[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TENNESSEE]

Effect of Variables on Reductions by Alcohol and Potassium in Ammonia

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The effects of certain variables on the time required for the reduction of an organic substrate by alcohol and potassium in ammonia, and on the time required for liberation of hydrogen from the alcohol by the metal, have been measured. The most interesting effects found are that (1) oxygen vigorously catalyzed both reactions (reduction and hydrogen liberation), (2) alkoxide ion has no effect on reduction while it greatly retards hydrogen liberation, and (3) certain reductions go to completion in an unusually brief period, $<3 \times 10^{-3}$ sec. Mechanistic aspects of the reduction are discussed and the point is stressed that any mechanism must take cognizance of the competition for protons by two anions, electrons and substrate carbanions.

Introduction

Although reductions by alkali metals in liquid ammonia have been exploited extensively,[1] our knowledge of the fundamental, intricate nature of these reactions is incomplete.[2] Because of the great utility of these reactions it has seemed worthwhile to initiate a program of experimentation designed explicitly to help elucidate the detailed mechanism of the reduction of organic compounds by alkali metals in ammonia.

It is generally agreed that reductions (1) by metals (M) in ammonia occur by the pick up of electrons ($e^{\ominus}$) by a substrate (S:) to produce a carbanion ($:S:^{=}$) which in turn picks up protons from some acid (AH) to produce the reduced, or hydrogenated, product (HSH).[3,4] These ideas must eventually be considerably ramified to show whether one or both electrons are picked up before the first proton is taken on and whether a given step is reversible or rate determining. For an exact understanding of these and other ramifications a knowledge of the kinetics of the reduction reaction is being sought.[5]

$$S: + 2M + 2AH \xrightarrow{NH_3} HSH + 2MA \qquad (1)$$

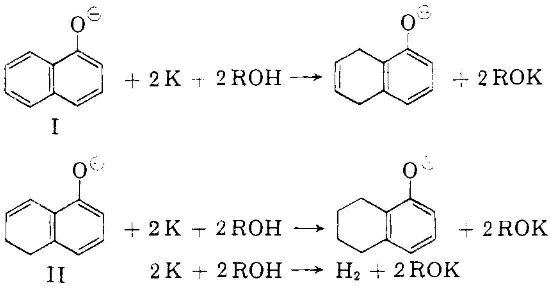
Reported in the present communication are some preliminary experiments which, although not detailed kinetic measurements, do show qualitatively the effect of certain variables on the reduction reaction's rate. It has also been of interest to show the effect of these same variables on the omnipresent competing reaction for alkali metals, hydrogen liberation. In a solution of electrons (from the metal), proton source and reducible substrate, the substrate competes with the proton source for electrons, equations 2 and 3, and *the substrate carbanion competes with electrons for the proton source*, equations 3 and 4. A knowledge of the relative influence of variables on the competing hydrogen liberation and reduction reactions should reveal details of each.

$$2\,e^{\ominus} + S: \longrightarrow :S:^{=} \qquad (2)$$

$$2e^{\ominus} + 2AH \longrightarrow 2A^{\ominus} + H_2 \qquad (3)$$

$$:S:^{=} + 2AH \longrightarrow 2A^{\ominus} + HSH \qquad (4)$$

The technique employed has been to determine the total time for complete reaction after mixing of an ammonia solution of alkali metal (potassium) with one containing a stoichiometric amount of substrate (1-naphthoxide ion (I) or 5,6-dihydro-1-naphthoxide ion (II))[6] and/or excess proton source (*t*-amyl alcohol or ethyl alcohol) with and without certain additives. For the reactions studied, equations 1 and 3 are rewritten below and the experimental results are summarized in Tables I and II.



