Electrochemical Reactions of Organic Compounds in Liquid Ammonia. I. Reduction of Benzophenone

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Abstract: The electroreduction of benzophenone in liquid ammonia was studied by cyclic voltammetry. In anhydrous solutions, the reduction occurs in two reversible one-electron steps producing the anion radical and the dianion. In the presence of alcohol, the first reduction is unaffected and the second reduction wave becomes irreversible and is shifted toward positive potentials, following qualitatively the criteria for a rapid reaction of the dianion with the proton donor.

Liquid ammonia is an amphiprotic, very weakly acidic, slightly ionized solvent in which solvated electrons are stable. Its unique properties have been exploited by organic chemists to achieve numerous reductions of unsaturated compounds by alkali metals dissolved in liquid ammonia.[2] The overall reaction can be written

$$R + 2M + 2HA \xrightarrow{NH_3} RH_2 + 2M^+ + 2A^- \quad (1)$$

where R is the reducible compound, M the alkali metal, and HA a proton source (generally an alcohol) and is known as the Birch reduction in the case of the aromatic hydrocarbons or simply reduction by dissolved metals for the other compounds. The overall reaction shown in eq 1 occurs in several steps. It is generally accepted[2] that the first step is the formation of solvated electrons followed by the reversible reaction of these to produce anion radicals.

$$R + e^-_{solv} \rightleftharpoons R\cdot^- \quad (2)$$

After this first step two reaction schemes have been proposed: (1) addition of a second electron followed by protonation (an EEC scheme) or (2) protonation of the radical anion followed by a second electron addition and protonation[3] (an ECE scheme). It is also possible that the radical anions undergo dimerization or disproportionation reactions. The proton source also plays an important role in the reduction; indeed the rate of the reaction, the nature, and the yield of the products vary greatly with the nature of the proton source. Although the method is used extensively in organic synthesis, few attempts have been made to work out the mechanism of the reaction on a quantitative basis.[4-6] Some electrochemical studies of inorganic substances have been carried out in liquid ammonia,[7,8] but the electrochemistry of organic substances in this medium has received little attention. Studies of the electrochemical behavior of organic compound in the absence and presence of proton donors could provide information about the details of the mechanism of reduction. Modern electrochemical techniques have proven to be very powerful in the elucidation of reaction mechanisms of organic compounds in nonaqueous solvents.[9] Moreover, electrochemical methods, through control of the electrode potential, allow selective reduction to the radical ion or dianion to be carried out and, by observation of current changes or potential shifts upon addition of a proton donor, provide information about the reaction paths of the electrogenerated species. Finally, the usefulness of liquid ammonia as a solvent in chemical syntheses,[1-3] as well as some interesting reported electrosyntheses in related amine solvents,[10] suggests that liquid ammonia may be a useful medium for electrosynthesis as well. Several problems arise in the use of liquid ammonia in these studies. Since the dielectric constant of liquid ammonia is small (23.7 at −36°[7]), solution resistances are high and *iR* compensation must be employed for accurate potential measurements. The solubility of many organic compounds in ammonia is small, often necessitating the use of cosolvents in synthetic work.

In this paper we report on the electroreduction of benzophenone. This substance is readily soluble in ammonia, it is easily reducible, its electrochemical behavior in other nonaqueous solvents is well known,[9] and the reactions of benzophenone with alkali metals in liquid ammonia have been examined in some detail.[11] It will be shown in this paper that our results agree in general with the earlier work of Wooster. The reduction of benzophenone occurs in two one-electron steps to produce first the anion radical and then the dianion, both of which are stable in liquid ammonia. The protonation leading to the diphenyl methanol[11] occurs through the dianion.

Experimental Section

In all the experiments, vacuum techniques were used to purify the ammonia and to transfer it into the cell. The main purpose

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(2) (a) H. Smith, "Chemistry in Nonaqueous Ionizing Solvents," Vol. I, Part 2, G. Jander, H. Spandau, C. C. Addison, Ed., Interscience, New York, N. Y., 1963; (b) M. Smith in "Reduction," R. L. Augustine, Ed., Marcel Dekker, New York, N. Y., 1968.

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(10) See, for example, (a) H. W. Sternberg, R. E. Markby, I. Wender, and D. M. Mohilner, *J. Amer. Chem. Soc.*, **89**, 186 (1967); (b) *J. Electrochem. Soc.*, **113**, 1060 (1966); (c) R. A. Benkeser and E. M. Kaiser, *J. Amer. Chem. Soc.*, **85**, 2858 (1963).

