Photochemical Generation and Detection of an Elusive Rotamer of Matrix-isolated Mesityl Oxide. Dispersive Kinetics of the Thermal Isomerization: Twisted s-*trans* ⟶ s-*cis* Forms

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The photochemical behaviour of mesityl oxide (4-methylpent-3-en-2-one) was investigated in a number of rare-gas matrices. A 'new' conformer, most probably the twisted s-*trans* form, generated by irradiation with UV light (λ_{max} 250 nm), was trapped and its UV and IR absorption spectra were recorded. The twisted s-*trans* isomer was unstable upon warming of the matrix and rearranged to starting material (s-*cis* isomer). Kinetic measurements of the twisted s-*trans* ⟶ s-*cis* rotational isomerization were performed in an argon matrix in the temperature range 37–41 K, and these data were analysed in terms of dispersive kinetics with time-dependent rate coefficients.

Conformational analysis of α,β-unsaturated aldehydes and ketones has attracted a great deal of interest in recent years.[1–4] The barriers to rotation around the formal C_{sp^2}–C_{sp^2} single bond are expected to be in the order of a few kJ mol^{-1}.[3] Small barriers of this type can be measured directly at low temperature. Application of matrix-isolation spectroscopy to such conformational problems has been previously reported.[5–7] This paper involves the application of matrix-isolation spectroscopy to studies of conformational isomerism in mesityl oxide (4-methylpent-3-en-2-one). In this study a metastable rotamer, most probably the twisted s-*trans* form of mesityl oxide (henceforth referred to as s-*trans*), generated photochemically in rare-gas matrices, has been characterized spectroscopically and the kinetics of thermal s-*trans* ⟶ s-*cis* isomerization is shown to follow complex (dispersive) kinetics.

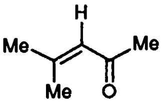
Experimental

A description of the apparatus and sample preparation was presented previously.[8] Temperature was measured directly on a CsI deposition window with accuracy ±0.5 K using a chromel–gold (0.07% iron) thermocouple. Argon (Matheson, prepurified, 99.998% min.) was further purified according to the procedure described in ref. 8*a*. Research-grade krypton and xenon, supplied by Matheson, were used without further purification. Mesityl oxide supplied by Eastman was purified by gas chromatography prior to sample preparation. Photochemical reactions were carried out with a 1000 W mercury–xenon lamp (Hanovia, No. B977B0010) as the light source. Interference filters (Oriel, No. G-572) were used as indicated.

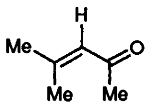
Results and Discussion

Photochemical Generation of the s-trans *Rotamer from Matrix-isolated Mesityl Oxide.*—Mesityl oxide **1** can exist in the form of two rotamers, described as twisted s-*cis* and twisted s-*trans*, neglecting rotamers of methyl groups. In view of experimental[1,2,9,10] and theoretical[3,11] data the s-*cis* conformation is considered to be the more stable form.

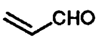
Two approaches have been applied to trap unstable conformers in matrices. The first is based on fast quenching of a gaseous sample onto a surface maintained at cryogenic temperatures, which allows the trapping of high-energy conformers observed in the gas phase.[7,12] Under our experimental conditions, we should be able to trap out conformers separated by barriers of *ca.* 4 kJ/mol or higher. The second approach leading to the stabilization of metastable conformers in matrices can be achieved by direct irradiation of substrate molecules with light.[5–7,8*b*,13] This method of photochemically inducing rotation in matrices is not universal and may depend very much upon the size of the rotating group,[13] and on competitive non-radiative and radiative processes.



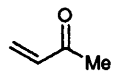
s – cis (**1**)



s – trans (**1**)



(**2**)



(**3**)

As in the examples of acrolein (acrylaldehyde) **2**[5,7] and methyl vinyl ketone **3**,[5,6] irradiation of matrix-isolated compound **1** gives a photoproduct which can be assigned to a high-energy conformer. Photoreaction of compound **1** in matrices could, in principle, lead to the trapping of various enols **4**–**7**[14] which should be stable under cryogenic conditions. Our efforts to trap such enols (which would be easily detected by their characteristic OH-frequencies) were unsuccessful despite irradiation of the sample at regions covering π–π* or n–π* absorptions. Perhaps a singlet-state phototransfer of a hydrogen atom actually results in the formation of the *Z*-s-*cis* enol **4**, which rapidly reverts to ground-state ketone **1**. Failure to detect the *Z*-enol upon irradiation of *ortho*-alkyl-substituted phenyl aldehydes and ketones in gas matrices has previously been noted.[15]

