Table IV. Chromic Acid Cooxidation of Isopropyl Alcohol and Glycolic Acid at 25° ([$HClO_4$] = 0.628 *M*)

[Isopropyl alcohol], *M*	[Isopropyl alcohol-*d*], *M*	[Glycolic acid], *M*	[Glycolic acid-d_2], *M*	$10^2 k_{\text{exptl}}$, sec^{-1}	k_H/k_D
1.56		0.36		3.30[a]	
	1.56	0.36		0.55	6.0
1.56			0.36	0.57	5.8
	1.56		0.36	0.092 0.099	34.4

[a] Average of three measurements: 3.26, 3.30, and 3.33.

substrates. These results are consistent only with a mechanism in which breaking of the bonds in both substrates is fully synchronous and the extent of bond breaking in the transition state has reached about the same level. The results also provide the most convincing support for the correctness of the three-electron oxidation mechanism.

Experimental Section

Materials. Glycolic acid (Eastman Kodak) was crystallized from petroleum ether (mp 74-76°). Isopropyl alcohol (Baker Instra-Analyzed) and sodium dichromate (J.T. Baker, Reagent) were used without further purification. Acrylonitrile (Practical) was distilled and the fraction boiling between 77 and 79° was collected. Perchloric acid solutions were prepared from 60% perchloric acid (B & A reagent).

Isopropyl alcohol-*d* and glycolic acid-d_2 were prepared by the method described earlier.[1,3]

Kinetic Measurements. Reaction rates were determined spectrophotometrically at 350 nm using Cary 14, Cary 15, and Zeiss PMQII spectrophotometers equipped with thermostated cell holders. Pseudo-first-order rate constants were calculated from the slopes of the linear parts of the log (absorbance) vs. time plots (Figure 1). Rate constants obtained from multiple determinations were within ±5% of each other.

Product Analysis. In a typical experiment isopropyl alcohol (20.0 ml, 7.8 *M*), glycolic acid (10.0 ml, 3.6 *M*), perchloric acid (5.0 ml, 9.69 *M*), and sodium dichromate (0.2 ml, 1.745 *M*) were allowed to react in a 100 ml volumetric flask, the total volume made up to the mark with distilled water. The reaction products were isolated and identified by previously described methods.[1,3]

Acknowledgment. One of us (J. R.) wishes to express his gratitude to the Department of Chemistry of the University of Geneva for the hospitality and assistance offered during the preparation of the manuscript.

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Effect of Cationic Micelles on the Acidity of Carbon Acids and Phenols. Electronic and ^1H Nuclear Magnetic Resonance Spectral Studies of Nitro Carbanions in Micelles[1]

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Abstract: The acid dissociation constants (K_a values) for five α-substituted 4-nitrophenylacetonitriles [$4\text{-}NO_2C_6H_4CH(R)CN$ where R = H, C_6H_5, *p*-ClC_6H_4, *p*-$NO_2C_6H_4$, and CN] and for 1-nitroindene, 4-nitrophenol, and 2,6-di-*tert*-butyl-4-nitrophenol were determined in aqueous buffer solutions both with and without micelle forming concentrations of the cationic surfactant, cetyltrimethylammonium bromide (CTABr). For all compounds, the presence of 10^{-2} *M* CTABr causes an increase in K_a values, but the effect is most pronounced for the nitro carbanion forming ionizations of the 4-nitrophenylacetonitriles; e.g., the K_a of bis(4-nitrophenyl)acetonitrile is increased 10^4-fold. The nature of the interaction between nitro carbanions and CTABr molecules was investigated by visible and ^1H NMR spectroscopy. CTABr micelles cause an unprecedented red shift in the visible spectra of several nitro carbanions; identical red shifts are observed when water is replaced by a wide variety of organic solvents, suggesting that the interaction between water and a nitro carbanion increases the energy of its $\pi \rightarrow \pi^*$ transition, possibly because of hydrogen bonding between water and the nitro group. The association between aromatic carbanions and CTABr molecules causes upfield shifts in the ^1H NMR signals for the aromatic protons of the carbanion and for the $N^+(CH_3)_3$ protons of the surfactant, indicating that the carbanion interacts tightly with the cationic head groups of neighboring surfactant molecules. Line broadening studies show that the ionization of aromatic acid molecules solubilized in a cationic micelle increases the rigidity of the micelle-solubilisate aggregate.

Cationic micelles[3] enhance the acid dissociations of phenolic pH indicators,[4] phenols,[5] carboxylic acids,[6] and the N-conjugate acids of methyl orange[7] and *p*-chlorobenzylidene-1,1-dimethylamine.[8] The effect of cationic micelles on carbanion formation by carbon acids has not been reported but is interesting, because the reaction involves proton loss from carbon rather than a hydrophilic oxygen or nitrogen atom, and the negative charge in carbanions is more delo-

Table I. The Effect of CTABr Micelles on the Acid Dissociation of Carbon Acids and Phenols

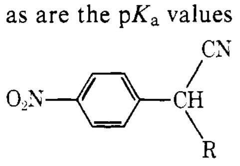
Compd	$pK_{a,w}$[a]	$pK_{a,CTABr}$[b]	ΔpK_a
1	13.2 (13.4)[c]	11.3	1.9
2	10.9	8.3	2.6
3	10.7	8.0	2.7
4	10.35	5.75	4.6
5	2.35 (1.89)[d]	−0.18[e]	2.5
6	2.0	1.5	0.5
7	7.15 (7.15)[f]	6.35	0.8
8	6.92 (6.65,[f] 7.20[g])	5.13	1.79

