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## Electrohydrodimerization Reactions

### V. Liquid Ammonia as a Solvent for Reductive Coupling of Diethyl Fumarate, Cinnamionitrile, and Acrylonitrile

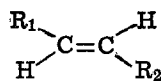
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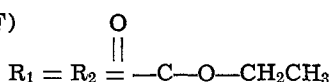
#### ABSTRACT

Cyclic voltammetric (CV) and controlled potential coulometric investigations of the reduction of several activated olefins in anhydrous liquid ammonia containing either 0.1M methyl-tri-n-butylammonium iodide or 0.1M potassium iodide as supporting electrolytes are reported. For diethyl fumarate and cinnamionitrile the studies provide evidence for formation of a radical anion, which undergoes dimerization and polymerization reactions, and of dianion formation at more negative potentials. The effect of adding isopropanol and glacial acetic acid was also investigated.

The reduction of activated olefins in aprotic media has been the subject of numerous investigations [see (1, 2) and references therein]. Diactivated olefins (R) react via formation of the radical anion and produce, depending upon the acidity of the medium, hydrodimer (R<sub>2</sub>H<sub>2</sub>), reduced monomer (RH<sub>2</sub>), and polymer. At more negative potentials, where dianion is produced, extensive polymerization apparently occurs, so that the second reduction waves observed in voltammetry are frequently much smaller than the first waves. We have previously shown that anhydrous liquid ammonia is a useful medium for studies of the electroreduction of organic compounds (3, 4) and that stable dianions of benzophenone and nitrobenzene could be prepared in this solvent. This stability of radical anions and dianions in ammonia can be attributed to the low acidity of the solvent, the possibility of preparing highly pure solutions through the use of vacuum line techniques and solvent treatment with sodium, and the fact that these studies are carried out at low temperatures, decreasing the rate of homogeneous chemical reactions following the electron transfer steps. Previous studies of amalgam reductions leading to hydrodimerization in liquid ammonia have also been described (5). In this paper we describe preliminary cyclic voltammetric and coulometric experiments on the reduction of several activated olefins in liquid ammonia; the structures of the substances studied are shown below



Diethyl fumarate (DEF)



Cinnamionitrile (CN)  $R_1 = -C_6H_5$   $R_2 = -CN$

Acrylonitrile  $R_1 = H$   $R_2 = -CN$

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Key words: cyclic voltammetry, coulometry, electrochemical dimerizations, organic electrochemistry.

#### Experimental

General experimental techniques were the same as those reported previously (2-4); a detailed description is available (6). The four-compartment cell, containing separate chambers for the working, reference, and auxiliary electrodes, and an intermediate chamber between the working and auxiliary compartments was employed. A gold working microelectrode, polished with AB ALPHA polishing alumina (Buehler Limited, Evanston, Illinois) before each experiment, was employed in cyclic voltammetric experiments and a 3 cm by 8 cm platinum electrode was used in coulometry. A silver wire (Ag. R.E.) isolated in a separate compartment closed with a sintered-glass disk was used as reference electrode. All experiments were carried out with a Princeton Applied Research Corporation Model 170 electrochemistry system using positive feedback resistance compensation. All experiments were conducted on a high vacuum line (10<sup>-5</sup> Torr) at -43°C.

#### Results and Discussion

*Diethyl fumarate.*—The cyclic voltammetric (CV) reduction of DEF in DMF solution shows a fairly reversible first reduction wave at fast scan rates and has been characterized by reversible reduction to the radical anion followed by a coupling reaction (2). The second reduction wave is very small or even characterized by a current decrease in polarography or RDE voltammetry, which has been ascribed to production of the dianion which initiates a rapid polymerization reaction removing parent from the vicinity of the electrode. In liquid ammonia, the CV reduction occurs in two reversible waves at fast scan rates (Fig. 1a) with the reversal wave heights decreasing at slower scan rates (Fig. 1b) indicating decomposition reactions of the electrogenerated species. Typical data for CV experiments for DEF are shown in Table I. The theory of CV for electrode reactions with following dimerization reactions has been presented (7, 8); application of this theory in estimating the rate constant for the dimerization step from the variation of  $i_{pa}/i_{pc}$  for the first reduction wave yields a value of about 0.1 M<sup>-1</sup> sec<sup>-1</sup>.

