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*Electrochemical Hydrogenation and
Hydrogenolysis in Aqueous Media*

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FINAL REPORT

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Electrochemical studies are usually performed with compounds which are reactive at potentials within the "potential window" of the chosen medium; i.e. a system is selected so that the compound can be reduced at potentials where the electrolyte, solvent and electrode are inert. The reactions described here are distinctive in that they occur at very negative potentials at the limit of the cathodic "potential window". We have focused here on preparative reductions at mercury cathodes in media containing tetraalkylammonium (TAA^+) electrolytes. Using these conditions the cathodic reduction of functional groups which are electroinactive within the accessible "potential window" has been achieved and several simple, but selective organic syntheses were performed. Quite a number of functional groups are reduced at this limit of the cathodic "potential window". They include a variety of benzenoid aromatic compounds, heteroaromatics, alkynes, 1,3-dienes, certain alkyl halides, and aliphatic ketones.

At very negative potentials neither the TAA^+ cation nor the electrode are inert, instead they combine to form reduced TAA-metals. Recent work has led us to formulate the hypothesis that TAA-metals are involved in many organic reductions done in the presence of TAA^+ salts at very negative potentials. These species are formed at the electrode surface and may act as mediators for electron-transfer to the organic substrates. A simplified mechanism for this catalytic sequence is shown below.

All cathodic reductions described below were performed at mercury pool cathodes in solutions containing tetraalkylammonium (TAA^+) electrolytes and most were carried out at a constant current. For preparative scale experiments, in general, the constant-current method is preferable to that of constant potential. The equipment for constant-current experiments is simpler, much less expensive and more suitable for large scale reactions. For the particular conditions described here, experiments at constant potential are difficult. The current often varies erratically throughout constant-potential experiments, reaction times are unpredictable and often impractically long. This is the result of participation of the cathode material in the reaction sequence. The mercury pool surface is visibly disrupted, droplets of mercury separate from the surface and in many instances the black precipitate of the TAA-mercury covers the cathode surface.

Benzene and Substituted Benzenes

The electron affinity of benzene is very low (-1.15 eV in the gas phase) and its reduction requires strong reducing agents. The common method for reduction of benzenes, the Birch reduction, involves solvated electrons. These are generated by dissolving alkali or alkaline earth metals in liquid NH_3 , low boiling amines or HMPA. The products are usually the corresponding 1,4-dihydrobenzenes which are obtained in high yield.

Using aqueous $(\text{C}_4\text{H}_9)_4\text{NOH}$ or $(\text{C}_4\text{H}_9)_4\text{NBF}_4$ in THF-water, benzene could be reduced at mercury to 1,4-dihydrobenzene. During the reduction a black solid was observed. Under these conditions benzene shows no polarographic wave. CV, however, gives some suggestion that $(\text{C}_4\text{H}_9)_4\text{N}$ -mercury is a catalyst for this process.

An example that demonstrates the possibilities inherent in the Hg cathode $-(C_4H_9)_4N^+$ electrolyte method, for the preparation of products which are inaccessible by other methods, is found in the reduction of diphenyl ether (12). The only products of 12 from reduction with alkali metals in amine solvent were phenol and benzene, presumably arising from cleavage at the radical anion stage. Similarly phenol and benzene were formed by

cathodic reduction in aqueous $(C_4H_9)_4NOH$ or in dry DMF containing $(C_4H_9)_4N^+$ salts. However, upon addition of water to the organic solvent, hydrogenation of the benzene nuclei took place and formation of the previously unknown 13 and 14 competed with the reductive cleavage. Depending on the amount of water and the solvent, either 13 or 14 could be obtained in good yields (Table 1). Increasing the amount of water in DMF increased the yield of 13 up to 38% at 12% H_2O (at higher concentrations of water hydrogen evolution was significant). In this solvent 14 was formed only in small amounts. This is not surprising, since isolated benzenes are not efficiently reduced in DMF. In THF-8% H_2O , 13 was obtained (43% after transfer of 3 Fmol^{-1}). But, in this solvent 13 could be reduced and upon additional charge transfer (5 Fmol^{-1}) the tetrahydroderivative 14 was the major product.

