

ON THE PHOTOLYSIS MECHANISM OF AZIBENZIL*

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Summary

The photolysis of azibenzil was investigated in solution as well as in the absence of solvent, at room and low temperatures, in degassed samples or in the presence of O₂. According to the e.p.r. spectra obtained and to the decay kinetics of the corresponding intermediates we proposed a general photolysis scheme in good agreement with some reaction paths suggested by other authors.

Introduction

The conversion of α -diazoketones to the corresponding ketenes was shown for the first time by Wolff [1, 2] and Schroeter [3]. Later, it was found that their decomposition with Wolff rearrangement [4 - 11] can be produced by light, temperature and catalyst. Many other authors bring experimental arguments, even in the case of azibenzil, to show that the intermediates involved in the photochemical Wolff rearrangement must be in its ground state singlet [12 - 16].

However, as Trozzolo showed [17] we must consider also the formation of the corresponding triplet radical on the photolysis of azibenzil.

Experimental

Azibenzil was synthesized according to the methods of Nenitzescu-Solomonica [18] and Miller [19].

For irradiating azibenzil we used a HBO 500 W lamp and to determine its concentration during the irradiation we measured the optical density in

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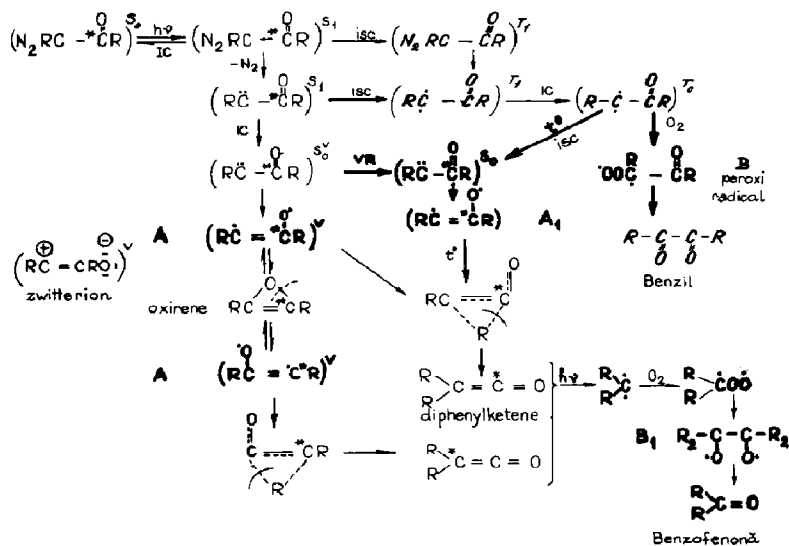


Fig. 1. General reaction scheme of the azibenzil photolysis: R = phenyl; ///, Trozolo's path; |||, Strausz's path; ||||, our path.

a Pye Unicam SP 1800 spectrophotometer. Quantum yield was determined by using the chemical actinometer with $Fe(C_2O_4)_3 \cdot K_3$. E.p.r. spectra of the intermediate species were performed using an "ART 1" spectrometer, which works in X band modulated in high frequency (100 kHz), made in the Bucharest Institute of Atomic Physics. For the measurements of g -values we used disulphonated peroxyamine and Mn^{2+} as standards.

Results and Discussion

According to the literature data as well as to our experiments we suggest the general reaction scheme presented in Fig. 1.

Concerning the primary process, it is known that on irradiation of azibenzil (and other diazo compounds) the electronic state of ketocarbene radicals may be either singlet or triplet depending on the multiplicity of the state which is the precursor – the excited azibenzil molecules.

On irradiation of polycrystalline azibenzil with ultra-violet light *in vacuo*, at 77 K, we obtained the e.p.r. spectra shown in Fig. 2.

