

PHOTOENOLIZATION OF *o*-METHYL SUBSTITUTED BENZALDEHYDES DISPERSED IN DURENE SINGLE CRYSTALS*

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Summary

The solid state photoenolizations of 2,4,5-trimethylbenzaldehyde, 2,4- and 2,5-dimethylbenzaldehydes in a durene single crystal have been investigated as a function of light intensity and of temperature. The data show that photoenolization of these guests is a monophotonic process. Arrhenius plots for the overall reaction observed from the three guests show two distinct linear regions with change in slope within a narrow temperature region. Different temperature dependent processes which might be involved in the solid state photoenolization reaction of these guests in durene are discussed. The non-resolved character of the well polarized absorption of the photoenol in the durene single crystal at 10 K is indicative of the dissociative nature of its first excited singlet state. It is proposed that the photoenol is initially formed in its triplet state.

Introduction

Aromatic carbonyl compounds with alkyl substituents in an *ortho* position are known to form enols on u.v. irradiation [1]. The enols thus produced are hydroxy-*o*-quinodimethanes (*o*-xylylenes) formed by intramolecular hydrogen transfer from the methyl substituent to the carbonyl group in the *ortho* position. Photoenolization has been mostly studied in liquid solutions by steady-state [1 - 4] as well as by conventional flash [5] or nanosecond laser [6, 7] photolysis techniques. Photoenols are characterized by their broad transient absorption responsible for the yellow colour developed in the solution during photolysis. For example, the non-resolved absorptions of the enols formed from 2,4-dimethylbenzophenone [6] and 2-methylacetophenone [7] with maxima respectively at 4300 and 3900 Å disappear within 3 to 4 seconds in deaerated solutions of cyclohexane at room temperature. However, results obtained on the *o*-quinonoid enol

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generated from polycrystalline 2,3,5,6-tetramethylbenzophenone [8] indicate that the thermal destruction of this species is much slower in solid samples at room temperature.

In the present investigation, we attempted to obtain information on the mechanism of photoenolization carried out on isolated guest molecules dispersed in a crystal matrix. The durene crystal which we have chosen as matrix is particularly convenient as it permits the photochemistry to be done in a rigid environment over the whole temperature range used in these experiments. Furthermore, the yellow coloured enols absorb in a wavelength region where durene is transparent. In this mixed crystal system, thermal destruction of the enol, even at room temperature, is negligible within the time scale of our spectroscopic measurements.

We observed the solid state photoenolization process in durene single crystals doped with the following *o*-methyl substituted benzaldehydes: 2,4,5-trimethylbenzaldehyde (TMB), 2,4- and 2,5-dimethylbenzaldehydes (2,4-DMB and 2,5-DMB). The electronic spectra of the guest molecule as well as that of 3,4-dimethylbenzaldehyde (3,4-DMB — see later) in the host crystal at low temperatures are sharp and well resolved, as was also observed for TMB by Fischer [9]. The spectral characteristics indicate that dispersed substitutional solutions are indeed formed, in agreement with expectations based on the similar geometries between host and guest molecules.

Experimental

Samples of TMB in durene were obtained from commercially available durene (Eastman Kodak 2295) purified by several successive recrystallizations from ethanol. The absorption and emission spectra of the recrystallized product indicate that this method of purification does not exclude the aldehydic impurity of durene which was previously identified as TMB [9]. Further purification of the recrystallized durene by column chromatography on Woelm neutral aluminium oxide considerably reduces the amount of TMB present so that it does not interfere with the results obtained on the photochemistry of other guests deliberately introduced into durene. This further purified durene was therefore used as a single crystal matrix in the present study.

3,4-DMB was synthesized by L. Blanco of Laboratoire des Carbocycles, Orsay, using the Sommelet reaction [10] from 3,4-dimethylbenzylchloride (K and K 15933) and hexamethylenetetramine (Touzart and Matignon). 2,5-DMB (Aldrich 15.106-8) and 2,4-DMB (Aldrich 15.104-1) were purified by distillation under reduced pressure.