$$2K + 2ROH \longrightarrow H_2 + 2ROK$$

Experimental

Apparatus.—Liquid ammonia solutions were prepared and mixed in a three-arm reactor sketched in Fig. 1. Before each run this apparatus was washed, dried at 90° and allowed to cool while a stream of dry nitrogen passed through it. The reactor was immersed in a Dewar flask (C) of boiling ammonia (−33°) and the "T-bore" stopcock closed to all arms. Solutions, one of alkali metal and the other of substrate, proton source and additives, were prepared in arms A and A'. To initiate reaction the stopcock was opened to all arms while a constant head of nitrogen was maintained in arms A and A'. The reaction-arm (B) was usually initially filled with nitrogen, air or oxygen. Flow rate was controlled by variation of the nitrogen head in A and A', or, for the fastest flow (50 ml. mixed in <1 sec.), arm B was evacuated before mixing. A stopwatch was used to measure the time required after mixing for the disappearance of the intense blue color characteristic of alkali metal (electrons) in ammonia. The sharp change, dark blue to colorless, occurred in a second or less in all but the long re-

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(1) *Cf.* (a) A. J. Birch, *Quart. Revs.*, **4**, 69 (1950); A. J. Birch, H. Smith and R. E. Thornton, *J. Chem. Soc.*, 1339 (1957); (b) W. Hückel, A. Munkner and B. Graf, *Ann.*, **614**, 47 (1958); (c) G. W. Watt, *Chem. Revs.*, **46**, 289 (1950).

(2) Of the many applications of reductions by metals-in-ammonia, most have involved syntheses from which the only quantitative data published concern the stoichiometry of the reactions. Even this is not usually available because most investigators have employed excess reducing agent and have been interested in only qualitative knowledge of the products. No quantitative data are available on the kinetics of any reduction by an alkali metal in homogeneous media. No systematic competition experiments have been carried out to quantitatively compare effects by the many variables associated with metal-in-ammonia reductions.

(3) The symbol S: is used to represent a system with at least one pair of π-electrons.

(4) The most significant recent studies and discussions of reductions by metals in ammonia have been made by A. J. Birch.[1a] Birch has contributed particularly to our understanding of the protonation of the substrate anion.

(5) The first reaction studied in detail (kinetics and isotope effects) is that between alcohols and alkali metals in ammonia: E. J. Kelly, Ph.D. thesis submitted to the University of Tennessee, March, 1959.

(6) J. F. Eastham and D. L. Larkin, THIS JOURNAL, **80**, 2887 (1958).

action times, when a slow fading of the blue could be perceived. Rough experiments showed that the color is obvious at metal concentration below 10^{-3} molar.

Reduction of Potassium 1-Naphthoxide (I).—After condensation of 25 ml. of anhydrous ammonia into each arm A and A′ of the reactor, 2.4 g. of *t*-amyl alcohol (dried over sodium and fractionated) and 0.38 g. of potassium were added to arm A. After the initial reaction was complete, 1.38 g. of freshly recrystallized 1-naphthol was added to arm A[7] and 0.76 g. of potassium was added to arm A′. The total volume of solution was brought to 40 ml. in each arm by condensation of additional ammonia and the two solutions were mixed in a nitrogen atmosphere. The blue color disappeared in 29 seconds (line 3, Table I). In other runs, one or another of the reactants was omitted and/or its concentration changed, a portion of the solvent was replaced with ether, excess alkoxide ion was formed in arm A before the solutions were mixed, a portion of the ammonia solvent was replaced with anhydrous ether, the solution in arm A was made 0.02 *M* in water, absolute ethyl instead of *t*-amyl alcohol was used, or atmospheres of air or oxygen replaced the nitrogen. Results are summarized in Table I where about one-third of the actual runs made are reported. The times reported were reproduced in all cases with less than 15% deviation in duplicate and in some cases triplicate runs.

After each of several runs involving reduction, the ammonia solution was evaporated and the residue dissolved in water. Spectrophotometric analysis of an aliquot always showed no absorption above 300 mμ and hence complete reduction. In a few runs, including those involving oxygen's presence, the aqueous solution was acidified and the precipitated 5,8-dihydro-1-naphthol was distilled (b.p. 120° (1 mm.)) and recrystallized to give an 80% yield of pure product, m.p. 72–73°.[5] The product from reaction of the naphthoxide ion with metal in the absence of alcohol was not investigated.

