(22) U. Sowada, G. Bakale, K. Yoshino, and W. F. Schmidt, *Chem. Phys. Lett.*, **34**, 466 (1975).
(23) E.g., R. E. Weston and H. A. Schwarz, "Chemical Kinetics", Prentice-Hall, Englewood Cliffs, N.J., 1972.
(24) R. A. Holroyd and M. Allen, *J. Chem. Phys.*, **54**, 5014 (1971).
(25) W. Tauchert and W. F. Schmidt, Proceedings of the 5th International Conference on Conduction and Breakdown in Dielectric Liquids, Noordwijkerhout, The Netherlands, July 1975.

Discussion

D. A. ARMSTRONG. Would you say whether the rate constants that you plotted against V_0 were zero-field-strength rate constants; also tell us which liquids they were for?

G. BAKALE. The rate constants in the k vs. V_0 plot were all low-field results where v_d is proportional to E, the electric field. (The symbols are explained in Figure legend.)

L. KEVAN. (1) It is interesting in your electron mobility data vs. temperature in ethane that you find a break near 180 K (see ref 19 and 20). This is about where the simple electron localization criterion Fueki and I developed (paper in this issue) changes sign. In liquid propane, your data vs. temperature do not show a break and the electron localization criterion does not change sign.

G. BAKALE. We agree that this temperature region should be studied further since it may provide information on electron localization; however, we could not do these experiments in our glass cells.

L. KEVAN. (2) In alkaline ice glass (10 m NaOH–H_2O) hot electrons may also be produced at moderate electric fields. (T. Huang, I. Eisele, and L. Kevan, *J. Chem. Phys.*, 1973). Thus it appears that scavenger rate constant effects on field-dependent mobilities of hot electrons could be studied to compare with your results in liquids.

G. BAKALE. We would like to see such studies done since we believe such studies would provide information on the electronic states in both liquids and glasses.

M. SILVER. One must be very careful when applying the Bagley "sink" formula for the field emptying out of traps (see ref 19 and 20). This comes from a one-dimensional analysis. One should use the Onsgaer three-dimensional field-dependent escape probability from a localized center. The two approaches agree at very high fields but disagree at moderate to low fields.

G. BAKALE. We recognize that the Bagley model may be an oversimplification but consider it adequate as a first-order approximation to explain the apparent increase in the electron mobilities at high (~100 kV/cm) fields which we observed.

R. A. HOLROYD. What is the temperature dependence of the rate constant in xenon?

G. BAKALE. We saw a slight negative temperature dependence of $k(e^- + SF_6)$ in liquid xenon, but the narrow liquidus range of xenon over which we could make measurements prevented our accurately determining this dependence.

M. SILVER. The result that the rate constant in high mobility systems decreases with electric field is very interesting. From the standpoint of bias random walk [D. Haarer and H. Mohwald, *Phys. Rev. Lett.*, **34**, 1447 (1975)], in the hot electron regime, the distribution of velocities is distorted in the field direction and the number of new sites encountered per unit time is increased and therefore the rate constant for attachment should go up. It would be very important to compare these field effects (for high mobility electrons) at many temperatures and for different scavengers. Your results might be in conformity with the random walk ideas if the cross-section for attachment was decreasing with increasing electron energy faster than the encounter rate with new sites was increasing.

Mechanistic Studies of Metal–Ammonia Reductions

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Mechanisms are discussed for the reactions of the ammoniated electron with alkyl sulfides, alkyl sulfones, acetone, bromate ion, ammonium nitrate, nitrous oxide, and benzylaniline. Mechanisms for the reactions of protonic acids with metal–ammonia solutions are also discussed. The ionization constant for ethanol in liquid ammonia at −45° has been estimated from conductivity studies. Kinetic data are presented for the reaction of ethanol with sodium in liquid ammonia at −45°. Mechanisms are suggested for the reduction of benzene by the alcohol–metal–ammonia system.

The unique properties of metal–ammonia solutions present unusual opportunities for the study of reduction reactions. A large variety of organic and inorganic molecules are reduced by reaction with the metals, either in the presence or absence of a proton donor. Encyclopedic summaries[1-8] of the chemistry of metal–ammonia solutions indicate the magnitude of scientific expenditure in this area. In view of the synthetic utility of metal–ammonia solutions, it is surprising to still find a paucity of available kinetic data necessary in formulating mechanisms.

The objective of this paper is to review some recent studies of the reactions of metal–ammonia solutions and to suggest mechanisms for a number of other metal–ammonia

reactions. Because of the abundance of synthetic data, it has been necessary to be selective, and the choice of the systems discussed does not in any way reflect upon the merit of other work.

