Laser Flash Photolysis of Azocumenes. Direct Observation of Stepwise Decomposition

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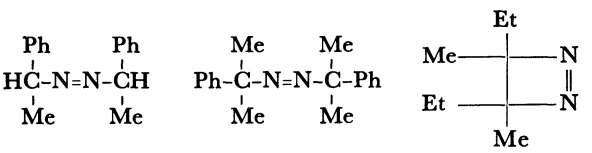
The mechanism of the decomposition of α,α′-azocumene and 2,2′-di-*p*-tolyl-2,2′-azopropane was studied by means of laser flash photolysis (λ=347 nm) and the optical absorption of 1-methyl-1-phenylethyl (α-cumyl) and α-cumyldiazenyl radicals was observed. The α-cumyl radicals were formed in two modes, a fast mode occurring during the flash and a slow mode after the flash. The ratio of the optical densities pertaining to the two modes depended on the absorbed dose rate. The higher the absorbed dose per flash, the more dominant was the fast mode. The transient band at λ=285 nm which decayed simultaneously with the grow- in of the α-cumyl radicals was assigned to α-cumyldiazenyl radicals. The experimental results strongly suggested the occurrence of the stepwise decomposition mechanism. The dose rate dependent kinetics of the slow formation process was explained in terms of the competition between the unimolecular decomposition and the dimerization of α-cumyldiazenyl radicals. The rate constants of the decomposition and the dimerization were estimated to be 1.1×10^5 s^{-1} and 5×10^9 M^{-1} s^{-1}, respectively.

Azo compounds are well-known as very effective initiators for the free radical polymerization of vinyl compounds.[1] Both thermal and photochemical decomposition reactions of azo alkanes were studied by several workers, and two mechanisms were discussed: simultaneous scission of the two C–N bonds (Eq. 1)[2] and stepwise cleavage of the C–N bonds involving the diazenyl radical as a transient (Eq. 2).[3]

$$R_1\text{-}N{=}N\text{-}R_2 \longrightarrow R_1\cdot + N_2 + \cdot R_2 \quad (1)$$

$$R_1\text{-}N{=}N\text{-}R_2 \longrightarrow R_1\text{-}N{=}N\cdot + \cdot R_2 \longrightarrow R_1\cdot + N_2 + \cdot R_2 \quad (2)$$

As far as *thermolysis* is concerned, Engel[4] arrived at the conclusion that "azoalkane thermolysis seems to proceed by a continuum of mechanisms between 1 and 2; the more unsymmetrical the azo compound the more unsymmetrically it cleaves." Actually, evidence for a concerted two bond cleavage according to reaction 1 was obtained for the thermolysis of symmetrical azo compounds: 1,1′-diphenylazoethane,[5] α,α′-azocumene,[6,7] and a cyclic azoalkane:[8]



1,1′-diphenylazoethane | α,α′-azocumene | dl-3,4-diethyl-3,4-dimethyldiazetine

On the other hand, the occurrence of the heat-induced stepwise decomposition according to reaction 2 was evidenced in the case of *cis*-1,1′-azoadamantane, a symmetrical compound.[9] Dannenberg and Rocklin[10] carried out a theoretical study on the thermolysis of trans-azoethane, also a symmetrical compound, and arrived at the conclusion that the initial step is trans → cis isomerization which is followed by dissociation into diazenyl and ethyl radicals.

The mechanism of the *photolysis* of azo compounds was studied by relatively few researchers up to now. Porter et al.[11] postulated a stepwise mechanism based on their work with unsymmetrical compounds such as Ph–N=N–C(CH_3)$_2$Ph and Ph_2CH–N=N–CH_2Ph. Upon irradiation *trans*-1-(1,1-dimethylallylazo)alkanes of the type R–N=N–C(CH_3)$_2$CH=CH_2 with UV light (337 nm) evidence was obtained by Engel and Gerth[12] for the intermediacy of thermally labile cis-isomers. Diazenyl radicals were found to play "a more general role" in the decomposition of the cis isomers with R equal to phenyl, methyl, cyclohexyl, ethyl etc. In these cases the recombination of diazenyl and 1,1′-dimethylallyl radicals (occurring at the allylic site) was observed. However, with the symmetrical compound (R: H_2C=CHC(CH_3)$_2$) this turn-around reaction was not observed.

