Electrochemical Reduction of Trimethylacetyl Chloride at Carbon and Mercury Electrodes in Acetonitrile

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In previous reports we have established that the electrochemical reductions of heptanoyl chloride,[1] phenylacetyl chloride,[2] hydrocinnamoyl chloride,[2] cyclohexanecarbonyl chloride,[3] and 2,4,6-trimethylbenzoyl chloride[4] at carbon and mercury electrodes in acetonitrile containing tetraalkylammonium perchlorates leads to the production of aldehydes. Experiments involving the use of acetonitrile-d_3, deuterium oxide, and diethyl malonate-d_2 have indicated that heptaldehyde and cyclohexanecarboxaldehyde arise from acyl radical intermediates, whereas phenylacetaldehyde, hydrocinnamaldehyde, and 2,4,6-trimethylbenzaldehyde are derived from both acyl radicals and acyl anions. Moreover, we have reported that, depending on the electrolysis potential and on whether a proton donor is present or absent, phthaloyl dichloride can be electrochemically reduced to 3-chlorophthalide, phthalide, biphthalyl, and dihydrobiphthalide.[5] In addition, the preceding papers contain summaries of four other publications[6-9] dealing with the electrochemical reduction of acyl halides.

In the last decade or so, there have been several investigations concerning the chemical reduction of trimethylacetyl chloride. Entwistle and co-workers[10] used tetrahydroborate in the presence of metal ions with dimethylformamide in acetonitrile to reduce trimethylacetyl chloride to trimethylacetaldehyde in 32% yield. Reduction of trimethylacetyl chloride with tri-*n*-butyltin hydride in the presence of tetrakis(triphenylphosphine)palladium(0) and triphenylphosphine in benzene was carried out by Four and Guibe[11] to produce trimethylacetaldehyde in 80% yield. Leblanc, Moise, and Tirouflet[12] reduced trimethylacetyl chloride with carbonyldi-η^5-cyclopentadienyltantalum hydride and carbonyldi-η^5-cyclopentadienylniobium hydride in diethyl ether to afford trimethylacetaldehyde, but the yield of aldehyde was not reported. Pentacoordinated hydrogenosilanes were employed by Corriu, Lanneau, and Perrot[13] to form trimethylacetaldehyde in 95% yield.

Ingold and co-workers[14] used tri-*n*-butyltin hydride to probe the mechanism of reduction of trimethylacetyl chloride to trimethylacetaldehyde. A radical intermediate was ruled out because the yield of aldehyde did not change when the reaction was carried out in the presence of galvinoxyl, an inhibitor of free-radical processes, whereas isobutane was the major product when the reaction was initiated with free radicals generated by the decomposition of *tert*-butylhyponitrile. Ultimately, these investigators were not able to elucidate the actual mechanism for the conversion of trimethylacetyl chloride to trimethylacetaldehyde.

In the present work, we have examined the electrochemical reduction of trimethylacetyl chloride at both carbon and mercury electrodes in acetonitrile containing tetraalkylammonium perchlorates. Trimethylacetaldehyde and trimethylacetic anhydride, the latter arising via hydrolysis of the starting material, are the only products recovered.

Experimental Section

Reagents. Acetonitrile was purchased from American Burdick & Jackson Laboratories, Inc.; prior to use, it was distilled over calcium hydride to remove water. Tetramethylammonium perchlorate (TMAP) and tetraethylammonium perchlorate (TEAP), from the G. Frederick Smith Chemical Co., were employed without additional purification as supporting electrolytes. Trimethylacetyl chloride, obtained from Aldrich Chemical Co., was transferred from original containers into electrochemical cells with the aid of syringes. All deaeration procedures were carried out with zero-grade argon (Air Products).

Electrodes, Cells, Instrumentation, and Procedures. For cyclic voltammetric studies, we used a three-electrode cell of conventional design[15] that accommodated either a carbon or mercury working electrode. A glassy carbon rod (Tokai Electrode Manufacturing Co., Tokyo, Japan), press fitted into a shroud of Teflon, provided a disk-shaped working electrode with an area of 0.077 cm^2; descriptions of the construction, polishing, and cleaning of this electrode have been reported previously.[16] Alternatively, the working electrode was a hanging mercury drop (obtained with a Metrohm Model EA290 capillary system) having an area of 0.014 cm^2. All potentials are quoted with respect to a reference electrode consisting of a saturated cadmium amalgam in contact with dimethylformamide saturated with both cadmium chloride and sodium chloride;[17,18] this electrode has a potential of −0.76 V versus the aqueous saturated calomel electrode at 25 °C.

