

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TENNESSEE, KNOXVILLE 16, TENNESSEE]

Reactions of Metal-Ammonia Solutions. III. Kinetics, Isotopic Exchange and Fractionation in the Reactions of Sodium and Ethanol in Tritiated Ammonia

BY EUGENE J. KELLY,^{1a} HENRY V. SECOR,^{1b} CHARLES W. KEENAN^{1c} AND JEROME F. EASTHAM^{1c}

RECEIVED OCTOBER 7, 1961

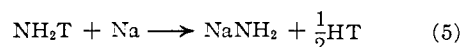
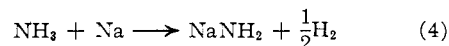
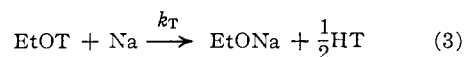
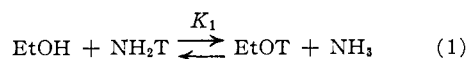
Detailed techniques and apparatus are described for forming solutions of metals and other reactants in ammonia labeled with tritium, quantitatively collecting gas evolved from these solutions, and radioassaying this evolved gas. When a proton donor (ethanol) is mixed with a metal (sodium) in tritiated ammonia, five reactions which may occur (*cf.* equations 1-5) involve isotopic exchange between solvent and proton donor and attack of electrons on each to liberate hydrogen or tritium. With the experimental data collected and mathematical expressions derived, it is shown that exchange of tritium between ammonia and ethanol as a proton donor is instantaneously fast relative to attack of electrons on the alcohol, and that isotopic fractionation, *i.e.*, relative rates of hydrogen (2) and of tritium (3) liberation, changes as the liberation reaction proceeds. The interpretation of this change in fractionation, that it is a consequence of a change in the nature of the alcohol, is consistent with the finding that the kinetic order of the hydrogen liberation changes after 25% reaction of the donor. This reaction begins by a process (initial 25% of reaction) whose rate is first order in alcohol but independent of the metal concentration, and then becomes a process which is first order in each reactant. Rate constants of these processes are determined and the mechanism of the liberation reaction 2 discussed.

Since Weyl² initiated the study of solutions of metals in ammonia, this system has had a unique fascination for the chemist. This fascination centers on the fundamental particle in chemistry the electron, for metal-ammonia systems apparently constitute a true solution of electrons. Despite extensive study, particularly by physical means, the exact nature of this solution of electrons is not known. The known physical data, as well as the chemical reactions of the system, have been reviewed periodically.³ Conspicuous by its absence from such reviews, however, is any kinetic analysis of the reactions of electrons in ammonia.

With the belief that kinetic analysis of the reactions of electrons in ammonia would assist in understanding their physical nature and might extend the chemical utility of these solutions, we have determined the rates of several simple reactions of alkali metals in ammonia.⁴ It has proved useful to include in these determinations a study of the effect of replacing one reactant, hydrogen, with its radioactive isotope, tritium; *i.e.*, to measure certain kinetic isotope effects.

The first reaction investigated was the liberation of hydrogen by a metal, sodium, from a weak acid, ethanol, in ammonia. This rather simple reduction is of considerable practical significance because so many utilitarian reactions of other substrates with metals in ammonia require the presence also of an alcohol.^{3c} In order to study the effect on this reduction of replacing the active hydrogen in alcohol with tritium, it was necessary to consider the exchange of active hydrogen between alcohol and ammonia. Finally, in a metal-ammonia-alcohol system, liberation of hydrogen from ammonia itself can occur and had to be considered. The various possible reactions of the sodium-am-

monia-ethanol system containing tritium are symbolized by equations 1-5, in which the symbol $1/2$ HT is used to represent tritium atoms in labeled hydrogen.



Previous work on the liberation reaction 2 was reported about forty years ago.⁵ Chablay studied the reactions of various metal-ammonia solutions with several alcohols.^{5a} Although he gave no specific data, Chablay stated that calcium and lithium each reacted more vigorously than other alkali and alkaline earth metals and that in general the rate of reaction varied with the nature of the alcohol in the order: primary > secondary > tertiary. He suggested that with certain ratios of ammonia to alcohol for the reaction, insoluble complexes were formed between the alcohol and its alkoxide salts. Kraus and White studied the specific reaction of sodium and ethanol in ammonia and reported that the reaction was "vigorous" at first, but rapidly slowed down, with the result that after 2.5 hr., the reaction had gone to only 70% completion.^{5b} White, Morris and Anderson also studied this reaction of sodium with ethanol and suggested that during the course of the reaction a complex having the formula EtOH·EtONa may be formed.^{5c} The report by Chablay was far more extensive than that of the other early authors, but all of the early work was of a qualitative nature.

To study reactions 1-5, we used an apparatus (Fig. 1) which provided for the rapid formation of a solution containing known initial concentrations of the reactants at the boiling point (-33.4°)

(5) (a) E. Chablay, *Ann. Chim.*, [9] **8**, 145 (1917); (b) C. A. Kraus and G. W. White, *J. Am. Chem. Soc.*, **45**, 768 (1923); (c) G. W. White, A. B. Morrison and E. Anderson, *ibid.*, **46**, 961 (1924).

(1) (a) Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee; (b) Chemetron Corporation, Newport, Tennessee; (c) Department of Chemistry, University of Tennessee, Knoxville, Tennessee.

(2) W. Weyl, *Ann. Physik*, **121**, 601 (1864).

(3) Recent reviews include (a) W. L. Jolly, "Progress in Inorganic Chemistry," Vol. I, Interscience Publishers Inc., New York, New York, 1959, p. 235; (b) M. C. R. Symons, *Quart. Revs.*, **13**, 99 (1959); and (c) A. J. Birch, *ibid.*, **12**, 17 (1958).

(4) Papers I and II in this series appeared in *J. Am. Chem. Soc.*, **81**, 6523 (1959), and **82**, 1831 (1960). The findings in the present paper were first presented at the 136th Meeting, Am. Chem. Soc., Atlantic City, New Jersey, 1959, abstr. p. 17-N.

