was used and, being a rather weak acid, this exaggerated the effect. The same titration using a 0.2cc. offset gave the curve shown in Fig. 5. It is quite possible to decrease the offset further if great care be observed to ascertain that the burets are quite accurate. If such care be not observed small and irregular potential readings may be obtained or else the cusps may turn downward indicating that the wrong buret is in the lead. For ordinary use with 0.1 *N* or 0.05 *N* solutions an offset of 0.2 cc. has been found to be most satisfactory.

Summary

It has been found that in many cases the method described above and referred to as "differential titration" is simpler and more accurate than electro-titration as usually practised. The reasons for this are summarized as follows.

1. The necessity of plotting curves is eliminated.
2. The use of the troublesome calomel half-cell is avoided.
3. Slight errors due to "drifting" (very slow change of potential at an electrode upon standing) are compensated.
4. By the use of solutions almost identical in composition all trouble from diffusion is avoided.

Pittsfield, Massachusetts

[Contribution from the Chemistry Department of the University of California]

A NEW OXIDE OF NITROGEN, NITROSO-NITROGEN TRIOXIDE, AND ITS BEARING ON THE OXIDATION OF NITRIC OXIDE

By R. Leonard Hasche[1]

Received April 21, 1925 Published August 5, 1925

In an earlier paper,[2] the negative temperature coefficient of the rate of reaction between nitric oxide and oxygen was attributed to the formation of an unstable intermediate compound which is more stable at low temperatures than at high. It was the purpose of this investigation to discover whether such an intermediate would be sufficiently stable at liquid-air temperatures to be isolated. Two previous attempts have been made to prepare and identify the compound formed from the interaction of nitric oxide and liquid air or liquid oxygen. Helbig[3] in 1903 by passing an electric discharge through liquid air obtained a light green solid which was very unstable. He pumped off the liquid air and a light blue, amorphous solid remained which by his analysis corresponded to the formula N_2O_3. Raschig[4] prepared a compound by passing nitric oxide through liquid air

---

[1] National Research Fellow in Chemistry.

[2] Patrick and Hasche, This Journal, **47,** 1207 (1925).

[3] Helbig, *Atti accad. Lincei,* **5,** 166 (1903).

[4] Raschig, *Chem.-Ztg.,* **35,** 1096 (1911).

or oxygen and by analyses determined its formula to be NO_3. Both of these results seem questionable. The blue compound that Helbig analyzed might not be the same as the green solid that was suspended in the liquid air, while Raschig's results are open to the objection that he probably did not remove all of the oxygen before he commenced his analysis.

Experimental Part

The compound was prepared and analyzed in the apparatus shown in Fig. 1.

Oxygen from a steel storage cylinder was dried and purified by passing through the towers A and B containing calcium chloride, soda lime and potassium hydroxide. It then passed through the liquid air trap C, which removed the last traces of moisture and carbon dioxide, and condensed in the bulb D which was surrounded by a Dewar vessel F containing liquid air. During condensation, Stopcocks b and c were kept closed. When the bulb D had been filled about three-fourths full of liquid oxygen, Stopcock a was warmed and then closed and the tip of Tube E broken to allow entrance of the nitric oxide. The nitric oxide gas was prepared by the action of concd. sodium nitrite solution on an acid solution of ferrous sulfate. It was stored in reservoirs over water and washed with sulfuric acid before passing into the liquid oxygen. A delivery tube was inserted into the tube E, the tip of the former dipping below the surface of the liquid oxygen. An immediate formation of a light green substance, resembling freshly precipitated chromium hydroxide, resulted when the nitric oxide started to flow into the liquid air. It was necessary to change the delivery tube several times, as the tip soon became clogged with solid nitrogen trioxide. It should be pointed out that the blue nitrogen trioxide always formed when the delivery tube was raised above the surface of the liquid oxygen. The solid that formed in the delivery tube was blue in the colder part of the tube, at the end, and brown in the warmer part of the tube. These two substances were then products formed from the interaction of nitric oxide and oxygen at a higher temperature than that of liquid air or were decomposition products of the green material suspended in the liquid. Passage of the nitric oxide through the liquid

