Electrochemical Formation and Decomposition of Halogenated Acetophenone Anion Radicals

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The electrochemical reduction of a series of chloro-, bromo-, and iodoacetophenones in N,N-dimethylformamide has been shown to be a one-electron process with the formation of an unstable anion radical. The anion radical decomposes to form an acetylphenyl radical and halide ion. The acetylphenyl radical abstracts a hydrogen atom from the solvent system to form acetophenone, which is reduced at more negative potentials to complete the reaction sequence. Since the reduction of p-chloroacetophenone in the presence of cyanide ion results in the formation of the p-cyanoacetophenone anion radical, the intermediacy of an acetylphenyl radical is suggested. Although the decomposition rates of the ortho- and para-halogenated acetophenone anion radicals are quite rapid ($>10^4$ s^{-1}), the kinetics for the decomposition of the m-chloroacetophenone anion radical to the acetylphenyl radical ($k = 10$ s^{-1}) has been shown to be consistent with a simulated ECE model mechanism, with the second electron transfer being the reduction of acetophenone to its anion radical. The acetylphenyl radical is apparently not reduced further to the anion under anhydrous, aprotic conditions at the platinum cathode. The results obtained here are contrasted with previously reported decomposition pathways of halogenated aromatic anion radicals.

Electrochemical and electron spin resonance studies of halogenated aromatic compounds have shown that loss of anionic substituents is a frequently observed pathway for anion radical decomposition.[2-8] However, the fate of the resultant phenyl radical is apparently dependent on the nature of the substituent remaining on the ring. The nitrophenyl radical, which is produced via decompositions of halogenated nitrobenzene anion radicals, abstracts a hydrogen atom from the solvent to form nitrobenzene.[2-4] Radicals which are produced from the decomposition of halogenated benzophenone and pyrimidine anion radicals[9,10] are not reduced to carbanions, but abstract hydrogen atoms to form benzophenone and pyrimidine, respectively. However, cyanophenyl radicals, which are produced by the decomposition of halogenated benzonitrile anion radicals, are subsequently reduced to carbanion intermediates.[6] Recent reports indicate that the lifetime of the halogenated anion radical is a factor which determines whether the overall mechanism is an one-electron reduction to produce a radical, which subsequently abstracts a hydrogen atom, or a two-electron process to produce a carbanion intermediate.[6,11] If the lifetime of the anion radical is sufficient to allow the species to diffuse from the electrode surface into the bulk solution, the resultant radical cannot be reduced by heterogeneous electron transfer. There is, however, the possibility of homogeneous electron transfer between the resultant radical and the parent anion radical to produce a carbanion intermediate. Recently, an additional mode of halogenated anion radical decomposition, which involves dimerization of the anion radicals to form a dianion, has been reported.[7,12]

The reductive electrochemical behavior of acetophenone has been studied in a variety of solvents with pinacol formation a predominant product.[13] α-Substituted halogenated acetophenones have been shown to undergo reductive cleavage of the carbon–halogen bond by a two-electron mechanism.[14] Although polarographic studies of halogenated acetophenones have been carried out in aqueous media,[15] reductive cleavage of ring-substituted halogenated acetophenones has not been studied in detail in solvents of low proton availability. Polarographic half-wave potentials for halogenated acetophenones have been reported in nonaqueous solvents;[16,17] however, a detailed study of the electrode reaction mechanism and products has not been reported. Fraenkel and co-workers briefly examined the polarographic behavior of p-fluoroacetophenone in dimethylformamide; however, an ESR spectrum was not obtained at temperatures as low as -100 °C.[25] The present study is principally concerned with the electro-chemical formation of a series of bromo- and chloroacetophenones and their subsequent mode of decomposition. We intend to report in a future communication on the mode of decomposition of fluoroacetophenones in solvents of low proton availability.

Experimental Section

Instrumentation. The cyclic voltammetric and chronoamperometric studies were performed on a previously described three-electrode potentiostat.[18] A digital-controlled, multipurpose-function generator and a circuit for electronic compensation of ohmic potential loss were incorporated into the instrument. All measurements were made with electronic compensation of ohmic potential loss using the procedures of Smith and co-workers.[19] Large-scale, controlled-potential reductions were performed on a second potentiostat which used a Harrison Model 6824A amplifier (±50 V, 1 A) in the control circuit. Readout in the cyclic voltammetric and chronoamperometric experiments was to a Hewlett-Packard Model 7035B X-Y recorder for slow-time experiments. Data at rapid scan rates and times less than 1 s were obtained by a Tektronix Model 5103N storage oscilloscope. The latter was equipped with a type 5A20N differential amplifier, type 5B10N time base plug ins, and a Model C-5 Polaroid camera.