Controlled-potential electrolyses were performed in two-compartment (divided) cells that incorporated either reticulated vitreous carbon[16] or mercury pool[19] cathodes. After each experiment, the electrolyzed solution was partitioned between diethyl ether and aqueous brine. Then the ether extract was dried over anhydrous magnesium sulfate and concentrated, and the ether-soluble electrolysis products were separated, identified, and quantified (through the use of *n*-tetradecane and *n*-heptane as internal standards) with the aid of gas chromatography, as

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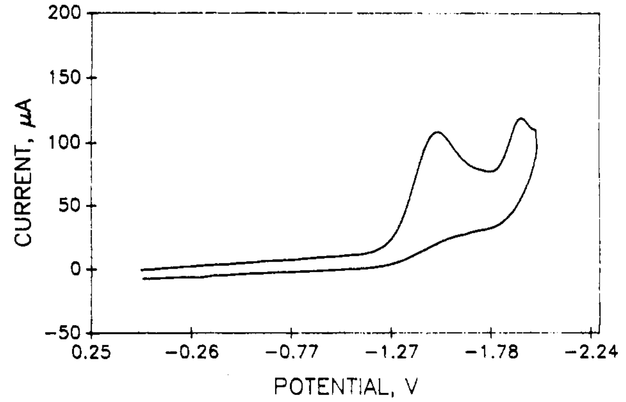

Figure 1. Cyclic voltammogram for the reduction of 3 mM trimethylacetyl chloride at a glassy carbon electrode in acetonitrile containing 0.1 M TEAP at a scan rate of 50 mV s^{-1}.

described in a recent paper;[20] all tabulated product yields represent the absolute percentage of starting material incorporated into a particular species. Mass spectra were acquired with a Kratos Model MS80 RFQQ gas chromatograph-mass spectrometer system or a Hewlett-Packard Model 5890 Series II gas chromatograph coupled to a Hewlett-Packard Model 5971 mass-selective detector.

Product Identification. We identified the two products, trimethylacetaldehyde and trimethylacetic anhydride, obtained from electrochemical experiments involving trimethylacetyl chloride by comparing gas chromatographic retention times for the suspected species with those of commercially available authentic samples. These identifications were confirmed with the aid of mass spectrometry (70 eV): (a) for trimethylacetaldehyde, *m/z* (relative intensity) 86 (M^+, 23), 57 (88), 43 (16), 41 (100), 39 (30), 29 (67); (b) for trimethylacetic anhydride, *m/z* 85 (58), 57 (100), 41 (28), 39 (11), 29 (15).

Results and Discussion

Cyclic Voltammetric Behavior of Trimethylacetyl Chloride. As illustrated in Figure 1, the reduction of trimethylacetyl chloride in acetonitrile containing 0.1 M TEAP at a glassy carbon electrode gives a cyclic voltammogram showing two irreversible waves with peak potentials of −1.49 and −1.91 V at a scan rate of 100 mV s^{-1}. In acetonitrile containing 0.05 M TMAP, the peak potentials shift to −1.55 and −1.93 V at 100 mV s^{-1}. Using a hanging mercury drop electrode and a scan rate of 50 mV s^{-1}, one observes only a single irreversible wave with a peak potential of −1.50 V in acetonitrile containing 0.1 M TEAP, whereas in the presence of 0.05 M TMAP the peak potential for the lone wave shifts to −1.23 V.

At potentials corresponding to the first wave for a carbon electrode or to the only wave for a mercury electrode, cleavage of the carbon–chlorine bond to afford trimethylacetaldehyde takes place. Separate experiments demonstrated in the present investigation that the second wave for a carbon cathode arises from the combined reductions of trimethylacetaldehyde and trimethylacetic anhydride. For a glassy carbon electrode in acetonitrile containing 0.1 M TEAP, trimethylacetaldehyde exhibits one irreversible wave with a peak potential of −1.91 V at a scan rate of 50 mV s^{-1}, whereas trimethylacetic anhydride shows a single irreversible wave having a peak potential of −1.97 V under similar conditions. Only one cathodic wave is seen when trimethylacetyl chloride is reduced at a hanging mercury drop electrode, because the aldehyde and anhydride undergo reduction at potentials that are too negative for this system.