Rather recently, the photofragmentation of azomethane in the vapor phase was studied.[13] In this case, the fragmentation was complete within 2 ns and by coherent anti-Stokes Raman spectroscopy the nascent vibrational distribution appeared consistent with a theoretical prediction of stepwise bond scission.

The present paper describes results obtained upon the laser flash photolysis of α,α′-azocumenes in solution. These compounds were selected because, in spite of their UV band at 367 nm, they possess an absorption window between 270 and 340 nm. This enabled us to observe the absorption of transient species, i.e., 1-methyl-1-phenylethyl (α-cumyl, hereafter) and diazenyl radicals. As will be shown below

the photolysis of the α,α′-azocumenes occurred according to the stepwise mechanism.

Experimental

Materials. α,α′-Azocumene (AC) and 2,2′-di-*p*-tolyl-2,2′-azopropane (DMAC) were synthesized by a procedure described in the literature.[14] Cyclohexane of Uvasol(R) quality was obtained from E. Merck and was used without further purification.

Irradiations. Solutions of α,α′-azocumenes freed from oxygen by bubbling with purified argon were irradiated by 347 nm laser flashes of a ruby laser operated in conjunction with a frequency doubler. The flash duration was about 20 ns.

Actinometry was performed with benzene solutions of benzophenone (1.15×10^{-3} M†) containing naphthalene (1.03×10^{-1} M). The absorbed dose per flash was calculated from the concentration of naphthalene triplets formed by energy transfer from benzophenone with $\varepsilon_{T\text{-}T}=1.32\times10^{4}$ $M^{-1}cm^{-1}$ at 425 nm[15] and $\phi(T)=1$. The maximum laser output was 4.5×10^{-4} Einstein per dm^3. The laser beam diameter was 0.6 cm at the sample position.

Results

Figure 1 shows transient absorption spectra with peaks at 272, 310, and 322 nm of a solution of AC in cyclohexane (4.7×10^{-3} M) photolyzed with an absorbed dose of 7.9×10^{-5} E l^{-1}.* These peaks were observed immediately at the end of the flash. The peaks at 272 and 322 nm grew-in further after the pulse. The three bands, which were also observed with DMAC in cyclohexane solution, are similar to those reported for benzyl,[16] *o*-, *m*-, *p*-methylbenzyl[17] and cumyl radicals.[18] They are, therefore, assigned to α-cumyl and 1-methyl-1-(*p*-tolyl)ethyl radicals, for AC and DMAC, respectively.

In addition to the absorption of α-cumyl radicals, a fast decaying transient absorption was observed in the region between 270 and 305 nm. The difference

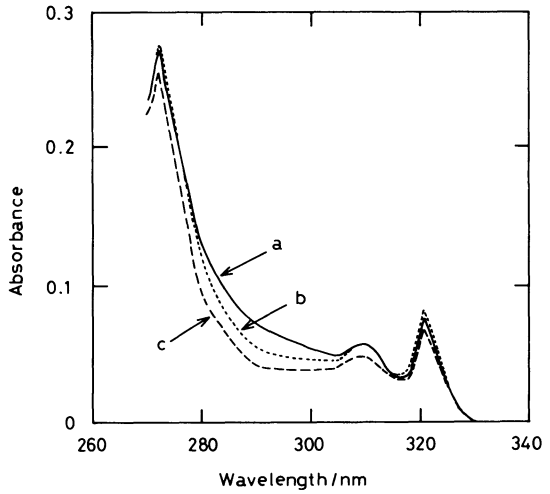


Fig. 1. Transient absorption spectra of 4.7×10^{-3} M α,α′-azocumene in cyclohexane recorded at the end of the flash (a), 8 μs (b), and 16 μs (c) later. $D_{abs}=7.9\times10^{-5}$ Einstein/l.

† 1 M=1 mol dm^{-3}, * l=dm^3.