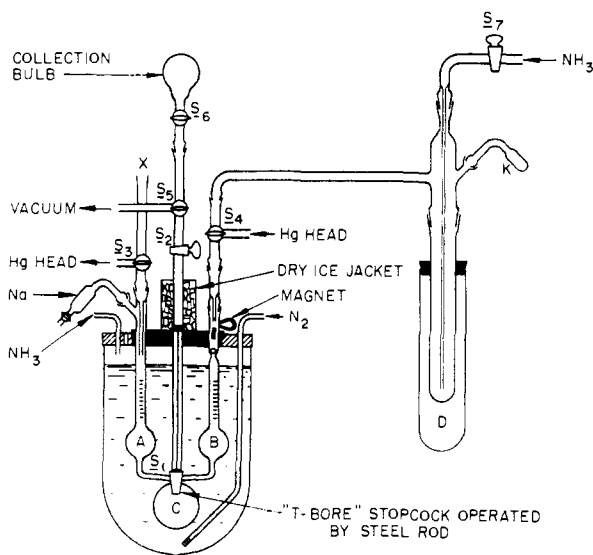


Fig. 1. Apparatus.

of the solvent in a closed system. This paper reports: (i) the details of how data on the rates of liberation of hydrogen and of tritium were collected, (ii) the application of a derived relationship between these rates to help reveal the mechanism of the liberation reaction 2, (iii) an evaluation of the rate of isotopic exchange 1 relative to the liberation reaction and (iv) a kinetic analysis of the liberation reaction (2).

Experimental

Reagents.—Commercial Solvents Corporation absolute ethanol was treated with magnesium and fractionally distilled directly into the reservoir of a carefully dried micropipet which was especially constructed to allow its use in delivering 0.5- to 1.0-g. portions of the alcohol into small dry glass bulbs through their capillary necks in an atmosphere of nitrogen. The bulbs, which were virtually filled by alcohol, were sealed, weighed and stored in a vacuum desiccator.⁶

Small cubes of about 0.1 g. each of reagent grade sodium (from the General Chemical Division of Allied Chemical and Dye Corporation) were cut from the interior portion of a lump of the metal under mineral oil. The desired amount of the metal sample was approximated by transferring an appropriate number of the cubes, lightly coated with mineral oil, into dry xylene in a weighing bottle. A special addition tube, used on the reactor described in the next section, was carefully cleaned, dried, evacuated, weighed and filled with helium. Cubes of alkali metal were quickly transferred from the weighing bottle to the addition tube. The tube was again evacuated (to remove the xylene and to degas the metal surface) and weighed (to obtain an accurate value for the weight of the metal sample). The addition tube containing the metal was then filled with gaseous ammonia and attached to the reactor.

The unlabeled ammonia was E. I. du Pont de Nemours Co. highest purity anhydrous grade ammonia. Tritium labeled ammonia was obtained from the Oak Ridge National Laboratory where it was prepared by the reaction of magnesium nitride with tritiated water.⁷ Just before use as solvent for a reaction, the ammonia was distilled twice, once from its storage cylinder and once from alkali metal in the manner described in the next section.

Apparatus.—The reactor system used for this work (Fig. 1) is a modification of one previously reported.⁸

(6) Details of the equipment and procedure used for preparation of the bulbs of alcohol are given by E. J. Kelly, Ph.D. Thesis, The University of Tennessee, 1959, p. 57.

(7) The authors are indebted to Dr. Percy Staats for making the labeled ammonia available to us.

Bulb C served as the actual reaction chamber. This bulb had a volume of 55 ml., and its neck, terminating at stopcock S₂, held an additional 45 ml., giving a total chamber volume of 100 ml. A removable jacket for Dry Ice was placed around the neck just below stopcock S₂. Bulb C was connected to burets A and B via a 4-mm., "T-bore" stopcock S₁, which was operated by a knob connected to the stopcock by a steel rod. A No. 15 rubber stopper, bored to accommodate the steel rod, buret and neck of the reaction chamber, served to structurally reinforce the apparatus and to hold it in a large unsilvered Dewar flask of coolant liquid ammonia.

Buret A was equipped with an addition bulb, for alkali metal, and a constriction in buret B served to hold in place a sealed bulb of alcohol. Each buret had a calibrated volume of 25 ml. and terminated in joints which connected them to separate manostats and to separate ammonia purification reactors similar to D. The latter had volumes of 100 ml. each, were equipped with addition bulbs K, and were mounted in unsilvered Dewar flasks. The manostats⁹ enabled the operator to both observe and control pressures in the burets.

Stopcock S₅ connected the top of the reaction chamber to a vacuum line and to gas collection bulbs which had volumes of 125 ml. each and were used either in trains of four to eight bulbs, or singly (Fig. 1). Stopcock S₁ was lubricated with Dow-Corning "Hy-Vac" silicone lubricant. The other stopcocks and joints were lubricated with Apiezon-T.

Reaction Procedure.—Prior to each experiment, the entire apparatus was disassembled, carefully cleaned and relubricated. A fragile, sealed glass bulb of alcohol (0.5 to 1.0 g.) was placed on the constriction in buret B and a glass-coated, magnetic iron bar was placed on top of the bulb. The apparatus was assembled, "baked-out" under vacuum with infrared lamps, cooled under vacuum and filled with gaseous ammonia to a pressure about 100 mm. above atmospheric. A temporary plug in the side arm of buret A was removed and the addition bulb containing sodium (0.2 to 1.0 g.) quickly attached. At the same time, additional bulbs K, each containing about 2 g. of metal, were attached to the ammonia purifiers. The entire system was again evacuated.

The purifiers were immersed in Dry Ice-acetone baths and approximately 30 ml. of liquid ammonia distilled into each of them from storage tanks. In most experiments, at least one tank was of ammonia labeled with tritium. Alkali metal was added to the purifiers from addition bulbs. While the purification process was taking place, the large Dewar flask was filled with liquid ammonia which was maintained at $-33.4 \pm 0.1^\circ$ by bubbling nitrogen through it slowly. Any hydrogen produced in the system by the purification process was removed by opening the entire system (A, B, C, D) to the vacuum line several times, for a fraction of a second each time. Burets A and B and chamber C were then separated from one another by rotating stopcock S₁.

The coolant baths were removed from the purifiers and, after about 15 ml. of liquid ammonia had distilled into each buret, the addition tube on buret A was rotated to add the alkali metal, and the bulb of alcohol in buret B was crushed by moving a horseshoe magnet outside the buret. Distillation of the ammonia was continued until each buret contained 25.0 ml. of solution. An evacuated collection bulb was attached as shown in the drawing, with stopcock S₅ connecting the bulb to stopcock S₂ on the reactor. Dry Ice was packed in the jacket on the neck of the reaction chamber and the pressure in the burets equalized at 100 mm. of mercury above atmospheric pressure.

Stopcock S₁ was then opened three ways, connecting the two burets with the evacuated reaction chamber. In a total time of about 0.1 second, the reactant solutions jetted into the reaction chamber. Stopcock S₁ was immediately closed.

To remove hydrogen liberated in the closed glass reactor (bulb C) at any desired time, stopcock S₂ was opened and then stopcock S₆ on the evacuated gas collection bulb was opened for a fraction of a second and then closed. Stopcock S₂ was then closed and the collection bulb replaced. Rather

(8) J. F. Eastham and D. R. Larkin, *J. Am. Chem. Soc.*, **81**, 3652 (1959). The drawings in this reference may assist the reader in interpreting Fig. 1.

