350. *The Structure and Reactions of Dinitrogen Tetroxide.**

By Zoltán G. Szabó, Lajos G. Bartha, and Béla Lakatos.

A study of the reaction between dinitrogen tetroxide and iodide ions as a function of the iodide-ion concentration, temperature, and pressure shows that, in addition to the symmetrical $O_2N{\cdot}NO_2$ and its monomer, a tetroxide of another structure is present. Structural, kinetic, and energetic considerations unequivocally show that this tetroxide is the ring molecule suggested by Longuet-Higgins. The results include evidence that an equilibrium occurs between the three types of molecule (see Scheme A).

The other structure which may play a role in the formation of the tetroxide (II), *viz.*, nitrosonium nitrate, can be regarded only as an intermediate state. From the Longuet-Higgins molecule nitrosonium and nitrate ions can be formed *via* the nitrosonium nitrate (see Scheme B, p. 1793).

On the other hand, on interaction of NO^+ and NO_3^- ions nitrosonium nitrate is formed and ring closure gives the Longuet-Higgins molecule.

Concerning the kinetics of the reaction it has been concluded that the nitrogen dioxide dissociated from the tetroxide (I) determines the velocity of the transformation in the following two steps :

$$NO_2 + N_2O_4 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ONO_2{\cdot}NO + NO_2;\ NO_2 + I^- \xrightarrow{k_2} NO_2^- + \tfrac{1}{2}I_2$$

The former reaction shows the tetroxide molecule (II) to be formed *via* the intermediate (III) which dissociates as shown (p. 1790). The high concentration of the tetroxide (II) (31% at 0°) favours the formation of Longuet-Higgins's type of molecule again rather than of nitrosonium nitrate, as no appreciable dipole moment can be detected.

The consistent interpretation of experimental data obtained for the physical and chemical properties of dinitrogen tetroxide was rendered extremely difficult by the discrepancy between the symmetrical structure (I) established on the basis of physical measurements [1] and the conclusions drawn from chemical reactions,[2] according to which the structure of dinitrogen tetroxide can only be one from which the ions NO^+ and NO_3^-, on the one hand, and NO_2^+ and NO_2^-, on the other, can be simultaneously derived.

In order to reconcile the physical and chemical properties of dinitrogen tetroxide, Addison and Lewis [1c] and also Seel *et al.*[2c] assumed an equilibrium between the symmetrical

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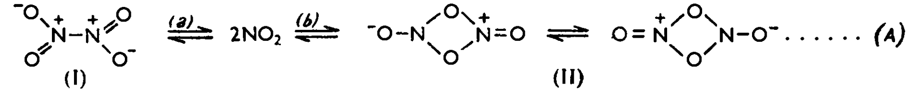
* Read, in abstract, at the First Hungarian Physicochemical Meeting, Szeged, 1954; cf. *Magyar Kém. Folyóirat*, 1955, **61**, 161.

[1] Röntgen spectra : Broadly and Robertson, *Nature*, 1949, **164**, 915. Infrared and Raman spectra : *e.g.*, (*a*) Sutherland, *Proc. Roy. Soc.*, 1933, *A*, **141**, 342; Harris and King, *J. Chem. Phys.*, 1934, **2**, 51, 321 ; (*b*) Perkins and Wilson, *Phys. Rev.*, 1952, **85**, 755. Dipole moment : *e.g.*, (*c*) Addison and Lewis, *J.*, 1953, 1869. Specific heat : (*d*) Giauque and Kemp, *J. Chem. Phys.*, 1938, **6**, 40. Specific conductivity; (*e*) Addison, Allen, Bolton, and Lewis, *J.*, 1951, 1289.

[2] With metals : *e.g.*, (*a*) Addison *et al.*, *J.*, 1949, S211, and subsequent papers. With halides : (*b*) Seel *et al.*, *Z. anorg. Chem.*, 1950, **261**, 75, and subsequent papers. With azides : (*c*) Seel, Nógrádi, and Breit, *ibid.*, 1952, **269**, 102. Hydrolysis and alcoholysis : *e.g.*, (*d*) Denbigh and Prince, *J.*, 1947, 790; Yoffe and Gray, *J.*, 1951, 1412. With metal oxides, hydroxides, and carbonates : *e.g.*, (*e*) Addison and Lewis, *J.*, 1953, 1319, 1874. With olefins : (*f*) Levy and Scaife, *J.*, 1946, 1093; 1948, 52. Formation of N_2O_4 from nitrosonium and nitronium salts : *e.g.*, Seel, *loc. cit.*; (*g*) Exner, *J.*, 1872, 1072. Electrolysis in presence of ionic partner : (*h*) Angus, Jones, and Phillips, *Nature*, 1949, **164**, 433. (*i*) With labelled alkylammonium nitrates : Clusius and Vecchi, *Helv. Chim. Acta*, 1953, **36**, 930.

tetroxide favoured by physical methods, the ring structure proposed by Longuet-Higgins,[3] and nitrosyl nitrate.[4]

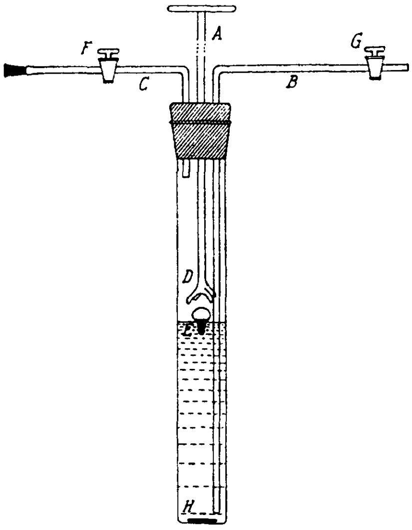
During the present investigations direct experimental evidence has been found for the existence of such equilibrium for the liquid dinitrogen tetroxide :



(I) (II) ...... (A)

On the basis of kinetic measurements we conclude that tetroxide (II) arises through the intermediate nitrosonium nitrate and may be identified with the structure suggested by Longuet-Higgins. The dependence of the reaction between dinitrogen tetroxide and iodide ions in aqueous solution on iodide-ion concentration, temperature, and pressure has been examined, it being thought that the foregoing equilibrium, if real, would be very sensitive to such variations. Indeed, depending on the parameters referred to above, various amounts of nitrate, nitrite, iodine, and nitric oxide have been determined.

