

88 per cent ethyl nitrate, a flame cannot be induced on sparking. If more nitrogen dioxide is added to that mixture so that its concentration is approximately doubled, a flame can be propagated once more. The role of the methane is probably similar to that in the hydrogen-oxygen reaction.

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The Ion N_2O_3^+ . Binding by One-Electron Transfer

It has been shown spectroscopically (the evidence will be published shortly¹) that the nitrosonium ion in solution forms a molecular compound with nitrogen dioxide: $\text{NO} \overset{+}{\text{N}}\text{O}_2$ (I). As the compound may also be produced from nitric oxide and a solution of nitronium ion, one might also consider representing it

thus: $\text{NO} \overset{+}{\text{N}}\text{O}_2$ (II). Actually, its spectral properties indicate that it has an intermediate constitution, but one which much more closely resembles structure I than II. Thus the high vibration frequency ($2,240 \text{ cm}^{-1}$), depending on the multiple link in the NO-component of the complex, is displaced only one-seventh of the way from the frequency of the nitrosonium ion ($2,300 \text{ cm}^{-1}$) towards the frequency of nitric oxide ($1,880 \text{ cm}^{-1}$).

We regard the components of this compound ion as being held together by a one-electron bond, that is, by the reversible electron-transfer which would interconvert structures I and II. It is reasonable that structure I should make a considerably larger contribution than II to the wave-function of the meso-

meric complex $\text{NO} \overset{+}{\text{N}}\text{O}_2$; for the oxidation-levels of the components of I (which may be denoted by the nitrogen-oxidation numbers 3 and 4) are not as widely separated as are the oxidation-levels of the components of II (the oxidation numbers of which are 2 and 5). Therefore structure I should have a smaller tendency to pass by a redox electron-transfer into II, than II should have to pass into I; that is, the mesomeric state will more closely resemble I.

This case may help to clarify the position of Weiss's univalent electron-transfer theory of molecular compounds², some critics of which forget that (as Weiss implies, but does not emphasize) electron-transfers are in principle always reversible³. A practically irreversible one-electron transfer to form an ionic bond, as in a Wurster salt, to the normal state of which the structure $\overset{+}{\text{N}}\text{O} \overset{-}{\text{N}}\text{O}_2$ contributes every-

thing, and $\overset{+}{\text{N}}\text{O} \overset{+}{\text{N}}\text{O}_2$ nothing, and a perfectly balanced transfer to give a fully homopolar one-electron bond, as in the hydrogen molecule-ion, to which the

structures $\overset{+}{\text{H}}\overset{+}{\text{H}}$ and $\overset{+}{\text{H}}\overset{+}{\text{H}}$ make equal contributions, evidently constitutes limiting cases of a more general picture of compound formation by one-electron bonds varying in type from fully homopolar to fully electrostatic. Our ion N_2O_3^+ belongs to the general case of a partly homopolar and partly electrostatic bond: structure I contributes much more than II, but not everything. If we consider N_2O_3^+ to be produced from NO and NO_2^+ , we may approximately describe it as having been formed through a Weiss transfer; whereas, if we think of it as derived from NO^+ and NO_2 , then our first approximate description might well be that the binding arises from the incursion of exchange.

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¹ By Goulden and Millen, probably in *J. Chem. Soc.*

² *Nature*, **147**, 512 (1941); *Trans. Farad. Soc.*, **37**, 780 (1941); *J. Chem. Soc.*, 245 (1942); 462 (1943).

³ Cf. Bateman, Hughes and Ingold, *J. Chem. Soc.*, 243 (1944).

Preparation of High Specific Activity Hydrogen Sulphide (H_2S^{35}) from Neutron-Irradiated Potassium Chloride

THE recent note of U. Croatto and A. G. Maddock¹ pointing out the desirability of producing radio sulphur in its lowest, rather than in its highest, valency form, as it ordinarily occurs when potassium chloride is irradiated with slow neutrons, has prompted us to comment on the method used in this laboratory for producing H_2S^{35} from neutron-irradiated potassium chloride.

Neutron-irradiated potassium chloride was put in a quartz container which was first evacuated and then sealed with about 25 cm. of hydrogen in it. This container was heated to $1,100^\circ \text{C}$. for three hours and then permitted to stand overnight at 550°C . Chemical examination of both the gas and solid phase showed that more than 95 per cent of the sulphur activity which was originally present in the solid phase was now in the gas phase and all of it was in the form of hydrogen sulphide.

It might be appropriate to comment at this time on the other aspect of the letter by U. Croatto and A. G. Maddock, namely, that of the state of oxidation of the sulphur formed from the reaction $\text{Cl}^{35(n,p)}\text{S}^{35}$. We have found that if the pre-irradiation treatment of the potassium chloride is sufficiently drastic, one can alter, at least in part, the oxidation state of the radiosulphur produced². Recently, we subjected a group of potassium chloride crystals of various sizes to an outgassing procedure which consisted of heating to 700°C ., pumping with a diffusion pump for 72 hr. and then irradiating the crystals in an atmosphere of hydrogen in the Oak Ridge pile. Chemical examination showed that the smallest crystals had about 40 per cent of their sulphur activity in the -2 state and 60 per cent in the $+6$ state. The fraction of activity in the hexavalent