IV.—*The Interaction between Iodine Pentoxide and Nitric Oxide.*

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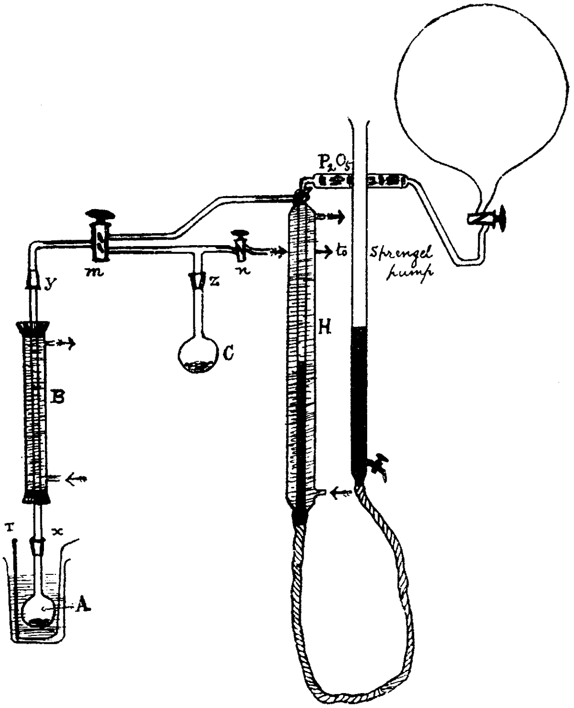
WHILST studying the combustion of charcoal in certain gases, one of us observed that iodine pentoxide and nitric oxide react with each other, giving iodine and nitrogen peroxide (Shah, J., 1929, 2666). We have now examined the reaction in detail, and have found that at 120°, in presence of sodium hydroxide, all the nitric oxide is converted into nitrite and nitrate. The course of the reaction has been followed by measuring (*a*) the diminution in volume of the gas, *i.e.*, the volume of nitric oxide used, (*b*) the amount of iodine produced, and (*c*) the amount of nitrite formed.

EXPERIMENTAL.

The apparatus shown in Fig. 1 was used. The bulb *A* which contained iodine pentoxide (0·2—0·5 g.) was connected through a small water condenser *B* to a three-way tap *m* by means of ground joints *x* and *y*. The other limbs of the tap *m* were joined to the gas burette *H* with the nitric oxide reservoir and by means of the ground joint *z* to a bulb *C* containing coarsely powdered moist sodium hydroxide. Connexion with the Sprengel pump and pressure column was made, when required, by opening the tap *n*. From trial experiments it was found (*a*) that the reduction of iodine pentoxide with nitric oxide begins at 80° and is rapid at 120° and (*b*) that the time required to complete the reaction at 120° varies with the amount of nitric oxide used in the experiment.

FIG. 1.



Procedure.—After complete evacuation of the apparatus from *A* to *C*, the taps *m* and *n* were closed and the bulb *A* was immersed in a paraffin-bath at room temperature. A measured volume of nitric oxide, purified by fractionation in liquid air, was next admitted, and the tap *m* turned off. The bulb *A* was then heated to 120° for time *t* (mins.), and the iodine produced was condensed in *B*. After the heating was over, the bulb *A* was immersed in ice-water and kept at 0° for ½ hour to condense residual iodine vapour.

The connexion with the bulb *C* was next made, and the remaining gas absorbed by the moist sodium hydroxide. After ½ hour, a test was made for the presence of unabsorbed gas by connecting the apparatus with the pump through the tap *n*: not the slightest fluctuation of mercury in the pressure column was observed, showing that, all gas having been absorbed, the reaction was quantitative.

The bulb *A* was now detached from the ground joint *y*. The unchanged iodine pentoxide was neutralised with freshly prepared sodium bicarbonate solution, and iodine in the condensing tube *B* and the bulb *A* was dissolved in potassium iodide. The resulting solution was titrated with standard sodium thiosulphate, giving a measure of the iodine produced. The contents of the bulb *C*, *viz.*, sodium hydroxide, nitrite, and nitrate, were dissolved in water, diluted to 100 c.c., and titrated with standard potassium permanganate, which gave the amount of nitrite formed.

