shown in previous work to give a major fraction of a "reactive form" of $C_7H_7^+$, which is believed to have the **1** structure, and a minor fraction of an "unreactive form", thought to have the **2** structure;[4-7] however, $C_7H_7^+$ ions produced in this manner are likely to contain substantial excess internal energy, and the reactive population may consist of more than one structural form. The broad PDS band peaking at 290 ± 10 nm, which arises from photodissociation of >50% of the $C_7H_7^+$ ions in the population, is not compatible with the pulse-radiolysis observation of **1** at 363 nm in solution or the present 353-nm argon matrix absorption. Furthermore, the PDS is not compatible with **2** since the gaseous spectrum of **2** is expected to the blue of the acid solution (and solid argon) observations. The ICR experiment has the advantage of precise knowledge of the ion mass and the disadvantage of possible excess internal energy, which can facilitate structural rearrangement of many ions in the population. The cryogenic matrix technique certainly quenches internal energy and the pulse-radiolysis method gives a spectrum on a $10^{-6}$-s time scale, although neither can absolutely prevent the observation of benzyl cation reaction products. However, the pulse-radiolysis observation of the same 363-nm transient absorption with the different dibenzylmercury and benzyl bromide precursors in solution strongly favors identification of the 363-nm band as a common fragment and not a reaction product with the precursor. Further kinetic studies[31,32] of **1** in solution are consistent with this identification. As discussed above, the 353-nm argon matrix and 363-nm pulse-radiolysis identifications of **1** are mutually supportive. It is therefore suggested that the $C_7H_7^+$ population giving rise to the broad 350- to 260-nm PDS band is complicated by more than one structural form different from **1**.

The photoelectron spectrum of benzyl radical[22] contains no band in the region 3.5 eV above ionization which would correspond to a 353-nm absorption for the ion. This suggests that the 3.5-eV transition for **1** involves an electron promotion type of transition such as $\pi \rightarrow \pi^*$ or, less likely, that the structure of **1** is substantially different from benzyl radical.

Several exploratory experiments have been performed codepositing benzyl bromide vapor with argon from a separate source onto the sapphire window and an electrode positioned in the center of the window.[33] Applying +300 V dc to the electrode to sustain a discharge on the surface of the sample during codeposition gave no products; however, a 30-min codeposition with a Tesla coil discharge on the electrode produced a substantial 263-nm absorption ($A = 0.2$) without significant absorption in the 350-nm region. Apparently, the tropylium structure is the most stable isomer under electrical discharge conditions.

## Conclusions

Codeposition of benzyl bromide vapor with argon emerging from a microwave discharge onto a sapphire plate at 22 K produced new absorptions at 263 and 353 nm. Agreement with the 274-nm absorption of tropylium salts in concentrated acid and the 363-nm absorption of benzyl cation in 1,2-dichloroethane solution identifies the argon matrix absorptions. Photolysis in the **1** absorption, which is below the dissociation threshold, isomerizes **1** to **2**, possibly involving another $C_7H_7^+$ structure absorbing at 325 nm. Further photolysis in the **2** absorption, which is above the dissociation threshold, destroys the **2** band and reproduces a small **1** absorption. The matrix quenches internal energy and makes some $2 \rightarrow 1$ rearrangement possible. The photochemical interconversion of **1** and **2** supports their identification in these experiments and is consistent with $1 \rightleftharpoons 2$ equilibrium at low internal energies in gas-phase studies.

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# Intramolecular Electron Transfer and Dehalogenation of Anion Radicals. 3. Halobenzonitriles and Cyanobenzyl Halides[1-3]

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**Abstract:** One-electron reduction of halobenzonitriles and cyanobenzyl halides produces the anion radicals which then undergo intramolecular electron transfer leading to dehalogenation. Kinetic spectrophotometric pulse radiolysis allowed the observation of the halobenzonitrile anion radicals and the determination of their dehalogenation rates. The rates varied from $10^4$ to >$10^7$ s$^{-1}$ depending on the halogen and its position relative to the cyano group. The production of $X^-$ was measured in steady-state radiolysis experiments, and the participation of cyanophenyl radicals as intermediates was also deduced from observation of chain reactions. The anion radicals of cyanobenzyl halides were not observed since they dehalogenate very rapidly. The cyanobenzyl radicals produced by this process were monitored spectrophotometrically. The rates of dehalogenation of the anion radicals studied here are at least 5 orders of magnitude higher than the corresponding values determined previously for analogous nitro derivatives, but the pattern of reactivities is similar in both series of radicals.