Chemicals. All electroactive chemicals were obtained from commercial sources. If necessary, compounds were further purified by sublimation or recrystallization. Tetraethylammonium perchlorate was prepared according to the method of Kolthoff and Coetzee.[20] Tetraethylammonium cyanide was prepared by the method of Andreades and Zahnow.[21] Dimethylformamide (DMF) (Eastman reagent grade) was purified by a combination of two methods, that of Faulkner and Bard[22] and that of Thomas and Rochow.[23] Approximately 2 L of DMF was stored over 300 g of anhydrous copper sulfate for at least 48 h. The DMF was then distilled at a reduced pressure of 1 mmHg at 35 °C using a Nester Faust spinning band column at a reflux ratio of four. The middle 50% cut was collected and redistilled again with the same conditions at a reflux ratio of four. The middle 70% cut was immediately passed through a 5-cm column of Woelm activated alumnia before being collected over activated Linde Type 4A molecular sieves. The solvent was immediately transferred to a vacuum line for use.

Electrodes and Cell. All electrochemical experiments were performed on an all-glass vacuum line.[24] The solvent (DMF) was distilled into the cell on the vacuum line; traces of oxygen, if present, were removed by several freeze–pump–thaw cycles. After the cell and its contents were brought to room temperature, helium was introduced until normal atmospheric pressure was attained. The helium was purified by successive passage of the gas through BASF Catalysis R3-11 to remove oxygen and magnesium perchlorate to remove traces of water.

An aqueous saturated calomel electrode was used throughout as the reference electrode. The reference electrode compartment was isolated from the working and auxiliary electrodes in all experiments by means of a glass frit and a bridge which contained a 0.1 M solution

of tetraethylammonium perchlorate (TEAP) in dimethylformamide (DMF). No attempt was made to position the reference electrode to minimize IR loss; however, electronic compensation as stated above was employed in all experiments. The auxiliary electrode for the microscale experiments was a piece of platinum foil, which was positioned within 1 cm of and parallel to the working electrode surface. The auxiliary electrode for coulometric studies was a large coil of platinum wire, which was isolated by a glass frit from the working electrode compartment. The working electrode in the chronoamperometric experiments was a modified Beckman platinum button electrode (no. 39273) with a geometric area of approximately 0.25 cm². The working electrode for most cyclic voltammetric experiments was the above platinum button; however, a platinum bead electrode was used to analyze the results of controlled-potential electrolysis experiments. The working electrode for the controlled-potential coulometry experiments was a large cylindrical piece of platinum gauze. Stirring of the cell contents in the exhaustive experiments was accomplished with a magnetic stirring bar and stirrer.

Product Studies. The yields of acetophenone in the exhaustive electrolysis experiments were determined by gas chromatography. The gas chromatograph was a Beckman GC4 equipped with flame ionization detectors. SE-30 and DC-200 columns at temperatures of 100–120 °C were employed for acetophenone analysis at a nitrogen flow rate of 1 mL/s. Electrolyzed solutions of the halogenated acetophenones were analyzed directly for products; calibration curves were prepared daily.

Electron spin resonance studies were obtained on a Bruker ER-420 dual cavity spectrometer. The anion radicals were produced in situ in a Scanco electrolytic cell using a platinum gauze working electrode.

Results and Discussion

The cyclic voltammetric data for six isomers of ring-substituted bromo- and chloroacetophenones are summarized in Table I. Since all of the above isomers exhibit similar electrochemical behavior, the experimental results for p-chloroacetophenone and m-chloroacetophenone have been chosen for discussion and interpretation.

The cyclic voltammetric behavior for p-chloroacetophenone in DMF is shown in Figure 1A. Two reduction waves are seen near −1.82 and −2.04 V on the first cathodic sweep. Upon reversal of the direction of potential sweep, a single oxidation wave corresponding to the oxidation of the product formed

Table I. Cyclic Voltammetric Data for Several Substituted Acetophenones[a]

| compd | registry no. | first wave | | second wave |
		$E_p{}^b$	$E_{p/2}{}^b$	$E_p{}^b$
p-chloroaceto- phenone	99-91-2	−1.82	−1.74	−2.04
o-chloroaceto- phenone	2142-68-9	−1.80	−1.71	−2.04
m-chloroaceto- phenone	99-02-5	−1.84	−1.78	−2.04
p-bromoaceto- phenone	99-90-1	−1.74	−1.64	−2.04
o-bromoaceto- phenone	2142-69-0	−1.74	−1.61	−2.04
m-bromoaceto- phenone	2142-63-4	−1.71	−1.65	−2.04
p-iodoaceto- phenone	13329-40-3	−1.67	c	−2.04
p-cyanoaceto- phenone[d]	1443-80-7	−1.49	−1.43	−2.22
acetophenone	98-86-2	−2.04	−1.98	−2.69