The signal of ketocarbene appears at low field in its triplet ground state as Trozolo [17] pointed out and analyzed for the first time, on irradiation of azibenzil with $\lambda = 3500 \text{ \AA}$ in a variety of organic glasses at 77 K. He showed that when the glass was warmed, the triplet radical reacted with O_2 to form benzil (0 - 12%, depending on O_2 concentration) and only a small amount of diphenylketene (0 - 12%), which means that the ground state triplet of ketocarbene does not undergo the Wolff rearrangement efficiently at low temperature. On the contrary, at room temperature the yield of diphenylketene was about 90%, in this case its ground state singlet being involved.

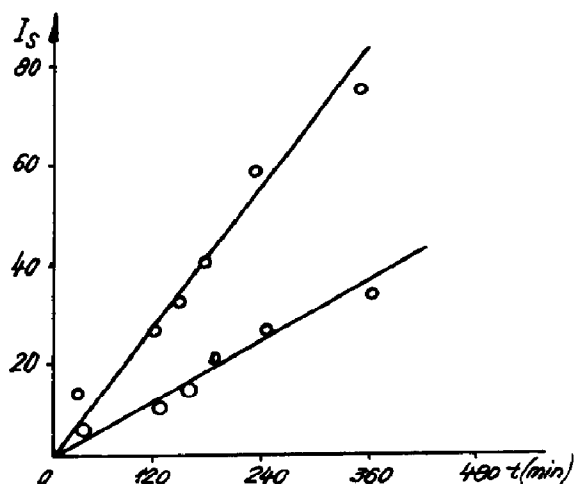
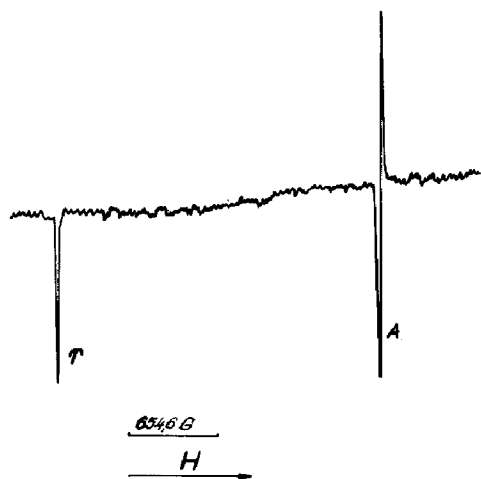


Fig. 2. E.p.r. spectrum obtained by the photolysis of polycrystalline azibenzil with u.v. light, in vacuum at 77 K: ketocarbene triplet signal (T) and transient species signal (A).

Fig. 3. Radical accumulation on irradiation of azibenzil in vacuum at 77 K: ketocarbene in its ground triplet state (T) and transient species (A).

As Fig. 2 shows we obtained besides the triplet signal another one (A) with the following spectral parameters: $g = 2.0029$ and $H = 11.6$ G.

Recording these spectra at various irradiation times we obtained a zero kinetic order with respect to both species which indicates that during the irradiation radical accumulation occurs (Fig. 3).

On warming the sample the triplet signal disappears, so that at -78 °C for example, we detected only the signal centred at the free electron value, of course with lower intensity. This behaviour on warming is due to the ketocarbene triplet which undergoes intersystem crossing to the singlet state as scheme (1) indicates.

The intensity of the centred signal in turn decreases gradually with respect to the temperature and vanishes at about 10 °C.

For one of the investigated temperatures, -20 °C, we found first order kinetics for the decay of this species, strong evidence for a unimolecular rearrangement (Fig. 4).

We assigned its spectrum to the radical $(\text{RC}=\overset{\text{O}}{\text{C}}\text{R})^\cdot$ excited vibrationally which results from the vibrationally excited ground singlet ketocarbene (A in Fig. 1). The rearrangement to diphenylketene can occur via a bridge cyclic intermediate and via the competing conversion to oxirene. The formation of oxirene was conclusively demonstrated by Strausz *et al.* [16] using ^{13}C azibenzil labelled in the carbonyl group. The presence of the paramagnetic species A, does not require absolutely the participation of the zwitterion $\text{RC}=\overset{\ominus}{\text{C}}\text{R}-\overset{\oplus}{\text{O}}$ in this reaction path which Strausz *et al.* [16, 20] proposed for computational reasons.

