mL). After 3 h at 25 °C, the suspension of crystals was allowed to stand at 5 °C for 12 h. The orange needles of the product were collected and were washed with THF (2 × 1 mL) and dried under a stream of N_2; 0.16 g, 91%. Anal. Calcd for $C_{36}H_{50}ClO_4P_2Rh$: C, 58.7; H, 5.5; Cl, 4.8; P, 8.4. Found: C, 58.7; H, 5.8; Cl, 4.5; P, 8.1.

[Rh((*S*)-chairphos)(NBD)]ClO_4·$^3/_8$$CH_2Cl_2$. A solution of (*S*)-chairphos (0.37 g) in CH_2Cl_2 (2 mL) was added dropwise to a stirred solution of [Rh(NBD)$_2$]ClO_4 (0.33 g) in CH_2Cl_2 (4 mL). The orange solution was filtered and then was gradually diluted with THF (~2 mL) until crystallization began. After 2 h at 25 °C, more THF (2 mL) was added, and 2 h later the mixture was held at 5 °C for 12 h. The red-orange prisms of the product were collected and were washed with THF (2 × 2 mL) and were dried under N_2; 0.62 g, 98%. The CH_2Cl_2 of crystallization was quantitatively confirmed by ^1H NMR. Anal. Calcd for $C_{35}H_{36}ClO_4P_2Rh\cdot{}^3/_8CH_2Cl_2$: C, 56.4; H, 4.9; Cl, 8.2; P, 8.2. Found: C, 56.3; H, 5.1; Cl, 7.9; P, 8.4.

(c) **Circular Dichroism Spectra. [Rh((*S*,*S*)-skewphos)Y]ClO_4, Y = $(CH_3OH)_2$, Leucine Precursors.** A suspension of [Rh(*S*,*S*)-skewphos)(NBD)]ClO_4 (2.61 mg) in methanol (3.0 mL) was stirred under argon until all of the solid had dissolved. Hydrogen gas (1.7 mL) was then injected, and the sample was shaken (~5 min) until the 472-nm absorption peak, characteristic of coordinated NBD, had disappeared to give the dimethanolo adduct. An aliquot of this solution (0.34 mL) was transferred to a 1-mm cell under argon, and the circular dichroism spectrum was measured with a JASCO J-41A spectropolarimeter. The same sample was then injected with 5.4 μL of a 0.76 M solution of the leucine precursor, β-isopropyl-α-benzamidoacrylic acid in methanol solution, and the spectrum was recorded. A second aliquot of the stock methanolo complex solution (0.34 mL) was injected with 20 μL of a 0.203 M solution of the alanine precursor, α-acetamidoacrylic acid in methanol solution, and the spectrum was recorded.

[Rh((*S*)-chairphos)Y]ClO_4. A stock solution of the dimethanolo complex was prepared in the manner described for the skewphos analogue. Thus [Rh((*S*)-chairphos)(NBD)]ClO_4·$^3/_8$$CH_3Cl_2$ (2.8 mg) in methanol (3 mL) was reduced with hydrogen gas (1.7 mL). The circular dichroism spectra were obtained with the same substrate to complex ratios as for skewphos.

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Intramolecular Electron Transfer and Dehalogenation of Anion Radicals. 4. Haloacetophenones and Related Compounds[1]

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Abstract: Halogen-substituted acetophenones and several other carbonyls and carboxyl derivatives were reduced with e_{aq}^- in irradiated aqueous solutions to produce the anion radicals. In certain cases, reduction by $(CH_3)_2\dot{C}O^-$ was also used. The anion radicals undergo intramolecular electron transfer and dehalogenation to yield inorganic halide ions. The rates of these reactions varied over a wide range (10^1–10^7 s^{-1}) and were strongly dependent on the nature of the halogen and the other substituent and their relative positions in the molecule. The results obtained here are discussed along with previous measurements on cyano and nitro derivatives. The rate of dehalogenation is found to be dependent on the electron affinity of the other substituent on the ring. Hammett's substituent constants do not correlate with the observed rates. However, spin density distribution in the anion radicals, as derived from ESR parameters, yields a good qualitative correlation. Increased spin density on the ring carbon bearing the halogen is accompanied by an increase in the rate of C–X bond scission. The spin density represents in this case the negative charge density, since protonation of the anion radicals results in minor changes in spin densities but causes a dramatic decrease of the rate of dehalogenation.

