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Electrolytic Reduction of *tert*-Butyl Bromide at Mercury Cathodes in Dimethylformamide

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A polarogram or cyclic voltammogram for reduction of *tert*-butyl bromide at mercury in dimethylformamide containing a tetraalkylammonium salt exhibits two waves, signaling stepwise generation of the *tert*-butyl radical and carbanion. Electrolyses of the alkyl bromide at a mercury pool cathode and at potentials corresponding to the first wave produce isobutane (40–43%), isobutylene (43–45%), and 2,2,3,3-tetramethylbutane (9–10%). Experiments with perdeuterated *tert*-butyl bromide have revealed that the first two products arise via disproportionation of *tert*-butyl radicals, whereas the third compound is formed by combination of radicals. At potentials on the second wave for *tert*-butyl bromide, electrolyses in dimethylformamide containing either tetramethylammonium or tetra-*n*-butylammonium perchlorate yield equal quantities of isobutane (47–50%) and isobutylene (47%), but little 2,2,3,3-tetramethylbutane (<1%) is formed; interestingly, when tetraethylammonium perchlorate is the electrolyte, the products are isobutane (55%), isobutylene (30%), pivalaldehyde (14%), and 2,2,3,3-tetramethylbutane (<1%). Electrolyses done in the presence of deuterated reagents have demonstrated that electrogenerated *tert*-butyl carbanions are protonated by water and, to a lesser extent, tetramethylammonium and tetraethylammonium cations to yield isobutane. Hydroxide ion, formed when water is deprotonated by the alkyl carbanion, attacks unreduced *tert*-butyl bromide to give isobutylene.

Alkyl halides comprise an important class of compounds in organic chemistry; therefore, it is not surprising that the electrochemistry of these species has been of considerable interest. Two recent summaries[1,2] as well as other review articles[3-9] about the electrochemical behavior of alkyl halides have appeared, but confusion persists in the literature concerning the mechanism of reduction. Points of controversy include the number of electrons transferred to the carbon–halogen bond and thus the nature of the intermediates generated which undergo follow-up chemical reactions. Recent studies have demonstrated that the course of reduction is influenced by the electrode potential,[10] the cathode material,[11] the nature and purity of the supporting electrolyte–solvent,[12,13] the initial concentration of the alkyl halide,[11] the steric hindrance at the carbon–halogen site,[14] and even the time scale of the electrolysis.[15]

Several earlier papers[13,16-18] have dealt with the polarographic characteristics of *tert*-butyl bromide in various nonaqueous solvents; and in a recent publication[19] we confirmed, with the aid of polarography and cyclic voltammetry, that this alkyl bromide is reduced in stepwise fashion to the *tert*-butyl radical and the *tert*-butyl carbanion at a mercury cathode in dimethylformamide containing tetraalkylammonium perchlorates. However, there has been no previous report concerning the products formed by electrolytic reduction of *tert*-butyl bromide, nor have the identities and reactions of electrogenerated intermediates been substantiated. In the present paper are described the results of large-scale controlled-potential electrolyses of *tert*-butyl bromide at mercury pool cathodes in dimethylformamide containing various tetraalkylammonium salts; the number of electrons transferred and the products formed at each stage of reduction have been ascertained, the role played by adventitious water in the mechanism of reduction has been elucidated, and the nature of the intermediates generated at each stage of reduction has been verified through the addition of proton donors and deuterium-labeled trapping agents to the supporting electrolyte–solvent system. In addition, comparisons of the data and conclusions discussed here are made with those of prior work from our laboratory pertaining to primary[10] and secondary[14] alkyl halides.

Experimental Section

Reagents. Burdick & Jackson "distilled in glass" grade dimethylformamide was employed as solvent throughout this research. Further purification of the solvent was carried out by means of vacuum distillation (50 °C, 14 torr) through a 30 in. × 1.2 in. glass column packed with $^1/_8$-in. glass helices; the purified dimethylformamide was stored in a collection flask at room temperature under nitrogen in the dark.

Tetramethylammonium perchlorate, tetraethylammonium perchlorate, and tetra-*n*-butylammonium perchlorate were purchased from the G. Frederick Smith Chemical Co., and were used without further purification as supporting electrolytes for large-scale controlled-potential electrolyses.

Because of its tendency to undergo slow decomposition, *tert*-butyl bromide (MCB, 98%) required purification by means of

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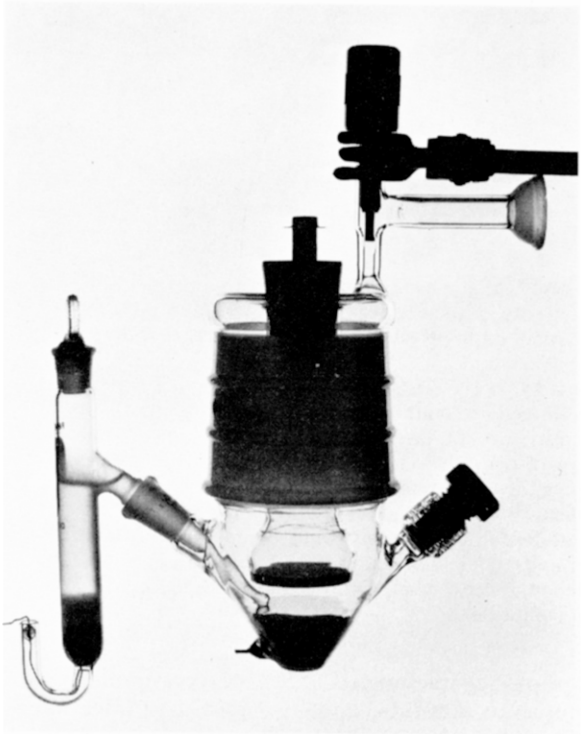

Figure 1. Electrochemical cell used for controlled-potential electrolyses of *tert*-butyl bromide at mercury pool cathodes.

vacuum distillation; a clear fraction was collected (53 °C, 400 torr) in a Schlenk tube and was stored under nitrogen in the dark at -10 °C. Mercury (Ventron, ACS reagent), hexamethylethane (Aldrich, 99%), *tert*-butyl alcohol (Fisher, certified), neopentyl alcohol (Aldrich, 99%), isobutane (Matheson, C.P.), isobutylene (Matheson, C.P.), *n*-butane (Matheson, instrument grade), 1-butene (Matheson, C.P.), ethylene (Matheson, C.P.), *n*-decane (Aldrich, 99+%), diethyl malonate (Fisher, purified), deuterium oxide (Cambridge Isotope Laboratories, 99.83 atom % D), diethyl malonate-d_2 (MSD Isotopes, 98.25 atom % D), *tert*-butyl-d_9 bromide (MSD Isotopes, 98.11 atom % D), dimethylformamide-d_7 (MSD Isotopes, 99.5 atom % D), 2-methylpropane-2-d_1 (MSD Isotopes, 98.7 atom % D), and methylcellulose (MCB) were used as received. Trimethylacetaldehyde (Sigma) or 2,2-dimethylpropanal, hereafter called pivalaldehyde, was freshly distilled before being used. All deaeration and drying procedures were carried out with either Matheson PP or Air Products UHP nitrogen.

