

mental value of  $15 \pm 4$  obtained by Mysels, Cox and Skewis for films in the range  $1-10\mu$  is therefore in satisfactory agreement with the Gibbs theory.

This concord between theory and experiment confirms that the elasticity of thick soap films under quasi-static conditions is governed by the Gibbs effect. It does not mean, however, that the other effects mentioned here are unimportant in foams under other conditions; the evidence for long-range forces in very thin films, for example, is compelling.

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<sup>1</sup> cf. Kitchener, J. A., and Cooper, C. F., *Quart. Rev.*, **13**, 71 (1959).

<sup>2</sup> Mysels, K. J., Cox, M. C., and Skewis, J. D., *J. Phys. Chem.*, **65**, 1107 (1961).

<sup>3</sup> Clayfield, E. J., and Matthews, J. B. (private communication of data); cf., *Proc. Second Intern. Cong. Surface Act.*, **1**, 172 (1957).

### Photochromism of *o*-Nitrotoluenes

THE crystals of 2-(2',4'-dinitrobenzyl)-pyridine (I), which are colourless when kept in the dark, turn blue when exposed to light<sup>1</sup>. Hardwick, Mosher and Passailaigue<sup>1</sup> by using a cryoscopic technique have demonstrated that the change in colour is not confined to the crystals but occurs in dilute solutions as well. A similar change in colour has also been observed with 4-(2',4'-dinitrobenzyl)-pyridine (II)<sup>2</sup>.

Now, by using the flash photolysis technique, I have established the fact that *o*-nitrotoluene and a variety of compounds, all derivatives of *o*-nitrotoluene, are photochromic. In this work, a light pulse of high intensity was obtained by the discharge of 1,800 joules (9  $\mu$ F., 20 kV.) through four straight quartz tubes (Lindqvist, L., Institute of Physical Chemistry, University of Uppsala) giving a flash duration of 5  $\mu$ sec. ( $1/e$  time). Light emitted from the lamps of wave-lengths shorter than 250  $m\mu$  was absorbed in a filter surrounding the test solution. The transmission of 20 cm. of the solutions was recorded photoelectrically. All investigations were performed at room temperature ( $24^\circ \pm 1^\circ$  C.) with the concentration of the compound being about  $10^{-4}$  M. No detectable stray light from the exciting flash entered the recording system and the absorption spectra of the coloured

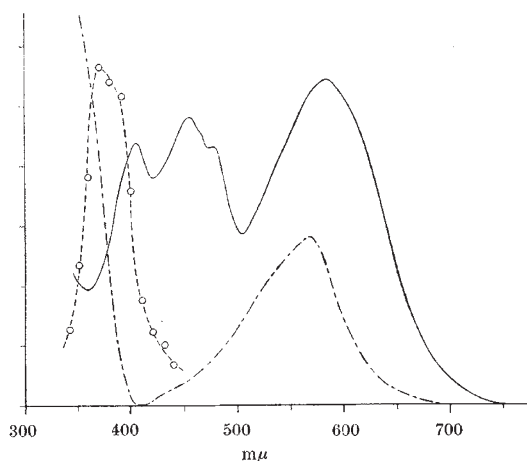


Fig. 1. Absorption spectra of ethanol solutions of *o*-nitrotoluene (—), 2-(2',4'-dinitrobenzyl)-pyridine (---), and 2-(2'-nitro,4'-cyanobenzyl)-pyridine (-·-·) after exposure to ultra-violet light. The ordinate is proportional to optical density with different proportionality constants for the different solutions

solutions were determined at maximum optical density during the flash. The kinetics of the fading reaction were evaluated from the change with time of the light transmission of the coloured solution after the flash.

Compounds examined were *o*-nitrotoluene (III), 2,4-dinitrotoluene (IV), 2-(2'-nitro,4'-aminobenzyl)-pyridine (V) and 2-(2'-nitro,4'-cyanobenzyl)-pyridine (VI) as well as I. It was shown that all these compounds have the property of becoming coloured on exposure to light and then becoming colourless in the dark.

The colourless compounds do not appreciably absorb light of wave-lengths longer than 330  $m\mu$ .

The absorption spectra of three of the coloured solutions are presented in Fig. 1. The irradiated solutions of I and VI maintained their colour long enough at  $-70^\circ$  C. to measure the spectra by means of a cryoscopic technique using a Cary 14 spectrophotometer<sup>3</sup>. The spectrum of the irradiated solution of III was obtained at room temperature by means of flash photolysis using a small Bausch and Lomb grating monochromator.

In absolute ethanol the fading reaction in all cases followed the kinetics of a first-order reaction. Rate constants are given in Table 1.

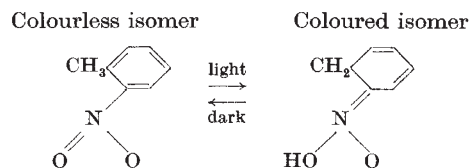
Table 1. RATE CONSTANTS FOR THE FIRST-ORDER FADING REACTIONS IN ABSOLUTE ETHANOL AT ROOM TEMPERATURE

Compound	Rate constant (sec. <sup>-1</sup> )
<i>o</i> -Nitrotoluene	$1.3 \times 10^2$
2-(2',4'-Dinitrobenzyl)-pyridine	$1.2 \times 10^{-1}$
2-(2'-Nitro,4'-cyanobenzyl)-pyridine	$3.7 \times 10^{-1}$

The cycle of becoming coloured and then reverting to the colourless state could be repeated several times without noticeable change in the behaviour of the solution. After 5-10 cycles, however, a change in the rates of the fading reaction was observed; in the cases of I and VI the rates are increased, but in the case of *o*-nitrotoluene the rate is decreased. This behaviour appears to be due to irreversible side reactions which render the solutions acidic since the same phenomena were observed when acid is added to the solution.

A detailed study has been made<sup>4</sup> of the fading reaction of I in water solutions under different conditions of pH and the rate of the fading reaction has been found to be increased by a factor of  $10^5$  when going from pH 12 to 2.

A probable mechanism for the change in colour is as follows:



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<sup>1</sup> Hardwick, R., Mosher, H. S., and Passailaigue, P., *Trans. Farad. Soc.*, **56**, 44 (1960).

<sup>2</sup> Mosher, H. S., Souers, C., and Hardwick, R., *J. Chem. Phys.*, **32**, 1888 (1960).

<sup>3</sup> Sousa, J. A., and Weinstein, J., *J. Org. Chem.* (in the press).

<sup>4</sup> Wettermark, G., *J. Amer. Chem. Soc.* (in the press).