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KINETIC STUDIES OF TRANSIENT PHOTOCHEMICAL ISOMERS OF 2-CYCLOHEPTENONE, 1-ACETYLCYCLOHEXENE AND 2-CYCLO-HEXENONE*

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Summary

Nanosecond laser photolysis and conventional gas discharge flash photolysis have been used to search for electronic spectra of transient species or states following the photoexcitation of dilute solutions of 2-cycloheptenone, 1-acetylcyclohexene and 2-cyclohexenone in methylcyclohexane. In addition to the long lived *trans* isomer of 2-cycloheptenone previously observed, the spectrum of a short lived transient with a first order rate constant of the order of 10^7 s^{-1} was observed for each of the three enones. Arrhenius parameters derived from the temperature dependence of these rate constants are presented. Neither the addition of piperylene nor the deoxygenation of the solutions had any effect on the formation or decay kinetics of any of the transients. It thus appears that these short lived species are not triplet states of the parent molecules. We propose that the existing evidence is best explained by assuming that the intermediates produced by photolyzing either 2-cyclohexenone or 1-acetylcyclohexene are highly strained *trans* isomers of these molecules, and that in the case of 2-cyclo-heptenone the short lived transient is a higher energy conformer of the *trans* isomer. Attempts to stabilize these very short lived intermediates by matrix isolation photolysis in argon at 14 K proved unsuccessful.

Introduction

The effect of the geometric constraints imposed on photochemical processes involving *cis–trans* isomerization by incorporating an ethylenic bond in a medium or small ring has been the subject of considerable inves-

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tigation and speculation (see, for example, refs. 1 - 3). The actual detection and characterization of photolytically produced *trans* cyclenes with eight or fewer atoms in the ring* has proved to be a difficult task. Success has been achieved with some conjugated systems for which accessible excited states of relatively low energy exist. Eaton and Lin [4] produced and characterized *trans*-2-cyclooctenone by photolyzing its *cis* isomer in solution at room temperature. The analogous *cis–trans* photo-isomerization of 2-cycloheptenone (I) has also been reported [5, 6] but in this case the *trans* isomer was found to be stable only at temperatures below —160 °C. The formation of *cis,trans*-1,3-cyclooctadiene has been reported to result from both sensitized [3] and direct [7] photolysis of its *cis,cis*-isomer.

Despite the degree of distortion necessary to accommodate a *trans* ethylenic bond in a six-carbon cyclic alkene, these species have been implicated as transients in photo-isomerization [3], photocyclo-addition [2] and photoprotonation [1] reactions. Recently, Bonneau *et al.* [8] have reported a transient observed during the laser photolysis of 1-phenylcyclohexene which they identify as the *trans* isomer of that molecule.

Eaton [2], in reviewing the photochemistry of alicyclic enones, has pointed out that 1-acetylcyclohexene (II) behaves more like 1-acetylcycloheptene than like 1-acetylcyclopentene. He proposes that the cycloheptene and cyclohexene reactions involve strained *trans* intermediates whereas the reactive species in the case of the cyclopentene is a triplet state species. This is in contrast to the photochemical behavior of 2-cyclopentenone, 2-cyclohexenone (III) and (I). For this latter homologous series, the cyclohexene behaves more like the cyclopentene (both presumably involving reactive triplet intermediates) than like the cycloheptene which has been shown to form a labile *trans* isomer [5, 6]. This difference in behavior was attributed to the fact that the incorporation of the sp^2 hybridized carbon in the ring of III would make the *trans* isomer more strained and less stable than in the case of II.

Our success in using flash and laser photolysis [9] as well as matrix isolation spectroscopy [10] to study the photo-isomerization of 1,3,5-cyclooctatriene encouraged us to use these techniques to obtain direct spectroscopic evidence for the roles of *trans* isomers and triplet species in the photochemistry of I, II and III. Although we were successful in detecting a long lived transient which behaved as would be expected of the previously identified *trans* isomer I [5, 6], we shall not report the details of our observations on this species**. In this paper we confine our discussion to our ob-

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*To simplify the discussion we shall refer to all molecular conformers related to the *cis* configuration about the ethylenic bond by a torsional twist of greater than 90° as *trans*. We recognize that in seven-membered or six-membered rings the "true" 180° *trans* orientation would require a totally unrealistic distortion of the rest of the molecule.