Reduction of Potassium 5,6-Dihydro-1-naphthoxide (II).—When 5,6-dihydro-1-naphthol[6] was reduced with potassium and ethyl alcohol under the conditions described above for 1-naphthol, the blue color was discharged before the reactants got into arm B. The apparatus was then adapted and working conditions adjusted so that the blue color persisted a measurable distance through the long arm of the "T" connecting B to A and A′. This arm was made of 2-mm. capillary, 25 mm. in length, and calibrated. The nitrogen pressure was regulated to cause a flow rate of 13.3 ml./sec. and excess stopcock grease was removed carefully from the "T" joining the arms. Under these conditions when a reaction solution initially 0.12 *M* in II, 0.24 *M* in potassium and 0.34 *M* in alcohol was discharged into B the boundary between blue and colorless solution was distinct at the 12 mm. mark where it persisted for virtually the entire period of discharge, 6 sec. A conventional flow calculation shows that the electrons (blue color) persisted for somewhat less than 3×10^{-3} sec. (line 1, Table II). In other runs the substrate or alcohol was omitted and alkoxide ion was added; results are summarized in Table II.[8]

The above reaction solution was evaporated and the residue dissolved in water. By spectrophotometry an aliquot of the aqueous solution (no absorption above 300 mμ) was shown to contain no 5,6-dihydro-1-naphthol. Acidification of the aqueous solution and distillation (b.p. 115° (1 mm.)) and recrystallization of the precipitate gave a 79% yield of 5-hydroxytetralin, m.p. 69–70°.

Discussion

The first line in Table I shows that complete reaction between the metal (or its electrons) is quite slow with the substrate in the absence of a proton source. Hydrogen liberation, line 2, from the same quantity of metal and excess proton source is also a rather slow reaction in the absence of a substrate. Under the same conditions, reduction (all three reactants present) proceeds much faster, line 3. Subsequent lines in Table I show the effects

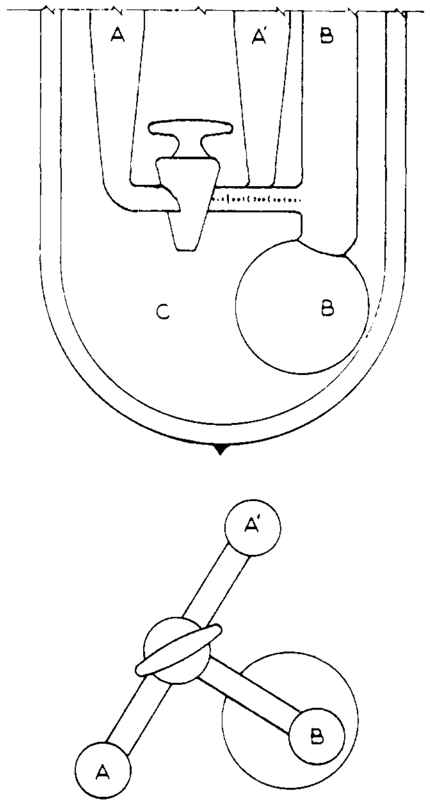

Fig. 1.—Liquid ammonia reactor: upper, side view; lower, top view.

TABLE I

	Initial molarity of reactants				
	Naphthoxide[a]	Alcohol[b]	Potassium	Additives[c]	Reaction time in sec.
1	0.28	...	0.24	....	2600
2	..	0.46[b]	.24	....	1620
3	0.12	.46	.24	....	29
4	.12	.37	.24	....	26
5	.12	.34	.24	....	27
6	.13	.46	.26	Air[d]	<2
7	..	.46	.26	Air[d]	170
8	.12	.37	.24	0.04 *M* H_2O	24
9	.12	.34[b]	.24	....	19
10	..	.34	.24	....	840
11	..	.34	.24	O_2[d]	20
12	.12	.34	.24	O_2[d]	<3
13	..	.34	.24	Ether[e]	622
14	..	.34	.24	Ether[e] and 0.34 *M* KOEt	10600
15	.12	.34	.24	Ether[e] and 0.34 *M* KOEt	17

[a] Potassium 1-naphthoxide (I). [b] Lines 2 through 8 represent runs made with *t*-amyl alcohol; lines 9–15, with ethyl alcohol. [c] Unless otherwise indicated atmosphere for all runs was nitrogen. [d] These gases replaced the usual nitrogen in these runs. [e] Ether was 25% by volume.