(11) (a) C. B. Wooster, *ibid.*, **50**, 1388 (1928); **51**, 1856 (1929); **56**, 2436 (1934); (b) C. B. Wooster and W. E. Holland, *ibid.*, **56**, 2438 (1934); (c) C. B. Wooster, *ibid.*, **59**, 377 (1937).

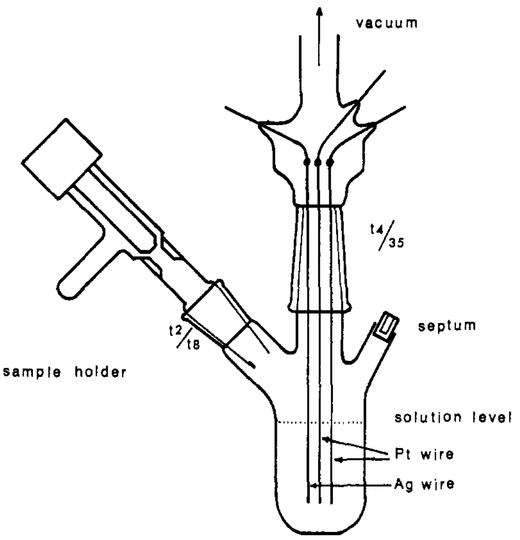

Figure 1. A simple electrochemical cell.

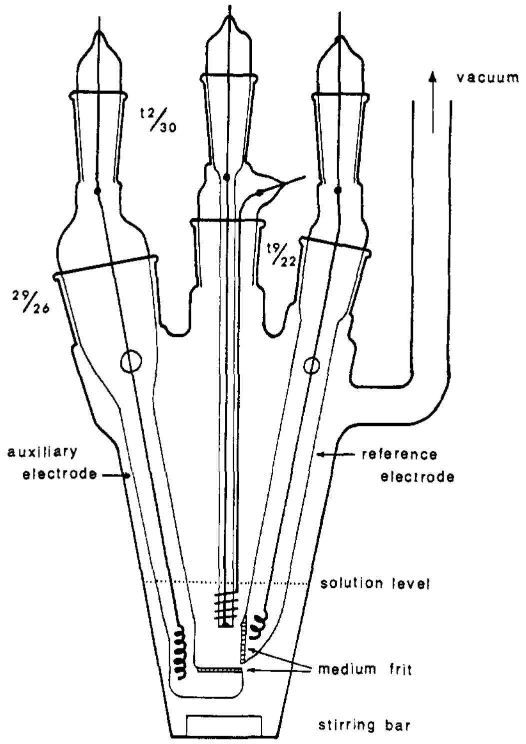

Figure 2. A three-compartment electrochemical cell.

was to avoid the presence of oxygen and to eliminate any trace of water from the solvent and the cell.

Cell. For this study we used two different cells. The first one (Figure 1) is an undivided cell with three electrodes: two platinum wires used as the working and the auxiliary electrodes and a silver wire acting as a pseudoreference. The cell is provided with a sample holder made with a 4-mm high-vacuum Teflon stopcock that can be rotated to drop the sample into the cell. The vacuum-tight rubber septum allows the introduction of known amounts of alcohol. This cell is very convenient for preliminary studies. However, with it as the experiment continues, the medium gradually turns acidic because of the production of ammonium ions at the auxiliary electrode. The cell used in the quantitative work was a three-compartment cell (Figure 2) designed to minimize the distances between the electrodes. Not shown in Figure 2 are a side arm, connected to the cell with a ground joint, in which the supporting electrolyte can be dried under vacuum, a rubber septum, and the sample holder. The solution volume for this cell is 60 ml.

Electrodes. All the results reported in this paper were obtained with a platinum wire, a silver wire, or a gold disk working electrode. The use of a platinum disk sealed in soft glass as a working electrode was unsuccessful. During our study a platinum electrode, disk or wire, activated by repeated cycling of potential in H_2SO_4,[12] which showed good electrochemical behavior for the oxidation of ferrocyanide ion in 1 *M* KCl aqueous solution,[13] sometimes did not work properly in liquid ammonia. In these cases the observed reduction waves had characteristics of very slow electron-transfer reactions. However, in other cases, platinum wire electrodes pretreated this way gave a good response. Apparently, electrode reactions on platinum in liquid ammonia, as in ethylenediamine,[10b] depend upon the nature of the platinum surface, but we did not investigate these surface effects further. Gold disk electrodes (gold plated on a platinum disk sealed in soft glass) and silver wire electrodes gave more reproducible behavior. The reference electrode used was either a $Ag|AgNO_3$ (10^{-2} *M*), KI (10^{-1} *M*) electrode,[14] separated from the working compartment with a medium glass frit, or a silver wire coiled around the working electrode to minimize the ohmic drop between these two electrodes. The potential of the silver pseudoreference was found to be very stable but shifted slightly after addition of alcohol; in these cases the $Ag|Ag^+$ reference electrode was used.