[a] Taken from pH at half-ionization at 25° in aqueous buffer solutions. Literature values given in parenthesis. [b] In buffered aqueous CTABr solution. [c] R. S. Stearns and G. W. Wheland, *J. Am. Chem. Soc.* 69, 2025 (1947), and ref 16. [d] H. D. Hartzler, *ibid.*, 86, 2174 (1964). [e] Estimated from H_0 value for the HCl concentration required for half-neutralization. [f] L. A. Cohen and W. M. Jones, *ibid.*, 85, 3397 (1963). [g] I. M. Kolthoff, M. K. Chantooni, and S. Bhowmik, *ibid.*, 88, 5430 (1966).

calized than in carboxylate ions. We report here that the pK_a values for carbon acids **1–6** are markedly decreased by

$$H_2O + R_3C{-}H \longrightarrow H_3O^+ + R_3C{:}^- \qquad (1)$$

cationic micelles of hexadecyltrimethylammonium bromide (CTABr) as are the pK_a values of the nitrophenols **7** and **8**.



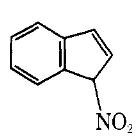
1, R = H

2, R = C_6H_5

3, R = p-ClC_6H_4

4, R = p-$O_2NC_6H_4$

5, R = C≡N



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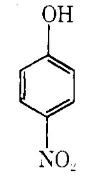

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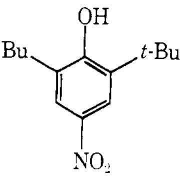

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In order to understand this effect, we investigated the influence of cationic micelles and organic solvents on the visible and ^1H NMR spectra of several of the carbanions, and these results are reported as well.

Results

The Effect of CTABr on pK_a Values. Practical reasons limited our choice of carbon acids to water soluble compounds that form stable colored anions somewhere in the pH range 1–13. We found that 1-nitroindene (**6**) and several α-substituted p-nitrophenylacetonitriles ionize to produce colored solutions which are stable when dilute ($\leq 10^{-4}$ M) if excessive light or alkali are avoided. The anions of **1** and **4** fade within minutes when exposed to ordinary room illumination, but reliable pK_a values can be obtained by working with fresh solutions in the dark.

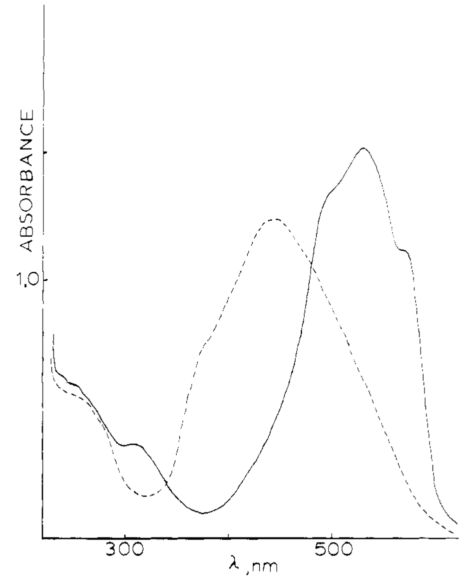


Figure 1. The absorption spectra of ca. 10^{-4} M 4-nitrophenylacetonitrile in aqueous 1.0 M NaOH (dashed curve) and in 0.02 M NaOH with 0.01 M CTABr (solid curve).

Table II. The Effect of CTABr and Me_2SO on the Visible Spectra of Carbanions and Phenoxide Ions

Compd	λ_{max},[a] nm (H_2O)	λ_{max},[b] nm (CTABr)	λ_{max},[c] nm Me_2SO
1	445	535	535
2	484	581	589
3	495	593	593
4	630	642	660
5	468	468	468
6	358	384	417
7	401	400	430
8	450	452	455

[a] In dilute aqueous solution, sufficiently alkaline to ensure complete conversion to anion. [b] In $\geq 10^{-2}$ M CTABr. [c] In $\geq 99\%$ Me_2SO containing 0.01 M tetramethylammonium hydroxide.

The pK_a values measured in aqueous buffer solutions, with and without CTABr, are given in Table I. The addition of micellar concentrations of CTABr decreases the pK_a values of all eight compounds. The α-substituted p-nitrophenylacetonitriles (**1–5**) are much stronger acids (by 10^2–10^4-fold) when taken into CTABr micelles, while 1-nitroindene is affected only to the same extent as a carboxylic acid (by about threefold[6]), probably because the negative charge is less delocalized into the aromatic ring in this nitro anion. Similarly, the more hydrophobic phenol **8** is affected more than **7**.

The Effect of CTABr on Visible Spectra. Micelles of CTABr have a large effect on the visible spectrum of some nitro carbanions. Colorless solutions of 10^{-4} M p-nitrophenylacetonitrile **1** in 0.02 M NaOH are made deep purple by the addition of 10^{-3} M CTABr. Without CTABr, the NaOH concentration must be raised to nearly one molar before much colored species is produced and, in this case, the color is orange (λ_{max} 445 nm) rather than purple (λ_{max} 535 nm, shoulder at 575 nm); see Figure 1. Similar behavior is observed with several of the anions, and in Table II are the λ_{max} values for the anions of compounds **1–8** in water, aqueous CTABr, and in Me_2SO. The spectra of the first three anions are red shifted by more than 90 nm in going from water to 10^{-2} M CTABr.