Bond Cleavage Reactions. Several overall general mechanisms have been suggested previously to characterize bond cleavage reactions.[9,10] In Figure 1, a general scheme is presented in this paper where A and B can represent either individual atoms or radical groups. Note that the different possible net reactions and corresponding sets of products are indicated by Roman numerals. A more general scheme is obtained when the scheme given in Figure 1 is coupled with the one presented by Jolly.[9]
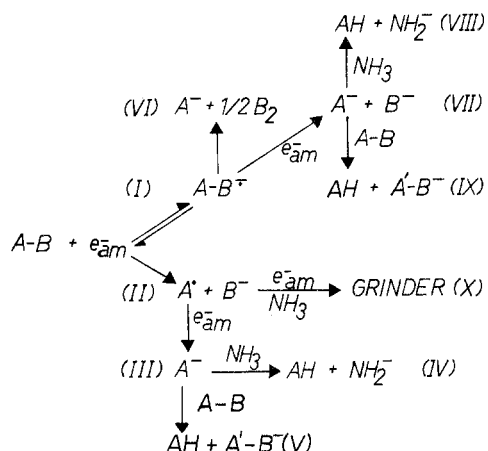
Figure 1. A proposed general mechanism to explain bond cleavage reactions.

Figure 2. Isokinetic plot for the reaction of sodium with simple alkyl sulfides in ammonia.[16]

Net reaction I corresponds to radical anion formation. There exists an almost complete lack of rate data reported for reactions of this type. The rate constant for the reaction of the ammoniated electron with pyridine[11] has been reported to be 4×10^4 M^{-1} sec^{-1} at $-34°$. In this case, the pyridine radical anion dimerizes and hence does not lead to bond cleavage.[1]

Examples corresponding to net reaction VI are found in the reactions of propionamide, hydroquinone, and phenol with the ammoniated electron.[12] These compounds[2] react as weak acids with the ammoniated electron according to the following general scheme:

$$HA + e_{am}{}^- \rightarrow A^- + \tfrac{1}{2}H_2 \tag{1}$$
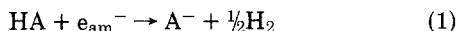
Moreover, these weak acids are capable of forming radical anions prior to bond cleavage. Radical anions of monobenzenoid substances[1,13,14] have been reported in a number of solvent systems, and, in the case of propionamide, the carbonyl group can facilitate electron attachment as previously suggested for acetamide.[15] For these reactions, the following scheme has been suggested[12] to account for the observed second-order rate expression:
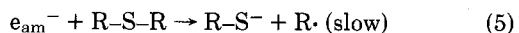
$$e_{am}{}^- + HA \rightleftharpoons HA \cdot^- \tag{2}$$

$$HA \cdot^- \rightarrow A^- + \tfrac{1}{2}H_2 \tag{3}$$
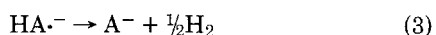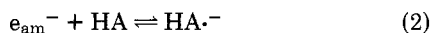
If reaction 3 is the slow step, then the rate expression becomes

$$-d(e_{am}{}^-)/dt = k_3 K_2 (e_{am}{}^-)(HA) \tag{4}$$

where $K_2 = (HA \cdot^-)/(e_{am}{}^-)(HA)$ and the observed second-order rate constant is $k_3 K_2$.

The reactions of sodium with simple alkyl sulfides in liquid ammonia are in accord with net reaction IV. The following scheme has been suggested[16] for these reactions:

$$e_{am}{}^- + R–S–R \rightarrow R–S^- + R \cdot \text{ (slow)} \tag{5}$$

$$R \cdot + e_{am}{}^- \rightarrow R^- \tag{6}$$

$$R^- + NH_3 \rightarrow RH + NH_2{}^- \tag{7}$$

where R denotes an alkyl group. Figure 2, obtained from the results reported by Jones and Dewald,[16] gives a plot of $\Delta H^{\ddagger}$ vs. $\Delta S^{\ddagger}$ for these reactions. The linearity of the plot supports their suggestion of a common rate-determining step for the reactions in this series. The isokinetic temperat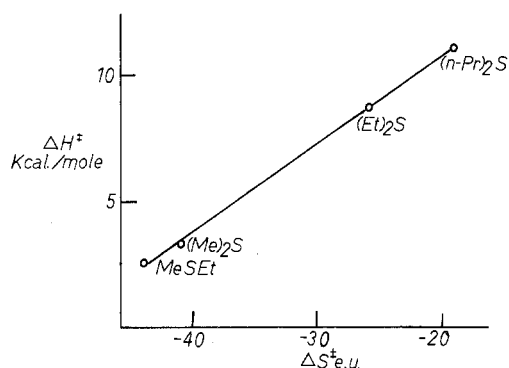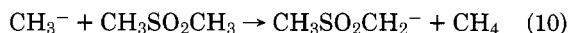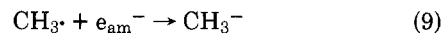ure ($348°$ in Figure 2) 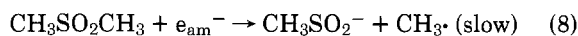indicates that the reaction rates are controlled by $\Delta H^{\ddagger}$ values, consistent with the electronic effects being paramount.[17] Moreover, the inductive effects of the alkyl groups were found to strongly influence the rates of cleavage. The cleavage of diphenyl sulfide also has been reported to proceed via the phenyl radical.[18] This was shown by using the acetone enolate ion to trap phenyl radicals.