## Introduction

Anion radicals of nitroaromatic compounds, containing a halogen atom at various positions on the ring or on a side chain, were found in certain cases to undergo an intramolecular electron transfer and to release halide ions.[2,3] Rates of dehalogenation in the range of $1-10^6$ s$^{-1}$ were determined for the anion radicals of various nitrobenzyl and nitrophenacyl halides. The rates were strongly dependent on the nature of the halide and its position relative to the nitro group.[2,3] On the other hand, when the halogen was further removed from the ring or attached directly to the ring, no significant C–X bond scission was observed. These findings were explained by differences in C–X bond strength and by the charge distribution on the ring. The rate of dehalogenation should

104   *J. Am. Chem. Soc., Vol. 103, No. 1, 1981*

*Neta and Behar*

also depend strongly on the distribution of the charge or the unpaired electron between the ring and the substituents. As a result, the replacement of the nitro group by a substituent of lower electron affinity is expected to facilitate the release of halide ions. In the extreme case where no other substituent is present except for the halogen or halomethyl group, no evidence for the existence of the anion radical has been obtained, and dehalogenation was proposed to take place immediately upon addition of an electron.[5] In the present study the effect of the cyano group on the stability of the anion radical and the rate of dehalogenation has been examined. As expected, since the group has a lower electron affinity than that of the nitro it allows a more rapid C–X bond scission in the anion radical.

## Experimental Section

The cyano compounds were obtained from Aldrich, except for the *p*-cyanobenzyl chloride which was from Pfaltz and Bauer. They were of the purest grade commercially available and were used without further purification. 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 or nitrous oxide.

Steady-state irradiations were carried out in a Gammacell 220 $^{60}$Co source with a dose rate of $3.1 \times 10^{17}$ eV g$^{-1}$ min$^{-1}$. The inorganic halide ions released by the irradiation were determined by ion-selective electrodes.

Pulse irradiation was carried out with an ARCO LP-7 linear accelerator supplying 5–50-ns pulses of 7-MeV electrons. The energy deposited in the solution produced 2–5 $\mu$M of radicals per pulse. Kinetic spectrophotometric experiments with signal averaging utilized the computer-controlled pulse radiolysis apparatus described previously.[6]

## Results and Discussion

Radiolysis of aqueous solutions leads to the formation of $e_{aq}^-$, which react with aromatic nitriles with diffusion-controlled rates, $k = (1–2) \times 10^{10}$ M$^{-1}$ s$^{-1}$,[7] and produce intensely absorbing anion radicals.[8–11] The H and OH radicals, also produced in the radiolysis, add predominantly to the aromatic ring to yield cyclohexadienyl radicals. To avoid interference by the latter reactions, we used *t*-BuOH to scavenge the OH radicals, and the small contribution by H atoms can be usually neglected. The $(CH_3)_2C(OH)\dot{C}H_2$ radical from *t*-BuOH is relatively unreactive[12] and is not expected to react with nitriles. 2-Propanol scavenges both OH and H efficiently, but the $(CH_3)_2\dot{C}OH$ radical thus produced reduces the cyano compounds considerably more slowly than does $e_{aq}^-$ (see below). This reduction interfered with the kinetic measurements of the formation and decay of the anion radicals, and, therefore, *i*-PrOH was not used in the pulse experiments.

**Cyanobenzyl Halides.** The reaction of $e_{aq}^-$ with cyanobenzyl halides produces initially the anion radical which should exhibit an intense absorption at ~310–320 nm, judging from the results with benzonitrile[8,9] and halobenzonitriles (see Figure 2 and ref 10). However, the spectrum observed immediately after the pulse with a solution of *p*-cyanobenzyl bromide has only weak absorptions in this range. This spectrum (Figure 1) has an intense maximum at 280 nm ($\epsilon = 34000$ M$^{-1}$ cm$^{-1}$) and two weak absorptions peaking at 310 and 322 nm. It resembles the spectrum of benzyl radical which exhibits the main peak at 258 nm ($\epsilon =$
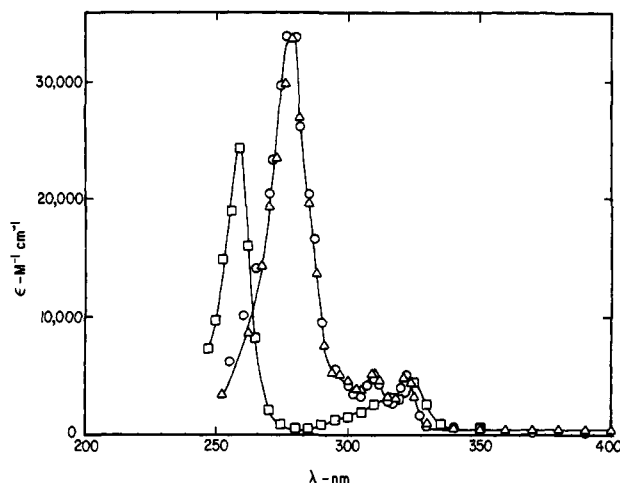