Instrumentation and Procedures. Shown in Figure 1 is the cell used for controlled-potential electrolyses; the cell was comprised of two parts built around a 55/50 standard-taper joint. Because *tert*-butyl bromide decomposes slowly, it was desirable to complete the electrolyses as quickly as possible; thus, the ratio of the area of the working electrode to the volume of solution was maximized. In addition, the cell was designed to be used in a "gas-tight" configuration because electrolysis of *tert*-butyl bromide yields volatile hydrocarbon products. To the upper part of the cell was connected a Kontes extended-tip Teflon valve with a 2-mm bore which provided an exit for nitrogen during deaeration of the solution. Sealed into the center of the upper part of the cell was the auxiliary-electrode compartment, consisting of a length of 24-mm pyrex tubing closed at its bottom with a 3-cm diameter, coarse-porosity, sintered glass disk; a carbon rod, held in place with a stopper, served as the auxiliary electrode. To minimize mixing of the contents of the auxiliary-electrode compartment with the solution in the lower, tapered working-electrode compartment, a gel of methylcellulose–supporting electrolyte–solvent was placed on top of the sintered glass disk. Before each electrolysis, mercury was placed in the lower part of the cell to give a working electrode with a surface area of 7.1 cm^2; a short piece of platinum wire, sealed through the wall of the cell, provided electrical contact to the mercury pool. There were two ports in the working-electrode compartment; a 10/18 standard-taper joint accommodated the sidearm of the reference electrode, and an Ace Glass threaded adapter served as a nitrogen inlet and allowed for the introduction and removal of samples through a Teflon-backed septum secured by a nylon bushing. The reference electrode, which made contact with the test solution through a cracked-glass junction, consisted of a saturated cadmium amalgam in contact with dimethylformamide saturated with both cadmium chloride and sodium chloride;[20,21] all potentials reported in the present work are with respect to this reference electrode, which has a potential of -0.75 V vs. the aqueous saturated calomel electrode.

A Princeton Applied Research Corporation (PARC) Model 173 potentiostat–galvanostat equipped with a PARC Model 176 current-to-voltage converter having positive-feedback *IR* compensation capability was employed for all electrolyses. During the electrolyses, the output of the current-to-voltage converter was connected to a Tektronix RM564 storage oscilloscope which aided setting of an appropriate amount of *IR* compensation, to an Esterline Angus L1101S strip-chart recorder which monitored the current decay, and to a house-built digital coulometer[22] which integrated the electrolysis current.

At the start of an experiment, fresh mercury, a magnetic spin bar, and 10 mL of supporting electrolyte–solvent were placed into the working-electrode compartment of the cell; approximately 5 mL of supporting electrolyte–solvent was poured over the methylcellulose gel, and the carbon electrode was placed into the auxiliary-electrode compartment. Deaeration of the solution was accomplished by insertion of a stainless-steel syringe needle through the septum in the sampling port. After the deaeration ($\sim$20 min), the needle was removed and the Teflon valve was closed to seal the cell. Preelectrolysis of the supporting electrolyte–solvent was begun at the potential at which the electrolysis was to be done, and internal standards (*n*-butane and *n*-decane) were injected into the cell; the preelectrolysis was continued until a steady-state background current ($\sim$0.1 mA) was reached. Then the electrolysis circuit was briefly opened, *tert*-butyl bromide was injected into the cell, and the electrolysis was commenced; typically, the electrolysis lasted between 20 min and 1 h, by which time the current had decayed to the background level.

Upon completion of an electrolysis, samples were taken from the sealed cell and were injected directly into a Varian Model 3700 gas chromatograph equipped with dual flame-ionization detectors. Gaseous products were separated on a 12 ft × $^{1}/_{8}$ in. stainless-steel column packed with a chemically bonded stationary phase consisting of *n*-octane on 100–120 mesh Porasil C. Higher boiling products were separated on a 12 ft × $^{1}/_{8}$ in. stainless-steel column packed with 15% Carbowax 20M-TPA on 80–100 mesh Chromosorb WHP. Gas chromatographic peak areas were measured with the aid of a Hewlett-Packard 3380S integrator. Quantitation of products was accomplished with the aid of internal standards (*n*-butane was used for gaseous species and *n*-decane was used for higher boiling compounds); experimentally determined gas chromatographic response factors were measured for each product. Because isobutane and isobutylene are volatile electrolysis products, it was necessary to analyze both the solution and the gas phase above the solution for these species. Reported yields for the various products are absolute and reflect the percentage of starting material incorporated into a particular compound. To verify the identity of each electrolysis product, a Hewlett-Packard Model 5992 gas chromatograph–mass spectrometer was employed; mass spectra were obtained by use of electron-impact ionization at 70 eV. Retention times and mass spectra for all products were compared with those of commercially available authentic samples.

A series of controlled-potential electrolyses was carried out in which special care was taken to lower the water content of the supporting electrolyte–solvent: (a) dimethylformamide was dried for 6–8 h over freshly activated 4–8 mesh Davison Type 4-Å molecular sieve beads; (b) supporting electrolytes were dried in a vacuum oven at 130 °C for 24 h and were stored in a vacuum desiccator over Drierite; (c) nitrogen used for purging and drying operations was passed through two 2 ft × $^{3}/_{4}$ in. glass columns containing activated 8–12 mesh molecular sieve beads; (d)

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Table I. Coulometric Data and Product Distributions for Electrolytic Reduction of 0.0025 M Solutions of *tert*-Butyl Bromide at Mercury in Dimethylformamide

			product distribution, %				
supporting electrolyte[a]	potential, V	*n* value	isobutane	isobutylene	2,2,3,3-tetramethylbutane	pivalaldehyde	total recovery[b]
0.1 M TMAP	−1.40	0.94	43	44	9		98
0.1 M TMAP	−1.70	1.02	50	47	<1	1	99
0.1 M TBAP	−1.50	0.94	42	43	10		97
0.1 M TBAP	−1.80	0.98	47	47	<1	3	98
0.1 M TEAP	−1.40	0.88	40	45	10		98
0.1 M TEAP	−1.80	1.35	55	30	<1	14	99
1.0 M TEAP	−1.80	1.55	76	11	<1	6	93

[a] TMAP = tetramethylammonium perchlorate, TBAP = tetra-*n*-butylammonium perchlorate, TEAP = tetraethylammonium perchlorate. [b] In most of the entries, a small amount (1–3%) of *tert*-butyl alcohol is included in the total recovery.

glassware was dried and stored in an oven at 140 °C; (e) mercury used as the working electrode was dried in a sealed flask by being purged with dry nitrogen for 90 min with rapid stirring; (f) the electrolysis cell was assembled as quickly as possible and was purged with dry nitrogen for 90 min; and (g) all transfers of mercury and solution into the cell were made via a stainless-steel cannula. Throughout the course of each experiment, the water content of the supporting electrolyte–solvent was monitored with a Varian Model 3700 gas chromatograph equipped with a thermal conductivity detector; a 6 ft × $^1/_8$ in. stainless-steel column packed with 80–100 mesh Porapak S was employed. Typical water concentrations present during the preelectrolysis ranged from 3 to 5 mM; however, by the end of an electrolysis (~60 min later), the water content increased to 5–7 mM. In the absence of special drying procedures, the water level during routine electrolyses was found to vary from 40–60 mM.