The cleavage of alkyl sulfones by the ammoniated electron[19] conforms to net reaction V. Using dimethyl sulfone as an example, the following mechanism[19] has been suggested:

$$CH_3SO_2CH_3 + e_{am}{}^- \rightarrow CH_3SO_2{}^- + CH_3 \cdot \text{ (slow)} \tag{8}$$

$$CH_3 \cdot + e_{am}{}^- \rightarrow CH_3{}^- \tag{9}$$

$$CH_3{}^- + CH_3SO_2CH_3 \rightarrow CH_3SO_2CH_2{}^- + CH_4 \tag{10}$$

For these reactions, the rate expression was found to be second-order, first-order with respect to both the alkyl sulfone and the ammoniated electron.[19] One would predict that the oxygens on the sulfone group should dominate the electronic effects governing the cleavage process. Hence, one would expect that the activation energies of a series of simple alkyl sulfones should be essentially invariant. This was found to be the case.[19] The reaction of diphenyl sulfone was found to be too rapid to permit rate studies by conventional methods. However, unlike the simple alkyl sulfones, the phenyl group can readily accept an electron forming a radical anion, and the following scheme presents a possible mechanism for the overall reaction (net reaction VIII):

$$C_6H_5SO_2C_6H_5 + e_{am}{}^- \rightleftharpoons C_6H_5SO_2C_6H_5 \cdot^- \tag{11}$$

$$C_6H_5SO_2C_6H_5 \cdot^- + e_{am}{}^- \rightarrow C_6H_5SO_2{}^- + C_6H_5{}^- \tag{12}$$

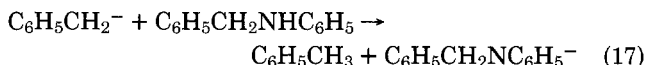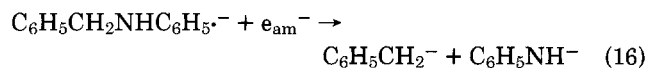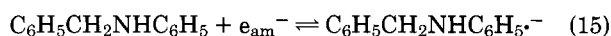$$C_6H_5{}^- + NH_3 \rightarrow C_6H_6 + NH_2{}^- \tag{13}$$
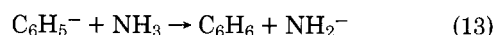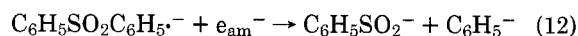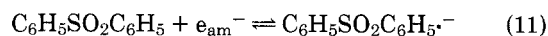
The above mechanism is consistent with a third-order rate expression, that is, second-order with respect to the ammoniated electron and first-order with respect to diphenyl sulfone. Moreover, the above scheme is in agreement with the observations of Rossi and Bunnett.[18]

Benzylaniline is reduced by metal–ammonia solutions according to the overall reaction[2]

$$2C_6H_5CH_2NHC_6H_5 + 2e_{am}{}^- \rightarrow$$
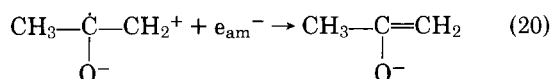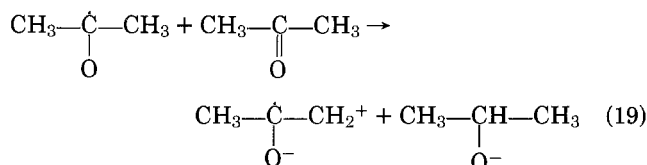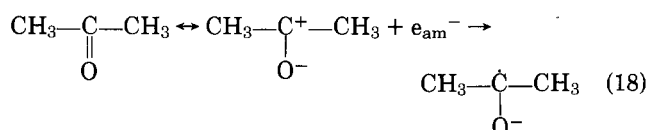$$C_6H_5NH^- + C_6H_5CH_3 + C_6H_5CH_2NC_6H_5{}^- \tag{14}$$
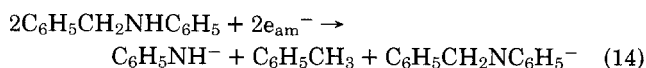
In this reaction, one can speculate that the substrate is initially cleaved to anilide and benzyl anions with the carbanion being protonated by the substrate giving toluene and the diphenylamide ion as shown by the following sequence:

$$C_6H_5CH_2NHC_6H_5 + e_{am}^- \rightleftharpoons C_6H_5CH_2NHC_6H_5 \cdot^- \quad (15)$$

$$C_6H_5CH_2NHC_6H_5 \cdot^- + e_{am}^- \rightarrow$$
$$C_6H_5CH_2^- + C_6H_5NH^- \quad (16)$$

$$C_6H_5CH_2^- + C_6H_5CH_2NHC_6H_5 \rightarrow$$
$$C_6H_5CH_3 + C_6H_5CH_2NC_6H_5^- \quad (17)$$

The above mechanism is representative of net reaction IX.