**Our observations on the first order *trans–cis* thermal isomerization of I were hindered by competition from the dimerization reactions of *trans*-I. Furthermore, we have been informed by R. Bonneau that he and coworkers have determined that, under conditions similar to the ones we used, a *trans–cis* photo-isomerization is induced by the

servation of three very short lived photochemical transients — one each for the enones I, II and III — which have not previously been reported.

Experimental section

The samples of I used in these studies were from two different commercial sources. The UV and IR spectra of these samples were identical with those in the literature. Further purification of this material by vapor phase chromatography was performed for the initial samples used, but this procedure was found to have no effect on the observed spectra or photochemistry and was not used for subsequent samples.

Solutions of II and III were prepared from research grade commercial samples which were further purified by vapor phase chromatography and then stored at temperatures below —80 °C. The solvent for all samples was spectral grade methylcyclohexane. Deoxoygenation of the samples was accomplished by three cycles of cooling to 77 K, evacuating to a pressure of less than 10^{-3} Torr and thawing under vacuum. The piperylene used in the quenching studies was a freshly vacuum distilled commercial sample.

Both the Nd laser apparatus [11] and the gas discharge apparatus [9] have been previously described in some detail. Laser photolysis was accomplished using the third harmonic at 353 nm. The laser pulse had a halfwidth duration of 35 ns. The laser beam, reduced to a 4 mm X 8 mm cross section, was projected on one side of a 10 mm X 10 mm silica cell with polished sides. The analyzing light beam passed in a crossed beam arrangement through a 2 mm wide section adjacent to the laser beam entrance window. The gas discharge photolysis used a pulse with a halfwidth duration of 4 μs from six oxygen-filled flash tubes surrounding a jacketed 20 cm quartz cell.

A monochromator–photomultiplier–oscilloscope arrangement was used to detect transient optical density changes over the 255 - 600 nm wavelength range at intervals of 20 nm and oscilloscope sweep rates in the range 10^8 - 10^{-1} cm s^{-1}. The regions where positive results were obtained were reinvestigated at wavelength intervals of 5 nm.

Data for the Arrhenius plots using the laser apparatus were obtained by placing the sample cell in a brass block heated by resistance wire, or by placing the cell in an insulated jacket through which a controlled flow of dry cold nitrogen gas was passed.

The general procedure employed in the matrix isolation studies has been described previously [10]. A cryogenic refrigerator (Air Products and

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analyzing beam of the flash photolysis apparatus and it is this process, rather than the thermal process, that is probably primarily responsible for the first order rate constant of 8.8×10^{-2} s^{-1} which we determined at 25 °C. We understand that the results of a more thorough study of the complicated kinetics of *trans*-I are presently being prepared for publication by Bonneau *et al.*

Chemical Displex) was used to cool samples to 14 K. Infrared spectra were recorded using a Perkin–Elmer model 180 spectrophotometer.

Results

Gas discharge flash photolysis

Flashing solutions of I, II or III dissolved in methylcyclohexane resulted in the observation of no transient spectral changes in the 255 - 600 nm wavelength region other than those due to the very long lived *trans* isomer of I (see refs. 5 and 6 and footnote to p. 30).