One-electron reduction of organic halides leads in most cases to the immediate release of a halide ion with formation of an alkyl or aryl radical.[3]

$$\mathrm{RX} + e^- \rightarrow \dot{\mathrm{R}} + \mathrm{X}^- \tag{1}$$

However, when the molecule contains an electron affinic substituent such as NO_2 or CN, the initial electron adducts were shown to have finite lifetimes before releasing the halide,[4-6] e.g.

$$\mathrm{XCH_2C_6H_4NO_2} + e^- \rightarrow \mathrm{XCH_2C_6H_4N\dot{O}_2^-} \rightarrow \mathrm{X^-} + \mathrm{\dot{C}H_2C_6H_4NO_2} \tag{2}$$

In these cases the dehalogenation reactions have been viewed as intramolecular electron-transfer processes, where an electron is transferred from the $N\dot{O}_2^-$ or $\dot{C}N^-$ groups, and the conjugated π system, to the halogen atom to cause the C–X bond scission. The rates of these processes were found to depend on the nature of the halogen (I > Br > Cl) and its relative position to the other subsitutent on the ring (*o* > *p* > *m*).[4-6] For example, the anion radicals of nitrobenzyl halides undergo dehalogenation with rates ranging from <5 s^{-1} for *m*-$(ClCH_2)C_6H_4N\dot{O}_2^-$ to 5.7 × 10^5 s^{-1} for *p*-$(ICH_2)C_6H_4N\dot{O}_2^-$.[4] The variations in the rates were rationalized by the differences in C–X bond dissociation energies and by the spin density distribution at the various positions. Contrary to the case of nitrobenzyl halides, the anion radicals of halonitrobenzenes did not undergo dehalogenation,[5] because the aromatic C–X bonds are much stronger than the benzylic analogues. Replacement of NO_2 by CN allows greater electron density to reach the halogen and thus increases the rates of dehalogenation considerably.[6] In order to further examine the effect of the substituent on the rate of dehalogenation, a study of haloacetophenones and related compounds has been undertaken. The

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results indicate that the acetyl group has an intermediate effect between those of nitro and cyano groups.

Experimental Section

p-Iodoacetophenone was obtained from Pfaltz and Bauer, *m*-(chloromethyl)acetophenone was from Chemical Procurement Laboratory, and the other substrates were from Aldrich. The alcohols and inorganic compounds were Baker Analyzed reagents. Water was purified by a Millipore Milli-Q system.

Solutions were prepared freshly before irradiation and were deoxygenated by bubbling with pure nitrogen. Steady state irradiations were carried out in a Gammacell 220 Co^{60} source with a dose rate of 3 × 10^{17} eV g^{-1} min^{-1}. The yields of halide ions were determined by using the corresponding ion-selective electrodes. Pulse irradiation was carried out with an ARCO LP7 linear accelerator delivering 5–50 ns pulses of 7 MeV electrons. The dose absorbed per pulse usually produced 2–5 μM radicals. The transient absorption spectra and kinetics with signal averaging were measured by the computer controlled pulse radiolysis apparatus described previously.[7]