FIG. 1.



EXPERIMENTAL

Apparatus and Technique.—The reaction vessel was a 40 × 4 cm. glass tube (Fig. 1), the open end of which was closed by a three-bored rubber plug after it had been filled with the required quantities of reactants. In the middle bore of the plug a glass rod (*A*) was inserted, the lower end of which terminated in four claw-like points (*D*). This rod served for breaking the phial (*E*) containing the dinitrogen tetroxide. The claws pushed the phial forward, preventing it from emerging over the liquid surface. The two outside bores were used for inserting glass tubes each fitted with a tap. Tube *B*, by means of which nitrogen was previously passed through the system, reached to the bottom of the reaction vessel. Tube *C*, reaching about 1 cm. into the vessel, was employed for collecting the nitric oxide evolved after the reaction was over.

Klemenc and Rupp's method[5] was used for preparing dinitrogen tetroxide, the liquid being distilled into glass globes of about 1·5 cm. diameter, which were then sealed.

The reaction vessel, containing 250 ml. of potassium iodide solution of a chosen concentration,* and equipped with the phial containing the tetroxide, was placed in a bath at the required temperature, and then nitrogen was passed through the system for 2 hr. After simultaneous closure of taps *F* and *G*, the tube used for introducing nitrogen was drawn up above the liquid surface. After this, with constant stirring, the phial with the dinitrogen tetroxide was broken by rapidly pushing down the glass rod. Stirring was effected by a small electromagnetic stirrer *H*.

When reaction was complete, the iodine, nitrate, nitrite, and nitric oxide contents of the mixtures were determined.

After the tube *C* had been attached by means of ground joints to ½ l. gas-analytical test-tubes,[6] previously evacuated, the nitric oxide was collected by opening tap *F*. Then 3% hydrogen peroxide solution was poured into the 3 or 4 test-tubes containing nitric oxide to oxidize it to nitric acid, which was determined alkalimetrically.[7]

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* The concentration of potassium iodide solution is throughout given in g. per 100 ml. of solution.

[3] Longuet-Higgins, *Nature*, 1947, **159**, 743.
[4] Addison, Lewis, and Thompson, *J.*, 1951, 2838.
[5] Klemenc and Rupp, *Z. anorg. Chem.*, 1930, **104**, 51.
[6] Szabó, *Z. analyt. Chem.*, 1943, **126**, 219.
[7] Moser, *ibid.*, 1911, **50**, 428; Szabó and Bartha, *Analyt. Chim. Acta*, 1952, **6**, 416.

Iodine was determined by titration with sodium thiosulphate.

Nitrate and nitrite were determined by decomposing the nitrite in a portion of the solution by boiling diluted sulphuric acid, and then the nitrate remaining unchanged was determined. In another sample the contents of both were determined together. In the two determinations both the nitrate and the nitrite were reduced to ammonia by ferrous hydroxide in the presence of copper as catalyst, and the ammonia was distilled into standard acid.[7a]

Reaction between Dinitrogen Tetroxide and Iodide Ion.—Dodé [8] and Seel *et al.*[2b] have discussed the reaction between dinitrogen tetroxide and iodide ions in detail. The reaction leads to formation of nitrite, nitrate, nitric oxide, and iodine, according to the two principal processes :

$$N_2O_4 + 2I^- \longrightarrow 2NO_2^- + I_2 \qquad (1)$$

$$N_2O_4 + I^- \longrightarrow NO_3^- + NO + \tfrac{1}{2}I_2 \qquad (2)$$

From the two studies it became evident that during and after these two principal reactions, other processes occur. Nitric oxide, liberated according to (2), reacts with unchanged dinitrogen tetroxide to give dinitrogen trioxide :

$$2NO + N_2O_4 \longrightarrow 2N_2O_3 \qquad (3)$$

Further, the iodine and the nitrite react thus : [9]

$$2NO_2^- + \tfrac{1}{2}I_2 \rightleftharpoons NO_3^- + NO + I^- \qquad (4)$$

and this reaction competes with the tri-iodide equilibrium (5) for the iodine :

$$I^- + I_2 \rightleftharpoons I_3^- \qquad (5)$$

Dodé [8] considered reaction (2) to proceed, not directly, but through hydrolysis :

$$N_2O_4 + H_2O = HNO_3 + HNO_2 \qquad (6)$$

$$HNO_3 + HNO_2 + KI = KNO_3 + NO + \tfrac{1}{2}I_2 + H_2O \qquad (7)$$

and, in addition, he assumed that the nitrous acid formed during hydrolysis, before further reacting, undergoes partial disproportionation :

$$3HNO_2 = HNO_3 + 2NO + H_2O \qquad (8)$$

In this process, however, the possibility of hydrolysis must be excluded for, according to our investigations [10] and those of Denbigh and Prince,[2d] this hydrolysis is much too slow to be of significance here. The great difference between these two rates of reaction has already been mentioned by Prahl and Raschig,[11] and, moreover, in discussing an analogous reaction involving the NO_2–NO mixture and alkaline potassium iodide, they proved that hydrolysis does not play any role in the process. Our investigations on the dependence of hydrolysis on temperature and pressure [10] also undoubtedly prove these relationships. According to our further experimental evidence, hydrolysis occurs only if 1 mole of the tetroxide reacts with less than 1 g.-ion of the iodide.