Single crystals of purified durene doped with either TMB, 3,4-DMB, 2,5-DMB or 2,4-DMB, at concentrations between 10^{-3} and 10^{-2} g/g, were grown by slowly lowering the deaerated melt in an oil bath through a sharp temperature gradient. Crystal specimens with conoscopically identified bc' or ac' faces developed were cut from ab cleavage sections.

Photolysis of the samples were carried out by 3030, 3130 or 4358 Å

radiations, isolated from a medium pressure mercury lamp Osram HBO 200 W by a Huet M 25 monochromator having a $f/3$ aperture and equipped with a 610 grooves/mm grating blazed at 3000 Å. The intensity of the lamp was held constant with a voltage stabilizer.

Single crystals were positioned by means of a metal support in a cryostat designed in this laboratory by A. Lopez Campillo. This cryostat has three quartz double windows incorporated into stiff Styrofoam thick walls. The double windows were evacuated cylindrical cells provided with two optically plane and parallel windows. The dimensions of the cryostat were adjusted to the cell compartment of a Bausch and Lomb Spectronic 505 spectrophotometer. For absorbance measurements, the single crystals were placed in the analyzing light beam between the two double windows of the cryostat. Photolysis was carried out through the third front window perpendicular to the two others. Once photolyzed, the sample was then rotated by 90° in order to monitor the absorption changes in the region of the crystal submitted to the photolyzing light. Temperatures between 160 K and room temperature were obtained, with accuracies of ± 1 K, by blowing cold nitrogen gas from a liquid nitrogen tank, through insulated tubes, into the cryostat. The rate of nitrogen flow, controlling the temperature in the cryostat, was adjusted by regulating the current in a small heating coil placed inside the liquid nitrogen tank. The temperature in the cryostat was measured by means of a thermocouple placed in the gas stream near the sample. Spectra at 10 K were taken in an 'Air Liquide' cryostat using cold helium gas as a coolant.

We have observed that the light beam of the spectrophotometer has a wavelength dependent polarization. Therefore measurements of polarized absorptions using this beam produce biased spectra which depend on the orientation of the sample. In order to correct for this artifact, all the absorption spectra mentioned in this work were recorded using a light beam completely polarized by means of a HNP'B UV Polaroid. A single polarizer was introduced in our double beam spectrophotometer before the light beam splits into the reference and analyzing beams so as to equally polarize them.

Results and discussion

Evidence for photoenol formation

A yellow coloration due to an absorption peaking around 4050 Å is developed in durene single crystals doped with TMB during 3130 Å radiation photolysis from room temperature down to 160 K. This absorption is mainly polarized along the c' durene crystalline axis. This is illustrated in Fig. 1 which shows absorption spectra of oriented samples recorded with a polarized light beam before and after photolysis at room temperature. This yellow coloration and the related absorption disappear slowly in the dark, more rapidly in daylight at room temperature. While the thermal bleaching of this absorption becomes slower as the temperature decreases, its photo-

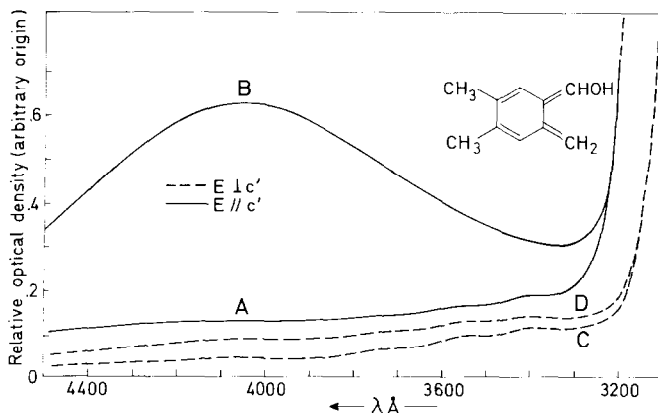
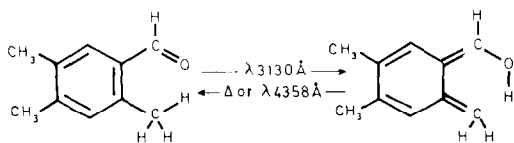


