as ^{13}C shifts in analogous carbon compounds to the electronic substituent effects.[2] The magnitudes of these ^{15}N and ^{13}C shift differences (up to 25 ppm) associated with changing the ring substituents are so large as to be clearly due to changes in the paramagnetic contribution for the screening constant. The basic assumption in these Hammett shift correlations is that, because the paramagnetic term depends on the π-electron density at the nucleus undergoing the transition, any inductive or conjugative interactions of the substituents which might affect the electronic distributions about that nucleus should have an important influence on its chemical shift. Even if this assumption is correct, then the substantially greater sensitivity of ^{15}N over ^{13}C shifts in these correlations might arise from additional shift effects produced by substituents as a result of changing the degree of mixing in states corresponding to n $\rightarrow \pi^*$ or other optical transitions involving π orbitals of the imines.

However, when the ^{15}N chemical shifts of our series of para-substituted *N*-(arylmethylidene)cyclohexanamines **2** are plotted against the corresponding shifts of the N-protonated hydrotrifluoroacetates **4**, it is found that there is a good overall linear correlation with a slope of 0.963 and a correlation coefficient of 0.994. The near unit slope indicates clearly that the effect of 4 substituents in the phenyl ring on the shifts is nearly the same for series **2** and **4**. We can only conclude on the basis of these results that the n $\rightarrow \pi^*$ contribution to the ^{15}N shifts in the **2** series is essentially constant and is *not* substantially influenced by substituent groups in the 4 position of the phenyl ring. This seems to be the only way to rationalize the fact that there is essentially no change in the effects of 4 substituents when the n $\rightarrow \pi^*$ contribution is cut off on conversion to the salt series **4**. Substituent influences on the unshared nitrogen electrons through interactions with the substituent groups involving the n and π orbitals should not be very large because the n orbital is essentially orthogonal to the p orbitals of the double bond system. It is much more likely that the substituents would influence the energy of mixing in of the π^* state (or other appropriate excited states), but this does not seem to be important.

Overlying the influence of the nitrogen unshared pair on the shifts is a considerable substituent effect which is associated with the conjugated π system made up of the phenyl and $-CH{=}N-$ (or $-CH{=}{}^{+}NH-$) groups and which responds in a rather simple way to 4 substituents, probably through changes in the π-electron densities and/or bond orders of the imine and immonium nitrogen. The fact that the ^{15}N shifts for *both* the **2** and **4** series seem to be inherently more sensitive to substituent effects than analogously situated carbons[8] is not easy to explain. Possible contributors are differences in bond lengths, polarizability, and nuclear charge.

References and Notes

(1) (a) Supported by the Public Health Service, Research Grant No. GM-11072 from the Division of General Medical Sciences, and by the National Science Foundation. (b) Present address: Department of Chemistry, University of Southern California, Los Angeles, Calif. 90007.
(2) Westerman, P. W.; Botto, R. E.; Roberts, J. D. *J. Org. Chem.* **1978**, *43*, 2590–2596.
(3) For a comprehensive survey on nitrogen coupling constants, see Axenrod, T. "Correlations of Nitrogen Coupling Constants with Molecular Structure", in "Nitrogen NMR"; Witanowski, M., Webb, G. A., Eds.; Plenum Press: London, 1972.
(4) Binsch, G.; Lambert, J. B.; Roberts, B. W.; Roberts, J. D. *J. Am. Chem. Soc.* **1964**, *86*, 5564–5570.
(5) See Webb, G. A. "Nitrogen Chemical Shift Calculations", in "NMR of Nuclei other than Protons"; Axenrod, T., Webb, G. A., Eds.; Wiley: New York, 1974; Chapter 4.
(6) Pople, J. A. *J. Chem. Phys.* **1962**, *37*, 53–59, 60–66; *Mol. Phys.* **1964**, *7*, 301–310.
(7) For a comparison of shifts in related nitrogen compounds, see ref 2, Chapter 4. For carbon compounds, see Stothers, J. B. "Carbon-13 NMR Spectroscopy"; Academic Press: New York, 1972.
(8) Dhami, K. S.; Stothers, J. B. *Can. J. Chem.* **1965**, *43*, 510–520.

