631. *The Preparation and Magnetic Susceptibility of Clathrate Compounds of Nitric Oxide and of Oxygen.*

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Methods have been devised for preparing clathrate compounds of quinol and oxygen, and of quinol and nitric oxide. The specific susceptibilities of the compounds have been measured, and the values of χ for the enclosed molecules calculated. For oxygen in the clathrate compound, $\chi = 108{\cdot}8 \times 10^{-6}$, which agrees within experimental error with measurements in the gas phase. For nitric oxide in its compound, $\chi = 51{\cdot}_6 \times 10^{-6}$. This value is higher than the recorded results for gaseous nitric oxide, but the difference may not be significant. It is pointed out that the magnetic properties of these compounds at very low temperatures might be of interest.

Powell and his collaborators (*J.*, 1948, 815) described in detail the structures of a number of adducts formed by quinol and molecules or atoms of suitable dimensions, such as methanol, sulphur dioxide, and inert gases. In these so-called clathrate compounds, each trapped molecule is totally enclosed in a cage formed by the molecular arrangement of the β-quinol lattice. It was thought that the physical properties of molecules thus trapped in an environment different from that normally present in the pure material, might prove of interest; in particular, it seemed likely that the magnetic properties of clathrate compounds of paramagnetic substances would be easy to study. Of the common paramagnetic gases, oxygen and nitric oxide were chosen, as these are the only ones of suitable size which do not react with quinol.

Experimental

Preparations.—(a) *The oxygen clathrate compound.* A hot concentrated solution of quinol is air-free ethyl alcohol in a Monel-metal pressure bomb was allowed to cool slowly during 24 hours under a pressure of 25—40 atm. of oxygen. The faintly yellow crystals obtained were filtered off and dried in a vacuum desiccator; they are perfectly stable under normal conditions at room temperature, but on exposure to strong sunlight gradually turn brown. When dissolved in water, the compound evolves a gas, and analysis by Dr. B. Lambert and Mr. A. B. Webster, by absorption in Fieser's solution, showed this to contain 97·6% of oxygen. The volume of gas obtained from a known weight of sample was measured in a nitrometer and corresponded in different samples to clathrate compounds in which 40—50% of the available spaces had been filled, *i.e.*, the compound is in the range $3C_6H_4(OH)_2,0{\cdot}4$—$0{\cdot}5O_2$. The densities of the samples were consistent with this interpretation.

(b) *The nitric oxide clathrate compound.* A warm saturated solution of quinol in ethyl alcohol was boiled to remove dissolved air, and poured into a stainless-steel bomb. The bomb was evacuated with a rotary oil pump and quickly cooled in liquid oxygen. Nitric oxide, prepared by the method of *Inorg. Synth.*, **2**, p. 126, in an evacuated vessel, was passed through an evacuated train of traps containing sodium hydroxide solution to remove nitrogen peroxide, and sodium hydroxide pellets to remove water, and condensed into the bomb. The quantities of sodium nitrite and ferrous sulphate used in the preparation were chosen so that a final pressure of about 40 atm. would be obtained in the bomb at room temperature. After its valve had been closed, the bomb was removed from the liquid oxygen and finally immersed in hot water. It was shaken for some time to redissolve all the quinol and then allowed to cool slowly for about 24 hours. Excess of nitric oxide was removed by evacuating the bomb, and the crystals were filtered off from the mother-liquor. They were washed with a saturated solution of quinol in ethyl alcohol to remove small amounts of quinhydrone formed by oxidation of the quinol, and were then dried in a vacuum desiccator. The crystals evolved nitric oxide when dissolved in solvents. The samples were analysed by adding air-free water to a known weight in an evacuated vessel, and measuring the pressure developed by means of a mercury manometer. The purity of the nitric oxide was found by repeating this analysis, an alkaline solution of sodium sulphite being used in place of water to dissolve the clathrate compound. This reagent is a quantitative absorbent for nitric oxide (Divers, *J.*, 1899, **75**, 82). The samples contained amounts of nitric oxide which corresponded to about 50% of the available space. The purity of the nitric oxide evolved from one sample was found to be 98·5%. Crystals of this clathrate compound were also obtained by using water as a solvent, but these samples contained much smaller quantities of nitric oxide.

The nitric oxide compound forms crystals which are stable in dry air, but when finely powdered slowly turn violet.

Magnetic Susceptibilities.—The susceptibility measurements were made with a Gouy apparatus. The sample was contained in an egg-shell-thick glass tube, suspended by a fine copper wire from one arm of a Sartorius microbalance. The lower end of the specimen was centred in the magnetic field of an electromagnet which provides fields of about 8000 gauss. The current through the electromagnet was kept at a fixed value by manual adjustment of a small series resistance, a potentiometric arrangement being used to measure the current accurately. The magnet was usually operated near the flat part of its hysteresis curve.

The apparatus was calibrated by using air-free distilled water in the sample tube. It was assumed for water that the specific susceptibility, χ, is $-0{\cdot}720 \times 10^{-6}$, and for air at room temperature, the volume susceptibility, κ is $0{\cdot}029 \times 10^{-6}$. The reproducibility of the apparatus with water is about $\pm 0{\cdot}1\%$, as shown by the following data (by R. E. Richards and C. O. L. Juulman):

Temp.	Press., mm.	*d*	Force on H_2O, mg.	Temp.	Press., mm.	*d*	Force on H_2O, mg.
	(Specimen No. 1)				(Specimen No. 2)		
19·76°	763·0	0·99825	22·108	19·60°	739·3	0·99829	22·074
20·35	762·0	0·99813	22·110	19·00	744·4	0·99841	22·094
20·40	760·2	0·99812	22·105	20·20	743·9	0·99816	22·067
19·63	757·2	0·99828	22·113	20·00	742·9	0·99820	22·070

The systematic difference between the results for the two specimens is probably due to differences in their purity. Experiments carried out with organic liquids such as benzene showed no systematic differences of this kind for different fillings of the tube, since these substances are easier to purify and free completely from dissolved oxygen. (These results are to be published shortly.)

