

PHOTOCHROMISM AND PHOTOCHEMISTRY OF 2,3,4,4-TETRACHLORO-1-KETO-1,4-DIHYDRO-NAPHTHALENE ( $\beta$ -TKN)

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Crystals of  $\beta$ -TKN, grown from solutions at room temperature, become purple coloured when exposed to ultraviolet light. At room temperature the thermal bleaching takes about 24 hours. The coloured photoproduct (P) is also produced upon irradiation of solutions of  $\beta$ -TKN and of its isomer 2,2,3,4-tetrachloro-1-keto-1,2-dihydronaphthalene ( $\alpha$ -TKN), although crystals of  $\alpha$ -TKN do not show a light-induced coloration. Scheibe et.al. (1) attributed the photochromism of  $\beta$ -TKN to a homolytic photodissociation of an aliphatic C-Cl bond, yielding the 2,3,4-trichloro-1-naphthoxyl radical (TCNR) and atomic chlorine. They argued that the naphthoxyl radical should be identified with P. Subsequent e.s.r. experiments on polycrystalline  $\beta$ -TKN proved the photochemical formation of radical pairs, but the attribution of the visible absorption to the TCNR turned out to be doubtful (2,3). In the present work it is shown that the mechanism for colour production proposed by Scheibe is incorrect and an alternative mechanism is derived.

We have analyzed the photochemical formation of paramagnetic species in single crystals of photochromic  $\beta$ -TKN (4). It appears that two types of radical pairs are produced upon irradiation. The triplet state of these pairs has been studied by e.s.r. Initially radicals are formed from neighbouring  $\beta$ -TKN molecules which belong to successive layers of molecules perpendicular to the b-axis (e.g. molecules I and II in fig. 1). Very probably the reaction involves homolytic photodissociation of an aliphatic C-Cl bond followed by addition of the released Cl atom to the aromatic ring of the neighbouring molecule. "Secondary" radical pairs are generated in a consecutive photoreaction in which the Cl atom is released again and reacts with a  $\beta$ -TKN molecule in the next layer along b.

However, the triplet e.s.r. and visible absorption which are simultaneously generated in the crystal upon irradiation appear to have widely different lifetimes. An additional spectroscopic study of the chemically produced TCNR proves definitely that P is diamagnetic. In the course of the identification of the chemical structure of P, it is established that this product is formed in a unimolecular photoreaction. The infrared spectrum of P has been obtained by observing the change in the infrared spectrum of solid  $\beta$ -TKN in KBr upon irradiation. About 1% of  $\beta$ -TKN is converted to P and is completely restored during the thermal bleaching. The IR spectrum of P suggests its identification with the carbenium ion (A) resulting from heterolytic photodissociation of an aliphatic C-Cl bond of  $\beta$ -TKN. The similarity of the visible absorption spectra of P and of A produced by reaction of either  $\alpha$ - or  $\beta$ -TKN with  $\text{SbCl}_5$  supports the view that the two species are identical (fig. 2).

In order to determine the spatial requirements for observing photochromism in the solid state, the crystal structures of  $\alpha$ -TKN and of two non-photochromic high temperature modifications of  $\beta$ -TKN have been resolved by X-ray methods. In photochromic  $\beta$ -TKN a very short intermolecular O-Cl distance of 2.973 Å appears to be an essential feature which is absent in the non-photochromic modifications and in crystalline  $\alpha$ -TKN. There are no restrictions to the formation of A in these structures but only in the photochromic crystal the lifetime of A is substantially

enhanced owing to steric hindrance of the recombination with  $\text{Cl}^-$ .

We conclude that in photochromic  $\beta$ -TKN crystals both homolytic and heterolytic C-Cl bond cleavage occur. In carbon tetrachloride solution the coloured carbenium ion A can be obtained photochemically from either  $\alpha$ - or  $\beta$ -TKN.