Both the orange and purple forms of **1** must be anions, because both can be repeatedly neutralized and regenerated by adding acid followed by excess base. The orange species can be converted to the purple by adding CTABr; the color change occurs immediately upon mixing. No purple color appears until the CTABr concentration surpasses its CMC (*ca.* 8×10^{-4} M at 25°)[3] but, at higher CTABr concentrations, the absorbance at 535 nm increases up to a maximum value in the manner characteristic of micelle influenced reactions. This increase in absorbance with increased CTABr concentration for 8×10^{-5} M **1** in 0.8×10^{-2} and 1.6×10^{-2} M NaOH is shown in Figure 2. Both curves

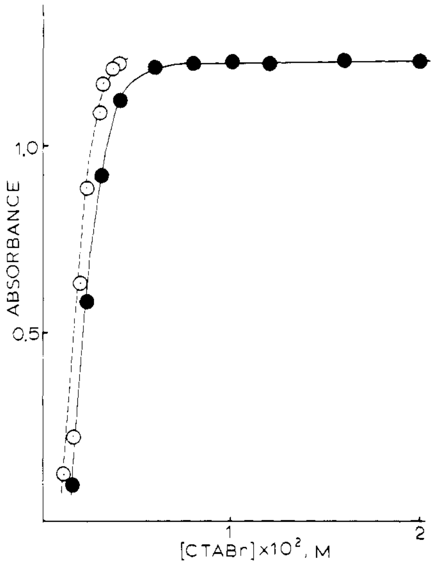


Figure 2. The effect of CTABr on the absorbance at 535 nm of 8×10^{-5} *M* 4-nitrophenylacetonitrile in 8×10^{-3} and 16×10^{-3} *M* NaOH (closed and open circles, respectively).

bend up at the CMC, rising steeply at first, then more slowly, and finally reaching a maximum level where further CTABr does not increase absorbance. At this surfactant concentration, all **1** is incorporated into micelles and ionized. Hexadecyltrimethylammonium hydroxide micelles give similar results except that the solutions quickly turn blue-green. The blue-green color is due to photodecomposition of the carbanion in highly alkaline solutions (see below). Neither sucrose monopalmitate, a nonionic surfactant, nor low concentrations (≤ 0.1 *M*) of tetramethylammonium hydroxide (TMOH) give purple solutions of **1** in water.

The salts NaF, NaCl, NaBr, and sodium acetate (all 1.0 *M*) reduce the purple coloration of 10^{-4} *M* solutions of **1** containing 10^{-2} *M* NaOH and 10^{-2} *M* CATBr; see Table III. The salts reduce the intensity of the peak at 535 nm but do not change λ_{max} or introduce new peaks, indicating that the salt effects are not the result of a new reaction but due to a saturation of the micelle surface (the Stern layer) with added electrolyte, inhibiting the formation of carbanion. The spectral intensities decreased in the order: $F^- \approx OAc^- > Cl^- > Br^-$; the same order has been observed in other cases of salt effects on micelle-catalyzed reactions[9] and micelle structure.[10]

Both the orange and purple species obey Beer's law over the concentration range $0.1\text{-}1.0 \times 10^{-4}$ *M*, indicating that the anion is probably monomeric in both media at such concentrations. The absorbance increases linearly with the concentrations of **1** at 445 nm in 1.0 *M* NaOH and at 535 nm in 9.7×10^{-3} *M* NaOH with 10.9×10^{-3} *M* CTABr. Both sets of data were analyzed by a least-squares linear fit program, the extinction coefficients and correlation coefficients (ten points/line) being ϵ_{445} 1.39×10^4 ($r = 0.9995$) and ϵ_{535} 2.11×10^4 ($r = 0.9979$) for the orange and purple species, respectively. The large extinction coefficients suggest π to π^* transitions.[11]

Alkaline solutions of **1** in a wide variety of solvents have similar purple colors. For example the visible spectra of **1** in dry Me_2SO or DMF (both with TMOH), in aqueous pyridine or acetone (both with NaOH), and in formamide with KOH all have the same λ_{max} at 535 nm. In methanolic KOH, the color is similar (λ_{max} 542 nm, shoulder at 510 nm). In aqueous Me_2SO, the orange and purple species can be interconverted by varying the solvent composition. Superimposed spectra of 1.3×10^{-5} *M* **1** with 0.1 *M* TMOH in Me_2SO-water mixtures containing more than 0.20 mole fraction of Me_2SO intersect in an isosbestic point at 491 nm. The spectra of **1** in solutions containing less Me_2SO do not intersect at the isosbestic point, because these solutions are not "alkaline[12] enough for complete ionization of **1**. In Me_2SO-water mixtures containing only 0.01 *M* TMOH, very high proportions of Me_2SO are required to ionize **1** and convert all **1** anion to the purple form; see Table IV. Similar color changes were observed by adding water to an alkaline formamide solution of **1**. The fact that the ionization and orange-purple color change have different solvent dependencies explains Stewart's[13] observation that **1** is not a useful Hammett indicator for the H_- scale.

Table III. Salt Effects on the Visible Spectrum of *p*-Nitrophenylacetonitrile Anion[a]

Salt	Abs[b] (λ 445 nm)	Abs[c] (λ 535 nm)	Abs[d] (λ 535 nm)
	1.33	1.76	1.31
NaF	1.26	1.71	Insoluble
NaOAc	1.25	1.06	1.24
NaCl	1.22	0.83	1.20
NaBr	1.19	0.39	1.17

[a] Absorbance values for a 1-cm sample of 10^{-4} *M* *p*-nitrophenylacetonitrile with 1.0 *M* salts in various media. [b] In aqueous 1.0 *M* NaOH. [c] In aqueous 10^{-2} *M* NaOH with 10^{-3} *M* CTABr. [d] In Me_2SO containing 0.1 *M* tetramethylammonium hydroxide.