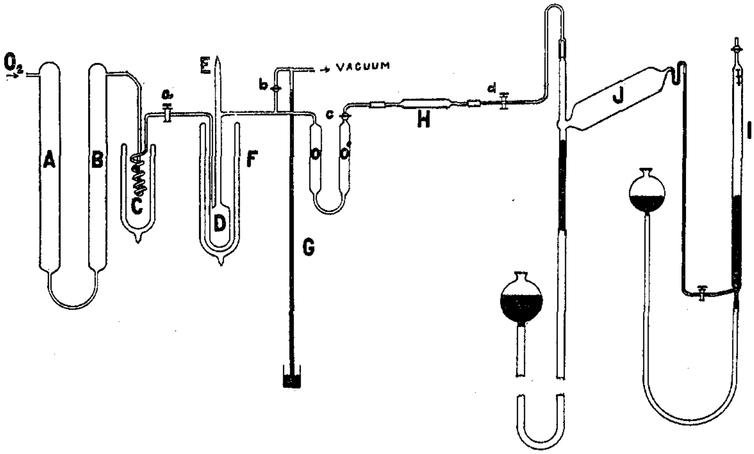


Fig. 1.

oxygen was continued until a paste was formed, the tube E was sealed off and the oxygen pumped off very slowly through Stopcock b. It was very important that the Dewar vessel F be completely filled with liquid air and that evacuation be carried out slowly, as the green compound was very unstable and decomposed when any warm oxygen diffused back into the bulb, especially during the latter part of the evacuation. The green compound decomposes just above the boiling point of oxygen, leaving the powdery, blue compound that Helbig described and found to be N_2O_3. By observing these two precautions, I was able to obtain the pale green solid free from any traces of the blue decomposition product. Evacuation was continued until the mercury in the manometer G showed a constant vacuum, when connection with the pump was broken. Stopcock b was then closed, the Dewar vessel F removed and the mixture of nitrogen oxides analyzed.

Due to the extreme instability of the substance, the following method of analysis was used.

The oxides of nitrogen were reduced to nitrogen by passage through the tared tube H containing copper wire which had been reduced from the oxide by pure hydrogen. The tube was connected to the apparatus by heavy-walled rubber tubing and shellac was applied to make the joints gas-tight. Preliminary to the run, the tube was evacuated by a Toepler pump through Stopcock d. It was then heated electrically to 700–800° and the gases were slowly drawn over the copper. The glass tubing of the stopcock d was thermometer capillary tubing to allow the slow passage of the gases through the reduction tube. The tubes (O) and (O′) were drying tubes containing calcium chloride and phosphorus pentoxide. The nitrogen was pumped off by the Toepler pump and collected in the measuring buret I. The gas in the buret was tested in alkaline pyrogallol and ferrous sulfate pipets to make sure that no traces of nitrogen dioxide, nitric oxide or oxygen were present. In one or two experiments a small amount of nitric oxide was found by the ferrous sulfate test and the proper correction made in the calculation of the analyses. After the tube H had cooled, it was disconnected from the apparatus, the shellac removed with alcohol and the tube was reweighed. From the weight of oxygen given by the increase in weight of the copper tube and the weight of nitrogen corresponding to the volume measured and corrected to standard conditions, the formula of the compound was deduced.

Table I

Results of the Analyses

Expt.	Wt. of N_2 G.	Wt. of O_2 G.	% of N_2
1	0.0381	0.0590	39.21
2	.0196	.0296	39.95
3	.0183	.0280	39.73
4	.0264	.0404	39.45
5	.0694	.1069	39.40
6	.0469	.0760	38.14
		Av.	39.31
		Av. (without Expt. 6)	39.53

Calcd. for N_3O_4: 39.64%. Calcd. for N_2O_3: 36.84%.