When we carried out this photolysis also at 77 K but in the presence of atmospheric oxygen, we obtained a similar e.p.r. spectrum which on warming

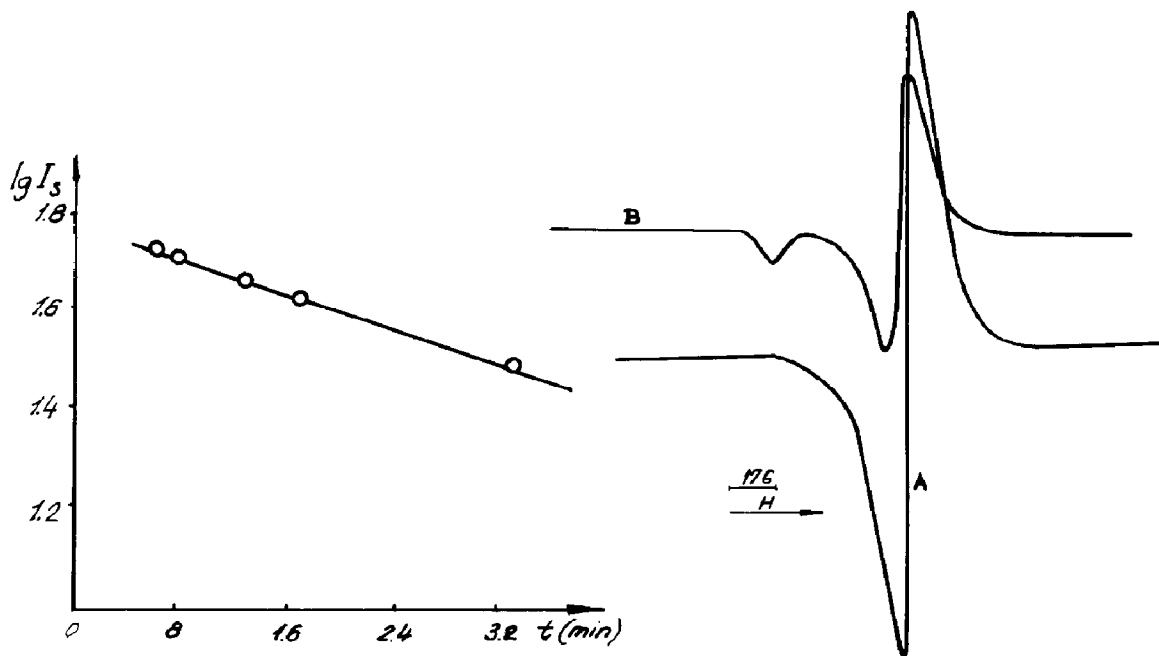


Fig. 4. Variation of the signal intensity ($\log I$) vs. time at -20°C of the excited vibrationally transient, A.

Fig. 5. E.p.r. spectra of the transient species A recorded at 77 K, and of the peroxy-radical B at -78°C .

to -78°C gave a different signal: $g_{\perp} = 2.0013$ and $g_{\parallel} = 2.0342$ (Fig. 5). This new species, being less thermally resistant than the radical (A), vanishes at about -20°C , whereas the other one persists up to 10°C . We assigned it to

the peroxyradical $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\overset{\text{O}}{\text{O}}\cdot$ (B in the photolysis mechanism, Fig. 1) which appears from the reaction of the triplet ground state ketocarbene with O_2 . This supposition agrees with the following arguments: (i) on warming to -78°C the irradiated sample of azibenzil at 77 K in which we previously bubbled O_2 , we obtained a much more intense spectrum B than in the presence of air; (ii) the form of the spectrum B is typical for an asymmetric radical, like this peroxy species; (iii) one can isolate benzil from the sample as Trozzolo [17] also mentioned.