Laser photolysis

When either air-saturated or degassed solutions of I in methylcyclohexane at a concentration of 3×10^{-2} M were exposed to a laser pulse of 353 nm radiation, a transient absorbance change with a half-life of less than $1 \mu s$ was observed over the wavelength interval from 260 to 290 nm. The initial absorbance increase observed at a time interval of 80 ns after initiation of the laser pulse is plotted *versus* wavelength as the dotted curve in Fig. 1. The disappearance of this transient is characterized by a further increase in absorbance to produce the broken curve. This latter spectrum corresponds to that of the long lived *trans* isomer. The similarity of the
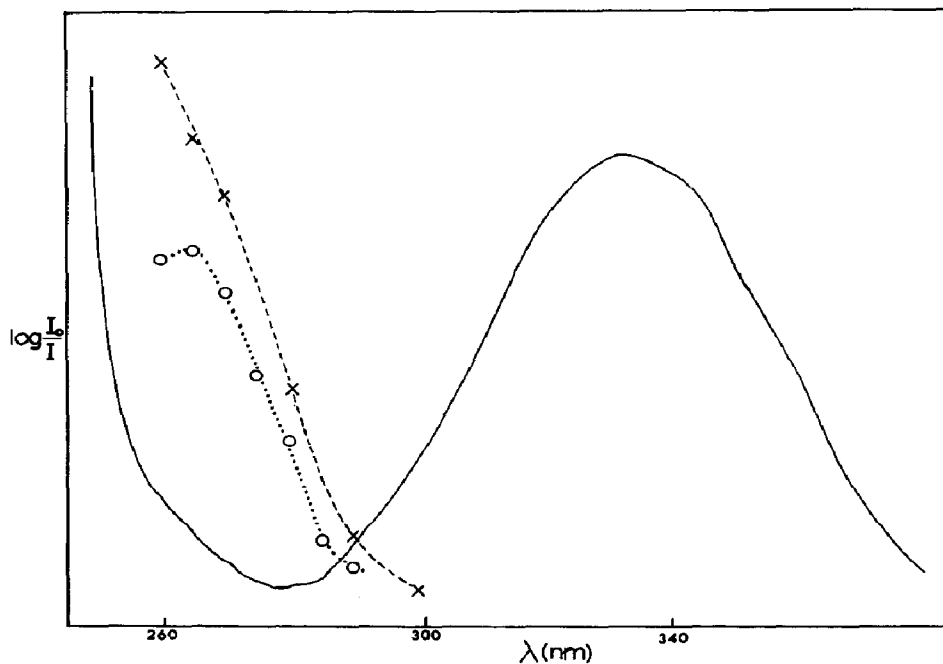

Fig. 1. The absorption spectrum of *cis*-I (solid curve) and the differential absorbance spectra of long lived (broken curve) and short lived (dotted curve) photolytically produced transients.

spectrum observed immediately after the flash and that obtained following the decay of the short lived transient leads to two possible interpretations of this result. The spectrum represented by the dotted curve may be characteristic of the transient or it may be due to the *trans* isomer formed during the laser pulse. In either case the subsequent increase in intensity of *trans* absorption indicates that this isomer of I is a product of the decay of the observed short lived species or state. The fact that the dotted curve in Fig. 1 peaks at 265 nm, whereas the broken curve is still rising at 260 nm, appears to indicate that the short lived transient does absorb in this region. This conclusion is qualified by the fact that the uncertainty of our absorbance measurements below 270 nm increases rapidly owing to absorbance by the parent species. (The spectrum of I shown as the solid curve in Fig. 1 is for a considerably more dilute solution than that which we actually used in the laser experiments.)

The decay of the short lived transient photochemical product of I is first order and has a rate constant of $(5 \pm 1) \times 10^6 \, \mathrm{s}^{-1}$ at 25 °C. Addition of piperylene at concentrations as high as 0.1 M had no observable effect on either the magnitude of the observed transient absorbance change or its decay rate. The temperature dependence of the decay rate was studied at 10 °C intervals over the range 24 - 54 °C. The resulting data yielded a linear plot of log k *versus* $1/T$. The Arrhenius parameters derived from this plot are $E_a = 7.5 \pm 1 \, \mathrm{kcal \, mol}^{-1}$ and $A = 2 \times 10^{12} \, \mathrm{s}^{-1}$.