a The solutions are 0.1 M tetraethylammonium perchlorate in DMF; the scan rate is 100 mV/s. b Potentials are in volts vs. an aqueous saturated calomel electrode. c Prepeak is observed at approximately −1.50 V. d The first wave corresponds to a one-electron reduction to a stable anion radical. The second wave results from the reduction of the anion radical to the corresponding dianion, which was unstable under the experimental conditions with the above scan rate.
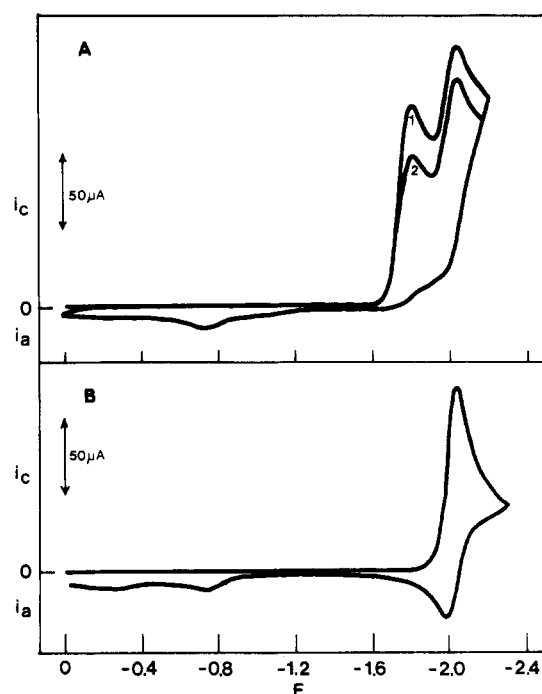

Figure 1. Cyclic voltammograms in DMF with 0.1 F TEAP as the supporting electrolyte at a scan rate of 0.1 V/s: (A) 2.3×10^{-3} F p-chloroacetophenone, (B) 2.0×10^{-3} F acetophenone. The numbers 1 and 2 represent cycles, 1 and 2, respectively, on a platinum button electrode with an area of 0.25 cm².

is evident at −2.03 V. Subsequent cycles show that the second cathodic wave grows in magnitude relative to the first wave; thus, the electron transfer process at −2.03 V must arise from the decomposition of the products formed by the process at −1.82 V. The electrode product generated at −1.82 V must be relatively unstable since no reoxidation wave is observed when the scan is reversed between the two cathodic peaks ($E_{switching}$ = −1.9 V) at scan rates up to 100 V/s. The species generated by the initial cathodic process can be identified as acetophenone by comparison with an authentic cyclic voltammogram of acetophenone in DMF (Figure 1B). The absence of additional discernable electron transfer processes indicates that acetophenone is the only stable electroactive product in the potential range of interest in the reduction of p-chloroacetophenone in DMF.

The number of electrons involved in the two cathodic processes can be estimated by the comparison of chronoamperometric $it^{1/2}/C$ values for similar compounds. The initial reduction reaction of acetophenone, which has been reported as a one-electron process[25] to an anion radical, gave a diffusion-controlled $it^{1/2}/C$ value of 38 A s$^{1/2}$ mol^{-1} cm^3, from t = 1 ms to t = 1 s at an applied potential of −2.3 V. A chronoamperometric measurement for p-chloroacetophenone at a potential of −2.3 V, which includes both cathodic waves (see Figure 1A), gave a diffusion-controlled value of 72 A s$^{1/2}$ mol^{-1} cm^3 from t = 1 ms to t = 1 s. This value is indicative of an overall two-electron process for both cathodic processes. Since the second reduction wave is the one-electron reduction of acetophenone to its anion radical, the reduction dehalogenation of p-chloroacetophenone (E_p = 1.82 V) must be a one-electron process.

Controlled-potential coulometry was used to verify the cyclic voltammetric and chronoamperometric results, which indicated a one-electron reductive dehalogenation to acetophenone (see Table II). Exhaustive electrolyses of p-chloroacetophenone at millimolar concentration levels and at a potential between the first and second cathodic waves (−1.9 V) gave an n value of 1 (n_{exptl} = 1.05). A pulsed electrolysis

Table II. Coulometric Data for Halogenated Acetophenones[a]

compd	concentration, mM	$-E_{applied}$[b]	n_{exptl}, F/mol	yield of acetophenone,[c] %
p-chloroacetophenone	1.6	1.80	0.99	83, 89[d]
o-chloroacetophenone	2.3	1.80	0.96	77, 91[d]
m-chloroacetophenone	2.2	1.84	1.02	74, 87[d]
p-bromoacetophenone	1.5	1.80	0.98	71
o-bromoacetophenone	2.4	1.76	0.98	73
m-bromoacetophenone	2.8	1.76	1.10	78
p-iodoacetophenone	2.3	1.72	0.92	62

[a] The DMF solutions contained 0.10 M tetraethylammonium perchlorate. [b] Potentials are in volts vs. an aqueous saturated calomel electrode. [c] Unless the data are specified otherwise, the yields were determined by flame ionization gas chromatography and are calculated upon the original amount of halogenated acetophenone. Acetophenone was the only product found by either cyclic voltammetry or gas chromatography. Less than 5% of the starting material remained upon termination of the electrolysis. Triethylamine was not detected by gas chromatography in the exhaustive electrolysis mixture, indicating the absence of a Hofmann elimination reaction between a possible phenyl carbanion and the quaternary ammonium cation. [d] Analysis by cyclic voltammetry.