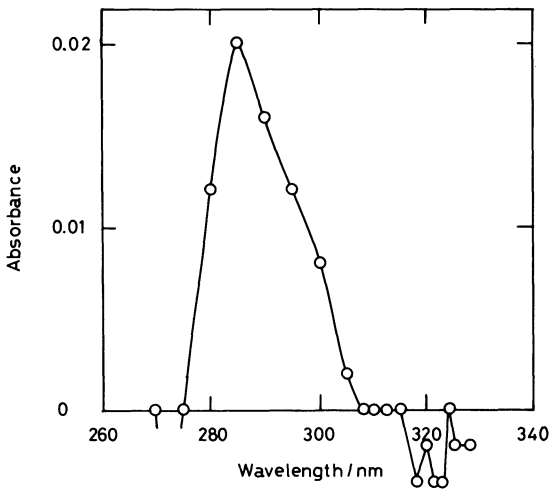


Fig. 2. Difference spectrum obtained by subtraction of spectrum (b) from spectrum (a) in Fig. 1.

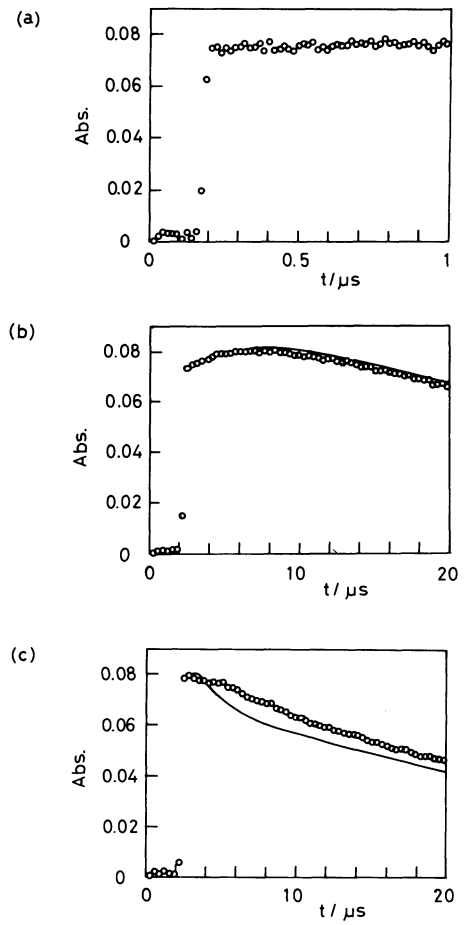


Fig. 3. Kinetic traces observed with 4.7×10^{-3} M α,α′-azocumene in cyclohexane (○), and simulated kinetic traces (—) at 322 (a) and (b), and 290 nm (c).

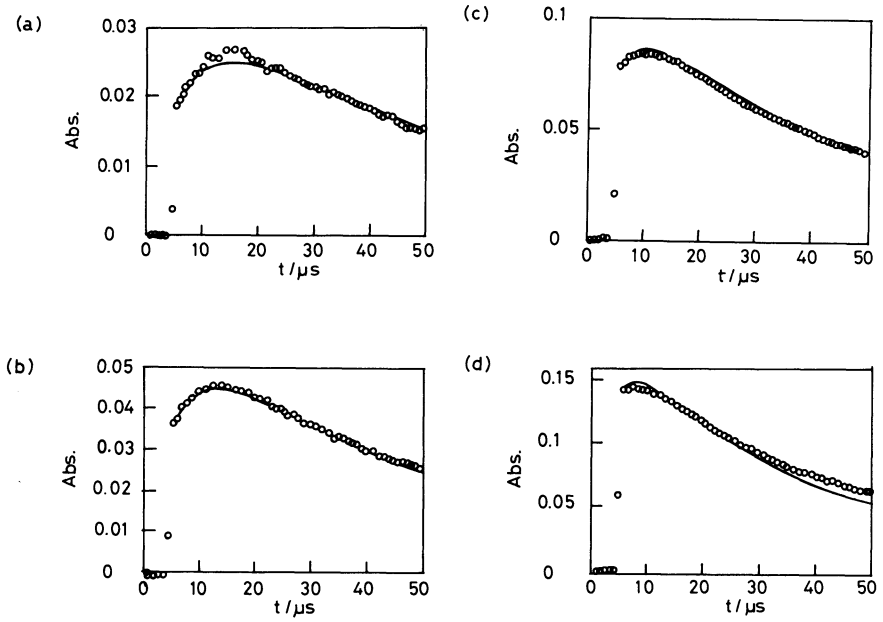


Fig. 4. Kinetic traces demonstrating changes in the 322 nm band observed with 4.7×10^{-3} M α,α′-azocumene in cyclohexane at absorbed doses of 2×10^{-5} (a), 3.7×10^{-5} (b), 8×10^{-5} (c), and 1.5×10^{-4} Einstein l^{-1} (d) (O).
Kinetic traces simulated with $\phi=0.36$ and $\varepsilon=4500\ M^{-1}\ cm^{-1}$ (—). Rate constants used are given in the text.

spectrum obtained by subtracting spectrum (b) from spectrum (a) in Fig. 1 is shown in Fig. 2. It has an absorption maximum at 285 nm.