When a 3×10^{-2} M solution of II in methylcyclohexane was exposed to a laser pulse, a transient absorption change was observed over the wave-
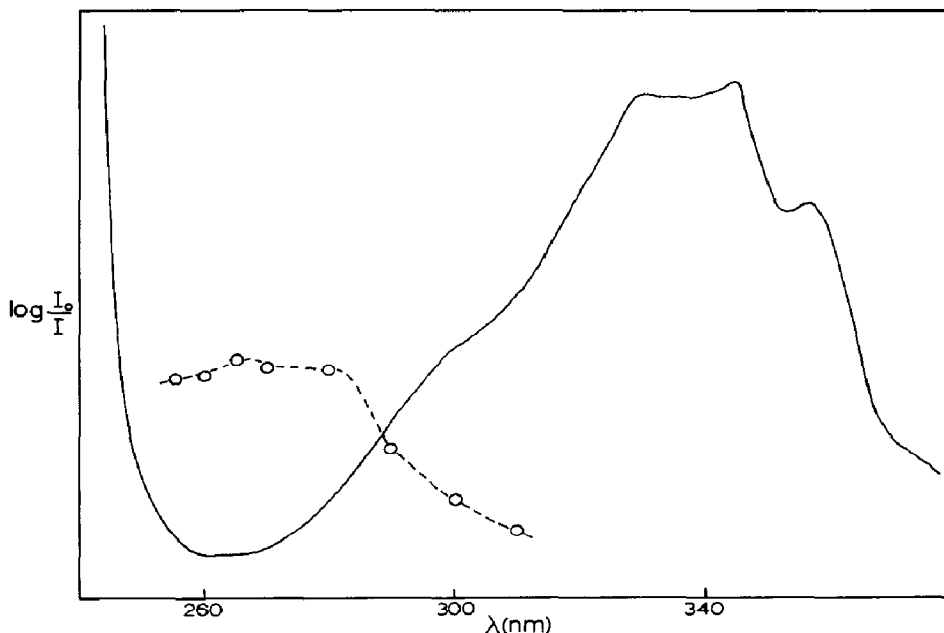

Fig. 2. The absorption spectrum of II (broken curve) and the differential absorbance spectrum of its observed transient photolysis product (broken curve).

length region from 265 to 310 nm. The effect clearly extended to shorter wavelengths but the high extinction coefficient of the parent molecule prevented observation at wavelengths less than 265 nm. The absorbance increase observed at a time interval of 50 ns after initiation of the laser flash is plotted *versus* wavelength as the broken curve in Fig. 2. The absorbance change was found to be linearly related to the intensity of the laser pulse. Analysis of the decay curve for this phenomenon showed it to be a first order process with a rate constant at 25 °C equal to $(2.7 \pm 0.2) \times 10^7 \text{ s}^{-1}$. The absorbance relaxed to its pre-flash value and examination of the UV spectrum of the sample after exposure to as many as 30 flashes showed no permanent change. (The facts that less than 5% of the sample in the cell is actually exposed to each laser pulse and that only a small percentage of the molecules of the exposed sample are converted to the transient reduces the significance of this result. We estimate, however, that 30 flashes resulted in a minimum cumulative conversion of 4% of the molecules of II in our sample to the observed transient. A decrease of this size in the concentration of II would certainly have been detectable, and thus it is clear that most, if not all, of the transient reverts to II.) Deoxygenation of the sample prior to flashing produced no change in either the intensity of the transient absorbance or in its rate of decay. Addition of piperylene at concentrations as high as 0.1 M also had no observable effect.