**Figure 1.** Absorption spectra of *p*- and *m*-cyanobenzyl radicals, monitored by pulse radiolysis of aqueous solutions of *p*-BrCH$_2$C$_6$H$_4$CN (△), *p*-ClCH$_2$C$_6$H$_4$CN (○), and *m*-BrCH$_2$C$_6$H$_4$CN (□). All solutions contained $1 \times 10^{-3}$ M of the nitrile and 1 M *t*-BuOH at pH 12. The spectra were not corrected for the bleaching of the parent compounds. This causes the slight difference below 275 nm between the spectrum shown by △ and ○.

25000 M$^{-1}$ cm$^{-1}$) and two weaker maxima at 307 and 318 nm.[13] It can be, therefore, assigned to *p*-cyanobenzyl, produced by dehalogenation.

$$BrCH_2C_6H_4CN + e_{aq}^- \rightarrow (BrCH_2C_6H_4CN)^-\cdot \quad (1)$$

$$(BrCH_2C_6H_4CN)^-\cdot \rightarrow Br^- + \dot{C}H_2C_6H_4CN \quad (2)$$
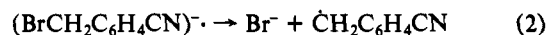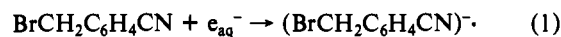
In an attempt to resolve reaction 2 from (1) the concentration of *p*-cyanobenzyl bromide was increased to the limit of solubility (~3 mM) in 2 M *t*-BuOH solution at pH 12. At this concentration the decay of $e_{aq}^-$ as observed at 550 nm followed a pseudo-first-order rate of $6 \times 10^7$ s$^{-1}$, leading to $k_1 = 2 \times 10^{10}$ M$^{-1}$ s$^{-1}$. The formation of the benzyl radical absorption at 310 nm followed an identical rate within experimental error. It is, therefore, concluded that reaction 2 must proceed with $k_2 > 6 \times 10^7$ s$^{-1}$.

Similar experiments were performed with *p*-cyanobenzyl chloride. The spectrum observed in this case (Figure 1) is identical with that obtained from *p*-cyanobenzyl bromide and lends further support to its assignment to the *p*-cyanobenzyl radical. The kinetics of formation of this radical was again identical with that of the $e_{aq}^-$ decay so that only a lower limit of $>3 \times 10^7$ s$^{-1}$ can be estimated for the dechlorination reaction parallel to (2).

The spectrum obtained upon reaction of $e_{aq}^-$ with *m*-cyanobenzyl bromide (Figure 1) is different from that with the para derivatives. It has $\lambda_{max} = 259$ nm and $\epsilon_{max} = 25000$ M$^{-1}$ cm$^{-1}$ and thus resembles the spectrum of benzyl radical more closely.[13] It can be similarly assigned to *m*-cyanobenzyl radical. The CN group at the meta position exerts little effect on the spectrum as compared with its effects at the para position. This difference is a result of the weaker interaction between the unpaired electron and the CN group in the meta as compared with the para radical. The rate of reaction 2 for *m*-cyanobenzyl bromide is expected to be much slower than that for the para derivative, on the basis of the previous findings with the nitro compounds.[2] However, the difference between the rate of $e_{aq}^-$ decay and the rate of buildup of *m*-$\dot{C}H_2C_6H_4CN$ was not large. At $1.5 \times 10^{-3}$ M substrate the $e_{aq}^-$ decayed with a pseudo-first-order rate of $2.1 \times 10^7$ s$^{-1}$, leading to $k_1 = 1.4 \times 10^{10}$ M$^{-1}$ s$^{-1}$. The rate of buildup of the benzyl radical was slightly slower, $k_2 = (1.3 \pm 0.5) \times 10^7$ s$^{-1}$. It should be noted that the rate determined for dehalogenation of *m*-BrCH$_2$C$_6$H$_4$NO$_2^-\cdot$ was only 60 s$^{-1}$,[2] indicating the large difference in the electron affinities of the NO$_2$ vs. CN groups.