Procedure. Because the benzophenone dianion reacts rapidly with proton sources, it was necessary to avoid any trace of water in the system and great care was exercised during the preparation of the solutions. The ammonia (Matheson 99.9%) was condensed under vacuum in a trap containing a small piece of clean sodium to remove all traces of water and oxygen.[15] After the required amounts of chemicals were introduced into the reference and auxiliary compartments, the supporting electrolyte side arm, and the sample holder, the cell was connected to the vacuum line (10^{-5} Torr) and evacuated at least 20 hr. From time to time the cell and the supporting electrolyte (when possible) were heated with a torch to eliminate all remaining traces of water from the walls of the cell and from the salt. The required amount of ammonia was then transferred from the trap to the cell by distillation. The temperature of the solution was kept constant by a Dry Ice–acetone cold bath. Before adding the benzophenone into the cell, the absence of water was verified by the absence of a reduction wave occurring before the reduction of the supporting electrolyte.[14] As opposed to Herlem's results,[14] we found it was easy to eliminate the water from the cell, especially when KI was used as the supporting electrolyte. All electrochemical experiments were performed with a Princeton Applied Research Corp. Model 170 electrochemistry system (PAR) using positive feedback to compensate for the ohmic drop between the working and the reference electrodes. For scan rates greater than 200 mV/sec a storage oscilloscope (Tektronix, Type 564) was used to record the cyclic voltammograms.

Results and Discussion

A typical cyclic voltammogram of benzophenone reduction in anhydrous liquid ammonia at −50° is given in Figure 3. The data for the system are summarized in Table I. For both waves, the values of $E_{pc} - E_{pa}$ are close to those for a Nernstian one-electron reaction, the values of i_{pa}/i_{pc} are essentially 1, and the peak potentials do not vary with the scan rate (up to 5 V/sec). According to these facts we can conclude that the reduction of benzophenone consists of two reversible one-electron processes producing the stable radical anion and dianion

$$R + e^- \rightleftarrows R\cdot^- \qquad (3)$$

$$R\cdot^- + e^- \rightleftarrows R^{2-} \qquad (4)$$

To our knowledge this is the first time that a reversible

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[12] A. J. Bard, *Anal. Chem.*, 35, 1602 (1963).

[13] R. N. Adams, "Electrochemistry at Solid Electrodes," Marcel Dekker, New York, N. Y., 1969, Chapter 3.

[14] (a) M. Herlem, *Bull. Soc. Chim. Fr.*, 1687 (1967); (b) M. Herlem, J. J. Minet, and A. Thiebault, *J. Electroanal. Chem.*, 30, 203 (1971).

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Table I. Electrochemical Data for the Reduction of Benzophenone in Anhydrous Liquid Ammonia (10^{-1} *M* KI) at $-50°$ [a]

Wave	E_{pc},[b] V	$E_{pa} - E_{pc}$,[c] mV	i_{pc},[d] mA	i_{pa},[d] mA	i_{pa}/i_{pc}
I	−1.25	48 ± 5	2.9	2.8	0.97
II	−1.78V	48 ± 5	2.9	2.9	1.0

[a] Abbreviations: E_{pc}, cathodic peak potential; E_{pa}, anodic peak potential; i_{pc}, cathodic peak current; i_{pa}, anodic peak current for reversal wave. [b] V *vs.* Ag|AgNO$_3$ 0.01^{-2} *M*, KI 0.1 *M* reference electrode; potentials are independent of the scan rate (50–5000 mV/sec). Mean values of several determinations. The main source of error is the variation of the reference potential from experiment to experiment. [c] The theoretical peak separation for a Nernstian reaction at $-50°$ is 44 mV. [d] Values for a typical experiment, electrode area 0.5 cm^2.