To determine the identity and fate of electrogenerated intermediates, deuterium-labeled trapping agents were employed in a series of experiments. A Hewlett-Packard Model 5992 gas chromatograph–mass spectrometer was used to measure the extent of isotopic labeling in the product of interest (isobutane). Prior to mass spectrometric analysis, isobutane was separated from other products on a 3 ft × $^1/_8$ in. stainless-steel column packed with *n*-octane chemically bonded to 100–120 mesh Porasil C; the amount of deuterium incorporated into isobutane was determined by comparison of several isotope ratios in the actual sample to those of an isotope-dilution calibration curve.

Preparation of Di-*tert*-butylmercury. All procedures were conducted under nitrogen. A Grignard synthesis was carried out by slow addition of 4.4 mL (40 mmol) of *tert*-butyl chloride to 35 mL of anhydrous diethyl ether containing 0.95 g (39 mmol) of magnesium turnings. This mixture was gently heated and refluxed for 20 min and then cooled to −10 °C. Mercuric chloride (2.7 g, 10 mmol), which had been pulverized and then dried in a desiccator over Drierite for 24 h, was added with rapid stirring to the cooled solution over a 1-h period. Next, the solution was warmed to room temperature, stirred for 2 h, and then cooled to −10 °C. To the reaction mixture was added dropwise 40 mL of a deaerated 5% aqueous solution of ammonium chloride. Then the ether layer was transferred via a cannula to a Schlenk flask containing a few grams of anhydrous sodium sulfate. After being dried, the ethereal solution was transferred by cannula to another Schlenk flask. A gentle stream of nitrogen was used to purge the ether from the flask, leaving behind a residue of white crystals which were purified by means of room-temperature vacuum sublimation (0.1 torr).[23,24] Purified crystals were stored in a Schlenk tube under nitrogen in the dark at −10 °C: mp 60–61 °C (lit.[23,25] 58–60 °C); NMR (C_6D_6) δ 1.24 (s, 18, CH_3), J (^{199}Hg–CH_3) = 104 Hz;[25,26] mass spectrum (70 eV), *m/e* 316, $(C_4H_9)_2Hg^+$ (0.9%); 258, $C_4H_8Hg^+$ (0.1%); 202, Hg^+ (4.4%); 114, $C_8H_{18}^+$ (2.0%); 57, $C_4H_9^+$ (100%).

Preparation of Tetramethylammonium-*d*$_{12}$ Perchlorate. Tetramethylammonium-*d*$_{12}$ chloride (1.004 g, 8.26 mmol, KOR Isotopes, 99 atom % D) was dissolved in 20 mL of water, and 1.696 g (8.18 mmol) of anhydrous silver perchlorate (Alfa Products) was dissolved in 1 mL of water. Both solutions were heated nearly to boiling, and the hot silver perchlorate solution was added dropwise with rapid stirring to the hot tetramethylammonium-*d*$_{12}$ chloride solution. Heating and stirring of the solution were continued until the silver chloride precipitate coagulated. Next, the hot solution was filtered through paper, the clear filtrate was collected and reheated to boiling until the first appearance of a precipitate, and the mixture was cooled slowly to room temperature and then placed in an ice bath. Finally, the cold mixture was filtered, and the needle-like crystals of tetramethylammonium-*d*$_{12}$ perchlorate were washed with several 1-mL portions of ice-cold water. These crystals were dried in air for 24 h and were stored in a vacuum desiccator over Drierite.

Results and Discussion

Voltammetric Behavior of *tert*-Butyl Bromide. Although a full account of the polarographic and cyclic voltammetric behavior of *tert*-butyl bromide has been published elsewhere,[19] it is useful to review key points of that report. A normal dc polarogram for a 1 mM solution of *tert*-butyl bromide in dimethylformamide containing 0.1 M tetramethylammonium perchlorate exhibits a pair of closely spaced waves nearly equal in height. We estimate that the half-wave potentials are −1.23 and −1.46 V, respectively, for the first and second wave. Transfer of a single electron to the carbon–bromine bond, resulting in formation of a *tert*-butyl radical, is responsible for the first wave, whereas *tert*-butyl bromide undergoes two-electron reduction to yield the *tert*-butyl carbanion at potentials corresponding to the second polarographic wave. In a cyclic voltammogram, recorded at a scan rate of 50 mV s^{-1}, stepwise reduction of *tert*-butyl bromide is again revealed by the appearance of two, poorly resolved, irreversible waves with peak potentials of −1.34 and −1.51 V; the peak height of the first wave is several times greater than the peak height of the second wave. We determined that the size of the first peak for the alkyl bromide is appropriate for a one-electron reduction, and that the second peak is unusually small because *tert*-butyl radicals generated at potentials corresponding to the first wave are consumed via follow-up chemical reactions.

Controlled-Potential Electrolyses at Mercury Pool Cathodes. Shown in Table I are coulometric data and product distributions obtained from electrolyses of *tert*-butyl bromide in dimethylformamide containing 0.1 M tetraalkylammonium perchlorate. Tetramethylammonium, tetraethylammonium, and tetra-*n*-butylammonium perchlorate were all employed as supporting electrolytes in order to examine the dependence of the

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Table II. Coulometric Data and Product Distributions for Electrolytic Reduction of 0.0025 M Solutions of *tert*-Butyl Bromide at Mercury in Dimethylformamide Containing Added Proton Sources

				product distribution, %				
proton source[a]	supporting electrolyte[b]	potential, V	*n* value	isobutane	isobutylene	2,2,3,3-tetramethylbutane	2,2-dimethylpropanol	total recovery
0.010 M DEM	0.1 M TMAP	−1.40	1.00	45	44	9		98[c]
0.010 M DEM	0.1 M TMAP	−1.70	1.83	91	5	<1	1	97[c]
0.010 M DEM	0.1 M TEAP	−1.40	0.85	42	43	11		96[c]
0.010 M DEM	0.1 M TEAP	−1.80	2.15	79	2	<1	14	95[c]
1.0 M H_2O	0.1 M TMAP	−1.24	0.90	40	45	9		97[d]
1.0 M H_2O	0.1 M TMAP	−1.70	1.58	77	19	<1		97[d]
1.0 M H_2O	0.1 M TEAP	−1.80	1.65	76	16	<1	4	97[d]

[a] DEM = diethyl malonate. [b] TMAP = tetramethylammonium perchlorate, TEAP = tetraethylammonium perchlorate. [c] A small amount (1–3%) of *tert*-butyl alcohol may be formed in these electrolyses, but coelution of a decomposition product of DEM and *tert*-butyl alcohol precludes the determination of the latter species. [d] A small quantity (1–3%) of *tert*-butyl alcohol is included in the total recovery.

course of the reduction on the identity of the tetraalkylammonium cation.