Table IV. The Visible Spectrum of *p*- Nitrophenylacetonitrile Anion in Me_2SO-H_2O Mixtures[a]

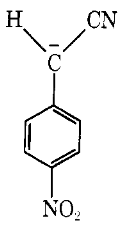
Me_2SO, mol %	H_-[b]	Absorbance (λ 445 nm)	(λ 535 nm)
4.4	12.0	0.050	0.034
7.3	12.5	0.090	0.080
14.3	13.6	0.160	0.254
21.7	14.5	0.160	0.417
29.8	15.4	0.140	0.496
91.7	22.2	0.068	0.615

[a] For 1.83×10^{-5} M *p*-nitrophenylacetonitrile in Me_2SO-H_2O solutions containing 0.01 *M* tetramethylammonium hydroxide. [b] Extrapolated from data, ref 13.

The data in Table II indicate that the carbanions derived from **1**, **2**, and **3**, give equivalent, or nearly equivalent, color changes when water is replaced by either Me_2SO or aqueous CTABr. The carbanions derived from **4** and **6** are affected less by CTABr micelles than by Me_2SO, and that derived from **5** is not solvent sensitive. Any explanation of the large spectral changes caused by CTABr must also account for these differences (see Discussion).

An orange-purple color change for **1** has been observed before.[14] Schaal[15] suggested that the orange and purple colors were due to mono- and dianions of **1**, respectively. Ridd[16] discounted this suggestion by demonstrating that the orange species in $NaOH-H_2O$ and the purple species in NaOMe-HOMe have equivalent stoichiometric dependencies on base concentration. Both Ridd[16] and Stewart[13] considered that each color corresponded to a different chemical species, one a proton abstraction product **9** and the second formed by nucleophilic addition of ^-OH or ^-OR to the ring, e.g., **10** or **11**. They made no assertion as to which species was purple. Despite uncertainty on this point, studies of the kinetics of proton transfer from **1** in water[17] and in ethanol-ether[18] have been reported. In both cases, the results are consistent with rate determining proton abstraction from the cyano carbon acid.

^{1}H NMR Spectra. The ^{1}H NMR spectrum of un-ionized **1** in $Me_2SO\text{-}d_6$ is characterized by a two proton singlet (δ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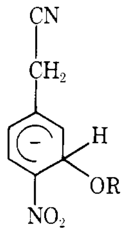
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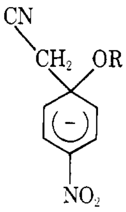
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4.32 ppm, downfield from NaDDS) for the methylene protons and an AA′BB′ pattern with doublets (J = 8.5 Hz) centered at δ 7.67 and δ 8.30 ppm for the C_2,C_6, and C_3,C_5 protons. A similar spectrum has been reported by Crampton.[19] If methanolic TMOH is added to the Me_2SO solution, the methylene proton signal merges with the solvent hydroxy signal, while added NaOD in D_2O causes the methylene proton signal to disappear, while the HOD signal intensity increases. Both results suggest that methylene proton ionization occurs in either media. The addition of less than an equivalent of methanolic TMOH to a Me_2SO solution of **1** broadens the aromatic proton signals of un-ionized **1** and produces additional proton signals upfield due to the carbanion. With an equivalent or more of TMOH in Me_2SO-methanol (61 mol % Me_2SO), the C_3,C_5 proton signals of the carbanion appear as a two proton intensity "triplet" centered at 7.47 ppm, and the C_2 and C_6 protons give rise to a pair of doublets centered at 6.34 ppm; i.e., the ring protons of the carbanion give an ABXY spectrum with the C_3 and C_5 signals overlapping ($\Delta\delta$ 0.1 ppm) more than the C_2 and C_6 proton signals ($\Delta\delta$ 0.2 ppm). A 0.1 m solution of **1** in a Me_2SO-D_2O solution (26 mol % Me_2SO) containing a 20-fold excess of NaOD gives rise to a broadened triplet and pair of doublets centered at 7.6 and 6.6 ppm, respectively. Adding D_2O to an Me_2SO-methanol-TMOH solution of **1** causes the aromatic proton signals to broaden and shift downfield toward those observed for Me_2SO-D_2O-NaOD solutions of **1**. Although the aromatic proton signals of a red-brown aqueous Me_2SO solution are broader and further downfield than the corresponding signals of a purple methanolic Me_2SO solution of **1**, in both cases, the same coupling pattern is clearly recognizable, and no additional peaks attributable to nucleophilic ring addition are observable. Compound **1** is too insoluble in water to permit a ^1H NMR study of its anion in D_2O solutions where the orange species predominates and spectra in alkaline Me_2SO-D_2O solutions where both orange and purple species are present represent the average of both components; i.e., exchange between orange and purple species is rapid. Our data show that the aromatic proton signals of the orange species are closer together and not as far upfield as those of the purple species. The chemical shift and coupling pattern for the C_2,C_6 and C_3,C_5 proton signals of **1** in all alkaline solutions are consistent with methylene proton loss. The complicated coupling pattern results from hindered rotation about the C_1-C_α bond which makes the ortho protons no longer equivalent.[19] Moreover, the spectra are inconsistent with either structure **10** or **11**. The fact that both aromatic signals have equivalent integrations (two protons each) rules out nucleophilic addition to form **10**. In structure **11**, both sides of the molecule are equivalent, and the ortho and meta protons would appear as doublets. Also the chemical-shift difference between the ortho and meta proton signals of **11** would be larger than that observed. For example, the C_5 and C_6 proton signals (in Me_2SO-d_6) of the Meisenheimer complex derived from methoxide ion addition to 2,4-dinitroanisole are at 7.25 and 5.06 ppm, respectively.[20]

Table V. Broadening of the CTABr ^1H NMR Spectrum by Added Aromatic Anions[a]