reduction to a stable dianion has been observed for the electrochemical reduction of benzophenone. Such a scheme is in agreement with the earlier work of Wooster[11] who demonstrated that a stable mono- or disodium derivative of benzophenone could be prepared in liquid ammonia by adding the correct proportion of sodium. On the basis of this scheme and with the values of the potential given in Table I, it was possible to reproduce exactly by computer simulation the experimental voltammogram given in Figure 3. The reversible one-electron reduction for the first wave is also in agreement with the electrochemistry of benzophenone in other nonaqueous solvents. The polarographic behavior of benzophenone in *N,N*-dimethylformamide (DMF) has been reported by Wawzonek and Gundersen.[16] They gave the values −1.21 and −1.78 V *vs.* Hg pool for the half-wave potentials, but they gave no indication about the reversibility of the waves. The difference between the half-wave potentials was approximately the value we have observed. The potential of the second reduction wave observed by Wawzonek[16] is much more negative than the value reported by Given and Peover[17] (−1.53 V *vs.* Hg pool in DMF). A small difference between the two reduction waves (−0.23 V) was also found in pyridine.[18] It seems that in the last two cases the studies were performed in a solvent which was not completely dry. Cyclic voltammetry in these pyridine solutions shows the second reduction wave to be irreversible with no anodic reversal current associated with it. Michielli and Elving[18] identify an oxidation wave 1.4 V more positive than the second reduction wave as oxidation of benzophenone dianion, but based on the results here, this degree of electrochemical irreversibility for the $R\cdot^-/R^{2-}$ couple appears unreasonable and the results in pyridine probably represent rapid protonation of the dianion.

Since the two reduction waves observed are reversible, we can deduce from the peak potentials the equilibrium constant for the disproportionation reaction

$$2R\cdot^- \rightleftharpoons R + R^{2-} \tag{5}$$

The constant $K = 10^{-12}$ (at $-50°$) shows that the equilibrium is completely displaced to the left and the benzophenone radical anion does not disproportionate.

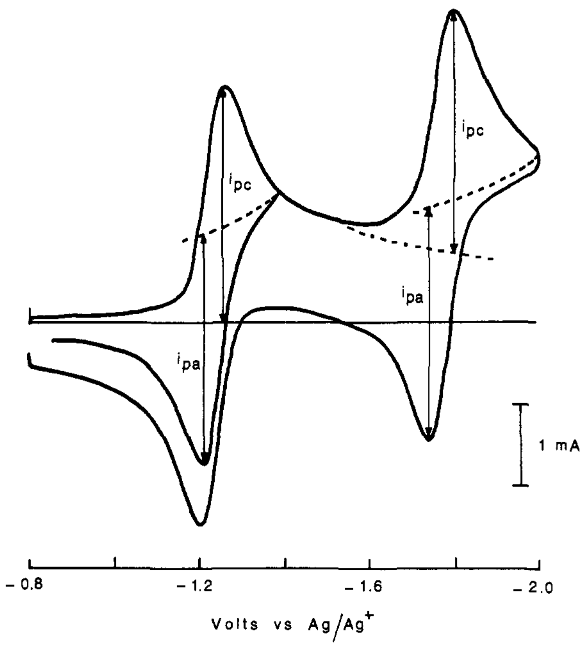

Figure 3. A cyclic voltammogram of benzophenone in anhydrous liquid ammonia at $-50°$. The solution was 1 m*M* in benzophenone and 0.1 *M* in KI. The scan rate was 200 mV/sec, and the electrode area was 0.5 cm^2.

Wooster[11] has also shown that this reaction does not proceed to the right because benzyl alcohol has little effect on the radical anion but reacts very rapidly with the dianion. We will comment on this point later. During the experiments we have always observed a slight amount of black film formation on the working electrode. Accordingly, there may be some tendency for the radical anion or dianion to dimerize (or polymerize). However, for the first electron transfer, the ratio of the anodic peak current (i_{pa}) to the cathodic peak current (i_{pc}) was always very close to 1 even at slow scan rates (50 mV/sec). We can conclude that the radical anion is stable and that the dimerization (or polymerization), if it occurs, is a slow side reaction. The dianion is also stable and ammonia itself is not acidic enough to protonate it.

Conductance studies[11c] indicate that the mono- and the disodium derivatives of benzophenone are only slightly dissociated into free ions with the association constants for the ion pairs being about 10^4. Since the electrochemical studies were performed with a large excess of supporting electrolyte, all of the radical ions and the dianions produced are present in the solution in the form of ion pairs. For the benzophenone in DMF, Kalinowski[19] found that the half-wave potential for the first reduction depends upon the nature of the supporting electrolyte cation. The fact that the reduction was easier in the presence of Li^+ ion rather than with $(n\text{-Bu})_4N^+$ (−1.67 and −1.82 V *vs.* sce) was attributed to a greater association constant for the lithium ion–ketyl radical ion pair. In liquid ammonia we did not find any difference in the first peak potentials observed with KI, NaI, LiNO$_3$ (all 0.1 *M*), or with $CH_3(n\text{-Bu})_3NI$ (saturated, *ca.* 0.07 *M*) as supporting electrolyte. This result may suggest that the ion-pairing constant is the same in all cases. Krigowski[20]

(16) S. Wawzonek and A. Gundersen, *J. Electrochem. Soc.*, **107**, 537 (1960).