experiment was necessary due to apparent film formation on the platinum surface causing the electrode to become passive after several minutes into the electrolysis. In this experiment the potential of the working electrode is pulsed from +0.1 to −1.9 V at a frequency of 0.1 Hz. The resultant current is integrated in the usual way using the instrumentation described in the Experimental Section. Cyclic voltammetric examination of the product after electrolysis indicated acetophenone as the sole electroactive product in the region of 0.0 to −2.5 V. The absence of any wave at $E_p = -1.8$ V indicated that the electrolysis was indeed exhaustive. Direct gas chromatographic analysis of the resultant electrolyzed solution gave an 83% yield of acetophenone. No other products were detected by gas chromatographic analysis at column temperatures up to 250 °C with the GLC system as specified (infra supra). Thin-layer chromatography of the electrolyzed solution indicated two products, one with an R_f consistent with acetophenone. The second product which was isolated by thin-layer chromatography was not p-chloroacetophenone or the acetophenone pinacol.

m-Chloroacetophenone. Although the cyclic voltammetric peak potentials of $E_{pc} = -1.84$ and -2.03 V for m-chloroacetophenone were similar to the other chloro- and bromoacetophenones, the cyclic voltammetric data at fast scan rates indicated that the decomposition of the initial electrode product was appreciably slower than the radical anions of o- and p-chloroacetophenone. Reoxidation of the initial electrode product is observed at scan rates of 1 V/s, and the system appears chemically reversible at 10 V/s (Figure 2) when the scan is reversed between the two cathodic peaks ($E_{switching} = -1.9$ V). Controlled-potential coulometry at $E_{applied} = -1.85$ V using the pulse mode (amplitude of pulse = 1.5 V, frequency = 0.1 Hz) gave an experimental n value of 1.02 from integration of total current passed. Cyclic voltammetry of the exhaustively electrolyzed solution indicated acetophenone as the only electroactive product. Gas chromatographic analysis of the electrolyzed solution indicated a 74% yield of aceto-
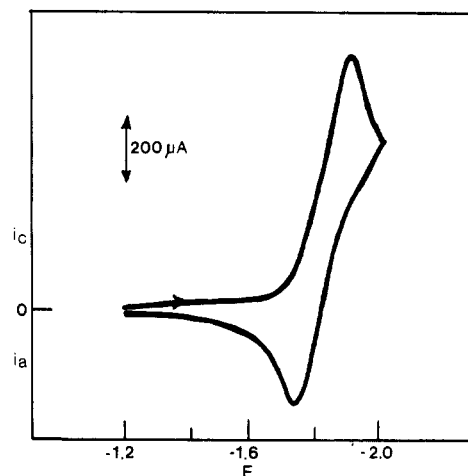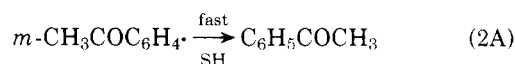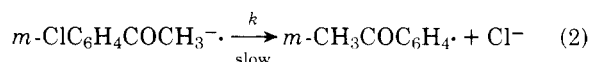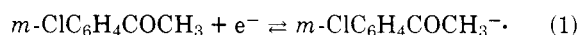

Figure 2. Cyclic voltammogram of 2.9×10^{-3} F m-chloroacetophenone in 0.1 F TEAP–DMF at a scan rate of 5 V/s. The platinum electrode area is 0.25 cm^2.

phenone; no other products were detected by gas chromatographic or electrochemical techniques.