Results and Discussion

The radiolysis of water produces hydrated electrons which react with ketones with diffusion-controlled rates[8] to yield ketyl radical ions

$$XC_6H_4COCH_3 + e_{aq}^- \rightarrow XC_6H_4\dot{C}O^-CH_3 \quad (3)$$

The hydroxyl radicals, also produced by the radiolysis, react with the ketones to form different products. In order to study the ketyl radicals without interference by the reactions of OH, the latter are scavenged by an alcohol. Both *t*-BuOH and *i*-PrOH were used in this study. *t*-BuOH yields $(CH_3)_2C(OH)\dot{C}H_2$ which is relatively unreactive[9] and is not expected to react with the ketones. *i*-PrOH, on the other hand, yields the reducing radicals $(CH_3)_2\dot{C}OH$, or $(CH_3)_2\dot{C}O^-$ at high pH, which then reduce acetophenones and benzophenones efficiently.[9]

$$(CH_3)_2\dot{C}O^- + XC_6H_4COCH_3 \rightarrow (CH_3)_2CO + XC_6H_4\dot{C}O^-CH_3 \quad (4)$$

Ketyl radicals are thus produced by reaction 3 ($k \sim 10^{10}$ M^{-1} s^{-1})[8] and reaction 4 ($k \sim 10^8$–10^9 M^{-1} s^{-1}).[9] Ketyl radicals from the haloacetophenones presently studied may undergo dehalogenation

$$XC_6H_4\dot{C}O^-CH_3 \rightarrow X^- + \dot{C}_6H_4COCH_3 \quad (5)$$

In order to monitor reaction 5 it is necessary to avoid its overlap with the formation reactions (3 and 4) and with the radical–radical decay. If reaction 5 is relatively rapid it is advantageous to avoid the slower formation reaction 4, i.e., to produce the ketyl radicals by reaction with e_{aq}^- only, using *t*-BuOH as the OH scavenger. On the other hand, if reaction 5 is slow the use of *t*-BuOH has a drawback in that the ketyl radicals may decay more rapidly by reaction with $(CH_3)_2C(OH)\dot{C}H_2$ than by reaction 5. In such cases it becomes important to use *i*-PrOH in order to produce a one-radical system which could minimize the second-order decay relative to reaction 5.

Anion radicals from halocetophenones and benzophenones have pK_a values[10] in the range of 9–10.

$$XC_6H_4\dot{C}(OH)CH_3 \rightleftarrows XC_6H_4\dot{C}O^-CH_3 + H^+ \quad (6)$$

In order to insure complete dissociation, most experiments were carried out at pH >12.

The absorption spectra of the anion radicals from several haloacetophenones are shown in Figures 1 and 2. They all exhibit intense maxima around 320 nm and weaker ones around 460 nm, in agreement with previously reported spectra of similar radicals.[10,11] The spectrum of the anion radical of *p*-bromobenzophenone (Figure 1) shows maxima at slightly higher wavelengths and is also in agreement with previous reports.[10,11]

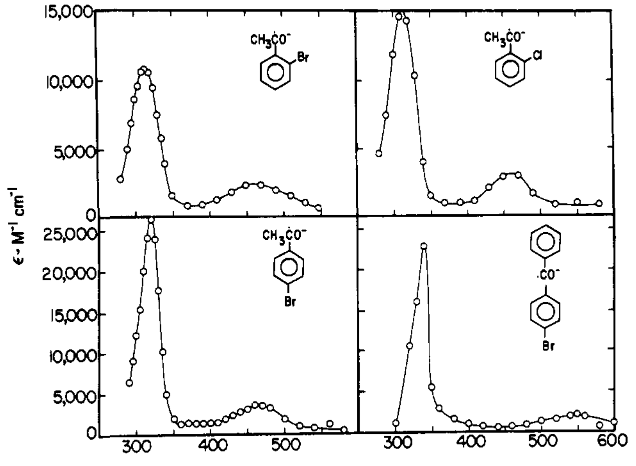

Figure 1. Transient absorption spectra of the anion radicals of chloro- and bromoacetophenones and of bromobenzophenone. Observed in the pulse radiolysis of deoxygenated aqueous solutions containing ~1 mM substrate and 1 M *t*-BuOH at pH 12.2. The extinction coefficients were calculated by assuming yields of $G = 2.8$ and using KSCN dosimetry. The spectra were not corrected for possible bleaching of the parent compounds at the lower wavelengths.