Finally, under the same experimental conditions, *i.e.*, with minute iodide concentration, the nitrite formed in reaction (1) is oxidized by the excess of dinitrogen tetroxide to nitrate : [9]

$$N_2O_4 + 2NO_2^- \longrightarrow 2NO_3^- + 2NO \qquad (9)$$

This side reaction of the tetroxide has also been studied in a separate series of experiments. In a concentrated solution of alkali nitrite, dinitrogen tetroxide was caused to react by the same technique as for the iodide reaction. The gases evolved were absorbed by sodium hydroxide in which, besides nitrite, only an excess of nitric oxide was found. On increase of temperature, the concentration of the nitrite formed increases linearly while the quantity of nitric oxide diminishes.

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[8] Dodé, *Bull. Soc. chim. France*, 1942, **9**, 449, 461.

[9] Seel *et al.*, ref. 2*b*.

[10] Szabó, Bartha, and Lakatos, *Acta Chim. Acad. Sci. Hung.*, in the press.

[11] Prahl and Raschig, *Z. angew. Chem.*, 1929, **42**, 253.

The possible reactions are as follows :

$$N_2O_4 + NO_2^- \longrightarrow NO_3^- + N_2O_3 \quad \ldots\ldots \quad (9a)$$

$$NO_2 + NO_2^- \longrightarrow NO_3^- + NO \quad \ldots\ldots \quad (9b)$$

$$NO_2 + NO \rightleftharpoons N_2O_3 \quad \ldots\ldots \quad (9c)$$

It must be assumed that, at a higher temperature, reaction (9*b*) prevails over (9*a*). However, the excess of nitric oxide can be considered as a result of reaction (9*b*) only if reaction between the nitrite and the nitrogen dioxide proceeds more rapidly than reaction (9*c*), but that is against all available evidence. In order to interpret the excess of nitric oxide, therefore, besides the above three processes, further reactions must be assumed which may lead to formation of nitric oxide. Disproportionation of nitrous acid, formed by hydrolysis of the tetroxide,[8] may be considered as such a process; *i.e.*, the rate of hydrolysis decreases with rising temperature, and, accordingly, the amount of nitric oxide resulting from disproportionation of the nitrous acid will do so, too. Hence, at a higher temperature, the excess of nitric oxide is smaller. Now it follows from the foregoing that, with nitrite ions present, hydrolysis of the tetroxide would be comparable with, or even more rapid than, the oxidation of nitrite. On the other hand, from this it necessarily follows also that, since reaction with the iodide proceeds by orders of magnitude more rapidly than the hydrolysis, the rate of reaction between the tetroxide and iodide ions is much higher than that between the tetroxide and nitrite.

On the basis of these experiments it is obvious that under the above conditions oxidation of the nitrite ions by the tetroxide cannot take place. In addition, however, a more rigid proof can be made based on the above experiments, namely, that, in reaction between the tetroxide and the iodide, the nitrate arises from a primary reaction and not through a secondary oxidation of the nitrite formed likewise in a primary step.

Obviously, all these reactions exert a greater or smaller influence on the ratio of nitrate to nitrite produced in the two principal reactions. Hence, to draw any concrete conclusion from this ratio on the influence of iodide-ion concentration, temperature, and pressure, all the side reactions must be eliminated or minimized. This was effected by suitable choice of experimental method and conditions. With the present technique the whole of the dinitrogen tetroxide undergoes reaction with the iodide ions, and the relatively good reproducibility of our results shows that side reactions have been suppressed. All runs were done in duplicate or triplicate and the reproducibility was within ±2%.

Results

Effect of Iodide-ion Concentration.—These experiments were carried out at 0°. The results (Table 1 and Fig. 2) show that, other conditions being unchanged, with rising iodide-ion concentration the quantity of the nitrate produced diminishes, and that of the nitrite increases.

TABLE 1. *Effect of iodide-ion concentration.* (Temp. 0°.)

		N_2O_4 (%) converted into :			
KI (%)	N_2O_4 (g.) taken	NO_2^-	NO_3^-	NO	Total (%)*
10	0·2958	24·2	77·8	76·0	101·1
	0·2731	22·8	77·0	75·6	99·1
	0·2683	24·4	76·0	76·4	100·6
25	0·2883	38·9	61·0	58·8	99·3
	0·3418	41·0	60·2	60·6	101·4
50	0·3121	56·4	43·6	44·8	100·6
	0·2950	57·9	42·0	43·8	100·8
65	0·3240	62·7	37·2	36·6	99·6
85	0·3103	68·9	31·0	31·6	100·2
	0·1818	68·8	30·6	31·4	99·8
93	0·3116	69·3	30·2	30·0	99·4
	0·1437	69·1	30·4	31·0	99·8

* The totals are based on the nitrite plus the mean of the nitrate and nitric oxide.

Effect of Temperature (see Table 2).—These experiments were carried out in 10, 25, 35, and 50% solutions of potassium iodide, covering a temperature range 0—60°. With 10% potassium iodide, between 0° and 10°, the quantity of nitrate increases rapidly, at about 10° it passes through a maximum, then decreases gradually. The nitrite produced varies inversely, showing a minimum at 10° (Fig. 3, Curve *A*).

With 25% potassium iodide solution the results (Fig. 3, Curve *B*) are similar, but the maximum and the minimum both appear at about 15° and are somewhat lower than those obtained for the 10% solution.

With 35% potassium iodide (Fig. 3, Curve *C*), at first, the variation of nitrate is the same as it is subsequently after the maximum. From 10° upwards, the quantity of nitrate increases. The maximum, found at about 15°, is considerably lower than that mentioned above. The amounts of nitrite vary in the reverse direction throughout.