Two potentials are listed for electrolyses done with each supporting electrolyte; the more positive value corresponds to a potential on the first polarographic wave for *tert*-butyl bromide, and the more negative potential corresponds to a value on the plateau of the second wave. At the more positive potential, a coulometric *n* value near unity is observed with all three supporting electrolytes, a result in accord with the observed polarographic behavior. However, at the more negative potential, an *n* value approximately equal to one is found in the presence of tetramethylammonium and tetra-*n*-butylammonium perchlorates and an *n* value of 1.35 is seen with 0.1 M tetraethylammonium perchlorate. Thus *n* values obtained from electrolyses at the more negative potential are in disagreement with the *n* value predicted from polarographic experiments. Other alkyl halides which undergo stepwise reduction exhibit analogous behavior.[10,14] As will be discussed later, an apparent *n* value near unity is observed at the more negative potential because a substantial portion of starting material undergoes non-electron-consuming reactions.

Products obtained from controlled-potential electrolyses of *tert*-butyl bromide include isobutane, isobutylene, 2,2,3,3-tetramethylbutane, and pivalaldehyde; a small amount of *tert*-butyl alcohol is observed at all potentials and is thought to originate via hydrolysis of starting material, because the yield of the alcohol is directly proportional to the length of electrolysis. Although previous studies in our laboratory of primary and secondary alkyl halides have failed to reveal the formation of any aldehydic products,[10,14] traces of aldehydes have been observed in other investigations of the electrolytic reduction of alkyl and aryl halides in dimethylformamide containing tetraethylammonium bromide.[13,28]

Similar coulometric *n* values and product distributions are obtained when either tetramethylammonium perchlorate or tetra-*n*-butylammonium perchlorate is employed as supporting electrolyte. Significant differences in the data occur at the more negative potential in the presence of tetraethylammonium perchlorate. An *n* value of 1.35 is observed and, more importantly, we detected substantial amounts of ethylene and triethylamine, products derived from a Hofmann elimination reaction involving tetraethylammonium cation and a strong base—a process reported in previous investigations of the electrochemistry of alkyl halides.[13,22,28,29] In Table I the last entry further demonstrates the role of tetraethylammonium cation as a proton donor; reduction of *tert*-butyl bromide at −1.80 V in the presence of 1 M tetraethylammonium perchlorate gives an *n* value of 1.55 along with a concomitant increase in the yield of isobutane. Another notable feature of the results obtained with different supporting electrolytes is the quantity of pivalaldehyde, the yield of which is several times greater in the presence of tetraethylammonium perchlorate than in the presence of the other tetraalkylammonium salts.

In polarograms showing the stepwise reduction of 1-iododecane and 2-iodooctane, the appearance of the first wave is thought to be due to the ability of mercury to stabilize incipient free radicals.[10,14,22] Indeed, large quantities of dialkylmercury compounds are formed as products of electrolyses of these alkyl iodides at mercury pool cathodes held at potentials corresponding to the first polarographic wave.[10,14] Since *tert*-butyl bromide exhibits stepwise reduction at mercury, the possibility was considered that a dialkylmercury species is formed during electrolyses at potentials on the first wave. Accordingly, di-*tert*-butylmercury was synthesized, and its electrochemical and gas chromatographic characteristics were examined. Decomposition of the dialkylmercury compound in the electrolysis cell or in the gas chromatograph was conceivable, because these materials are known to be sensitive to heat,[23,25,26,30] light,[25,30] and air.[25,26,31] However, di-*tert*-butylmercury was found to be stable under experimental conditions employed in our work. Thus, the possible presence of di-*tert*-butylmercury, as a product or intermediate in the electrolysis of *tert*-butyl bromide, is rejected. This conclusion is in agreement with the results of an earlier study involving the reduction of *tert*-butyl bromide at a lead cathode in acetonitrile; preparative-scale controlled-potential electrolyses failed to yield an appreciable amount of organolead species.[32]

Electrolyses in Dimethylformamide Containing Added Proton Sources. Summarized in Table II are coulometric data and product distributions for controlled-potential electrolyses of *tert*-butyl bromide in dimethylformamide containing 0.1 M tetraalkylammonium perchlorate in the presence of a deliberately added proton source (diethyl malonate or water). Results from experiments with tetra-*n*-butylammonium perchlorate as supporting electrolyte have been omitted, because they closely parallel those found in the presence of tetramethylammonium perchlorate. Presumably, addition of a proton source should not affect the *n* value or the product distribution derived from an electrolysis performed at po-

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tentials corresponding to the formation of radical intermediates. From a comparison of results obtained at the more positive potentials in Tables I and II, it is evident that diethyl malonate or water has virtually no influence on the coulometric data or product distributions. Conversely, results in Tables I and II acquired at the more negative potentials where carbanions are suspected as intermediates reveal that addition of diethyl malonate or water has a dramatic effect.

Comparison of second entries in Tables I and II demonstrates the effect of diethyl malonate on the reduction of *tert*-butyl bromide in dimethylformamide containing tetramethylammonium perchlorate. Diethyl malonate causes an increase in the *n* value from 1.02 to 1.83 along with a rise in the yield of isobutane at the expense of the quantity of isobutylene. Thus clearer evidence for the carbanionic character of the electrochemical process is seen. There are two ways by which diethyl malonate can act to cause the above changes in the data. Diethyl malonate can either protonate *tert*-butyl carbanions directly or intercept the base (or bases) responsible for the dehydrohalogenation of *tert*-butyl bromide. Deprotonated diethyl malonate does not react with unreduced starting material, so that more than 90% of the alkyl bromide is consumed electrochemically. Diethyl malonate has exhibited analogous behavior during the reductions of primary and secondary alkyl halides at potentials leading to the production of carbanion intermediates.[10,14]

In the fourth entry of Table II are results of an electrolysis of a dimethylformamide solution of *tert*-butyl bromide containing 0.1 M tetraethylammonium perchlorate and 0.010 M diethyl malonate. In comparison to the data of entry 6 in Table I, the presence of diethyl malonate causes several significant differences: (a) the *n* value increases from 1.35 to 2.15, lending further support for the intermediacy of carbanions; (b) a substantial growth in the yield of isobutane is observed, whereas the quantity of isobutylene decreases dramatically—chemical destruction of starting material is almost completely suppressed, allowing quantitative electrolytic consumption of *tert*-butyl bromide; (c) formation of Hofmann elimination products derived from tetraethylammonium cation is nearly excluded; and (d) the most important result is the appearance of a new species, 2,2-dimethylpropanol, which is the product of two-electron reduction of pivalaldehyde. Four electrons per molecule of *tert*-butyl bromide are consumed for each molecule of 2,2-dimethylpropanol formed; the yields of electron-consuming products (isobutane and 2,2-dimethylpropanol) give a calculated *n* value of 2.14 which agrees with the measured *n* value of 2.15.

Note that the appearance of 2,2-dimethylpropanol requires its precursor, pivalaldehyde, to become reducible when diethyl malonate is present during a controlled-potential electrolysis at −1.80 V. We have obtained polarographic and controlled-potential electrolytic data which support this fact. In dimethylformamide containing 0.1 M tetraethylammonium perchlorate, pivalaldehyde exhibits a single polarographic wave with a half-wave potential of −1.94 V, which shifts to −1.83 V in the presence of 0.010 M diethyl malonate. A controlled-potential electrolysis of a 0.0025 M solution of pivalaldehyde in dimethylformamide containing 0.1 M tetraethylammonium perchlorate and 0.010 M diethyl malonate at −1.80 V resulted in an *n* value of 1.5 and the formation of 2,2-dimethylpropanol in 75% yield.