Kinetics for Anion Radical Decomposition. Single potential step chronoamperometry was used to evaluate the kinetics for the decomposition of the m-chloroacetophenone anion radical. In this experiment, the potential was stepped from −1.50 V, at which no electron transfer is taking place, to a final potential of −2.30 V, so as to cause the concurrent reduction of both m-chloroacetophenone and acetophenone present at the electrode surface. The chronoamperometric $it^{1/2}/C$ decreased smoothly from a value of 79 A s$^{1/2}$ mol^{-1} cm^3 at long ($t \geq 1$ s) times to a value of 39 A s$^{1/2}$ mol^{-1} cm^3 at short times ($t < 5$ ms). Although electrode surface problems were noted in the long-term exhaustive reduction of m-chloroacetophenone, chronoamperometric i–t data show no evidence of electrode fouling; reproducible runs were obtained on the same electrode surface over a time window of 5 ms to 10 s. Comparison of these chronoamperometric data to acetophenone, which has an $it^{1/2}/C$ value of 38 A s$^{1/2}$ mol^{-1} cm^3, indicates kinetic control of the current due to formation of electroactive acetophenone at these potentials. These $it^{1/2}/C$ values correspond to $n = 1$ at short times ($t = 5$ ms), i.e., one-electron reduction of halogenated acetophenone to an anion radical (eq 1), and to $n = 2$, i.e., one-electron reduction to the anion radical and one-electron reduction of a product, acetophenone (eq 3), produced as a result of anion radical decomposition (eq 2 and 2A). The data were analyzed for an ECE-type process in which the effect of the homogeneous chemical reaction between the acetophenone anion radical and m-chloroacetophenone was considered (eq 4).[26] A dimensionless working curve in which $N_{app} = it^{1/2}/it^{1/2}{}_{k=0}$ is a calculated function of log kt was constructed by conventional digital simulation techniques (Figure 3).[27] The value chosen for the equilibrium constant for the solution redox reaction was 10, and it is consistent with the observation that the reduction of acetophenone occurs at more negative potentials than m-chloroacetophenone. The experimental results at three different concentrations of m-chloroacetophenone are consistent with the theoretical curve projected for this model if the rate constant for the decomposition of the radical anion is taken as 5 s^{-1}.
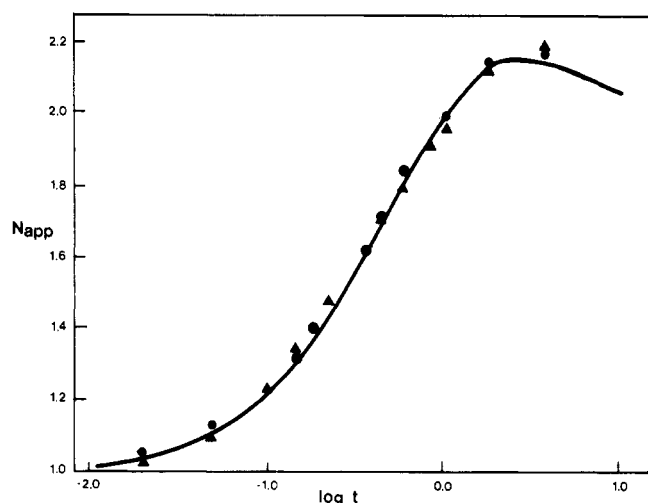
$$m\text{-ClC}_6\text{H}_4\text{COCH}_3 + \text{e}^- \rightleftharpoons m\text{-ClC}_6\text{H}_4\text{COCH}_3{}^-\cdot \quad (1)$$

$$m\text{-ClC}_6\text{H}_4\text{COCH}_3{}^-\cdot \xrightarrow[\text{slow}]{k} m\text{-CH}_3\text{COC}_6\text{H}_4\cdot + \text{Cl}^- \quad (2)$$

$$m\text{-CH}_3\text{COC}_6\text{H}_4\cdot \xrightarrow[\text{SH}]{\text{fast}} \text{C}_6\text{H}_5\text{COCH}_3 \quad (2A)$$
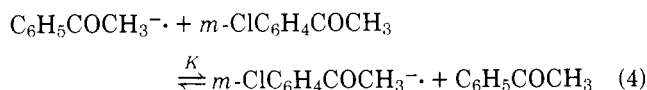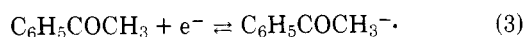
Figure 3. Single potential step chronoamperometric data for the decomposition of m-chloroacetophenone at concentrations of (●) 1.8 × 10^{-3} F and (▲) 3.6 × 10^{-3} F. The solid line is calculated for a first-order rate constant of 5 s^{-1}.

$$C_6H_5COCH_3 + e^- \rightleftharpoons C_6H_5COCH_3^{-} \cdot \tag{3}$$

$$C_6H_5COCH_3^{-} \cdot + m\text{-}ClC_6H_4COCH_3$$

$$\overset{K}{\rightleftharpoons} m\text{-}ClC_6H_4COCH_3^{-} \cdot + C_6H_5COCH_3 \tag{4}$$

The rate of carbon–halogen bond fragmentation of halogenated aromatic radical ions has been shown to be directly related to the free electron density at the carbon site of the reaction.[30] Since we are postulating the intermediacy of a σ-type acetylphenyl radical, which is produced upon exclusion of the halide ion from a π-type anion radical, such a correlation would be anticipated. The free electron density on the acetophenone radical anion has been calculated using a McLachlan modification of LCAO Hückel calculations.[31] The calculated McLachlan spin density is −0.0504 (mean value) for the meta position vs. +0.1683 as the mean value for the ortho and + 0.2605 for the para positions on the acetophenone radical anion. In addition, the hyperfine coupling constants for the acetophenone anion radical ESR spectrum compare favorably with the calculated values in that higher electron density is present at the ortho and para positions than at the meta position. Substitution by halogens will alter the absolute values of the McLachlan spin densities; however, the relative magnitudes of the calculated spin densities can be shown to be similar for chloro-, bromo-, and iodo-substituted acetophenones. Electron density calculations using Hückel LCAO molecular orbital calculations were carried out in our laboratory for the chloroacetophenone anion radicals (Table III). The calculated electron density for the para carbon in p-chloroacetophenone (1.193) is considerably larger than the mean value for the ortho carbon in o-chloroacetophenone (1.068). In contrast, the mean value for the meta position in m-chloroacetophenone (1.035) is significantly less than either of the above. The mean values are based upon two values each for the ortho and meta positions because assymmetry is introduced by applying a negative correction to the Coulomb integral of the ring carbon adjacent to the oxygen atom of the carbonyl group.[31] The increased stability of m-chloroacetophenone (k = 5 s^{-1}) compared to o- and p-chloroacetophenone (k > 10^3 s^{-1}) is thus consistent with decreased electron density in the meta position.