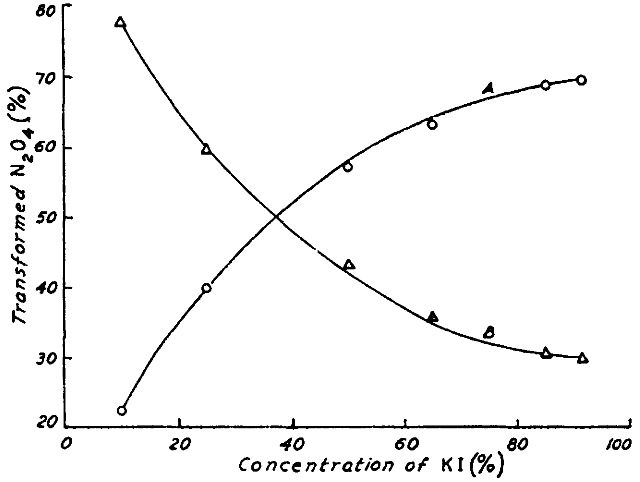


FIG. 2.
N_2O_4 (%) *converted into* (*A*) *nitrite and* (*B*) *nitrate.*

TABLE 2. *Effect of temperature.*

Temp.	N_2O_4 taken (g.)	N_2O_4 (%) converted into : NO_2^-	NO_3^-	NO	Total (%) *	Temp.	N_2O_4 taken (g.)	N_2O_4 (%) converted into : NO_2^-	NO_3^-	NO	Total (%) *
(*a*) 10% KI Solution.											
0°	0·2958	24·2	77·8	76·0	101·1	20°	0·2943	30·0	70·8	70·4	100·6
	0·2731	22·8	77·0	75·6	99·1		0·3340	29·2	70·0	70·4	99·4
	0·2683	24·4	76·0	76·4	100·6	40	0·2858	43·2	56·4	55·6	99·2
5	0·3181	21·2	78·8	79·6	100·4		0·3216	44·2	56·0	57·2	100·8
	0·3347	21·0	79·6	79·8	100·7	60	0·3098	52·2	48·0	49·2	100·8
10	0·3446	17·1	83·8	83·2	100·6		0·3323	51·7	48·6	48·4	100·2
	0·3147	17·9	83·0	82·8	100·8						
15	0·3374	25·3	75·0	72·6	99·4						
	0·2864	25·6	75·6	74·2	100·6						
(*b*) 25% KI Solution.											
0	0·7653	34·8	65·6	66·6	100·9	20	0·7692	33·1	67·0	67·8	100·5
	0·7664	35·2	64·0	65·4	99·9		0·7987	33·6	66·4	67·6	100·6
5	0·8343	35·9	63·8	62·8	99·2	40	0·7560	45·6	54·4	53·0	99·3
	0·8002	34·7	63·2	65·0	98·8		0·8361	46·5	55·4	54·0	101·2
10	0·7790	35·4	64·0	64·4	99·6	60	0·7709	55·0	45·4	45·6	100·5
	0·8158	34·5	65·2	65·4	99·8		0·7256	55·5	44·8	44·0	99·9
15	0·8121	29·8	70·2	71·4	100·6						
	0·8348	29·0	69·6	70·4	99·0						
(*c*) 35% KI Solution.											
0	0·7380	42·0	58·4	59·4	100·9	15	0·6094	49·9	50·6	51·0	100·7
5	0·6298	46·4	53·2	54·6	100·3	20	0·6741	51·6	48·2	47·6	99·5
10	0·6248	52·4	47·6	47·0	99·7	25	0·7106	55·9	43·0	44·8	99·8
(*d*) 50% KI Solution.											
0	0·9934	47·4	52·4	54·4	100·8	25	1·0283	59·5	40·0	39·6	99·3
	1·0245	46·2	53·2	55·8	100·7		0·9828	60·1	39·4	40·8	100·2
10	0·9352	50·7	49·2	49·8	100·2	40	0·9350	67·0	33·2	34·2	100·7
	0·9757	50·6	49·4	48·2	99·4		0·8766	68·9	31·4	31·8	100·5
15	0·9206	53·0	47·2	45·8	99·5	60	0·9213	72·5	27·6	25·8	99·2
	0·9616	53·7	46·2	45·6	99·6		0·9042	72·7	27·2	26·8	99·7
20	1·0357	57·2	42·6	43·2	100·1						
	0·9416	57·9	42·0	41·8	99·8						

* See footnote to Table 1.

The results with 50% potassium iodide solution are quite different (Fig. 3, Curve *D*). With rising temperature, the percentage of dinitrogen tetroxide converted into nitrite increases uniformly, while that of the nitrate diminishes, and no maximum (or minimum) is found.

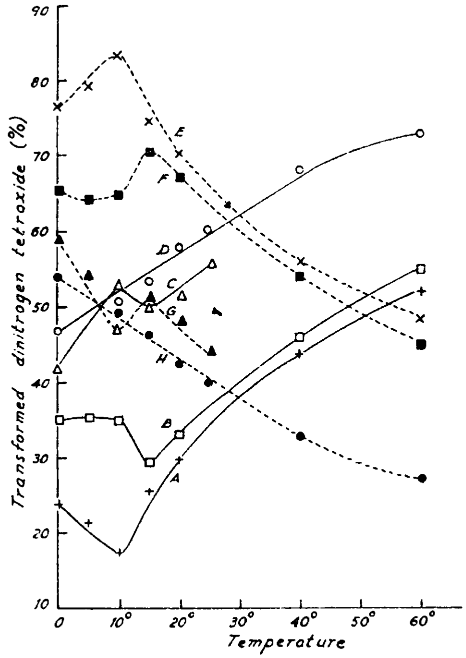


Fig. 3. *Transformation products of* N_2O_4 *in* KI *solution.*

Concn. (%) *of* KI *soln.*	10	25	35	50
Nitrite, curve	*A*	*B*	*C*	*D*
Nitrate, curve	*E*	*F*	*G*	*H*

Effect of Pressure.—Some experiments were carried out at a pressure corresponding to the vapour tension of the potassium iodide solution : the reaction changed in type, the nitrite becoming the principal product (see Table 3).