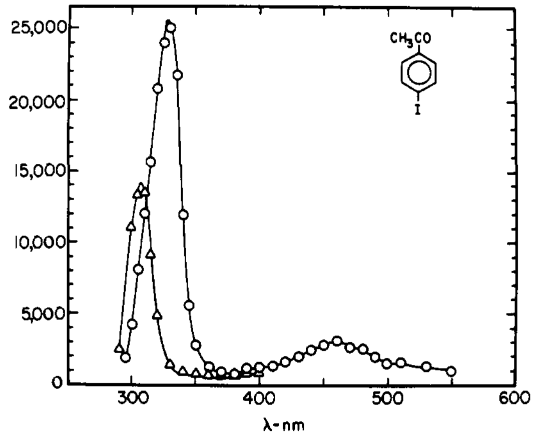

Figure 2. Transient absorption spectra of the anion radical of *p*-iodoacetophenone at pH 12.2 (○) and of its protonated form at pH 4.0 (△). Observed in the pulse radiolysis of deoxygenated aqueous solutions containing 2 × 10^{-4} substrate and 0.5 M *t*-BuOH.

The reactions of the anion radicals were followed by monitoring the decay of their absorptions around 320 nm. The decay of the anion radicals of *o*-chloro-, *o*-bromo-, *p*-bromo-, and *p*-iodoacetophenone in the presence of *t*-BuOH followed first-order kinetics with rates ranging from 1.5 × 10^3 to 5 × 10^5 s^{-1}. These rates were independent of the dose per pulse, i.e., radical concentration, and of the solute concentration over a tenfold range. These findings clearly indicate that the radicals do not decay by reactions with other radicals, nor by reaction with the parent compound. The decay must, therefore, represent the intramolecular electron transfer reaction 5 which results in dehalogenation. The substituted phenyl radicals produced by this reaction are expected to exhibit only weak absorptions below 300 nm[12] and could not be observed. On the other hand, the production of halide ions was experimentally confirmed. The yields of X$^-$ in steady state radiolysis experiments are summarized in Table I.

The yields of Cl$^-$ and Br$^-$ from the haloacetophenones resemble those obtained from the halobenzonitriles[6] and suggest similar mechanisms. In the presence of *t*-BuOH $G(X^-)$ is usually similar to $G_{e_{aq}^-}$ (2.8) if dehalogenation takes place efficiently. The slightly higher values (Table I) are caused by subsequent reactions of the phenyl radicals as discussed previously.[6] The very high $G(X^-)$

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Table I. Yields of Halide Ions in Irradiated Solutions of Haloacetophenones

substrate	concn, mM	additives (1 M)	pH	$G(X^-)$
o-$ClC_6H_4COCH_3$	1.5	t-BuOH	12.2	6.1
	1.5	i-PrOH	12.2	500
p-$ClC_6H_4COCH_3$	1.5	i-PrOH	12.2	~5
o-$BrC_6H_4COCH_3$	1.2	i-PrOH	12.2	1800
	1.9	i-PrOH	9.2	140
	1.9	i-PrOH	4.7	3.0
	1.2	i-PrOH	3.7	1.1
	1.2	t-BuOH	12.0	3.8
p-$BrC_6H_4COCH_3$	1.3	i-PrOH	12.1	250
	1.3	i-PrOH	4.3	1.6
	1.1	t-BuOH	12.0	2.5
m-$BrC_6H_4COCH_3$	1.3	i-PrOH	12.2	6.1
	1.0	t-BuOH	12.2	~1.0
p-$BrC_6H_4COC_6H_5$	0.2	i-PrOH	12.0	0.6