We have investigated also the photolysis of azibenzil in benzene solution. The formation of diphenylketene during the irradiation (with $\lambda = 313\text{ nm}$) at 17°C is confirmed by the shifting of the azibenzil absorption band from 430 nm to 409 nm with a continuous increase of the optical density (Fig. 6). By prolonged irradiation the absorption at $\lambda = 409\text{ nm}$ decreases which shows that diphenylketene formed from the azibenzil photolysis decomposes also photochemically.

A zero kinetic order is obtained from optical density measurements at $\lambda = 320\text{ nm}$ (absorption band of azibenzil) which permits us to calculate a rate constant $k_0 = 2.12 \times 10^{-7}\text{ mol l}^{-1}\text{ s}^{-1}$. We determined also the quan-

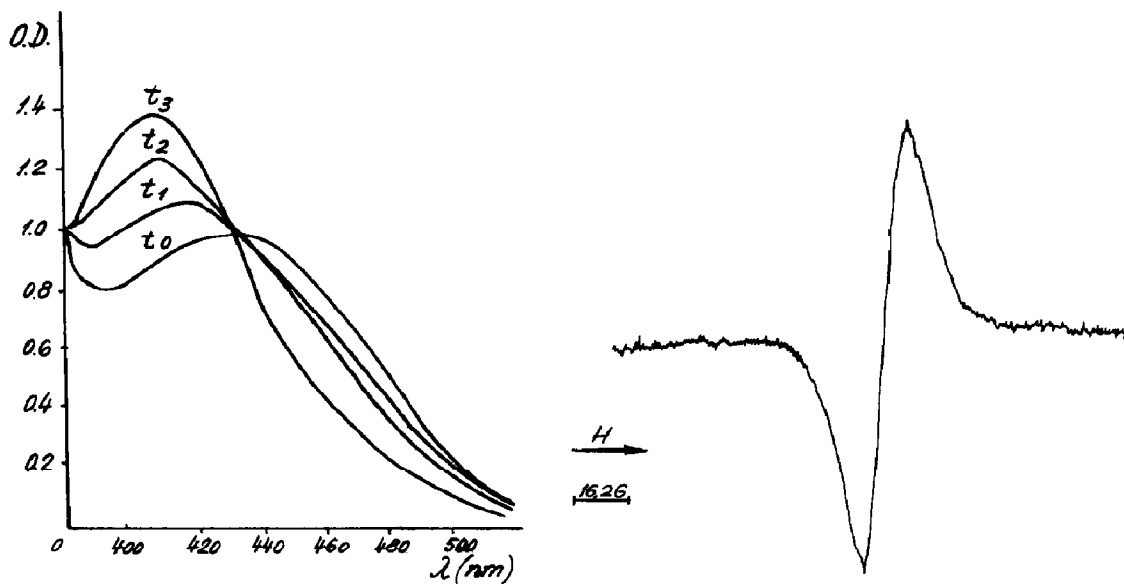


Fig. 6. Absorption spectra of the azibenzil sample in benzene, during the photolysis at 17 °C, in the presence of atmospheric O₂.

Fig. 7. E.p.r. spectrum obtained on the photolysis of azibenzil in benzene at 77 K in the presence of atmospheric O₂.

tum yield of the reaction and found a value $\Phi = 0.5$ suggesting that in solution the deactivation of excited azibenzil molecules takes place with the same chance as the photolysis (probably due to internal conversion [21]).

On the other hand, the irradiation of the azibenzil in benzene, also in the presence of atmospheric O₂ but at 77 K gives an e.p.r. spectrum (Fig. 7) with the following parameters: $g = 2.0031$ and $\Delta H = 12.7$ G. Characteristic of this spectrum is the absence of the ketocarbene triplet signal which is in very good agreement with the behaviour of the sample on warming to -78 °C. Indeed in this case the e.p.r. spectrum is not modified by the appearance of the peroxyradical signal (B), which involved absolutely the presence of the ketocarbene in its ground state triplet to react with O₂. We ascribe this spectrum to a species with the same chemical structure as the species A, but unexcited vibrationally, which results from the ground state singlet of ketocarbene unexcited vibrationally (noted A₁ in Fig. 1). This means that vibra-

tionally relaxation process $(\text{RC}-\text{CR})^{\text{S}\circ} \xrightarrow{\text{V.R.}} (\text{RC}-\text{CR})^{\text{S}\circ}$ is much more favoured under these conditions.