(9) See G. W. White, *ibid.*, **45**, 780 (1923). For the drawing of a similar manostat.

than a single collection bulb, a train of bulbs was employed during the early stages of a reaction to enable fast sampling. Except in the early stages of the reaction, when it was left filled constantly, the Dry Ice condenser on the reaction chamber was filled shortly before taking each sample and emptied immediately thereafter.

Product Analysis.—For analysis of its contents, each collection bulb was in turn attached to a vacuum line which provided for freezing, transferring, mixing and metering gases. Ammonia was separated from hydrogen and tritium by freezing at liquid nitrogen temperature. After being transferred from the frozen ammonia *via* a Toepler pump into a gas buret, the total volume of hydrogen and tritium was measured. Aliquots of this volume were transferred to an ionization chamber, which was then filled with hydrogen and assayed for tritium content by the ion current method.¹⁰

Before determination of its activity, the ammonia, which had been removed from the collection bulb and frozen, was exhaustively evacuated, allowed to come to room temperature and expanded into a gas buret. Aliquots of the gaseous ammonia were transferred to the ionization chamber, which was then filled with hydrogen and assayed for tritium content by the ion current method. To make these assays comparable to those of the hydrogen, it was necessary to correct the ion current observed with ammonia for (a) the per cent ammonia in the counting gas and (b) the time the ammonia had been in the chamber before counting. Because the ionization potential of ammonia is significantly lower than that of hydrogen,¹¹ correction a was anticipated and easily made by means of a calibration curve based on the determination of the ion current produced by a constant amount of tritium in various mixtures of ammonia and hydrogen. Correction b was not expected; we have tried brass, gold-plated brass and stainless steel ionization chambers but have been unable to find an ionization chamber which will consistently yield a constant ion current from a small amount of tritiated ammonia in a hydrogen counting gas. It is believed that the slow decrease in ion current with time is caused by the adsorption of ammonia on the metal parts inside the chamber.¹² To correct for this decrease, the ion current from each ammonia aliquot was re-determined at measured time intervals and the data plotted so that extrapolation revealed the ion current at time zero, *i.e.*, before any adsorption occurred. After corrections a and b, the ammonia assay values could be compared directly with those of hydrogen.¹⁰

Alternate Apparatus.—Although most of the data on equations 1–5 were collected using the three-tube reactor system, described above, in a few runs it was advantageous to use a one-tube reactor. This latter reactor was similar to that in Fig. 1 without burets A and B and similar to one previously described.¹³ To prepare for a run, a solution of alkali metal in ammonia was prepared in the reactor, in which a sealed bulb of alcohol had been placed. To initiate reaction, the alcohol bulb was crushed and the reactants vigorously stirred by the introduction of a stream of gaseous ammonia at the bottom of the tube. Hydrogen was removed and analyzed as described above.

Tests and Evaluation of Procedure.—The apparatus and technique used were extensively tested. For example, after putting 50 ml. of liquid ammonia into bulb C (the reactor proper in Fig. 1), known volumes of hydrogen were introduced into the reactor and then collected in evacuated bulbs. When two collection bulbs were used, the reactor was opened to the first bulb and then to the second bulb.

(10) K. E. Wilzbach, A. R. VanDyken and L. Kaplan, *Anal. Chem.*, **26**, 880 (1954). Although the absolute value of radioactivity may be slightly in error due to the difficulty in absolute standardization of tritium by ionization counting, the relative values reported are self-consistent because each was determined with the same counting gas in the same ion chamber and compared with the same secondary standard.

(11) A. Eucken (Ed.), "Landolt-Börnstein, Zahlenwerte und Funktionen aus Physik, Chemie, Astronomie, Geophysik, Technik," 6th Ed., Vol. I, Part 3, Springer-Verlag, Berlin, 1960, pp. 359–363.

(12) Evidence for this is the fact that all of our chambers give a constant ion current when relatively small amounts of tritium-hydrogen gaseous mixtures are added to the chamber filled with unlabeled ammonia as a counting gas. Here some adsorption of the ammonia should not alter the ion current appreciably.

(13) W. C. Johnson and W. C. Fernelius, *J. Chem. Ed.*, **6**, 445 (1929).

The gas was always quantitatively removed by the first bulb; no hydrogen gas could be found in the second bulb. Such was the case even when as much as 40 ml. of hydrogen was present in the reactor.

Tests were also made to ascertain that molecular hydrogen, in contact with reaction solution, did not undergo isotopic exchange. At the end of a typical (excess) alkali metal-ethanol reaction in labeled ammonia, unlabeled hydrogen was introduced into the reaction and left for several hours. Upon removal, it was found that the hydrogen had gained no activity. After being radioassayed, occasionally samples of the hydrogen collected from a run were spot checked by combustion analysis to be certain that no air was present. The purity of the ammonia collected from a run was also spot checked by gas chromatography. The purity of these collected gases indicated that the reaction in progress, the removal of product from that reaction, and the product analyses, all proceeded without atmospheric contamination.

The success with which our reactor system allowed preparation and maintenance of contaminant-free reactants could be qualitatively observed after all of the alcohol in a run had reacted and excess alkali metal remained to react with the ammonia equation (4). The rate of reaction 4 generally increased lithium < sodium < potassium.¹⁴ With sodium it was routinely possible to maintain a reaction solution which decomposed no more than about 1% per day; in some runs this decomposition was only one-tenth of 1% per day. Correction of the data on the alcohol-metal reaction for competition by the ammonia-metal reaction is discussed subsequently. Routinely in runs with lithium, reaction 4 was too slow to observe. In some runs with lithium, after the alcohol had reacted, excess metal was so dilute, <10⁻⁶ M, as to give only the faintest blue coloration to the ammonia, yet this solution could be maintained indefinitely (at least for several days) with no apparent loss of the color (metal).

Variability in apparent fractionation and actual rate of the metal-ammonia reaction was in contrast to the reproducibility of findings for the metal-alcohol reaction. Measured rate constants for hydrogen liberation from alcohol by metal were duplicable (*cf.* Fig. 4 and related discussion) and fractionations by this reaction, although a function of its percentage completion, were the same from one run to another (*cf.* Fig. 3).

