

Reduction of the Benzene Ring and of the Olefinic Double Bond by Electrolytically Generated Electrons

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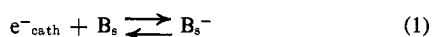
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Abstract: Benzene and olefins can be reduced electrochemically in ethanol containing hexamethylphosphoramide (HMPA). The reduction of these substrates is believed to be due to electrochemically generated solvated electrons. The relative amounts of cyclohexadiene, cyclohexene, and cyclohexane obtained in the reduction of benzene depend on ethanol concentration, current density, and temperature in a manner consistent with the proposed mechanism. Benzene can also be reduced electrochemically in pure ethanol. In the absence of HMPA, however, the current efficiency is only of the order of 1% as compared to a current efficiency of 95% in ethanol-HMPA.

The dark blue solutions obtained by dissolving alkali metals in liquid ammonia provide convenient and stable sources of solvated electrons. These solutions have been used for a long time for the reduction of inorganic and organic compounds. The mechanism of the reduction of the benzene ring in alkali metal-liquid ammonia in the presence of ethanol as a proton donor has been investigated by Krapcho and Bothner-By,^{2,3} among others.⁴⁻⁶

Electrochemical reduction of the benzene ring has been carried out in liquid ammonia,⁷ ethylenediamine,⁸ and methylamine.⁹ In these solvents two different charge-transfer steps must be considered: direct electron transfer from the cathode to the benzene



or release of electrons into the solvent (S), followed by addition of the solvated electron to the benzene ring, according to eq 2 and 3. We have previously shown¹⁰



that in ethylenediamine the charge-transfer step is the release of electrons into the solvent according to eq 2. We also have shown that reduction of the benzene ring by electrolytically generated electrons can be achieved in ethanol containing hexamethylphosphoramide ($[(\text{CH}_3)_2\text{N}]_3\text{P}=\text{O}$, HMPA).¹¹ That the blue solutions

of alkali metals in HMPA^{12,13} contain solvated electrons has been recently confirmed.^{14,15} We now present further work on the electrochemical reduction of benzene and report the electrochemical reduction of the olefinic double bond.

Experimental Section

Reagents. Lithium chloride, HMPA, the olefins, benzene, and naphthalene were of the highest purity available commercially. HMPA was purified by vacuum distilling and collecting the fraction boiling between 88 and 92° (3 mm). The olefins, benzene, and naphthalene were analyzed by glpc and were found to be free of impurities. Ethylenediamine was purified as described previously.¹⁰

Apparatus. The electrolysis vessel, an H cell of 150-ml capacity, the reference electrode, and special arrangement of the Luggin capillary used have been previously reported in detail.¹⁰ Instead of the zinc amalgam reference electrode described previously,¹⁰ a silver wire was used. Aluminum or platinum of 5.5 cm² total immersed surface served as the cathode and a carbon rod as the anode.

Procedure. The H cell and reference cell were filled with a solution of ethanol and HMPA, 0.3 M in LiCl. Eleven mmoles (about 1 to 2 ml) of the substrate to be reduced was placed in the cathode compartment which contained 65 ml of the solution. The H cell was placed in an ice or ice-salt bath to maintain the required temperature of the electrolyte ($28 \pm 1^\circ$ or $-2 \pm 1^\circ$) during electrolysis. During electrolysis, catholyte and anolyte were vigorously stirred by glass-enclosed magnetic stirring bars. Reductions were carried out at a constant current density of 0.091 A/cm² and in some cases 0.0036 A/cm² and the charge passed through the solution was integrated by a current integrator. The cathode potential remained fairly constant at -2.4 ± 0.1 V (vs. Ag wire) throughout the electrolysis. The electrolysis was interrupted after sufficient charge (0.00761 faraday) had been passed to reduce about 15% of the unsaturated compound present.

Recovery and Analysis of Reduced Material. The catholyte was poured into 200 ml of water and acidified, and the aqueous solution was extracted with 5 ml of decane. (In the case of naphthalene, the reduction products were exhaustively extracted with pentane.) The decane extract was analyzed by glpc. A 12 ft \times 1/8 in. column packed with 5% FFAP on 100-120 Chromosorb G was used. In all cases the results were checked against synthetic samples having approximately the same composition and having been sub-

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jected to the same treatment as the electrolyzed material, including extraction from ethanol-HMPA-water by decane.

