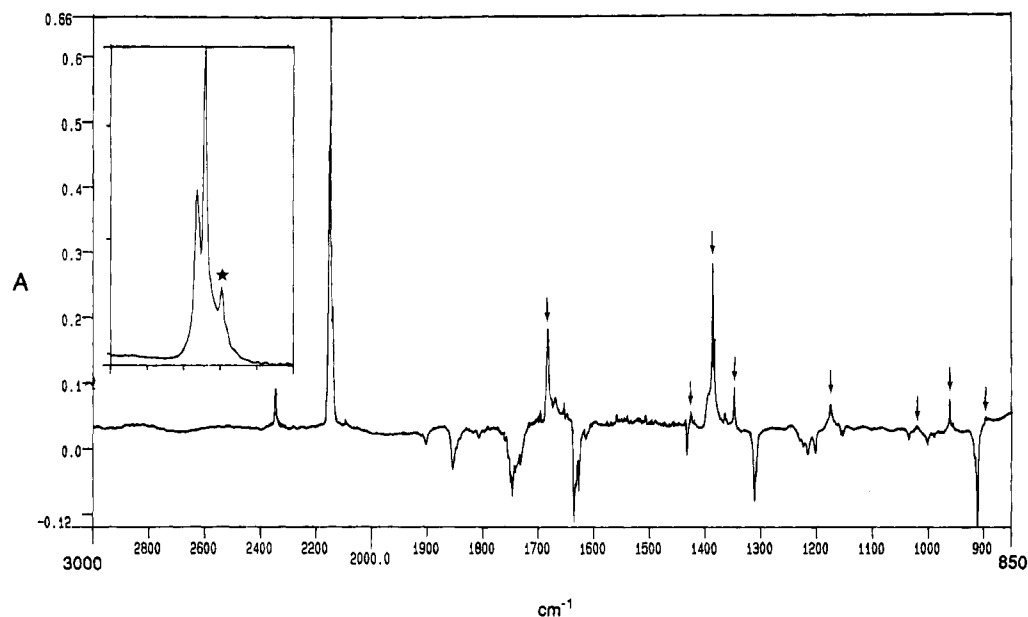
Figure 7. IR difference spectrum (Ar, 14 K) showing the photolysis (366 nm, 4 h) of **2** (bottom) to "photo-Z"-**5** (top). The inset shows the expanded ketene region (2200–2100 cm^{-1}). Bands due to "photo-Z-**5** (positive peaks) at 2152, 2149, 1684, 1425, 1387, 1383 (sh), 1348, 1175, 1020, 962, and 897 cm^{-1} marked by ↓. The intensity of the band at 1387 cm^{-1} is significantly diminished by coincidence with a band of **2** at 1388 cm^{-1}. CO (2139 cm^{-1}) marked by ★. The small deviations in frequencies with respect to "photo-Z"-**5** produced by irradiation of s-Z/s-E-**5** (Figure 6b) are probably due to CO being formed and trapped in the same matrix cavity as "photo-Z"-**5**. Bands due to **2** (negative peaks) at 1903, 1855, 1748, 1635, 1628, 1435, 1388, 1313, 1218, 1198, 1156, 1024, 999, and 913 cm^{-1}.

Scheme 3

7

8
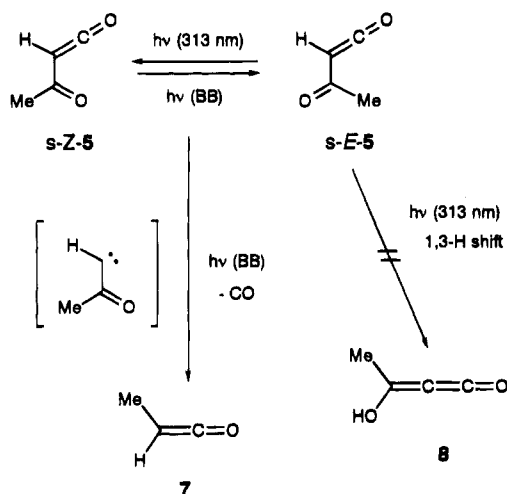
1,3-migration process. The characteristic features of the IR spectrum of **8** are the strong absorption at 3467 (ν_1), 2113 (ν_2), 1672 (ν_3), and 1248 (ν_4) cm^{-1} (see Table S2 in the supplementary material). Although ν_2 and ν_3 are close to those observed for the "photoproduct" (2156, 2154, 2149, 2130, and 1687 cm^{-1}) ν_4 is significantly different from the observed value at 1387 cm^{-1}. [Hydroxy(methyl)-methylene]ketene (**8**) is calculated to lie 81 kJ mol^{-1} above acetylketene (s-E-**5**). Rearrangement of **8** to s-E-**5**, via a four-centered transition structure, is predicted to have a barrier of 127 kJ mol^{-1}, which is vastly higher than one would have inferred from the annealing experiment at 35 K.

