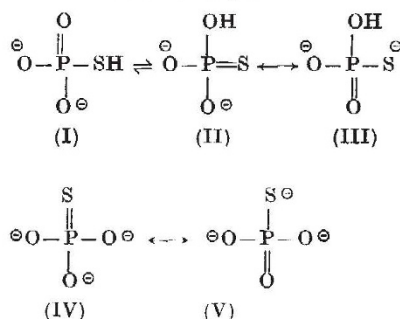


(where  $R_1$  and  $R_2$  is H or alkyl) react, it is obvious that an increased negative charge on the phosphorothioate ion should increase the reaction rate. However, the fact that uncharged molecules, like ethylene oxide, react exclusively with the triply charged anion would indicate that coulombic forces alone do not give a satisfactory explanation.

Obviously the  $\text{HPSO}_3^{2-}$  ion and the  $\text{PSO}_3^{3-}$  ion can exist in several forms, for example:



Of the protomeric and mesomeric forms of the  $\text{HPSO}_3^{2-}$  and the  $\text{PSO}_3^{3-}$  ions shown above, II and IV containing doubly bonded sulphur would be expected to be the least reactive with alkylhalogenides and with ethylene oxide. The fact that the  $\text{HPSO}_3^{2-}$  ion reacts extremely slowly in this type of reaction suggests that in aqueous solution this ion is predominantly present as the unreactive form II, while in the reactive  $\text{PSO}_3^{3-}$  ion the contribution of the mesomeric form (V) is the most important.

Recent investigations by Steger and Martin<sup>3,4</sup> on the configuration of the various ionic species of phosphorothioic acid in solid hydrated form leave little doubt that the above assumptions are correct. Infra-red and Raman spectra confirm forms (II) and (V), respectively.

Due to the greater electronegativity of oxygen compared with sulphur the double bond should mainly exist between phosphorus and oxygen in the  $\text{PSO}_3^{3-}$  ion. The probable explanation for the predominant existence of form (II) of the  $\text{HPSO}_3^{2-}$  ion is that the three oxygen atoms are equal in respect to proton bonding, thus leaving the double bond in this ion mainly between phosphorus and sulphur.

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<sup>1</sup> Åkerfeldt, S., *Svensk Kem. Tidskr.*, **75**, 231 (1963).

<sup>2</sup> Åkerfeldt, S., *Acta Chem. Scand.*, **17**, 329 (1963).

<sup>3</sup> Steger, E., and Martin, K., *Z. Anorg. Allgem. Chem.*, **308**, 330 (1961).

<sup>4</sup> Steger, E., and Martin, K., *Z. Anorg. Allgem. Chem.*, **323**, 108 (1963).

### Structure of the Viscous Phase of Liquid Sulphur

A FEW years ago McLaughlin presented arguments against the polymerization theory of liquid sulphur<sup>1</sup>. No further arguments against the theory have so far been offered by other investigators. On the contrary, an increasing number of experiments have contributed to the general acceptance of the theory. An examination of the objections raised by McLaughlin therefore seems to us of enough interest to present our counter-arguments.

Roughly speaking, the polymerization theory states that from about 160° C upwards the eight-atomic sulphur rings break open and combine to form very long chain-like polymers. When a small amount of iodine is added to the sulphur the iodine will react with the free valencies at the ends of the chains and so the chemical activity of the chain ends is neutralized. This hinders polymerization and so reduces the chain-length, so that if the amount of iodine is increased the viscosity of the polymeric sulphur decreases.

From this picture McLaughlin concluded that the decrease in viscosity would depend on whether iodine was added at the measuring temperature or before heating up to that temperature. In the former case the long polymers would have been formed already, and McLaughlin expected that the iodine would no longer have any influence on the chain-length or the viscosity. The results proved not to be in accordance with this conclusion, and he therefore rejected the starting point of his reasoning, the polymerization theory.

In our opinion, McLaughlin's arguments do not hold in that at high temperatures the polymeric molecules and the rings in liquid sulphur must not be seen as definite and inactive molecules but as the results of an equilibrium maintained by continual reactions. It will, therefore, always be possible for the added iodine to take part in these chemical reactions.

The best evidence for the persistence of reactions at higher temperatures lies in the work of Gardner and Fraenkel<sup>2</sup>, who even calculated the rate of one of the chemical reactions involved from the line-widths of their electron spin resonance measurements.

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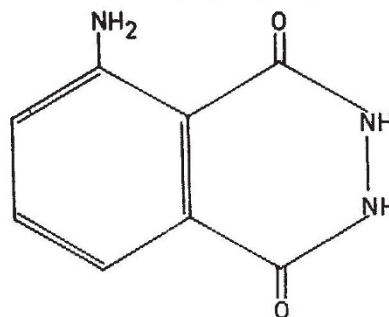
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<sup>1</sup> McLaughlin, E., *Nature*, **186**, 78 (1960).

<sup>2</sup> Gardner, D. M., and Fraenkel, G. K., *J. Amer. Chem. Soc.*, **78**, 3270 (1956).

### Di-imide and the Chemiluminescence of Luminol

THE light emitted when luminol reacts with hydrogen peroxide is usually<sup>1</sup> supposed to come from excited luminol molecules formed by the decomposition of a luminol peroxide<sup>2</sup>. However, Albrecht<sup>3</sup> has proposed that luminol molecules are excited by di-imide,  $\text{N}_2\text{H}_2$ , formed during the oxidation of luminol by hydrogen peroxide.



Luminol

Di-imide was formerly postulated only as a reactive intermediate, but it has recently been isolated as a solid at low temperatures<sup>4</sup> and detected in gases by mass spectrometry<sup>5</sup>. A growing body of evidence indicates that it is the reducing agent in solutions containing either hydroxylamino-*O*-sulphonic acid<sup>6</sup>, or hydrazine<sup>7</sup> or *p*-toluene-sulphonyl hydrazine<sup>8</sup>, which are used to hydrogenate unsaturated compounds.

We find that luminol in aqueous solutions of these reagents emits light even in the absence of hydrogen