Table 3. *Effect of pressure.* (*Experiments in* 25% KI *solution*; *temp.* 0°.)

	N_2O_4 (%) converted into :			Total		N_2O_4 (%) converted into :			Total
Pressure	NO_2^-	NO_3^-	NO	(%)	Pressure	NO_2^-	NO_3^-	NO	(%)
1 Atm.	34·8	65·6	66·6	100·9	V. p. of KI soln.	89·7	10·2	10·2	99·9
	35·2	64·0	65·7	99·9		90·6	9·6	10·4	100·6

The experimental observation that, other conditions being unchanged, with increasing quantity of dinitrogen tetroxide, the amount of nitrate produced increases while that of the nitrite diminishes, may be attributed to the effect of pressure. With smaller concentrations of tetroxide the opposite course is observed. Accordingly, we have endeavoured to take nearly the same amount of tetroxide into reaction in each experimental run.

DISCUSSION

Equilibrium between Dinitrogen Tetroxide and Nitrogen Dioxide.—The experiments summarized above may be interpreted as follows.

It is only the nitrogen dioxide radicals, and the tetroxide (II), or rather the nitrosonium and nitrate ions split off from this molecule, that are involved in the reaction with the iodide ions. Reaction (1) (p. 1786) proceeds with the nitrogen dioxide radicals :

$$NO_2 + I^- \longrightarrow NO_2^- + \tfrac{1}{2}I_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1a)$$

Reaction (2) really involves nitrosonium ions :

$$NO^+ + I^- \longrightarrow NO + \tfrac{1}{2}I_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2a)$$

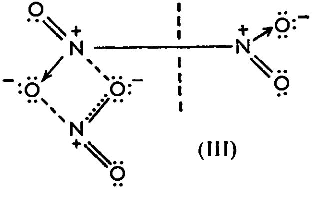
The effect of iodide-ion concentration therefore may be explained as follows. At first, both the nitrogen dioxide and the ions produced from the tetroxide (II) react with the iodide ions. Thereafter, the dinitrogen tetroxide of structure (I) (which cannot react directly), dissociates to replenish the reactive species. However, the increase of iodide-ion concentration results in a steadily diminishing possibility of establishment of equilibrium (*b*) (see p. 1785) as well as in the steadily decreasing amount of nitrogen dioxide capable of becoming tetroxide (II), owing to the preferential reaction with the iodide ions. With lower iodide-ion concentration, more nitrogen dioxide molecules can be transformed into tetroxide (II), so reaction (2*a*) asserts itself more intensely. A high iodide-ion concentration, therefore, facilitates formation of nitrite and, conversely, a low one favours production of nitrate.

The establishment of equilibria is indicated also by the effect of temperature on the concentrations of the end-products. For 10, 25, and 35% potassium iodide the results were as expected. Those for 10% potassium iodide were of particular interest: on increase of temperature, the quantity of nitrate at first increased rapidly; with increasing nitrogen dioxide concentration, more and more nitrogen dioxide was converted into dinitrogen tetroxide of structure (II). The percentage, however, of the dinitrogen tetroxide transformed into nitrate diminished after having reached a maximum; at higher temperatures, tetroxide (II) partly decomposed to nitrogen dioxide again, fewer and fewer molecules breaking up into ions, *i.e.*, into components involved in the " nitrate " reaction.

With 50% potassium iodide, however, the reaction proceeds differently. On rise of temperature, increasing amounts of nitrogen dioxide arise from structure (I), but establishment of equilibrium (*b*) is limited for the same reason as is given for the effect of iodide-ion concentration. Owing to the extremely high iodide-ion concentration, most of the nitrogen dioxide undergoes reaction with the iodide ions rather than conversion into tetroxide (II), so there is no maximum value of nitrate. To a smaller extent, the similar limiting role of the iodide-ion concentration is manifested in the experiments with 25 and 35% potassium iodide, as shown by the constancy (in 25% potassium iodide) or decrease (in 35% solution) of dinitrogen tetroxide converted into nitrate before it can reach its maximal value. Results obtained for 35% solution particularly illustrate the opposing effects of the two rival factors, (i) iodide-ion concentration and (ii) temperature, on the concentration of structure (II): the quantity of nitrate, after an initial decrease, increases again to reach a maximum, thus showing the superiority of (ii). For a 50% solution, there is no trace of such a maximum.

The results of pressure variation are also consistent. On decrease of pressure, the equilibrium N_2O_4 (I) $\rightleftharpoons 2NO_2 \rightleftharpoons$ N_2O_4 (II) undergoes a shift in favour of the nitrogen dioxide, so the concentration of the N_2O_4 (II) yielding the ions decreases, the " nitrate " reaction being inferior to the " nitrite " reaction.

Mechanism of Reaction : Kinetic Considerations.—It is only the nitrogen dioxide radicals and the tetroxide (II), or rather the nitrosonium and nitrate ions split off from the latter, that are involved in the reaction. The velocity of the whole transformation is determined by the following two reactions of the nitrogen dioxide: (i) in one a portion reacts with the iodide ions, (ii) in the other it is converted into tetroxide (II) to react further, after dissociating into ions.