Figure 3 shows kinetic traces recorded at 290 and 322 nm at an absorbed dose of 7.8×10^{-5} E l^{-1}. As can be seen from Fig. 3a, the absorption at 322 nm was formed to some extent during the flash. It increased further within about 5 μs and then decreased, as is shown in Fig. 3b. At 290 nm, on the other hand, the absorption formed during the flash decreased steadily after the flash.

Figure 4 shows kinetic traces obtained at 322 nm at various absorbed doses. It can be seen that with increasing absorbed dose the initial absorption increased while the extent of the grow-in absorption did not increase. Moreover, the grow-in rate depended significantly on the absorbed dose per flash. At $D_{absd}=2\times10^{-5}$ E l^{-1}, for example, the absorption increased until 10 μs but, at $D_{absd}=1.4\times10^{-4}$ E l^{-1}, only until 2 μs after the flash. The decay of the 322 nm band dose not fit first order or second order kinetics. However, the half lifetime slightly decreased with increasing absorbed dose, suggesting the occurrence of radical-radical reactions as will be dealt with in the next section. A similar kinetic behavior was observed with DMAC. In Fig. 5 the initial optical density (OD_0) and the maximum optical density (OD_{max}) at 322 nm were plotted against the absorbed dose per flash. Straight lines passing through the origin were obtained for OD_0 but not for OD_{max}. From the slope of the straight line (OD_0 vs. D_{absd}) the following $\phi\varepsilon$ values were

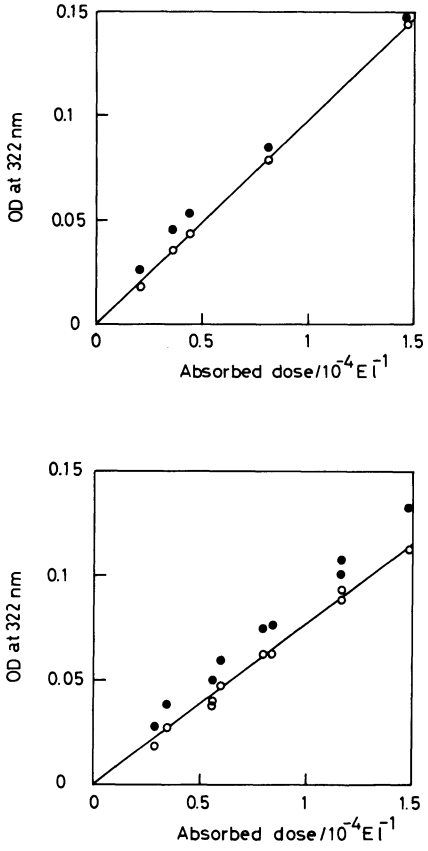


Fig. 5. Absorbed dose dependences of the initial (O) and the maximum (●) optical density observed at 322 nm.
(a) 4.7×10^{-3} M α,α′-azocumene in cyclohexane (b) 5.0×10^{-3} M 2,2′-di-*p*-tolyl-2,2′-azopropane in cyclohexane.

calculated for the α-cumyl radicals produced during the flash: 1630 and 1280 M^{-1} cm^{-1} for AC and DMAC, respectively.

Discussion

Engel and Steel have shown that the triplet-sensitized decomposition of AC (ϕ=0.31) occurs as efficient as the direct photolysis (0.36).[19] This fact suggests the intermediacy of the triplet AC in C–N bond scission.

For many azo compounds, it is well-known that the cis-isomers undergo remarkably facile thermal decomposition. *cis*-AC produced by UV irradiation of *trans*-AC in a poly(methyl methacrylate) matrix at −196 °C had a half lifetime of the order of 10 min at −100 °C,[20] while *trans*-AC has a lifetime of 20 min in toluene at 69 °C.[14] Thus, photoinduced trans-cis isomerization and the thermal instability of *cis*-AC suggest the intermediacy of *cis*-AC in decomposition. The present experimental results show that there exist two sources for α-cumyl radical production. On the basis of the fast mode of the α-cumyl radical formation that was completed during the laser pulse, it is assumed that both the triplet and the cis-isomer of α,α′-azocumene at room temperature have lifetimes much shorter than the laser pulse width of 20 ns.