Treatment of Data.—The various runs made involved changes in initial concentration of reactants from 0.2 to 1.0 M in sodium and from 0.2 to 0.4 M in alcohol and changes in the ratio of reactants (sodium and alcohol) from 1:1 to 4:1. The type of data obtained directly from our experiments are shown in the first three columns of Table I. In this run ethanol and sodium were each dissolved initially in 25 ml. of labeled ammonia, 0.358 $\mu\text{C./ml.}$ at STP,¹⁶ so that upon mixing, the concentration of sodium (0.96 M) was approximately three times that of the alcohol. Reaction of the excess metal with the solvent is indicated by the data after about 8 hr., when all of the alcohol had reacted and when both the volume of hydrogen liberated per hour and the radioactivity of the liberated hydrogen had dropped to a relatively constant low level. Although the rate of hydrogen evolution by the metal-ammonia reaction, 0.3 ml. per hour in this run, was almost insignificant relative to the rate of metal-alcohol reaction, other experiments have shown that this competing side reaction 4 was occurring continuously in our experiments.^{14,16} Therefore, before further treatment, data like those in Table I were corrected for the metal-ammonia reaction. Thus, for this run, each volume of hydrogen collected was decreased by the product of 0.3 ml./hr. and the time over which it was collected. In a similar manner, the radioactivity liberated

(14) While it is generally accepted that the rate of decomposition of metal-ammonia solutions is controlled by trace contamination, to our knowledge no experimental technique has yielded an ammonia solution of sodium or potassium which undergoes no decomposition. Few reports on these solutions give a quantitative evaluation of their stability.

(15) The units of radioactivity used throughout are microcuries and gaseous volumes are corrected to STP.

(16) For example, in runs with the one-tube reactor, the rate of reaction 4 was observed to be about the same before addition of the alcohol to the metal-ammonia solution as it was after all of the added alcohol had reacted.

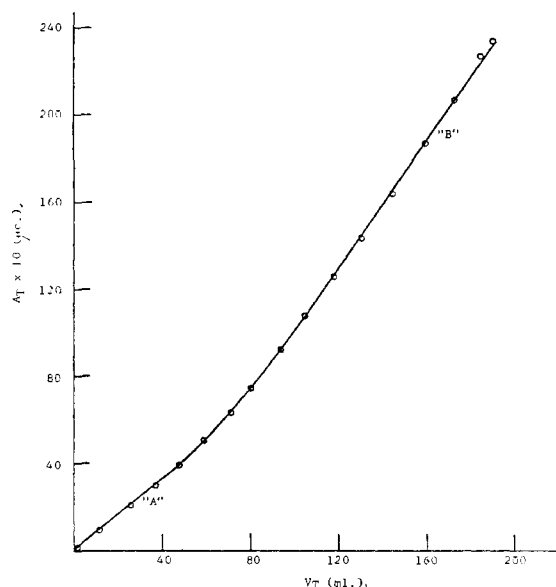


Fig. 2.—Change in activity of hydrogen liberated as a function of volume liberated. Data are from Table I.

was decreased by 0.006 $\mu\text{c.}/\text{hr.}$ ¹⁷ The corrected data, which represent only the metal-alcohol reaction (equations 2 and 3), are recorded in the last two columns of Table I in terms of the total volume of hydrogen liberated, V_t , and total activity of that hydrogen, A_t , after successive periods of reaction t .

TABLE I
CHARACTERISTIC EXPERIMENTAL DATA

Time (t) after which product taken	Volume of product (ml.)	Activity of product ($10^2 \times \mu\text{c.}/$ ml.)	V_t (ml.)	A_t ($\mu\text{c.}$)
~3 sec.	2.27	6.54	2.27	0.15
10 sec.	10.10	8.00	12.37	0.96
30 sec.	14.39	7.99	26.76	2.11
1 min.	10.84	8.35	37.6	3.01
2 min.	10.74	8.86	48.3	3.96
4 min.	11.48	9.61	59.8	5.06
8 min.	11.91	10.65	71.7	6.23
12 min.	9.15	12.24	80.8	7.45
20 min.	13.21	13.35	94.0	9.22
28 min.	11.52	13.71	105.5	10.80
40 min.	12.88	14.01	118.3	12.6
60 min.	12.38	14.35	130.6	14.3
80 min.	14.14	14.37	144.6	16.4
2 hr.	15.52	14.85	159.9	18.7
3 hr.	13.34	15.19	173.0	20.7
5 hr.	13.02	15.39	185.4	22.7
8 hr.	5.65	13.33	190.1	23.4
16 hr.	2.28	3.44	190.1	23.4
24 hr.	2.62	1.81		
32.1 hr.	2.40	1.80		
42.5 hr.	3.01	2.20		

Discussion

Development of V_t versus A_t Plots.—In analyzing the experimental data, it has proved most useful to make plots of the volume V_t of hydrogen

(17) It must be emphasized that these corrections were quite small—so small that, even if one questions the precision in measuring the extent of metal-ammonia reaction, this does not bring into question the precision of measuring the extent of metal-alcohol reactions. For example, in Table I it is seen that during the first hour of reaction, when the correction was 0.3 ml., the total volume of hydrogen liberated was 130.6 ml.

liberated in a given reaction time *versus* the activity A_t of tritium liberated in the same time, *cf.* Fig. 2. To illustrate the utility of such plots, let it be assumed that during some fraction of the over-all reaction, the rates of formation of hydrogen (H_2) and labeled hydrogen (HT) are described by the following equations.¹⁸

$$\frac{2d[\text{H}_2]}{dt} = \frac{-d[\text{EtOH}]}{dt} = k_{\text{H}}[\text{EtOH}]^b[\text{Na}]^a$$

$$\frac{d[\text{HT}]}{dt} = \frac{-d[\text{EtOT}]}{dt} = k_{\text{T}}[\text{EtOT}]^b[\text{Na}]^a$$

Then one may write equation 6, in which α is the isotope effect or fractionation factor, $k_{\text{H}}/k_{\text{T}}$.

$$\frac{d[\text{H}_2]}{d[\text{HT}]} = \frac{\alpha}{2} \left(\frac{[\text{EtOH}]}{[\text{EtOT}]} \right)^b \quad (6)$$

Before beginning our experimental work, we thought it likely that the exponent b would be unity and that the ratio $[\text{EtOH}]/[\text{EtOT}]$ in this equation would be a reaction constant. Concerning this ratio, one may reason that if the exchange equilibrium 1 were effectively instantaneous relative to the liberation reaction 2 and 3, then

$$K_1 = \frac{[\text{NH}_3][\text{EtOT}]}{[\text{NH}_2\text{T}][\text{EtOH}]}$$

$$\frac{[\text{EtOH}]}{[\text{EtOT}]} = \frac{[\text{NH}_3]}{K_1[\text{NH}_2\text{T}]} \quad (7)$$

