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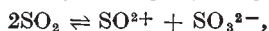
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May 4.

<sup>1</sup> Scott Blair, G. W., Veinoglou, B. C., and Caffyn, J. E., *Proc. Roy. Soc., A*, **189**, 69 (1947).

<sup>2</sup> Nutting, P. G., *J. Franklin Inst.*, **191**, 679 (1921).

### Ionic Reactions in Liquid Dinitrogen Tetroxide

THE fact that liquids other than water may serve as media for inorganic reactions is widely recognized; reactions in the well-known liquid ammonia and liquid sulphur dioxide systems are explained by postulating the ionization:



although neither liquid has an appreciable electrical conductivity. Frankland and Farmer<sup>1</sup> in 1901 first considered the possibility that liquid dinitrogen tetroxide might serve as an ionizing medium, but were unable to find any inorganic salt which was soluble in the liquid. In view of the high solubility of many organic compounds, they concluded that the liquid was of a non-ionizing character and resembled in behaviour such organic solvents as benzene.

We have now obtained evidence that ionic reactions can be conducted in liquid dinitrogen tetroxide medium. Where electron-transfer can readily occur, all reactions so far investigated in this medium can be interpreted on the basis of the ionization:



The existence of the nitrosyl radical is already established in other media<sup>2,3</sup>, and we have found no evidence for dissociation of the  $\text{N}_2\text{O}_4$  into  $\text{NO}_2^+$  and  $\text{NO}_2^-$  under these conditions. Thus the alkali metals, including lithium, react rapidly but quietly with liquid dinitrogen tetroxide to yield the nitrate and nitric oxide:



The reaction is not affected, except in velocity, by dilution of the dinitrogen tetroxide with an inert solvent such as benzene. The insoluble nitrate produced is free from nitrite. At temperatures approaching the boiling point of dinitrogen tetroxide (21.3°) the nitric oxide is evolved (although at low temperatures, or under pressure, some nitric oxide remains associated in the liquid phase as blue dinitrogen trioxide), and the reaction can be considered as a simple electron transfer from the sodium atom to the  $\text{NO}^+$  ion, giving the resonance-stabilized nitric oxide molecule. Attempts to explain this reaction on the basis of dissociation of the medium into  $\text{NO}_2^+$  and  $\text{NO}_2^-$  would involve the intermediate formation of the alkali metal nitrite, which we have found to be stable in contact with liquid dinitrogen tetroxide. Although some metallic oxides when allowed to react with dinitrogen tetroxide yield nitrite as well as nitrate, this is probably at least a two-stage reaction which may be explained thus:

$\text{MO} + (2\text{NO}^+ + 2\text{NO}_3^-) \rightarrow \text{M}(\text{NO}_3)_2 + 2\text{NO}^+ + \text{O}^{2-}$ , followed by  $\text{MO} + 2\text{NO}^+ + \text{O}^{2-} \rightarrow \text{M}(\text{NO}_2)_2$ , and the formation of nitrite here does not necessarily imply the presence of  $\text{NO}_2^-$  in the medium.

Ammonium chloride (in liquid ammonia) and thionyl chloride (in liquid sulphur dioxide) have many properties commonly associated with aqueous hydrochloric acid solutions. The corresponding compound in the liquid dinitrogen tetroxide system, nitrosyl chloride, is soluble in this medium and such solutions attack many of the metals which are resistant to the tetroxide alone, the degree of attack depending on the concentration of the nitrosyl chloride; nitric oxide is evolved, the insoluble product being either the metal chloride or the chloride associated with nitrosyl chloride as a complex of the type  $(\text{NO})_x[\text{MCl}_y]$ .

The ionic dissociation of dinitrogen tetroxide (equation 1) is fully reversible in the liquid phase. Thus the reaction:

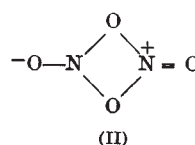
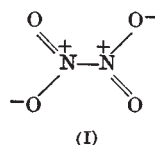


(comparable with the reaction between an aqueous solution of hydrogen chloride and an insoluble hydroxide) is complete in the direction indicated. However, if dry diethylammonium chloride is added to liquid dinitrogen tetroxide at 0° the reaction:



proceeds readily. The medium is immediately coloured red by the nitrosyl chloride produced, and diethylammonium nitrate may be crystallized from the solution; the process resembles that of hydrolysis. At higher temperatures the products of reaction (3) undergo further mutual interaction.