We have also considered the potential involvement of long-lived excited states of **5** in these matrix photolyses, since in a few cases a strong blue phosphorescence had been observed upon argon matrix photolysis of other α-oxo ketenes.[4a] We have performed ab initio calculations on the geometries and energies of several possible

Table 4. Calculated Vertical Transition Energies^{a,b} of Acetylketene (5)

| | s-Z-**5** | | | s-E-**5** | |
state^c	transition energy	f^d	state^c	transition energy	f^d
TA″	300 (4.13)	0.000	TA″	321 (3.86)	0.000
TA′	292 (4.25)	0.000	TA′	293 (4.23)	0.000
SA″	274 (4.53)	0.000	SA″	289 (4.29)	0.000
TA″	260 (4.77)	0.000	TA″	267 (4.64)	0.000
SA″	230 (5.40)	0.000	SA″	234 (5.31)	0.000
TA′	212 (5.84)	0.000	TA′	214 (5.79)	0.000
TA′	187 (6.62)	0.000	TA′	191 (6.50)	0.000
TA′	182 (6.81)	0.000	TA″	181 (6.87)	0.000
SA′	180 (6.90)	0.320	SA′	174 (7.12)	0.410
SA″	174 (7.12)	0.028	SA″	172 (7.21)	0.028

^{a} CIS/6-311+G**//MP2/6-31G* values. ^{b} In nm (eV in parentheses). ^{c} S stands for singlet and T for triplet. ^{d} Oscillator strength

excited states of acetylketene. The first ten transition energies of s-Z and s-E-acetylketene were calculated by using the configuration interaction including the all-singly-excited configurations (CIS)[13] approach, with the 6-311+G** basis set. As seen in Table 4, the first singlet excited states are 4.3–4.5 eV higher than the corresponding singlet ground states. However, there are two low-lying triplet excited states. Full geometry optimization of the first singlet excited state (RCIS/6-31G*) and the lowest triplet state (UCIS/6-31G*) of s-Z-**5** indicate that both structures are planar and have kinked C=C=O geometries ($\angle$CCO = 137 and 128°, respectively, Figure 8). As a consequence, these excited states are expected to exhibit IR spectra very different from the spectra of the ground state species. This is readily confirmed by explicit frequency calculations of the optimized excited-state structures. No observable IR bands are calculated in the 1900–2500 cm^{-1} region.

Furthermore, on photolysis of **2** at 435 nm (see section C), there is not enough energy available to populate an excited state of **5**. The reaction **2** → **5** + CO is calculated
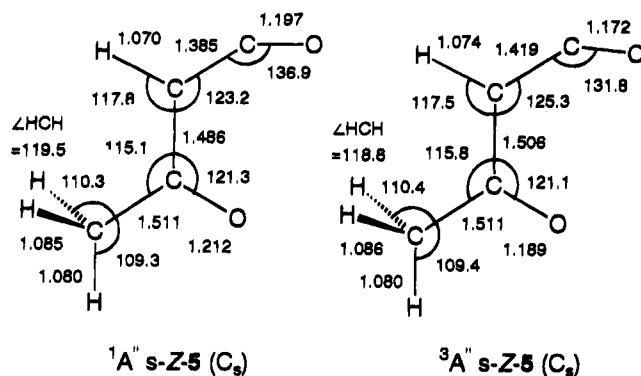
Figure 8. Optimized geometries of the first singlet excited state (^{1}A″, CIS/6-31G*) and the lowest triplet state (^{3}A″, UMP2/6-31G*) of s-Z-acetylketene (bond lengths (Å) and bond angles (deg)).

Figure 9. Rotational profile (MP2/6-31G*) for acetylketene (calculated as a function of the CCCC torsional angle).

to be endothermic by 21 kJ mol^{-1} (Table 3). Photolysis of **2** at 435 nm will, therefore, lead to an excess energy of 254 kJ mol^{-1} (or 471 nm or 2.63 eV) for acetylketene (**5**), significantly less than the excitation energy of the ground state to the first excited singlet state or to the lowest triplet state (Table 4).