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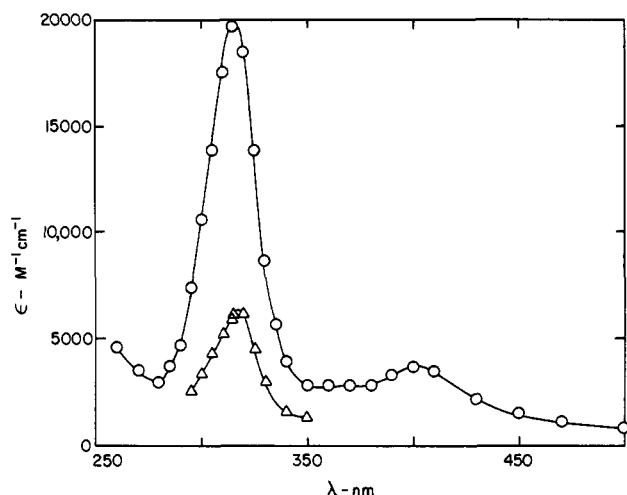(13) Mittal, J. P.; Hayon, E. *Nature (London)* **1972,** *240,* 20 and references therein.

*Electron Transfer of Anion Radicals*

*J. Am. Chem. Soc., Vol. 103, No. 1, 1981* 105



**Figure 2.** Absorption spectrum of $(m\text{-ClC}_6\text{H}_4\text{CN})^-$, monitored with aqueous solution of $1 \times 10^{-3}$ M $m\text{-ClC}_6\text{H}_4\text{CN}$ containing 1 M $t$-BuOH at pH 12 (O). The spectrum of $(m\text{-BrC}_6\text{H}_4\text{CN})^-$ is similar ($\triangle$) but is obtained here only in partial yield so that the extinction coefficient scale does not apply.

**Table I.** Rates of Dehalogenation of Anion Radicals

| parent compd | $k$, s$^{-1}$ |
|---|---|
| $p$-CNC$_6$H$_4$CH$_2$Br | $>6 \times 10^7$ |
| $m$-CNC$_6$H$_4$CH$_2$Br | $(1.3 \pm 0.5) \times 10^7$ |
| $p$-CNC$_6$H$_4$CH$_2$Cl | $>3 \times 10^7$ |
| $p$-CNC$_6$H$_4$Br | $>3 \times 10^7$ |
| $m$-CNC$_6$H$_4$Br | $(8 \pm 2) \times 10^6$ |
| $o$-CNC$_6$H$_4$Cl | $(9 \pm 2) \times 10^6$ |
| $p$-CNC$_6$H$_4$Cl | $(5 \pm 1) \times 10^6$ |
| $m$-CNC$_6$H$_4$Cl | $(4.2 \pm 0.6) \times 10^4$ |
| $p$-CNC$_6$H$_4$F | $(6.5 \pm 2) \times 10^5$ $^a$ |

$^a$ From ref 10.

**Halobenzonitriles.** The absorption spectra of the anion radicals of $m$-chloro- and $m$-bromobenzonitrile are presented in Figure 2. A similar spectrum with $\lambda_{max} = 315$ nm was also observed with the $p$-Cl derivative. These spectra are very similar to that of the benzonitrile anion radical.[8,9] The extinction coefficient determined for the $m$-Cl anion radical (20 000 M$^{-1}$ cm$^{-1}$ at 315 nm) is also similar to that observed with benzonitrile. However, the absorption monitored with the $m$-Br and $p$-Cl derivatives is significantly lower. These anion radicals decayed much more rapidly than the former one, resulting in an overlap of their formation with their decay and, therefore, the full yield was not experimentally observed. The spectrum of the anion radical of $p$-bromobenzonitrile was not observed at all since the decay in this case was very rapid.