The analyses confirm the formula N_3O_4. In order to determine whether the green compound that I have analyzed and the blue compound that Helbig obtained on evacuation were the same, analyses of the blue solid were made, and the results confirmed those of Helbig; the formula of the blue substance was not N_3O_4 as given by Raschig but N_2O_3.

Several experiments were carried out to discover whether the substance N_3O_4 could be prepared under different conditions. Colorless, solid nitric oxide was frozen out in Bulb D. When the air was admitted while the Dewar vessel containing liquid air was kept around the bulb, the pure substance N_3O_4 resulted; when the Dewar vessel was removed and air admitted, some blue nitrogen trioxide was formed together with the substance N_3O_4. When oxygen under pressure was admitted, a mixture of green, blue and brown solids was obtained. The brown material was probably a mixture of nitrogen tetroxide and trioxide. The reaction, $N_3O_4 \longrightarrow N_2O_3 + NO$, is irreversible. I was never able to re-form the green compound by replacing the Dewar vessel after the substance had been warmed until it decomposed to the blue nitrogen trioxide.

Discussion

We may consider the green solid of the formula N_3O_4 to be a derivative of nitrogen trioxide and as such it would be called nitroso-nitrogen trioxide. However, its extreme instability and instantaneous formation would seem to indicate that it is a peroxide, not a derivative of nitrogen trioxide but of polymerized nitric oxide molecules. G. N. Lewis[5] has recently proposed the electronic formula: $:\overset{\cdot\cdot}{\underset{\cdot}{O}}:\overset{\cdot\cdot}{\underset{\cdot}{O}}:$ containing two unpaired electrons, as best expressing the strong paramagnetic susceptibility of the oxygen molecule. This structure would show it to be unsaturated and to have a tendency to form a peroxide, whenever possible. At the low temperature of liquid air it is very conceivable that such a peroxide of nitric oxide would be sufficiently stable to be isolated. Many cases are known at higher temperatures in which peroxidation is the first step in the addition of oxygen. The formation of a peroxide is doubtless a very rapid reaction; in the present case the compound forms instantaneously and, being stable over a narrow range of temperature, it can be isolated.

Before we arrive at a conclusion regarding any mechanism for the formation of this compound, one other point should be considered—the polymerization of nitric oxide. At room temperature and atmospheric pressure, the polymer is practically completely dissociated, since its physical properties show that it behaves as a monomolecular gas within the limits of experimental error. Olszewski and Adwentowski[6] present evidence that nitric oxide is polymerized to a considerable extent at its boiling point. The density of nitric oxide at its boiling point of —150.2° is 1.269. This, compared with the corresponding values for oxygen of —181.4° and 1.1187, shows that the former is about 30% high. The specific heat of nitric oxide according to Regnault[7] increases with rising temperature which can be

---

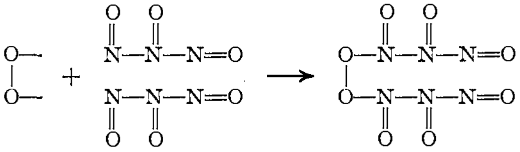
[5] Lewis, THIS JOURNAL, **46**, 2027 (1924).

[6] Olszewski and Adwentowski, *Ion*, **2**, 1 (1910).

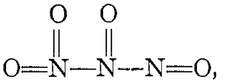
[7] Regnault, *Jahresber.*, **79**, 73 (1853).

explained as being due to the polymer dissociating as the temperature rises.

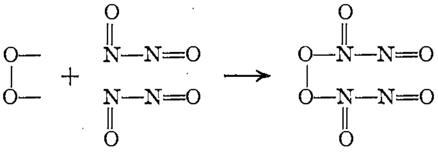
We may consider, then, at the temperature of liquid air that the polymer N_3O_3 reacts with oxygen according to the scheme:



(1)

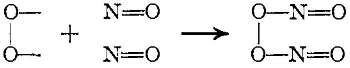
This shows that the molecule is doubled to N_6O_8, which seems likely, since the structure for N_3O_4,  $O{=}\overset{\overset{O}{\|}}{N}-\overset{\overset{O}{\|}}{N}-N{=}O$, would scarcely explain its instantaneous formation. In accord with the structure for N_6O_8 given in Reaction 1, it might be called di-trinitrosyl peroxide.