Reaction Pathways. The coulometric and kinetic data are consistent with a one-electron reduction to a anion radical. The anion radical undergoes a unimolecular reaction with formation of an acetylphenyl radical and halide ion. The

Table III. Calculated Electron Spin Densities for Chloroacetophenone Anion Radicals[a]

anion radical	registry no.	position	electron density
o-chloroacetophenone	68225-75-2	2	1.070
		6	1.065
		7	1.986
m-chloroacetophenone	68225-76-3	3	1.019
		5	1.053
		7	1.986
p-chloroacetophenone	68225-77-4	4	1.193
		7	1.989

[a] MO parameters from ref 31 and 34: k_{C-O} = 1.7, h_O = 1.55, $k_{C_{1B}-C_1}$ = 0.90, $h_{C_{1B}}$ = −0.20, h_{C_6} = −0.05, k_{C-Cl} = 0.40, h_{Cl} = 2.00, h_{CH_3} = 2.0, k_{C-CH_3} = 0.90.

suggested intermediacy of an acetylphenyl radical is further substantiated by radical trapping experiments. Several recent reports have demonstrated that nucleophilic anions can trap aryl radicals to form new stable anion radicals[3,28] in reactions known as the $S_{RN}1$ mechanism of aromatic nucleophilic substitution.[29] Cyclic voltammetric experiments of chloroacetophenones in which the halogenated acetophenone is reduced in the presence of a strong nucleophile such as cyanide ion indicate clearly the intermediacy of an acetylphenyl radical (Figure 4A). On the initial cathodic scan, the only reductive process noted prior to acetophenone reduction is the reduction of p-chloroacetophenone. However, on the anodic
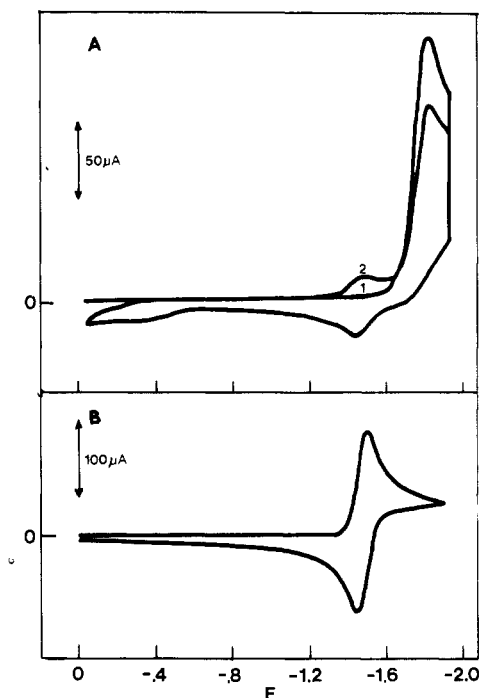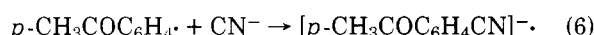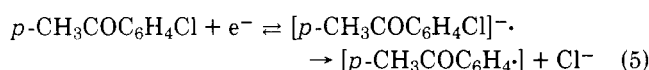

Figure 4. Cyclic voltammograms in DMF at a scan rate of 0.1 V/s on a planar platinum electrode. (A) 1.8 × 10^{-3} F p-chloroacetophenone and 0.4 F tetraethylammonium cyanide. The potential scan was interrupted at −1.8 V for 30 s to accentuate the formation of the p-cyanoacetophenone anion radical. Numbers 1 and 2 represent cycles 1 and 2, respectively. (B) 2.5 × 10^{-3} F p-cyanoacetophenone and 0.1 F tetraethylammonium perchlorate.

Table IV. Rate Constants for the Decomposition of Chloro-Substituted Anion Radicals

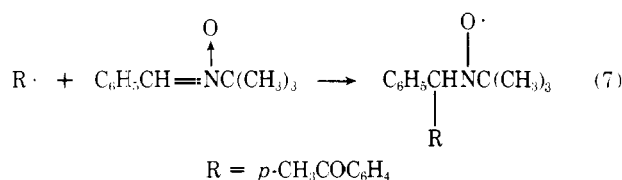| radical anion	log k
m-chloronitrobenzene	<-3[a]
p-chloronitrobenzene	<-3[a]
m-chlorobenzophenone	<-1[b]
p-chlorobenzophenone	1[b]
m-chloroacetophenone	1[c]
p-chloroacetophenone	5[d]
m-chlorobenzonitrile	≥ 10[e]
p-chlorobenzonitrile	≥ 10[e]