Competition Experiments. Since reduction of benzene yields cyclohexene and cyclohexane along with cyclohexadiene, competition experiments between benzene and cyclohexene could not be analyzed without ambiguity. Instead of using benzene and cyclohexene, we used benzene and 4-methylcyclohexene to obtain $k_{\text{benzene}}/k_{4\text{-methylcyclohexene}}$ ratios in our competition experiments. We then determined the ratio $k_{4\text{-methylcyclohexene}}/k_{\text{cyclohexene}}$ in a separate experiment. From this ratio, which was very close to unity (0.929), and the ratios $k_{\text{benzene}}/k_{4\text{-methylcyclohexene}}$, we calculated the ratio $k_{\text{benzene}}/k_{\text{cyclohexene}}$.

Results and Discussion

Reduction of Benzene. Benzene was reduced in ethanol-HMPA (66.6 mol % ethanol) with an aluminum cathode to give a mixture of 22.8% cyclohexadiene, 10.0% cyclohexene, and 67.2% cyclohexane with an over-all current efficiency of 95%. The electrolysis was interrupted after 15% of the available benzene had been reduced, *i.e.*, the reduction was carried out in the presence of a large excess of benzene. The formation of cyclohexane in the presence of excess benzene is in good agreement with the result previously reported for the reduction of tetralin under the same conditions where decalin was obtained as the main product.¹¹ In contrast, electrochemical reduction of benzene in methylamine⁹ and of tetralin in ethylenediamine⁸ produces only the di- and tetrahydro derivatives, *i.e.*, cyclohexadiene and cyclohexene in the case of benzene and hexalin and octalin in the case of tetralin. That benzene is not reduced past the olefin stage in amine solvents is readily explained by assuming that the reduction of the isolated double bond is much slower than the reduction of benzene to olefins. On the other hand, the fact that benzene is reduced to cyclohexane in ethanol-HMPA even in the presence of excess benzene indicates that some other factor is controlling the reaction in this case. It is obvious that the proton availability in ethanol-HMPA is vastly greater than in ethylenediamine and this difference provides the basis for an explanation of the different product distributions in these two solvents. The effect of proton availability is best understood by considering the rate equation for the reduction of benzene. The rate of benzene reduction, $-dB/dt$, has been shown² to be proportional to benzene (B), electron (e^-), and proton donor (P) concentrations

$$-dB/dt = k_b(B)(e^-)(P) \quad (4a)$$

and we shall assume that the same rate law also holds for the reduction of cyclohexene

$$-dC/dt = k_c(C)(e^-)(P) \quad (4b)$$

where (C) is the concentration of cyclohexene. A competitive reduction, where benzene and cyclohexene are exposed to the same electron and proton donor concentration, gives the ratio of specific rate constants² according to the formula

$$k_b/k_c = \frac{\log(B/B_0)}{\log(C/C_0)} \quad (5)$$

where B/B_0 and C/C_0 are the ratios of final to initial concentrations of benzene and cyclohexene.¹⁶ Elec-

(16) Equation 5 was originally derived² for a case of homogeneous kinetics. Use of this equation to describe the kinetics of the electrochemical "follow-up reactions" discussed in this paper implies that, for given current density and ethanol concentration, steady-state concentration

profiles will exist for the solvated electrons and for the proton donors inside the very thin reaction layer next to the electrode surface where the reaction actually takes place. The conditions of convective mass transport employed in our experiments probably justify such an assumption as a first approximation. A more exact treatment could only be given for an electrode whose detailed hydrodynamic characteristics are better understood such as, for example, the rotating disk or disk-ring electrodes.