Micellar Catalysis of Proton-Transfer Reactions. 2.[1] Hydrolysis of Covalent *p*-Tolylsulfonylmethyl Perchlorate Catalyzed by Arenesulfinate Anions in the Presence of CTAB. Irrelevance of the Hydrophobicity of the Arene Moiety of the Sulfinate

Gerard B. van de Langkruis and Jan B. F. N. Engberts*

Department of Organic Chemistry, University of Groningen, Nijenborgh, Groningen, The Netherlands

Received July 10, 1978

During the last decade, studies of catalysis and inhibition of chemical processes by micellar aggregates of surfactant molecules have developed beyond the qualitative stage and many of the recent results have now been summarized in pleasing reviews.[2] Nevertheless, there is still only limited insight into the factors which determine the catalytic efficiency of a particular surfactant aggregate. Recent work from these laboratories[1] has shown that the rates of arenesulfinate, formate, and hydroxide-catalyzed hydrolysis of covalent arylsulfonylmethyl perchlorates[3,4] (Scheme I) are greatly enhanced (by factors of 10^3–10^4) in the presence of micelles of cetyltrimethylammonium bromide (CTAB). Since electronic effects of substituents on the pK_A values of para-substituted benzenesulfinic acids are relatively small,[5] it could be anticipated that dynamic basicities within a series of p-$XC_6H_4SO_2^-$ ions (**2a**, X = CH_3; **2b**, X = H; **2c**, X = Br; **2d**, X = NO_2) solubilized by CTAB will be rather insensitive to electronic effects of X but might instead respond to the hydrophobicity of the substituent. The present study reports an attempt to find such a relationship. Hydrophobic fragmental constants as defined by Rekker[6] (f_X; X = CH_3, H, Br, NO_2) for the system octanol–water were employed to quantify relative hydrophobicities of the sulfinate anions **2a–d.**

Results and Discussion

Binding of Arenesulfinate Ions to CTAB. Since the efficiency of micellar CTAB catalysis will be directly affected by the strength of sulfinate–micelle interaction as well as by the location of the sulfinate ion in the micelles, we will first discuss these factors.

The binding between the sodium sulfinates **2a–d** and CTAB micelles was investigated by measuring the change in absorbance of **2a–d** in the presence of varying concentrations of CTAB according to the method of Riegelmann et al.[7] The plots were analyzed by using a Langmuir-type model as delineated by Sepulveda[8] (eq 1). Herein $(CTAB)_n$ is a portion of a micel consisting of n detergent molecules necessary for sorbing one sulfinate anion.

$$p\text{-}XC_6H_4SO_2^- + (CTAB)_n \overset{K}{\rightleftarrows} [(CTAB)_n \cdot p\text{-}XC_6H_4SO_2^-]$$

2a–d

The values obtained for K and n are listed in Table I. The data show that, although the sulfinate anions interact strongly with the micelles, there is no evident relationship between K or n and the magnitude of f_X. Thus it appears that the modest changes in n and K as a function of X do not primarily originate from hydrophobicity effects.

NMR spectroscopy was used to obtain information about the solubilization site of the sulfinate anions. Ever since the

Scheme I

$$\underset{\text{1, R = } p\text{-}CH_3C_6H_4}{RSO_2CH_2OClO_3} + B \xrightarrow{\text{slow}} RSO_2CH^-OClO_3 + BH^+$$

$$RSO_2CH^-OClO_3 \xrightarrow[H_2O]{\text{fast}} RSO_2H + HCOOH + ClO_3^-$$

B = Brönsted base (i.e., H_2O, OH^-, RSO_2^-, HCO_2^-)

0022-3263/79/1944-0141$01.00/0

Table I. Effect of CTAB (2×10^{-3} M) on the Sulfinate and Carboxylate Ion Catalyzed Hydrolysis of 1 at 25.0 °C

base	registry no.	pK_A[a]	f_X[b]	$K \times 10^3$ M^{-1}	n	k_m, $M^{-1}\,s^{-1}$	k_m/k_w
2a, p-$CH_3C_6H_4SO_2^-$	17223-96-0	2.30	0.702	6 ± 2[d]	1.35 ± 0.07	280 ± 17	14×10^3
2b, $C_6H_5SO_2^-$	16722-50-2	2.26	0.175	4 ± 1[d]	1.45 ± 0.07	210 ± 13	10×10^3
2c, p-$BrC_6H_4SO_2^-$	68001-97-8	2.58	1.131	8 ± 2[d]	1.22 ± 0.05	260 ± 37[e]	10×10^3
2d, p-$NO_2C_6H_4SO_2^-$	30904-36-0	2.27	−0.078	4 ± 1[d]	1.60 ± 0.05	15 ± 11[e]	0.7×10^3
3a, HCO_2^-	71-47-6	3.75				174	3×10^3
3b, $CH_3(CH_2)_2CO_2^-$	461-55-2	4.81				1860	9×10^3

[a] The pK_A's of the sulfinic acids bound to CTAB micelles were obtained by substracting 0.5 pK_A units from the pK_A of the acid in water at 25 °C (ref 14).[5] [b] Hydrophobic fragmental constant (ref 6). [c] k_w refers to the reaction in water in the absence of CTAB (see text). [d] Sulfinate concentration 1.0×10^{-3} M. [e] Rates were measured conductometrically.