The experimental results of the photolysis of α,α′-azocumenes in cyclohexane can be accounted for by the following equations:

$$\mathrm{Ph\text{-}C(CH_3)_2\text{-}N{=}N\text{-}C(CH_3)_2\text{-}Ph} \longrightarrow \mathrm{Ph\text{-}C(CH_3)_2\text{-}N{=}N\cdot} + \cdot\mathrm{C(CH_3)_2\text{-}Ph} \quad (3)$$

$$\mathrm{Ph\text{-}C(CH_3)_2\text{-}N{=}N\cdot} \longrightarrow \mathrm{Ph\text{-}C(CH_3)_2\cdot} + \mathrm{N_2} \quad (4)$$

$$\mathrm{Ph\text{-}C(CH_3)_2\text{-}N{=}N\cdot} + \mathrm{Ph\text{-}C(CH_3)_2\text{-}N{=}N\cdot} \longrightarrow \mathrm{Ph\text{-}C(CH_3)_2\text{-}N{=}N\text{-}N{=}N\text{-}C(CH_3)_2\text{-}Ph} \quad (5)$$

$$\mathrm{Ph\text{-}C(CH_3)_2\cdot} \longrightarrow \text{product} \quad (6)$$

$$\mathrm{Ph\text{-}C(CH_3)_2\cdot} + \mathrm{Ph\text{-}C(CH_3)_2\cdot} \longrightarrow \text{product} \quad (7)$$

Figure 6 shows a plot of the ratio OD_{max}/OD_0 vs. the absorbed dose per flash which corresponds to the absorbed dose rate. It seems that both curves (obtained with AC and DMAC, respectively) are approaching the value of two on extrapolation of the absorbed dose rate to zero. At low absorbed dose rates the ratio of the concentrations of α-cumyl radicals formed by reaction 3, i.e., during the pulse, and reaction 4, i.e., after the pulse, is expected to be unity because the dimerization reaction 5 cannot compete with the unimolecular decomposition of diazenyl radicals according to reaction 4. This condition results in OD_{max}/OD_0=2. Reaction 6 stands for the reaction of α-cumyl radicals with intact α,α′-azocumene, the solvent and impurities.

To estimate the individual rate constants, a series of kinetic traces obtained within a wide range of absorbed doses (2×10^{-5}—1.5×10^{-4} E l^{-1}, see Fig. 4)

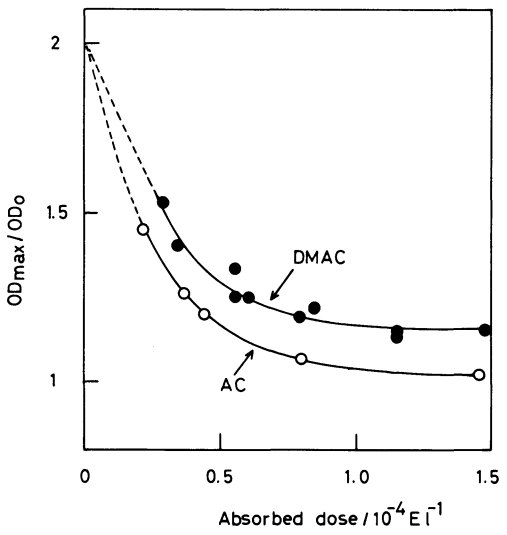


Fig. 6. Absorbed dose dependence of OD_{max}/OD_0 at 322 nm for α,α′-azocumene (○) and 2,2′-di-*p*-tolyl-2,2′-azopropane (●).

were simulated with the aid of a personal computer.

One can write equations for the rate of disappearance of the α-cumyldiazenyl radicals and the α-cumyl radicals:

$$-dA/dt = k_4A + 2k_5A^2 \quad (8)$$

$$-dB/dt = -k_4A + k_6B + 2k_7B^2 \quad (9)$$

where A and B represent the instantaneous concentrations of the α-cumyldiazenyl radicals and α-cumyl radicals respectively.

