

of the freezing point cell, or prolonged storing of the mixture in a liquid air-bath, failed to induce crystallization.

As shown graphically in Fig. 7, pyridine and N-methylphthalimide form a single compound, $C_6H_4(CO)_2NCH_2C_6H_5N$, which undergoes dissociation to N-methylphthalimide and solution at a temperature just below its melting point, which, as indicated by a short extrapolation, is approximately 82° . The eutectic is 2.2 mole per cent. N-methylphthalimide, f. p. -42.7° .

Discussion of Results

The fact that pyridine forms no solid addition compound with formamide in the temperature range indicated is not surprising, inasmuch as pyridine has a much lower tendency to donate its unshared electron pair than ammonia. Even with N-phenylformamide, which would be expected to be a stronger acid than formamide itself, no solid compound is observed. Of the remaining five amides, N,N-diethylacetamide, N,N-diphenylacetamide, N,N-diphenylformamide, N-methyldiacetamide and N-methylphthalimide, the last-named would be expected, on the basis of the electron theory, to possess the most positive carbonyl carbon atom, *i. e.*, the carbonyl carbon atom of lowest electron density. It may possibly be significant, therefore, that, although no solid compound

is formed between N,N-diethylacetamide, N,N-diphenylacetamide, N,N-diphenylformamide, or N-methyldiacetamide and pyridine, even down to eutectic temperatures as low as -51.0 and -64.7° , nevertheless N-methylphthalimide and pyridine form a solid 1:1 compound stable at temperatures up to 80° . At present, however, the structure of the compound $C_6H_4(CO)_2NCH_2C_6H_5N$ is entirely problematical. Evidence for the type of bonding in such a solid binary compound can be obtained only by studies of the chemical reactions and crystal and molecular structures of the compound, and of the deviations from ideality in dilute solutions included in the system. Investigations of this type are in progress in this Laboratory.

Summary

1. Temperature-composition data are presented for the seven systems consisting of pyridine with each of the following amides: formamide, N-phenylformamide, N,N-diethylacetamide, N,N-diphenylacetamide, N,N-diphenylformamide, N-methyldiacetamide and N-methylphthalimide.

2. It has been shown that N-methylphthalimide and pyridine form a 1:1 addition compound, the existence of which cannot be accounted for logically in terms of hydrogen-bonding.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF KANSAS]

The Absorption of Oxygen by Sodium in Liquid Ammonia: Evidence for the Existence of Sodium Superoxide

BY WILLIAM H. SCHECHTER, HARRY H. SISLER¹ AND JACOB KLEINBERG

It is well known that potassium, rubidium and cesium combine directly with oxygen² to form superoxides³ of the formula MO_2 , in which the oxygen exists as an ion of the structure $:\ddot{O}:\ddot{O}:^4$. Similar compounds of alkaline earth metals have not yet been isolated in the pure form, although calcium superoxide (as an admixture to the extent of 8.7% in calcium peroxide) and barium superoxide (about 8% in barium peroxide) have been obtained by the action of 30% hydrogen peroxide on the corresponding hydroxides.⁵ Magnetic studies on the impure calcium superoxide prepared in this manner demonstrate the presence of the O_2^- ion in this substance.⁶

(1) Present address: Department of Chemistry, The Ohio State University, Columbus, Ohio.

(2) (a) Joannis, *Compt. rend.*, **116**, 1370 (1893); (b) Holt and Sims, *J. Chem. Soc.*, **65**, 432 (1894); (c) Rengade, *Ann. chim. phys.*, [8] **11**, 348 (1907); (d) Kraus and Whyte, *THIS JOURNAL*, **46**, 1781 (1926).

(3) The investigators cited above believed that they had obtained tetroxides of the formula M_2O_4 ; however, later work (ref. 4) showed the correct formula to be MO_2 .

(4) Neuman, *J. Chem. Phys.*, **3**, 31 (1934).

(5) Traube and Schulze, *Ber.*, **54**, 1626 (1921).

(6) Ehrlich, *Z. anorg. Chem.*, **252**, 370 (1944).

Up to the present the existence of sodium superoxide has not been reported. Joannis^{2a} described the preparation in liquid ammonia at -50° of an oxide of the formula Na_2O_3 , whereas Kraus and Whyte^{2d} found no evidence for any oxide higher than the peroxide in the same solvent at -33° . Preliminary experiments in this Laboratory at approximately -77° in liquid ammonia indicated the formation, by the direct combination of the elements, of a higher oxide than sodium peroxide. The results, however, were not consistent, indicating that the oxide formed was unstable; hence the oxygen uptake of sodium in liquid ammonia at -77° was studied quantitatively. In the present report an apparatus is described for the study of low temperature reactions in liquid ammonia involving gas absorption, and evidence for the existence of sodium superoxide is presented.

Experimental

The apparatus employed (Fig. 1) is suitable for use only at temperatures at which the vapor pressure of the solvent has a known, moderately low value. The volume of gas absorbed by a solution can be calculated from the observed change in volume in the gas buret C; if the reaction is not too rapid, it is possible to determine its rate.

