Oxidation of Radical-ions and the Photolysis of Their Peroxides

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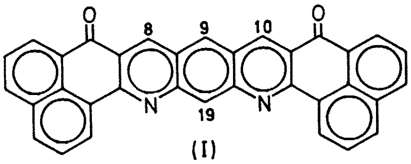
Summary The stable radical anions $(I^{\cdot-})$ absorb oxygen to form a diamagnetic peroxide $^{-}I{\cdot}O{\cdot}O{\cdot}I^{-}$, whose photolysis (500—700 nm) leads to the rupture of a C–O bond and reformation of 1/2 of the original radical-ions without evolution of oxygen.

IN the course of preparation of model compounds of condensed aromatic polymers the diketone (I) was synthesized.[1] On reaction of its suspension in hexamethylphosphoramide (HMPA) with an equivalent amount of biphenylsodium, $(B^{\cdot-})$, the respective radical-anion $(I^{\cdot-})$ is formed quantitatively, *i.e.*,



(I)

$$B^{\cdot-} + (I) \rightarrow B + (I^{\cdot-})$$

The resulting orange solution of $(I^{\cdot-})$ is stable, no changes are observed even after a few weeks of storage, and its optical spectrum is shown in Figure 1; λ_{max} 837 nm (ϵ 2·8 × 10^4). The relevant e.s.r. spectrum consists of a 1 : 3 : 3 : 1 quadruplet (*a* 5·2 gauss) tentatively interpreted as due to splitting by protons 8, 9, and 10, assumed to be magnetically equivalent (see Figure 2).

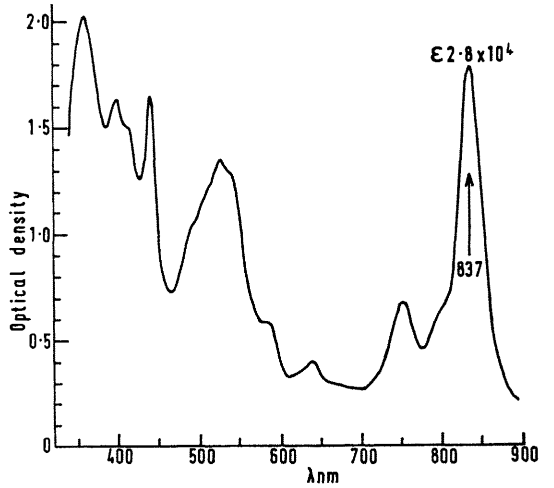


FIGURE 1. *Spectrum of the solution of the radical-ion (red-brown).*

On exposure to air the orange solution turns green; apparently $(I^{\cdot-})$ is oxidized. Quantitative studies showed that one mole of O_2 is absorbed by 2 moles of the radical-ion. The product is diamagnetic, λ_{max} 683 nm (ϵ 2·1 × 10^4). The oxidized species seems to be a peroxide of structure (II).

The peroxide is light-sensitive, 500–700 nm light being photolytically active; its preparation and storage therefore require darkness. Even in the absence of light a slow decomposition with half-life of about 3—4 hours takes place at ambient temperature.

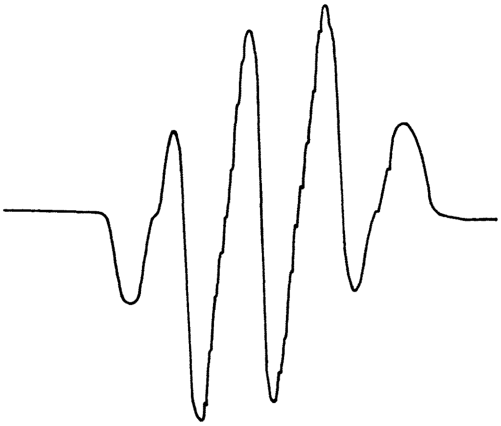
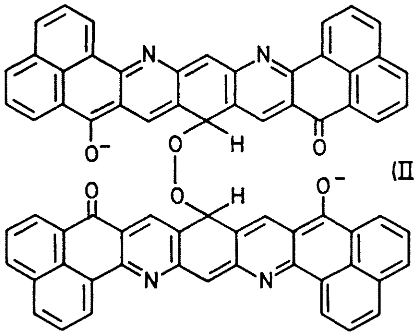


FIGURE 2. *E.s.r. spectrum of the radical-ion. A quadruplet* 1 : 3 : 3 : 1, *a* 5·2 *gauss with further splitting indicated by the "teeth" on the lines.*

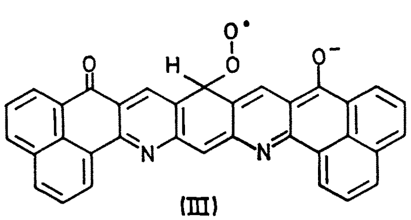
The photolysis was studied by placing a sample of (II) kept in an evacuated cell into the compartment of a Cary-14 spectrophotometer. Its irradiation with the i.r. source, shielded with Corning filters CS1-57 and CS3-69, led to the first-order decomposition which was followed by recording the optical density at 683 nm as a function of time.