Table I. Cyclic voltammetric data for reduction of diethyl fumarate in liquid ammonia<sup>a</sup>

Concentration, C (mM)	Scan rate, v (mV/sec)	First wave			Second wave		
		$i_{pc}$ ( $\mu$ A)	$i_{pa}/i_{pc}$	$-E_{pc}^b$ (V)	$i_{pc}$ ( $\mu$ A)	$i_{pa}/i_{pc}$	$-E_{pc}^b$ (V)
A. 0.1M Methyl-tri-butylammonium iodide							
1.5	50	28	0.41	0.87	10	0.42	1.40
	100	36	0.48	0.88	16	0.87	1.41
	200	49	0.64	0.89	24	0.86	1.42
	500	71	0.87	0.91	52	0.96	1.45
	20,000	620	1.0	0.94	450	1.0	1.50
$i_{pc}(l)/v^{1/2}C = 1.95$							
3	50	49	0.64	0.87	13	0.66	1.40
	100	63	0.54	0.88	24	0.33	1.41
	200	84	0.60	0.90	41	0.68	1.44
	500	123	0.78	0.92	82	0.9	1.48
	$i_{pc}(l)/v^{1/2}C = 2.0$						
4.6	50	65	0.50	0.85	15	0.46	1.42
	100	90	0.53	0.86	29	0.43	1.39
	200	128	0.53	0.87	56	0.70	1.40
	500	200	0.67	0.88	120	0.80	1.42
	$i_{pc}(l)/v^{1/2}C = 2.4$						
B. 0.1M KI <sup>c</sup>							
2.3	50	12.5		0.74			1.33
	100	22.5		0.75			1.34
	200	29		0.76			1.35
	500	38		0.77			1.37
	$i_{pc}(l)/v^{1/2}C = 0.98$						

<sup>a</sup> Solution contained indicated supporting electrolyte in anhydrous liquid ammonia.

<sup>b</sup> vs. Ag-wire reference electrode.

<sup>c</sup> Second reduction wave and reversal waves were to ill-defined for precise current measurements.

The addition of alkali metal ions has been shown to increase the rate of the coupling reaction in DMF, probably by formation of ion pairs with the radical anions (2). The CV reduction of DEF is similarly affected by the addition of KI in liquid ammonia (Fig.

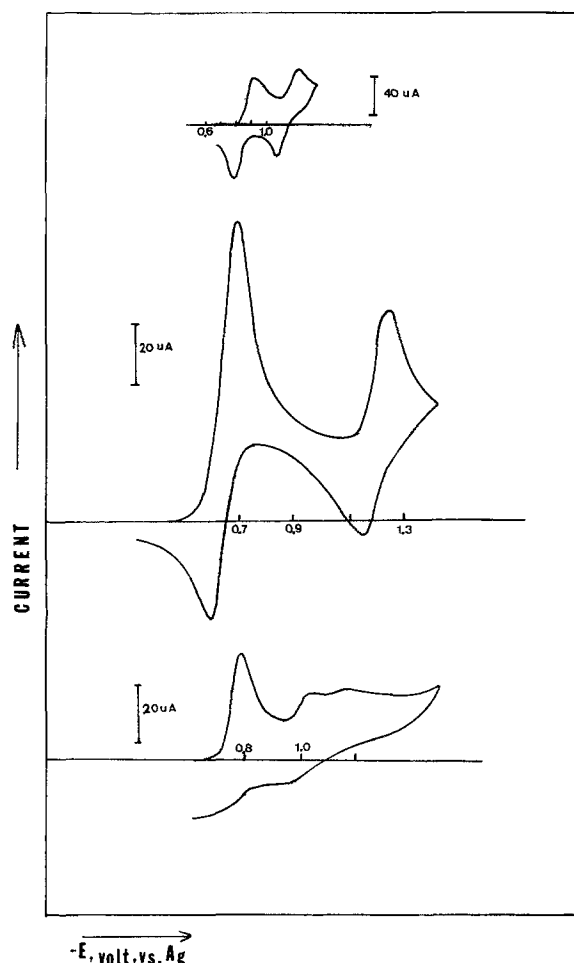


Fig. 1. Cyclic voltammograms of diethyl fumarate in liquid ammonia: (a) 1.75 mM DEF, 0.1M MTBAI,  $v = 20$  V/sec; (b) 3 mM DEF, 0.1M MTBAI,  $v = 0.2$  V/sec; (c) 3.5 mM DEF, 0.1M KI,  $v = 0.2$  V/sec.