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(20) T. M. Krigowski, *J. Electroanal. Chem.*, **35**, 436 (1972).

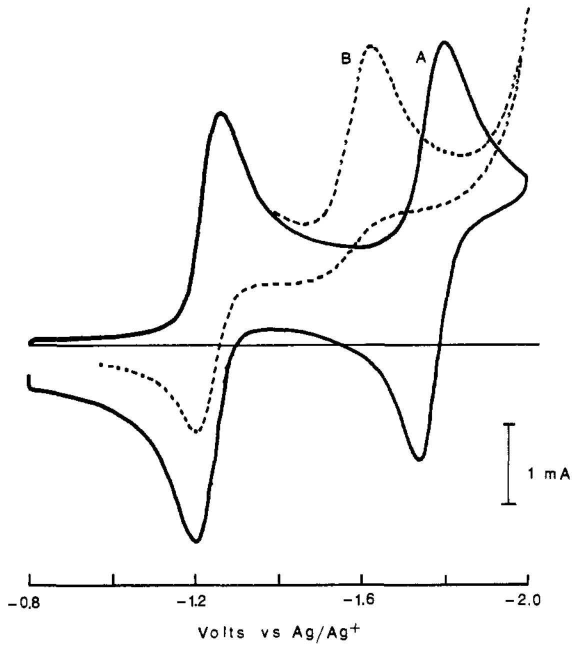

Figure 4. A cyclic voltammogram of benzophenone in liquid ammonia at 50°: (A) anhydrous, (B) 0.28 *M* ethanol.

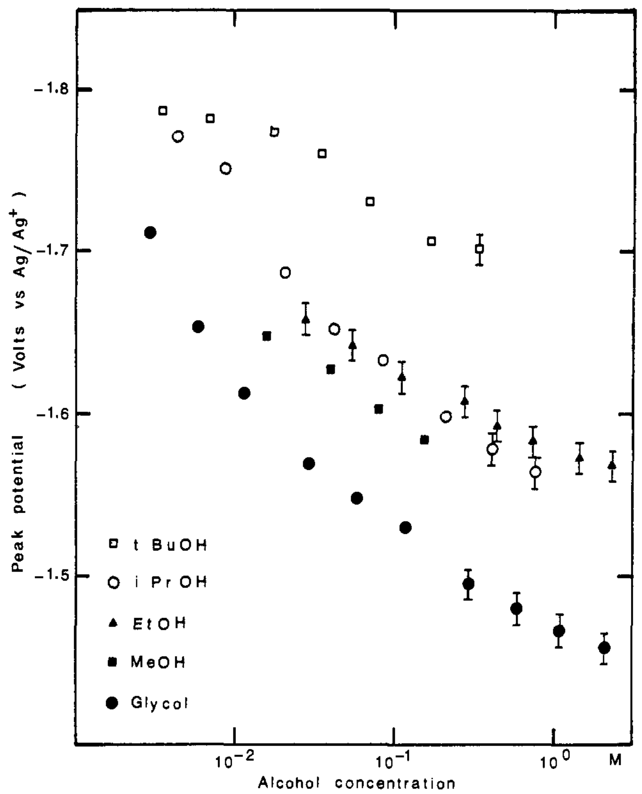

Figure 5. The effect of the nature and the concentration of alcohol on the position of the second reduction wave of benzophenone in liquid ammonia.

has related the shifts of the half-wave potentials of the reduction of 1,2-naphthoquinone as a function of the cation and the solvent to the Gutmann[21] donor number (*D*) of the solvent. The main result of this study is that the effect of the nature of the cation decreases as the donor number (the solvating power of the solvent) increases. If the donor number of liquid ammonia is as high as suggested by Herlem and Popov,[22] we can expect that the nature of the cation will have no effect on the reduction potential of benzophenone, because the cations are completely solvated and form solvent separated ion pairs with the ketyl radical anions. However, the situation may be more complex. It has been shown that ion pairing did not influence nitrobenzene radical ion esr spectra in liquid ammonia[23] but had a strong effect on the spectrum of cyclooctatetraene radical.[24] It is also probable that the dianion is also associated with the supporting electrolyte cation to form ion pairs and triple ions. Accordingly, it should be noted that the value $K = 10^{-12}$ derived for the disproportionation reaction 5 of the radical ion is the effective constant in the medium used, 0.1 *M* KI in liquid ammonia.

