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THE PHOTOCHROMISM OF 4,4'-DIACETAMIDO-2,2'-STILBENE SULPHONIC ACID

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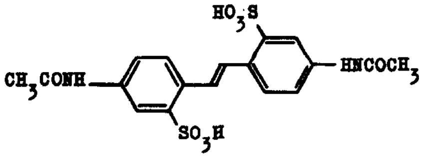
Since photochromic properties of 4,4'-diacetamido-2,2'-stilbene disulphonic acid (I) and its salts were observed by Mallison and Stobbe (1) in 1912 only a few investigations have been devoted to possible explanations of this phenomenon (2,3). From these papers the following facts are known.



I (Sodium salt: Ia)

a. I, its alkali and earth alkali salts are photochromic in the solid state. The light-induced colouring is not observed in vacuo, a hydrogen or carbondioxide atmosphere. Air, especially oxygen, is necessary for the appearence of a red colour, which is enhanced in the presence of moisture. A red sample loses colour in the dark or upon heating (1).

b. The colouring of the substance is a reaction of second order in the stilbene derivative; the bleaching follows first order kinetics (2).

c. When a suspension of I in colophonium is exposed to light for a long time the compound loses its photochromic properties. A non-photochromic modification can be separated from the resin (3).

Stobbe supposed that a chemical transformation to an epoxide, an aminoxide or a peroxide might be responsible for the colouring.

We would like to suggest the formation of a charge-transfer complex of I in an excited state and oxygen as a better explanation for this typically topochemical (4) phenomenon. This proposition is supported by the following observations.

1. The IR spectra of Ia and its coloured form (KBr-disks) are identical. However, when the KBr-disk of Ia is irradiated some new bands in the 800-650 cm^{-1} region appear, which do not disappear after keeping the sample in the dark. A similarly modified spectrum is found with KBr-disks of I and Ia, previously heated to about 140°. These changes in the IR spectrum may be described to a change of crystal structure (5). They are also found in the non-photochromic modification of Ia, which is obtained by heating a suspension in paraffin oil at 180°.

   Debye-Scherrer diagrams of the two crystalline modifications are different. Crystallization of the non-photochromic form from water gives the photochromic one again.
2. UV spectra of aqueous solutions of Ia and its coloured form are identical. However, spectra traced from KBr disks differ slightly. In the latter case the spectrum of the red compound shows a broadened absorption band with an inflexion of low intensity at 450 nm. Similar inflexions at the long-wavelength side of the first absorption band have been found for many compounds in the presence of oxygen (6) and have been described to charge-transfer complexes by Mulliken (7).
3. As the photochromic behaviour of I and its salts is clearly dependent on a special arrangement of molecules in the crystal, a salt with rather bulky cations (tetra butylammonium) was investigated. The compound (mp: 310°) shows a similar red colouring after irradiation in the presence of oxygen, but the phenomenon appears to be irreversible. The colour does not fade in the dark.
4. At a low temperature (-80° C) I shows also photochromic behaviour in glycerol solution. Only weak colouring is observed under these circumstances, possibly because of the low oxygen concentration.

5. Red coloured products (λ_{max}: 450 nm, inflexion), as formed in the presence of oxygen, are also obtained by treatment of Ia with bromine, iodine (vapour) or nitrogenoxide, even without irradiation. In these cases no other explanation than the formation of charge-transfer complexes seems to be possible.

   The red compound, obtained with bromine, turns pale upon heating leaving a bromine-free colourless powder. It shows no photochromic behaviour and does not turn red with any of the above mentioned vapours. Crystallization from water gives again the photochromic modification.
6. The red products obtained by treatment with oxygen and irradiation, bromine or nitrogenoxide are paramagnetic as shown by their ESR spectra (in all cases g = ca 2). When the sample holder is evacuated the ESR signal diminishes strongly. The reversibility points to an equilibrium between Ia and oxygen on one side and the red product on the other, and seems to exclude the formation of an organic free radical due to oxidation by oxygen.
7. Compound Ia acts as a sensitizer in the photochemical oxidation of dimethylsulfoxide (DMSO) (8). The amount of dimethylsulfon, which is formed by bubbling oxygen through UV-irradiated DMSO increases five or six fold after addition of small amounts (0,1%) of Ia under otherwise identical reaction circumstances.
8. From a hot saturated solution of Ia in oxygen-free water the compound crystallizes in a colourless form, even when the solution is irradiated during cooling. By addition of a drop of hydrogen peroxide to the cooling solution the precipitate turns red after some time. The red colour is formed faster if also a mineral acid has been added.

From these facts it may be concluded that I and its salts both in the solid state and in solution easily interact with oxygen under the influence of light. In the solid state red-coloured products are obtained with properties corresponding to those of compounds formed by treatment of Ia with bromine or nitrogenoxide. In the latter cases the coloured compounds should be charge-transfer complexes. A similar structure appears to be valid for the red products obtained from the light induced interaction of I or Ia and oxygen. Acid induced acceptor properties of oxygen have been observed before (9).

The photochromic behaviour of I and Ia in the presence of oxygen is connected with a special crystalline modification. It is attractive to suppose that oxygen molecules are inserted between two molecules of the donor compound, which is in accordance with the second order kinetics found by Padoa (2).

(1) H.Stobbe, H.Mallison, Ber. 46, 1226 (1912).
(2) M.Padoa, A.Zazzaroni, Atti della Reale Accademica dei Lincei 24, 828 (1915).
(3) H.Stobbe, Berichte über die Verhandl. der Sächs. Akad. der Wiss., Leipzig (Math. Phys. Klasse) 74, 161 (1922).
(4) M.D.Cohen, G.M.J.Schmidt, J. Chem. Soc. 1964, 1966.
(5) L.J.Bellamy, The infra-red Spectra of complex Molecules, Methuen and Co Ltd London 1960, p.380.
(6) D.F.Evans, J. Chem. Soc. 1960, 1987.
(7) H.Tsubomura, R.S.Mulliken, J.Amer.Chem.Soc. 82, 5966 (1960).
(8) G.O.Schenck, C.H.Krauch, Ber. 96, 517 (1963).
(9) W.IJ.Aalbersberg, J.Gaaf, E.L.Mackor, J.Chem.Soc. 1961, 905.