(III)

The data now recorded are consistent with the consideration that the nitrogen dioxide radicals thermally dissociated from the tetroxide react, not with one another, but with an undissociated tetroxide to form the intermediate (III) by what may be regarded as bimolecular gas reaction (10). Owing to the fact that neither the tetroxide (I) nor the nitrogen dioxide * reacts with water, to a first approximation water may be considered as an indifferent medium but, since the reaction is between polarized systems, the action of water may be merely one of physical catalysis. The

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* According to Denbigh and Prince's experiments,[2d] the hydrolysis of tetroxide is slower at 40° than at 25°. This fact, as well as the authors' studies on the hydrolysis of tetroxide, suggest that the nitrogen dioxide fails to undergo hydrolysis.

decomposition of the intermediate (III) yields the tetroxide (II), as shown. On the basis of this consideration, therefore, the mechanism of the two reactions of nitrogen dioxide is as follows :

$$NO_2 + N_2O_4 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ONO_2{\cdot}NO + NO_2 \quad . \; . \; . \; . \; . \quad (10)$$

$$NO_2 + I^- \xrightarrow{k_2} NO_2^- + \tfrac{1}{2}I_2 \quad . \; . \; . \; . \; . \; . \; . \; . \quad (1a)$$

Whence $\mathrm{d}y/\mathrm{d}t = k_1[N_2O_4][NO_2]$ and $\mathrm{d}x/\mathrm{d}t = k_2[NO_2][I^-]$

where $[NO_3^-] = y$ and $[NO_2^-] = x$

Putting $[N_2O_4] = [N_2O_4]_o - \tfrac{1}{2}[NO_2^-] - [NO_3^-] = a - \tfrac{1}{2}x - y$

and $[I^-] = [I^-]_o - [NO_2^-] - [NO_3^-] = b - x - y$

we have, on division of $\mathrm{d}y/\mathrm{d}t$ by $\mathrm{d}x/\mathrm{d}t$:

$$\mathrm{d}y/\mathrm{d}x = k_1(a - \tfrac{1}{2}x - y)/k_2(b - x - y)$$

As the iodide-ion concentration is virtually constant during any one run, this equation can be reduced to :

$$\mathrm{d}y/\mathrm{d}x = k_1[N_2O_4]/k_2[I^-] = k_1(a - \tfrac{1}{2}x - y)/k_2[I^-]_o$$

Solution of this equation, with $y_{x=0} = 0$, gives

$$y = (a + 1/2A)(1 - e^{-Ax}) - x/2$$

where $A = k_1/k_2b = \kappa/b$ and $\kappa = k_1/k_2$ (*i.e.*, $\kappa = Ab$)

If the initial iodide-ion concentration is high, then, since $A \ll 1$, e^{-Ax} can be put equal to $1 - Ax$, giving $y \simeq aAx$, whence $\kappa = by/ax$. The κ values thus calculated are summarized in col. 4 of Table 4, which also gives the values from Table 1 in terms of molar concentrations.

TABLE 4.

Concns. (10^{-3} moles/l.)						
$N_2O_4 = a$	$NO_2^- = x$	$NO_3^- = y$	$\frac{by}{ax} = \kappa$	$\frac{by}{x}$	$\frac{x}{y}$	$[I^-] = b$ (moles/l.)
3·215	1·556	2·502	301·3	0·969	0·622	0·602
2·968	1·354	2·286	342·6	1·017	0·592	
2·916	1·424	2·216	321·5	0·937	0·643	
3·133	2·438	1·912	377·0	1·181	1·275	1·506
3·715	3·046	2·236	297·6	1·105	1·362	
3·392	3·826	1·478	343·0	1·163	2·589	3·012
3·206	3·712	1·346	340·6	1·092	2·758	
3·521	4·416	1·314	330·9	1·165	3·361	3·915
1·976	2·738	0·600	567·8	1·122	4·437	5·120
3·372	4·666	1·030	335·2	1·130	4·498	
3·386	4·668	1·052	372·9	1·262	4·563	5·602
1·562	2·150	0·478	797·3	1·245	4·530	

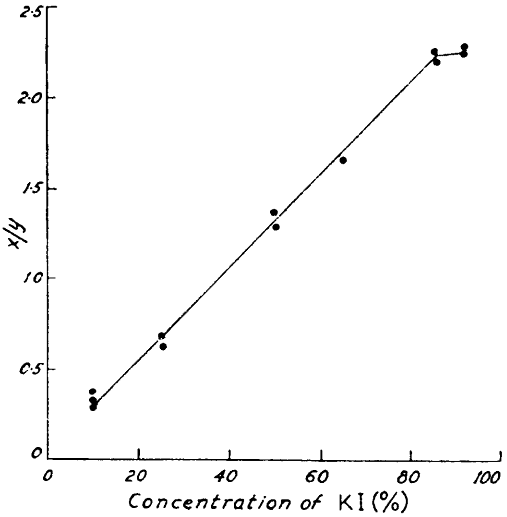
The values of *by*/*ax* are nearly constant if the quantity of tetroxide *a* is nearly the same. It follows from the experimental method that, because of the large excess of iodide ions, the concentration of tetroxide is independent of the quantity of N_2O_4 used, for more tetroxide reacts in a larger volume. Therefore, the tetroxide concentration may be regarded as being constant and can be introduced into κ. So the values k_1/k_2 are constant. On the basis of this consideration, therefore, the quotient x/y should be a linear function of the iodide ion-concentration, and this is proved by the results (see Fig. 4; for break in the curve, see below).

No conclusion could be drawn as to the dependence of the reaction upon temperature. Values of log κ plotted against $1/T$ did not give a straight line. This fact suggests that κ

represents, not only the quotient k_1/k_2, but also a term depending on the rate constants of other processes. Since, if the dioxide–tetroxide (II) transformation controlled the rate, the log κ–$1/T$ should be linear, it is clear that another process takes part in the measured reaction velocity. This divergence may be interpreted by the assumption that, during the reaction, not an equilibrium but a stationary state is involved, so that the rate of dioxide–tetroxide (II) transformation as well as that of the dioxide–iodide reaction is greater than, or at least equal to, the tetroxide–dioxide dissociation rate. This means that the activation energy of the processes consuming dioxide cannot be larger than 11 kcal., *i.e.*, the energy of activation of the reaction $N_2O_4 \longrightarrow 2NO_2$.[12]

By assuming this stationary state, the results can be reinterpreted. Increase of temperature gives rise to an increase in dioxide concentration, and, therefore, also the reaction $NO_2 + O_2N{\cdot}NO_2 \longrightarrow ONO_2{\cdot}NO + NO_2$ yields more tetroxide (II) and the amount of nitrate increases. Above a certain temperature, however, the nitrogen dioxide–iodide ion reaction becomes faster than the rate of formation of tetroxide (II). Thereafter the quantity of nitrate decreases steadily.

