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TRANSIENT PHENOMENA IN THE PHOTOCHEMISTRY OF *TRANS*-AZOCUMENE[1]

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Summary: Laser flash photolysis work demonstrates that the dominant process at room temperature in the photolysis of *trans*-azocumene is its isomerization to the cis isomer; cumyl radicals are also produced within 20 ns of excitation.

The mechanism for the decomposition of diazene compounds has been the subject of extensive work[2-7]. Stepwise and concerted mechanisms have been proposed (reactions 1 and 2), although experimental[2,4,5] and theoretical[8] evidence tend to support the intermediacy of diazenyl radicals proposed by Pryor[2].

$$R_1\text{-N=N-}R_2 \longrightarrow \underset{\textbf{I}}{R_1\text{-N=N}^{\bullet}} + R_2^{\bullet} \longrightarrow R_1^{\bullet} + N_2 + R_2^{\bullet} \qquad (1)$$

$$R_1\text{-N=N-}R_2 \longrightarrow R_1^{\bullet} + N_2 + R_2^{\bullet} \qquad (2)$$

CIDNP[7,9], ESR[10] and laser photolysis techniques[11] have been employed to aid in the detection of diazenyl radical intermediates I. In the last year we have explored the possibility of detecting aryldiazenyl radicals directly using optical absorption spectroscopy. Recently, Suehiro *et al.*[10] have been rather successful in detecting these intermediates (I; R_1=Ar) in solution employing ESR techniques. The radicals, generated by photocleavage of the N-S bond in aryl(arylthio)diazenes, were reported to have lifetimes of a few microseconds at room temperature. In another recent publication,[11] on the photolysis of *trans*-azocumene (II), it has been proposed that the corresponding diazenyl radicals, $PhC(CH_3)_2N_2^{\bullet}$, have a lifetime of ~9 µs in cyclohexane at 293K. Given that the cleavage of phenyldiazenyl and cumyldiazenyl radicals produce a highly reactive and a highly stabilized radical, respectively (and that this must be reflected in the bond energies), it seems unlikely that these two diazenyl radicals would have comparable lifetimes. For comparison, in the case of acyl radicals the rate constants for decarbonylation are a direct function of the stability of the radical formed[12].

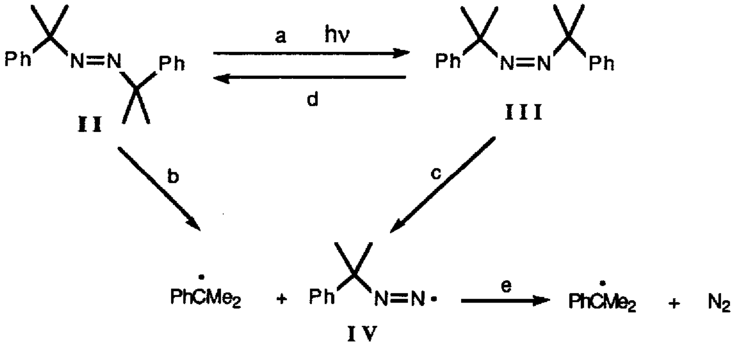
The photolysis of *trans*-azocumene could proceed via two distinct mechanisms, depending on whether *cis*-azocumene (III) plays a role or not in the generation of cumyl radicals, Scheme I.

We have reexamined the photochemistry of *trans*-azocumene using laser photolysis techniques. We conclude that cumyldiazenyl radicals must be short lived, with lifetimes of <20ns.

Results and discussion:

Laser excitation of a 0.02M deaerated solution of *trans*-azocumene in cyclohexane at 292K leads to the transient spectrum of Figure 1, recorded between 3.3 and 4.9 µs following excitation. The band around 315nm is readily scavenged by oxygen and is produced "instantaneously", (<20ns) in our time scale. We assign these

Scheme I



signals to cumyl radicals on the basis of their similarity with the reported spectroscopic data on this[13] and other benzylic radicals[14]. The failure to detect a biphasic growth of the cumyl signal (i.e. steps **b** and **e** in Scheme I) suggests that step **e** does not take place in the time scale we monitor; i.e. it is either too fast or too slow. Since diazenyl radicals of this type are not known to undergo intermolecular reactions and their deazatization is known[4] to compete with escape from the solvent cage, we believe that the correct explanation is that they are too short lived to be detected in our experiments. That is, both steps **b** and **e** lead to formally instantaneous formation of radicals. Engel[15] has reported a value of 0.36 for the nitrogen quantum yield for the photolysis of *trans*-azocumene in solution. This value which incorporates all modes of nitrogen formation (i.e. paths **b+e** and **c+e**) cannot be compared directly with the quantum yield for "instantaneous" cumyl radical formation due to

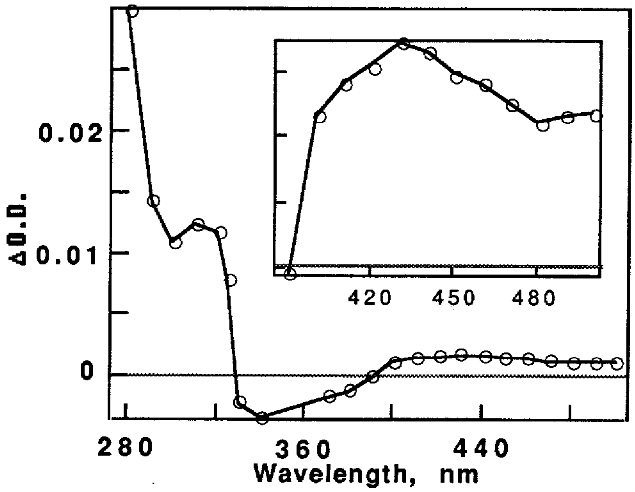


Figure 1. Transient spectrum obtained following laser excitation of a 0.02 M sample of *trans*-azocumene in cyclohexane monitored between 3.3 and 4.9 μs after excitation.The insert shows a detail of the data at λ> 400 nm.