The IR frequencies of argon matrix-isolated mesityl oxide are tabulated in Table 1. The $\nu_{C=O}$ and $\nu_{C=C}$ regions are additionally displayed in Fig. 1(*a*) and subsequent changes in the spectrum upon irradiation are presented in Fig. 1(*b*). The photoproduct is distinguished by a set of four bands: 1678s, 1652sh, 1268s and 995w. It seems likely that the photoproduct

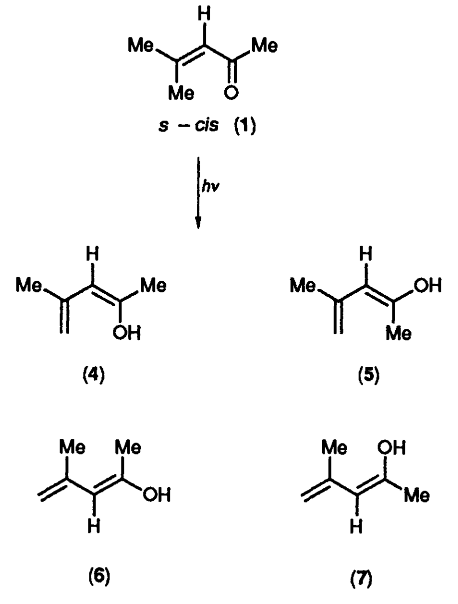


Table 1 Observed vibrational frequencies (cm^{-1}) of argon matrix-isolated mesityl oxide[a]

3015w	1458s	1163s
2990m	1445m	1070w
2943w	1432m	1020w
2921w	1388m	959m
1728w	1361s	902w
1708vs	1355m	824w
1678vw	1268w	623s
1645m	1231s	456w
1629s	1178w	

[a] $M/R = 600$, $T = 12$ K, 40 Torr (1 Torr = 133.322 Pa).

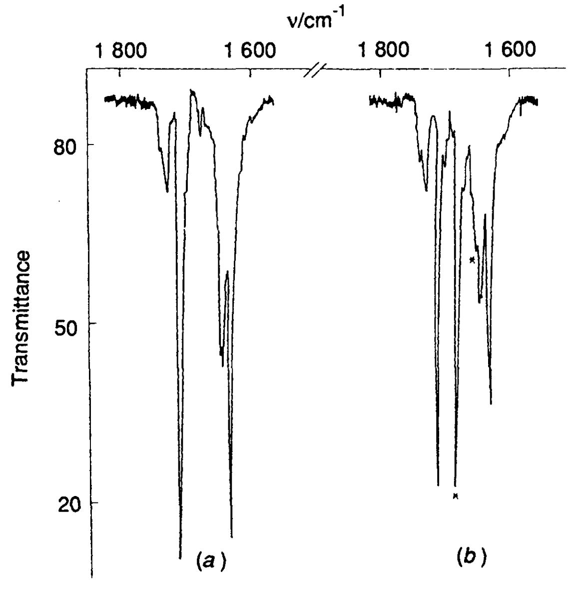


Fig. 1 The $\nu_{C=O}$ and $\nu_{C=C}$ stretching region of the IR spectrum of argon matrix-isolated mesityl oxide ($M/R = 600$, $T = 12$ K, 40 Torr): (*a*) before irradiation; (*b*) after irradiation for 90 min through a 250 nm interference filter. Asterisks indicate the bands of the photoproduct

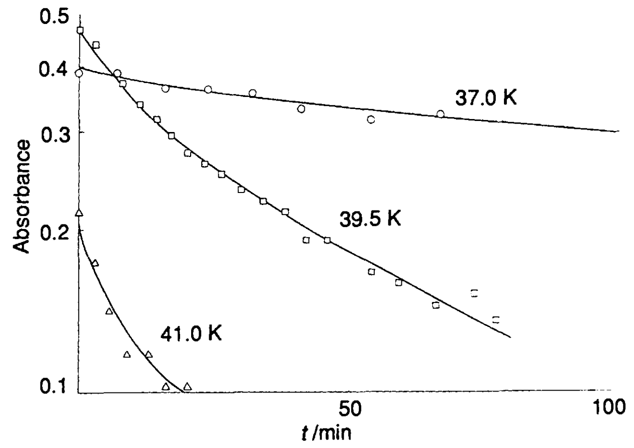


Fig. 2 First-order kinetic plot for the s-*trans* ⟶ s-*cis* rotational isomerism of argon matrix-isolated mesityl oxide

represents a less stable rotamer of compound **1**; *e.g.*, s-*trans*, since, judging by the magnitude of band intensities, both photoproduct and reactant have a number of identical bands, and the existence of a photostationary state between the photoproduct and starting material supports such an interpretation.