Table 1. Reduction of diphenyl ether (12);

0.25 M $(C_4H_9)_4NBF_4$

<u>Solvent</u>	<u>H₂O(%)</u>	<u>mAcm⁻²</u>	<u>Fmol⁻¹</u>	<u>yield(%)</u>	
				<u>13</u>	<u>14</u>
DMF	0	8	3	--	--
DMF	12	8	5	38	3
THF	8	8	3	43	6
THF	8	24	5	trace	52

Thus reduction of benzenoid aromatics reveal that the solvent, the electrolyte cation, the current density and the water content are all important variables. In general it is important to have a rather negative potential (large TAA⁺) and a proton source (water) present under conditions where hydrogen evolution or attack on the solvent does not occur. Under such conditions difunctional molecules can be selectively reduced by control over the number of Faradays/mole which are passed. This kind of predictable selectivity should give the electrochemical method real advantage over alkali metal reductions and the possibility to use materials other than liquid ammonia and alkali metal is quite attractive.

Alkynes and Alkenes

In the literature, much has been reported and tabulated concerning the electroreduction of alkynes and alkenes. The bulk of this data involves activated substrates, compounds which are conjugated or substituted with electron withdrawing groups. The reduction of these compounds takes place at more positive potentials than isolated triple and double bonds due to the ability of the activating groups to stabilize the radical anion formed. The simple, isolated alkynes and alkenes, however, reduce beyond the "accessible" potential range of the common electrolyte-solvent systems.

Reduction of alkynes and alkenes in wet THF or diglyme with $(C_4H_9)_4N^+$ electrolytes seems to be effective. Reduction of 1-hexyne at a constant current (16 mA cm^{-2}) in THF- H_2O (8%) with 0.25 - 0.5 M $(C_4H_9)_4NBF_4$ as the electrolyte led to the formation of 1-hexene in a good yield (65%). The reactant was completely consumed after transfer of 2.8 F mol^{-1} and the only byproduct formed was hexane (5%). Upon additional charge transfer the amount of hexane increased somewhat, but at a very small rate and after transfer of 4 F mol^{-1} its yield was only 10%. Thus it seems that cathodic reduction at these conditions is feasible for terminal alkynes, but very inefficient for the corresponding alkenes. Indeed attempts to reduce 1-nonene under the same conditions as those employed for 1-hexyne were unsuccessful. After transfer of 4 F mol^{-1} less than 10% 1-nonane was obtained and most of the reactant was recovered.

Cathodic reduction of disubstituted alkynes is possible but proceeds with relatively low current efficiency. Reduction of 4-octyne under similar conditions as used for 1-hexyne yields only $\approx 50\%$ 4-octene after transfer of 8 F mol^{-1} . It is interesting to note that the ratio trans/cis for the cathodically obtained 4-octene was $\approx 3/1$. Other methods involving electron-

transfer reductions yield the corresponding trans isomers almost quantitatively.

It has been of interest to know if the electrochemical method can provide functional group selectivity. As test cases the inter- and intramolecular competition between reduction of benzene rings and terminal alkynes were studied. It was found that the amount of water in the solvent has a large effect on the ratio alkyne/benzene that reacted and that it could be used to control the ratio of alkene/dihydrobenzene products. The composition of the reduction product of an equimolar mixture of 1-hexyne/benzene in diglyme is shown in Table 2. Since this was an attempt to only determine the relative rates, reactions were not carried out to completion and the product was analyzed after $\approx 50\%$ conversion ($1F\ mol^{-1}$). It was shown that at 1% H_2O reduction of 1-hexyne predominates while at 8-12% H_2O 1,4-dihydrobenzene is the major product.