$$(\text{XC}_6\text{H}_4\text{CN})^- \cdot \rightarrow \text{X}^- + \dot{\text{C}}_6\text{H}_4\text{CN} \tag{3}$$
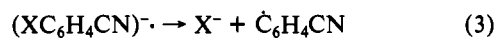
The decay of the anion radical absorptions followed a first-order process in all cases and the rate constants are summarized in Table I. These values are assigned to the intramolecular reaction 3. Intermolecular electron transfer from $(\text{XC}_6\text{H}_4\text{CN})^-$ to the halogen of another $\text{XC}_6\text{H}_4\text{CN}$ to yield $\text{X}^-$ cannot account for the observed rates, since at the concentrations used the second-order rate constants would be unreasonably high. Only in the case of $m$-ClC$_6$H$_4$CN, where reaction 3 is slower, was it possible to verify that the rate is independent of the concentration.

The production of cyanophenyl radical by reaction 3 could not be followed. Phenyl radicals exhibit only weak absorptions below 300 nm,[14] and the formation of cyanophenyl radical in this region could not be experimentally verified because it was masked by other absorptions. It is, therefore, desirable to prove the occurrence of reaction 3 by other means. This was done by determining the

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**Table II.** Yields of Halide Ions in Irradiated Solutions of Halobenzonitriles

| compd | concn, M | additives | pH | $G(\text{X}^-)$, ions/100 eV |
|---|---|---|---|---|
| $p$-CNC$_6$H$_4$Br | $5 \times 10^{-4}$ | | 12.0 | $10 \pm 0.5$ |
| | $5 \times 10^{-4}$ | N$_2$O satd | 12.0 | $5.8 \pm 0.4$ |
| | $1 \times 10^{-3}$ | 0.7 M $i$-PrOH | 12.2 | 300 |
| | $1 \times 10^{-3}$ | 0.7 M $i$-PrOH | 8.5 | 25 |
| | $1 \times 10^{-3}$ | 0.7 M $i$-PrOH | 2.0 | $0.7 \pm 0.1$ |
| $m$-CNC$_6$H$_4$Br | $1 \times 10^{-3}$ | 0.5 M $t$-BuOH | 12.4 | $8.2 \pm 0.5$ |
| | $1 \times 10^{-3}$ | | 12.2 | $15.6 \pm 1.0$ |
| | $1 \times 10^{-3}$ | N$_2$O satd | 12.2 | $7.8 \pm 0.5$ |
| | $1 \times 10^{-3}$ | 0.7 M $i$-PrOH | 12.3 | 1100 |
| | $1 \times 10^{-3}$ | 0.7 M $i$-PrOH | 9.1 | 80 |
| | $1 \times 10^{-3}$ | 0.7 M $i$-PrOH | 4.0 | $3.0 \pm 0.4$ |
| | $1 \times 10^{-3}$ | 0.7 M $i$-PrOH | 0 | $0.3 \pm 0.2$ |
| $m$-CNC$_6$H$_4$Cl | $2 \times 10^{-3}$ | 0.5 M $t$-BuOH | 12.2 | $7.2 \pm 1.2$ |
| | $2 \times 10^{-3}$ | 0.5 M $t$-BuOH | 4.5 | $0.6 \pm 0.2$ |

yield of halide ions in steady-state radiolysis experiments. These experiments have also provided an evidence for the presence of phenyl radicals as is shown below.

$\gamma$ radiolysis of deoxygenated aqueous solutions of $m$-chloro-, $m$-bromo- and $p$-bromobenzonitrile at pH 12 produced the corresponding halide ion. With use of $t$-BuOH as an OH scavenger $G(\text{X}^-) \approx 7-8$ ions/100 eV was found. This yield is higher than the yield of $e_{aq}^-$ in these solutions ($G \approx 2.8$ ions/100 eV). It indicates that reaction 3 takes place efficiently, but it also shows that an additional process contributes to the production of $\text{X}^-$. The radical from $t$-BuOH is not likely to cause this result since it is not expected to reduce the nitriles.[12] In fact, experiments in the absence of $t$-BuOH gave even higher yields (Table II). The observed $G$ values of 10–15 ions/100 eV indicate that a chain reaction is occurring, since the total radical production in water cannot exceed $G \approx 7$ ions/100 eV. This chain process can be explained by the assumption that the cyanophenyl radical produced by reaction 3 causes further reduction of the parent compound. But direct reduction of this kind is very unlikely. It is conceivable, however, that the phenyl radical adds to the parent compound as demonstrated in other cases,[15] and the adduct reduces another molecule. Addition takes place at various ring positions, e.g., eq 4. Radicals of the cyclohexadienyl type are known to be oxidized