10^2C_{anion}, M	R^b	$W_{1/2}$N-Me,[c] Hz	$W_{1/2}$C-CH_2,[d] Hz
0.0[e]	0.00	1.3	2.8
0.8[e]	0.05	1.3	2.5
1.5[e]	0.10	1.3	3.0
3.0[e]	0.20	2.3	4.0
3.8[e]	0.25	3.5	6.8
7.6[e]	0.49	5.0	13.2
1.0[f]	0.07	1.5	3.0
2.2[f]	0.14	1.5	3.0
4.4[f]	0.28	3.0	6.0
6.6[f]	0.42	9.0	18.0

[a] Change in width of half-height for the prominent signals of 0.16 M CTABr in D_2O, at 31°. [b] $R = C_{anion}/C_{CTABr}$. [c] $W_{1/2}$ = width at half-height, for the N-methyl proton singlet of CTABr. [d] For the C-methylene proton multiplet of CTABr (appears as a broad singlet). [e] The Na salt of **5**. [f] The K salt of **6**.

Dianion formation is ruled out, because the aromatic proton signals would be much further upfield in such a species, and because the visible spectra of the anions of **2** and **3** are just as solvent sensitive as that of **1**, even though the former compounds have only one acidic proton. The possibility of charge transfer complex formation at concentrations less than 10^{-4} M is ruled out by the linearity of the Beer's law plots and the similarity of the extinction coefficients. The possibility of radical anion formation is unlikely; neither orange nor purple (CTABr) solutions of **1** with NaOH give an ESR spectrum.

The ^1H NMR spectrum of the aromatic proton region of **2** in Me_2SO-d_6 is characterized by two multiplets (two protons each) at 8.15 and 7.60 ppm and an unsymmetrical multiplet (five protons each) at 7.30 ppm. The addition of 0.5 equiv of TMOH (without methanol) broadens and shifts the p-nitrophenyl proton multiplets to 7.45 and 6.65 ppm and causes the large multiplet, due to the unsubstituted phenyl protons, to spread out making the difference between the ortho, para, and meta protons more apparent. Because the nitro group is attracting electron density, the p-nitrophenyl ortho protons appear as the most upfield multiplet. The anion of **2** is too insoluble in Me_2SO-D_2O mixtures for ^1H NMR study. The ^1H NMR spectrum of the potassium salt of **5** in Me_2SO-d_6 consists of two AA′BB′ "doublets" centered at 7.80 and 6.68 ppm. The addition of an equal volume of D_2O broadens the peaks and shifts them downfield to 7.94 and 6.84 ppm. In this case both the meta and ortho protons are shifted to the same extent, indicating little change in the relative electron densities at the meta and ortho sites upon changing the solvent.

The ^1H NMR spectrum of CTABr in D_2O is considerably changed by the addition of small amounts of the anions of **5** or **6**. The addition of less than 0.5 equiv of the sodium salt of **5** broadens both the N-methyl and C-methylene proton signals of 0.16 M CATBr, while causing little change in the chemical shift of either proton signal (see Table V). The addition of equivalent amounts of the potassium salt of **6** to 0.15 M CTABr causes the N-methyl signal to shift upfield (by 0.15 ppm, measured relative to water[21]) and broadens both the N-methyl and C-methylene proton signals (see Table V). CTABr solutions containing more than 0.5 equiv of either anion are very viscous and do not give well resolved spectra.

It has been shown before that the nature of the interaction between aromatic compounds and surfactant molecules in micelles can be determined from changes in the surfactant ^1H NMR spectrum.[9,23] The signal broadening indicates that, on a time average, the surfactant and aromatic anion are associating tightly, forming a rigid nonspherical mixed aggregate (hence the viscosity increase) with a greater relaxation time than either the free anion or pure CTABr micelle. The fact that the HOD singlet and the CTABr *C*-methyl triplet were not broadened[24] implies that the aromatic anion is associating primarily with the *N*-methyl ends of neighboring surfactant molecules, leaving the micelle interior and solvent little changed. The upfield shift of the *N*-methyl proton singlet caused by **6** anion is consistent with this view since only those parts of the surfactant molecules close to the incorporated aromatic ring are shifted upfield by ring current effects. Both the broadening and shifts caused by the anion of **6** are comparable to those caused by tosylate anion,[9] which probably resides between surfactant cationic head groups at the micelle surface. This suggests that the anion of **6** is somewhat hydrated even when taken into micelles.

The addition of 0.07 *M* CTABr to a 0.42 *M* solution of the potassium salt of **6** causes an upfield shift of the C_2 and C_3 proton signals of **6** anion; the former is shifted 0.16 ppm upfield, the latter 0.03 ppm. Additional CTABr causes enough signal broadening to obscure the spectrum of **6** anion. This result implies that there is an increase in the anionic character in the ring when the anion is taken into a micelle, and that the association between aromatic anion and surfactant molecules is tight.

Photodecomposition. It has long been known that purple alkaline solutions of **1** turn green with time.[25] We found that the color of a 10^{-4} *M* solution of **1** in 0.02 *M* NaOH with 5×10^{-3} *M* CTABr changed more rapidly under a sun lamp (70% conversion in 5 min) than in the cell compartment of a Cary 14 spectrophotometer under constant exposure to light (λ 535 nm, 50% conversion in 4 hr), and that the color change is very slow in total darkness. The color change occurred just as rapidly in deoxygenated solutions under nitrogen as in solutions exposed to air. Photodecomposition was especially pronounced at high alkali concentrations (with or without CTABr), and all solutions were prepared in the dark. Reproducible pK_a values could not be obtained for tris(4-nitrophenyl)methane, 2-nitrofluorene, and 2,5-dinitrofluorene because of the high photoreactivity of their alkaline CTABr solutions.