Table 2. Reduction of an equimolar mixture of 1-hexyne/benzene;
 0.1 M $(C_4H_9)_4NBF_4$ in diglyme, $I = 12.8\ mAcm^{-2}$, $Q = 1\ Fmol^{-1}$

<u>$H_2O(\%)$</u>	Yield(%)	
	<u>1-hexene</u>	<u>1,4-dihydrobenzene</u>
1	26	10
4	26	33
8	14	41
12	8	38

The inertness of olefins to cathodic reduction makes this method rather selective for reduction of benzene nuclei in molecules which also contain

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double bonds. Cathodic reduction of 21 and 24 in THF-H₂O (4-12%) with 0.25 M (C₄H₉)₄NBF₄ gave the corresponding 1,4-dihydrobenzene derivatives 22 and 25 in good yield (60%). The reactants were completely consumed after transfer of 6 Fmol⁻¹ and the corresponding byproducts 23 and 26 were formed in relatively small amounts (15%). At lower water concentrations the composition of the cathodic products of 21 and 24 was similar, but the current efficiency of the reactions was lower.

The double bond of allylbenzene 27 is more reactive than the double bonds of 21 and 24 and competing reaction of the two functional groups

is observed. The competition depends on the water content (Table 3). The double bond reacted preferentially at low water concentration while the benzene ring was mainly reduced at the higher water concentrations. Thus depending on the amount of water 28 or 29 are obtained as major

Table 3. Reduction of allylbenzene (27);
0.25 M $(C_4H_9)_4NBF_4$ in THF, $I = 3.2 \text{ mAcm}^{-2}$

<u>H₂O(%)</u>	<u>Fmol⁻¹</u>	Relative Yields(%) ^a			
		<u>27</u>	<u>28</u>	<u>29</u>	<u>30</u>
1	4	30	56	1	13
8-12	4	3	24	54	20
6	4	1	24	31	44
6	6	1	9	26	64

^aThe chemical yield of the crude product was $\approx 80\%$.

products. At medium water concentrations mixtures of 28 and 30 were formed. But these conditions were optimal if the reduction of both the benzene and the double bond functionalities was the target, and after transfer of 6 Fmol⁻¹ 30 was obtained in good yield.

From the limited data available, it seems that terminal alkynes can be efficiently reduced to the corresponding alkenes at mercury cathodes in $(C_4H_9)_4N^+$ electrolyte solutions. The cathodic reduction can be carried out in an organic-aqueous medium in which base related complications, associated with

other electron-transfer reductions, can be avoided. Efficient reduction of alkenes has not proven possible. In competition, both benzenoid and alkyne functionalities are reduced. Selectivity can be improved by controlling the water content of the medium so that a terminal alkyne can be converted to an alkene in the presence of a benzenoid aromatic functionality.

Polycyclic Aromatic Hydrocarbons

Polycyclic aromatic hydrocarbons contain extended conjugated π -electron systems and are electroactive within the cathodic "potential window" of many organic solvent/tetraalkylammonium electrolyte combinations. For many of them reduction potentials were measured and reported. It is important to note that the reduction of polycyclic aromatics involves consecutive electron-transfers and protonations. The nature of the product depends on the number of electrons and protons consumed and higher numbers result in more hydrogenated, less conjugated and thus less electroactive products. A simplified reduction scheme for polycyclic aromatics is shown below. The products are divided into three groups; [A] are reduced within the potential window and [B] require drastic reduction conditions as those described for the substrates in chapter 3.

Our focus here is on the formation of highly hydrogenated products. This process is of special interest for coal chemistry and the compounds which have been studied can be considered models for coal.

Anthracene 31 has been the subject of many electrochemical studies. It exhibits two polarographic waves at $E_{1/2} = -1.99$ and $-2.71V$ (SCE)

in DMF-0.01 M phenol with 0.25 M $(C_4H_9)_4NBr$ as the supporting electrolyte. Preparative electrolysis in this solution at -2.20V (SCE) gave 90% 9,10-dihydroanthracene (**32**). More saturated products were obtained under conditions permitting reduction of isolated benzene nuclei (as described in section 3). The products **32** - **36** were isolated and identified.