The results of seven experiments, typical of the 25 performed, are given in the tables. The recorded volumes of nitric oxide are reduced to *N.T.P.*

The interaction between iodine pentoxide and nitric oxide at 120°.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.	XII.
Expt. No.	NO used, c.c.	*t*.	Products, mg.		Calc. values, mg.		$NaNO_2$ corr. to I_2 (IV), mg.	$NaNO_2$ (V—VIII), mg.	NO from IV, c.c.	NO from IX, c.c.	NO total (X+XI) c.c.
			I_2.	$NaNO_2$.	I_2.	$NaNO_2$.					
1	26·33	30	54·54	47·51	59·69	40·57	37·06	10·45	24·06	2·26	26·32
2	25·06	60	54·85	41·10	56·78	38·59	37·28	3·82	24·21	0·83	25·04
3	29·47	90	62·2	51·16	66·77	45·38	42·26	8·90	27·44	1·92	29·36

I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.	XII.
Expt. No.	NO used, c.c.	*t*.	Products, mg.		Calc. values, mg.		I_2 corr. to $NaNO_2$ (V), mg.	I_2. (IV—VIII), mg.	NO from V, c.c.	NO from IX, c.c.	NO total (X+XI). c.c.
			I_2.	$NaNO_2$.	I_2.	$NaNO_2$.					
4	27·37	60	62·18	42·18	62·03	42·16	62·07	0·11	27·39	0·02	27·41
5	25·74	90	59·17	38·41	58·33	39·65	56·52	2·65	24·94	0·78	25·72
6	29·93	105	74·43	37·90	67·82	46·10	55·80	18·63	24·61	5·48	30·09
7	35·48	135	88·42	43·94	80·41	54·66	65·97	22·45	29·11	6·60	35·71

The amounts of iodine and nitrite (columns IV and V) when compared with those (columns VI and VII) deduced from the equation

$$10NO + 2I_2O_5 = 2I_2 + 5N_2O_4(\longrightarrow 5NaNO_2) . \qquad (1)$$

lead to the following conclusions:

(*a*) The iodine and nitrite values agree only in Expt. 4, *i.e.*, in one out of the 25 experiments the reaction proceeded solely according to equation (1).

(*b*) The iodine values are low and the nitrite values are high in Expts. 1, 2, and 3. This indicates that the reaction shown in equation (1) was not completed : nitrogen peroxide and nitric oxide that had escaped oxidation by iodine pentoxide gave the trioxide and led to the formation of more nitrite according to

$$5N_2O_4 + 10NO = 10N_2O_3(\longrightarrow 20NaNO_2) \quad . \quad . \quad (2)$$

The peroxide by itself (5 mols.) would yield nitrite (5 mols.) as in (1) which must be deducted. In addition, the nitric oxide in (2) yields 15 mols. of nitrite instead of 5 mols. as in (1).

(*c*) The iodine values are high and the nitrite values low in Expts. 5, 6, and 7, as if nitrogen peroxide and iodine pentoxide had reacted thus :

$$5N_2O_4 + I_2O_5 = I_2 + 5N_2O_5 \quad . \quad . \quad . \quad . \quad (3)$$

This was tested in separate experiments by heating pure nitrogen peroxide with iodine pentoxide in sealed vessels at 120° : iodine pentoxide was reduced and iodine evolved. The nitrogen pentoxide thus produced may decompose, giving nitrogen peroxide and oxygen. In none of our 25 experiments was any gas (oxygen) left unabsorbed by sodium hydroxide, indicating that, even if the decomposition had occurred, the mixture of nitrogen peroxide and oxygen behaved as nitrogen pentoxide in its absorption by sodium hydroxide. Baekland (*J. Amer. Chem. Soc.*, 1904, **26**, 392) observed that such a mixture of nitrogen peroxide and oxygen evolved by heating lead nitrate was completely absorbed by the product when the temperature was allowed to fall.

Thus nitric oxide (10 mols.) can lead either to iodine (2 mols.) and nitrite (5 mols.) as in equation (1), or to iodine (3 mols.) and nitrate according to equations (1) and (3), *i.e.*,

$$10NO + 3I_2O_5 = 3I_2 + 5N_2O_5 \quad . \quad . \quad . \quad . \quad (4)$$

Hence the excess of iodine above that corresponding to the nitrite formed is a measure of the nitric oxide reacting in the latter way.

Discussion.

The interaction between iodine pentoxide and nitric oxide can be explained in two ways. (*a*) We have proceeded above on the assumption that the initial product of this interaction is nitrogen peroxide as in (1) and that nitrogen pentoxide is obtained on subsequent oxidation as in (3). We are unable to adduce decisive evidence in support of this view. (*b*) The fact that nitrogen peroxide reduces iodine pentoxide with the production of iodine is important. Nitrogen pentoxide may be the primary product, according to (4), and nitrogen peroxide may then be produced on subsequent interaction with nitric oxide, thus

$$5N_2O_5 + 5NO = 7{\cdot}5N_2O_4 \quad . \quad . \quad . \quad . \quad . \quad (5)$$

This assumption is equally tenable.

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