Effect of Proton Donors. The addition of a proton source to the solution produces a large effect on the second reduction wave of benzophenone (Figure 4). For example, when ethanol is added, the first peak is unchanged but the second wave becomes irreversible and is shifted toward positive potentials, following qualitatively the criteria of a reversible electron transfer followed by a fast irreversible chemical reaction (or for a rapidly established reversible following reaction with a large equilibrium constant).[25] Because of the filming of the electrode mentioned previously, it was difficult to obtain very reproducible currents. However, in some experiments the filming was not too important and the intensity of the first peak remained constant over a wide range of alcohol concentrations with the ratio i_{pa}/i_{pc} close to 1. We can, therefore, eliminate the possibility of protonation of the radical anion to produce a radical reducible at the same potential as the benzophenone itself (ECE mechanism[26]). This agrees with earlier results[11] which showed that benzyl alcohol did not react with the benzophenone radical ion produced by reaction of sodium metal in liquid ammonia. Previous studies of the effect of proton sources on the reduction of benzophenone in DMF showed a dependence on the strength of the acid. The presence of water caused shifts in both reduction waves with only small changes in the wave heights.[16] The authors suggest a slow reaction of $R\cdot^-$ and a faster reaction of R^{2-} with water. The addition of a stronger acid such as benzoic acid or phenol causes a positive shift in both waves, with the height of the first wave growing at the expense of the second,[17] showing reaction of $R\cdot^-$ with the proton donor. It is possible that in liquid ammonia the use of acids stronger than alcohol would show changes in the first reduction wave, but it is not possible to carry out this study by electrochemical techniques because in the presence of strong acid the concentration of the solvated proton, NH_4^+, becomes important and this species is then more easily reduced than benzophenone.

The effect of the nature and the concentration of the proton source on the peak potential of the second cyclic voltammetric wave is shown in Figure 5. The positive shift of the second peak increases with increasing con-

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[21] V. Gutmann, *Chem. Brit.*, 7, 102 (1971).

[22] M. Herlem and A. I. Popov, *J. Amer. Chem. Soc.*, **94**, 1431 (1972).

[23] F. J. Smentowski and G. R. Stevenson, *ibid.*, 90, 4461 (1968).

[24] F. J. Smentowski and G. R. Stevenson, *ibid.*, **89**, 5120 (1967); *J. Phys. Chem.*, 73, 340 (1969).

[25] R. S. Nicholson and I. Shain, *Anal. Chem.*, 36, 706 (1964).

[26] (a) R. S. Nicholson and I. Shain, *ibid.*, 37, 178 (1965); (b) J. M. Saveant, *Electrochim. Acta*, 12, 753 (1967).

centration and acidity of the alcohol.[27,28] This suggests a reaction mechanism such as

$$NH_3 + AH \rightleftharpoons NH_4^+ + A^- \qquad \text{(fast)}$$

$$R^{2-} + NH_4^+ \rightleftharpoons RH^- + NH_3 \qquad \text{(fast)}$$

$$RH^- + NH_4^+ \rightleftharpoons RH_2 + NH_3 \qquad \text{(slow)}$$

which would lead to a first-order dependence in dianion and second-order dependence in alcohol (AH), with the rate constant of the overall reaction dependent on the acidity constant of the alcohol.

The effect of the various parameters on the peak potential in the case of a reversible electron transfer followed by a chemical reaction has been studied theoretically by Saveant and Vianello.[29]

For the system

$$A + ne \rightleftharpoons B \qquad (6)$$

$$mB + m_zZ \xrightarrow{k} \text{products} \qquad (7)$$

the position of the peak potential, for large values of the rate constant k, is given by the relation

$$E_p = E + \frac{RT}{(m+1)nF}\ln k - \frac{RT}{(m+1)nF}\ln v + \frac{m_zRT}{(m+1)nF}\ln C_Z^* + \frac{(m-1)RT}{(m+1)nF}\ln C_A^* \qquad (8)$$

where E is a constant containing the normal potential and the diffusion coefficients of A and B, v is the scan rate, n is the number of electrons exchanged in the electrochemical reaction, m and m_z are the stoichiometric coefficients in the chemical reaction 7, and C_Z^* and C_A^* are the bulk concentrations of Z and A. At −50° the coefficient $2.3RT/nF$ is equal to 44 mV for $n = 1$. Therefore, the order of reaction in B can be deduced from the variation of the peak potential with the scan rate and the order in Z can be obtained from the shift of the peak with the concentration of Z.