Entries 6 and 7 of Table II demonstrate the influence of water on the reduction of *tert*-butyl bromide at potentials corresponding to the production of carbanion intermediates. Electrolyses of *tert*-butyl bromide in dimethylformamide containing 1.0 M water result in sizable increases in the coulometric *n* value with accompanying increases in the yield of isobutane at the expense of isobutylene; compare these results to those of entries 2 and 6 in Table I. It is noteworthy that pivalaldehyde becomes electroactive at −1.80 V when 1.0 M water is present in the supporting electrolyte–solvent. More importantly, the yield of pivalaldehyde decreases from 14% in the absence of water to 4% in the presence of water, the latter figure being revealed by the yield of 2,2-dimethylpropanol. This observation suggests that *tert*-butyl carbanions are protonated by water; to be discussed later in more detail is experimental proof for the occurrence of this reaction that we have obtained from electrolyses done in the presence of deuterium oxide.

Electrolyses of *tert*-Butyl Bromide in Dimethylformamide Containing 3–5 mM Water. To investigate further the effect of water on the course of the reduction, electrolyses of *tert*-butyl bromide were carried out at potentials corresponding to formation of carbanions in supporting electrolyte–solvent systems containing 0.003 to 0.005 M water. For concentrations of *tert*-butyl bromide ranging from 0.0025 to 0.025 M in dimethylformamide containing 0.1 M tetramethylammonium perchlorate and limited amounts of water, we found virtually no difference in the *n* value or the product distribution from what is reported in entry 2 of Table I. These observations suggest that other species besides water must be important in protonating *tert*-butyl carbanions and that the conjugate bases of such species must be efficient at dehydrohalogenating *tert*-butyl bromide. On the other hand, when 0.0025 M *tert*-butyl bromide is electrolyzed in dimethylformamide containing 0.1 M tetraethylammonium perchlorate, there is a significant difference between results obtained when the system contains 0.050 M water or only 0.003 to 0.005 M water. Compared to the former experiment (Table I, entry 6), the latter electrolysis showed an increase in the *n* value from 1.35 to 1.53, an increase in the yield of isobutane from 55 to 61%, a rise in the yield of pivalaldehyde from 14 to 17%, and a decrease in the yield of isobutylene from 30 to 17%; in addition, more of the Hofmann elimination product, ethylene, was seen. Taken together, these results indicate that a large proportion of *tert*-butyl carbanions is protonated by the tetraethylammonium cation, that more of the alkyl bromide undergoes reduction than dehydrohalogenation, and that protonation of the *tert*-butyl carbanion by water is in direct competition with the nucleophilic substitution reaction responsible for the production of pivalaldehyde.

Electrolyses Performed with Deuterium-Labeled Reagents. A series of controlled-potential electrolyses were conducted in which various deuterium-labeled species (including *tert*-butyl bromide and dimethylformamide) were employed. Coulometric *n* values and percentages of the total amount of isobutane formed that incorporated deuterium are listed in Table III.

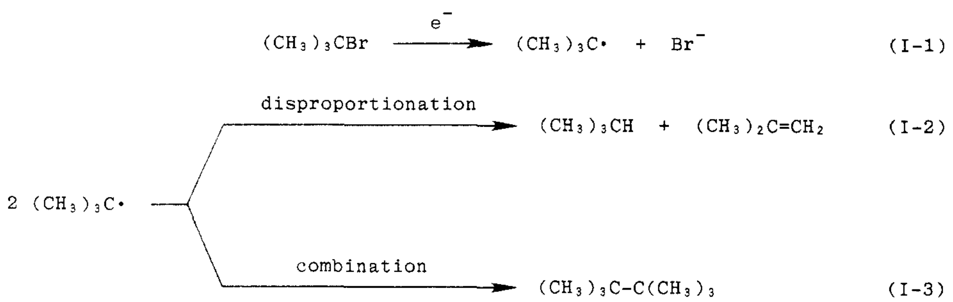
To verify the presence of radical intermediates at potentials corresponding to the first polarographic wave, an electrolysis of perdeuterated *tert*-butyl bromide was done at −1.30 V in dimethylformamide containing 0.1 M tetramethylammonium perchlorate (entry 1, Table III). Under these conditions, disproportionation of *tert*-butyl radicals is the only process which affords perdeuterated isobutane. Mass spectrometric analysis of the isobutane produced revealed that approximately 95% of it formed via radical disproportionation. This result is reasonable in view of the nearly equal amounts of isobutane and isobutylene

Table III. Coulometric Data and Percentage of Deuterium Incorporation for Electrolytic Reduction of 0.0025 M Solutions of *tert*-Butyl Bromide at Mercury in Systems Containing Deuterium-Labeled Reagents

deuterium-labeled reagent	supporting electrolyte[a]	potential, V	*n* value	$[H_2O]$, M	deuterium incorporation, %[b]
2.5 mM $(CD_3)_3CBr$	0.1 M TMAP	−1.30	0.96	0.015[c]	95
50 mM D_2O	0.1 M TMAP	−1.70	1.01	0.005	42
0.1 M $(CD_3)_4N^+$	0.1 M TMAP-d_{12}	−1.70	1.03	0.015[c]	34
2.5 mM $(CD_3)_3CBr$	0.1 M TMAP	−1.70	1.08	0.008	5
$DCON(CD_3)_2$	0.1 M TMAP	−1.70	0.99	0.014	1
50 mM D_2O	0.1 M TEAP	−1.80	1.48	0.008	26

[a] TMAP = tetramethylammonium perchlorate, TEAP = tetraethylammonium perchlorate. [b] Percentage of the total amount of isobutane formed that incorporated deuterium. [c] This is an approximate value based on concentrations of water typical for this series of electrolyses.

Scheme I



observed (entry 1, Table I). In an earlier study[14] of the reduction of 1,1,1,3,3-pentadeuterio-2-iodooctane at a potential corresponding to its first polarographic wave, an analogous result was obtained; virtually all of the octane arises through radical disproportionation.

Entries 2, 3, 4, and 5 in Table III pertain, respectively, to experiments done with deuterium oxide, perdeuterated tetramethylammonium perchlorate, perdeuterated starting material, and perdeuterated solvent in order to obtain direct proof for the existence of carbanion intermediates and to establish the relative importance of these various species as proton donors for *tert*-butyl carbanions. Although the results of these studies have been presented and discussed in a recent communication,[33] main points will be summarized here. We conclude that water is the dominant proton donor and that the tetramethylammonium cation is an important second source, though proton transfer between the electrolyte cation and the *tert*-butyl carbanion apparently occurs directly as well as indirectly via proton (deuteron) scrambling. No more than 5% of the isobutane produced arises from protonation of *tert*-butyl carbanions by the starting material, and the solvent (dimethylformamide) is an exceedingly poor proton donor. A similar conclusion regarding the poor proton-donating tendency of dimethylformamide was reached by de la Torre and Sease,[28] who investigated the electrochemical reduction of iodobenzene to the phenyl carbanion.