Table II. Rates of Dehalogenation of Anion Radicals

radical	rate,[a] s^{-1}
o-$ClC_6H_4\dot{C}O^-CH_3$	$(1.5 \pm 0.5) \times 10^3$ [b]
o-$BrC_6H_4\dot{C}O^-CH_3$	$(5 \pm 1) \times 10^5$
p-$ClC_6H_4\dot{C}O^-CH_3$	$\sim 10^2$ [c]
p-$BrC_6H_4\dot{C}O^-CH_3$	$(5 \pm 1) \times 10^3$
p-$IC_6H_4\dot{C}O^-CH_3$	$(1.4 \pm 0.2) \times 10^5$
m-$BrC_6H_4\dot{C}O^-CH_3$	$\sim 10^2$ [c]
p-$BrC_6H_4\dot{C}O^-C_6H_5$	<7 [c]
p-$BrC_6H_4\dot{C}HO^-$	4×10^2 [d]
o-$BrC_6H_4\dot{C}OHCH_3$	$(9 \pm 2) \times 10^3$ [e]
p-$IC_6H_4\dot{C}OHCH_3$	$(4 \pm 1) \times 10^3$ [f]
m-$(ClCH_2)C_6H_4\dot{C}O^-CH_3$	$(1.5 \pm 0.5) \times 10^4$ [d]
p-$ClC_6H_4\dot{C}O_2^{2-}$	$(4 \pm 1) \times 10^7$
p-$FC_6H_4\dot{C}O_2^{2-}$	$(6 \pm 1) \times 10^5$

[a] Measured at pH 12.0–12.2 in the presence of t-BuOH as OH scavenger unless otherwise indicated. [b] The same rate was also obtained in the absence of alcohol. [c] Measured in the presence of i-PrOH. [d] The same value was obtained with the use of either t-BuOH or i-PrOH. [e] pH 7. [f] pH 4.

values observed in the presence of i-PrOH indicate efficient chain processes[6] which propagate by reactions 4, 5, and 7. From the

$$\dot{C}_6H_4COCH_3 + (CH_3)_2CHOH \rightarrow C_6H_5COCH_3 + (CH_3)_2\dot{C}OH \quad (7)$$

results at pH 12 (Table I) it is evident that o-chloro-, o-bromo-, and p-bromoacetophenone undergo reaction 5 efficiently, while p-chloro- and m-bromoacetophenone and p-bromobenzophenone do not.

The rates of the dehalogenation reaction 5 are summarized in Table II. A value of $1.5 \times 10^3\ s^{-1}$ was determined for the anion radical of o-chloroacetophenone in the presence of t-BuOH or in the absence of any OH scavenger. However, when i-PrOH was used the decay became slower and appeared to follow second-order rate law. The same phenomenon was found with the p-Br analogue. These findings are rationalized by the occurrence of chain reactions involving i-PrOH, which lengthen the apparent lifetime of the anion radicals and change the observed decay into second-order termination reactions.

The decay rates of the anion radicals of p-chloro- and m-bromoacetophenone are lower than those of the other four radicals discussed above. The slow rates in the presence of t-BuOH may be affected by mixed radical–radical reactions. Since the p-Cl and m-Br derivatives do not exhibit chain reactions with i-PrOH (Table I), their decay rates may be more accurately determined in the presence of this alcohol. The values of $10^2\ s^{-1}$ given in Table II are only estimates since the decay did not follow pure first-order rate law.

p-Bromobenzophenone showed a similar behavior. An upper limit of the decay rate of $<7\ s^{-1}$ (Table II) was determined in the presence of i-PrOH at pH 12.2. The anion radical of p-bromobenzaldehyde underwent first-order decay with a rate of $4 \times 10^2\ s^{-1}$ in the presence of either t-BuOH or i-PrOH.

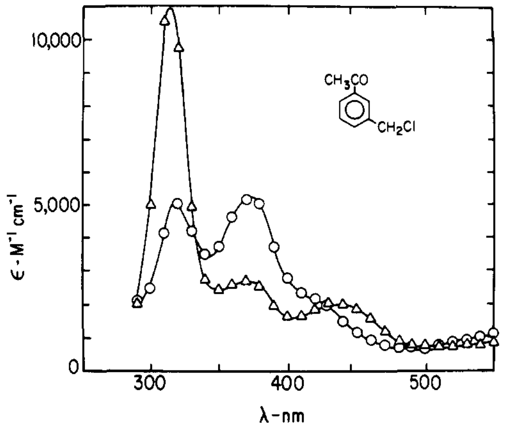

Figure 3. Transient absorption spectra of the anion radical of m-(chloromethyl)acetophenone (△) and of the benzyl radical produced from it (○). Observed in the pulse radiolysis of deoxygenated aqueous solutions containing 5×10^{-4} M substrate, 1.5 M i-PrOH, and 0.5 M acetone at pH 12.2. Recorded 8 (△) and 200 (○) μs after the pulse.