1c), although the kinetics of the reactions were not studied in this case. The addition of a threefold excess of a proton donor, either the weak acid, isopropanol (i-PrOH), or the strong acid, acetic acid (HOAc) to the DEF/MTBAI/ $NH_3$  system has essentially no effect on the first reduction wave, but decreases the reversal current of the second wave and shifts the second wave to more positive potentials. The extent of the shift increases linearly with the log of the proton donor concentration; for acetic acid  $\Delta E_p/\Delta \log[HOAc] = 39$  mV; and for i-PrOH,  $\Delta E_p/\Delta \log[i-PrOH] = 57$  mV. These results suggest that protonation of the radical anion species does not occur, even with the strong acid HOAc, while the dianion reacts with acid. This scheme is reminiscent of that found with benzophenone (3), and the CV reaction order treatment of Savéant and Vianello (8) probably applies here as well. From the limiting slopes of the peak shift with log proton donor concentration we find a reaction order of dianion ( $m_z$ ) and proton donor ( $m_z$ ) of 0.5 and 1.9, respectively, for i-PrOH and 0.4 and 1.2 for HOAc. This half-order dependence on dianion is the same as that observed for benzophenone dianion and probably indicates kinetic complications in the electron transfer reaction or interferences due to the dianion polymerization reaction.

Controlled potential coulometry of DEF in the presence of either MTBAI or KI as supporting electrolyte (Table II) at potentials beyond the first reduction peak show  $n_{app}$  values less than one, even in the presence of proton donor. This result suggests, as do the similarly low values of  $n_{app}$  in DMF, that a slow polymerization reaction of the radical anion occurs on the coulometric time scale. CV experiments after coulo-

Table II. Controlled potential coulometry results

Compound	Concentration (mM)	Conditions	$n_{app}$
DEF	4.3	0.1M MTBAI	0.6
	10	0.1M MTBAI	0.5
	20	0.1M MTBAI + 40 mM i-PrOH	0.5
DEF	7	0.1M KI	0.4
DEF	3	0.1M KI + 14 mM HOAc	0.5
CN	10.4	0.1M MTBAI	0.16
	13.6	0.1M MTBAI + 40 mM i-PrOH	0.04
CN	20	0.1M MTBAI	0.27
AN	3	0.1M MTBAI	0.05
	14	0.1M MTBAI	0.17
AN	10	0.1M KI + 10 mM i-PrOH	0.96
AN	20	0.1M KI + 20 mM i-PrOH	0.88
AN	20	0.1M KI + 10 mM HOAc	2

metric reduction showed no reduction or oxidation peaks.

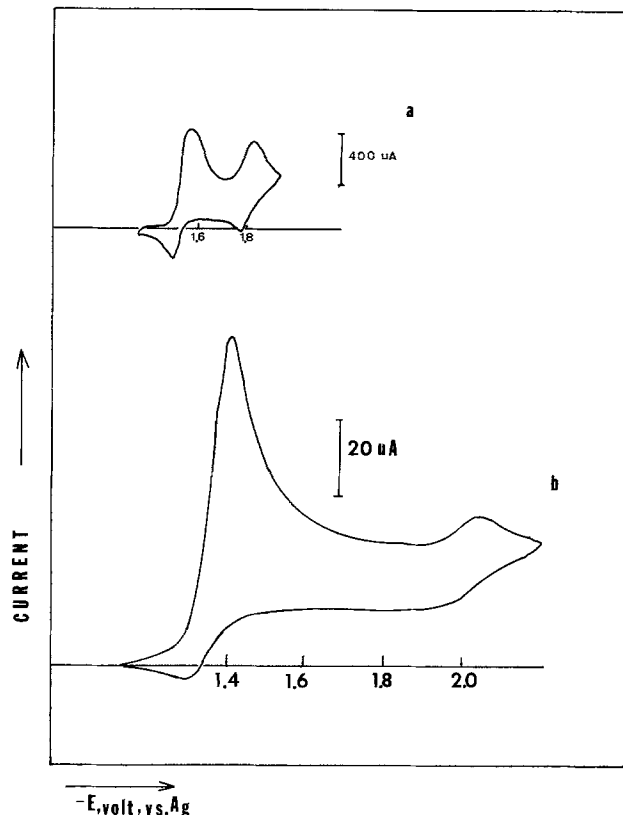


Fig. 2. Cyclic voltammograms of 3.2 mM cinnamionitrile in liquid ammonia containing 0.1M MTBAI with a  $v$  of (a) 20 and (b) 0.2 V/sec.