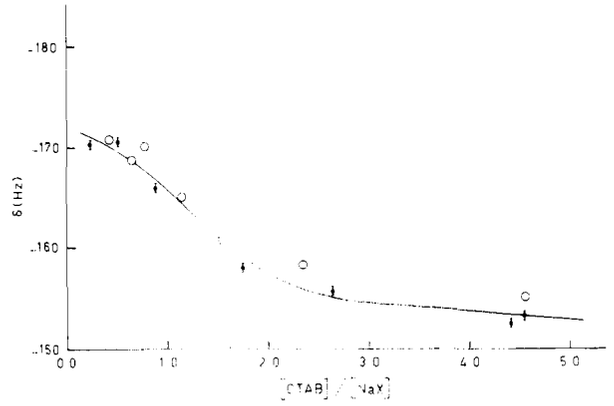

Figure 1. Chemical shift of the CTAB N-methyl protons (upfield from the HOD frequency) as a function of CTAB concentration at constant salt (NaX) concentration of 2×10^{-2} M: (●) X = p-$CH_3C_6H_4SO_2^-$; (○) X = p-$CH_3C_6H_4SO_3^-$.

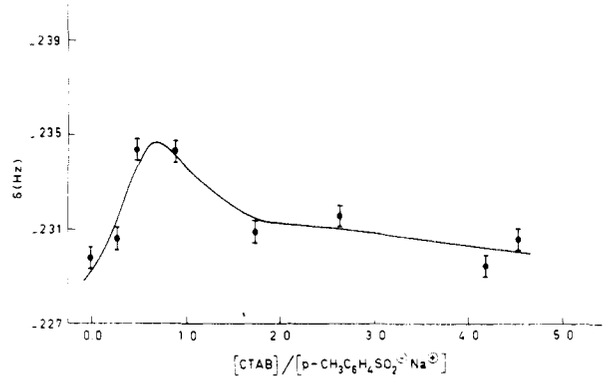

Figure 2. Chemical shift of the p-methyl protons of **2a** (upfield from the HOD frequency) as a function of CTAB concentration at a constant concentration of **2a** (2×10^{-2} M).

work of Eriksson[9] on uncharged aromatics, chemical shift changes of the aggregated surfactant molecules and of sufficiently hydrophobic solubilizates have been rationalized in terms of specific mutual interaction between both components as determined by the average position of the solute within the micelle. Figure 1 portrays the upfield shift of the micellar CTAB N-methyl protons upon increasing incorporation of p-toluenesulfinate ions (**2a**) into the micelle. These upfield shifts are best interpreted in terms of insertion of the aromatic ring of **2a** into the micellar interior, the depth of the penetration being such that the surfactant N-methyl protons experience the magnetic anisotropy effect of the π system of the solute. Quite similar effects have been observed by Bunton et al.[10,11] for sodium p-toluenesulfonate bound to CTAB micelles and their results have also been incorporated in Figure 1. In Figure 2, the p-methyl proton chemical shift of **2a** is plotted as a function of CTAB concentration. A maximum upfield shift of 6 Hz is observed at about 1:1 CTAB/**2a** ratio. Finally we note that the CTAB $C(CH_2)_{14}C$ protons display two partially resolved peaks upon incorporation of **2a** into the micelle. The one at lower field is shifted 3 Hz downfield whereas the other one is shifted by more than 20 Hz upfield. From these data we conclude that the mutual effect of CTAB and **2a** on chemical shifts are reminiscent of those for the analogous system containing sodium p-toluenesulfonate[10,11] instead of **2a**. This strongly suggests that both types of aromatic ions are located at rather similar average locations in the CTAB micelles.