Equation 8 can be resolved to give[21]

$$\ln\{A_0(k_4+2k_5A)/A(k_4+2k_5A_0)\} = k_4t, \quad (10)$$

where A_0 is the initial concentration of the α-cumyldiazenyl radicals produced by reaction 3. Equation 10 may be rearranged to give

$$A = A_0k_4/\{(k_4+2k_5A_0)\exp(k_4t)-2k_5A_0\}. \quad (11)$$

By substituting this value for A into Eq. 9, we obtain

$$dB/dt = A_0k_4^2/\{(k_4+2k_5A_0)\exp(k_4t)-2k_5A_0\} - k_6B - 2k_7B^2. \quad (12)$$

This differential equation can be solved numerically by the Runge-Kutta method,[22] with the condition A_0=B_0 at t=0, where B_0 is the initial concentration of the α-cumyl radicals.

To estimate values of A_0 and B_0 one has to know the extinction coefficient of the α-cumyl radical at 322 nm. According to Nelsen and Bartlett[14] the quantum yield of the photodecomposition of α,α′-azocumene in benzene at 26.3 °C is 0.6. This rather high value very probably dose not only refer to scission of C–N bonds according to reactions 1 and 2 but also to other AC consuming reactions. For the

present case it appears more relevant to refer to the quantum yield of N_2 formation in order to estimate the quantum yield of α-cumyl radicals formed according to reactions 1 and 2. $\phi(N_2)=0.36$ has been determined by Engel and Steel[19] in the photolysis of AC in benzene. Dividing the slope of the straight line in Fig. 5a by 0.36 yields $\varepsilon(322\text{ nm})=4500\ M^{-1}\ cm^{-1}$ for AC. This extinction coefficient is quite similar to those obtained for *o*-, *m*-, *p*-methylbenzyl radicals which fall in the range 3000—6000.[17]

An iterative curve fitting procedure on the basis of Eq. 12 was applied to the experimental kinetic traces of Fig. 4. The solid lines in Fig. 4 are best fits obtained with the following rate constants: $k_4=1.1\times10^5\ s^{-1}$, $k_5=5\times10^9\ M^{-1}\ s^{-1}$, $k_6=1.65\times10^4\ s^{-1}$, and $k_7=1.8\times10^8\ M^{-1}\ s^{-1}$. With these rate constants the kinetic traces observed with DMAC in cyclohexane could also be reproduced. The unimolecular decay rate constant of the α-cumyldiazenyl radical k_4 can be compared with rate constants $(1.8—330)\times10^5\ s^{-1}$ obtained for substituted phenyldiazenyl radicals in water/*t*-butyl alcohol mixture.[23] The dimerization rate constant of the α-cumyldiazenyl radical is the same as that obtained for the phenyldiazenyl radical.[23]

The full line in Fig. 3 is the simulated kinetic trace representing the absorbances of both the α-cumyldiazenyl radical and the α-cumyl radical on the assumption that extinction coefficients at 290 nm are equal to 2000 and 2600 $M^{-1}\ cm^{-1}$, respectively. The difference between the experimental and the simulated curves might be explained on the basis of strongly absorbing products formed in the dimerization of α-cumyl radicals. According to Skinner et al.[24] the dimerization of α-cumyl radicals gives the following distribution of isomers: 1,2-diphenylethane:*o*-semibenzene:*p*-semibenzene=1:0.1:0.2.[24] The *p*-semibenzene is characterized by its strong UV absorption band peaked at 262 nm in cyclohexane and the extinction coefficient is estimated to be 25000—40000 $M^{-1}\ cm^{-1}$. From the spectrum of p-semibenzene the extinction coefficient at 290 nm can be estimated to be about 3500—6000 $M^{-1}\ cm^{-1}$.[24] Thus we can expect a contribution of about 10% of p-semibenzene to the transient absorption at 290 nm which compares well with the difference shown in Fig. 3c.

In conclusion, the present results clearly indicate the stepwise decomposition of α,α'-azocumenes on photolysis. This contrasts strongly the conclusion arrived at in the thermolysis studies,[6,7] where it is shown that on heating α,α'-azocumene is decomposed by a concerted process according to reaction 1. It can be conjectured that upon UV irradiation an electronically excited repulsive state is produced resulting in the occurrence of rapid fragmentation. This problem could probably be solved by a highly time-resolved flash photolysis technique.

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