Tetrahedron Letters, Vol. 34, No. 8, pp. 1271-1274, 1993
Printed in Great Britain

0040-4039/93 $6.00 + .00
Pergamon Press Ltd

Lactones as Minor Products of the Electrochemical Reduction of Glutaryl Dichloride at Mercury Cathodes in Acetonitrile

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Key Words: Electrochemical Reduction; Glutaryl Dichloride; 5-Chlorovalerolactone; Valerolactone

Abstract: *Electrochemical reduction of glutaryl dichloride at a mercury electrode in acetonitrile containing 0.1 M tetraethylammonium perchlorate results in the formation of 5-chlorovalerolactone, valerolactone, and a polymeric species.*

Recently, we have established that the electrochemical reduction of acyl halides in acetonitrile containing tetraalkylammonium salts can lead to the formation of aldehydes. Heptanoyl chloride is reduced to heptaldehyde at both carbon and mercury cathodes;[1] phenylacetaldehyde and hydrocinnamaldehyde are produced by the electrolysis of phenylacetyl chloride and hydrocinnamoyl chloride, respectively, at mercury electrodes;[2] reduction of cyclohexanecarbonyl chloride at mercury affords cyclohexanecarboxaldehyde;[3] and the reduction of trimethylacetyl chloride at either a carbon or mercury cathode generates trimethylacetaldehyde.[4] On the other hand, electrolytic reduction of phthaloyl dichloride produces 3-chlorophthalide, phthalide, biphthalyl, and dihydrobiphthalide.[5] These publications, which contain detailed information about experimental procedures, provide brief reviews of several previous papers[6-9] dealing with the electrochemistry of aromatic acyl halides. Because there have been no previous reports pertaining to the electrolytic behavior of acid chlorides of aliphatic dicarboxylic acids, we describe here the results of a study of the reduction of glutaryl dichloride at mercury cathodes in acetonitrile containing 0.1 M tetraethylammonium perchlorate (TEAP). We have found that 5-chlorovalerolactone and valerolactone arise via reductive intramolecular cyclization of the starting material.

As shown in Figure 1, a cyclic voltammogram for reduction of glutaryl dichloride at a hanging mercury drop electrode exhibits three irreversible waves with peak potentials of -1.34, -1.43, and -1.75 V in acetonitrile containing 0.1 M TEAP at 100 mV s^{-1}. A current spike appears in the cyclic voltammogram at -1.38 V which we attribute to an adsorption process; in fact, when cyclic voltammograms are recorded for reduction of the acyl halide at a glassy carbon disk, blockage of the electrode surface by an adsorbed species appears to be so effective that no current is observed on the second and all succeeding repetitive cathodic voltage scans. In addition, the current spike seen with a hanging mercury drop varies in prominence as the potential is cycled repetitively, which influences the distinctness with which the second main reduction wave for glutaryl dichloride can be seen; in some instances, the second wave is clearly delineated because the current spike is nearly absent. On the basis of our previous work concerning the electrochemical behavior of aliphatic acyl halides,[1,3,4] we propose that the first step in the reduction of glutaryl dichloride is a one-electron process to yield a radical-anion which cyclizes intramolecularly to give the radical precursor of 5-chlorovalerolactone, whereas reductive cleavage of the carbon-chlorine bond of any electrochemically generated 5-chlorovalerolactone to afford valerolactone is responsible for the second wave. We attribute the third wave for glutaryl dichloride to reduction of glutaric anhydride; a cyclic voltammogram for reduction of glutaric anhydride at a hanging mercury drop electrode reveals one irreversible wave at -1.77 V in acetonitrile containing 0.1 M TEAP at a scan rate of 50 mV s^{-1}, and deliberate addition of glutaric anhydride to a solution of glutaryl dichloride causes the third wave to increase in magnitude.