FIG. 4.



The reaction between tetroxide (II) and iodide ions was assumed to be very rapid, being faster than that between dioxide and iodide ions. A number of analogous reactions, *e.g.*, between potassium iodide and chlorine[13] or chlorine dioxide,[14] as well as the fact that these processes do not take place with perfectly dry potassium iodide, indicate that the electron transfer can only take place after the polarization of the electron system of the dioxide molecule. On the other hand, the reaction between the Longuet-Higgins structure and the iodide ion may be regarded as a reaction between an ion and a quasi-ion and so is extremely rapid. This assumption is supported by the consistency of calculations based upon it. Nevertheless, these kinetic considerations and results confirm the fact that the Longuet-Higgins formula cannot represent the total amount of the tetroxide, for if this were the case one would have obtained much more larger quantities of nitrate, increasing with increasing iodide concentration.

Structure of Dinitrogen Tetroxide (II).—On the basis of the various reactions of dinitrogen tetroxide, as already mentioned, it became necessary to assume, in addition to the known tetroxide structure (I), the existence of a structure which would explain the almost invariable formation of nitrate. This structure is the Longuet-Higgins formula, while the nitrosonium nitrate, as proposed *inter alia* by Seel *et al.*,[2b] must be regarded as an

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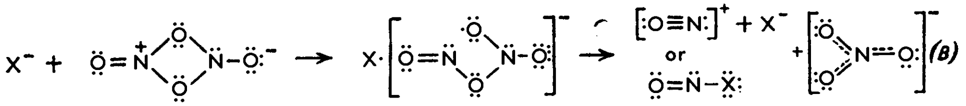
[12] Carrington and Davidson, *J. Phys. Chem.*, 1953, **57**, 418.

[13] Parsons, *J. Amer. Chem. Soc.*, 1925, **47**, 1817.

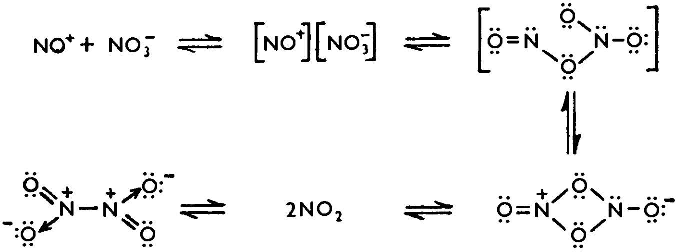
[14] Szabó, Beck, and Bergh, unpublished.

intermediate stage in the reactions. Tetroxide (I), together with the dioxide formed in the thermal dissociation, turns into the structure suggested by Longuet-Higgins to produce, first, with heteropolar or strongly polar partners and with temporary addition of electrons, the asymmetrical nitrosonium nitrate as critical complex, and thereafter, the nitrosonium and nitrate ions :



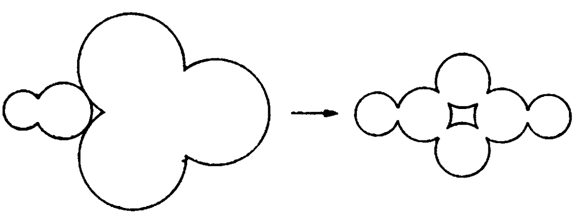
It appears from the mechanism that, in the Longuet-Higgins formula, the N^+ is able to compensate the electron affinity of oxygen, but after taking up the electron, because of the electron affinity of the three oxygen atoms, the N–O bond will break. Depending on the electronegativity of X, either •NO + •X or NOX arises. If the reaction partners are of less polar character, then the fission of the Longuet-Higgins ring proceeds more symmetrically, in the NO_2^+ and the NO_2^- direction.[15]

In interpreting the dinitrogen tetroxide reactions, the intermediate existence of nitrosonium nitrate seems to be more probable in terms of the mechanism of the formation of dinitrogen tetroxide during the various reactions. In the reaction of nitrosonium salts with tetra-alkylammonium nitrates, quantitatively yielding dinitrogen tetroxide,[2b] the nitrosonium ion should be joined up with two unpaired electrons while, simultaneously, the nitrate ion should be linked *via* its two oxygen atoms through 1–1 unpaired electrons to achieve the Longuet-Higgins formula directly from the ion-pairs. Now, neither the nitrosonium ion nor the nitrate ion has a single unpaired ion, and moreover, both of them are excited only with difficulty. Hence, the reaction proceeds as follows :



Such a course is rendered possible also by the fact that it corresponds to the principle of tending to reach a state of minimum energy. For during the passage from the heteropolar nitrosonium and nitrate ions towards the dinitrogen tetroxide, the dipole moment decreases steadily.

FIG. 5.



When establishing the structure of $(NO^+)(NO_3^-)$ ion-pairs, the nitrosonium nitrate formula must not be taken into account again because all the oxygen atoms of the nitrate ion are equivalent. Therefore, when a molecule is formed, the nitrogen atom of the nitrosonium ion must be joined with two oxygen atoms, so as to give a state of minimum energy (Fig. 5). From this bonding the Longuet-Higgins structure arises through a simple electron rearrangement. In this structure the oxygen atoms possess two π bonds, making an angle of 90° each, while the nitrogen atoms have two σ bonds of 120° each, so the ring

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[15] See, *e.g.*, Levy and Scaife, ref. 2*f*.

exhibits a stress of (420°—360°)/4 = 15° for each angle, which is likewise in accordance with the properties of the molecule.