Kraus and White[21] reported that acetone reacts with sodium in a 1:1 mole ratio without the evolution of hydrogen. On the other hand, Birch[22] reported that acetone is recovered largely unchanged on treatment with sodium in liquid ammonia, and suggested that the lack of reduction resulted because of the enolate salt formation. Recently, Rossi and Bunnett[18] reported that the reaction of acetone with potassium metal in ammonia yields the acetone enolate ion and produces approximately 40% isopropoxide ion as a by-product. We suggest the following scheme for the reaction of acetone with the ammoniated electron:

$$CH_3-\overset{\|}{\underset{O}{C}}-CH_3 \leftrightarrow CH_3-\overset{+}{\underset{O^-}{C}}-CH_3 + e_{am}^- \rightarrow$$
$$CH_3-\overset{\cdot}{\underset{O^-}{C}}-CH_3 \quad (18)$$

$$CH_3-\overset{\cdot}{\underset{O}{C}}-CH_3 + CH_3-\overset{\|}{\underset{O}{C}}-CH_3 \rightarrow$$
$$CH_3-\overset{+}{\underset{O^-}{C}}-CH_2^+ + CH_3-\overset{}{\underset{O^-}{CH}}-CH_3 \quad (19)$$

$$CH_3-\overset{}{\underset{O^-}{C}}-CH_2^+ + e_{am}^- \rightarrow CH_3-\overset{}{\underset{O^-}{C}}=CH_2 \quad (20)$$

The mechanism is consistent with the following stoichiometric reaction:

$$2CH_3COCH_3 + 2e_{am}^- \rightarrow$$
$$CH_3-\overset{}{\underset{O^-}{C}}=CH_2 + CH_3-\overset{}{\underset{O^-}{CH}}-CH_3 \quad (21)$$
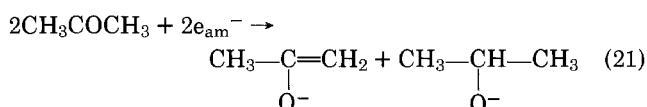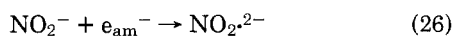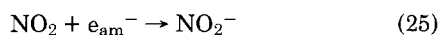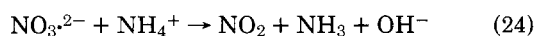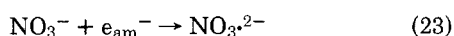
Note the 1:1 mole ratio which was recently confirmed by Jones and Dewald.[23] Moreover, the acetone enolate ion can readily be prepared by the reaction of acetone with the amide ion.[18] Evidence for the radical formed by reaction 18 has been demonstrated by pulse radiolysis and by ESR for a number of carbonyl compounds.[24]

The reaction of ammonium nitrate with metal–ammonia solutions is an interesting system in that virtually no hydrogen is evolved.[2] Burgess and Holden reported that ammonium nitrate and potassium react in a 1:3.1 ratio.[25] The following overall reaction has been proposed[2,26]

$$2NH_4NO_3 + 6K \rightarrow 2NH_3 + K_4N_2O_4 + 2KOH \quad (22)$$
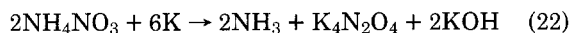
The following scheme can account for the products of the above reaction:

$$NO_3^- + e_{am}^- \rightarrow NO_3 \cdot^{2-} \quad (23)$$

$$NO_3 \cdot^{2-} + NH_4^+ \rightarrow NO_2 + NH_3 + OH^- \quad (24)$$

$$NO_2 + e_{am}^- \rightarrow NO_2^- \quad (25)$$

$$NO_2^- + e_{am}^- \rightarrow NO_2 \cdot^{2-} \quad (26)$$

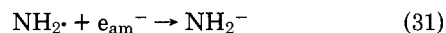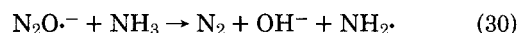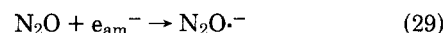$$2NO_2 \cdot^{2-} \rightarrow N_2O_4^{4-} \quad (27)$$
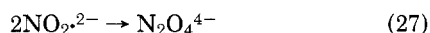
We have found that some hydrogen is indeed evolved in

this reaction. In a typical experiment in which 6.72×10^{-4} mol of NH_4NO_3 was allowed to react with 3.10×10^{-4} mol of Na, 6.58×10^{-6} mol of hydrogen was recovered. This would indicate that the rate constants for reactions 23 and 24 are much larger than $k(NH_4^+ + e_{am}^-)$.
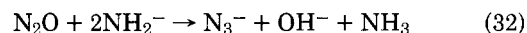
Nitrous oxide reacts with metal–ammonia solutions according to the following:[9]

$$N_2O + 2e_{am}^- + NH_3 \rightarrow N_2 + OH^- + NH_2^- \quad (28)$$
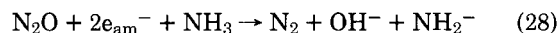
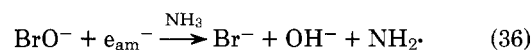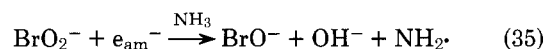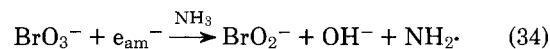Since nitrous oxide is capable of readily accepting an electron, a possible pathway for the reaction is as follows:

$$N_2O + e_{am}^- \rightarrow N_2O \cdot^- \quad (29)$$

$$N_2O \cdot^- + NH_3 \rightarrow N_2 + OH^- + NH_2 \cdot \quad (30)$$

$$NH_2 \cdot + e_{am}^- \rightarrow NH_2^- \quad (31)$$

In addition, the following side reaction occurs:[9]