The solid samples were finely powdered and packed as evenly as possible into the Gouy tube, and in the case of the oxygen compound the uniformity of this packing is responsible for the largest error (about 1—2%). A small correction was applied for the air contained in between the particles of solid in the tube; this was calculated from the measured density of the packed sample and from the known density of the crystals.

The oxygen compound. The results obtained for the specific susceptibility ($\chi \times 10^6$) at 17° are given below:

Filling 1	3·318, 3·322, 3·310	Mean = 3·317
Filling 2	3·276	

Average value of χ at $17° = +\,3{\cdot}29_7 \times 10^{-6}$.

The sample was analysed in the nitrometer after the susceptibility measurements, and found to have 39·0% of the available spaces filled. The purity of the oxygen evolved was 97·6%.

The specific susceptibility ($\times 10^6$) of quinol has been given as $-0·586$ (Palacious and Foz, *Anal. Fís. Quím.*, 1935, **33**, 627), $-0·604$ (French, *Trans. Faraday Soc.*, 1945, **41**, 676), and $-0·588$ (Mikhail and Baddar, *J.*, 1944, 590). The values 0·587 and 0·604 $\times 10^{-6}$ lead to a specific susceptibility for the oxygen enclosed in the clathrate compound of 108·6 and 109·0 $\times 10^{-6}$, respectively. The experimental values of χ for gaseous oxygen at 17° range from 104·5 to 110·0 $\times 10^{-6}$ (Selwood, "Magnetochemistry," p. 117, Interscience Publ., New York). The theoretical value calculated by Van Vleck is 107·7 $\times 10^{-6}$ ("Electric and Magnetic Susceptibilities," O.U.P.). This shows that the susceptibility of the oxygen molecules in the clathrate compound is very little affected by their environment. Facilities for measuring the value of χ for the clathrate compound at very low temperatures are not available, but the value might well be of interest as the diamagnetic O_4 complex could not be formed under these conditions.

The nitric oxide compound. When the finely powdered nitric oxide compound was packed into the Gouy tube, rapid decomposition occurred, with eventual formation of quinhydrone and benzoquinone. This is probably due to small amounts of liberated nitric oxide which are oxidised by the air to nitrogen peroxide, which reacts with the quinol. More nitric oxide and also water are liberated from this reaction, and cannot escape from the tightly packed tube of powder, so that further decomposition of the clathrate compound ensues. Accordingly, susceptibility measurements were made immediately after packing the tube, and the sample was then quickly removed and analysed. In spite of these precautions, however, the accuracy of the measurements is considerably lower than in the case of the oxygen compound. The results are shown below.

Sample no.	Spaces filled, %	Purity, %	$\chi_{\text{Clathrate}} \times 10_6$	Temp.	$\chi_{\text{NO}} \times 10^6$	$\chi_{\text{NO}} \times 10^6$, corr. to 17°
1	51·1	98·5 (ass.)	$1·62_6$	18°	50·4	50·6
2 (*a*)	49·1	98·5	$1·56_7$	17·6	51·0	51·1
(*b*)	48·2	98·5	$1·64_6$	17	53·8	53·8

Average value at 17° = $51·_8 \times 10^{-6}$.

(In this table χ for quinol is assumed to be $-0·604 \times 10^{-6}$. If it is taken as $-0·587 \times 10^{-6}$, an average value of χ_{NO} at 17° of $51·_4 \times 10^{-6}$ is obtained.)

The experimental values of $\chi \times 10^6$ for gaseous nitric oxide at 17° have been given as 47·7 (Burris and Hause, *J. Chem. Physics*, 1943, **11**, 442), 49·2 (Bauer, Weiss, and Pickard, *Compt. rend.*, 1918, **167**, 484), and 49·3 (Sone, *Sci. Rep. Tohoku Univ.*, 1922, **11**, 139). The value calculated by Van Vleck (*op. cit.*) is 48·3 $\times 10^{-6}$.

The specific susceptibility of the nitric oxide molecule in the clathrate compound appears to be higher than in the gas phase, but, owing to the difficulty of handling this compound, this difference may not be significant. More precise results could probably be obtained by using an evacuated Gouy tube.

The normal state of the nitric oxide molecule is a regular $^2\Pi$ doublet, the energy difference between the $^2\Pi_{\frac{1}{2}}$ and the $^2\Pi_{\frac{3}{2}}$ state being about 352 cal./mole. The effective Bohr magneton number of nitric oxide therefore varies with temperature, and at 17° is 1·83. At low temperatures this number should fall to zero, in accordance with equations given by Van Vleck (*op. cit.*, p. 269), but since this gas liquefies at 121° K, and forms diamagnetic N_2O_2, it has not been possible to verify this below 112·8° K. The nitric oxide clathrate compound would provide a method of extending the measurements to very low temperatures. It is possible that these two low-lying energy levels of nitric oxide might be perturbed by some kind of interaction between the nitric oxide molecules and the cage, and give rise to the disrepancy between the values of the susceptibility of the gas and that found for the clathrate compound.

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