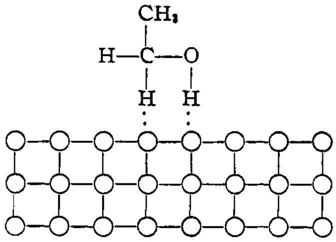
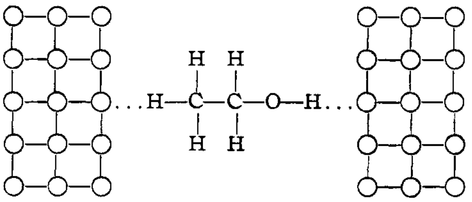


whereas in the dehydration an attack on the substrate molecule is necessary *from two opposite sides*, *i. e.*, from the two walls of a molecular crack.



The fact that, at least in the alcohol dehydration, the hydrogen atom and the hydroxyl group are most probably split off from different carbon atoms, is in favor of this view. Even in the opposite case of formic acid a similar mechanism seems probable by analogy to solution catalysis. Acid–base catalyzed hydrolysis, which is about the reverse of dehydration, is well known[14] to be a prototropic change, requesting an electron shift by the simultaneous action of a proton donor from one end and a proton acceptor from the other end of the reactant molecule. In the extreme form of dual ionization catalysis, this view of the prototropic character of the heterogeneous dehydration has recently been expressed by Bremner.[15] Experiments to check this view are planned.

Summary

The velocity of the simultaneous dehydration and dehydrogenation of the vapors of ethanol and of formic acid on many different oxides and salts as catalysts has been examined. Activation energies and frequency factors were measured by a reflux flowing system with the use of special methods of continuous product gas analysis.

With ethanol, the dehydration has the greater activation energy, whereas with formic acid the dehydrogenation activation energy is greater. A systematic dependence of the activation energy on the chemical nature and the mode of preparation of the catalysts does not exist.

A linear relationship between the activation energy and the logarithm of the frequency factor has been shown to exist, identical for both reactions, but different for the two reactants.

After taking into account the casual variations of the activation energies, it is shown that the different degree of selectivity is mainly due to differences of the frequency factors.

For these reasons, the actual ratio of reaction velocities at a reference temperature gives an adequate picture of the variations of the two selectively active surface areas.

The results indicate that factors producing sintering or recrystallization most generally reduce the rate of dehydration to a larger degree than that of dehydrogenation, independently of the chemical nature of the catalyst.

It is concluded that probably dehydrogenation takes place on the flat surface of the secondary particles, and dehydration within cracks of molecular dimensions. Arguments in favor of this view are discussed.

ATHENS (PIRAEUS), GREECE RECEIVED OCTOBER 25, 1948

[14] R. Bell, J. Baker, *et al.*, in G.-M. Schwab "Handbuch der Katalyse," Vol. 2, Vienna, 1941.

[15] J. G. M. Bremner, *Research*, 1, 281 (1948).

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

Further Studies on the Oxidation of Sodium in Liquid Ammonia

BY WILLIAM H. SCHECHTER,[1] JOSEPH K. THOMPSON AND JACOB KLEINBERG

The data in the literature on the oxidation of sodium in liquid ammonia have been of a conflicting nature. Joannis[2] stated that a substance of the formula $Na_2O \cdot NH_3$ is first formed and this is further oxidized to Na_2O_3 when a solution of sodium in liquid ammonia at $-50°$ is oxidized by a slow stream of oxygen. The investigations of Kraus and Whyte[3] on the slow oxidation of sodium in liquid ammonia have shown that sodium monoxide ammonolyzes in liquid ammonia to give a mixture of hydroxide and amide. The analyses of Joannis upon which the formation of $Na_2O \cdot NH_3$ are based would also correspond to a mixture of hydroxide and amide and it is, therefore, highly likely that this mixture was the first product of oxidation. Joannis' claim for the existence of Na_2O_3 is based solely on an analysis for sodium, the oxygen content being calculated by difference. The work of Kraus and Whyte[3] has demonstrated that the amide in the mixture of hydroxide and amide formed by the ammonolysis of sodium monoxide may be further oxidized to nitrite. Consideration of the stoichiometry of these reactions leads to fact that the sodium content of the final mixture ($3NaOH$ to $1NaNO_2$) is very nearly that which would be present in a substance of the

---

[1] Present address: Department of Chemistry, Sterling College, Sterling, Kansas.

[2] Joannis, *Compt. rend.*, 116, 1370 (1893).

[3] Kraus and Whyte, THIS JOURNAL, 48, 1781 (1926).

formula Na_2O_3. It would appear, therefore, that Joannis' assertion of the formation of Na_2O_3 is invalid.

Kraus and Whyte[3] have declared that the highest oxide formed in the rapid oxidation of sodium in liquid ammonia at −33° is the peroxide. Proof for this declaration is based solely upon the volume of oxygen apparently absorbed by the metal in solution. In a previous report from this Laboratory[4] it was shown that sodium in liquid ammonia appears to absorb, from oxygen which is being cycled rapidly through the solution at −77°, a volume approaching that required for sodium superoxide. Moreover, after evaporation of the ammonia the remaining yellow and white mixture liberates, upon decomposition, a quantity of oxygen greater than that which can be accounted for solely on the basis of sodium peroxide.