$$N_2O + 2NH_2^- \rightarrow N_3^- + OH^- + NH_3 \quad (32)$$

We have found that sodium bromate reacts upon mixing with sodium–ammonia solutions at $-65°$. The following stoichiometric reaction has been reported:[2]
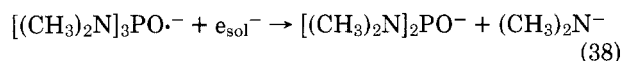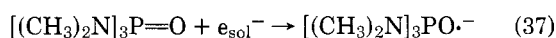
$$NaBrO_3 + 6Na + 3NH_2 \rightarrow NaBR + 3NaOH + 3NaNH_2 \quad (33)$$
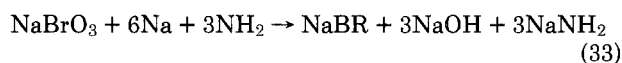
We suggest the following mechanism in order to account for the reaction products:

$$BrO_3^- + e_{am}^- \xrightarrow{NH_3} BrO_2^- + OH^- + NH_2 \cdot \quad (34)$$

$$BrO_2^- + e_{am}^- \xrightarrow{NH_3} BrO^- + OH^- + NH_2 \cdot \quad (35)$$

$$BrO^- + e_{am}^- \xrightarrow{NH_3} Br^- + OH^- + NH_2 \cdot \quad (36)$$

where the amide ion is formed by the reaction of $NH_2 \cdot$ with e_{am}^-. The above mechanism is an example of the scheme which we termed "grinder" in Figure 1.

The reaction of hexamethylphosphoramide (HMPA) with alkali metals has been reported to yield two anions,[27] the dimethylamine anion and the diamidophosphite anion. Therefore, the following scheme appears to be operative:

$$[(CH_3)_2N]_3P=O + e_{sol}^- \rightarrow [(CH_3)_2N]_3PO \cdot^- \quad (37)$$

$$[(CH_3)_2N]_3PO \cdot^- + e_{sol}^- \rightarrow [(CH_3)_2N]_2PO^- + (CH_3)_2N^- \quad (38)$$

Here the nature of the decomposition products is now governed by the reactions of the dimethylamine anion. Analysis of the decomposition products showed the presence of dimethylamine, and lesser amounts of trimethylamine and methane.[28] Also, it is interesting to note that the stability of metal–HMPA solutions increases by a factor of 3 to 4 when the temperature is lowered from 25 to $10°$.[28] This variation in stability with temperature would correspond to an activation energy of approximately 11 to 15 kcal/mol. At $-45°$, we have found that HMPA is not readily cleaved by sodium–ammonia solutions. The slowness of this reaction would correspond to a second-order rate constant of less than $10^{-6} M^{-1} sec^{-1}$.

Reactions of Weak Acids. One of the most important class of reactions that metal–ammonia solutions undergo is the reaction with a protonic acid to give hydrogen and the corresponding salt of the acid.[9] Weak acids, especially ethanol, are frequently used as the proton source in the reduc-

TABLE I: Summary of Rate Constants for the Reaction of Ethanol with Sodium in Liquid Ammonia at −45°

Run no.	$(e_{am}^-)_i$ $10^3\,M$	$(EtOH)_i$ $10^2\,M$	$10^5 k_{obsd}$, sec^{-1}	$10^6 k'$, $M\,sec^{-1}$
R41R	1.26	1.13	7.0 ± 1.0^a	1.1 ± 0.3^a
R42R	1.44	2.30	9.0 ± 0.5	2.4 ± 0.2
R37R	1.34	3.79	8.2 ± 0.2	5.5 ± 0.4
R36R	6.90	1.10	8.6 ± 0.8	1.0 ± 0.1
R35R	1.67	1.14	8.1 ± 0.5	0.40 ± 0.04
R39R	0.809	1.30	7.4 ± 0.3	0.66 ± 0.03
		Av	8.0 ± 0.7	

^{a} Standard deviation.

TABLE II: Summary for the Conductance Data for the Determination of the Ionization Constant for Ethanol in Liquid Ammonia at −45°

| EtOH $10^3\,M$	Λ	$\alpha = \Lambda/\Lambda_0$	K_{eq}, M
2.39	0.0620	2.34×10^{-4}	1.5×10^{-10}
8.56	0.0294	1.11×10^{-4}	1.2×10^{-10}
15.8	0.0232	8.75×10^{-5}	1.4×10^{-10}
28.6	0.0152	5.77×10^{-5}	1.1×10^{-10}
42.7	0.0129	4.87×10^{-5}	1.2×10^{-10}
		Av	1.3×10^{-10}

tion of aromatic compounds by metal–ammonia solutions.[5,8] A mechanism in which the weak acid can readily form a radical anion has been discussed above. For the case wherein a weak acid cannot initially form a radical anion, Jolly[9,29] has suggested the following mechanism:

$$HA \rightleftharpoons NH_4^+ + A^- \qquad (39)$$

$$NH_4^+ + e_{am}^- \rightarrow NH_3 + \tfrac{1}{2}H_2 \qquad (40)$$
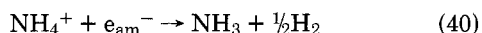
The kinetics of the reactions of sodium with water,[30] alcohols,[30–32] and urea[33] have been studied. The results of these studies appear to substantiate Jolly's mechanism. Krapcho and Bothner-By[34] reported findings that provide strong evidence that the reverse step of reaction 39 is much faster than reaction 40. Brooks and Dewald,[35] using the stopped-flow technique, reported that $k_{40} = (1.2 \pm 0.2) \times 10^6\ M^{-1}$ sec^{-1} at −34°. There is agreement that k_{-39} is expected to have a magnitude characteristic of a diffusion-controlled reaction.[9] Therefore, assuming equilibrium conditions exist in reaction 39, the rate expression for ethanol becomes

$$-d(e_{am}^-)/dt = k_{40}K_{39}[(e_{am}^-)(EtOH)/(EtO^-)] \quad (41)$$

where $K_{39} = (NH_4^+)(EtO^-)/(EtOH)$. Furthermore, the following side reactions should be considered:

$$NH_3 + e_{am}^- \rightarrow NH_2^- + \tfrac{1}{2}H_2 \qquad (42)$$

$$NH_2^- + EtOH \rightarrow NH_3 + EtO^- \qquad (43)$$
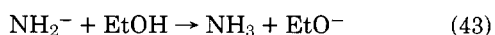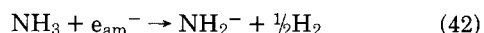
Kinetic studies have shown that the platinum-catalyzed decomposition reaction 42 is zero order in dissolved alkali metal.[36] We also have investigated the decomposition reaction in our glass system containing bright platinum electrodes and found that the reaction is consistent with zero-order kinetics. Therefore, the rate expression becomes

$$-d(e_{am}^-)/dt = k_{40}K_{39}[(e_{am}^-)(EtOH)/(EtO^-)] + k' \quad (44)$$

where k' corresponds to the zero-order decomposition reaction. The general curve fitting program developed by Dye and Nicely[37] was used to evaluate the kinetic data for the reaction of sodium with ethyl alcohol. The results of the study are summarized in Table I. Note the constancy of the
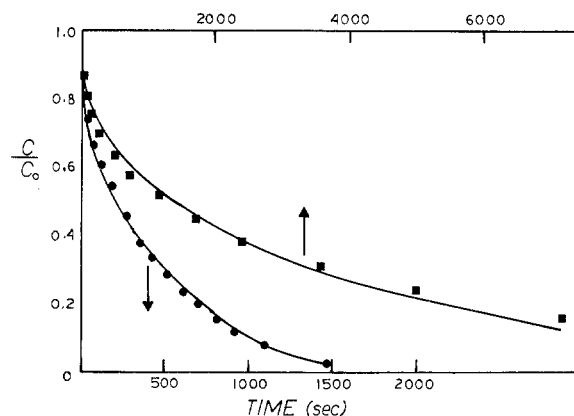

Figure 3. Typical C/C_0 vs. time plots for the reaction of sodium with ethanol in liquid ammonia. The circles are run no. R39R, and the squares are data reported by Kelly, et al.[31] The solid lines represent calculated curves.

observed rate constants ($k_{obsd} = k_{40}K_{39}$). Moreover, the zero-order decomposition constant, k', is small and varies by approximately an order of magnitude depending on the experiment. An example of the fit of the data to the rate expression (eq 44) is shown in Figure 3. Electrical conductivity experiments were performed in order to determine the ionization constant for ethyl alcohol in liquid ammonia according to eq 39 at −45°. The results of this study are given in Table II. The ionization constant was calculated by using the simple Ostwald dilution equation[38] assuming unit activity coefficients. The value of the equivalent conductance of ammonium ethoxide at infinite dilution has not been reported. A value of 265 (Kohlrausch units) for ammonium ethoxide was used in the calculations. This value was obtained by assuming that NH_4EtO and NH_4BrO_3 should have similar equivalent conductivities, and hence the reported value for NH_4BrO_3[39] was corrected for viscosity to yield 265. Note the constancy of the ionization constants given in Table II. Assuming an activation energy of 5.0 kcal/mol for reaction 40,[11] k_{40} is estimated to be $7.2 \times 10^5\ M^{-1}\ sec^{-1}$ at −45°. Therefore, we calculate a value of 9.4×10^{-5} for $k_{40}K_{39}$, which is in good agreement with the observed rate constant.

Figure 3 also shows the fit of the data reported by Kelly et al.[31] to eq 44. Taking their data and estimating the initial ethoxide ion concentration by using the ionization constant for ethanol at −45°, k_{obsd} was calculated to be 4.3×10^{-5}. This value is about a factor of 4 smaller than one would expect based on our results. However, the magnitude of the calculated rate constant is highly sensitive to the initial ethoxide concentration which may account for the above disparity.