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[7] This technique formed potassium 1-naphthoxide in arm A. One reason for using the naphthoxide ion instead of free naphthol was to have present only one proton source throughout the reduction.

[8] The very brief time reported in Table II represents a maximum possible reaction time. From the geometry of the flow system and the nature of the mixing fluids one can estimate that an appreciable fraction of the reduction period was required for complete mixing of the reactants.

on reduction and hydrogen liberation of varying the alcohol and its concentration and of the presence of certain additives: water, oxygen, ether and alkoxide ion.

TABLE II

	Initial molarity of reactants				
	Dihydro-naph-thoxide[a]	Ethyl alcohol	Potas-sium	Additives[b]	Reaction time in sec.[c]
1	0.12	0.34	0.24	Ether	3×10^{-3}
2	.12	..	.24	Ether	128
3	..	.34	.24	Ether	622
4	..	.34	.24	Ether and 0.34 *M* KOEt	10,600
5	.12	.34	.24	Ether and 0.34 *M* KOEt	3×10^{-3}

[a] Potassium 5,6-dihydro-1-naphthoxide (II). [b] All reactions in a nitrogen atmosphere and with 25% by volume ether solvent. [c] See footnote 8.

From lines 3, 4 and 5 it is apparent that the concentration of excess alcohol does not significantly affect the rate of reduction. The nature of the alcohol, tertiary (line 3) or primary (line 9), apparently does affect the reduction rate somewhat. The nature of the alcohol has an even greater effect on hydrogen liberation (compare lines 2 and 10). The effect for both reactions is an acceleration by the primary over the tertiary alcohol. These effects are dwarfed however by one unexpectedly discovered when the reduction fortuitously was carried out in air instead of in nitrogen. As is shown in line 6, reduction with the reaction solution exposed to air went to completion in less than one-tenth of any time previously encountered. The hydrogen liberation reaction, line 7, was similarly accelerated by air.

The ingredient in air first considered responsible for this catalysis was water. However, addition of a small amount of water to the reduction run under nitrogen had no appreciable effect (compare lines 4 and 8). It then was found that *oxygen effectively promotes both the hydrogen liberation* (lines 10 and 11) *and the reduction* (lines 9 and 12). It should be stressed that little oxygen could have been consumed by reaction with alkali metal under the conditions employed; the substrate was still efficiently reduced. An attractive hypothesis for the action of oxygen in these reactions is that it acts as an electron transfer agent through equation 5.[9] The novel effect of oxygen facilitating a reduction is being studied further.

$$K + O_2 \longrightarrow K^{\oplus} + O_2^{\ominus} \qquad (5)$$

For many reactions it is convenient to add to the liquid ammonia a better organic solvent, such as ether. Ether, up to 25% by volume, apparently has no significant effect on the reaction rates (compare lines 10 and 13, and 9 and 15). Alkoxide ion, on the other hand, has a profound effect on the rate of hydrogen liberation (compare lines 13 and 14). It would appear that with sufficient added alkoxide ion the reaction between alcohol and metal could be brought virtually to a halt. However, this same alkoxide ion has no effect on the reduction reaction.[10]

It is not difficult to envision how the strongly basic alkoxide ion might tie up protons making them less available for attack by electrons (equation 3). Less obvious though is how this is done without at the same time making these same protons less available to attack by carbanions (equation 4). By what mechanism can a proton be made relatively less available to the smallest of all anions, an electron, and remain at the same time abundantly available to a large organic anion?

Initially several different compounds were briefly applied in this study in seeking a suitable substrate, one that would be efficiently reduced to a single product under a variety of conditions. The difficulty with most compounds tested was that they were reduced too rapidly. No accurate measurement could be made of the time required for reduction. For example, 1-naphthol itself is reduced far more rapidly than the 1-naphthoxide ion; the presence of a negative charge on the substrate slows the rate of pick up of negative electrons. A group which is particularly rapidly reduced is the styrene-type double bond; here even a net negative charge on the substrate does not slow reduction appreciably.