Fig. 1. Polarized absorption spectra of the 2,4,5-trimethylbenzaldehyde photoproduct in durene single crystal at room temperature. Spectra recorded before (A and C) and after (B and D) photolysis at room temperature. The electric vector E of the light beam is polarized along c' (A and B) and perpendicular (C and D) to the durene c' axis.

chemical bleaching with 4358 Å Hg line is efficient over the whole 160 - 290 K temperature range used here.

Similar yellow colorations and polarized broad absorptions were also created in durene doped with either 2,5-DMB or 2,4-DMB during photolysis with 3130 or 3030 Å Hg lines respectively, these radiations corresponding to the intense $S_2 (\pi\pi^*) \leftarrow S_0$ absorptions of these aromatic carbonyl compounds. The polarized absorptions created in samples containing 2,5-DMB and 2,4-DMB have maxima at 4000 Å and 4050 Å respectively. No coloration and related absorption appear on irradiated single crystals of purified durene or of durene doped with 3,4-DMB which does not contain an *o*-methyl substituent.

On the basis of these observations, the broad polarized absorption at 4050 Å is attributed to the photoenol created from TMB by hydrogen transfer from the methyl substituent to the carbonyl group in the six-membered cyclic transition state which is essential for this tautomerization to take place:



The broad polarized absorptions at 4000 and 4050 Å observed respectively in photolyzed mixed crystals of durene doped with 2,5-DMB and 2,4-DMB were also attributed to the corresponding photoenols.

Studies of the reaction mechanism

This monomolecular process was previously studied chiefly in liquid

solutions where the photoenol produced has a short lifetime because of its thermodynamic instability. In the present work the longer lifetime and consequently the higher stationary concentration of the photoenol generated in a solid environment allowed us to perform new studies using conventional steady state photolysis techniques. In order to get more information on the mechanism responsible for the formation of the photoenol from the three guest molecules in the durene host, the relative rate of the species produced was measured both as a function of the photolyzing light intensity at room temperature and as a function of temperature for a given light intensity. To our knowledge such studies have not previously been carried out for photoenolization processes.

In both series of experiments performed with the three guest molecules, the relative rates of photoenol production were measured by monitoring the absorption changes at the broad polarized band maxima during photolysis. However, owing to the inner filter effect of the product, possible back photoprocess and secondary reactions, the absorbance change levels off at high radiation doses. Therefore the rates were determined from the initial linear regions of the curves obtained by plotting the optical density at the band maximum *versus* time of irradiation.

Light intensity dependence of the photoenolization reaction

The relative photolyzing light intensity was modified, within a factor of 9, by using wire screens placed at a sufficient distance from the sample to ensure uniform illumination. The transmission of the screens was measured separately by spectrophotometry. For experiments run at the maximum light intensity where no screen was used, the transmission was taken as 100%. In Fig. 2 are plotted, on a logarithmic scale, the initial rates of photoenol production in durene doped with 2,5-DMB, 2,4-DMB or TMB as a function of the wire screen transmission. The slopes of the lines drawn through experimental points are all equal to unity. These results show that each of the three guest molecules exhibits an intensity exponent of unity in the photoenol formation process. The reaction mechanism is most probably monophotonic and the reactive state a triplet state as in the intermolecular hydrogen abstraction case. A biphotonic mechanism yielding an intensity exponent of unity [11] would necessitate efficient triplet-triplet absorption from a triplet state intermediate of much longer lifetime than is the case for aromatic carbonyl compounds; for TMB for example, the lifetime of the lowest triplet state is 33 ms at 1.8 K [12].

Temperature dependence of the photoenolization reaction

In Fig. 3 are plotted, on a semi-logarithmic scale, the initial rates of photoenol production from the three guests as a function of reciprocal temperature, at a constant 100% photolyzing light intensity. In contrast to what might be expected for such Arrhenius plots, the experimental points do not fit a unique straight line but present, for the three cases, two distinct linear portions with a discontinuity in the slope within a narrow temperature region. This region is approximately the same for the three guests studied.