(II)

The spectrum of the solution photolysed *in vacuo* resembles that of the original radical-anion $(I^{\cdot-})$ (see Figure 3), but the optical density at 837 nm is only one-half of that of $(I^{\cdot-})$ prior to its oxidation. The photolysed solution is paramagnetic and its e.s.r. spectrum is identical with that of the original radical-anion although again only one-half as intense. Oxygen is not evolved during the photolysis and this observation, coupled with the e.s.r. and spectroscopic evidence, implies that the C–O bond, and not the O–O bond is ruptured, *i.e.* the reaction seems to proceed according to the equation, (II) → $(I^{\cdot-})$ + (III). The intermediate radical (III) rapidly rearranges into some diamagnetic species, because no other paramagnetic compound was observed in the e.s.r. spectrum.

In order to isolate products of the reaction other than (I$^{\cdot-}$), the photolysed solution was oxidized by admitting oxygen in the dark. Thereafter, the excess of oxygen was pumped out and the evacuated solution photolysed again. The cycle: oxidation, evacuation, and vacuum photolysis, was repeated a few times until the absorption peak at 837 nm virtually disappeared. The changes in the resulting spectra of the photolysed solution are shown in Figure 3, where curve (A) represents the spectrum of the solution photolysed only once and curve (B) that of the ultimate products resulting from the multiple photolyses. The acidification of the repeatedly photolysed solution with trifluoroacetic acid led to the formation of a brown precipitate, which is soluble in dilute bases. The elemental analysis corresponds to $C_{34}H_{16}N_2O_4$. This result, coupled with the acidic properties of the product, suggests structure (IV).



(III)

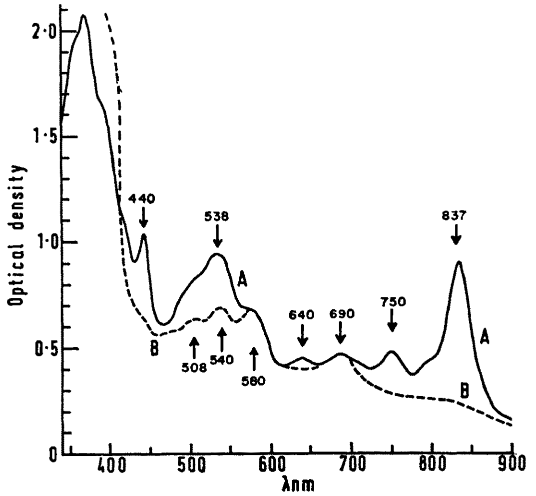
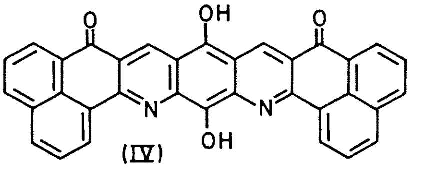


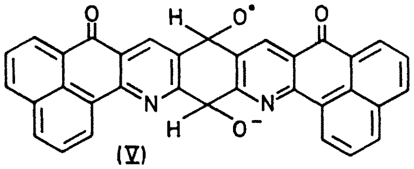
FIGURE 3. *The spectrum of the photolysed solution. Curve A. Once photolysed* in vacuo. *Curve B. Multiple photolysis as described in the text performed until all the radical-ions disappear.*

The spectrum of alkali solution of the brown precipitate [assumed to be (IV)] shows two absorption maxima at 508 and 540 nm revealed also in curve B of Figure 3. This proves that the precipitate is a component of the solution produced by the repetitive photolyses.

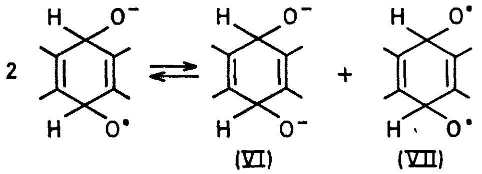


(IV)

It seems that (III) rearranges into (V), and the latter undergoes a rapid disproportionation through electron-transfer process. Thus, a dianion (VI) and a diradical (VII) are formed. We suggest that the diradical rearranges into (IV) which, being more acidic than the non-protonated (VI), transfers protons to it. Hence, the salt of (IV) and the protonated (VI), or its rearrangement product, are probably formed in the reaction.



(V)



This tentative mechanism was presented as a series of consecutive steps. It is possible, however, that the photolysis produces products (I$^{\cdot-}$) and (V) by concerted decomposition of (II). It is most probable that peroxide (II) is not planar, but that the two aromatic moieties are located one above the other, being linked by the O_2 bridge. Forces arising from mutual polarizibility of the aromatic fragments favour such geometry, which should facilitate the formation of (I$^{\cdot-}$) and (V) in one step. The concerted mechanism accounts also for the low energy requirement of this process.

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[1] W. Bracke, submitted to *J. Org. Chem.*