**Cinnamionitrile.**—The CV reduction of CN at high scan rates (Fig. 2) also shows two reduction waves with appreciable anodic currents on reversal. Typical CV data for CN are shown in Table III. At slower scan rates the second reduction peak decreases in size and the reversal currents decrease. For CN, as opposed to DEF, the value of  $i_p/v^{1/2}C$  decreases significantly with

Table III. Cyclic voltammetric data for reduction of cinnamionitrile in liquid ammonia<sup>a</sup>

Concentration, C (mM)	Scan rate, $v$ (mV/sec)	$i_{pc}$ ( $\mu A$ )	$-E_{pc}^b$ (V)	$-E_{pc}^c$ (2) (V)
1.6	50	38	1.27	1.90
	100	55	1.28	1.88
	200	73	1.28	1.88
	500	105	1.33	1.90
$i_{pc}/v^{1/2}C = 3.3$				
3.2	50	52	1.26	1.90
	100	88	1.27	1.90
	200	120	1.28	1.90
	500	140	1.36	1.88
$i_{pc}/v^{1/2}C = 3.1$				
7.2	50	82	1.27	
	100	133	1.27	
	200	195	1.28	
	500	280	1.33	
$i_{pc}/v^{1/2}C = 2.2$				
10	50	127	1.25	
	100	175	1.27	
	200	240	1.28	
	500	300	1.34	
$i_{pc}/v^{1/2}C = 1.6$				
20	50	170	1.24	
	100	212	1.25	
	200	280	1.27	
	500	395	1.35	
$i_{pc}/v^{1/2}C = 0.8$				

<sup>a</sup> Solution contained 0.1M MTBAI.

<sup>b</sup> First wave, V vs. Ag-wire reference electrode.

<sup>c</sup> Second wave. Peak too ill-defined at higher concentrations for precise measurement.

increasing concentration of CN, suggesting that the polymerization reaction of the radical anion is important, even on the CV time scale. Treatment of the  $i_{pa}/i_{pc}$  data for the first reduction wave, assuming a following coupling reaction of the radical anion, yields a dimerization rate constant of about  $5.7 M^{-1} sec^{-1}$ . The CV behavior in the presence of proton donor resembles that of DEF: the first wave is unaffected by additions of *i*-PrOH or HOAc, while the second wave is shifted to more positive potentials. The limiting  $E_p$  vs. log proton donor concentration plots for the second wave yield reaction orders  $m$  and  $m_z$  of 0.4 and 2, respectively, for *i*-PrOH and 0.7 and 1 for HOAc. Controlled potential coulometry of CN (Table II) in the absence of proton donor or with *i*-PrOH showed very low  $n_{app}$  values suggesting abundant polymerization.

**Acrylonitrile.**—The CV reduction of AN at all scan rates up to 20 V/sec in both MTBAI and KI electrolytes occurs in a single irreversible wave (Fig. 3); typical CV data are shown in Table IV. The very low  $i_p/v^{1/2}C$  values observed with MTBAI as electrolyte are evidence of a very rapid polymerization of AN, as is also observed in aprotic solvents in the absence of proton donor. In the KI electrolyte however the  $i_p/v^{1/2}C$  values are larger and closer to those of DEF and CN. Controlled potential coulometric reduction of AN (Table II) also shows evidence of polymerization in MTBAI. In a KI + *i*-PrOH medium, however,  $n_{app}$  values close to one are obtained, suggesting significant formation of the hydrodimer product. Product analysis

Table IV. Cyclic voltammetric data for reduction of acrylonitrile in liquid ammonia

