Reverse Photochromism of Stenhouse Salts

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It has been found that Stenhouse salts show reverse photochromism.

Among the large number of photochromic compounds known, very few show reverse photochromism†[1] (in which coloured species bleach upon irradiation and the colours return in the dark). We have found that Stenhouse salts (1),[2] five-carbon cyanine dyes with an OH group at the second carbon atom, show reverse photochromism in solutions or polymer matrices and we report here this property for (1; X = Cl) in solution.

The photochromic behaviour of more than ten Stenhouse salts was studed by u.v.–visible spectroscopy. Red to violet solutions of (1) in several alcohols were irradiated with u.v. or visible light for *ca.* 30 s and the thermal recoveries of the strong bands of (1) in the visible region (λ_{max} *ca.* 480—600 nm) were followed at λ_{max}. The photobleaching–thermal recolouration processes were repeated several times to examine the reversibility and typical examples are shown in Figure 1.
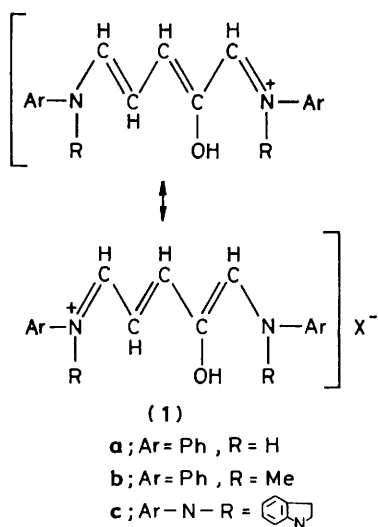
All the Stenhouse salts examined showed reverse photochromism with good reversibilities in visible light especially for the simple salts like (1a)—(1c) shown in Figure 1. Irradiation with u.v. light lowered the reversibility because of the increase in irreversible side reactions. The thermal recolouration rates followed a first order rate equation and the recolourations were complete within 15 min at room temperature after irradiation ceased. The rates were strongly dependent on the temperature and the concentration of added acid.

As the temperature was lowered, both the photobleaching efficiency and the recolouration rate diminished. At below *ca.* −50 °C, the thermal recovery rates became slow enough to follow the absorption spectral change. The rate constants

(1)

a; Ar = Ph , R = H

b; Ar = Ph , R = Me

c; Ar—N—R =
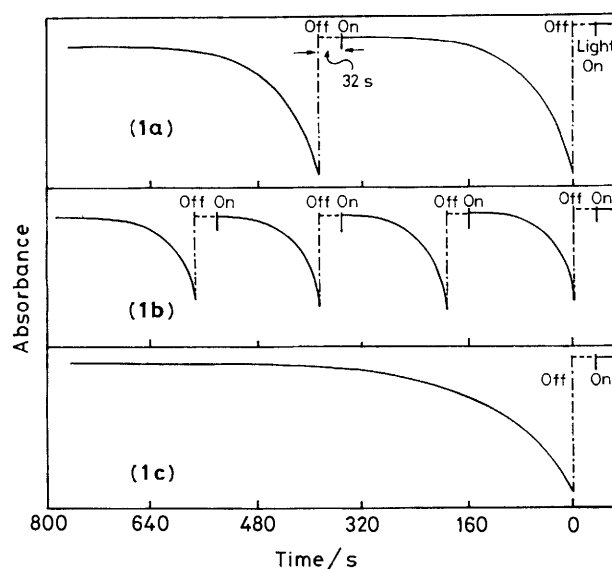
Figure 1. Reverse photochromic behaviour of (1a)—(1c) in glycerol at 27 °C. Irradiation period is 32 s. The absorption maximum wavelength (λ_{max}), irradiation light wavelength (λ_{irr}), and recolouration rate constant (k) calculated from the curve are as follows: (1a); $\lambda_{max} = 518$ nm, $\lambda_{irr} \geqslant 420$ nm, $k = 1.4 \times 10^{-2}$ s^{-1}, (1b); $\lambda_{max} = 484$ nm, $\lambda_{irr} \geqslant 400$ nm, $k = 2.9 \times 10^{-2}$ s^{-1}, (1c); $\lambda_{max} = 560$ nm, $\lambda_{irr} \geqslant 470$ nm, $k = 7.5 \times 10^{-3}$ s^{-1}.

† In this paper, the definition of photochromism is in accordance with that described in ref. 1, *i.e.* a reversible change of a single chemical species between two states having distinguishably different absorption spectra, such change being induced in at least one direction by the action of electromagnetic radiation.

Table 1. Recolouration rate constants of (1a)—(1c) in MeOH at various temperatures, and the activation energies calculated from them.

| Stenhouse salt	$10^3 k/s^{-1}$				E_a, kcal[a]/mol
	0 °C	8 °C	17 °C	25 °C	
(1a)	3.1	6.0	12	24	12.8
(1b)	5.4	12	28	58	15.0
(1c)	2.2	3.8	6.7	11	9.9

[a] 1 kcal = 4.18 kJ.

(2)

(k) of (1a)—(1c) in MeOH at several temperatures and the activation energies (E_a) calculated from them are represented in Table 1.

Addition of acids resulted in a large increase in recolouration rate and, consequently, in a decrease in the photobleaching efficiency. In the case of (1b) in MeOH at 0 °C, for example, the rate increased by a factor of ca. 10 on addition of 10 times the molar quantity of HCl, and the apparent photobleaching was not observable in the presence of more than 100 times the quantity of HCl.

The recolouration rates were measured in typical alcoholic solvents (MeOH, EtOH, Pr^{i}OH, Bu^{t}OH, glycol, and glycerol), but there was no direct relationship between the rates and the polarities or viscosities of the solvents.

Mechanistic studies are in progress, but the enolic OH group in the molecule of (1) appears to play an important role since the parent cyanine dyes[3] with no OH group do not show reverse photochromism. However, a mechanism involving photochemical ketonization of the enol is probably excluded
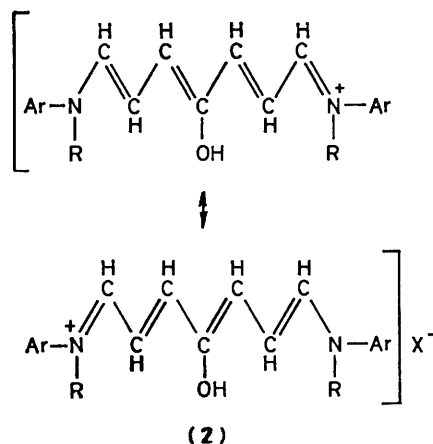
since seven-carbon cyanine dyes having a similar OH group at the fourth carbon atom (2)[4] do not show such photochromism.

References

1 'Techniques of Chemistry,' Vol III, 'Photochromism,' ed. G. H. Brown, Wiley, New York, 1971, pp. 98 and 308.
2 K. G. Lewis and C. E. Mulquiney, Tetrahedron, 1977, 33, 463, and references cited therein.
3 T. Zincke and W. Wuerker, Liebigs Ann. Chem., 1905, 338, 107.
4 W. Koenig, J. Prakt. Chem., 1913, 88, 193.