$$\tag{4}$$

$$\tag{5}$$
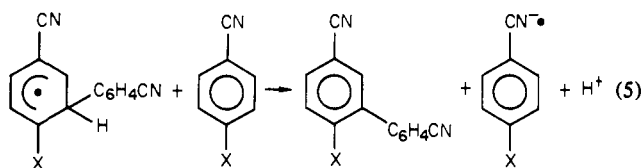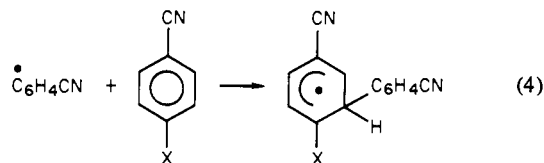
by various organic compounds[16] so that a slow reaction 5 is not surprising. The chain length is only of the order of 2–3, and termination is caused by radical–radical reactions. Further support for reaction 5 is obtained from the experiments with N$_2$O, where only OH radicals react with the cyano compound. The OH radicals are known to add to the aromatic ring. They may produce a low yield of $\text{X}^-$ by partial addition at the carbon bearing the halogen but will mostly add to the other ring positions. The finding of $G(\text{X}^-) \approx 6-8$ ions/100 eV indicates that the OH adduct radicals reduce the parent compound in a reaction similar to 5 to produce
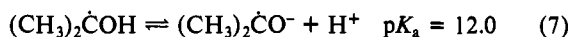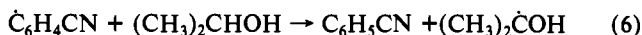
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the anion radical which then undergoes reaction 3.

A much longer chain is observed in the presence of $i$-PrOH where $G(X^-)$ as high as 1100 ions/100 eV is observed in alkaline solutions (Table II).[17] In this case a more efficient propagation takes place by the reaction of cyanophenyl radicals with $i$-PrOH (see eq 6) followed by the acid-base equilibrium (eq 7) and the

$$\dot{C}_6H_4CN + (CH_3)_2CHOH \rightarrow C_6H_5CN + (CH_3)_2\dot{C}OH \quad (6)$$

$$(CH_3)_2\dot{C}OH \rightleftharpoons (CH_3)_2\dot{C}O^- + H^+ \quad pK_a = 12.0 \quad (7)$$

reduction step (eq 8) and subsequently by reaction 3. Reaction

$$(CH_3)_2\dot{C}O^- + XC_6H_4CN \rightarrow (CH_3)_2CO + (XC_6H_4CN)^- \quad (8)$$
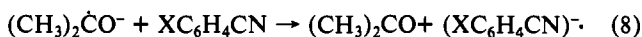
6 should take place with a rate constant of the order of $10^6$ $M^{-1}$ $s^{-1}$, judging from the value reported for $p$-$\dot{P}hCO_2^- + (CH_3)_2CH$- OH ($5.8 \times 10^6$ $M^{-1}$ $s^{-1}$).[18] The rate of reaction 8 was measured by pulse radiolysis experiments only with $m$-$CNC_6H_4Cl$ since the resulting anion radical in this case was sufficiently long-lived to allow this measurement to be made. A value of $k_8 = (2 \pm 0.5) \times 10^8$ $M^{-1}$ $s^{-1}$ is found for this compound and is expected to be similar for the other halobenzonitriles. The rate of reduction by $(CH_3)_2\dot{C}OH$ is much slower. The pulse experiments at pH 11, where only $\sim 10\%$ of the $i$-PrOH radicals are in the basic form, showed a rate constant of reduction of $\sim 1 \times 10^7$ $M^{-1}$ $s^{-1}$, resulting mostly from the contribution of reaction 8 rather than direct reduction by $(CH_3)_2\dot{C}OH$. The latter reduction is shown to be slow also from the yields of halide ions at pH 8–9 (Table II), where the chain length is significantly shortened.

At high acidities the yield of $X^-$ decreases to negligible values. Under these conditions the anion radicals protonate and the resulting radicals do not appear to dehalogenate. The $pK_a$ for protonation of the benzonitrile anion radical is 7.3,[8,9] and the corresponding values for the halo derivatives may be slightly lower. At pH 4.5 $(m$-$CNC_6H_4Cl)^-$ protonates and does not yield much $Cl^-$. However, $(m$-$CNC_6H_4Br)^-$ dehalogenates much more rapidly so that this process competes with the protonation reaction and yields $G(Br^-) = 3.0$ ions/100 eV at pH 4.0. In this case, a lower pH is necessary in order to suppress the dehalogenation.