Concentration of the Dinitrogen Tetroxide (II).—For establishment of the structure of tetroxide (II), its concentration, too, may play an important part. Leaving aside, for a moment, the foregoing consideration, a very slight concentration of form (II) would permit the existence of the nitrosonium nitrate structure since its concentration would be so low that it could not be detected by physical methods. The presence of tetroxide (II) in a larger amount, however, excludes the nitrosonium nitrate structure, for its detection by physical methods would doubtless be feasible. On the other hand, if tetroxide (II) is identified with the Longuet-Higgins structure, then the experimental fact that physical methods refer only to the presence of tetroxide (I) as well as of nitrogen dioxide, can be interpreted merely by the assumption of the close identity of the physical properties of the Longuet-Higgins structure with those of the tetroxide (I).[3] In consequence, detection of the latter was not feasible. This aspect, in turn, permits larger quantities of tetroxide (II) to be present in the tetroxide–dioxide system.

On the basis of the above considerations, it would be of great importance to determine experimentally the concentration of tetroxide (II). For this purpose the following assumption was made. With a sufficiently high concentration of the iodide ion, dinitrogen tetroxide would convert into nitrate and nitric oxide only as much of the tetroxide (II) as was present in the system at first, at the given pressure and temperature. In this case, therefore, the amount of tetroxide (II) consumed cannot be replaced, since, because of the high concentration of iodide ions, the whole of the nitrogen dioxide undergoes reaction with these.

In view of the above, in a reaction with potassium iodide saturated at a given temperature, the amount of nitrate, or nitric oxide, would directly give the tetroxide (II) concentration. In our opinion the result obtained in such a way would yield the right concentration of form (II) only if this same amount of nitrate could also be achieved with a somewhat more dilute potassium iodide solution. With this condition fulfilled, it may be stated that the results would be the same even if the experiment had been carried out in the more concentrated solution hypothetically preparable.

The last four data of Table 1 represent such experimental results. The percentage of reaction products shows no appreciable variation though rather different amounts of substances were made to react in solutions with various concentrations (Fig. 2). Fig. 4, too, shows clearly that the ratio x/y, in a concentrated potassium iodide solution, is no longer a linear function of the iodide-ion concentration. Consequently, in the most concentrated potassium iodide solutions, the nitrate can be formed only from the tetroxide (II), originally present as well, so the concentration of the nitrate represents also that of the tetroxide (II), which is, therefore, at 0°, about 31%.

The experimental results for the concentration of tetroxide (II), therefore, again indicate the presence of the Longuet-Higgins structure. Presence of about 31% of nitrosonium nitrate in the dinitrogen tetroxide–nitrogen dioxide system is inconceivable in the light of our knowledge of the results of physical investigations.

This aspect, however, can only be accepted if, as already pointed out, the physical properties of the tetroxide (II) are nearly the same as those of the tetroxide (I). The results of X-ray studies and of analyses on Raman spectra, having been obtained below −10°, can justify only the presence of tetroxide (I). Consequently, these investigations do not exclude the occurrence of a tetroxide of another structure at higher temperatures. However, the infrared spectrum of the tetroxide at higher temperatures (*e.g.*, at 20° [17]) could also be made consistent with a structure of ethylene type. The possibility of this co-ordination is, among others, supported also by the fact that the two frequencies, consequent upon Sutherland's calculations but unobserved by him, have since been found by Perkins and Wilson.[1b] At any rate, a number of bands of medium, or weak, intensity were considered by Sutherland to be combination lines, though in fact they might be lines of another tetroxide structure.

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[16] Seel, ref. 2*b*.

[17] Sutherland, ref. 1*a*.

The rather high concentration of the tetroxide (II) found in the present investigation requires reconsideration of the results of infrared spectra.

Comparison of N_2O_5, N_2O_4, and N_2O_3.—According to our results, the reactions and structure of dinitrogen tetroxide occupy a middle position between those of the pentoxide and the trioxide. The former has an ionic structure also in its solid phase. This was supported, *e.g.*, by the studies of Ingold *et al.* :[18] in the spectrum of pure N_2O_5 lines of nitronium and nitrate ions could be seen at —40°. Moreover, the presence of NO_2^+ ions was proved by spectral and *X*-ray evidence also.[19] On the other hand, a structural study of dinitrogen tetroxide indicated the absence of ions in the solid phase. The nitronium ion, beyond question, has a less polarizing effect than nitrosonium ion. In the dinitrogen trioxide, the nitrosonium ion, being more strongly polarized, forms a covalent bond with the more polarizable nitrite ion to such an extent that the reactivity of dinitrogen trioxide decreases; *e.g.*, nitric oxide evolved in the sodium metal–liquid tetroxide interaction, with the excess of tetroxide, produces dinitrogen trioxide remaining unaffected by the metal.[20] Alkali carbonates react with dinitrogen tetroxide to give alkali nitrate and nitric oxide, whereas with dinitrogen trioxide no reaction proceeds.[21]

Thanks are offered to Dr. P. Huhn for the mathematical discussion concerning the kinetic studies of the reactions.

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[*Received, June 22nd*, 1955.]

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[18] Ingold, Millen, and Poole, *Nature*, 1946, **158**, 480; Millen, *J.*, 1950, 2609.

[19] Cox, Jeffrey, and Truter, *Nature*, 1948, **162**, 259; Grison, Eriks, and de Vries, *Acta Cryst.*, 1950, **3**, 290.

[20] Addison and Thompson, *Nature*, 1948, **162**, 369.

[21] Oswald, *Ann. Chim.*, 1914, **1**, 45; Addison and Lewis, *J.*, 1953, 1319.