Discussion

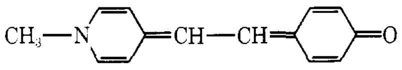
In this study we have shown the following. (1) Cationic micelles of CTABr markedly increase the acidity of certain carbon acids; the acid dissociations of compounds **1-5** are enhanced more than those of carboxylic acids[6] and phenols.[5] (2) The addition of micellar concentrations of CTABr changes the color of aqueous solutions of some nitro carbanions. (3) This color change is due to a solvent effect rather than a chemical reaction.

Both the decrease in pK_a values and the color change are related to the manner in which a carbanion associates with neighboring surfactant molecules in the micelle. The following discussion is an attempt to rationalize both phenomena in terms of specific interactions within the micelle.

The pK_a Value Changes. Cationic micelles lower the pK_a value of a solubilized acid by reducing the free-energy difference between the acid and its anion; a change in hydronium ion activity would not account for the specific dependence of ΔpK_a on acid structure. From the results of this study and earlier ones,[3-8] it appears that large decreases in pK_a values are observed when the acid and anionic forms are both hydrophobic enough to be incorporated almost totally into the micelle. Extensive incorporation implies that the free energy of both forms is reduced in micelles. With the hydrophobic acids studied, the free energy of the anionic form decreases more than that of the un-ionized form, because the anion is more polarizable and associates tightly with neighboring surfactant molecules. The especially large decrease in pK_a values observed for these carbon acids and phenols is because their more delocalized anions require less specific solvation by water than carboxylic acids and so give up less hydration energy when taken into micelles. Carboxylate anions are destabilized more than phenolate anions when transferred from water to a dipolar aprotic solvent.[26] We assert that the tight association between delocalized anions and the *N*-methyl ends of neighboring surfactant molecules promotes acid dissociation, because this tighter association stabilizes the whole micelle–anion aggregate.[6]

The difference in the ΔpK_a values observed for the two phenols **7** and **8** illustrates the importance of hydrophobicity. The bulky *tert*-butyl groups of **8** hinder hydrogen bonding to oxygen, consequently **8** forgoes less hydration energy when taken into CTABr micelles than does **7**, and its ionization is enhanced nearly ten times more than that of **7** by CTABr micelles.

The Color Change. The large red shifts in the visible spectra of the anions **1-4** and **6** in CTABr are unprecedented. For the anion derived from **1**, the shift corresponds to a difference in transition energies (ΔE_T) of 11 kcal/mol. Usually the solvent shifts caused by incorporation into micelles are small; even the very solvent sensitive $\pi \rightarrow \pi^*$ transition[27] for the merocyanin dye **12** is red shifted only 3 nm (ΔE_T = 0.4 kcal/mol) when taken into CTABr micelles (0.1 *M* CATBr).[28]


12

Because nearly identical red shifts are observed when **1** anion is transferred from water to such highly diverse media as formamide (dielectric constant, ε 109.5), Me_2SO (ε 46.6), and methanol (ε 32.6), we suggest that the shift is not due to an unspecific solvent polarization effect.[29,30] Rather it must be due to some unique difference between water and the other solvents. Water is an unique solvent in many ways,[31,32] but its high capacity for hydrogen bonding and its ability to solvate alkali metal cations, reducing ion pairing, are most likely the cause of the high electronic transition energies observed with water.

Kerber and Porter[33] observed a red shift with the anions of 1-nitroindene (**6**) and 9-nitrofluorene upon going from water to Me_2SO. This was paralled by upfield shifts in the ^1H NMR spectra of the anions. These workers suggest that the anions have greater anionic character distributed into the ring and less at the nitro group oxygen atoms when in Me_2SO rather than water, because the nitro group oxygen atoms are hydrogen bonded in water.[33] There has been no direct information about the hydrogen bonding capabilities of the nitro group in carbanions; however, our observation that the aromatic proton signals of **1** anion move downfield with added D_2O is consistent with hydrogen bonding to the nitro group oxygens which would reduce the anionic character in the ring, especially at positions ortho to the methylene group. Certainly nitro groups in conjugation with a carbanion are better able to donate electrons in a hydrogen bond than the nitro groups of neutral compounds, which have low hydrogen bonding capability.[34] Neutral aromatic nitro compounds normally blue-shift on going to nonpolar solvents.[11] The data in Table II suggest that large red shifts (90 nm) are observed only in nitro carbanions which have a high electron density at the nitro group, e.g., the anions of **1-3** and **6**. The spectrum of the anion of **4**, with two nitro groups to accommodate the extra electron pair, is only shifted 30 nm, and the spectrum of 5 anion, with two powerfully electron with-drawing -C≡N groups serving to withdraw electron density from the nitro group, is not shifted at all. Kerber[33] observed that the spectrum of the nitro carbanion from 9-nitrofluorene is red shifted, while Stewart[13] found that the spectrum of the carbanion from 9-cyanofluorene is not solvent dependent.

Ion pairing has been the traditional rationalization for spectral changes of carbanions,[35] and any distinction between a spectral change due to decreased hydrogen bonding and one due to a change in the cation–anion association cannot be made with total certainty. However, we observe the same spectral changes whether we use NaOH, KOH, or TMOH, meaning that any spectral change due to ion pairing is remarkably independent of the nature of the cation.