At a somewhat higher temperature, where N_3O_3 ceases to exist, the polymer N_2O_2 would react in a similar way to give di-dinitrosyl peroxide.



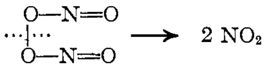
(2)

Similarly, in the gas phase monomolecular nitric oxide would react to give dinitrosyl peroxide.

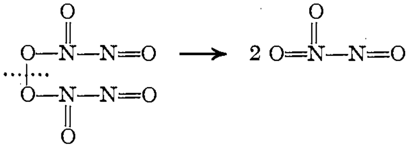


(3)

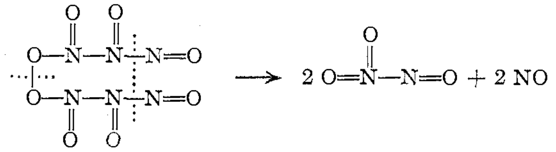
These three reactions, based on the assumptions of a peroxide and reaction of polymerized nitric oxide, explain many facts known about the oxidation of nitric oxide in the gas phase and down through liquid air temperatures. All of these peroxides, being relatively unstable, would be merely the first step in the oxidation at the temperatures in question and would either decompose or rearrange into the final product. We would restate the general principle given in the earlier paper:[2] "that compound is first formed which is the least stable" and "the slowest reaction produces the most stable end-product." Decomposition of the peroxides would occur in the following ways.



(4)



(5)


(6)

Briner[8] and Francesconi and Sciacca[9] have shown that when gaseous nitric oxide and oxygen react below about —50° the product is mainly nitrogen trioxide. Reactions 2 and 5 explain such a formation. At liquid-air temperature the di-trinitrosyl peroxide would form and decompose at a higher temperature, just above the boiling point of oxygen according to Reaction 6. It will be seen from Reactions 4 and 5 that the di-nitrosyl and di-dinitrosyl peroxides could not be distinguished from their decomposition products by analytical methods, since they have the same empirical formulas.

Summary

1. The compound formed from the interaction of nitric oxide and oxygen at liquid-air temperatures has been prepared and identified as a substance of the formula $(N_3O_4)_x$.

2. A mechanism for the formation of this new compound has been suggested which indicates that it is di-trinitrosyl peroxide.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 70]

THE ENTROPY OF SUPERCOOLED LIQUIDS AT THE ABSOLUTE ZERO

BY LINUS PAULING AND RICHARD C. TOLMAN

RECEIVED APRIL 23, 1925 PUBLISHED AUGUST 5, 1925

Introduction

In formulating the third law of thermodynamics Nernst[1] and Planck[2] assumed that a given substance at the absolute zero would have the same entropy in the form of a supercooled liquid as in the crystalline form. It was correctly pointed out by Lewis and Gibson,[3] however, that a supercooled liquid or glass at the absolute zero might be expected in many cases to have a greater entropy than the corresponding crystal, since there might be a greater randomness in the arrangement of the molecules of a liquid,

---

[8] Briner, *J. chim. phys.*, **21**, 24 (1924).

[9] Francesconi and Sciacca, *Gazz. chim. ital.*, **34**, I, 447 (1904).

[1] Nernst, *Nachr. Kgl. Ges. Wiss. Göttingen, Math.-physik. Klasse,* **1906,** p. 1.

[2] Planck, "Thermodynamik," Walter de Gruyter and Co., Berlin, **1921,** 6th ed., p. 273.

[3] Lewis and Gibson, THIS JOURNAL, **42,** 1529 (1920).