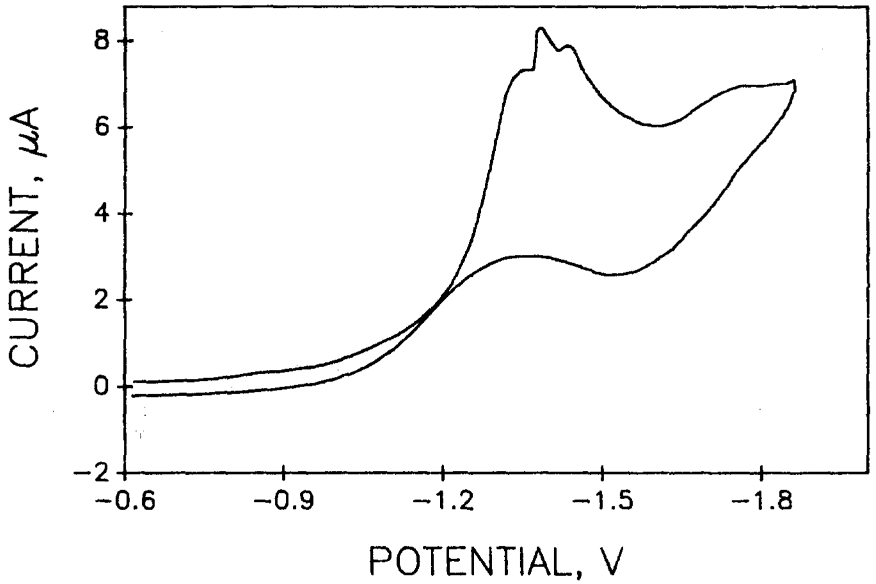


Figure 1. Cyclic voltammogram for reduction of 6 mM glutaryl dichloride at a hanging mercury drop electrode (area = 0.014 cm^2) in acetonitrile containing 0.1 M TEAP at a scan rate of 100 mV s^{-1}.

Coulometric data and product distributions for a series of controlled-potential electrolyses of glutaryl dichloride at mercury pool cathodes in acetonitrile containing 0.1 M TEAP at potentials before and after the peak of the first voltammetric wave are compiled in Table 1. Each tabulated value for *n* is the average number of electrons transferred to a molecule of glutaryl dichloride without any correction for starting material that is not consumed electrochemically, and all reported product yields (which were determined by means of gas chromatography[10]) represent the absolute percentage of starting material incorporated into a particular species. There appear to be no major differences in the coulometric *n* values or product distributions for the two potentials employed for the reductions. As shown in Table 1, two identifiable cyclic compounds, 5-chlorovalerolactone and valerolactone, were found as electrolysis products; valerolactone is formed because both potentials (-1.15 and -1.45 V) chosen for the experiments are on the rising part of the cyclic voltammetric wave for 5-chlorovalerolactone; thus, partial reduction of the latter compound takes place. Residual water in the solvent-supporting electrolyte system causes hydrolysis of glutaryl dichloride which leads to the formation of glutaric anhydride.

As is revealed in Table 1, the major electrolysis product is a grayish-white solid which starts to form immediately upon application of the potential; this material does not dissolve in solvents ranging from hexane to water. Analysis by means of FT-IR spectrometry showed a band at 1734 cm^{-1} which could be due to the carbonyl stretching mode of an ester. Mass spectrometry indicated that no mercury is incorporated into the solid, inasmuch as the characteristic isotope pattern of mercury was absent; the solid did not give reproducible mass spectroscopic parent-ion or fragmentation patterns. Elemental analysis (Galbraith Laboratories, Inc.) showed that the solid contained approximately 48% carbon, 6% hydrogen, and 21% oxygen, with the remainder most probably being chlorine. Although no precise formula is compatible with the preceding data, it is conceivable that the material is a polymer such as $X[(CH_2)_3CHCl\text{-}O\text{-}C{=}O]_n(CH_2)_3X$, where X = CHO or CO_2H. This species could arise via attack of the initially generated radical-anion of glutaryl dichloride on a molecule of unreduced starting material; reduction of this adduct to yield a new radical-anion which reacts with another molecule of starting material, and so on, would build the polymer.