In other words, although fractionation would tend to change the $[\text{EtOH}]/[\text{EtOT}]$ ratio, the large excess of solvent¹⁹ with its constant $[\text{NH}_3]/[\text{NH}_2\text{T}]$ ratio could act as a "reservoir" or "buffer" to maintain $[\text{EtOH}]/[\text{EtOT}]$ as a constant. Substitution of equation 7 in equation 6 and integration yields.

$$(\text{H}_2) = \frac{\alpha}{2} \frac{[\text{NH}_3]}{K_1[\text{NH}_2\text{T}]} (\text{HT}) + C \quad (8)$$

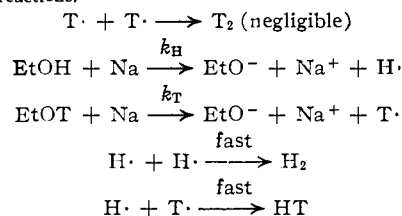
In equation 8, C must be zero, and (H_2) and (HT) may be expressed in terms of the total volume V_t and total activity A_t respectively, of the liberated gas, the volume of (HT) being negligible. Equation 8 is then transformed into equation 9, in which A_{NH_3} represents the specific activity

$$V_t = \frac{\alpha A_t}{2K_1 A_{\text{NH}_3}} = \frac{\alpha A_t}{2/3 A_{\text{NH}_3}} \quad (9)$$

of the solvent ammonia, and K_1 is assumed to have its statistical value of $1/3$.²⁰

Equation 9 indicates that a plot of V_t versus A_t should be linear. The slope of such a plot and

(18) These equations could apply, for example, to the following system of reactions.



(19) In every experiment the gram atoms of protons available to equilibrium 1 from the solvent ammonia were greater than the available protons in the alcohol by a factor of several hundred or more.

(20) The transformation of equation 8 into equation 9 is based on these facts: (i), since $[\text{NH}_2\text{T}] \ll [\text{NH}_3]$, the ratio $[\text{NH}_2\text{T}]/[\text{NH}_3]$ is proportional to the specific activity of the ammonia, A_{NH_3} ; (ii) since $[\text{HT}] \ll [\text{H}_2]$, the ratio $[\text{HT}]/[\text{H}_2]$ is proportional to A_t/V_t ; (iii) the proportionality constant for (i) and (ii) is the same.

knowledge of solvent activity would allow one to calculate a fractionation factor α for reactions 2 and 3. Deviation of the V_i versus A_i plot from linearity could indicate either that α changes because of a change in the mechanism of the liberation reaction as it proceeds or that the exchange reaction is not fast enough to maintain isotopic equilibrium 1 between ethanol and solvent.

In Fig. 2 there are plotted data (Table I) from a run in which the ethanol was equilibrated with the labeled solvent before being mixed with the metal; *i.e.*, both burets of the reactor initially contained labeled solvent. The plot is linear initially (region "A" in Fig. 2), when the liberation reaction is fastest, and after a change in slope it becomes linear again (region "B" in Fig. 2). The change in slope is not due to slowness of exchange reaction (*vide infra*); we interpret the change as indicating a change in mechanism for the liberation reaction.

Relative Rates of Exchange and Liberation Reactions.—Conclusive proof of the rapidity of exchange *via* equilibrium 1 has been obtained from experiments in which the equilibrium condition was approached from opposite sides. Table II shows the specific activity of the first hydrogen liberated from runs in which the alcohol solution (a) initially contained no tritium and (b) initially contained more than the equilibrium activity. In the first run shown, the alcohol was dissolved in unlabeled ammonia and the metal in tritium-containing ammonia; upon mixing, any tritium (activity) which appeared in the liberated hydrogen had to arise because exchange reaction 1 occurred before the liberation reactions 2 and 3. In this run (a, Table II), the very first hydrogen collected had a specific activity of $6.4 \times 10^{-3} \mu\text{c./ml.}$ The second run shown was identical with the first except that the initial position of labeling was reversed, alcohol in labeled solvent and metal in unlabeled solvent; upon mixing, the exchange reaction would tend to decrease the activity of liberated hydrogen. The activity of the hydrogen, $6.1 \times 10^{-3} \mu\text{c./ml.}$, first collected in this run (b, Table II), was es-

TABLE II
ACTIVITY OF INITIAL HYDROGEN AS A FUNCTION OF STARTING WITH LABELED OR UNLABELED ALCOHOL

Run ^a	Initial solvent for		Activity ($\mu\text{c./ml.}$)	First hydrogen collected
	Na	EtOH		Per cent. of total to be liberated
a	NH ₂ T	NH ₃	0.0064	2.41
b	NH ₃	NH ₂ T	.0061	0.23
c	NH ₂ T	NH ₂ T	.069 ^a	1.19
d	NH ₂ T	None ^b	.0088	2.18

^a In runs a, b and d the specific activity of the solvent after mixing of the reactant solutions was, in each case, approximately $0.04 \mu\text{c./ml.}$ In run c, the data for which are shown in Table I, the solvent activity was ten times greater. ^b Bulb of alcohol crushed under the solution of metal in the one-tube reactor.

entially identical with that found in the first run. These two runs, in which the exchange equilibrium (1) was initially displaced completely to the left and far to the right, respectively, may be compared with a third run (c, Table II) in which

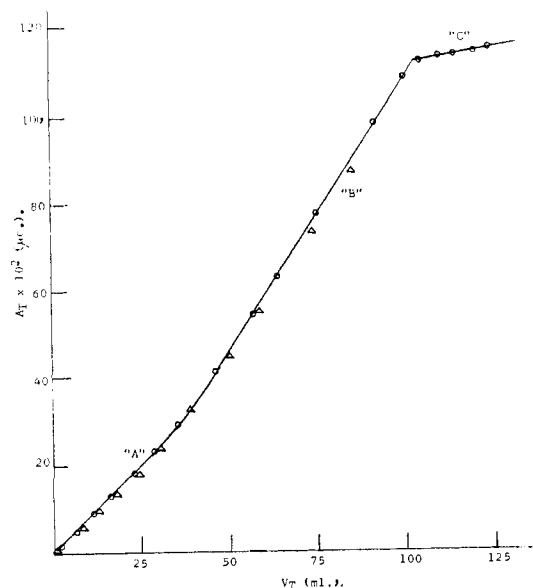


Fig. 3.—Uncorrected data, plotted as in Fig. 2; points represented by O from run initiated with no activity in the alcohol; points represented by Δ from run with excess activity initially in the alcohol solution.

equilibrium 1 was established before mixing. In each run the first sample of hydrogen, collected virtually as soon as the reactants were mixed, had an activity of $(6.5 \pm 0.4) \times 10^{-3} \mu\text{c./ml.}$ ²¹

