



Fig. 1

perature (up to 300° C.) and then (300–600° C.) again increases.

In the case of thallium-activated sodium chloride disks, decay did not follow the well-known exponential law of thallium-activated sodium chloride single crystal phosphors. The shape of the brightness versus time curve is satisfactorily accounted for by a hyperbolic expression. Experiments were carried out with thallium-activated sodium chloride single-crystal phosphors grown from the melt. These crystals showed an exponential decay law; however, after the crystals had been deformed by stressing, the exponential law changed to a hyperbolic one (Fig. 1). When the decay of the phosphorescence is represented in a (log-log) diagram, as in Fig. 1, the exponential decay law is represented by curve 1, while the shape of the diagram becomes a straight line after the stress had been applied (curves 2 and 3). Hence it seems that dislocations may seriously affect the decay of phosphorescence.

A detailed account of this work will be published elsewhere. I wish to thank Prof. Z. Gyulai, who directed the investigation.

Z. MORLIN

Institute of Experimental Physics,
Budapest University of Technology.

Reaction of Nitrates with Liquid Sulphur Dioxide

It has been known for some time that inorganic nitrates catalyse the formation of polysulphones from liquid mixtures of olefines and sulphur dioxide¹, but the mechanism of catalysis has never been clarified. It is now suggested that the effective catalyst is nitrogen dioxide and/or the sulphite radical ion formed as the primary products of the reaction between nitrates and sulphur dioxide. The following observations are consistent with this suggestion:

(1) If sufficient silver nitrate is allowed to react with liquid sulphur dioxide, a brown gas appears but may, in time, disappear again. The brown gas is

presumably nitrogen dioxide formed by processes such as $\text{NO}_3^- + \text{SO}_2 \rightarrow \text{NO}_2 + \text{SO}_3^-$, $\text{NO}_3^- + \text{SO}_3^- \rightarrow \text{NO}_2 + \text{SO}_4^{2-}$, and removed by further reactions with sulphur dioxide. In the presence of excess sulphur dioxide, the final products are likely to be nitrosyl pyrosulphate and nitric oxide², the overall reaction being:



It is worth noting that rapid oxygen atom transfer reactions such as $\text{ClO}_2^- + \text{SO}_3^{2-} \rightarrow \text{ClO}^- + \text{SO}_4^{2-}$ have been recognized³.

(2) The observation of Dainton and Ivin⁴ that the volatile products of the silver nitrate-sulphur dioxide reaction did not catalyse polysulphone formation is now consistent with this picture. Previously they had supposed that nitrogen dioxide was the end product.

(3) The only three completely soluble nitrates investigated by Snow and Frey¹ as catalysts for polysulphone formation were those of lithium, silver and ammonium, the efficiency increasing in that order. In liquid sulphur dioxide (dielectric constant 15.6 at 0° C.) the Bjerrum critical distance⁵ for ion-pair formation is calculated to be 19.6 Å. at 0° C. and it is to be expected that even with nitrate concentrations of $10^{-4} M$ there will be a considerable degree of association of the ions. Hence the rate-determining step for the initiation of polysulphone formation should probably be written as:



The cation would be expected to affect the ease of release of the oxygen ion, and it is interesting to note that the catalytic efficiency increases with increasing size of the (crystallographic) cationic radius.

(4) Nitrogen dioxide is known to attack olefines⁶. The sulphite radical ion may equally well be the effective catalyst, since it has been shown to initiate the polymerization of styrene⁷.

Attempts were made to follow the variation of the nitrogen dioxide concentration with time spectrophotometrically in mixtures of sulphur dioxide with ammonium or silver nitrate. These experiments were not successful, because of the very low solubility of the nitrates.

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K. J. IVIN

Department of Physical Chemistry,
University of Leeds.

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Interference in Soil Phosphorus Analyses by Snail Shells

IN some calcareous grassland soils in County Galway, certain fertility problems have been encountered with particular regard to soil phosphorus. While 'high' or 'very high' values for readily soluble phosphorus were sometimes obtained by routine analytical procedures¹, grazing and botanical observations indicated extreme phosphorus deficiency. Such