In fact, the UV absorption spectrum of the photolysed sample in an argon matrix is not very much different from that of matrix-isolated starting material, and in both cases is represented by a broad band with a maximum at 237 nm. This is consistent with Allinger's prediction that the UV absorption spectra of the individual rotamers should be closely similar.[3] The strongest bands of photoproduct at 1678 and 1268 cm^{-1} are also present in the spectrum of starting material but are of very low intensity. This strongly suggests that this species is also present in the gas phase before deposition at very low concentrations. If we assign the frequencies at 1708 cm^{-1} and 1678 cm^{-1} to the carbonyl stretches of s-*cis* and s-*trans* rotamers, respectively, we can then estimate the enthalpy difference between these two rotamers, assuming the relative ratio of both conformers to be unchanged upon quenching of the sample during matrix formation. The estimated value lies in the region 6.6–8.1 kJ mol^{-1}. Comparison of the spectra in Fig. 1(*a*) and Fig. 1(*b*) shows that $\nu_{C=O}$ of s-*cis* is higher than $\nu_{C=O}$ of the s-*trans* conformer, and additionally the intensity quotient $\nu_{C=O}/\nu_{C=C}$ for s-*cis* is much lower than that of the s-*trans* rotamer. Similar conclusions were drawn from conformational studies of methyl vinyl ketone.[5]

Dispersive Kinetics of s-trans ⟶ s-cis *Rotational Isomerization.*—The photoproduct generated from matrix-isolated compound **1** assigned to the less stable s-*trans* rotamer was unstable upon annealing of the matrix. Raising of the temperature of the photolysed sample in krypton and xenon matrices to >50 K caused almost immediate eradication of the bands belonging to the photoproduct, with concomitant increases in the bands due to starting material. Clearly, this is a low-energy transformation consistent with a thermal s-*trans* ⟶ s-*cis* isomerization in gas matrices.

To study the kinetics of this reaction we chose argon as host, since the spectra of mesityl oxide and its photoproduct are very well resolved under these conditions. Kinetic measurements were made in the narrow temperature region 37–41 K. After the thermal conversion of photoproduct into starting material, the spectrum was still well resolved, indicating limited diffusion in the matrix, which is usually manifest by a broadening of IR bands. The kinetics were followed by measuring the intensity of the bands at 1678 and 1268 cm^{-1} during the time course. Rotational isomerization (s-*trans* ⟶ s-*cis*) is a unimolecular process and should, in principle, follow first-order kinetics. The

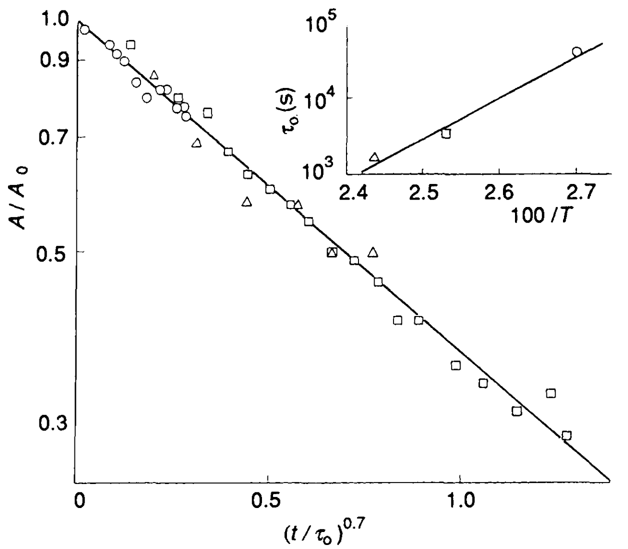


Fig. 3 First-order kinetic plot for the s-*trans* ⟶ s-*cis* rotational isomerism of argon matrix-isolated mesityl oxide presented in co-ordinates proper for the dispersive kinetics. Inset: Arrhenius plot of τ_0

results presented in Fig. 2 in the semilogarithmic format exhibit a multi-exponential character for the process, indicating more complex kinetics.

Kinetic observations of chemical reactions in a nonfluid medium are often difficult to analyse by applying classical kinetic equations. Complications may arise from the perturbation caused by solvent rigidity; different molecules in a rigid matrix may experience different microenvironments. This phenomenon, in principle, can lead to a distribution of activation barriers and to complex (dispersive) kinetics. Recent approaches to dispersive kinetics in condensed media [16,17] offer various mathematical models for the treatment of experimental data. Dougherty and co-workers [17] applied the method called 'distribution slicing' and showed experimentally that the rate dispersion may arise from a distribution of activation energies (E), with the Arrhenius pre-exponential factor (A) remaining constant. We have recently established that conformation-dependent charge delocalization in diamine radical cation in hydrocarbon matrices did not obey classical kinetics; [18a] the kinetic observations were successfully explained by a model of dispersive kinetics.[18b]