Effect of pH. It has been shown in previous studies[4-6] that protonation of the anion radical slows down the dehalogenation reaction very strongly. The same effect is found to hold for the acetophenone derivatives. The decay of the o-Br and and p-I ketyl radicals is found to be 2 orders of magnitude slower in neutral and acid solutions than at pH 12 (Table II). In the case of p-iodoacetophenone, the rate of protonation and the spectrum of the protonated radicals were also examined. The spectrum is shown in Figure 2 along with that of the anion radical and is found to be shifted to lower wavelengths as observed in similar cases.[10,11] The kinetics of protonation followed at pH 4 at 310–330 nm shows a diffusion-controlled rate $k = 2 \times 10^{10}\ M^{-1}\ s^{-1}$ for reaction of p-$IC_6H_4\dot{C}O^-CH_3$ with H^+. The rate of dehalogenation at pH 4 was $(4 \pm 1) \times 10^3\ s^{-1}$, independent of solute concentration.

***m*-(Chloromethyl)acetophenone.** Dehalogenation from a benzylic position was shown to be much faster than from a ring position.[4-6] The same effect is found to hold for the case of the haloacetophenone as exemplified by m-$(ClCH_2)C_6H_4COCH_3$. The spectrum of the anion radical of this compound is shown in Figure 3. Following the dehalogenation reaction 8 a spectrum

$$ClCH_2C_6H_4\dot{C}O^-CH_3 \rightarrow Cl^- + \dot{C}H_2C_6H_4COCH_3 \quad (8)$$

assignable to the m-acetylbenzyl radical is also observed (Figure 3). The kinetics were determined by following the decay at 300–320 and 460 nm and the concomitant buildup at 340–400 nm. An average value of $(1.5 \pm 0.5) \times 10^4\ s^{-1}$ was determined for reaction 8. This value was obtained in the presence of either t-BuOH or i-PrOH as OH scavengers. This behavior is expected since benzyl radicals do not initiate chain processes with i-PrOH.

***p*-Halobenzoic Acids.** One-electron reduction of benzoate ions produces a radical which absorbs at 322 and 445 nm.[13] Electron adducts of p-halobenzoate should exhibit similar absorptions. Only the p-fluoro derivative yielded a radical with sufficiently long lifetime to allow recording of its full spectrum with our experimental setup. The maxima were found at 310 nm (13 000 $M^{-1}\ cm^{-1}$) and 450 nm (3400 $M^{-1}\ cm^{-1}$) as determined at pH 13 in the presence of 1 M t-BuOH. The decay of the electron adduct followed first-order kinetics with a rate of $6 \times 10^5\ s^{-1}$, independent of dose and solute concentration. The electron adduct of p-chlorobenzoate decayed much more rapidly; $k = 4 \times 10^7\ s^{-1}$ was determined from the observed kinetics at 320 nm.

