

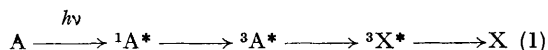
Photochromism of Tetramethyldianthrone—an Adiabatic Photoreaction in Solution

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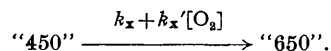
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Summary A transient with a half-life of about 200 ns was observed during the photocolouration of 1,3,1',3'-tetramethyldianthrone and is assigned to the triplet state of the photoproduct.

RECENT nanosecond laser photolysis investigations showed that the photocyclisation of aromatic amines proceeds *via* the excited triplet states of the photoproducts.¹ The spin-allowedness of the process $^3(\text{amine})^* \longrightarrow ^3(\text{dihydro-carbazole})^*$ seemed to be a major reason why in this case photoreaction competes effectively with ordinary triplet deactivation processes. We therefore expected that in another fast triplet state reaction, the photochromism of the dianthrone,² similar excited-state photoproducts might be involved, according to reaction (1) where X denotes the coloured photoproduct.

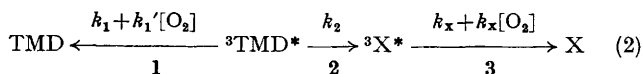


Flash experiments with a nitrogen laser (excitation 337.1 nm, half-time 12 ns) on solutions of 1,3,1',3'-tetramethyldianthrone (TMD) in methylcyclohexane at 23° gave the following results. In nitrogen-flushed solutions a transient with an absorption maximum at 450 nm was observed, and found to decay with a first-order rate constant $k_x = 6.7 \times 10^6 \text{ s}^{-1}$, while a stable photoproduct X with an absorption maximum at 650 nm was formed at a rate matching the decay of the 450 nm transient. When the nitrogen was replaced by oxygen, the rate constants for the decay of the 450 nm transient and the formation of the 650 nm photoproduct were increased by a factor of about ten, but with less than 15% decrease in the yield of final photoproduct. Taking a value of $1.1 \times 10^{-2} \text{ M}$ for the oxygen concentration in the oxygen-saturated solution,³ one obtains a bimolecular rate constant $k_x' = 6.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ for the oxygen-enhanced formation of product from the 450 nm transient:



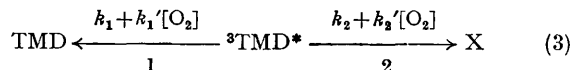
The latter reaction is thus nearly diffusion controlled.

If we assume that the triplet mechanism observed² at low temperatures also operates at room temperature, ${}^1A^* \rightarrow {}^3A^* \rightarrow X$, the most plausible assignment of the 450 nm transient would be a photoproduct triplet state ${}^3X^*$, whose transition to ground state X is enhanced by oxygen in the usual way. The relevant part of the sequence should then be as in reaction (2). The fact that oxygen



hardly affects the extent of formation both of the "450" intermediate (${}^3X^*$) and of the photoproduct (X) absorbing at 650 nm indicates that $k_2 \gg k_1 + k_1'[\text{O}_2]$ under these conditions.

An alternative explanation of the above observations would be that the 450 nm transient is actually the triplet ${}^3\text{TMD}^*$ observed earlier,² with its peak shifted from 490 nm at -160° to 450 nm at 23°, and that oxygen-quenching of ${}^3\text{TMD}^*$ results in formation of B almost to the same extent as in regular decay, reaction (3). A calculation based on



this assumption shows that k_2' should be about 10 times larger than k_1' , in order to explain the effects of oxygen. We believe that this, as well as the large temperature shift of the absorption peak in a hydrocarbon solvent, is unlikely. Moreover, quenching of a triplet molecule to its photoproduct is as yet unknown, though in principle it could take place. We therefore prefer the first explanation, *i.e.* formation of triplet photoproduct, with the latter being quenched by oxygen to its ground state.

According to Wild and his co-workers⁴ the triplet mechanism does not operate in the photochromism of TMD, and the photoproduct is formed directly from ¹A*. This mechanism is contradicted by our flash experiments at low temperatures.² If, for the sake of the argument, we assume such a singlet mechanism, the "450 nm" transient could be either ¹A* or ¹X* or ³X*. The first possibility is excluded by the observation that the fluorescence of TMD, as observed with the N₂ laser, has a life-time within that of the laser pulse. On the other hand, the molar extinction

coefficient of X at 650 nm is of the order of 10⁴ cm² mol⁻¹ (with a half-width of 2000 cm⁻¹), and a life-time of more than 100 ns is therefore not to be expected for ¹X*. Thus the only reasonable assignment of "450" remains ³X*.

The laser experiments were carried out with an Avco-Everett-N₂-laser⁵ at the Department of Physical Chemistry of the Hebrew University, Jerusalem.

(Received, 9th October 1972; Com. 1722.)

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