[a] Reference 2. [b] Reference 9. [c] This work. [d] The rate constant can be calculated from the positive shift in the reduction peak for the anion radical as a result of a follow-up chemical reaction. $E_p = E_{1/2} - (RT/hF)[0.78 - \ln (k/a)^{1/2}]$, where $a = 3.15$ s^{-1}; see ref 35 for details. Although the half-wave potentials for the chloroacetophenones can not be determined experimentally, they can be calculated from the reaction constant ρ and the appropriate σ-substituent constant. With $\rho = 0.31$ V, the half-wave potential for p-chloroacetophenone is calculated to be -1.94 V.[36] Since $E_p = -1.82$ V and $a = nFv/RT = 3.15$ s^{-1}, a rate constant of 10^5–10^6 s^{-1} is estimated for the decomposition of the p-chloroacetophenone anion radical. Using $\rho = 0.38$ V, which was reported for the benzophenones in DMF,[9] a rate constant of 10^4–10^5 s^{-1} is estimated for the decomposition of the p-chloroacetophenone anion radical. [e] Reference 6.

scan an oxidation wave at -1.43 V is seen, and on the subsequent cathodic scan a reduction wave at -1.49 V is observed. This redox couple compares favorably to the electrochemically reversible reduction of p-cyanoacetophenone (Figure 4B). These results suggest the reaction sequence shown in eq 5 and 6.

$$p\text{-CH}_3\text{COC}_6\text{H}_4\text{Cl} + \text{e}^- \rightleftharpoons [p\text{-CH}_3\text{COC}_6\text{H}_4\text{Cl}]^{-}\cdot$$
$$\rightarrow [p\text{-CH}_3\text{COC}_6\text{H}_4\cdot] + \text{Cl}^- \quad (5)$$

$$p\text{-CH}_3\text{COC}_6\text{H}_4\cdot + \text{CN}^- \rightarrow [p\text{-CH}_3\text{COC}_6\text{H}_4\text{CN}]^{-}\cdot \quad (6)$$

Confirmation of p-cyanoacetophenone anion radical formation was obtained by ESR spectroscopy. In this experiment, p-chloroacetophenone (2 mM) was reduced electrolytically at a potential of -1.85 V in an ESR cavity with tetraethylammonium cyanide (0.2 M) present as supporting electrolyte. In the absence of an applied potential, no spectrum could be recorded. Upon electroreduction of p-chloroacetophenone, a spectrum which was consistent with that reported by Rieger and Fraenkel for the p-cyanoacetophenone anion radical in DMF was recorded.[31]

Additional evidence for the intermediacy of an acetylphenyl radical was obtained by spin trapping ESR experiments. Spin trapping has been applied to the detection of radical intermediates produced by thermal and photochemical techniques.[32] Bard and co-workers[33] employed the spin trap reagent α-phenyl-N-tert-butylnitrone (PBN) to trap phenyl radicals produced by the electrochemical reduction of phenyldiazonium tetrafluoroborate in acetonitrile. Electrochemical reduction of p-chloroacetophenone (2 mM) at -1.8 V in tetraethylammonium perchlorate (0.1 M)/DMF in the presence of 10 mM PBN in an ESR cavity gave a six-line spectrum ($a_N = 14.75$ G, $a_H = 2.56$ G). This spectrum is consistent with that of a nitroxide, R = acetylphenyl group, which is produced by the reaction of electrochemically generated acetylphenyl radical with PBN (eq 7).

$$R\cdot + C_6H_5CH=NC(CH_3)_3 \longrightarrow C_6H_5\overset{\overset{\displaystyle O\cdot}{|}}{C}H\overset{}{N}C(CH_3)_3 \quad (7)$$
$$\overset{|}{R}$$

$$R = p\text{-CH}_3\text{COC}_6\text{H}_4$$

The combination of trapping experiments show that the acetylphenyl radical is indeed an intermediate in the electrode reactions for halogenated acetophenones. The n values from coulometry experiments and product analysis support the one-electron reduction to an anion radical, which decomposes to a free radical intermediate. The free radical intermediate is not reduced to the carbanion. The radical is either formed at sufficient distance from the electrode surface so as not to be electrochemically reduced or the potential at which the radical anion is formed is not sufficiently negative to reduce the resultant phenyl radical to its carbanion.