In Table 1 are displayed the apparent activation energies of the overall

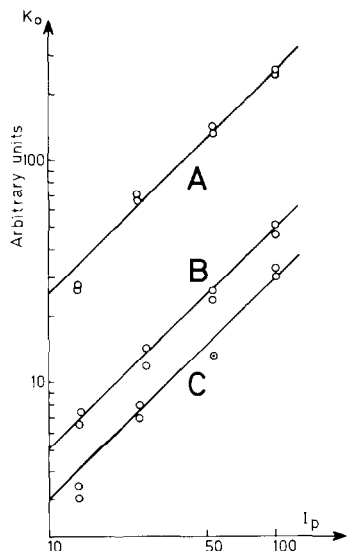


Fig. 2. Photolyzing light intensity I_p dependence of the initial rate K_0 of the photoenol formation in a durene matrix at room temperature from: A, 2,5-dimethylbenzaldehyde; B, 2,4-dimethylbenzaldehyde; C, 2,4,5-trimethylbenzaldehyde.

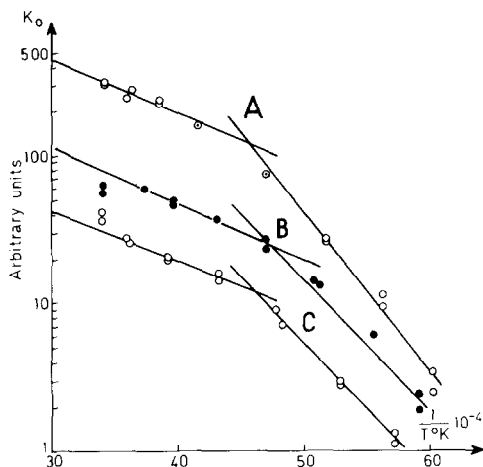


Fig. 3. Temperature dependence of the initial rate K_0 of the photoenol formation in a durene matrix from: A, 2,5-dimethylbenzaldehyde; B, 2,4-dimethylbenzaldehyde; C, 2,4,5-trimethylbenzaldehyde.

TABLE 1

Apparent activation energies (kcal/mol) for the photoenolization reaction from 2,5-DMB, 2,4-DMB and TMB

Guest involved	Temperature range	
	300 - 215 K	215 - 160 K
2,5-DMB	1.6	4.9
2,4-DMB	1.7	4.0
TMB	1.5	4.0

reaction determined from the two distinct linear portions of the Arrhenius plots for the three guest molecules.

These data show that the two temperature regions give two different apparent activation energies (~ 1.6 kcal/mol and ~ 4.3 kcal/mol) which are about the same within experimental error for the three guest molecules. This indicates that different rate controlling processes must be predominant in each of the two temperature regions. Furthermore, the relatively restricted temperature range of the transition between these two regions would suggest the existence of an abrupt structural modification of the first order phase transition type. However, such a phase transition is not known for durene. It is unlikely that the modification is a dynamic one, *e.g.* related to the

increasing rotation of the methyl groups, since this should not show up as an abrupt change without an accompanying structural modification.

Similar abrupt changes in Arrhenius plots were also found by Somersall *et al.* [13] for the phosphorescence emitted from various polymer films containing either ketones and/or naphthalenic groups. The changes in slope were observed at the temperatures corresponding to the onset of characteristic subgroup motion in the polymers, thus affecting the local accessibility of oxygen to quench the triplet state of the emitting group. In our case the changes in slope observed in Fig. 3 for the photoenolization reaction cannot be explained by an oxygen diffusion process setting in in the matrix around 215 K. The effect of oxygen would be to quench the reaction [6] at higher temperatures in contradiction to our observations. Furthermore, oxygen diffusion effects are unlikely to be important in the durene single crystal since we were able to conserve for months at about 270 K a sample of durene containing 2,4,5-trimethylbenzyl radicals without detectable loss of the latter.