Reduction of anthracene in 55% aqueous $(C_4H_9)_4NOH$ at 80°C, affected all three aromatic rings and after transfer of 10 Fmol^{-1} the hexahydroanthracene **33** was obtained in good yield (Table 4). Lower concentrations of $(C_4H_9)_4NOH$ or temperatures were ineffective. Reduction of anthracene to **33** could also be achieved at ambient temperature or 0°C in THF-H₂O (8%) with $(C_4H_9)_4NBF_4$. The yield of the major product **33** was 55%.

Table 4. Reduction of anthracene **31**;

55% aqueous $(C_4H_9)_4NOH$, 80°C, $I = 24 \text{ mAcm}^{-2}$

<u>Cell</u>	<u>Fmol^{-1}</u>	Yield(%)				
		<u>31</u>	<u>32</u>	<u>33</u>	<u>35</u>	<u>36</u>
divided	6	41	29	20	5	4
divided	10 or more	15	3	75	4	2
undivided	10 or more	3	4	65	14	3

Using the optimum conditions for the reduction of anthracene to 33 (entry 1, Table 5) and adding a base catalyzed isomerization step for the conversion of 33 to 34 it was possible to increase the cathodic yields of the octahydro-(35) and decahydro-(36) products. The "one pot" sequence is shown below:

	a) 10 Fmol ⁻¹								
31	<u>b) reflux 48h</u> →	33	+	34	+	35	+	36	other
	c) 10 Fmol ⁻¹	34%		9%		26%		21%	6%

Phenanthrene 37 shows a polarographic wave in dioxane-4% H₂O $E_{1/2} = -2.48V$ (SCE). It has been preparatively reduced in (C₄H₉)₄NOH under conditions similar to those employed for anthracene (Table 5). Depending on

Table 5. Reduction of phenanthrene (37);
55% aqueous (C₄H₉)₄NOH, 80°C, 24 mAcm⁻²

<u>mAcm⁻²</u>	<u>Fmol⁻¹</u>					Yield(%)	
		<u>37</u>	<u>38</u>	<u>octahydro^a</u> <u>phenanthrenes</u>		<u>decahydro^c</u> <u>phenanthrene</u>	
32	3	20	52	12		0	
11	10	0	0	74 ^b		17	
8	20	0	0	27		54	

^aMixture of three isomers

^bThe octahydrophenanthrene 39 constitutes 23% of this mixture

^cOne isomer in which the double bonds are nonconjugated

the amount of charge transferred, with a current density of 32 mAcm^{-2} , dihydrophenanthrene **38** or a mixture of octahydrophenanthrenes was the major product. At a lower current density (8 mAcm^{-2}), but with a longer reaction time decahydrophenanthrene was the major product and octahydrophenanthrenes were significant byproducts.

37

38

39

These studies in aqueous $(\text{C}_4\text{H}_9)_4\text{NOH}$ or mixed solvents containing $(\text{C}_4\text{H}_9)_4\text{N}^+$ show that the aromatic hydrocarbons can be converted to rather highly saturated products. In general, although mixtures will always result, it should be possible to drive the process to get isolable quantities of products like hexahydroanthracene **33**, octahydrophenanthrene **39** and tetrahydronaphthalene **44**. The aqueous $(\text{C}_4\text{H}_9)_4\text{NOH}$ system is of considerable interest for large scale work in that it requires no organic cosolvent and it is highly conductive.

Reductive Cleavage

Cleavage is a common reaction pathway for substrates which, upon reduction to the intermediate radical-anion stage, may split off relatively stable anions. Often such substrates contain heteroatoms which stabilize the

negative charge on the cleaved anion.