Entries 2 and 6 in Table III reveal how the choice of supporting electrolyte can affect the reduction of *tert*-butyl bromide in dimethylformamide containing 0.050 M deuterium oxide. Compared to tetramethylammonium perchlorate, the use of tetraethylammonium perchlorate results in significantly less incorporation of deuterium into the isobutane; although part of this decrease is probably due to the higher concentration (0.008 M) of residual water in the experiment done with tetraethylammonium perchlorate, we believe that the tetraethylammonium cation competes better than the tetramethylammonium cation as a proton donor for alkyl carbanions. In addition, because the tetraethylammonium cation is a more effective source of protons, there is less chemical consumption of unreduced *tert*-butyl bromide and the coulometric *n* value is higher (1.48) than when tetramethylammonium perchlorate is present.

Mechanism of Reduction at Potentials Corresponding to the First Polarographic Wave. Processes responsible for the products of electrolyses at potentials along the first polarographic wave for *tert*-butyl bromide are shown in Scheme I. Reduction of the alkyl bromide results in one-electron cleavage of the carbon–bromine bond to yield the *tert*-butyl radical and bromide ion (reaction I-1). Although *tert*-butyl bromide could dissociate into *tert*-butyl carbonium ion and bromide ion before or during the act of electron transfer, so that a *tert*-butyl radical would actually be formed by one-electron reduction of the carbonium ion, we have no evidence to support such a proposal. Pairs of *tert*-butyl radicals, presumably solvent-caged, either disproportionate to produce equal amounts of isobutane and isobutylene (reaction I-2) or combine to give 2,2,3,3-tetramethylbutane (reaction I-3).

Several pieces of evidence support the intermediacy of *tert*-butyl radicals at potentials on the first polarographic wave. First, we have demonstrated that electrolysis of perdeuterated *tert*-butyl bromide results in the formation of perdeuterated isobutane (Table III, entry 1), a product derived from disproportionation of radicals. Second, there can be little doubt that the hydrocarbon dimer, 2,2,3,3-tetramethylbutane, is produced via radical coupling, because S_N2 reactions for tertiary alkyl halides are unlikely.[34] Third, addition of a proton source has no effect on the coulometric *n* value or the product distribution (Table I, entries 1 and 5, and Table II, entries 1, 3, and 5). Fourth, no products (ethylene and triethylamine) of a Hofmann elimination are detected when tetraethylammonium perchlorate is employed as supporting electrolyte. Fifth, in a recent investigation[19] of the cyclic voltammetric behavior of *tert*-butyl bromide, we observed peaks associated with deprotonated diethyl malonate, formed by reaction of electrogenerated *tert*-butyl carbanion with diethyl malonate; however, these voltammetric peaks are not seen when *tert*-butyl bromide is reduced at potentials corresponding

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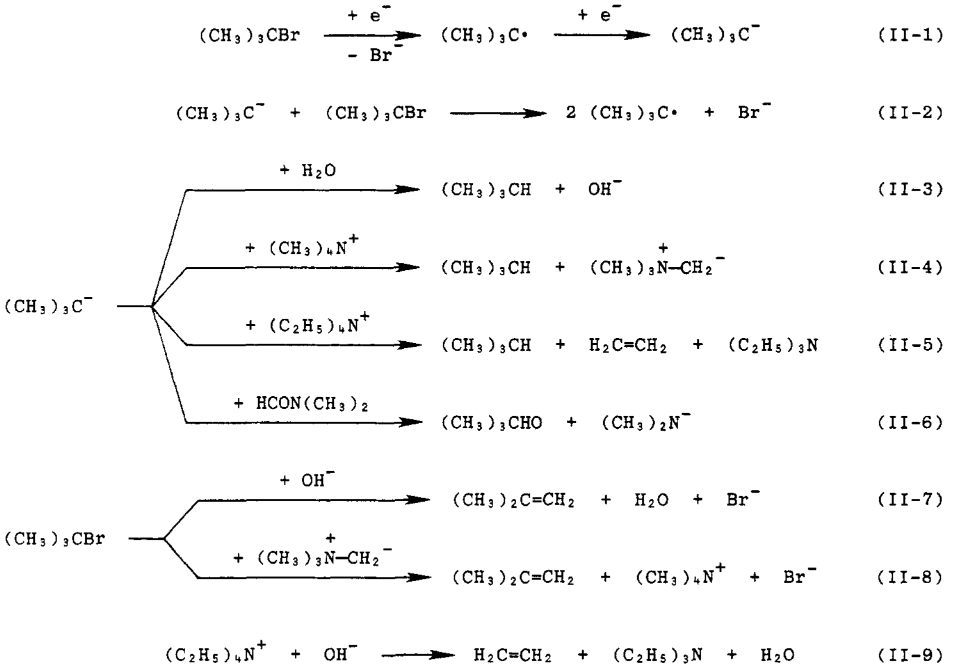
(33) Vieira, K. L.; Mubarak, M. S.; Peters, D. G. *J. Am. Chem. Soc.* **1984**, *106*, 5372–5373.

(34) Friedman, L.; Shechter, H. *J. Org. Chem.* **1960**, *25*, 877–879.

Scheme II



to the first polarographic wave.

Using the yields of isobutane and 2,2,3,3-tetramethylbutane shown for entries 1, 3, and 5 of Table I, we calculated[35] that the ratio of the number of moles of disproportionation product to the number of moles of combination product is approximately 8.6. Disproportionation–combination product ratios for *tert*-butyl radicals ranging from 4.4 to 10.1, obtained at or near room temperature in a variety of solvents, have been reported previously;[36-39] the factors which affect disproportionation–combination product ratios for organic radicals have been summarized by Gibian and Corley.[40] Therefore, it appears that electrogenerated *tert*-butyl radicals behave in a manner similar to those formed in homogeneous solution. This finding suggests that electroreduction of *tert*-butyl bromide produces solvent-caged radicals, as opposed to mercury-stabilized radicals.[41]

Adsorbed alkylmercury radicals are thought to be key intermediates in the stepwise reduction of 1-iododecane[10] and 2-iodooctane;[14] the production of didecylmercury (>99% yield) and of di-*sec*-octylmercury (>24% yield) during preparative-scale electrolyses of these alkyl iodides at mercury pool cathodes is supportive of this contention. However, the absence of di-*tert*-butylmercury as a product of the electrolysis of *tert*-butyl bromide argues against the possibility that stepwise reduction of the alkyl bromide is attributable to stabilization of the *tert*-butyl radical by mercury. These results imply that, as steric hindrance at the site of the carbon-halogen bond increases, there is a decrease in the yield of the diorganomercury species obtained from electrolyses of alkyl halides which exhibit two-step reduction.