Table I. Coulometric Data and Product Distributions for Electrolytic Reduction of Trimethylacetyl Chloride in Acetonitrile

			product distribution, %	
$[(CH_3)_3CCOCl]$, mM	electrode, potential[a]	*n*	trimethylacetaldehyde	trimethylacetic anhydride
	(A) 0.1 M TEAP			
10	C, −1.55	1.05	47	56
20	C, −1.55	1.20	44	45
10	Hg, −1.55	1.01	53	53
10	Hg, −1.55	1.01	42	54
30	Hg, −1.55	1.10	43	53
30	Hg, −1.55	1.01	44	58
	(B) 0.05 M TMAP			
10	C, −1.60	1.05	46	56
10	C, −1.60	1.00	36	52
20	C, −1.60	1.20	52	49
20	C, −1.60	1.00	38	54
20	Hg, −1.35	1.10	32	59

[a] C = reticulated vitreous carbon disk; Hg = mercury pool; TEAP = tetraethylammonium perchlorate; TMAP = tetramethylammonium perchlorate; potential is in volts versus a saturated cadmium amalgam reference electrode (see the Experimental Section).

Controlled-Potential Electrolyses of Trimethylacetyl Chloride. Coulometric data and product distributions for electrolyses of trimethylacetyl chloride in acetonitrile containing either 0.1 M TEAP or 0.05 M TMAP at reticulated vitreous carbon or mercury pool cathodes are compiled in Table I. Potentials for these experiments were chosen so that neither trimethylacetaldehyde nor trimethylacetic anhydride would be electroactive. As the results in Table I reveal, only one electrochemically generated species, trimethylacetaldehyde, is formed. Such behavior is similar to that seen for the reduction of two other aliphatic acyl halides, heptanoyl chloride[1] and cyclohexanecarbonyl chloride,[3] for which the main electrochemically formed products are heptaldehyde and cyclohexanecarboxaldehyde, respectively.

On the basis of the data in Table I, there is no compelling evidence that the choice of electrode material or supporting electrolyte plays any role in the formation of trimethylacetaldehyde. On the other hand, we have observed that electrochemical reduction of phthaloyl dichloride at carbon and mercury cathodes leads to the generation of different products.[5] Moreover, the yields of phenylacetaldehyde and hydrocinnamaldehyde produced from electrolyses of phenylacetyl chloride and hydrocinnamoyl chloride, respectively, at mercury electrodes change when the size of the supporting-electrolyte cation is varied.[2]

Due to the presence of residual water in the solvent-supporting electrolyte system, trimethylacetyl chloride undergoes some hydrolysis to afford 2,2-dimethylpropanoic acid which, in turn, reacts with a molecule of the acyl halide to form trimethylacetic anhydride (Scheme I, reactions 1 and 2). In an effort to lower the amount of residual water, an experiment was conducted in which activated molecular sieves (4 Å), placed in the assembled electrolysis cell containing a mercury pool, were stirred in contact with the solvent-supporting electrolyte solution for 90 min prior to the beginning of, and then (after injection of trimethylacetyl chloride) during, the electrolysis; the yield of trimethylacetic anhydride decreased only from 54% to 40%. A similar result has been obtained in a study of the electrochemical reduction of cyclohex-

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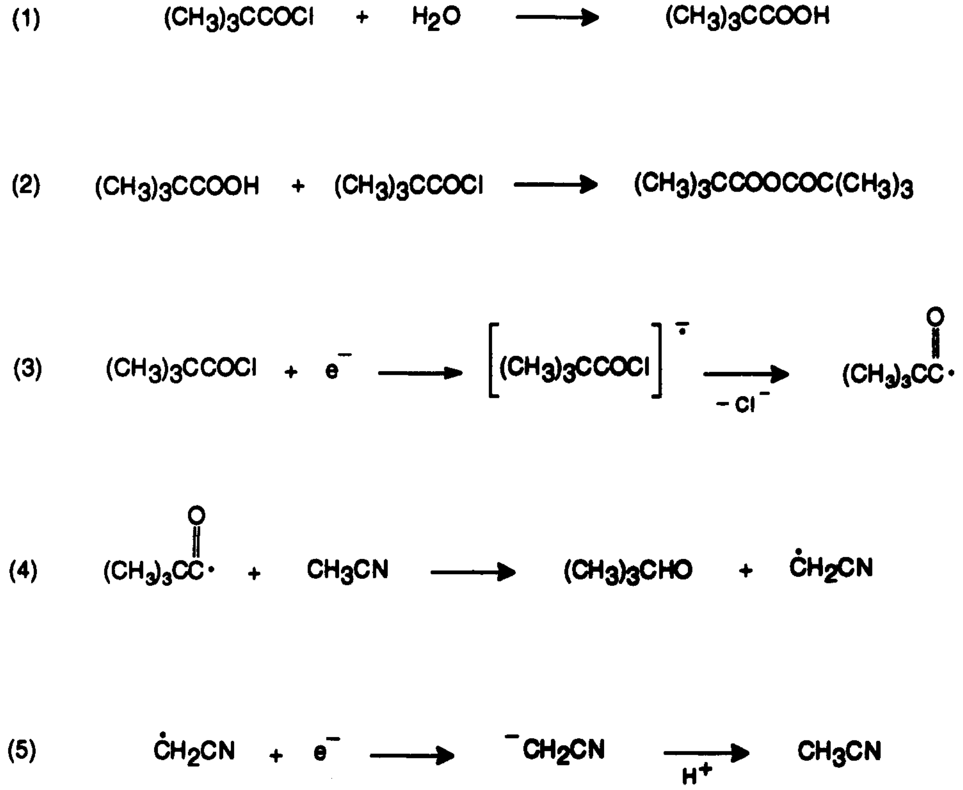
Scheme I