Concentration, C (mM)	Scan rate, $v$ (mV/sec)	$i_{pc}$ ( $\mu A$ )	$-E_{pc}$ (V vs. Ag R.E.)
A. 0.1M Methyl-tributyl ammonium iodide			
4.3	50	12	1.86
	100	20	1.86
	200	24	1.91
	500	27	1.96
$i_{pc}/v^{1/2}C = 0.55$			
5.8	50	5	1.78
	100	9	1.83
	200	15	1.86
	500	23	1.98
$i_{pc}/v^{1/2}C = 0.25$			
8.6	50	10	1.84
	100	12	1.86
	200	16	1.86
	500	19	1.96
$i_{pc}/v^{1/2}C = 0.07$			
11.5	50	6	1.86
	100	10	1.86
	200	15	1.90
	500	29	2.05
$i_{pc}/v^{1/2}C = 0.13$			
14.6	50	18	1.91
	100	20	1.90
	200	24	1.91
	500	37	1.96
$i_{pc}/v^{1/2}C = 0.06$			
23.2	50	16	1.93
	100	21	1.99
	200	28	2.00
	500	49	2.06
$i_{pc}/v^{1/2}C = 0.11$			
B. 0.1M Potassium iodide			
5.8	50	85	1.61
	100	120	1.62
	200	205	1.64
	500	285	1.67
$i_{pc}/v^{1/2}C = 1.7$			
10.3	50	70	1.62
	100	130	1.64
	200	220	1.68
	500	340	1.70
$i_{pc}/v^{1/2}C = 1.8$			
11.5	50	55	1.62
	100	93	1.64
	200	225	1.68
	500	430	1.70
$i_{pc}/v^{1/2}C = 2.1$			
20.12	50	95	1.62
	100	135	1.63
	200	195	1.64
	500	335	1.67
$i_{pc}/v^{1/2}C = 1$			

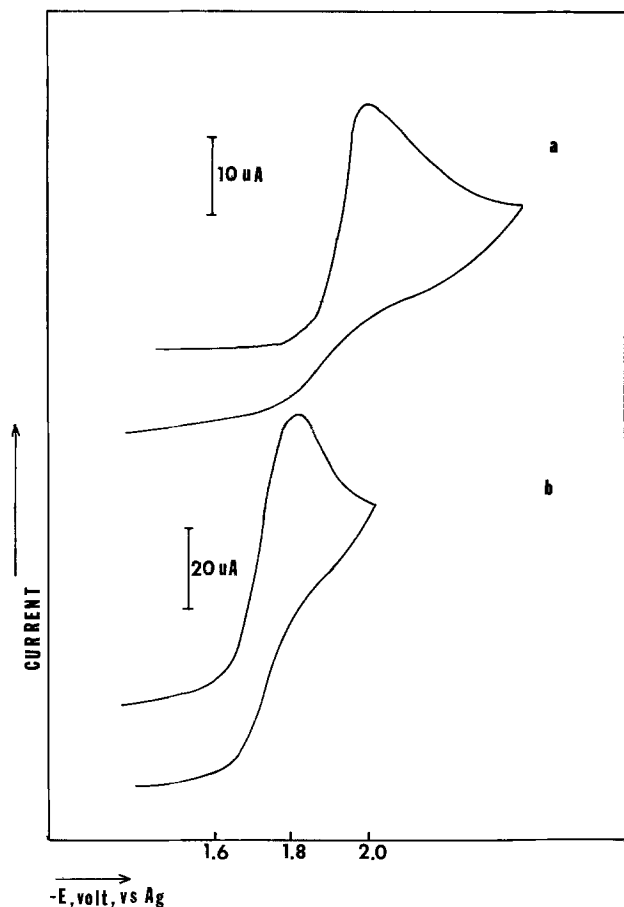


Fig. 3. Cyclic voltammograms of acrylonitrile in liquid ammonia; (a) 5.75 mM acrylonitrile, 0.1M MTBAI,  $\nu = 0.2$  V/sec; (b) 5.16 mM acrylonitrile, 0.1M KI,  $\nu = 0.2$  V/sec. Curves are of same form at higher scan rates.

of these solutions by gas chromatography was attempted, but unambiguous analyses were not obtained. The addition of HOAc yields  $n_{app}$  values near 2, probably signalling the production of some of the two-electron protonated product, propionitrile, in the presence of strong acid.

The preliminary results show the formation of radical anions and dianions of the deactivated olefins DEF and CN and suggest that with the addition of suitable amounts of proton donor, hydrodimerization reactions can be carried out in liquid ammonia. After this paper was submitted, a communication by Chiba *et al.* (9) appeared, in which the electrolytic reduction of acrylonitrile in liquid ammonia containing ammonium perchlorate as supporting electrolyte at a mercury cathode was described. These authors found a high yield of adiponitrile with some formation of propionitrile under these conditions with constant current electrolysis.

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