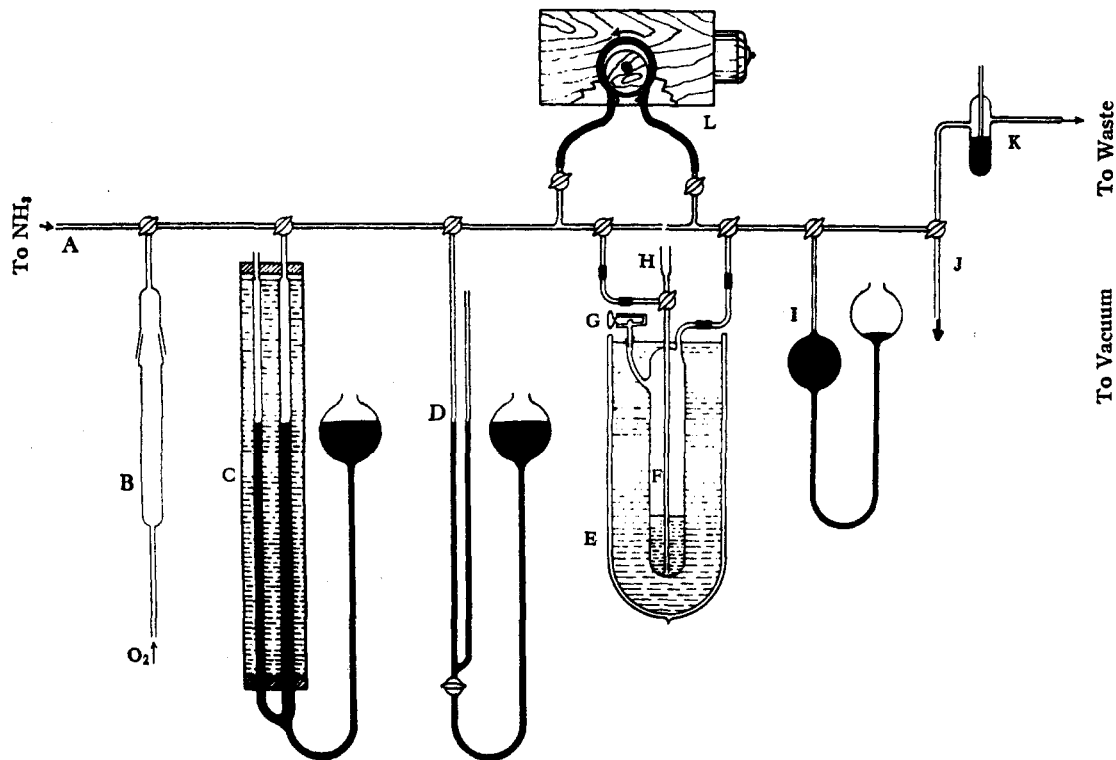


Fig. 1.

A sample of sodium of the desired size is cut in a dry-box containing phosphorus pentoxide. The metal is placed in the tared sampling stopcock G and the plug is rotated. After the ground glass cap has been replaced over the male joint, the stopcock is removed from the dry-box and weighed. The sampling stopcock is then placed at the point shown (Fig. 1) in the system, which has been previously dried by flushing for a considerable time with anhydrous (dried over sodium) ammonia.

The system is again flushed with ammonia, the stopcock J is closed, and the required volume of ammonia is condensed in the reaction cell F by means of the cold bath E, which consists of a mixture of equal volumes of carbon tetrachloride and chloroform to which Dry Ice has been added. The temperature of this mixture, by which the reaction cell is surrounded also during the process of oxidation, is between -77 and -79° .

When the ammonia has been condensed, oxygen is permitted to enter through the drying tube B, containing anhydrous magnesium perchlorate, until the buret C is almost filled. The system is then isolated by closing the stopcock above the drying tube. At this point, with the eccentric pump L turned on, oxygen from the buret is forced through the reaction cell and is collected in the reservoir I. With the manipulation of the appropriate stopcocks the gas is returned to the buret, and the cycling process is then repeated until the oxygen and the liquid ammonia are mutually saturated. During the cycling process and throughout subsequent operations, the level of the cooling liquid on the reaction cell is kept as nearly constant as possible, in order to avoid changes in oxygen volume. This is necessary because the sampling stopcock cannot be covered by the cooling bath.

Once the initial static volume in buret C has become constant, the pump L is turned on and, with the proper adjustment of stopcocks, oxygen at a rate of 850–900 cc. per minute is cycled through the reaction cell. (By regulated clamping of the rubber tubing leading to the pump, the rate of oxygen flow may be adjusted to any desired lower value.) By turning stopcock G the sodium

sample is dropped into the liquid ammonia. The system is kept at approximately atmospheric pressure during the oxidation by raising the mercury leveling bulb of buret C to continually higher levels as the oxygen is consumed. When the oxygen has proceeded to the point where there is no longer any noticeable change in the mercury level in the buret, the pump is turned off, the system permitted to come to apparent equilibrium and the final static volume obtained. The change in volume is then corrected for temperature, pressure and the vapor pressure of liquid ammonia to give the standard volume of oxygen absorbed by the known weight of sodium.

