

Constitution of Nitric Peroxide.

By

Edward Divers, *M. D., D. Sc., F. R. S.,*

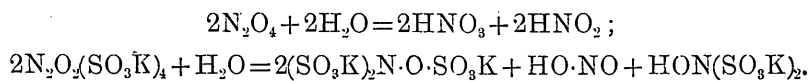
Emeritus Professor of Chemistry, Imperial University of Tokyo.

In a paper appearing with this (this vol., Art. 15), Haga has demonstrated that Fremy's *sulphazilate* is an oxime-peroxide and a tervalent nitrogen compound. If Hantzsch and Semple's suggestion is accepted (*Ber.*, 1895, **28**, 2744; *cf.* Piloty and Schwerin, *Ber.*, 1901, **34**, 1884 and 2354), that Fremy's salt is also a sulphonated nitric peroxide, it follows that the constitution of nitric peroxide is at last determined, being that of *nitrosyl peroxide*. Hantzsch and Semple must be right, for, after Haga's researches, a sulphazilate as a peroxy-aminesulphonate cannot be supposed to be other than a sulphonated nitric peroxide. It only remains, therefore, to show that nitric peroxide is a true peroxide in its chemical relations.

It is formed from nitric oxide and oxygen, just as sodium peroxide is formed from sodium and oxygen. Nitrous acid cannot, indeed, be shown to pass simply into it and back again, as a hydroxylaminedisulphonate (sulphonated nitrous acid) changes into a peroxyaminesulphonate, but that is only on account of its own instability and that of nitrous acid.

Its interaction with organic oximes, in which it converts these substances into peroxides and becomes hydrogenised into nitrous acid (Scholl), is in accordance with its nature as a true peroxide. Similarly, it converts a hydroxylaminedisulphonate into a peroxyamine-sulphonate (Haga).

Nitrosyl peroxide and a peroxyaminesulphonate both interact with water in essentially the same way, the apparent difference being due to the limits imposed by the sulphonation in the case of the latter substance. The former yields half its nitrogen as nitric acid and half as nitrous acid, whilst the latter yields half its nitrogen as a mixed anhydrosulphate (hydroxylaminetrisulphonate) and the other half as nitrous acid and sulphonated nitrous acid (hydroxylaminedisulphonate):



It would seem, therefore, that wholly on the evidence afforded by Haga's work, it can now be confidently asserted that dinitric peroxide is nitrosyl peroxide and a compound of exclusively tervalent nitrogen. The constitution of mononitric peroxide, in regard to these two points, remains to be considered, but can hardly be very different.

Hantzsch and Semple have suggested (*loc. cit.*) that the bluish-violet dissolved form of a peroxyaminesulphonate corresponds with mononitric peroxide, and its crystalline form with dinitric peroxide. Since then, Piloty and Schwerin (*loc. cit.*) have expressed the belief that *porphyrexide*, which has the colour of mononitric peroxide, may also be a derivative of this peroxide, because it contains the group :NO singly, as shown by the formula $(\text{C}_5\text{H}_9\text{N}_3) : \text{NO}$. Its molecular weight, however, has been only indirectly ascertained, that is, by cryoscopic determinations of those of its nitrate and its chloro-derivatives. That its molecular weight is not double as great is a remarkable fact, for, in its chemical behaviour, and especially in its

reversible relation with *porphyrexine*, $(C_5H_9N_3) :NOH$, porphyrexide seems to belong to the class of oxime-peroxides. Piloty and Schwerin do not indeed recognise this, and have instead come to the conclusion that the nitrogen of the group $:NO$ in porphyrexide and in mononitric peroxide must be quadrivalent. In the light of Haga's experimental results, this view of the matter has become untenable, since porphyrexide and the peroxyaminesulphonates appear to belong to the same class of nitroso-compounds, as Piloty and Schwerin themselves have pointed out.

In the few cases in which it has been possible to determine cryoscopically the molecular weight of a glyoxime-peroxide, this has been found to include $:NO$ twice. This result may be owing to the glyoxime constitution of these peroxides, but even so there is still no peroxide, except mononitric peroxide, and possibly porphyrexide, the molecular weight of which is such that it contains the group $:NO$ only once. The occurrence of many nitroso-compounds in a colourless, solid form, and in a bluish-violet liquid form, does not lend much assistance in deciding the molecular weights of the two forms of a peroxyaminesulphonate, since they contain not $:NO$ but $\cdot NO$. But it must not be left out of sight that Piloty (who thinks otherwise, and has been followed by Schmidt, Bamberger and others) has succeeded in showing that the white form of these compounds contains the group $\cdot NO$ twice, and that the deeply-coloured modification contains it only once. But here the latter is the form which must be treated as the chemically active one, whilst the double weight found for the white form has to be left uninterpreted chemically, as, for example, in the case of the formula $(C_8H_{17}NO)_2$ for nitroso-octane.

In the paper by Hantzsch and Semple (*loc. cit.*) there occurs, but in a foot-note only and without comment or explanation, the punctuated formula $O \cdot N : (SO_3K)_2$; whether this is to be regarded as a

printer's error for $O:N:(SO_3K)_2$ is uncertain, but if it is not it indicates some recognition by these chemists of the presence of univalent oxygen. However this may be, the possibility of the nitrogen being quadrivalent being inadmissible, the only solution of the matter seems to be to consider that both mononitric peroxide and porphyrexide are compounds of univalent oxygen, although still peroxides. The fact that a molecular quantity, such as that formulated by HO , NO_2 , $(SO_3K)_2NO$, or $(C_5H_9N_3)NO$, is never met with singly in chemical interactions militates against the acceptance of this explanation. Piloty and Schwerin, in discussing the quadrivalency of nitrogen, conceal this fact by stating that porphyrexide is produced from porphyrexine by the action of *half an atom* of oxygen. It is much more correct to hold with Haga that the molecule of peroxyaminesulphonate, and therefore also of mononitric peroxide and of porphyrexide, is not less than that represented by $[NO(SO_3K)_2]_2$, $(NO_2)_2$, or $(C_5H_9N_4O)_2$, as the case may be, if by molecule is meant the smallest chemically active weight of a substance. But still the fact remains that, when measured by comparison of their physical properties, the molecular weights of porphyrexide and red nitric peroxide are expressed by half the above formulæ, and probably the bluish-violet form of a peroxyaminesulphonate has also a molecular weight, which when physically considered, should be expressed by the formula, $NO(SO_3K)_2$. These weights, only physically determined, have no chemical significance, and should be distinguished from their doubles, the truly chemical molecular weights. But, as pseudo-chemical molecules, they must be represented to contain a univalent atom of oxygen.

It is, after all, not so difficult to admit that oxygen may be univalent in a peroxide. In fact, true peroxide may be defined and differentiated from other oxides, as being a compound in which some or

all of the oxygen is exerting on the rest of the compound only half its usual valency. Or, conversely, a peroxide may be defined as a compound containing oxygen which is either actually univalent or exteriorly and quasi-univalent. Apart from the unfamiliar nature of the conception of actually univalent oxygen, it seems natural enough to find a normal molecule of nitric peroxide dissociate at a gentle heat into two identical but simpler ones, in consequence of the linked oxygen atoms becoming parted and losing valency. On the other hand, the assumption that nitrogen is quadrivalent does not accord with the result actually obtained, when by cooling nitric peroxide it is found that the valency of the nitrogen decreases instead of increasing, $2\text{O}:\text{N}:\text{O}$ becoming $\text{O}:\text{N}:\text{O}\cdot\text{O}:\text{N}:\text{O}$.