$$(1)\quad (CH_3)_3CCOCl + H_2O \longrightarrow (CH_3)_3CCOOH$$

$$(2)\quad (CH_3)_3CCOOH + (CH_3)_3CCOCl \longrightarrow (CH_3)_3CCOOCOC(CH_3)_3$$

$$(3)\quad (CH_3)_3CCOCl + e^- \longrightarrow \left[(CH_3)_3CCOCl\right]^{\overset{\bullet}{-}} \xrightarrow[-Cl^-]{} (CH_3)_3C\overset{O}{\overset{\|}{C}}\cdot$$

$$(4)\quad (CH_3)_3C\overset{O}{\overset{\|}{C}}\cdot + CH_3CN \longrightarrow (CH_3)_3CHO + \dot{C}H_2CN$$

$$(5)\quad \dot{C}H_2CN + e^- \longrightarrow {}^-CH_2CN \xrightarrow[H^+]{} CH_3CN$$

anecarbonyl chloride at mercury in acetonitrile containing activated molecular sieves.[3] During an investigation of the reduction of heptanoyl chloride, we introduced activated neutral alumina into the solvent-supporting electrolyte before the start of an electrolysis, but the acyl chloride and alumina appeared to react chemically.

Some Mechanistic Aspects of the Reduction of Trimethylacetyl Chloride. On the basis of close similarities in the electrochemistry of heptanoyl chloride,[1] cyclohexanecarbonyl chloride,[3] and trimethylacetyl chloride, we feel confident that the behavior of trimethylacetyl chloride can be properly characterized by the reactions shown in Scheme I, although we have not undertaken work with deuterium-labeled reagents to trap key intermediates. Besides the processes (reactions 1 and 2) leading to the formation of trimethylacetic anhydride, we propose that trimethylacetyl chloride accepts one electron to yield a radical-anion which quickly loses a chloride ion to generate an acyl radical (reaction 3); this hypothesis is supported by the fact that experiments with acetonitrile-d_3, deuterium oxide, and diethyl malonate-d_2 have indicated that heptanoyl chloride[1] and cyclohexanecarbonyl chloride,[3] two other aliphatic acyl halides, give acyl radicals exclusively upon reduction and that a solvent molecule serves as donor of a hydrogen (deuterium) atom.

Once formed, the acyl radical abstracts a hydrogen atom from the solvent to afford trimethylacetaldehyde (reaction 4). For each result listed in Table I, the coulometric *n* value is approximately twice the size of what should be expected from the quantity of aldehyde arising from a one-electron process. Clearly, another electron-transfer reaction must occur during the electrolysis of the acyl chloride. On the basis of work with heptanoyl chloride[1] and cyclohexanecarbonyl chloride,[3] we suggest that $^\bullet CH_2CN$, formed by abstraction of a hydrogen atom from the solvent by a trimethylacetyl radical, can undergo subsequent reduction to $^-CH_2CN$ and that the latter anion can be protonated by adventitious water or by the supporting-electrolyte cation to give acetonitrile again (reaction 5); such a sequence of events would lead to anomalously high *n* values without affording novel products. Neither succinonitrile, formed from the coupling of $^\bullet CH_2CN$, nor any compound arising from attack of $^-CH_2CN$ on the carbonyl moieties[21,22] of trimethylacetaldehyde and trimethylacetic anhydride was detected. In addition, mass spectrometric analysis of solutions obtained from electrolyses of trimethylacetyl chloride indicated that, unlike other acyl halides the electrochemistry of which has been investigated,[1-4,6,9] no tetrameric species, 2,2,5,5-tetramethyl-3-hexene-3,4-diol bis(trimethylacetate), can be detected.

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