The data relative to the reduction of one styrene type double bond, that in the 5,6-dihydro-1-naphthoxide ion (II), was obtained using a flow technique and is given in Table II. A stoichiometric amount of *substrate II is reduced in less than 3×10^{-3} sec.* by the electrons from 0.2 *M* potassium and excess alcohol (line 1).[8] It was certainly surprising to find a stepwise reaction between a large organic ion and two other species occurring with such velocity. For this rapid reduction a proton source is needed (line 2), although the source may liberate hydrogen only slowly (line 3). The presence of alkoxide ion which greatly retards hydrogen liberation (line 4) still has no measured effect on the reduction (line 5).

A possible mechanism for reduction is

$$S\colon \overset{e^{\ominus}}{\rightleftarrows} \colon S\cdot^{\ominus} \xrightarrow[\text{fast}]{AH} A^{\ominus} + HS\cdot \xrightarrow[\text{slow}]{e^{\ominus}}$$

$$HS\colon^{\ominus} \xrightarrow[\text{fast}]{AH} A^{\ominus} + HSH$$

Although this scheme is highly speculative, it is consistent with the findings. Thus, in order to accommodate the great velocity with which reduction may occur, each step involves the transfer of one of the two most mobile of all chemical species, protons and electrons. Initial acceptance of an electron is rapid and reversible,[11] hence the necessity of a proton source to take the reaction to completion. If receipt of the first proton were not

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[9] J. Jortner and G. Stein, *Nature*, **175**, 893 (1955).

[10] Although the evidence probably is not needed, this divergent action of alkoxide ion on the two reactions is further evidence against the old "nascent hydrogen" theory of reduction. If some prior reaction between proton source and metal produces a "hydrogen" which actually causes reduction, then surely an additive which profoundly affects the rate of formation of hydrogen would also have some effect on the rate of reduction.

[11] For extensive evidence on the rapid reversible formation of related radical-anions ($:S\cdot^{\ominus}$) see T. L. Chu and S. C. Yu, THIS JOURNAL, **76**, 3367 (1954); R. L. Ward and S. I. Weissman, *ibid.*, **79**, 2086 (1957); D. Lipkin, D. E. Paul, J. Townsend and S. I. Weissman, *Science*, **117**, 534 (1953); and other papers by S. I. Weissman and co-workers.

unidirectional and fast as shown, *i.e.*, if it were rate determining or were reversible, then change in the alcohol concentration or addition of excess alkoxide ion should have a significant effect on the reduction rate. Pick up of the second electron is considered rate determining[12]; as observed, the presence of a negative charge on the substrate slows the reaction; albeit obscurely, oxygen could assist in the electron transfer here.

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[12] It is likely that the pick up of protons is faster than of electrons because of the negatively charged substrate used in this work. For reduction of neutral species protonation could be the slow step.

[Contribution from the Department of Chemistry, University of Arkansas]

The Stereochemistry of Hydrogenation of Isomers of Methyl Tetrahydrophthalate and Methyl Phthalate[1,2]

By Samuel Siegel and George S. McCaleb

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The hydrogenation of methyl phthalate or methyl Δ^1-cyclohexenedicarboxylate, in the presence of platinum oxide in acetic acid at room temperature yields only *cis*-methyl hexahydrophthalate. The result is independent of the pressure of hydrogen (1 to 200 atm.) and the concentration of the substrate (0.05 to 1.0 mole per liter). Methyl Δ^2-cyclohexenedicarboxylate yields the same result at about 1 atm. of hydrogen, but some of the *trans*-methyl hexahydrophthalate (6 ± 2%) is formed at a pressure of 130 atm. None (within 2%) of the isomeric unsaturated ester is found at the half point of reduction of either the Δ^1- or the Δ^2-ester. The results are consistent with the hypothesis that the hydrogenation of an aromatic compound proceeds stepwise, one of the possible intermediates being the tetrahydro derivative; *e.g.*, the stereochemical evidence does not require that an aromatic ring be saturated during a single period of residence on the catalyst.