Using the data obtained with ethanol (Table II) the reaction of benzophenone dianion with ethanol appears to be half order in dianion and second order in ethanol. According to eq 8 and for large values of alcohol concentration, a linear variation of E_p *vs.* log (AH) is expected with the same slope for all the alcohols. The results in Figure 5 show that this is not the case and the larger shift of the peak potential for ethylene glycol shows a reaction order greater than 2. These results suggest a more complex mechanism which we could not elucidate. There are several reasons why the reaction may be complex. Firstly, the dianion may be present in the solution in three different forms: triple ions, $R^{2-}\cdots 2Na^+$, ion pairs R^{2-}, Na^+, and free ions. As suggested by Dye and coworkers[30] these species may have different reactivities toward alcohol, resulting in a complex reaction scheme. Secondly, the alcohol may solvate the alkali metal ion or the ketyl radical[31] preferentially increasing the alcohol concentration in the vicinity of the dianion. Thirdly, the concentration profile near the electrode of all the species involved in the reaction is complex. For potentials more negative than −1.25 V, the benzophenone concentration at the electrode surface is zero. However, benzophenone can still diffuse toward the electrode and react with the dianion diffusing out from the electrode surface, perturbing the chemical reaction. Finally, we cannot *a priori* neglect the possibility of a disproportionation of the carbanion RH^- according to

$$2RH^- \rightleftharpoons RH_2 + R^{2-}$$

a reaction observed for some hydrocarbons.[32]

Table II. Influence of the Ethanol Concentration and the Scan on the Potential of the Second Reduction Wave of Benzophenone[a]

EtOH added, ml	[EtOH],[b] *M*	E_{pc},[c] V	dE_p/d log [EtOH], mV	dE_p/d log v,[d] mV
0.010	2.8×10^{-3}	-1.67_0		35 ± 5
0.020	5.7×10^{-3}	-1.65_5		
0.040	1.1×10^{-2}	-1.64_0		
0.10	2.8×10^{-2}	-1.61_5	55 ± 10	38 ± 5
0.20	5.7×10^{-2}	-1.60_0		
0.40	1.1×10^{-1}	-1.58_0		
1.0	2.8×10^{-1}	-1.55_5	50 ± 10	35 ± 5
2.0	5.6×10^{-1}	-1.54_0		
4.0	1.0×10^{-1}	-1.52_5		

[a] In the absence of ethanol, the second reduction wave in this experiment was irreversible, indicating the initial presence of a small amount of proton sources in the solution. The peak potentials are more positive than in Figure 5. However, the variation of E_p with the alcohol concentration has the same slope as in Figure 5. [b] The solution volume is 60 cm³. No correction was made for the volume change on mixing. [c] V *vs.* Ag|AgNO$_3$ 10^{-2} *M* reference electrode. [d] Between 50 and 500 mV/sec. With the same scan rates, the potential of the first reduction did not vary so that the shifts observed for the second reduction do not include any contribution from an uncompensated resistance effect.

Naphthalene and Benzene. In liquid ammonia with KI or Me(n-Bu)$_3$NI as supporting electrolyte, naphthalene shows only a one-electron reversible reduction at −2.20 V *vs.* Ag|Ag$^+$. This reduction occurs very close to the reduction of the supporting electrolyte and it is not possible to study the effects of the proton source. As expected, benzene is not reducible in liquid ammonia.

Mechanisms of the Reduction by Alkali Metal in Liquid Ammonia. In the case of benzophenone, there is little doubt about the mechanism of the reduction by alkali metal in the presence of alcohol. The solvated electron reacts with benzophenone to give the dianion which is rapidly protonated by the alcohol. This is in agreement with the mechanism proposed by Szwarc[33] for the protonation of perylene radical anion in tetrahydrofuran (THF) that occurs through the dianion, the concentration of which is maintained at a low level by the equilibrium

$$2Pe^- \rightleftharpoons Pe + Pe^{2-}$$

However, as we have found, the protonation reaction of the dianion may be complex. In the case of naphthalene or benzene, which are easily reducible by alkali metal and alcohol in liquid ammonia, the solvated electron is not reducing enough to produce the dianion. Therefore, the equilibrium concentration of the dianion will be very small and the reduction reaction will probably

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(27) M. Herlem and A. Thiebault, *Bull. Soc. Chim. Fr.*, 719 (1971).

(28) Reference 2a, p 40.