The constancy of the activity of the first hydrogen liberated, regardless of the initial position of equilibrium 1, is taken as proof that the exchange is instantaneous relative to hydrogen liberation, *i.e.*, that the proton donor is always maintained at isotopic equilibrium with the solvent regardless of fractionation of the isotopes from this donor by reaction. In one run (d, Table II) the alcohol was actually added directly (neat) with vigorous agitation to a solution of sodium in labeled ammonia. Even in this case the activity of the first hydrogen liberated, $8.8 \times 10^{-3} \mu\text{c./ml.}$, indicated that exchange was complete.²²

Interpretation of Change in Slope of V_i versus A_i Plots.—As an expected consequence of this rapid maintenance of equilibrium, plots V_i versus A_i for runs a and b do not show opposite changes in slope. In Fig. 3, the circles, which are the uncorrected data from run a (initially no activity in the alcohol), show the same change in slope as the triangles, which are data from run b (initially excess activity in the alcohol) and this change in slope is the same as that in Fig. 2 (initially equilibrium activity in the alcohol). The change in

(21) To make this comparison the activity of the hydrogen from run c was divided by 10, *cf.* footnote a on Table II.

(22) Unfortunately, the time required for liberation of the first samples of hydrogen (one second or less) could not be accurately measured during the experiments. However, with the rate equation and constant for this initial liberation reaction, one may calculate the time required for a given percentage reaction. Thus, knowing that in run b (Table II) the first sample of hydrogen constituted the first 0.23% of the liberation reaction, one can estimate the *maximum* time required for the exchange reaction. We may assume that the exchange reaction was 90% complete by the time 10% of that first sample had been liberated. If the exchange is first order in alcohol, as is the liberation reaction, then the exchange must have a half-life of less than 10^{-3} sec.

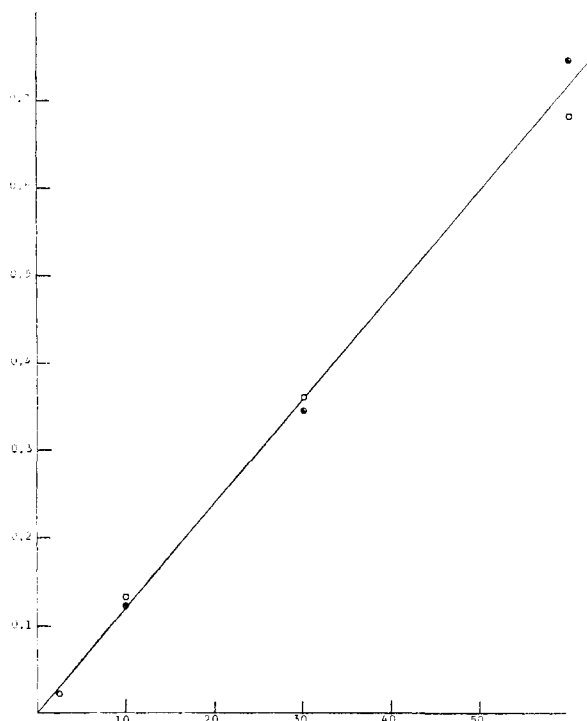


Fig. 4.—First order plot according to equation 11: $\log V_{\infty}/(V_{\infty} - 4V_t)$ vs. time minutes. Data from run with sodium to alcohol ratio of 2.8 (Table I) represented by \ominus , and from run with sodium to alcohol ratio of 1, by \bullet .

mechanism of hydrogen liberation indicated by this change in slope suggests that *as reaction proceeds, there is a change in the nature of the species from which hydrogen is liberated.* Although it may be the alcohol from which hydrogen is initially liberated to give the linear portion "A" of the plots, reaction products could combine with unreacted alcohol to give a new species from which hydrogen is liberated (with a different fractionation factor) to give the linear portion "B" of the plots. In all runs the first linear portion persists until approximately 25% of the hydrogen from alcohol has been liberated and the second linear portion covers the last 50% of hydrogen from alcohol.

The influence of a change in the proton donating species on the activity of the hydrogen liberated is shown clearly by the final portion, "C," of the plot in Fig. 3.²³ After all of the alcohol in the system had reacted, liberating approximately 100 ml. of hydrogen, the slow reactions 4 and 5 of ammonia with excess metal continued to liberate hydrogen. The specific activity of hydrogen liberated from ammonia was considerably less than that from alcohol, hence the decrease in slope shown in region "C" of Fig. 3. (The slope is inversely proportional to the fractionation factor of the particular species reacting.)

Kinetics of the Initial Liberation Reaction.—The concept that hydrogen liberated by the alcohol

(23) So that the continuing reaction of metal and ammonia would appear in Fig. 3, the data used in plotting Fig. 3 were not corrected for the metal-ammonia reaction in the manner discussed in the Experimental section. Another use of this type of plot is that the intersection of portion "B" and "C" may be used to accurately determine the end-point of the metal-alcohol reaction.

comes from at least two different species is supported by kinetic analysis of this reaction. It is not possible to fit the experimental kinetic data for the total reaction 2 to any simple monomial rate expression because the reaction decelerates so sharply as it proceeds. While the first one-fourth of the hydrogen was always liberated in about one minute, the third one-fourth of the reaction would require about 1 hr. However, plots of the fraction reacted *versus* time, using data from several runs in which initial reactant concentrations were widely varied, do reveal that the initial fast rate of hydrogen liberation from ethanol by sodium is insensitive to changes in the metal concentration. It appears from these plots that the initial fast reaction is over by the time 25% of the alcohol is consumed, corroborating the suggestion based on V_t *versus* A_t plots that the nature of the reactant proton donor changes after 25% reaction.

From these observations it appears that initially reaction 2 is first order in alcohol but that each molecule of alcohol which reacts accounts somehow for the removal of four molecules of alcohol from availability in this initial fast reaction. The initial rate of the reaction would be given by equation 10

$$-\frac{d[\text{EtOH}]}{dt} = k_1[\text{EtOH}] \quad (10)$$

which, if the assumptions are correct, could be integrated to yield

$$\ln \frac{V_{\infty}}{V_{\infty} - 4V_t} = k_1 t \quad (11)$$

The fit of experimental data to equation 11 is quite good, probably fortuitously so, considering the possible imprecision in time measurements while the reaction is proceeding so rapidly. Plotted in Fig. 4 are the data covering the first 20% of two runs in which the initial sodium concentrations differ by a factor of about 4. With the higher concentration of metal, the slope of the plot is slightly less, but from either run, the calculated rate constant (slope shown) is $1.65 \pm 0.04 \text{ min.}^{-1}$. With this rate constant (k_1), one may calculate that the first 12.5% of reaction ("half-life" of initial one-quarter of reaction) should require 25 sec. From seven runs involving sodium and alcohol (all for which we have data on the initial rate), we find the interpolated time required for 12.5% reaction to be $26.5 \pm 2.0 \text{ sec.}$ These runs involve variation of the initial sodium concentrations by a factor of over 5, and it was only in the runs at the higher metal concentrations that this "half-life" was as high as 26.5 sec.; in other words, the only effect observed from increasing the sodium concentration was to slightly decrease the initial reaction rate.