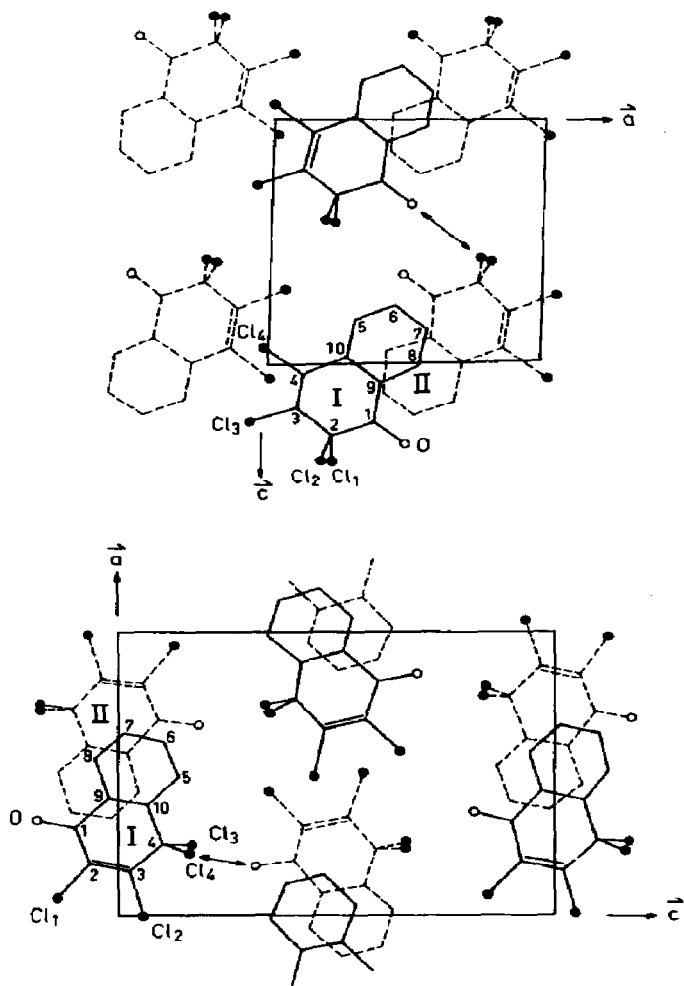


Fig. 1.

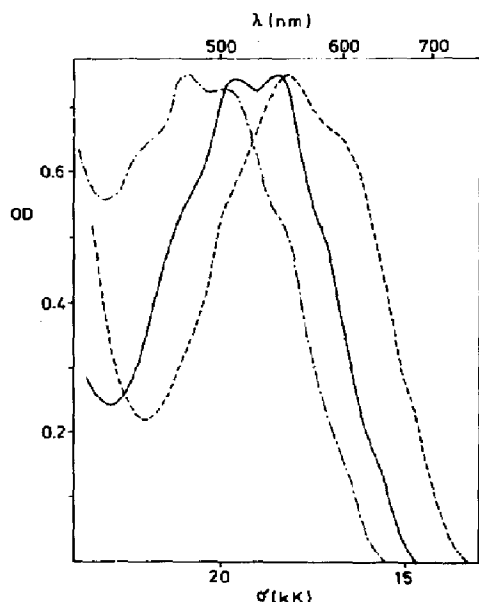


Fig. 2.

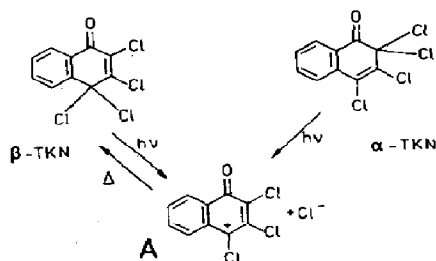


Fig. 3.

**Fig. 1.** The crystal structure of  $\alpha$ -TKN (top) and photochromic  $\beta$ -TKN (bottom) viewed along (010).  $\alpha$ -TKN molecules in the plane  $y = 0.78$  are indicated by thick lines, the dotted molecules in the plane  $y = 0.28$ . In the  $\beta$ -TKN structure (5) fully drawn molecules lie at  $y = 0.25$  and the dotted ones have  $y = 0.75$ . In both structures the double-headed arrow indicates the shortest intermolecular O-Cl distance.

**Fig. 2.** Absorption spectra of the coloured photoproduct P in crystalline  $\beta$ -TKN (—) and in  $\text{CCl}_4$  (-.-) at  $22^\circ\text{C}$ . The spectrum of the carbenium ion obtained by reaction of either  $\alpha$ - or  $\beta$ -TKN with  $\text{SbCl}_5$  in  $\text{SO}_2$  at  $-70^\circ\text{C}$  is indicated by the dashed line (----).

**Fig. 3.** Mechanism for the photochromism of  $\beta$ -TKN.

### references

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