After the absorption data have been obtained, the cold bath is removed and the ammonia allowed to boil off through the trap K to the waste jars. A slow flow of oxygen through the reaction cell is maintained during the removal of ammonia; this sweeps the last traces of ammonia from the system, thus preparing it for the analysis.

For the analysis the cell, now cooled by an ice-water-bath is connected with the measuring buret only, and both the cell and the buret contain oxygen at atmospheric pressure. A 10-ml. portion of catalyst solution (to be described presently) is added from H and the cell, which is connected to the rest of the system by means of Tygon tubing, is shaken to hasten the decomposition of oxide (or oxides); the quantity of oxygen liberated is calculated from the volume change in the buret. The decomposition of the cold, dilute, acidic solutions of hydrogen peroxide, formed upon the addition of acid to peroxides and superoxides of the alkali metals, is catalyzed by a solution which is 0.6 molar with respect to hydrochloric acid and 2 molar with respect to ferric chloride. To correct for the volume change due to the addition of the catalyst, a blank run is made with no oxide present.

Discussion of Results

The results of oxygen absorption studies are given in Table I. It is evident from these data that in liquid ammonia at -77° , sodium absorbs,

TABLE I
THE OXYGEN UPTAKE OF SODIUM IN LIQUID AMMONIA AT -77°

Na, g.	Dilution, cc. $\text{NH}_3/\text{g. Na}$	O_2 flow, cc./min.	Uptake, cc. (S. T. P.)		% of theoretical uptake	Analyses		% of theoretical liberation
			Calcd. for NaO_2	Obs.		cc. O_2 (S. T. P.) Calcd. for NaO_2	liberated Obs.	
0.0266	380	850-900	25.9	23.3	90	19.4	10.8	56
.0235	380	850-900	22.9	21.0	92	17.1	9.3	53
.0428	430	850-900	41.7	35.8	86	31.2	15.9	51
.0616	680	700-750	59.9	51.3	86	45.0	22.3	50
.0317	760	ca. 150	30.8	26.2	85	23.1	12.1	52
.0343	770	ca. 150	33.4	30.9	93	25.0	12.0	48
.0279	810	850-900	27.1	24.3	90	20.3	10.1	50
.0183	1200	850-900	17.8	16.0	90	13.4	7.3	54
.0213	1240		20.7	18.7	90	15.5	8.9	57
.0163	1780	850-900	15.8	14.4	91	11.9	5.6	47
.0293	1830	850-900	28.5	24.9	87	21.4	11.9	56
.0191	2490	850-900	18.6	16.8	90	13.9	6.9	50

from oxygen which is being cycled rapidly through the solution, a volume approaching that required for sodium superoxide. It is apparent that in liquid ammonia a temperature below -33° is essential for the formation of an oxide higher than sodium peroxide, since Kraus and Whyte^{2d} have demonstrated that the peroxide is the highest oxide formed by the rapid oxidation of sodium at the boiling point of ammonia.

As mentioned previously, the amount of oxygen absorbed by the sodium is calculated from the volume change in the buret during the oxidation. This calculation is made on the assumptions that oxygen behaves as an ideal gas under the conditions of the experiment, and that the absolute pressure of the ammonia in the buret is the same before and after the oxidation, *i. e.*, that it is equal to the vapor pressure of the liquid ammonia solution. The first assumption is valid within the experimental error, but the second is true only if sufficient time is allowed for the system to reach equilibrium. The calculated oxygen uptake data, as given in Table I, are based on the assumption that such equilibrium had been attained.

In no case was the theoretical absorption for sodium superoxide quite realized. It is possible that this may be accounted for in part by insufficient time having been allowed for the system to come to equilibrium after oxidation, and in part by contamination of the sodium during the sampling process. Nevertheless, there is no plausible explanation other than the formation of sodium

superoxide that will account for the absorption of such large quantities of oxygen.

The unstable nature of the superoxide is indicated by the results of the analyses, which were made after the ammonia had been permitted to evaporate and the product allowed to reach room temperature. Roughly half the volume of oxygen required for sodium superoxide is liberated upon analysis. At present we have no explanation for the approximately constant values obtained on analysis. The quantity of oxygen liberated is too large to be accounted for solely on the basis of decomposition of sodium peroxide. In each case the volume liberated is approximately 50% greater than that calculated for the peroxide. The reaction product before analysis is visibly heterogeneous, appearing to be a mixture of a yellow⁷ and a white substance.

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Summary

1. An apparatus for studying low temperature reactions in liquid ammonia involving gas absorption is described.

2. Evidence for the existence of sodium superoxide, based upon oxygen absorption in liquid ammonia at -77° , is presented.

LAWRENCE, KANSAS

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(7) Although pure sodium superoxide has not been prepared, it is of interest to note that potassium superoxide is yellow in color.