Rates of Dehalogenation The results summarized in Table II show that the rates of dehalogenation depend on the nature of the halide (Cl < Br < I) and on its position relative to the acetyl group ($m < p < o$). These trends are similar to those found with nitrobenzyl halides[4] and halobenzonitriles.[6] They have been rationalized by the differences in C–X bond dissociation energies and by the spin-density distribution at the various ring positions

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of the anion radicals. Quantitatively, the realtive rates *o*:*p* appear to be much higher in the acetyl compounds than in the cases of the CN and $\mathrm{NO_2}$ analogues, and rather resemble the ratio observed in the rates of intramolecular electron transfer in *o*- and (*p*-nitrobenzoato)pentamminecobalt(III) complexes.[14]

The rate of dehalogenation of $m\text{-}(\mathrm{ClCH_2})\mathrm{C_6H_4\dot{C}O^-CH_3}$ is at least 2 orders of magnitude faster than that of $m\text{-}\mathrm{BrC_6H_4\dot{C}O^-CH_3}$ and the ratio is expected to be much greater when compared with $m\text{-}\mathrm{ClC_6H_4\dot{C}O^-CH_3}$. This trend of increased rates at the benzylic positions relative to ring positions has also been observed previously with the $\mathrm{NO_2}$ and CN derivatives.[4-6] Despite the greater interaction of the halogen on the ring with the unpaired electron and the negative charge, the C–X bond is much weaker for the benzylic than for the ring position and this effect predominates to cause the faster decomposition.

A comparison of the absolute rates of dehalogenation observed here for acetophenones with those reported for the analogous nitro and cyano derivatives[4-6] shows an order of reactivity of $\mathrm{NO_2} < \mathrm{COCH_3} < \mathrm{CN}$. For example, for $(o\text{-}\mathrm{ClC_6H_4Y})^{-}\cdot$ and $(p\text{-}\mathrm{BrC_6H_4Y})^{-}\cdot$, where Y is $\mathrm{NO_2}$, $\mathrm{COCH_3}$, and CN, the rates of dehalogenation are <1, 1.5×10^3, 9×10^6, and <1, 5×10^3, $>3 \times 10^7$, respectively. This order reflects the relative electron affinity of the substituent Y. The nitro group has the greatest electron affinity and thus presents a higher barrier to the intramolecular electron transfer to the halogen. The order found here is not in line with the order of the Hammett σ constants,[15] i.e., $\mathrm{NO_2}$ (0.78), CN (0.63), and $\mathrm{COCH_3}$ (0.52). The σ constants may reflect the electron distribution in the molecule, which is not necessarily the same as in the radicals. On the other hand, the ESR hyperfine constants[16] for the para protons of the non-halogenated anion radicals correlate well with the the trend of dehalogenation rates. The hyperfine constants are 4.03, 6.60, and 8.42 G for the anion radicals of nitrobenzene, acetophenone, and benzonitrile, respectively, under the same conditions.[16] The rate of dehalogenation is found to increase with the hyperfine constant, reflecting the importance of the spin density in determining the rate of the intramolecular electron transfer and bond scission. It is further noticed that *p*-bromobenzophenone behaves similar to the nitro analogue as expected from the hyperfine constant (3.50 G)[16] and again with no correlation to the Hammett σ constant (0.46).[15] The correlation with the hyperfine constant is further supported by the behavior of *p*-bromobenzaldehyde, which exhibits slightly lower values than those of *p*-bromoacetophenone both in the rate of dehalogenation (Table II) and in the ESR parameters (6.5 G).[16] The hyperfine constant for the *p*-H in the electron adduct of benzoate has not been determined under similar conditions as the above anion–radicals. The value in aqueous solutions is 7.58 G,[17] and judging from the effect of solvent on the ESR parameters of nitro anion radicals,[18] the value for benzoate should be higher in aprotic solvents, i.e., it should be similar to that of the cyano derivative. The rates of dehalogenation for the halobenzoates (Table II) are also similar to those of the halobenzonitriles.[6]

The correlation between the rates of dehalogenation and the ESR hyperfine constants cannot be presented in a more quantitative manner because the wide variations in rates do not allow any one particular halogen derivative to be studied with all the substituents discussed. It is clear, nevertheless, that such a correlation holds in all cases studied. Although this correlation indicates the importance of spin density distribution in determining the rate of intramolecular electron transfer, the spin density parameter serves probably only as a representative of the negative charge density. When the charge is neutralized, upon protonation of the anion radical, the spin density changes only slightly but the rate of dehalogenation drops very markedly.

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