A more likely explanation for the new set of IR absorptions is the presence of high-energy conformers. It is well known that metastable conformers can be generated by direct UV,[19,21] or IR[19,21a,22] irradiation of matrix isolated molecules. Alternatively, these conformers can also be observed by high-temperature equilibration ("hot nozzle technique")[21c,23] of samples prior to matrix deposition. If the rotational barriers involved are sufficiently high (>6 kJ mol^{-1}), the metastable conformer can be observed under matrix conditions (4–20 K).[19] On annealing of the matrix at higher temperatures (35–40 K), the metastable conformer (corresponding to a local energy minimum on the potential energy surface) will convert back to the lower energy form if the rotational barrier is less than ca. 12 kJ mol^{-1}.[19,21b,22,23a,d] From our irradiation and annealing studies in argon matrices, one could easily come to the conclusion that the observed "photoproduct" is a high energy conformer of acetylketene. Since we have already observed and securely identified two low energy, virtually planar conformers of acetylketene (s-Z and s-Z), this "photoconformer" would presumably have a skewed conformation. However, all attempts to locate a higher-energy minimum on the C$_4$H$_4$O$_2$ potential energy surface were unsuccessful. The possible skew conformation was examined by calculating the energy profile using as coordinate the CCCC torsional angle and optimizing all remaining geometrical parameters at each point (at the MP2/6-31G* level). The resulting profile (Figure 9) indicates that there is no stable skew confor-
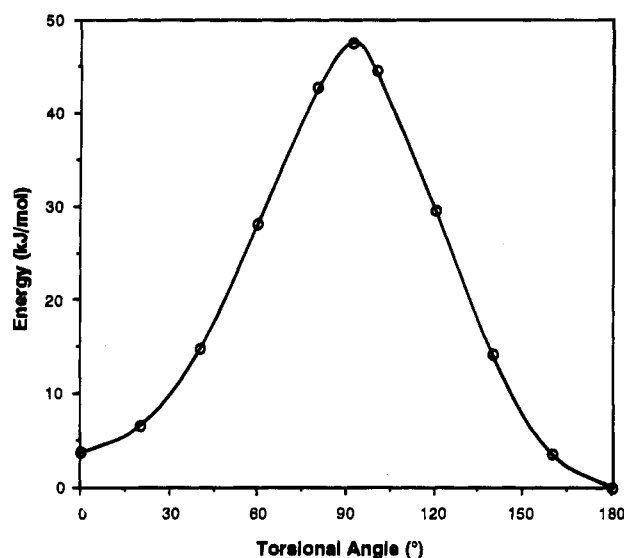
mation. We have also considered the s-Z and s-E forms with the methyl group in a staggered arrangement with respect to the carbonyl oxygen (cf. Figure 3). Both structures are found to be saddle points on the potential energy surface.

Another strong argument against a metastable conformer is the effect of the matrix environment. Any metastable acetylketene conformer should also, in principle, be existent and observable in the nitrogen or xenon matrices. However, care must be exercised in arguing along these lines, as there are a few examples known where conformational concentrations can be strongly dependent on the matrix gas.[19,23a] Nonetheless, in these cases the proposed metastable conformers would be associated with local energy minima.[19,23a] Finally, it is unlikely that a skewed conformer would have an IR spectrum very similar (both in frequencies and intensities) to the planar s-Z conformer, with all the bands are shifted in the same direction (viz. 3–8 cm^{-1} to higher frequency).

Matrix effects are known to cause complications in the analysis of IR spectra and due to their unpredictable nature frequently lead to misinterpretations.[16,19] The differentiation between conformational isomerism and matrix effects (i.e. multiple site trapping) is particularly difficult.[19] In the present case, we are confident that the observed splittings of IR bands (Figure 6b) are due to matrix site effects and not to conformational isomerism. Annealing of the matrix to 35 K leads to conversion of these "metastable" sites ("photo-Z"/"photo-E") back into the two stable sites (major/minor) for Z/E acetylketene (Figure 6d). This requires a UV-induced population of an alternate trapping site in the matrix lattice. Importantly, there is some precedent for such a process in the matrix photolysis of acrolein, although the effect is not as pronounced as in our case.[21c]

Furthermore we have obtained evidence that an UV-induced interconversion of sites is also possible in nitrogen matrices. Although irradiation of nitrogen matrix isolated s-Z/s-E-acetylketene normally leads to clean E → Z interconversion (Figure 4c), in one case (λ > 320 nm, 20 min) an initial *increase* in the minor s-E ketene band at 2141 cm^{-1} could be observed in the difference spectrum. Further photolysis at 313 nm resulted in the

(20) The UV spectrum of **5** is, however, not very characteristic, featuring a maximum at 220 nm, tailing off till 380 nm (Ar, 14 K).