In order to rationalize our observed temperature dependence of the overall photoenolization process, it is necessary to now discuss the various physical effects of an increase in thermal energy in this system.

First of all it should be noted that two triplet states are accessible over the temperature range studied. From the vibrational structure of the TMB phosphorescence in durene at 4.2 K [9], it was found that the lowest triplet state of this guest has a ${}^3\pi\pi^*$ character. However, a higher lying ${}^3n\pi^*$ triplet state at 400 cm^{-1} from the lowest state has been detected from the temperature dependence of the vibrational structure of the TMB phosphorescence in a durene matrix [14]. We have obtained some spectroscopic evidence, as yet unpublished, that for 2,5-DMB, 2,4-DMB as well as for 3,4-DMB, the lowest triplet state has ${}^3\pi\pi^*$ character and that close, higher lying ${}^3n\pi^*$ states are present at about 65, 100 and 350 cm^{-1} respectively.

It is well known that for intermolecular hydrogen abstraction reactions, the ${}^3n\pi^*$ triplet state of the aromatic carbonyl compound is much more reactive than the ${}^3\pi\pi^*$ state. If this is also the case for photoenolization reactions, then we might expect a certain temperature dependent reactivity of our guests towards hydrogen abstraction since, in the temperature range studied, the higher lying ${}^3n\pi^*$ state can be thermally populated in TMB, 2,5-DMB as well as in 2,4-DMB.

Experimentally, we observe essentially the same temperature dependence for the three guest molecules which, however, as we have stated above, have very different energy gaps between their ${}^3n\pi^*$ and ${}^3\pi\pi^*$ states. It follows that the observed temperature behaviour of the photoenolization reaction is not sensitive to the relative population of the ${}^3n\pi^*$ to ${}^3\pi\pi^*$ states. This can be interpreted as indicating that the ${}^3\pi\pi^*$ state is more reactive here than in the usual intermolecular case. However, another and possibly concurrent interpretation is that some process other than the reactive state population process is predominant in controlling the reaction rate.

We must now consider in some detail structural and dynamic aspects of the photoenolization process.

By optical detection of the e.s.r. of the TMB triplet state in durene, Sharnoff [12] has shown that at 1.8 K, the TMB carbonyl group is approximately parallel to the durene *c'* axis and therefore to the durene as well as to the TMB short axis. Such a conformation of the TMB molecule is not favourable for the photoenolization process which requires the formation of a suitable six-membered cyclic transition state. However, as the temperature increases, the rotation of the CO group around the C-C axis must become easier. It should be noted that for crystalline durene, the barrier to rotation of the methyl groups is about 1.6 - 2.0 kcal/mol [15]. This rotation in the durene matrix would therefore increase with temperature and it could also contribute, by a meshed "gear wheel" type action, to re-orient the guest CHO group to a steric position favourable to the abstraction reactions.

Another effect of increasing temperature is to induce the guest CH₃ group in the *ortho* position to occupy a dynamically more favourable orientation for the reaction to take place.

In view of the expected greater energy barrier to re-orientation of the carbonyl group as compared to the CH₃ group of the aldehyde, we consider that it is the rotation of the carbonyl group which controls the rate of the overall reaction in the low temperature range. At about 215 K, we consider the rotation of the CO group to become relatively free and the reaction would then be controlled predominantly by other processes giving a different activation energy.

Let us point out that in this higher temperature range, no guest phosphorescence can be detected from our samples of TMB, 2,4-DMB or 2,5-DMB in durene. This indicates that in these conditions the lowest triplet state of the aldehydes is mostly deactivated by radiationless processes, one of them being the photochemical enolization process. However, one cannot exclude the existence of temperature dependent photophysical radiationless processes which are known to deactivate triplet states of aromatic molecules in solid solutions. For example in the case of naphthalene-d₈/durene mixed crystals, the guest phosphorescence lifetime, which remains nearly constant at low temperatures, starts to decrease at temperatures higher than 200 K [16] which correspond to the temperature region where we observe the changes in slopes in Fig. 3. The drastic decrease in naphthalene-d₈ phosphorescence lifetime was discussed and finally attributed to an increase in radiationless transition rates at higher temperatures in the durene host [16]. Such a photophysical process certainly occurs in the mixed crystals studied in the present work, as evidenced by the absence of any phosphorescence at temperatures higher than about 200 K in mixed crystals of 3,4-DMB in durene where no photoenolization occurs.