Additional observations favor the conclusion that the first step in the reduction of *tert*-butyl bromide is one-electron scission of the carbon-bromine bond to yield a "free" *tert*-butyl radical. Because at least 95% of the isobutane is formed via disproportionation of radicals (Table III, entry 1), the presence of adsorbed *tert*-butyl or *tert*-butylmercury radicals is improbable. At reticulated vitreous carbon cathodes in dimethylformamide, reduction of 1-iododecane is a one-step, two-electron process leading to formation of the decyl carbanion, apparently because carbon (unlike mercury) cannot stabilize the decyl radical.[11] However, the stepwise pattern for the reduction of *tert*-butyl bromide is repeated for vitreous carbon electrodes;[11] therefore, we believe that the existence of the "free" *tert*-butyl radical is indicated.

Finally, because virtually all of the isobutane derived from electrolysis of *tert*-butyl bromide is formed via radical disproportionation and because nearly identical yields of isobutane and isobutylene are obtained, few if any of the *tert*-butyl radicals react with the solvent. This is a remarkable result, since dimethylformamide has been shown to be a good hydrogen-atom donor[42] and has been observed to react with alkyl radicals.[43]

Mechanism of Reduction at Potentials Corresponding to the Second Polarographic Wave. Summarized in Scheme II are the electron-transfer and follow-up chemical reactions occurring at potentials on the second polarographic wave for *tert*-butyl bromide. Initially, single-electron cleavage of the carbon–bromine bond occurs, generating *tert*-butyl radical and bromide ion; however, the alkyl radical undergoes immediate further reduction to the *tert*-butyl carbanion (reaction II-1). Alternatively, it is thermodynamically possible for the *tert*-butyl carbanion to reduce the starting material chemically with the resultant production of a pair of *tert*-butyl radicals (reaction II-2). Regardless of the rel-

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(35) In this computation we used the number of moles of isobutane instead of the number of moles of isobutylene, because any extraneous chemical decomposition of *tert*-butyl bromide will result in an erroneously high yield for isobutylene.

(36) Neuman, R. C., Jr.; Frink, M. E. *J. Org. Chem.* **1983**, *48*, 2430–2432.

(37) Tanner, D. D.; Rahimi, P. M. *J. Am. Chem. Soc.* **1982**, *104*, 225–229.

(38) Schuh, H.-H.; Fischer, H. *Helv. Chim. Acta* **1978**, *61*, 2463–2481.

(39) Sheldon, R. A.; Kochi, J. K. *J. Am. Chem. Soc.* **1970**, *92*, 4395–4404.

(40) Gibian, M. J.; Corley, R. C. *Chem. Rev.* **1973**, *73*, 441–464.

(41) The term "mercury-stabilized" is intended to indicate that stabilization towards further reduction is imparted to the radical by the presence of mercury, whether discrete adsorbed organomercury species are formed or not.

(42) Friedman, L.; Shechter, H. *Tetrahedron Lett.* **1961**, 238–242.

(43) Wawzonek, S.; Duty, R. C.; Wagenknecht, J. H. *J. Electrochem. Soc.* **1964**, *111*, 74–78.

ative importance of these processes, transfer of an electron to the radical must take place faster than either chemical or diffusional events; in fact, the only evidence for the presence of *tert*-butyl radicals is the trace of 2,2,3,3-tetramethylbutane detected after electrolyses at potentials corresponding to the second polarographic wave (Table I, entries 2, 4, 6, and 7).

Electrogenerated *tert*-butyl carbanions undergo rapid protonation by residual water present in the supporting electrolyte–solvent system (reaction II-3); proof for the occurrence of this process has been obtained by means of the previously mentioned experiments with deliberately added deuterium oxide (Table III, entries 2 and 6). Depending on the identity of the supporting electrolyte, the *tert*-butyl carbanion can react in a variety of other ways. First, in our discussion of electrolyses done in the presence of deuterium-labeled reagents (Table III, entry 3), we have already indicated that the tetramethylammonium cation serves as an important source of protons for *tert*-butyl carbanions (reaction II-4) when the concentration of water is low (<0.015 M). However, the relative importance of reactions II-3 and II-4 depends on the concentrations of water and tetramethylammonium ion. For equal concentrations of these two species, the former supplies protons in much greater abundance than the latter. Most probably, the kinetic acidity of various proton donors in the supporting electrolyte–solvent is the overriding factor governing protonation of *tert*-butyl carbanions; thus it is not surprising that water is the best proton source for the carbanion, because oxygen acids are known to transfer protons at much faster rates than carbon acids.[44] Second, when tetraethylammonium perchlorate is used as supporting electrolyte, one of the reactive β-hydrogens of the tetraethylammonium cation can protonate the *tert*-butyl carbanion (reaction II-5); the appearance of large quantities of ethylene and triethylamine implies that the tetraethylammonium ion is deprotonated by the carbanion. Furthermore, as described earlier in connection with our electrolyses of *tert*-butyl bromide in dimethylformamide containing deuterium oxide and either tetramethylammonium or tetraethylammonium perchlorate, the latter electrolyte is a better source of protons for *tert*-butyl carbanions (Table III, entries 2 and 6). Third, if tetra-*n*-butylammonium perchlorate is employed as supporting electrolyte for electrolyses of *tert*-butyl bromide, no significant amounts of Hofmann elimination products derived from the tetra-*n*-butylammonium cation are observed; electrolyses of primary[10] and secondary[14] alkyl halides have also failed to yield any substantial quantities of 1-butene and tri-*n*-butylamine. In comparison to the β-hydrogens of tetraethylammonium ion, those of the tetra-*n*-butylammonium cation are less susceptible to attack by a base, because steric, electronic, and statistical factors lower their reactivity. Thus, *tert*-butyl carbanions preferentially engage in other kinetically more favorable processes.

Perhaps the most dramatic difference brought about by a change in the identity of the supporting electrolyte cation is the appearance of pivalaldehyde in approximately 14% yield when tetraethylammonium perchlorate is the supporting electrolyte (Table I, entry 6). Apparently, the presence of tetraethylammonium ion in the double layer enhances nucleophilic attack of *tert*-butyl carbanion on the carbonyl site of dimethylformamide. Addition of the carbanion to the carbonyl moiety probably results in formation of a tetrahedral intermediate, which collapses to give pivalaldehyde and dimethylamide ion (reaction II-6); the dimethylamide ion is most likely protonated, although the production of dimethylamine has not been established.

In the absence of added proton sources, reactions II-7 and II-8 account for the observation of coulometric *n* values near unity and for the formation of almost equal amounts of isobutane and isobutylene; approximately half of the starting material undergoes non-electron-consuming reactions. Hydroxide ion, generated as a result of deprotonation of water by the *tert*-butyl carbanion, dehydrohalogenates unreduced *tert*-butyl bromide with high efficiency to form isobutylene (reaction II-7). Small, nonpolarizable anions are poorly solvated in dipolar aprotic solvents and, as a consequence, hydroxide is considered to be extremely reactive in dimethylformamide.[45] Because water is regenerated in the dehydrohalogenation step, small amounts of water in the supporting electrolyte–solvent system can be very effective in the protonation of carbanions.

As mentioned previously, invariant coulometric *n* values and product distributions obtained when the water concentration is lowered from 0.050 M to only 0.003 to 0.005 M lead us to believe that the deprotonated tetramethylammonium ion also participates in the dehydrohalogenation of *tert*-butyl bromide (reaction II-8).