Benzyl derivatives of aliphatic alcohols are not reduced below the discharge potential of $(C_2H_5)_4N^+$ in DMF [-2.9V (SCE)]. But, they show a wave around -3.1V (SCE) in solutions of $(C_4H_9)_4N^+$. Efficient reductive cleavage of benzyl methyl ether was achieved in THF-8% H_2O with 0.25 M $(C_4H_9)_4NBF_4$. Under these conditions, toluene, which is the cleavage product may also

be reduced and the product depended on the amount of charge transferred. The chemical yield of the isolated product was 70% and it contained 92% toluene after transfer of 2 Fmol^{-1} and 93% 2,5-dihydrotoluene after 4 Fmol^{-1} .

Reduction of benzo[b]thiophene 45 was also carried out in aqueous 55% $(C_4H_9)_4NOH$ and 0.1M $(C_4H_9)_4NBF_4$ in THF-8% H_2O . The products were 46 and 2-ethylbenzenethiol 47. Some results are shown in Table 6. The major product

Table 6. Reduction of benzo[b]thiophene (45); $I = 24 \text{ mAcm}^{-2}$

Electrolyte	Fmol^{-1}	Yield(%)		
		45	46	47
aqueous 55% $(C_4H_9)_4NOH$, $80^\circ C$	2	7	68	15
	6	8	6	77
0.1M $(C_4H_9)_4NBF_4$, THF-8% H_2O , $0^\circ C$	2	4	75	12
	4	8	0	54

of 45 in either solvent was 46 after transfer of charge equivalent to $2F \text{ mol}^{-1}$ and 47 after transfer of $4 F \text{ mol}^{-1}$ (or more). The chemical yield of 46 was somewhat better in the aqueous medium, while that of 47 was better in THF- H_2O . It was shown that 47 is the product of reductive cleavage of 46. Electrolysis of 46 ($2 F \text{ mol}^{-1}$) under conditions identical to those used for 45 gave 65% 47. Thus 45 is first hydrogenated to 46 which is consequently cleaved (upon additional charge transfer) to 47. It is interesting to note that 47 is the only product of 45 formed by alkali metal-liquid NH_3 reduction. Obviously solvated electrons are more powerful and less selective reducing agents than $(\text{C}_4\text{H}_9)_4\text{N}$ -mercury.

Summary

The studies described above demonstrate that a number of types of compounds, both aliphatic and aromatic, are cathodically reduced in the potential region -2.7 to -3.1 V (SCE) at mercury in a suitable solvent containing a TAA^+ electrolyte. It seems likely that other types of compounds will also reduce in this potential region and it is certain that more examples will be found within the functional group types already discovered.

The observation that so many compounds reduce in such a narrow potential range is curious. We hypothesize that one reason is that many of these reactions are catalyzed via the TAA^+/TAA -mercury couple. The mediated reactions then include reduction of compounds, like benzene, whose E° for single electron transfer is more negative than -3.1 V (SCE) . A second reason

for the possibility of reducing many compounds in this narrow potential range is that the reduction rates often depend on proton availability, which can be adjusted to make the process feasible.

Another curious observation is that many of the reactions described are rather selective and proceed with relatively high chemical and electrical yields. In general, it is believed that high energy processes are unselective. Reactions at very negative potentials should be, therefore, rather unselective. Furthermore, this potential range is one where the electrolyte and electrode are not inert. It seems that the "background decomposition" reaction is a very selective one generating TAA-mercury and it seems that TAA-mercury react rapidly and specifically with the organic substrates. We do provide a note of caution because the recovery of TAA^+ after bulk electrolysis has not been satisfactorily investigated, but the selectivity of organic reductions is remarkable. Especially remarkable is the selectivity exhibited when two different functional groups are present in the molecule, each of which can be reduced in this potential range. Several of these examples show that the electrochemical method is easily tuned to give better results than the alkali metal-ammonia alternative.

For the future it seems clear that this field is open to many fruitful investigations and developments. The creative organic chemist will develop more complex and more useful syntheses and the electrochemist will bring quantitative understanding to the mechanism(s) of this unusual, general and selective heterogeneous catalytic process. Because it is possible to obtain TAA-metals from metals other than mercury, the range of observed reactions may increase phenomenally - and in an understandable way. Indeed, this entire field is ripe for further discovery, better understanding and more useful applications.

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