From this discussion it appears that the apparent activation energy of 1.6 kcal/mol derived from higher temperature experiments results from at least two processes, the photoenolization reaction and the photophysical radiationless transition, each process having its own intrinsic activation energy. No data are available on the activation energies of intramolecular hydrogen abstraction in the photoenolization reaction in solution but in the

case of intermolecular hydrogen abstraction by benzophenone in liquid solutions [17] the activation energy for abstraction of a primary benzylic hydrogen is 2.5 kcal/mol.

Photoenol excited states

The *o*-quinonoid enol is well oriented in the durene single crystal since its absorption is well polarized along c' and in addition it is generated photochemically from a well oriented TMB guest. However, spectra recorded at low temperatures indicate that the broad absorption at 4050 Å remains unresolved even at 10 K. This is interpreted as indicating that the enol excited singlet state is dissociative, returning to the aldehyde by hydrogen transfer back to the CH_2 group. This explains the easy photolytic destruction of the enol as evidenced by the disappearance of its absorption on irradiation with 4358 Å radiation. The photochemical instability of the excited singlet state indicates that the formation of the enol does not involve this state. Consideration of the energies involved in the photolytic tautomerization process suggests that the photoenol is formed in an excited state: this is probably the triplet state since the excited singlet level is disallowed from the above discussion. Formation of photoenols in their triplet state has previously been suggested by Huffman *et al.* [3] in the case of chromones.

Further support for this interpretation of the unresolved character of the enol absorption is provided by results of experiments on *o*-durylene produced by photolysis ($\lambda = 2537$ Å Hg line) of durene in *n*-hexane at 77 K and identified by its fluorescence and excitation spectra measured at 77 K [18] (see Fig. 4). The vibrational structure is here relatively well resolved even though the polycrystallinity of the matrix creates inhomogeneous sites for *o*-durylene. The excited singlet state of *o*-durylene cannot tautomerize and therefore is stable as evidenced by the existence of its fluorescence. We

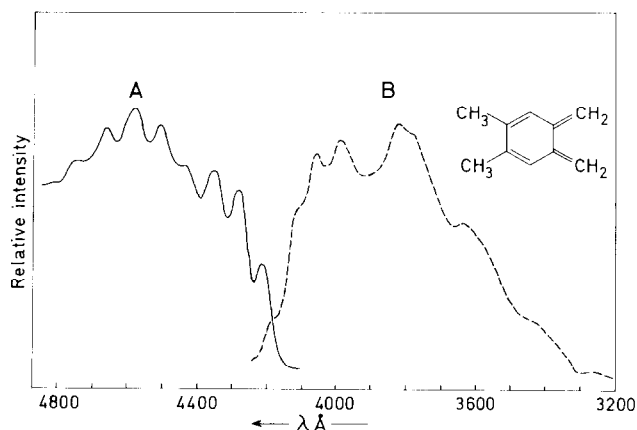


Fig. 4. Electronic spectra of *o*-durylene produced by photolysis of durene ($C = 10^{-3}$ M) in *n*-hexane at 77 K. A, Fluorescence excited by $\lambda = 3600$ Å radiation; B, excitation spectra of the fluorescence at $\lambda = 4750$ Å.

also note that the broad absorption of the photoenol shown in Fig. 1 is in the same wavelength region as the Franck-Condon envelope of the excitation spectrum of *o*-durylene, and that its displacement towards lower energies is in agreement with the expected OH-substituent effect on $\pi\pi^*$ transitions.

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