Hydroxide ion, formed via deprotonation of water by the *tert*-butyl carbanion, could attack the tetraethylammonium cation, causing the appearance of ethylene and triethylamine (reaction II-9). We tested the likelihood of such a process by vigorously stirring a dimethylformamide solution containing 0.1 M tetraethylammonium perchlorate and approximately 0.005 M tetramethylammonium hydroxide over an unpolarized mercury pool in the cell used for controlled-potential electrolyses; after 1 h, not a trace of ethylene had formed. Interestingly, polarization of the mercury pool at −1.80 V resulted in immediate formation of ethylene.[46] However, even in the presence of the polarized electrode, ethylene is formed at a rate too slow to account for more than a small fraction of the ethylene produced during actual electrolyses of *tert*-butyl bromide. Thus, most of the products of the Hofmann elimination generated during electrolyses of *tert*-butyl bromide result from abstraction of a β-hydrogen from tetraethylammonium cation by the *tert*-butyl carbanion.

Electrolyses of *tert*-butyl bromide at potentials corresponding to the second polarographic wave in the presence of diethyl malonate give rise to large increases in the coulometric *n* value and in the yield of isobutane at the expense of the yield of isobutylene, regardless of the identity of the supporting electrolyte (Table II, entries 2 and 4). We sought to determine the mechanistic role of diethyl malonate by carrying out an electrolysis of 0.0025 M *tert*-butyl bromide at −1.70 V in dimethylformamide containing 0.1 M tetramethylammonium perchlorate, 0.015 M water, and 0.010 M $CD_2(COOC_2H_5)_2$; the *n* value was 1.81 and 16% of the isobutane was monodeuterated. When the experiment was repeated, except for the use of 0.1 M tetraethylammonium perchlorate as electrolyte and a cathode potential of −1.80 V, the *n* value was 2.41 and 11% of the isobutane was monodeuterated; in addition, 2,2-dimethylpropanol (the reduction product of pivalaldehyde) was obtained in 17% yield, which accounts for the abnormally high *n* value. Together, these results imply that diethyl malonate functions predominantly as a proton donor for bases (hydroxide ion) generated as a consequence

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[44] Eigen, M. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 1–19.

[45] Parker, A. J. *Quart. Rev.* **1962**, *16*, 163–187.

[46] The potential of the cathode in this experiment was greater than 0.2 V more positive than the decomposition wave for tetraethylammonium ion.

of the protonation of *tert*-butyl carbanions, but not as a proton source for the carbanion itself. A qualitatively similar result was seen in a study involving a primary alkyl halide;[10] the electrolysis of 0.0025 M 1-iododecane at −1.70 V in dimethylformamide containing 0.1 M tetramethylammonium perchlorate, 0.002 M water, and 0.25 M $CD_2(COOC_2H_5)_2$ gave decane as the major product, of which only 17% was deuterated. It should be noted that the extent of deuterium incorporation is an upper limit because scrambling of the isotopic label between diethyl malonate and water could occur on the time scale of an electrolysis and because the same molecule of water might undergo more than one set of deprotonation–protonation reactions.

In conclusion, at potentials corresponding to its second polarographic wave, *tert*-butyl bromide undergoes reduction to yield the *tert*-butyl carbanion; the primary reaction of the carbanion is protonation, with adventitious water supplying the majority of protons. For low concentrations of water (<0.015 M), both tetramethylammonium and tetraethylammonium cations furnish substantial quantities of protons, whereas the solvent and the unreduced starting material donate few if any protons to the *tert*-butyl carbanion. In the presence of tetraethylammonium perchlorate, a significant portion of the *tert*-butyl carbanions react with dimethylformamide to form pivalaldehyde.

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Registry No. *t*-BuBr, 507-19-7; *t*-Bu·, 1605-73-8; *t*-Bu^-, 65114-21-8; $(CH_3)_3CH$, 75-28-5; $CH_3C(CH_3)=CH_2$, 115-11-7; $(CH_3)_3CC(CH_3)_3$, 594-82-1; $(CH_3)_3CCHO$, 630-19-3; $Me_4N^+ClO_4^-$, 2537-36-2; $Bu_4N^+ClO_4^-$, 1923-70-2; $Et_4N^+ClO_4^-$, 2567-83-1.

First Electron Spin Resonance Spectroscopic Study of Aliphatic RCOṄSR′ Radicals. ^{17}O and ^{33}S Hyperfine Splittings[1]

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The first ESR study of aliphatic RCOṄSR′ radicals is described. The ESR parameters for the amidyls in benzene or toluene from +18 to −50 °C are $a_N = 8.0–8.55$ G, $a_{^{33}S} = 10.5–10.8$ G, and $g = 2.0091–2.0094$. ^{17}O-Enriched PhCOṄS-*t*-Bu radical has also been generated, and the value $a_{^{17}O} = 2.70$ G (in benzene at 18 °C) has been determined. These ESR parameters confirm a higher π-orbital spin density on the nitrogen and sulfur, whereas a very low π-orbital spin density on the oxygen. In addition, the ESR parameters for the structurally interesting PhCOṄSS-*t*-Bu radical are also reported.

N-Alkylcarboxamidyl radicals (RCOṄR′) are among the most important intermediates in photochemical reactions.[2] Although a considerable amount of experimental and theoretical work has been devoted to determine the electronic structure in the ground state of RCOṄR′[3-5] and related radicals, *N*-alkoxycarboxamidyls[6] (RCOṄOR′), it has recently clearly demonstrated by variable-temperature ESR spectra of RCOṄSR′ radicals that they must have a π electronic structure in the ground state.[4c,d] While RCOṄR′ radicals are transient in lifetime,[4f,g] RCOṄOR′ radicals would be substantially stabilized by conjugative electron delocalization from the nitrogen to the alkoxy oxygen reinforced by the neighboring carbonyl group having an ability to accept the electrons.[6] Accordingly, the later radicals would be more long-lived. In this view, sulfur analogues, *N*-thiocarboxamidyls (RCOṄSR′) are also expected to be substantially stabilized in a similar manner, namely, conjugative electron delocalization from the nitrogen to the sulfur. In fact, we found in an earlier work that aromatic *N*-thiocarboxamidyl radicals persist over a long period, even in the presence of oxygen.[7] However, in contrast to a large body of the ESR work on RCOṄR′ and RCOṄOR′ radicals, only little attention has been paid to RCOṄSR′ radicals and much has remained unsolved.[7]

In the present paper we report the first ESR spectroscopic study of structurally simple aliphatic RCOṄSR′ radicals, 2. In this work, fortunately, we could observe ^{17}O and ^{33}S hyperfine splittings (hfs) for some 2 and could estimate the π-orbital spin density distribution in 2 on the basis of ESR parameters. In addition, we also report the ESR parameters for the structurally interesting *N*-dithiocarboxamidyl radical (RCOṄSSR′).

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[1] ESR Studies of Nitrogen-Centered Free Radicals. 27. Part 26: Miura, Y.; Kunishi, T.; Kinoshita, M. *J. Org. Chem.* **1985**, *50*, 5862.

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