The present investigation was undertaken with the principal purpose of preparing pure sodium superoxide. The results of the experiments described in this paper demonstrate that neither the gain in weight of sodium upon oxidation in liquid ammonia nor the volume of oxygen apparently absorbed constitutes a reliable criterion for assigning a formula to the product. Even at −77° sodium undergoes some conversion to amide and subsequently to nitrite if, during the course of oxidation, the blue color of the metal persists even for a short time. Amide formation may be avoided by the slow addition of a solution of the metal in liquid ammonia to another portion of ammonia through which oxygen is rapidly being passed. Under these conditions a yellow product of apparently constant composition is formed whether the reaction is carried out at −33 or −77°. Chemical analyses and magnetic measurements prove that this yellow substance contains a high percentage of sodium superoxide.

Experimental

Preliminary experiments were performed to check the observations of Kraus and Whyte[3] on the oxidation of sodium in liquid ammonia at −33°. The apparatus and technique used were essentially those previously described,[4] except that the oxygen was passed through the solution from a cylinder. The sodium–ammonia solution was kept at −30 to −35° with a Dry Ice–solvent-bath and oxygen was passed through the solution at approximately 60 cc. per minute. The product left after evaporation of the ammonia was treated with catalyst solution (1 *M* in hydrochloric acid and 2 *M* in ferric chloride), and from the known weight of sodium and the quantity of oxygen liberated the composition of the product was determined. The results of these experiments are shown in Table I, the percentage of oxygen in the product being expressed as per cent. sodium peroxide.

Since the data of Table I indicated in a qualitative way that the degree of oxidation is increased with increased dilution of the sodium, an apparatus was devised for the slow addition of a solution of sodium in liquid ammonia to another portion of ammonia through which oxygen is rapidly passed. The experiments utilizing this apparatus (Fig. 1) are described below.

TABLE I

PRELIMINARY DATA ON THE RAPID OXIDATION OF SODIUM IN LIQUID AMMONIA AT −33°

Na, g.	NH_3 vol., cc.	Dilution, cc. NH_3/g. Na	Analyses, % O_2 evolved, cc. (S. T. P.) Calcd. for Na_2O_2	Obs.	% Na_2O_2 indicated
0.0498	9	180	12.1	7.4	61
.0755	14	180	18.5	13.6	74
.0664	13	190	16.1	13.2	82
.0593	14	240	14.4	11.4	79
.0669	17	250	16.3	14.4	88
.0820	33	400	19.9	20.3	102
.0529	28	530	12.9	15.1	117
.0342	33	970	8.3	11.5	139
.0272	29	1100	6.6	8.0	121
.0427	58	1350	10.4	11.9	115

Rapid Oxidation in Solution.—Approximately 90 cc. of ammonia was condensed in reaction cell F, the maximum capacity of which was about 140 cc., and the cell was then thermostated to the desired temperature by use of a cooling bath. Then about 40 cc. of ammonia was condensed in the solution cell K whose maximum capacity was 90 cc. The solution cell was maintained at a temperature near the boiling point of liquid ammonia throughout any particular experiment by means of the cooling bath M. Oxygen, dried by passage through anhydrous magnesium perchlorate in B, was bubbled rapidly through the reaction cell F and the latter was brought to the temperature desired. A sample of freshly cut sodium, previously prepared in a dry-box containing phosphorus pentoxide, was then introduced into cell K by turning stopcock J. By the proper control of pinch clamp L the blue solution resulting from the introduction of the sodium could be added at any desired rate to the oxidizing solution in reaction cell F.

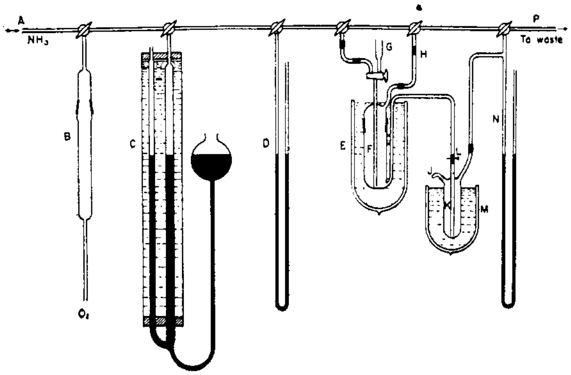


Fig. 1.

With care, the metal–ammonia solution could be added to the oxidizing solution sufficiently slowly so that it was oxidized immediately; under these conditions the liquid in cell F was never colored blue. When all the sodium–ammonia solution had been added, cell K was disconnected, the ammonia permitted to evaporate from F and the product analyzed in the following manner. The material was catalytically decomposed with an aqueous manganese dioxide suspension and the liberated oxygen collected in buret C. The sodium hydroxide solution remaining after decomposition was titrated with standard acid to determine sodium content. After titration, the solution was boiled almost to dryness and a qualitative test for nitrite made.