We mention also that the e.p.r. spectrum assigned to species A₁ disappears at about -20 °C whereas the spectrum of A obtained on irradiation of the polycrystalline azibenzil, persists up to $+10$ °C. This different thermal resistance can be explained by the fact that the radical A₁ leads irreversibly to diphenylketene whereas the vibrationally excited species A is involved in an equilibrium process with oxirene.

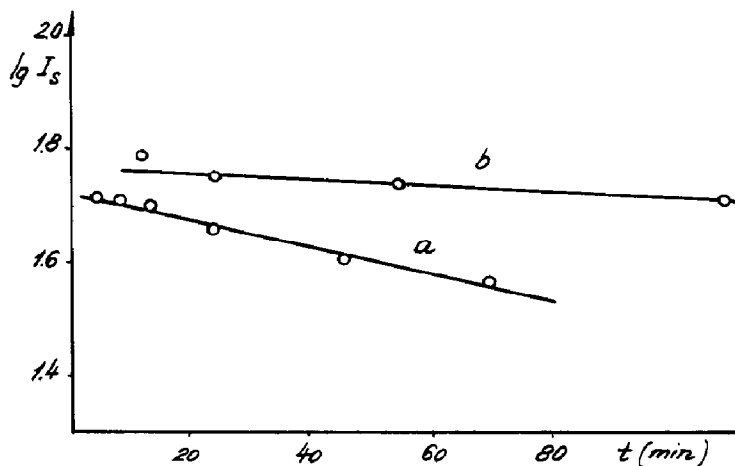


Fig. 8. Variation of the signal intensity ($\log I$) vs. time at -78°C of the azibenzil sample irradiated at 77 K: (a) sample degassed; (b) in the presence of atmospheric O_2 .

When the photolysis of the azibenzil sample in benzene also takes place at 77 K in vacuum one obtains a similar spectrum without the ketocarbene triplet signal. We concluded that in benzene in contrast to the polycrystalline sample ISC radiationless transitions [22] are not favoured so that neither ketocarbene triplet and in consequence nor its peroxide B appear in sensible amounts. This conclusion is confirmed by similar experiments performed in various other solvents: xylene, hexane, cyclohexane, ether, toluol.

By comparing the variation of the intensity signal with respect to time at -78°C , after irradiation in vacuum and in atmospheric O_2 at 77 K, we found unimolecular kinetics for both cases. But as Fig. 8 shows, the rate constant is higher *in vacuo*. We suppose that this behaviour is due to the diphenylketene photolysis into diphenylcarbene triplet radical [23, 24] which in turn reacts with O_2 to form an oxygenated transient (B_1 in scheme 1), whose spectrum must overlap the spectrum of species A_1 . In order to verify this supposition we carried out separately the photolysis of diphenylketene in benzene at 77 K and we obtained a similar spectrum on warming regardless of the form, position and thermal behaviour. In a previous paper [25] we showed that on photolysis of diphenyldiazomethane at 77 K when the diphenylcarbene triplet is formed, a transient species similar to B_1 with the same e.p.r. spectrum also appears.

In the case of the azibenzil photolysis both intermediates A_1 and B_1 whose spectra overlap, undergo unimolecular processes. But the transformation of the oxygenated radical B_1 into benzophenone (which was isolated and analyzed) is slower in comparison to the diphenylketene rearrangement of A_1 , which explains the difference of the decay rate *in vacuo* (only A_1) and in the presence of air ($A_1 + B_1$).

In conclusion our e.p.r. experiments on the photolysis of azibenzil confirm the presence of the ketocarbene triplet and put into evidence new transients such as A, A_1 , B and B_1 . Their formation agrees very well with the results of Strausz *et al.* [16] and Trozzolo [17] and permitted steps of this photolysis mechanism (presented in Fig. 1) to be more precisely known.

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