In contrast, the cyanophenyl radical intermediates formed as a result of the decomposition of chloro-, bromo-, and iodobenzonitriles are further reduced to the phenyl carbanion.[6] The further reduction of the cyanophenyl radical to its anion can be interpreted as the result of rapid formation (Table IV) of the cyanophenyl radical at the electrode surface. The potential of the electrode is sufficiently negative so as to cause concurrent reduction of the radical to the anion. Halogenated benzophenone radical anions, on the other hand, are stable enough to diffuse into the bulk solution before decomposition occurs since the resultant aryl radicals in this case are not reduced to the corresponding carbanion.[9] Although the halogenated acetophenone radical anions are less stable than the halogenated benzophenone radical anion, they are stable enough to diffuse into the bulk solution. There is, however, the possibility for a homogeneous redox reaction between unreacted radical anion and the resultant phenyl radical (eq 8).

$$RX^-\cdot + R\cdot \overset{K}{\rightleftharpoons} R^- + RX \quad (8)$$
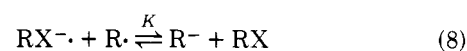
The equilibrium constant for this reaction should be greater than 1 if the reduction potential for the radical is less negative than the reduction potential for the halogenated aromatic species. Although reduction potentials for phenyl radicals have not been specifically measured, reductions of cyanophenyl radicals have been shown to occur at potentials equal to or more positive than the reduction of halogenated benzonitriles. Since it is improbable that the reduction potentials for these σ radicals should differ significantly,[37,38] one would expect the redox reaction (eq 8) to be favored to the right. Thus, the forward rate of the electron transfer from the π-halogenated anion radical to the σ-phenyl radical is apparently slower than the decomposition of the anion radical.

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Polymer-Anchored Cobalt Tetraarylporphyrin Catalysts for the Conversion of Quadricyclane to Norbornadiene[1]

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Received August 21, 1978

Methods are described for the preparation of carboxamide- and sulfonamide-linked polystyrene-anchored cobalt(II) tetraarylporphyrins containing 0.28 to 0.44% cobalt, which are highly active catalysts for the conversion of quadricyclane to norbornadiene. These cobalt catalysts gradually lose some of their activity upon repeated recycling. This loss in catalytic activity apparently arises from partial oxidation, since the loss of catalytic activity can be partially restored by treatment with a strong reducing agent such as titanium(III). The apparent activities of these catalysts are increased if the catalyst is finely powdered, thereby suggesting diffusion limitation of the catalytic activity. Applications are discussed of these catalysts in a proposed solar energy storage system based on the reversible valence isomerization of norbornadiene to quadricyclane.

The photosensitized conversion of norbornadiene (I) to quadricyclane (II) coupled with the transition metal complex catalyzed reversion of quadricyclane to norbornadiene presents a promising system for solar energy storage.[2-4] Both components I and II are liquids, with norbornadiene being
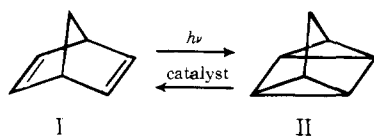
readily available and relatively inexpensive. Quantitative conversion of quadricyclane to norbornadiene produces 1.15 $\times 10^6$ J/L.[5] Quadricyclane is stable indefinitely under ambient conditions but can be rapidly converted to norbornadiene in the presence of appropriate catalysts.[6,7]

Since 1975 at the University of Georgia we have been studying appropriate sensitizers and catalysts for a model solar energy storage system based on this reversible valence isomerization of norbornadiene (I) to quadricyclane (II). In this connection we are studying both sensitizers and catalysts immobilized on macroreticular polystyrene beads. In an actual solar energy system based on this principle such isolation of the sensitizer is an attractive option, but similar isolation of the catalyst is mandatory in order to keep the active catalyst away from the photochemical reactor where the conversion of norbornadiene (I) to quadricyclane (II) is taking place.

Previous papers from this laboratory have discussed research directed toward the development of new sensitizer structures,[4,8,9] or toward the immobilization of sensitizers on polystyrene beads.[2] This paper discusses the preparation of

an immobilized catalyst for the conversion of quadricyclane (II) to norbornadiene (I).

An ideal catalyst for the conversion of quadricyclane (II) to norbornadiene (I) in a solar energy storage system should meet several requirements: (1) the active species should not be leached by the hydrocarbon reaction mixture; (2) it should not produce undesirable side reactions such as polymerization or dimerization; (3) it should be sufficiently active to evolve heat rapidly upon contact with quadricyclane. Cobalt(II) tetraarylporphyrins[10,11] covalently bonded to macroreticular polystyrene[12] were chosen as the most likely candidates for a catalyst to meet these criteria. In this work we have developed new methods for anchoring cobalt tetraarylporphyrins to polystyrene through carboxamide and sulfonamide linkages. Such a procedure has allowed us to obtain routinely polystyrene-anchored cobalt(II) tetraarylporphyrins containing 0.3 to 0.5% cobalt.

Results and Discussion

Syntheses of the Catalysts (Figure 1). Macroreticular polystyrene beads cross-linked with 20% divinylbenzene (Dow XFS 4022) were nitrated with nitric acid in acetic anhydride at room temperature.[13] The reaction proceeded at a moderate rate allowing control of the extent of the reaction by varying the time (see Experimental Section). Reduction of the resulting nitropolystyrene with stannous chloride in hydrochloric acid–acetic acid gave essentially complete conversion of the pendant nitro groups to amino groups. The completeness of the reduction was conveniently checked by noting the disappearance of the nitro infrared absorptions at 1521 and 1349 cm^{-1} while the presence of amino groups in the reduced