A least squares fit of a straight line to a plot of log k *versus* $1/T$ over the temperature range 25 - —45 °C yields the Arrhenius parameters $E_a = 0.4$ kcal mol^{-1} and $A = 5 \times 10^7 \text{ s}^{-1}$ for the decay of the transient.
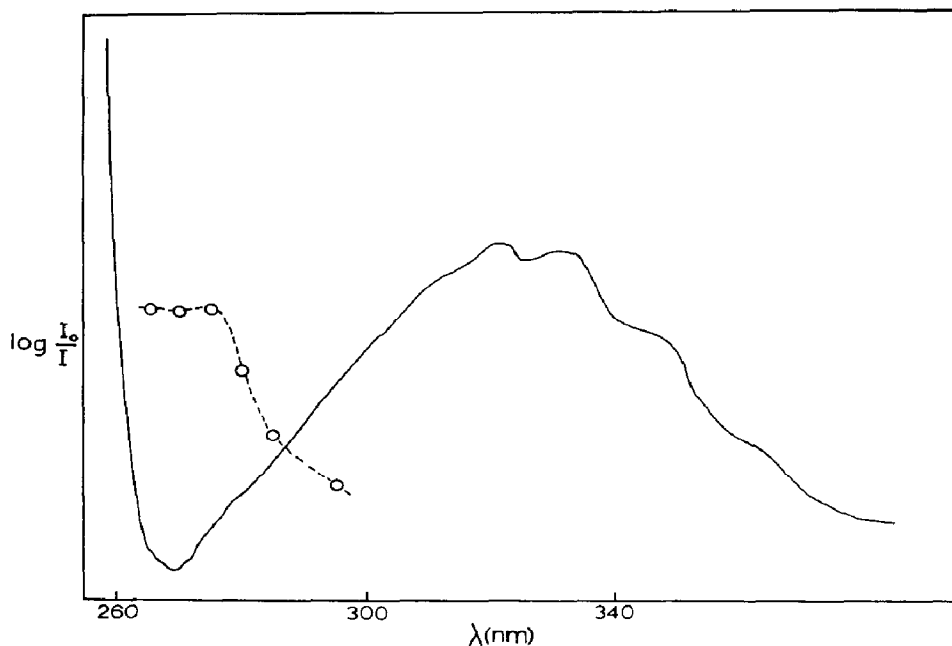

Fig. 3. The absorption spectrum of III (solid curve) and the differential absorbance spectrum of its transient photolysis product (broken curve).

Identical studies on 3×10^{-2} M solutions of III in methylcyclohexane produced very similar results. A plot of the transient absorbance change observed with these samples is shown as the broken curve in Fig. 3. The decay of this transient was also a first order process with $k = (1.9 \pm 0.2) \times 10^7$ s^{-1} at 25 °C. The post-flash absorbance relaxed to its pre-flashed value and multiply flashed samples showed no UV spectral changes. The effect was found to be linearly related to laser flash energy. Neither deoxygenation nor addition of piperylene produced any apparent effect. The Arrhenius parameters obtained by temperature dependence studies (in this case over the range from 20 °C to - 65 °C) are $E_a = 0.3$ kcal mol^{-1} and $A = 3 \times 10^7$.

Matrix isolation spectroscopy

Photolysis of I in solid argon (mole ratio Ar:I = 500) at 14 K produced only the IR spectrum previously attributed to its *trans* isomer [5, 6]. Warming this sample to 30 K produced no changes in the spectrum. Similar matrix photolysis of either II or III for as long as 4 h produced no change in the IR spectrum.

Discussion

Our initial suspicion concerning the identities of the short lived photochemically produced transients of I, II and III focused on triplet states of these molecules. Only in the case of III has the direct role of a triplet state in the photochemistry of these molecules been observed [12]. It has been presumed, however, that the failure to observe chemical evidence for the triplet states of I and II is due to their rapid conversion to reactive *trans* isomers [2]. Our failure to observe quenching by either oxygen or piperylene rules out the triplet state as the identity of any of the transients. If we assume that deactivation by piperylene would compete successfully with conversion of a shorter lived triplet state to any of our observed transients and if this deactivation process has a typical bimolecular rate constant of the order of 10^9 l mol^{-1} s^{-1}, then our failure to observe a reduction in the yield of the transient species by piperylene concentrations as high as 0.1 M limits the lifetime of a triplet precursor to a maximum of about a nanosecond. This conclusion is supported by the work of Wagner and Bucheck [13] who reported 3.0×10^8 s^{-1} as the rate constant for the decay of the triplet state of III which is responsible for the photodimerization of that molecule. As suggested by these workers, even shorter lifetimes should be expected for molecules like I or II for which the geometrical constraint against *trans* isomer formation is diminished.