trochemical reduction of benzene and cyclohexene in ethylenediamine and analysis of the reduction products showed that the ratio k_b/k_c in EDA was 200, *i.e.*, at the same electron and proton donor concentration (in this case the solvent EDA is the proton donor), benzene is reduced two hundred times faster than cyclohexene. This explains why in amine solvents the reduction of benzene comes to a halt when isolated double bonds are formed.^{8,9} In ethanol-HMPA, on the other hand, the ratio k_b^*/k_c^* was only 1.4. We believe, however, that this ratio is not really the ratio of the reaction rate constants but is rather essentially a ratio of the corresponding mass transfer coefficients, which should be proportional to the square roots of the diffusion coefficients of benzene and cyclohexene, respectively. From eq 4a and 4b one sees that the rates for benzene and cyclohexene reduction are proportional to the concentration (P) of the proton donor (ethanol). Therefore, as the ethanol concentration increases the rate of reduction increases until eventually it becomes diffusion controlled. By replacing EDA with ethanol-HMPA (66.6 mol % ethanol), we increased the proton availability to such an extent that the reduction became diffusion controlled. In the reaction layer near the electrode surface, where concentration of solvated electrons is high, reduction of benzene and cyclohexene to cyclohexane takes place at a faster rate than diffusion of benzene into the reaction layer. The fact that the ratio of the k^* 's is 1.4 indicates that even at these high ethanol concentrations the reduction is not completely diffusion controlled. If it were, we would probably observe a k_b^*/k_c^* ratio which would be even closer to unity since the diffusion coefficients of benzene and cyclohexene should be almost identical.

If the reduction of benzene and cyclohexene in ethanol-HMPA is essentially diffusion controlled, it should be possible to reduce the effect of diffusion control by reducing the rate of reaction. According to the rate expressions 4a and 4b, the rate should be reduced by decrease in electron or proton donor concentration, *i.e.*, by carrying out the reduction at lower current density or lower ethanol concentration. Another way of slowing down the rate of reaction would be to lower the reaction temperature, since rates of reactions are usually more temperature sensitive than rates of diffusion.¹⁷ Competition experiments between benzene and cyclohexene were carried out at lower ethanol concentration, lower current density, and lower temperature. The results, summarized in Table I, show that when ethanol concentration, current density, and temperature are lowered the reduction becomes more reaction controlled, as evidenced by the increase in k_b to k_c ratio. The degree to which the reduction of benzene is reaction controlled, in turn, determines the distribution of products since cyclohexadiene and cyclohexene are intermediates in the reduction of benzene to cyclohexane. That the product distribution is not dependent on cathode material may be seen by comparing experiments 2 and 5 in Table I. Essentially

profiles will exist for the solvated electrons and for the proton donors inside the very thin reaction layer next to the electrode surface where the reaction actually takes place. The conditions of convective mass transport employed in our experiments probably justify such an assumption as a first approximation. A more exact treatment could only be given for an electrode whose detailed hydrodynamic characteristics are better understood such as, for example, the rotating disk or disk-ring electrodes.

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Table I. Competitive Reduction of Benzene and Cyclohexene in EtOH-HMPA

Expt no.	Cathode material	Mol % EtOH	Temp, °C	Current density, A/cm ²	k_b/k_c	Benzene product distribution		
						Cyclohexadiene	Cyclohexene	Cyclohexane
1	Al	66.6	28	0.091	1.4	20.2	8.5	71.3
2	Al	5	28	0.091	8.2	81.3	16.4	2.3
3	Al	66.6	28	0.0036	2.5	53.1	10.1	36.8
4	Al	66.6	-2	0.0036	36.0	93.0	5.8	1.2
5	Pt	5	28	0.091	7.1	85.7	12.9	1.4

the same product distribution was obtained regardless of whether an aluminum (experiment 2) or a platinum cathode (experiment 5) was used.

Reduction of Olefins. The fact that cyclohexene, an internal olefin, was reduced in ethanol-HMPA at diffusion-controlled rates suggests that electrochemical reduction in solvents of high proton availability should prove an excellent method for the reduction of difficult to reduce, sterically hindered olefins. This expectation was fulfilled. The highly sterically hindered olefin, 2,3-dimethyl-2-butene, $(\text{CH}_3)_2\text{C}=\text{C}(\text{CH}_3)_2$, was reduced at only a slightly lower rate than hexene-1, hexene-2, and cyclohexene (Table II). In the absence of a com-

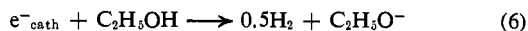
Table II. Competitive Reduction of Various Olefins and Cyclohexene in EtOH-HMPA^a

Expt no.	Test olefin	k_{o1}/k_c
1	Hexene-1	1.35
2	Hexene-2	0.90
3	2,3-Dimethyl-2-butene	0.59

^a Experimental conditions: aluminum cathode; solvent EtOH-HMPA (66.6 mol % EtOH); 0.3 M LiCl; temperature, 28°; current density, 0.091 A/cm²; charge passed, 0.00761 faraday.

peting olefin, 2,3-dimethyl-2-butene was reduced at a current efficiency of 30%. This result is impressive when compared with the chemical reduction of these olefins in ethylamine. Competitive reductions carried out by Krapcho and Nadel¹⁸ in lithium ethylamine showed that cyclohexene was not reduced in the presence of hexene-1 and 2,3-dimethyl-2-butene was not reduced in the presence of cyclohexene.