Although there are several discussions of the influence of hydrogen bond formation on electronic transitions, most deal with the blue shift in the absorption maximum of an $n \rightarrow \pi^*$ transition when the solvent is changed from an alkane to an alcohol.[29,36-38] There has been no theoretical discussion of the effect of hydrogen bonding on the $\pi \rightarrow \pi^*$ transition of a nitro carbanion. Quite possibly there is considerable charge reversal in a nitro group during a $\pi \rightarrow \pi^*$ transition[33,39] so that the Frank–Condon state is destabilized by the presence of a hydrogen atom at the H-bond distance optimum for the ground state.

If hydrogen bonding does lead to an increase in the spectral transition energy, then the fact that **1** anion in aqueous CTABr affords the same spectrum as in Me_2SO suggests that **1** anion is not hydrogen bonded within the micelle, implying that intramicellar water has less tendency to hydrogen bond with organic molecules than "normal" water. Although further experiments are needed to verify this point, it appears that the visible spectra of nitro carbanions may be useful probes of the hydrogen bonding capability of water in mixed aqueous organic solvents and in micelles.

Experimental Section

Materials. Purchased samples of all inorganic compounds as well as pyridine, 4-nitrophenol, 4-chlorophenylacetonitrile (Aldrich), and 4-chloronitrobenzene (Paragon) were of good quality and were used without further purification. Purchased CTABr (J. T. Baker, technical grade) was recrystallized twice from methanol-ether; the recovered solid was washed repeatedly with anhydrous ether and dried in vacuo.[40] Me_2SO and formamide were purified by distillation and stored over molecular sieves. Purchased phenylacetonitrile (Aldrich) was distilled [bp 110° (50 mmHg)]. 4-Nitrophenylacetonitrile (**1**) was prepared by nitration of phenylacetonitrile:[41] mp 115-116° (lit.[41] 116-117°); uv (H_2O) λ_{max} 269 nm; ir (Nujol) 1600 (phenyl) and 1515, 1350 (nitro) cm^{-1}; NMR ($CDCl_3$) δ 3.80 (s, 2, CH_2), 7.48 (d, 2, J = 8 Hz, ortho protons), and 8.15 ppm (d, 2, J = 8 Hz, meta protons).

(4-Nitrophenyl)phenylacetonitrile (**2**) was prepared from 4-chloronitrobenzene and phenylacetonitrile by the procedure of Davis and Pizzini.[42] The product was recrystallized twice from methanol: mp 68-69° (corr) (lit.[42] 70-72°); NMR ($CDCl_3$) δ 5.12 (s, 1, CHCN), 7.2 (s, 5, phenyl), 7.43 (d, 2, J = 8 Hz, C_2C_6 protons of 4-nitrophenyl), and 8.10 ppm (d, 2, J = 8 Hz, C_3C_5 protons of 4-nitrophenyl).

Anal. Calcd for $C_{14}H_{10}N_2O_2$: C, 70.58; H, 4.23; N, 11.76. Found: C, 70.14; H, 3.87; N, 11.49.

(4-Chlorophenyl)(4-nitrophenyl)acetonitrile (**3**) was prepared from 4-chloronitrobenzene and 4-chlorophenylacetonitrile by the same procedure.[42] The product was recrystallized three times from methanol: mp 107-108° (corr) (lit.[42] 110-112°); NMR ($CDCl_3$) δ 5.15 (s, 1, CHCN), 7.24 (m, 4, protons of 4-chlorophenyl), 7.44 (d, 2, J = 8 Hz, C_2C_6 protons of 4-nitrophenyl), and 8.16 ppm (d, 2, J = 8 Hz, C_3H_5 protons of 4-nitrophenyl).

Anal. Calcd for $C_{14}H_9ClN_2O_2$: C, 61.66; H, 3.33. Found: C, 61.53; H, 3.34.

Bis(4-Nitrophenyl)acetonitrile (**4**) was prepared by slowly adding 5 g (0.048 mol) of **2** to 150 ml of fuming nitric acid at 5° with vigorous stirring. After 15 min, the reaction mixture was poured onto crushed ice and the resulting yellow oil washed twice with cold water and once with dilute K_2CO_3 solution. Trituration with dry ether, at Dry Ice temperatures, afforded 3 g (45% yield) of a yellow gum, mp 15-20°, which was purified by chromatography with a silica gel column with CH_2Cl_2-pentane. The product had mp 40-45°; uv (aqueous NaOH) 630 nm; ir (Nujol) 2260 (CN), 1940 and 1810 (δ_{CH} overtone for para-substituted aromatic), 1530 and 1350 (nitro) cm^{-1}; NMR ($CDCl_3$) δ 5.36 (s, 1, CHCN), 7.52 (d, 4, J = 9 Hz, ortho protons), and 8.24 ppm (d, 4, J = 9 Hz, meta protons).

Anal. Calcd for $C_{14}H_9N_3O_4$: C, 59.38; H, 3.18. Found: C, 58.90; H, 3.38.

The same compound was obtained in lower yield by nitrating diphenylacetonitrile with cold fuming nitric acid, followed by chromatography on an alumina column ($CHCl_3$-pentane) where the product appeared as a blue band, and by reacting equimolar amounts of 4-chlorobenzene and 4-nitrophenylacetonitrile by the procedure of Davis and Pizzini.[42]

Sodium Salt of 4-Nitrophenylmalononitrile (**5**). To 2 g of sodium in 50 ml of absolute ethanol was added 6.8 g (0.10 mol) of malononitrile in 100 ml of dry ether followed by 230 ml of absolute ethanol and 16.1 g (0.10 mol) 4-chloronitrobenzene, with stirring. The mixture was heated at reflux for 4 hr and stirred at room temperature for 12 hr. The product precipitated as a red solid, recrystallized from aqueous ethanol: mp 225°; uv (H_2O) 468 nm (lit. 475); NMR (Me_2SO) δ 6.68 (d, 2, J = 9 Hz, ortho protons), and 7.80 ppm (d, 2, J = 9 Hz, meta protons).