From slope "A" in Fig. 2 and equation 9, the fractionation factor α for this initial first order reaction is found to be 3.0.

Kinetics of the Terminal Liberation Reaction.—During the second 25% of the liberation of hydrogen from alcohol, the reaction does not appear to be of definite kinetic order, but for the last half of the reaction, the data fit a rate expression 12 which is first order in each of the reactants; *i.e.*, second order over-all. To put equation 12 into

$$-\frac{d(\text{EtOH})}{dt} = k_2 (\text{EtOH})(\text{Na}) \quad (12)$$

a form applicable to our data we have used: (i) a factor a , which is the proportionality constant between the concentration of a reactant and the volume of hydrogen available from complete reaction of a given amount of solution at that concentration, (ii) the symbol Na_0 for the volume of hydrogen equivalent to all of the sodium employed in a run and (iii) the equivalences $[\text{EtOH}] = a(V_\infty - V_t)$, $-d[\text{EtOH}] = ad(V_t)$ and $[\text{Na}] = a(Na_0 - V_t)$. Equation 12 then becomes

$$\frac{adV_t}{dt} = a^2k_2 (Na_0 - V_t)(V_\infty - V_t)$$

which upon integration yields

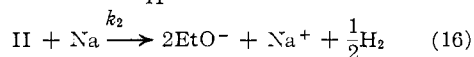
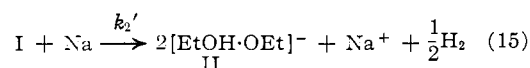
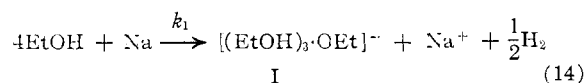
$$\ln \frac{(Na_0 - V_t)}{(V_\infty - V_t)} = a(Na_0 - V_\infty)k_2t + C \quad (13)$$

A plot, according to equation 13, of the data in Table I is shown in Fig. 5. The sharp decrease in rate as the reaction proceeds to 50% completion is apparent, but after 50% reaction (*i.e.*, after *ca.* 20 min.) the points satisfactorily define a straight line. From the slope of this line, and equation 13, one may calculate the second order rate constant k_2 , 1.41×10^{-2} liter mole $^{-1}$ min. $^{-1}$.

From slope "B" in Fig. 2 and equation 9, the fractionation factor α for this second order reaction is found to be 1.6. The fit of experimental data to equation 13 in Fig. 5 appears particularly good when one considers that at the last point on this plot the reaction of alcohol was about 98% complete.

A variety of other kinetic analyses of our data has been attempted,²⁴ but none, other than equations 11 and 13 for the initial reaction and terminal reaction, respectively, even approximately fit the experimental data.

Mechanism of the Alcohol-Metal Reaction.—The following consecutive, competitive reactions account for the total reaction 2



It is apparent that the product of reaction 2, the strongly basic ethoxide ion, greatly retards the reaction and does so effectively when there is only one mole of ethoxide ion per three of ethanol, *i.e.*, by the time the reaction is only one-quarter complete. This is rationalized in equation 14 by the formation of complex I, in which the three molecules of alcohol are proton bonded to one ethoxide ion. Initially, when no strong base is present, the reaction rate appears to be the rate of ionization of the alcohol, or at least the dissociation

(24) Although one can never be certain that every promising analysis has been tried, we attempted to test all probable ones. Analyses attempted include a variety of combination of orders with respect to both reactants, various steady state approximations for conceivable intermediates, inclusion of equilibrium ionization constants for the reactants and other standard treatments of kinetic data.

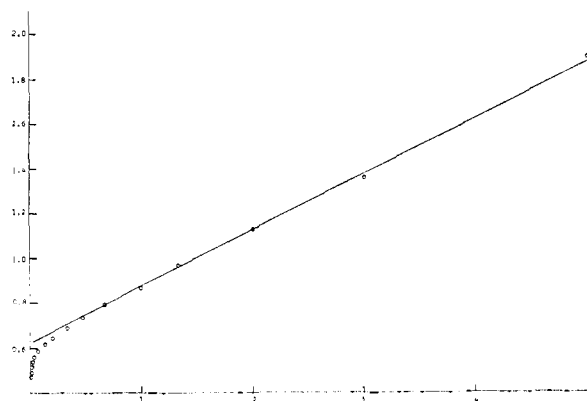
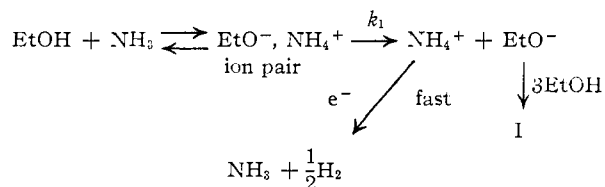


Fig. 5.—Second order plot according to equation 13: log $(Na_0 - V_t)/(V_\infty - V_t)$ vs. time in hours. Data from Table I.

of its ion pairs, as indicated in the second (rate-determining) step of the following scheme proposed as the mechanism for reaction 14



By this mechanism the rate of liberation of the first 25% of the hydrogen from an alcohol should be the same with other alkali metals; we have found the initial reaction rate of lithium with ethanol in ammonia to be the same as that of sodium.²⁵

The mechanism while the reaction proceeds from 25% to 50% completion must be left, for the present, as a moot question. One logical possibility, (direct reaction of complex I with electrons 15), would require that liberation of this second quarter of the hydrogen follow a rate equation like 12, but with a different second-order rate constant, k_2' . By whatever mechanism, by the time the reaction is 50% complete, there is available a quantity of ethoxide ion equimolar with the alcohol. It is suggested that these form a 1:1 complex (II) which is attacked by electrons in a bimolecular process to liberate the remaining available hydrogen as indicated in equation 16. The rate of this bimolecular process should differ (and does²⁶) according to which alkali metal is employed. Complexes like II are known to be formed by weak acids in solvents even more polar than ammonia.²⁶

Conclusions.—The different reactions which may occur when sodium and ethanol are mixed in tritium-labeled ammonia are established as having relative rates which decrease in the order: isotopic exchange (1), hydrogen liberation from alcohol (2)–(3) and hydrogen liberation from

(25) Kinetic analysis of data from the liberation of hydrogen from ethanol by lithium will be reported subsequently, along with fractionation factors for various of these liberation reactions.