When the addition of the sodium–ammonia solution to cell F was properly controlled the product remaining after evaporation of ammonia was yellow with occasional white traces and gave no test for nitrite ion. On the other hand, when the control was poor the product was a mixture of yellow and white substances and always gave a positive

---

[4] Schechter, Sisler and Kleinberg, THIS JOURNAL, **70**, 267 (1948).

nitrite test. Moreover, the oxygen content of the mixture was always appreciably less than that of the yellow material. The data for the experiments in which the control was excellent are collected in Table II.

TABLE II

RAPID OXIDATION OF SODIUM IN LIQUID AMMONIA

Vol. of NH_3–O_2 solution approximately 100 cc.

Na, g. (from titration)	Temp. of reaction cell bath	Vol. of oxygen evolved from product on analysis, cc. (S. T. P.)	Vol. of oxygen calcd. for NaO_2, cc. (S. T. P.)[2]	Atoms of oxygen per atom of Na
0.0591	Unthermostated	34.0	43.0	1.68
.0412	Unthermostated	23.3	30.0	1.67
.0126	Unthermostated	7.2	9.2	1.67
.0353	Unthermostated	20.6	25.8	1.70
.0424	Unthermostated	23.7	30.9	1.65
.0492	*ca.* −77°	27.8	35.9	1.67
.0453	*ca.* −77°	25.7	33.0	1.67
.0403	*ca.* −77°	22.9	29.5	1.67
.0536	*ca.* −77°	31.4	39.1	1.70
.0635	*ca.* −77°	36.2	46.3	1.67
.0324	*ca.* −77°	18.7	23.7	1.68

Magnetic Measurements on the Yellow Product.—The magnetic susceptibility of the yellow product described above was determined by the Gouy method. The apparatus for this purpose was constructed around an electromagnet with a field strength of 8000 gausses and an analytical balance with a sensitivity of ten divisions per milligram. Calibration of the magnetic field was based upon the magnetic susceptibility of water.

The material was highly paramagnetic, the value obtained for the specific susceptibility, χ_g, at 20° being 21.6×10^{-6} c.g.s. units. This corresponds to 67 ±5 weight per cent. of sodium superoxide, based on the value of 33.0×10^{-6} c.g.s. units recently found for the magnetic moment of pure sodium superoxide.[5] The possible error in this measurement is necessarily large since only small quantities of the yellow material could be obtained in the apparatus previously described. It was necessary to use samples accumulated from several runs and undoubtedly some decomposition occurred even though all sampling operations were performed in a dry-box. Initial attempts to design an apparatus for the production of larger quantities of the yellow material were unsuccessful.

Discussion of Experimental Results

The data of Table I definitely prove that sodium peroxide is not the highest oxidation product formed when sodium is oxidized in liquid ammonia at −33°. The data of Table II indicate that the rapid oxidation of sodium in liquid ammonia, effected by the slow addition of the metal–ammonia solution into another portion of ammonia through which oxygen is rapidly being passed, yields a yellow product the composition of which appears to be independent of the temperature of the reaction. The empirical formula $NaO_{1.67}$ corresponds to a mixture of $1Na_2O_2$ with $4NaO_2$. The yellow color of the product and its high degree of paramagnetism provides additional evidence that sodium superoxide is present in the material. The value of 67 ± 5% sodium superoxide as derived from a magnetic measurement agrees, as well as could be expected considering the accuracy of the measurement, with the figure of 73.7% calculated from the above composition.

If the control in manipulating the sodium–ammonia solution is poor and the blue color of the metal persists for a very short time (even at −77°), nitrite is formed. Undoubtedly this formation takes place through the reduction by the metal of any higher oxide to monoxide, followed by the sequence of reactions described in the introduction of this paper. The formation of nitrite even under conditions of rapid oxidation of the sodium demonstrates that neither the gain in weight due to reaction of the metal nor the volume of oxygen absorbed constitutes a reliable criterion for assigning a formula to the product.

Acknowledgment.—The authors are indebted to the Office of Naval Research for a grant which has made this and continuing investigations possible.

Summary

1. It has been shown that sodium peroxide is not the highest oxide formed by rapid oxidation of the metal in liquid ammonia at −33°. In general, the composition of the product has been found to be dependent on the method of oxidation.

2. Sodium, unlike potassium, is converted to some extent to the amide, even at −77°, during the course of the oxidation, if the blue color of the metal–ammonia solution is permitted to persist for even a short time. A method of oxidation has been developed which eliminates this undesirable side reaction over the entire liquid ammonia range from −33 to −77°.

3. Evidence is presented which indicates that a substance of empirical formula $NaO_{1.67}$ is formed when sodium is oxidized under conditions in which the side reaction described above is eliminated. The formula $NaO_{1.67}$ corresponds to a mixture of superoxide and peroxide in the ratio of four to one. Magnetic data lend credence to such a formulation.

LAWRENCE, KANSAS RECEIVED JANUARY 17, 1949

---

(5) Stephanou, Ph.D. Thesis, University of Kansas, 1949. The magnetic properties of sodium superoxide will be discussed in a forthcoming publication from this Laboratory.