The investigation of the stereochemistry of the hydrogenation of methyl phthalate and two isomeric methyl tetrahydrophthalates is part of a program to examine systematically the stereochemistry of the catalytic hydrogenation of aromatic and hydroaromatic compounds.[3] Although considerable data relating to this question are available, it is not sufficiently detailed to be of much use in advancing our understanding of the mechanism of this reaction beyond the qualitative stage which exists at present.[4]

Our first paper in this series[3] dealt with the stereochemistry of hydrogenation of the isomeric xylenes and tetrahydroxylenes. These compounds yield mainly the *cis* isomers of dimethylcyclohexane when reduced in acetic acid in the presence of platinum oxide at room temperature. The largest proportions of the *cis* product are obtained from *o*-xylene (95%) and 1,2-dimethylcyclohexene (82%). This predominance of *cis* products diminishes with the distance separating the substituents, *e.g.*, *m*-xylene, 86% *cis;* and *p*-xylene, 74% *cis.* Because the saturated products do not isomerize under the experimental conditions, the mixture must be formed directly during the reduction of the unsaturated compounds.

Although the isomerization of 1,2-dimethylcyclohexene was not detected under the conditions of the experiment, it yields approximately 18% of *trans*-dimethylcyclohexane. Consequently, the hydrogenation of the olefin must be stepwise, rather than the simultaneous addition of two atoms of hydrogen to one side of the double bond. An intermediate stage in the reduction must provide a path for the formation of both *cis* and *trans* isomers. This is consistent with the mechanistic concepts of Horiuti and Polanyi.[5] The fact that more *trans*-1,3-dimethylcyclohexane than is present in an equilibrium mixture is obtained upon hydrogenating *m*-xylene is evidence that the hydrogenation of the aromatic ring proceeds in steps also, rather than by the simultaneous addition of six hydrogen atoms.[6]

In the present study, the hydrogenation of methyl phthalate, methyl Δ^1-cyclohexenedicarboxylate and methyl Δ^2-cyclohexenedicarboxylate was investigated using platinum oxide as a catalyst and in the solvent acetic acid. The object was to determine whether the ester group gives rise to stereochemical results significantly different from those obtained with methyl groups as substituents on the unsaturated substrates.

The only product formed in the presently described hydrogenations of methyl phthalate or the Δ^1-ester is *cis*-methyl hexahydrophthalate. The result is independent of the pressure of hydrogen (1–200 atmospheres) and the concentration of the substrate (0.05–1.0 mole per liter). Methyl Δ^2-cyclohexenedicarboxylate yields the same result at about 1 atmosphere of hydrogen, but some of the *trans*-methyl hexahydrophthalate (6 ± 2%) is formed at a pressure of 130 atmospheres. None (within 2%) of the isomeric unsaturated ester is found at the half point of reduction of either the Δ^1-

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[2] Presented before the division of Organic Chemistry at the 133rd National Meeting of the American Chemical Society, San Francisco, Calif., April, 1958. Abstracted from the M.S. thesis of George S. McCaleb, University of Arkansas, January, 1958.

[3] S. Siegel and M. Dunkel, "Advances in Catalysis," Vol. IX, edited by A. Farkas, Academic Press, Inc., New York, N. Y., 1957, p. 15.

[4] R. L. Burwell, Jr., *Chem. Revs.*, **57**, 895 (1957).

[5] I. Horiuti and M. Polanyi, *Trans. Faraday Soc.*, **30**, 1164 (1934).

[6] R. P. Linstead, *et al.*, This Journal, **64**, 1985 (1942). See, also, A. A. Balandin, *Z. physik. Chem.*, **B2**, 289 (1929); *C. A.*, **23**, 2872 (1929); and "Advances in Catalysis," Vol. X, edited by D. D. Eley, W. G. Frankenburg and V. I. Komarewsky, Academic Press, Inc., New York, N. Y., 1958, pp. 96–129.