The Role of HMPA. The fact that benzene was reduced in ethanol-HMPA with a current efficiency of 95% means that out of every 100 electrons released into the solvent 95 were utilized for the reduction of the benzene ring. This result is remarkable in view of the fact that the molar ratio of ethanol to benzene was 40 to 1. Reduction of benzene under these conditions is possible only if the hydrogen evolution reaction 6



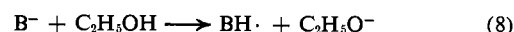
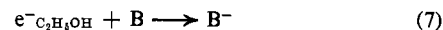
is suppressed. Suppression of the hydrogen evolution reaction, moreover, is essential for attainment of an electrode potential sufficiently cathodic for release of electrons into the solvent.¹⁹ This release occurs in

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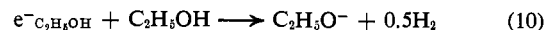
(19) A value of -2.7 V (vs. NHE) has been derived for the standard redox potential of the hydrated electron (J. H. Baxendale, *Radiation Res. Suppl.*, **4**, 139 (1964); E. J. Hart, S. Gordon, and E. M. Fielden, *J. Phys. Chem.*, **70**, 150 (1966)). It is reasonable to assume that the standard redox potential of the solvated electron in ethanol will not differ appreciably from this value. The free energy change involved in removing an electron from platinum is composed of the difference in free energy between the electron in platinum (e^-_{Pt}) and in the gas phase

ethanol-HMPA (66 mol % ethanol) at a potential of -2.4 V (vs. Ag wire) as may be readily verified by visual observation. At this potential, the surface of the cathode becomes covered by a thin layer of dark blue solution. That hydrogen evolution according to (6) does not take place is, we believe, due to HMPA being selectively adsorbed at the metal surface, thereby preventing decomposition of ethanol at the metal surface. As an aprotic compound, HMPA is not decomposed by hydrogen elimination, and as a highly polar compound, HMPA does not prevent release of electrons into the solvent. Strong support for this view of the role of HMPA was obtained by an experiment, wherein naphthalene was reduced electrochemically under the same conditions as benzene. In this experiment, the cathode potential was the same as that observed during the benzene reduction (-2.4 ± 0.1 V vs. Ag wire). A product analysis showed that naphthalene had been reduced to a mixture consisting of 7.1% dihydronaphthalene, 21.9% tetralin, 20.0% hexalin, 10.8% octalin, and 40.2% decalin with an over-all current efficiency of 96%. In view of the fact that the half-wave potential of naphthalene is about 1 V more anodic than the estimated half-wave potential of benzene,^{10, 20} the above result proves almost conclusively that the potential determining step in both cases is the release of electrons into the solvent. Apparently, HMPA adsorbed at the electrode surface prevents naphthalene from approaching the electrode surface close enough for direct electron transfer to take place between electrode and naphthalene.

In addition to suppressing the hydrogen evolution at the cathode, HMPA must also suppress hydrogen evolution in solution. Reduction of benzene is only possible if electron and proton transfer (7 and 8) are



faster than the two competing hydrogen-forming reactions (9 and 10). As far as the reactions of the sol-



vated electron in solution are concerned, no kinetic data are available for reactions 9 and 10. However, it is reasonable to assume²¹ that rate constants for the solvated electron in ethanol are very similar

(e^-_{g}) and the heat of hydration of e^-_{g} , neglecting entropy of hydration. On the basis of spectroscopic evidence (M. Anbar and E. J. Hart, *J. Phys. Chem.*, **69**, 1244 (1965)) the heat of solvation of e^-_{g} in ethanol differs very little from the heat of hydration of e^-_{g} , the difference being 1.1 kcal.