(21) (a) Lundell, J.; Räsänen, Raaska, T.; Nieminen, J.; Murto, J. *J. Phys. Chem.* **1993**, *97*, 4577. (b) Gebicki, J.; Plonka, A.; Krantz, A. *J. Chem. Soc., Perkin Trans. 2* **1990**, 2051. (c) Blom, C. E.; Müller, Günthard, Hs. H. *Chem. Phys. Lett.* **1980**, *73*, 483. (d) Krantz, A.; Goldfarb, T. D.; Lin, C. Y. *J. Am. Chem. Soc.* **1972**, *94*, 4022.

(22) For recent examples, see Kulbida, A.; Fausto, R. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 4257. (b) Kulbida, A.; Nosov, A. *J. Mol. Struct.* **1992**, *265*, 17.

(23) For recent examples, see Gatial, A.; Klaeboe, P.; Nielsen, C. J.; Sablinskas, V.; Powell, D. L.; Kondow, A. J.; Incavo, J. A. *J. Mol. Struct.* **1993**, *295*, 73. (b) Powell, D. L.; Gatial, A.; Klaeboe, P.; Nielsen, C. J.; Kondow, A. J. *J. Mol. Struct.* **1993**, *300*, 209. (c) Gatial, A.; Klaeboe, P.; Nielsen, C. J.; Sablinskas, V.; Piatrik, R.; Bobosik, V. *J. Mol. Struct.* **1992**, *266*, 289. (d) El-Bindary, A. A.; Horn, A.; Klaeboe, P.; Nielsen, C. J. *J. Chim. Phys.* **1993**, *90*, 1685.

normally observed *decrease* of both bands assigned to the s-E conformer. Although the observed effect is rather small, it clearly suggests the possibility of an initial photochemical population of the minor (stable) s-E ketene site before E → Z interconversion takes place (see Figure S3(a) in the supplementary material).

There is also some indication that simple annealing of an argon matrix isolated mixture of s-Z/s-E-acetylketene to 30 K allows to a small extent the population of the minor (2148, 2136 cm⁻¹) *and* the metastable sites, i.e. the "photo" sites (2152, 2130 cm⁻¹). On further annealing to 35 K, the metastable sites disappear again, leading to a net increase in the minor ketene bands (see section C and Figure S3(b) in the supplementary material). This behavior is very similar in nature to the one found for argon matrix isolated SF_6 and CO.[15b]

Conclusion

Acetylketene (**5**) has been generated by flash vacuum pyrolysis (FVP) and matrix photolysis from four different precursors. The IR spectra of both conformers (s-Z and s-E) were securely identified by matrix isolation IR spectroscopy and are in excellent agreement with ab initio calculations at the MP2/6-31G* level. High-level calculations predict both conformers to be virtually equal in energy, with a rotational barrier of ca. 39 kJ mol⁻¹. The population of these conformers can be changed by UV irradiation of nitrogen or xenon matrix isolated acetylketene, dependent on the wavelength employed. The matrix photochemistry of *argon* matrix isolated acetylketene is more complex: extensive photochemical and annealing studies in argon, together with ab initio calculations, now prove that the previously unidentified IR bands[4a] are formed by UV light-induced population of metastable matrix sites. The reported phenomenon is of considerable importance to all matrix-photochemical studies and once again demonstrates that care must be taken in the assignment of bands produced by photolysis, for example of ketenes in low-temperature matrices, where the effect can be very strong.

Supplementary Material Available: Tables of calculated (MP2/6-31G*) and experimental ketene stretching frequencies for compounds containing the C=C=O functional group (Table S1), calculated (MP2/6-31G*) IR spectrum of **8** (Table S2), calculated vertical transition energies (CIS/6-311+G**//MP2/6-31G*) of **2** (Table S3), and figures of IR spectra (Figures S1-S3) showing s-Z/s-E-**5** by FVP of **3**, the E/Z isomerization of **5** in xenon matrix, the photolytic population of minor acetylketene sites in nitrogen matrix, and annealing studies of E/Z-**5** in argon matrix (5 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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