(26) D. L. Martin and F. J. A. Rosoff (*Proc. Chem. Soc.*, **60**, (1959)) discuss the equilibrium $\text{HA} + \text{A}^- \rightleftharpoons \text{HA}_2^-$, where HA represents a weak acid and ion HA_2^- a complex similar to II. Others who have discussed the HA_2^- ion include H. V. Looy and L. P. Hammett, *J. Am. Chem. Soc.*, **81**, 3872 (1959). The specific complex II was at least suggested by the earliest work on reaction 2.⁵

ammonia (4)–(5). The maximum half-life of 10^{-2} sec. which we have estimated²² for the exchange is in agreement with the high rates estimated²⁷ for other comparable protolytic reactions. Our finding that reaction 2 decelerates so much is not unexpected; it has been known for some time that alkoxide ion slows the rate of the reaction of an alcohol with alkali metal. However, our quantitative evaluation of this deceleration, and its mechanistic interpretation, are new, and perhaps useful.

In effect our conclusion for hydrogen liberation from an electron–alcohol–ammonia system is as follows. When there is no base stronger than the solvent present, the alcohol produces ammonium ions (which are immediately reduced by electrons) more rapidly than electrons directly reduce the alcohol (or its ion pair). Strong base (e.g., alkoxide produced in the reaction) so complexes (proton bonds) the alcohol that its production of ammonium ions is sufficiently slow to allow direct reduction of the complex by electrons.

The quantitative effect of alkoxide on hydrogen liberation may be calculated with equations 11 and 13. For example, one interesting comparison is the time which would be required for 20% reaction of 0.1 *M* sodium with 0.1 *M* ethanol; first, initially

(27) R. A. Ogg, *Discussions Faraday Soc.*, **17** (1954); E. Grunwald, A. Lowenstein and S. Meiboom, *J. Chem. Phys.*, **27**, 630 (1957).

in pure ammonia and, second, initially with 0.1 *M* ethoxide ion in the ammonia. Reaction of 20% of the alcohol would, in the first experiment, require less than one minute; in the second, over 3 hr. In other words, addition of an equimolar amount of ethoxide ion to the ethanol would, in this experiment, increase the time for 20% reaction by a factor of about 200. Such knowledge as this might be of use in the reduction of other compounds by sodium and alcohol in ammonia, where it is desirable to avoid competition by reaction 2.^{3c}

Certainly competition by reaction 2 should be considered in the kinetic evaluation of any reactions of the alkali metals with other compounds in the presence of alcohol.²⁸ Also, our finding of a change in kinetic order after the initial 25% of reaction is of interest in connection with any "initial-rate" kinetic studies²⁹ which may involve alcohols and metals in ammonia.

Acknowledgment.—This research was made possible by Contract Number AT-(90-1)-1983 between The University of Tennessee and the U. S. Atomic Energy Commission.

(28) J. F. Eastham, C. W. Keenan and H. V. Secor, *J. Am. Chem. Soc.*, **81**, 6523 (1959).

(29) A. P. Krapcho and A. A. Bothner-By, *ibid.*, **82**, 751 (1960).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF KANSAS, LAWRENCE, KAN.]

Investigation of the Kinetics and Mechanism of the Anodic Oxidation of Aniline in Aqueous Sulfuric Acid Solution at a Platinum Electrode^{1,2}

BY DAVID M. MOHILNER,³ RALPH N. ADAMS AND WILLIAM J. ARGERSINGER, JR.

RECEIVED FEBRUARY 28, 1962

It is proposed that the anodic oxidation of aniline in aqueous sulfuric acid solution at a platinum electrode proceeds through a free radical mechanism and that the final product of this electrode reaction is primarily the octamer emeraldine, or a very similar compound. This mechanism is based upon measurement of kinetic parameters for the initial charge transfer step and upon direct comparison of the properties, including the infrared spectrum, of the precipitate formed on the anode and those of chemically synthesized compounds.

Introduction

Nearly a century ago, Letheby⁴ discovered that the final product of the anodic oxidation of aniline in aqueous sulfuric acid solution at a platinum electrode is a dark green precipitate. Subsequent investigators^{5–7} verified this result and called the precipitate "aniline black." Similar results were also reported^{8,9} for hydrochloric acid solutions of aniline. In 1935, a reaction scheme for the anodic oxidation of aniline at a carbon electrode was

suggested.¹⁰ No further research on this electrode reaction was carried out until the last decade when Khomutov and Gorbachev re-examined it.^{11–15} They again verified Letheby's original observation about the green precipitate. In addition, on the basis of current–time curves, two different mechanisms for the electrode reaction were proposed.

In the present paper, evidence is presented for a mechanism which is quite different from either of those of Khomutov and Gorbachev. It is based upon a characterization of the chemical nature of the final product of the anodic oxidation of aniline and upon an analysis of polarization curves.

(1) Presented at the 139th Meeting of the American Chemical Society, St. Louis, Mo., March, 1961.

(2) Taken in part from the dissertation of David M. Mohilner submitted to the Department of Chemistry and the Faculty of the Graduate School of the University of Kansas in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) Department of Chemistry, Louisiana State University, Baton Rouge, La.

(4) H. Letheby, *J. Chem. Soc.*, **15**, 161 (1862).

(5) J. J. Coquillion, *Compt. rend.*, **81**, 408 (1875); **82**, 228 (1876).

(6) M. A. Rosenstiehl, *ibid.*, **81**, 1275 (1875); *Ann. Chim. Phys.*, [5] **8**, 561 (1876).

(7) F. Goppelsroeder, *Compt. rend.*, **82**, 331, 1392 (1876).

(8) L. Gilchrist, *J. Phys. Chem.*, **8**, 539 (1904).

(9) J. W. Shipley and M. T. Rogers, *Can. J. Res.*, **B17**, 147 (1939).

(10) T. Yasui, *Bull. Chem. Soc. Japan*, **10**, 306 (1935).

(11) N. E. Khomutov and S. V. Gorbachev, *Zhur. Fiz. Khim.*, **24**, 1101 (1950).

(12) N. E. Khomutov and S. V. Gorbachev, *Soveshch. Elektrokhim.*, 1950, *Izdat. Akad. Nauk SSSR*, Moscow, 1953, pp. 579–585.

(13) N. E. Khomutov, *Zhur. Fiz. Khim.*, **25**, 607 (1951).

(14) N. E. Khomutov, *J. Gen. Chem. USSR*, **22**, 627 (1952).

(15) N. E. Khomutov, Reports of the Fourth Soviet Conference on Electrochemistry, Oct. 1–6, 1956, Consultants Bureau Inc., New York, N. Y., 1958.