competing geminate processes as well as photoisomerization followed by steps **c+e**. While we have not carried out transient quantum yield determinations in this system (they would be experimentally rather difficult), the signals from cumyl radicals are weak compared with those typically observed from other benzylic systems[13,14]. We suspect that the quantum yield for direct photocleavage (step **b**) leading to free radicals is ≤0.1.

The transient spectrum of Figure 1 also shows a region of bleaching between 330 and 390nm. These negative signals are attributed to the partial depletion of *trans*-azocumene which absorbs in this region. The positive signals in the 430 nm region are attributed to *cis*-azocumene, which had a lifetime of 5µs at 292K in cyclopentane (Figure 2); its decay followed first order kinetics. The lifetime increases to around 10 µs at 205K. Our data for *cis*-azocumene are in agreement with Engel's report[16] of λ_{max} at 434nm at 77K in a polymethylmethacrylate matrix, and a lifetime of 10 minutes at 173K. Oxygen saturation eliminated the signal at 315 nm, but had no significant effect on the intensity or lifetime (Figure 2) of the weak band at 430 nm .

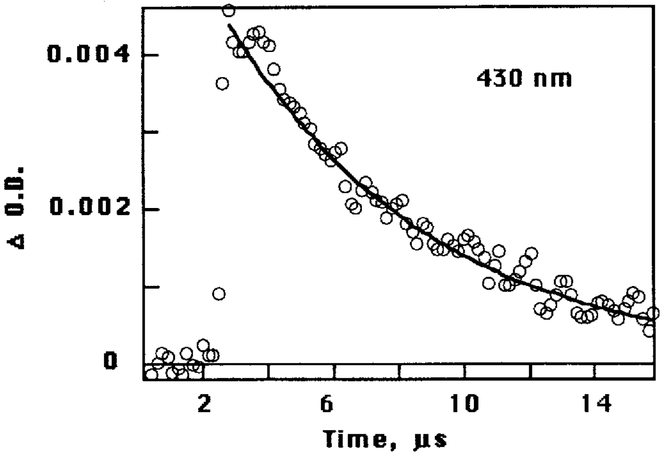
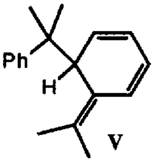


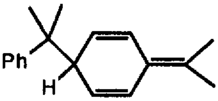
Figure 2. Decay trace monitored at 430 nm in cyclohexane at 292 K.

Thus, we conclude that the transient phenomena observed in the laser photolysis of *trans*-azocumene involves photocleavage to yield cumyl radicals and *cis*-azocumene. Diazenyl radicals are too short lived to be detected in our experiments. The lifetime of *cis*-azocumene is ~5µs; this decay must result from a combination of regeneration of *trans*-azocumene and cleavage of the cis isomer to yield cumyl radicals (i.e. steps **c** and **e** in Scheme I).[4,6,17] The absence of delayed cumyl formation suggests the former is the dominant process.

Why are our results in disagreement with a recent report on the lifetime (9 µs) of cumyldiazenyl, and what are the possible explanations for this discrepancy? It is clear that the assumption by Sumiyoshi *et al.*[11] that *cis*-azocumene could live less than 20 ns is not correct, since a direct measurement yields a lifetime of ~5 µs.

Sumiyoshi's[11] conclusion that the lifetime of cumyldiazenyl is ~9 µs is largely based on the detection of a delayed growth of the transient absorption monitored at 322nm. Our experiments with fresh and/or flow samples do not reveal this delayed growth. However, when a fresh static sample of *trans*-azocumene in cycloalkane is exposed to laser irradiation, the kinetics for the absorption signal monitored at 322nm is clearly a function of the accumulated irradiation dose. The initially observed signal decays cleanly with no residual absorption. However, after 20 pulses a substantial (>50% of maximum absorbance) residual is observed which, after 40 pulses, resembles the delayed process observed by Sumiyoshi *et al.*[11] Possibly this absorption and the long lived absorption reported by Sumiyoshi *et al.*[11] in the 285nm region (resulting from a spectral subtraction), may be related to the presence of a mixture of unstable ortho and para-semibenzenes (V and VI), produced via ring coupling of cumyl radicals. Bartlett[18] and McBride[19] have independently characterized these compounds and have found that they have intense maxima at 315 and 265nm for the ortho and para isomers respectively. Our own experiments confirm that after prolonged laser irradiation (~1000 shots) an absorption builds up in this (270-320nm) region.


V


VI

Experimental:

Trans-azocumene was prepared as previously described;[18] it was pure by NMR and HPLC. Cyclopentane and cyclohexane (spectroscopic grade) were used as received. The laser flash photolysis facility has been described in detail elsewhere[20]. A Molectron UV-24 nitrogen laser (337 nm, ~8 ns pulses, ≤10 mJ/pulse) was used for excitation. Unless otherwise mentioned, samples were deaerated with a stream of nitrogen.

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