Having concluded that they are not triplet states, we are left with the question of identifying the observed photochemical intermediates. The fact that these species decay to produce either the parent molecule or its *trans* isomer would seem to limit our choices to relatively unstable isomers.

In the case of the photolysis of I, we can think of only two alternatives. The only possible isomer of I that might be formed photochemically and then decay thermally to *trans*-I is the oxetene, $\Delta^{1,8}$-7-oxa-bicyclo[4.1.1]-octene (Ia):

Ia

The second alternative is a higher energy conformer of *trans*-I. Dreiding models with a 35° - 45° torsional distortion of the *trans* vinyl group suggest the two possible conformers below, of which Ib is likely to be of somewhat lower energy owing to steric repulsions between the hydrogen atoms on carbon atoms 3 and 6 of Ic.

Ib   Ic

A stable oxetene has been observed to result from the photolysis of 3,4-dimethylpent-3-en-2-one by Friederich and Schuster [14]. The lowest energy absorption maximum for this oxetene was found to occur at wavelengths less than 215 nm. Although uncertainties in our absorbance data below $\lambda = 270$ nm cast some doubt on our observation of an absorption maximum at $\lambda = 265$ nm (see Fig. 1), we are inclined to interpret the reported spectrum as favoring a high energy conformer such as Ib which would be expected to have a spectrum similar to I, rather than the oxetene which would not absorb in this region. The stability of the oxetene observed by Friederich and Schuster [14] and of the oxetene observed [15] to result from the photolysis of cyclooctatetraene oxide also leads us to doubt that Ia, once formed, would be as unstable as the observed transient.

The spectra of the transients observed following the laser excitation of II and III rule out the identification of these species as oxetenes or other unstable structural isomers of the parent molecules. The only remaining explanation that is consistent with the data is that the species we have observed are the highly strained *trans* isomers of II and III. The fact that the spectra of these intermediates is considerably shifted from that reported for the species identified as *trans*-1-phenylcyclohexene [8] is not very surprising. It is surely more appropriate to consider the latter molecule as a styrene derivative rather than as a simple substituted cyclohexene. Recent calculations have demonstrated the sensitivity of the potential surface of the lowest singlet and triplet excited states of the styrene molecule to

specific interactions of the lowest states in the ethylene and benzene state manifolds [16]. We assume that we are observing a red-shifted $\pi-\pi*$ state in the case of the enones and that a diagram similar to the one given by Bonneau *et al.* [8] would be appropriate to explain such a shift, but to anticipate a shift of the same magnitude seems inappropriate in terms of the anticipated differences in the dependence of the corresponding excited states on the twisting of the ethylenic bond.

The existence of *trans* isomers with similar lifetimes for both II and III does not conflict with the previous photochemical evidence on these species [2]. The fact that the photochemical dimerization and addition reactions of II do not appear to involve a triplet directly, whereas those of III do, can be interpreted in terms of a much more rapid rate of triplet to *trans* conversion in the case of II. It does seem surprising, however, that the *trans* isomer of the presumably more rigid III should be as stable as that of II.

Our failure to observe IR evidence for the stabilization of the short lived isomers of II and III is not at all surprising since extrapolation of the Arrhenius plots results in predictions of lifetimes for both of these species of less than 10^{-1} s at 14 K. In the case of the photochemistry of I, a similar extrapolation leads to a predicted lifetime of 3.5 h at 100 K. Our inability to detect this intermediate suggests that photolysis produces a vibrationally hot species that decays before it is thermally equilibrated.

Acknowledgments

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