The data presented here were analysed in terms of dispersive kinetics using the time-dependent rate coefficient in the form of equation (1) where the parameter $0 < \alpha \leqslant 1$ measures the

$$k(t) = Bt^{\alpha - 1} \qquad (1)$$

reactivity dispersion.[16] The lower the numerical value of α, the greater the dispersivity of the process. The limit of classical kinetics corresponds to $\alpha = 1$. The first-order kinetic equation (2) with the time-dependent rate coefficient [equation (1)]

$$-\frac{\mathrm{d}c}{\mathrm{d}t} = k(t) \cdot c \qquad (2)$$

gives, upon integration, the relation (3) which nicely fits the

$$\ln\frac{c}{c_0} = -\frac{Bt^\alpha}{\alpha} = -(t/\tau_0)^\alpha \qquad (3)$$

experimental results (Fig. 3) for when $\alpha = 0.7$. The values of $\tau_0 = (\alpha/B)^{1/\alpha}$ are shown in the Arrhenius co-ordinates in the inset to Fig. 3.

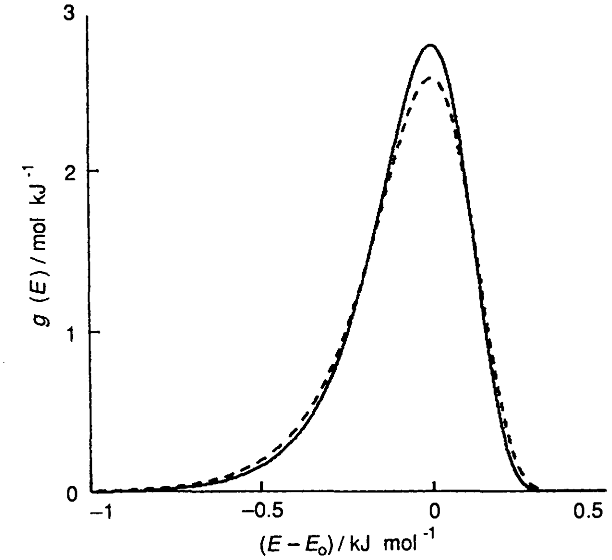


Fig. 4 Densities of activation energy distribution for the s-*trans* ⟶ s-*cis* rotational isomerism of argon matrix-isolated mesityl oxide at 37 K (solid line) and at 41 K (dotted line)

Phenomenologically, the decrease of the rate coefficient $k(t)$ with time according to equation (1) implies [16] that the activation energy for reaction increases as shown in equation (4)

$$E = E_0 + (1 - \alpha)RT\ln(t/\tau_0) \qquad (4)$$

where the effective energy E_0 can be determined from the Arrhenius plot of τ_0 (inset to Fig. 3). This enabled us to obtain the distribution function for activation energy $F(E)$ from the reaction progress: $F(t) = 1 - c/c_0$. The density of the activation energy distribution function [equation (5)] is depicted in

$$g(E) = \frac{\mathrm{d}F(E)}{\mathrm{d}E} \qquad (5)$$

Fig. 4. The first two moments of the activation energy distributions, *i.e.* the mean value of the activation energy $\langle E \rangle$ and the dispersion σ_E^2, are given by equations (6) and (7).

$$\langle E \rangle = E_0 - 0.577(1 - \alpha)RT/\alpha \qquad (6)$$

$$\sigma_E^2 = \frac{\pi^2}{6}[(1 - \alpha)RT/\alpha]^2 \qquad (7)$$

For the classical limit $\alpha = 1$, there is constant value for the activation energy of the reaction (equal to E_0), and the dispersion is equal to zero. These two equations clearly illustrate the physical meaning of parameter α.

For the data under discussion the effective activation energy estimated from the Arrhenius plot of τ_0 (inset to Fig. 3) is equal to 10.9 ± 1.2 kJ mol^{-1} ($\log A = 10.8$). This value may be taken as the mean activation energy for the process because, in the temperature region 37–41 K, the difference between the effective and mean activation energy values (amounting to some 80 J mol^{-1}), is negligible in comparison with the uncertainty of the effective activation energy determination. This value is in good accord with that predicted theoretically (8.8 kJ mol^{-1}).[3] The multiexponential character of the process arises from the dispersion of activation energy, which according to equation (7) varies over a rather narrow range 0.028–0.033 (kJ mol^{-1})^2 in the temperature region 37–41 K.

In the above discussion the ultimate contribution of temperature differences within the matrix on the dispersion of reactivity accounted for by equation (3) was neglected. This contribution, hard to evaluate for a matrix deposited on a window, seems not to be substantial, since a practically temperature independent dispersion of activation energy is seen. Therefore we believe that, as in many systems without the problem of temperature control,[16] the observed distribution in reactivity is mainly due to the differences of the microenvironments for the isolated molecules.

Acknowledgements

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