(29) J. M. Saveant and E. Vianello, *Electrochim. Acta*, 12, 629 (1967).

(30) E. R. Minnich, L. D. Long, J. M. Ceraso, and J. L. Dye, *J. Amer. Chem. Soc.*, 95, 1061 (1973).

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(32) N. H. Velhorst and G. J. Hoytink, *J. Amer. Chem. Soc.*, **87**, 4529 (1965); **89**, 209 (1967).

(33) M. Szwarc, *Accounts Chem. Res.*, 5, 169 (1972); G. Levin, C. Sutphen, and M. Szwarc, *J. Amer. Chem. Soc.*, **94**, 2652 (1972).

be very slow.[34] However, the protonation can occur through the radical anion. Since this species can exist for naphthalene in liquid ammonia, a kinetic study of the same type as that described by Szwarc[30] could provide an answer. However, in the case of benzene, it seems unlikely that it will be possible to study the mechanism of the reduction electrochemically, since it is not possible to observe the first step of the reaction to the radical anion.

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[34] For benzene, a 10% conversion (based on the sodium concentration) requires 2000 sec (at -45°). See Figure 3 in ref 6.

Endo- *vs.* Exocyclic Cyclopropyl Bond Rupture in Bicyclo[3.1.0]hex-2-ene

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Abstract: Highly excited bicyclo[3.1.0]hex-2-ene (BCH) produced by chemical activation isomerizes to give products arising from both endocyclic (65%) and exocyclic (35%) cyclopropyl bond rupture of BCH. Only endocyclic rupture to the diradical intermediate has been observed in thermal isomerizations, but both isomerization paths have been observed in the photoisomerization of derivatives of BCH. The results are discussed in terms of the estimated Arrhenius parameters for the two ring opening mechanisms and subsequent isomerizations.

Vinylcyclopropane isomerizations in general and bicyclo[3.1.0]hex-2-ene (BCH) rearrangements specifically are of current interest to both thermal kineticists and photochemists.[1–5] The present evidence in both thermal and photochemical reactions supports a mechanism of breaking of a bond in the cyclopropane ring to give a diradical intermediate rather than isomerization by a concerted process.[2,6,7] For BCH and its derivatives, thermally induced epimerization or structural rearrangement occurs by endocyclic bond rupture.[3,8] Photolysis of BCH derivatives in solution leads to products expected from exocyclic as well as endocyclic cyclopropane bond rupture.[4,9] No photochemical studies on the parent bicyclic molecule have been reported.

We wish to report some results on the high energy isomerization reactions of BCH using the technique of methylene chemical activation.[10,11] The results indicate that introduction into the molecule of sufficient energy by means other than a photochemical transition will lead to products arising from both types of cyclopropyl bond rupture. Since the products of exocyclic bond rupture are observed, this technique provides positive experimental data to determine the Arrhenius parameters for the reaction previously unobserved in pyrolysis. Thermochemical kinetic estimates provide an explanation why the exocyclic mechanism is not observed in thermal systems.

Experimental Section

Cyclopentadiene was prepared by cracking the commercially obtained dimer (Aldrich Chemical Co.). The starting material was stored at Dry Ice temperatures and subjected to several freeze–thaw degassing cycles before use. Gas chromatography indicated the impurities in the cyclopentadiene were less than 1%. Diazomethane was prepared by the reaction of 60% potassium hydroxide solution with *N,N'*-nitrosoylmethylurea using the procedure described by Frey.[12] It was stored at liquid nitrogen temperatures and distilled at -40° to fill the reaction vessel. The oxygen was bone dry grade (Matheson Gas) and was used without further purification.

The irradiation vessel was a 2-in. diameter 350 cm^3 cylindrical tube with Pyrex flats epoxied to the ends. The samples were filled on a greaseless, mercury-free, high-vacuum line capable of evacuating the vessel to $<10^{-4}$ Torr. The total pressure of the system was varied from 50 to 300 Torr. In most cases the ratio of diazomethane to cyclopentadiene was 1:14, but changes in this ratio by a factor of 2 did not significantly affect the relative yields. For all the results reported here, the ratio of oxygen to cyclopentadiene was 10%. The irradiations were carried out using a 200-W high-pressure mercury lamp. The light was passed through an interference filter with 40% transmission at 435.8 nm and a half-band width of 10 nm. Generally the irradiations lasted 3 hr although time dependence studies showed that the relative yields did not vary for irradiations between 0.5 and 5 hr.

The analysis of the product spectrum was done by using a gas sampling valve to inject an aliquot of the product mixture into a

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