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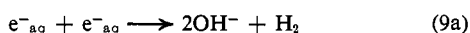
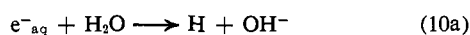
(21) T. A. Taub, D. A. Harter, M. C. Sauer, and L. M. Dorfman, *J. Chem. Phys.*, **41**, 979 (1964).

Table III. Electrolytic Reduction of Benzene in Ethanol^a

Expt no.	Cathode material	Reagent added	Molarity	Ref potential, V	Current efficiency, %	Product distribution, %		
						Cyclohexadiene	Cyclohexene	Cyclohexane
1	Al	None		-1.40	0.01	100	0	0
2	Al	Glacial acetic acid	0.808	-1.15 to -1.20	0	0	0	0
3	Al	Lithium ethoxide	0.234	-1.60 to -1.80	2.7	70.5	29.5	0
4	Pt	None		-0.90	1.4	52.7	42.3	5.0
5	Pt	Glacial acetic acid	0.808	-0.40	0	0	0	0
6	Pt	Lithium ethoxide	0.234	-0.90 to -1.50	1.2	25.0	58.8	16.2

^a Experimental conditions: solvent, EtOH 0.3 M LiCl; temperature, 28°; current density, 0.091 A/cm²; charge passed, 0.00761 faraday.

to those of the solvated electron in water. In the case of the hydrated electron, reaction 10a is comparatively slow²² with a k_{10a} of 16 $M^{-1} \text{sec}^{-1}$. In contrast reaction 9a is very fast,²² with a k_{9a}

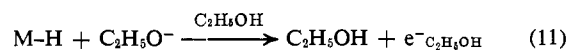


of $10^{10} M^{-1} \text{sec}^{-1}$, and we may assume similar rate constants for reactions 9 and 10. At the electrode surface the concentration of $e^-_{C_2H_5OH}$ is very high and one would expect hydrogen formation according to (9) to be the dominant reaction. The fact that reduction of benzene proceeds with a current efficiency of 95% indicates that HMPA as part of the solvent shell may stabilize the solvated electron to a large extent in (9). Stabilization of the solvated electron with respect to the unwanted hydrogen evolution reaction 9 does not imply stabilization toward the desired electron addition reaction 7. In liquid ammonia, for example, the reaction of the ammoniated electron to give hydrogen, $2e^-_{NH_3} \rightarrow H_2 + 2NH_2^-$, is extremely slow but the ammoniated electron reacts rapidly² with benzene to give benzene anion.

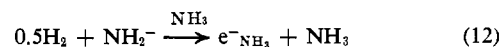
Reduction of Benzene in Ethanol in the Absence of HMPA. Benzene can also be reduced in ethanol in the absence of HMPA. Reductions in pure ethanol were carried out at the same current density as the reductions in ethanol-HMPA but differed from the latter in two respects: the electrolysis was accompanied by copious hydrogen evolution and the cathode potentials were 1-1.5 V more anodic than during the reduction in ethanol-HMPA. The results are summarized in Table III. On platinum, benzene is reduced at a much higher current efficiency than on aluminum (compare experi-

(22) E. J. Hart, S. Gordon, and E. M. Fielden, *J. Phys. Chem.*, **70**, 150 (1966).

ment numbers 1 and 4), and this may lead one to believe that benzene is reduced by a mechanism involving surface catalysis. In that case increasing the acidity of the solution should cause an increase in current efficiency since the rate of hydrogenation of organic compounds was shown^{23,24} to increase with acidity. However, we observed the opposite effect. Addition of glacial acetic acid (experiment numbers 2 and 5) completely suppressed the reduction of benzene, while decreasing the acidity by adding lithium ethoxide (experiment number 3) resulted in a very large increase in current efficiency. A conceivable, although admittedly speculative, explanation is that benzene is reduced in pure ethanol by solvated electrons formed by cleavage of metal-hydrogen bonds by ethoxide ion (eq 11). This



cleavage of a metal-hydrogen bond by ethoxide ion would be analogous to the splitting of the H-H bond by amide ion



a reaction shown²⁵ to proceed reversibly. Increase in alkalinity had no effect, within the limits of experimental error, in the case of the platinum electrode (experiment numbers 4 and 6). This may possibly be due to the difference in the nature of the metal-hydrogen bond which in the case of platinum may be more readily cleaved and consequently may not require the presence of a large excess of ethoxide ion.

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