Full details of the work will be published elsewhere, but it is of interest here to compare the behaviour of dinitrogen tetroxide outlined above with its reactions where bonds of a covalent character are involved. Levy and Scaife<sup>4</sup> have shown that it adds to olefinic double bonds to give exclusively dinitro-compounds or nitro-nitrites. Again, both ammonia and diethylamine react explosively with it, yet ammonium and diethylammonium chlorides and nitrates are unattacked, so that the conversion of the base into the ionic form shields it from decomposition by dinitrogen tetroxide. We are led to the conclusion that the dinitrogen tetroxide molecule may undergo dissociation in two ways during reaction, giving either  $(\text{NO}^+ + \text{NO}_3^-)$  or  $(\text{NO}_2^+ + \text{NO}_2^-)$ , and that the particular course followed depends upon whether the reacting groups are charged ions or covalent, uncharged molecules. It is not our desire here to support any particular structure for the dinitrogen tetroxide molecule; but our work on ionic reactions has shown that the molecule should be capable of dissociation into  $\text{NO}^+$  and  $\text{NO}_3^-$  units as a result of simple electron transfer processes. Ingold<sup>5</sup> considers that the results of Levy and Scaife<sup>4</sup> provide additional and conclusive proof of structure (I).



Ionic dissociation of this molecule (equation 1) would involve the breaking of the N-O bond and transfer of the oxygen atom, whereas ionization of molecule (II) postulated by Longuet-Higgins<sup>6</sup> would involve

no atom transfer, while at the same time satisfying physical evidence regarding symmetry<sup>7</sup>.

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<sup>1</sup> *J. Chem. Soc.*, 1356 (1901).

<sup>2</sup> Angus and Leckie, *Trans. Farad. Soc.*, **31**, 958 (1935).

<sup>3</sup> Klinkenberg, *Chem. Weekblad*, **35**, 197 (1938).

<sup>4</sup> *J. Chem. Soc.*, 1093 (1946).

<sup>5</sup> *Nature*, **159**, 743 (1947).

<sup>6</sup> *Nature*, **153**, 408 (1944).

<sup>7</sup> Sutherland, *Proc. Roy. Soc., A*, **141**, 342 (1933).

## A General Solution for the Force Constants of Polyatomic Molecules

It is well known that the fundamental vibration frequencies of polyatomic molecules can be predicted with an error of only 1 or 2 per cent by solving the secular equation with force constants obtained from related molecules<sup>1</sup>. The reverse process of solving for the constants in terms of the frequencies is, in general, impossible unless some special assumptions are made concerning the force field<sup>2</sup>. The following general solution is therefore of some interest.

The  $n$ th order secular equation can be written in matrix form as follows:

$$|dA - \lambda I| = 0. \quad (1)$$

The elements of  $d$  are the force constants  $d_{ij}$  in the general potential function:

$$2V = \sum_{i=1}^n \sum_{j=1}^n d_{ij} \Delta_i \Delta_j. \quad (2)$$

The  $\Delta_i$  are valence-type co-ordinates, expressed in terms of  $N$  further co-ordinates  $z_j$ :

$$\Delta_i = \sum_{j=1}^N a_{ij} z_j, \quad (3)$$

all possessing any required symmetry properties, and the elements of  $A$  (related to the inverse kinetic energy matrix  $G$  used by Wilson<sup>3</sup>), are defined as follows:

$$A_{ij} = A_{ji} = \sum_{k=1}^N a_{ik} a_{jk} \frac{M}{m_k}, \quad (4)$$

$m_k$  being the mass for the co-ordinate  $z_k$  and  $M$  some arbitrary mass, introduced in order that the  $A_{ij}$  shall be pure numbers.  $I$  is the unit matrix, and the quantity  $\lambda$  is defined as follows:

$$\lambda = 4\pi^2 \nu^2 c^2 M, \quad (5)$$

$\nu$  being the frequency of vibration in  $\text{cm}^{-1}$  and  $c$  the velocity of light in  $\text{cm. sec}^{-1}$ . The  $(N-n)$  null vibrations factorize out, giving (1). If the subscripts are ordered so that  $\Delta_i$  is the approximate normal co-ordinate for  $\nu_i$ , corresponding to the vibrational assignment, and if  $\nu_1 > \nu_2 > \dots > \nu_n$ , then the proposed general solution for the constants is obtained by equating to zero all elements below the diagonal of the determinant (1), thus reducing it to the product of  $n$  linear factors, and substituting  $\lambda_1$  to  $\lambda_n$  in order in the  $n$  diagonal elements; that is:

$$\left. \begin{aligned} \sum_{i=1}^n A_{ki} d_{ki} - \lambda_k &= 0, (k = 1, 2 \dots n). \\ \sum_{i=1}^n A_{qi} d_{pi} &= 0, (p > q). \end{aligned} \right\} \quad (6)$$

The corresponding (unnormalized) normal co-ordinates are given by:

$$z_i^{\nu_k} = \sum_{j=1}^k a_{ji} \frac{M}{m_i} k |A|_{kj} \quad (7)$$

$$\Delta_p^{\nu_k} = \sum_{j=1}^k A_{pj} k |A|_{kj}, (= 0 \text{ for } p < k). \quad (8)$$

where  $k |A|_{kj}$  are first minors of the  $k$ th order determinant formed from the first  $k$  rows and columns of the matrix  $A$ . The normal co-ordinate for  $\nu_i$  involves only the co-ordinates  $\Delta_i$  to  $\Delta_n$ ; the method, in effect, factorizes out the frequencies in descending order, the molecule increasing in rigidity as factorization proceeds. If only the constants for the  $m$  lowest frequencies are required, only elements in the last  $m$  rows of (1) need be considered, without introducing any fresh approximation.

The above solution is found to give surprisingly good results with actual examples, and is easy to apply. For molecules in which all the fundamentals fall into the category of 'group vibrations', factorization of the secular equation will clearly give a close approximation; where  $(\nu_i - \nu_{i+1})$  is small and  $\Delta_i$  and  $\Delta_{i+1}$  overlap, the approximation will not be so close, since the normal co-ordinate for  $\nu_{i+1}$  would then certainly involve  $\Delta_i$ ; but only the constants  $d_{ii}$ ,  $d_{i(i+1)}$  and  $d_{(i+1)(i+1)}$  will be much affected. The constants obtained in (6) are always real, and the normal co-ordinates defined in (7) and (8) correspond to the vibrations having idealized geometrical forms; thus, in valence vibrations the atomic displacement vectors lie directly along the appropriate valence bonds. Interactions which would normally be discarded are here generally found to be negligibly small; their retention gives the unambiguous solution.

The method can obviously be adapted to predict vibration frequencies, by substituting constants only in the diagonal elements of (1); the inconsistency in the force field can then be estimated by evaluating terms below the diagonal.

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<sup>1</sup> Crawford and Brinkley, *J. Chem. Phys.*, **9**, 69 (1941). See also Pitzer and others, *J. Res. Nat. Bur. Stand.*, **33**, 1, 191 (1947).

<sup>2</sup> Glockler and Tung, *J. Chem. Phys.*, **13**, 388 (1945).

<sup>3</sup> Wilson, *J. Chem. Phys.*, **7**, 1047 (1939); **9**, 76 (1941).

## Study of the Action of Ultra-violet Light on Urease by Means of the Ultracentrifuge

THE action of ultra-violet light on serum albumin has been studied with the ultracentrifuge by Svedberg and Brohult<sup>1</sup> and by Sanigar, Krejci, and Kraemer<sup>2</sup>. Irradiation of serum albumin at room temperature and at 0°C. causes the formation of low-molecular substances and a general inhomogenization of the protein.

It seemed worth while to perform a similar experiment with a protein having enzymatic activity in order to see if inhomogenization accompanies loss of activity, or is a process resulting from the absorption of quanta beyond those required on the average for inactivation. For irradiation, monochromatic light of 2537 Å. was used, at which a quantum yield of inactivation of 0.000926 has been found<sup>3</sup>. Inactiva-