Potassium salt of 1-nitroindene (**6**) was prepared by an adaption of the procedure of Kerber and Hodos.[43] Potassium metal (7.0 g, 0.18 g-atom) was added in small portions to a mixture of 40 ml of absolute ethanol and 30 ml of dry ether under nitrogen. This mixture was stirred under positive nitrogen pressure at 0° until all the metal dissolved, then a mixture of 17.5 g of freshly distilled indene and 14.7 g of freshly prepared[44] methylnitrate in 100 ml of dry ether was added dropwise over a 2-hr period at 0°, followed by the addition of 100 ml of dry ether. The reaction mixture was stirred an additional 12 hr under nitrogen at room temperature. The crude product was a yellow solid which was removed by filtration and recrystallized twice from acetone-chloroform. The purified product had mp 300°; uv λ_{max} (H_2O) 359 (absolute C_2H_5OH), 378 (dry ether), 393 nm (in agreement with lit.[33]); NMR (D_2O) in agreement with lit.[33]

2,6-Di-*tert*-butyl-4-nitrophenol was prepared by the method of Ströh.[45] The product was recrystallized twice from absolute ethanol-petroleum ether (1:3): mp 159-159.5° (lit.[45] 156°); NMR ($CDCl_3$) δ 1.44 (s, 18-20, $C(CH_3)_3$ protons), 5.83 (s, 1, -OH), and 8.00 ppm (s, 2, Ar-H protons).

pK_a Values. The pK_a of **1** in water was estimated from a well-defined plot of absorbance (λ 445 nm) vs. NaOH concentration; the pK_a was taken as 14-$[OH^-]_{1/2}$ where $[OH^-]_{1/2}$ is the base concentration corresponding to one-half maximum absorbance. The solutions were prepared by diluting weighed portions of NaOH with an aqueous carbonate-free 10^{-4} M solution of **1**, in the dark under nitrogen. The absorption spectra were taken immediately after mixing. Because highly alkaline solutions of **1** change color quickly, the maximum absorbance value could only be determined within 10%, and the reproducibility between three determinations was ±0.2 pK_a units. The pK_a of **1** in 4 × 10^{-3} M CTABr was determined in a similar manner, the uncertainty being ±0.1 pK_a units. The change in pK_a value caused by CTABr was much greater than the uncertainty in the individual pK_a values.

The pK_a values of all other compounds were determined from the half-neutralization pH values estimated from well defined sigmoidal plots of absorbance vs pH (or H_0). These values were in agreement with the average values calculated from eq 2, where

$$pK_a = pH_{obsd} + \log\left[\frac{A_{max} - A_{obsd}}{A_{obsd}}\right] \qquad (2)$$

A_{max} and A_{obsd} are the absorption values for fully dissociated and partially dissociated (at pH_{obsd}) solutions of the acids. No corrections were made for electrolyte effects or for the effect of CTABr on the glass electrode,[6] but such effects are small compared with the change in pK_a caused by CTABr; variations in ionic strength from 0.01 to 0.05 M caused no appreciable change in the pK_a values. Compounds **2**, **3**, and **4** were dissolved in a small amount of alcohol or acetone before dilution with water; the final solutions never contained more than 0.2% organic solvent.

Small aliquots of acetic or dilute hydrochloric acid were added to well stirred buffer solutions of the anion (with or without 10^{-2} M CTABr) in a thermostated bottle equipped with a pH electrode and, after each addition, a two-ml portion of the partially neutralized anion solution was transferred to a Beckman DB spectrophotometer, and the absorbance at the $\lambda_{\max}$ of the anion was measured. The temperature was maintained at 25 ± 1° by a Lauda K2/R constant temperature water circulator cooling both the mixing bottle and the spectrophotometer cell compartment. The pH was measured with a Corning Model 112 research pH meter and a Curtin combination electrode (calomel reference). Depending on the required pH range, either $1\text{-}5 \times 10^{-2}$ M acetate, phosphate, or carbonate buffers were used; for **2** and **3**, KOH was also used.

The neutral compounds **1–8** were colorless, or nearly so, while the anions were highly colored. In all cases, plots of absorbance vs. acidity were well defined, continuous, and reproducible. For compounds **2**, **3**, **5**, **7**, and **8**, the anion could be regenerated by adding base, and duplicate plots were always parallel and never separated by greater than 0.1 pH unit. Acidified solutions of **6** and alkaline solutions of **4** were unstable, but pK_a values with uncertainty of less than ±0.1 pK_a units were obtained with fresh solutions. In all cases, the uncertainties in the individual pK_a values were much less than the change in pK_a caused by CTABr.

Spectra. All electronic spectra were determined with a Cary 14 recording spectrophotometer, and all NMR spectra were taken with a Jeol JNM-MN-100 NMR spectrometer. Solutions of **1**, **2**, and **5** in Me$_2$SO-d_6 and Me$_2$SO-d_6-D$_2$O were prepared immediately before use. Me$_2$SO-methanol-TMOH solutions were made by combining weighed portions of 20% TMOH in methanol with a Me$_2$SO solution of **1**; the final concentration of **1** was 0.1 M. Alkaline Me$_2$SO-D$_2$O solutions were prepared by dissolving a weighed portion of sodium metal in the solvent at 0° and diluting the resulting slurry with additional warm solvent. These solutions were added to Me$_2$SO solutions of **1**; the final **1** concentration was 0.1 M. Chemical shifts were usually reproducible within 0.02 ppm.

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