Pulse radiolysis experiments have confirmed these arguments. The rate of protonation of $(m$-$CNC_6H_4Cl)^-$ was monitored by the decay at 315 nm (see eq 9). The rate increased linearly with

$$(m\text{-}ClC_6H_4CN)^- + H^+ \rightarrow (m\text{-}ClC_6H_4CNH)\cdot \quad (9)$$
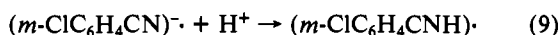
$[H^+]$ (Figure 3) according to $k_9 = 1.2 \times 10^{10}$ $M^{-1}$ $s^{-1}$. The intercept in Figure 3 indicates protonation by reaction with $H_2O$ with $k = 3 \times 10^5$ $s^{-1}$. These results are in agreement with previous determinations of the protonation rate of benzonitrile anion radical.[19] Parallel experiments with $o$-chloro-, $p$-chloro-, and
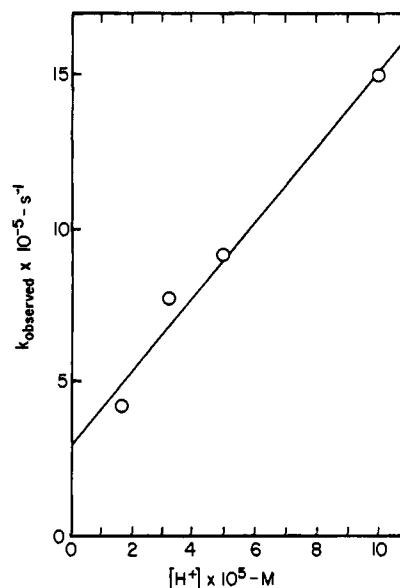
(17) Chain reactions of dehalogenation in the presence of $i$-PrOH were also found with halouracils (Bansal, K. M.; Patterson, L. K.; Schuler, R. H. *J. Phys. Chem.* **1972**, *76*, 2386 and references therein), and with haloaliphatic compounds (Anbar, M.; Neta, P. *J. Chem. Soc. A* **1967**, 837).

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**Figure 3.** Dependence of the protonation rate of $(m\text{-}ClC_6H_4CN)^-$ on $[H^+]$, monitored by the decay at 315 nm with solutions containing $6 \times 10^{-4}$ M $m$-$ClC_6H_4CN$ and 1 M $t$-BuOH.

$m$-bromobenzonitrile did not show any change in the decay rate between pH 12 and pH 4, since the very rapid dehalogenation reaction predominates in all these experiments. The protonation becomes important only at pH $\leq 3$, but this was not possible to follow experimentally, since at low pH $e_{aq}^-$ reacts with $H^+$ rather than with the nitrile.

**Rates of Dehalogenation.** The rates of dehalogenation of the anion radicals of cyanobenzyl halides and halobenzonitriles are summarized in Table I. In general, the nature of the halogen and its position relative to the cyano group exert strong effects on the rate of dehalogenation in a pattern similar to that found with nitro compounds.[2,3] The rates decrease in the order Br > Cl > F and ortho > para $\gg$ meta. The ratios of these rates for the different halogens and for the different isomers are of the same order of magnitude as those found with the nitrobenzyl halides. However, the absolute rates found for the nitriles are at least 5 orders of magnitude higher than those of the nitro derivatives. This large difference reflects the greater electron affinity of the nitro group, which diminishes the electron density near the halogen. This relatively low electron density presents a barrier to the release of $X^-$, and only the weaker C–X bonds undergo scission in this case. On the other hand, the cyano group allows a higher electron density near the halogen and thus presents a lower barrier for the dehalogenation even at the strong aromatic C–X bonds.

Judging from the rate measured for $m$-$CNC_6H_4CH_2Br$ and the ratios found for the nitrobenzyl halides,[2] the rates of dehalogenation of $(p$-$CNC_6H_4CH_2Cl)^-$ and $(p$-$CNC_6H_4CH_2Br)^-$ are estimated to be of the order of $10^9$ and $10^{10}$ $s^{-1}$, respectively. Even with these high decay rates the anion radicals have finite lifetimes and their parent compounds do not undergo a dissociative electron capture directly.