

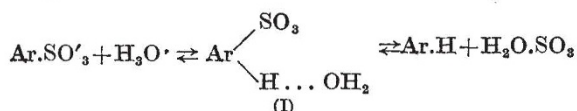
LETTERS TO THE EDITORS

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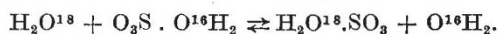
Relationship between Sulphonation and Desulphonation

THE familiar process of recovery of aromatic compounds from their sulphonic acids is probably almost universally regarded as one of hydrolysis. We have, however, confirmed our expectation that it might be more correctly comparable with the ordinary Dumas process of decarboxylation, and so involve their anions rather than the acids themselves; for a kinetic study of the desulphonation of *m*-cresol-sulphonic acid in 90 per cent acetic acid containing also hydrobromic or sulphuric acid showed its velocity to be independent of the concentration of the sulphonic acid, to conform to the first-order equation and to be proportional to the hydrogen ion activity of the solution, but independent of the nature of the inorganic anion. Sulphonic acids of mesitylene, phenol, *p*-cresol, and 4-nitrodiphenylamine, exhibited a similar behaviour.

We must therefore formulate the recognized reversible relationship between sulphonation and desulphonation as follows:



Sulphonation and desulphonation are thus essentially determined by the distribution of the acids, proton and SO_3 (in the Brønsted-Lowry sense), between the bases phenyl anion and water. Similarly the absence of oxygen exchange between sulphate ions, unless sulphuric acid be present¹, shows that here also the essential reaction is the distribution of SO_3 between H_2O^{16} and H_2O^{18} or, as it may be regarded, sulphonation of the two types of water:



The conclusion at which we arrive in this manner, that sulphonation directly involves $\text{H}_2\text{O.SO}_3$ rather than $\text{SO}_2(\text{OH})_2$, accords with the suggestion of Benford and Ingold² that nitration involves ($\text{H}_2\text{O.NO}_2$), and the deduction by one of us³ that nitrosation involves ($\text{H}_2\text{O.NO}$).

Furthermore, it will be seen that in the transition complex (I), water contributes to completion of the sulphonation forces by removal of the proton in the same way as it was suggested nitrite ion does in nitrosation³. This is in line with the observations of Martinsen⁴ on velocities of nitration and sulphonation.

This brief discussion will perhaps serve to illustrate the wider implications of our experiments for the general problem of substitution. It need scarcely be pointed out that reversibility of the sulphonation process is much facilitated by the negative charge of the sulphonate ion. The lack of such a charge in other cases commonly inhibits reversibility; but it is familiar in the cases of nitramines and chloramines, as well as sulphamic acids; and even neutral nuclear substituents may be readily displaced by proton if, for example, steric influences provide the necessary facility for attachment of proton to the nucleus⁵.

It is hoped to publish a more detailed account of this work elsewhere.

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¹ Winter, Carlton and Briscoe, *J. Chem. Soc.*, 31 (1940). Mills, *J. Amer. Chem. Soc.*, **62**, 2333 (1940).

² *J. Chem. Soc.*, 955 (1938).

³ Kenner, *Chemistry and Industry*, **60**, 443 (1941).

⁴ *Z. Phys. Chem.*, **50**, 385, 435 (1904); **59**, 605, 634 (1907); **62**, 713 (1908).

⁵ Compare, Baddeley, *Nature*, **144**, 444 (1939).

Rod and Cone Responses in the Human Eye

THERE is abundant evidence to show that the human eye has two distinct receptor mechanisms, one for vision in bright daylight and the other for vision at night. The sensitivity of the former, the photopic mechanism, is greatest for the longer wavelengths and is not much changed by dark adaptation. That of the scotopic mechanism is greatest for green and blue, and may be increased or reduced a thousand-fold by keeping the eye in darkness or light. From their distribution in the retina and in different animals, the cones are thought to be the photopic receptor organs and the rods the scotopic.

A new kind of evidence for the 'duplicity theory' has recently appeared from records of the potential changes developed in the human eye. Such records have been made before without adding much to what can be learnt from animals; but with modern technique the human electroretinogram can be seen to depend on two receptor systems with the characteristic photopic and scotopic properties. Leads have been taken from an electrode on the cheek and from a moist thread in contact with the front of the eyeball. The eye is exposed to a large field lit by brief flashes of light and the potential changes are recorded by an ink-writing oscillograph. With red light, which should stimulate mainly the cones (Wratten monochromatic filter No. 70), the response is a brief diphasic change, the cornea becoming initially negative (Fig. 1A). This response is very little affected by dark adaptation, though there is some increase in the first few minutes. With blue light, which should stimulate mainly the rods (Wratten filter No. 76), the response is a slower monophasic change with a longer latency (Fig 1B). This response is

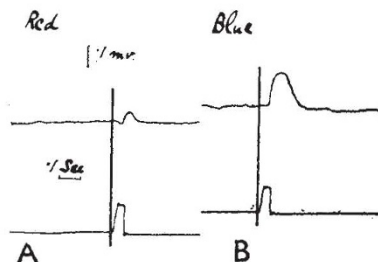


FIG. 1. A: ELECTRIC RESPONSE OF THE EYE TO A FLASH OF RED LIGHT, WRATTEN FILTER NO. 70. CENTRAL WAVE-LENGTH 690 $m\mu$. B: RESPONSE TO A FLASH OF BLUE LIGHT. WRATTEN FILTER NO. 76. CENTRAL WAVE-LENGTH 440 $m\mu$.