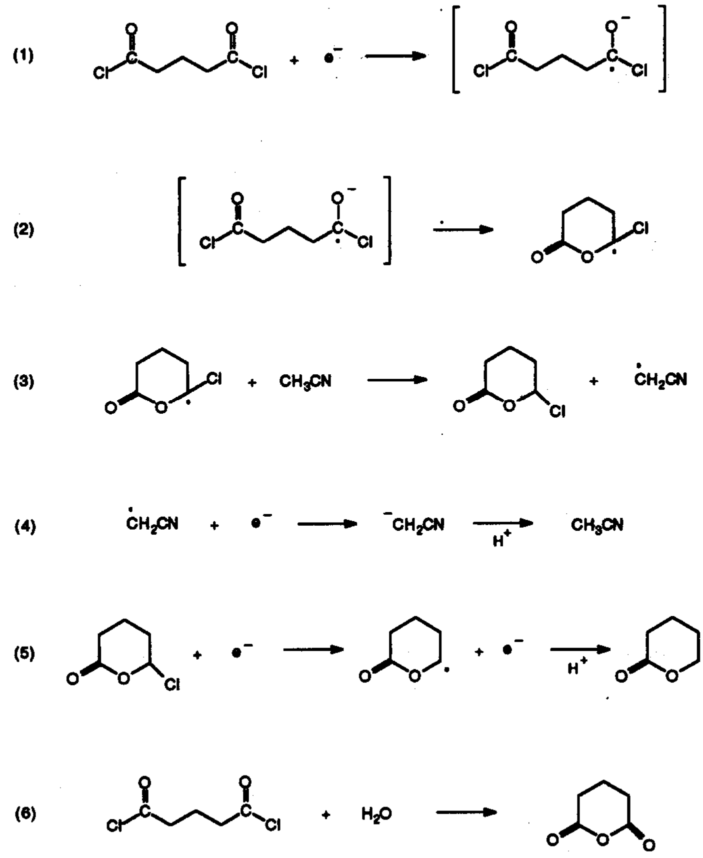
Table 1. Coulometric Data and Product Distributions for Controlled-Potential Electrolyses of Glutaryl Dichloride in Acetonitrile Containing 0.1 M TEAP at a Mercury Cathode

		Product Distribution,[a] %		
$[ClCO(CH_2)_3COCl]$, mM	*n*	5-Chlorovalerolactone	Valerolactone	Glutaric anhydride
(a) E = -1.15 V				
12	2.10	6	18	38
6	2.10	7	9	23
6	1.99	10	9	20
(b) E = -1.45 V				
20	2.16	12	14	20
20	2.10	9	11	39
12	2.19	14	18	34
6	2.05	9	8	25
6	2.20	14	7	8

[a] No unreduced glutaryl dichloride remained; the other product is a polymeric material (see text for further discussion).

Scheme 1 shows plausible reaction pathways for the formation of the various identified products. First, the acyl halide is reduced to a radical-anion which undergoes intramoleular cyclization with displacement of chloride ion to afford the radical precursor of 5-chlorovalerolactone (reactions 1 and 2); the absence of glutaric dialdehyde as a product suggests that cyclization must precede the loss of chloride ion, a scenario similar to what we have observed for the electrochemical reduction of phthaloyl dichloride.[5] Hydrogen atom abstraction from acetonitrile can occur to produce 5-chlorovalerolactone and $\cdot CH_2CN$ (reaction 3); studies of the electrochemical reduction of heptanoyl chloride[1] and cyclohexanecarbonyl chloride[3] in the presence of acetonitrile-d_3, deuterium oxide, and diethyl malonate-d_2 have demonstrated that acetonitrile serves as a donor of hydrogen atoms and not of protons.[1,3] We propose that, at potentials employed for the electrolysis of glutaryl dichloride, the solvent-derived radical ($\cdot CH_2CN$) is reduced to $^-CH_2CN$, followed by abstraction of a proton from residual water or the supporting-electrolyte cation to regenerate acetonitrile (reaction 4); no succinonitrile (formed by coupling of $\cdot CH_2CN$) and no species arising from attack of $^-CH_2CN$ on the carbonyl moieties of the starting material or products[11,12] were detected, yet we have found in previous work[1-4] that one-electron reduction of $\cdot CH_2CN$ is necessary to account for the anomalously high coulometric *n* values observed for electrolyses of acyl halides. Because the cyclic voltammetric waves for reduction of glutaryl dichloride and 5-chlorovalerolactone lie close to each other, two-electron reduction of the carbon-chlorine bond of 5-chlorovalerolactone is unavoidable, and the resulting anion can abstract a proton from water or supporting electrolyte to afford valerolactone (reaction 5). Finally, hydrolysis of the acyl halide, due to the presence of residual water in the solvent-supporting electrolyte, leads to formation of glutaric anhydride (reaction 6).

Scheme 1



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(Received in USA 29 October 1992; accepted 8 December 1992)