Hydrogenation of Unsaturated Compounds. The only reported kinetic studies of the hydrogenation reactions (Birch reductions) have been for the reduction of benzene to 1,4-cyclohexadiene by alkali metals and alcohols in liquid ammonia. The overall reaction is

$$C_6H_6 + 2e_{am}^- + 2ROH \rightarrow C_6H_8 + 2RO^- \qquad (45)$$
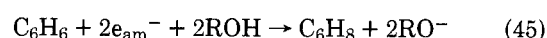
The mechanism originally suggested by Birch[5] appeared to be in agreement with kinetic data reported by Krapcho and Bothner-By.[34] These investigators reported that the reduction of benzene proceeds by the third-order rate law
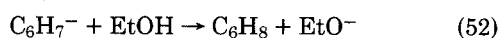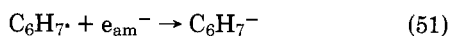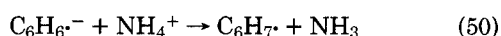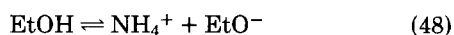
$$-d(C_6H_6)/dt = k_{46}(C_6H_6)(ROH)(Li) \qquad (46)$$

However, Jacobus and Eastham[40] later questioned the va-

lidity of the above rate expression and observed that the reaction rate in the presence of an initially saturated solution of ethoxide ions is

$$-d(C_6H_6)/dt = k_{47}(C_6H_6)(EtOH)(Li)^2 \qquad (47)$$

Jolly[29] suggested a mechanism in which protonation proceeds via the ammonium ion. Protonation of sodium naphthalide[41] by ethanol in liquid ammonia also was found to proceed via the ammonium ion. It is of interest to consider a modification of the mechanism for the reduction of benzene as suggested previously by Jolly.[29] In this scheme we again assume protonation via the ammonium ion as follows:

$$EtOH \rightleftharpoons NH_4^+ + EtO^- \qquad (48)$$

$$e_{am}^- + C_6H_6 \rightleftharpoons C_6H_6\cdot^- \qquad (49)$$

$$C_6H_6\cdot^- + NH_4^+ \rightarrow C_6H_7\cdot + NH_3 \qquad (50)$$

$$C_6H_7\cdot + e_{am}^- \rightarrow C_6H_7^- \qquad (51)$$

$$C_6H_7^- + EtOH \rightarrow C_6H_8 + EtO^- \qquad (52)$$

Applying steady-state treatment to $C_6H_7\cdot$ and $C_6H_7^-$, one obtains

$$\frac{d(C_6H_8)}{dt} = k_{50}K_{48}K_{49}\frac{(EtOH)(C_6H_6)(e_{am}^-)}{(EtO^-)} \qquad (53)$$

where $K_{48} = (NH_4^+)(EtO^-)/(EtOH)$ and $K_{49} = (C_6H_6\cdot^-)/(e_{am}^-)(C_6H_6)$.

The above rate expression can be shown to be equivalent to the fourth-order rate law reported by Jacobus and Eastham[40] if one considers the limited solubility product constant for lithium ethoxide is about 10^{-7}. In addition, charge balance requires that

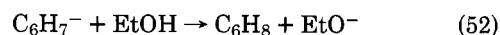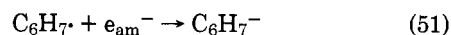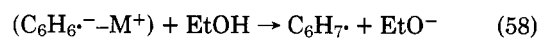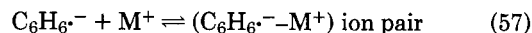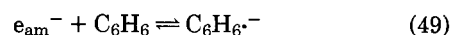$$(Li^+) = (e_{am}^-) + (C_6H_6\cdot^-) + (C_6H_7^-) + (EtO^-) \qquad (54)$$

and at high-metal concentrations eq 54 reduces to

$$(Li^+) \approx (e_{am}^-) \qquad (55)$$

Hence, the rate expression becomes:

$$\frac{d(C_6H_8)}{dt} = \frac{k_{50}K_{48}K_{49}}{K_{sp}}(EtOH)(C_6H_6)(e_{am}^-)^2 \qquad (56)$$

where $K_{sp} = (Li^+)(EtO^-)$. Note that the above expression is in agreement with that found by Jacobus and Eastham.[40] Unfortunately, not all of the constants in eq 56 are known. In order to have 95% reduction,[34] k_{50} should be about two orders of magnitude greater than $k(e_{am}^- + NH_4^+)$. Hence, if $k_{50} \approx 10^8 M^{-1} sec^{-1}$ and $K_{49} \approx 10^{-4} M^{-1}$ (estimated from the lack of an observed ESR signal for the $C_6H_6\cdot^-$ species when pure ammonia is the solvent), one calculates $k_{obsd} = 13$ which is in good agreement with the values reported by Jacobus and Eastham.[40] Furthermore, as pointed out by Jolly,[29] the observation[34] that the reduction rates with lithium, sodium, and potassium decreases in that order is predictable from the increase expected in the solubility of the alkoxides. The major defects of the above mechanism are the inability to explain low product yields when low concentrations of metal $[(Na) < 10^{-2} M]$ are used, and the role of a cosolvent which is frequently added.[5] In this connection, from the studies reported on the protonation of aromatic radical anions in solvent systems of lower dielectric constant than liquid ammonia, it has been shown that the state of ion pairing plays a major role in determining the reaction mechanism.[42-44] Therefore, we propose the following alternative mechanism involving ion pairing:

$$e_{am}^- + C_6H_6 \rightleftharpoons C_6H_6\cdot^- \qquad (49)$$

$$C_6H_6\cdot^- + M^+ \rightleftharpoons (C_6H_6\cdot^- - M^+) \text{ ion pair} \qquad (57)$$

$$(C_6H_6\cdot^- - M^+) + EtOH \rightarrow C_6H_7\cdot + EtO^- \qquad (58)$$

$$C_6H_7\cdot + e_{am}^- \rightarrow C_6H_7^- \qquad (51)$$

$$C_6H_7^- + EtOH \rightarrow C_6H_8 + EtO^- \qquad (52)$$

Applying steady-state treatment to the intermediates $C_6H_7\cdot$ and $C_6H_7^-$, and letting $(e_{am}^-) \approx (M^+)$, the following rate expression is obtained:

$$d(C_6H_8)/dt = k_{58}K_{57}K_{49}(e_{am}^-)^2(C_6H_6)(EtOH) \qquad (59)$$

where K_{57} is the ion-pairing constant. Note that eq 59 is again consistent with the observations of Jacobus and Eastham.[40] If one assumes that $K_{49} \approx 10^{-4}$ as before, K_{57} to be in the neighborhood of 10^3 for ion pairing,[45] and using the fourth-order rate constants reported by Jacobus and Eastham,[40] one calculates $k_{58} \approx 10^2$ to 10^3. This range of values is comparable to the rate constants reported for the protonation of various radical anions in other solvents.[42,43] Moreover, the influence of the ethoxide ion on the rate constant[40] can be explained by its formation of complex ions with ethanol.[9,31] We are presently undertaking a systematic study of the yield obtained for the reduction of benzene as a function of ionic strength and dielectric constant in the hope of obtaining experimental results that would enable us to distinguish between the above suggested mechanisms.

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Discussion

J. BELLONI. How do you explain the differences between the kinetics and hence mechanisms of e_{am}^-–hydrazine and e_{am}^-–substituted hydrazine reactions? Why can you definitely rule out a mechanism for phenylhydrazine beginning by ionization of the molecule as we showed for N_2H_4 similar to the ethanol mechanism?

R. R. DEWALD. Hydrazine does not react with the ammoniated electron. However, substituted hydrazines, especially those having electron-withdrawing groups, are acidic in ammonia and hence react with the ammoniated electron. In other cases, resonance effects can facilitate electron attachment which leads to bond cleavage. In the phenylhydrazine case, a mechanism similar to the alcohol reaction would not account for the products of the reaction. I would like to point out, however, that the mechanism we presented is formulated to account for the reaction products and we have no kinetic data to support the mechanism.

U. SCHINDEWOLF. The equilibrium for the reaction

$$e^- + C_6H_6 \rightleftharpoons C_6H_6 \cdot^-$$
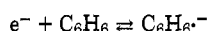
in mixtures of methylamine and liquid ammonia is shifted to left with increasing temperature. This indicates that ΔH is negative and also that $\Delta S > 0$.

J. L. DYE. The temperature dependence of the equilibrium constant for the formation of benzenide radical anion in tetrahydrofuran also shows a decreasing equilibrium constant with increasing temperature. By ESR techniques the benzenide signal disappears as the temperature is raised above about −50°C, similar to the results of Tuttle and Weissman.

U. SCHINDEWOLF. What is the catalyzed zero-order reaction that you were referring to

R. R. DEWALD. I was referring to the following reaction

$$e_{am}^- + NH_3 \rightleftharpoons NH_2^- + \tfrac{1}{2}H_2$$
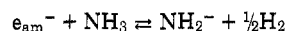
which is platinum catalyzed.[9]

U. SCHINDEWOLF. Why do you assume that ion pairing, $C_6H_6 \cdot^- + M^+ \rightleftharpoons C_6H_6 \cdot^-, M^+$, is important in the reduction of benzene? What is the evidence?

R. R. DEWALD. It is well established[42–44] that ion pairing plays an important role in the protonation of a number of aromatic radical anions in solvent systems of lower dielectric constants than liquid ammonia. Moreover, Krapcho and Bothner-By[34] reported that the addition of salts, particularly LiBr, resulted in a marked increase in the reduction rate.

A. M. KOULKES-PUJO. In the case of HMPA, were you referring to the reaction of e_{am}^- with HMPA? The reaction of $e_{HMPA}^- +$ HMPA is very slow, if there is a reaction occurring at all.

R. R. DEWALD. Yes, I was referring to e_{am}^-. I agree that the reaction of $e_{HMPA}^- +$ HMPA is very slow corresponding to second-order rate constant of less than $10^{-2}\ M^{-1}\ \text{sec}^{-1}$ at room temperature.

A. M. KOULKES-PUJO. For reaction of DMSO with e_{am}^-, you suggested an intermediate step involving the formation of DMSO·$^-$. Is there any evidence for a DMSO·$^-$ species?

R. R. DEWALD. Chung et al. (*J. Phys. Chem.*, **78**, 1882 (1974)) reported the formation of methyl-radical–methanesulfenate anion pairs by dissociative electron capture in γ-irradiated crystalline dimethyl-d_6 sulfoxide at 77 K. These authors also regarded $Me_2SO \cdot^-$ as an unstable product of electron capture whose structure naturally lends itself to a facile dissociation process.