Reaction of Perchlorate 1 in the Presence of CTAB. Taking into account the contributions of all Brönsted bases present in solution (H_2O, OH^-, product HCO_2^- and $ArSO_2^-$), k_{obsd} for hydrolysis of 1 is not expected to be constant during a kinetic run.[1] As shown previously,[1] CTAB micelles speed the reaction of 1 with OH^- by a large factor (k_{OH^-} ca. 10^8 $M^{-1}\,s^{-1}$ vs. $k_{OH^-} = 9.2\ 10^4$ $M^{-1}\,s^{-1}$ in the absence[12] of surfactant at 25 °C). Therefore, if the initial pH of the reaction mixture is 5.5, it can be calculated (and found experimentally) that a plot of k_{obsd} vs. product concentration deviates substantially from linearity in the lower concentration region. If instead an initial pH of 3.5 (HCl) was used, the kinetics did obey first-order requirements (starting concentration of **1**, ca. 3.10^{-5} M) for 2–3 half-lives. The k_{obsd} values (2×10^{-3} M CTAB) obtained were extrapolated to zero product concentration as described before[1] to yield k^0_{obsd}. The second-order rate contributions of added sodium arenesulfinates **2a–d**, k_m, were obtained from the slope of a linear plot of k^0_{obsd} vs. sulfinate concentration (Table I). For **2b** the kinetic data were also analyzed by means of eq 1[13] in which k_{H_2O}, k_{OH^-}, k_F, and k_S are rate constants for H_2O, OH^-, HCO_2^- (product), and p-$CH_3C_6H_4SO_2^-$ (product), respectively, and α_F, α_S, and α_S' are the degrees of ionization (from pK_A[14] and pH) of formic acid, p-$CH_3C_6H_4SO_2H$, and $C_6H_5SO_2H$, respectively.

$$k_{obsd} = k_{H_2O}[H_2O] + k_{OH^-}[OH^-] + [\text{product}]\{\alpha_F k_F + \alpha_S k_S\} + [\mathbf{2b}]\alpha_S' k_m \quad (1)$$

From a series of runs using known substrate concentrations and carried out after each other in the same solutions, k_m can be found by substracting the rate contributions of products (HCO_2^-, p-$CH_3C_6H_4SO_2^-$), H_2O, and OH^- from k_{obsd} and plotting these values against the concentration of **2b**. The k_m values obtained by the two methods agreed within experimental error (±6%).

The k_m values for **2a–d** may be compared with the rate constants in the absence of surfactant (k_w) estimated from the Brönsted plot for hydrolysis of 1 ($\beta = 0.51$ for a series of carboxylate anions).[3] Large rate accelerations in the order of 10^3–10^4 are indicated if it is assumed, on the basis of previous data[1] and the values of K and n in Table I, that both reactants are essentially quantitatively sorbed in the surface layer of

CTAB micelles. It is of course hard to estimate in how far orientation of the reactants in the micelles contributes to or hampers the overall catalytic efficiency of the micellar reaction. For instance, it is likely that the nonionic perchlorate **1** will penetrate deeper into the hydrophobic core of the micelles than the ionic reactants **2a–d.** Nevertheless it is highly possible that one of the important factors responsible for the pronounced micellar effects will be concentration of the reactants into a relatively small volume element in the micellar pseudophase.[2,15] The finding that binding constants as well as k_m values are only modestly influenced by the nature of X in the series **2a–d** is consistent with this rationalization but constitutes no proof for it. We emphasize—as pointed out repeatedly[2,15,16]—that it is at the moment hardly feasible to separate "concentration" and "medium" effects on k_m/k_w.

The main conclusion to be drawn from the kinetic data in Table I is that the k_m/k_w values for **2a–d** are within a small range, implying that the substituent effect of X on the kinetic basicity of the sulfinate ions in the micellar-catalyzed process is small and not governed by the hydrophobicity of X.

In view of the unexpected observation[1] that the rate of the formate-catalyzed hydrolysis of **1** is also greatly accelerated by CTAB, we have also determined the effect of CTAB micelles on k_m/k_w for the more hydrophobic butyrate anions. The kinetic analysis was carried out by means of eq 1 employing butyric acid concentrations in the range 2.38×10^{-4}–11.9×10^{-4} M. The rate acceleration was linear with the butyrate anion concentration for ten kinetic runs at different butyrate concentrations. As shown in Table I, k_m/k_w amounts to 9×10^3 which is three times larger than the corresponding value for formate anions. This dependence of the catalytic factor on the chain length of the reactants has been noted before,[2,15] but in the absence of information on the binding of both carboxylate anions to CTAB micelles, a detailed explanation is premature.

Experimental Section

Materials. *p*-Tolylsulfonylmethyl perchlorate (**1**) was prepared as described previously.[3] Cetyltrimethylammonium bromide (CTAB; Merck, p.a. quality) was purified by the method of Duynstee and Grunwald.[17] The sodium arenesulfinates **2c** and **2d** were obtained via reduction of the corresponding sulfonyl chlorides with sodium sulfite. The water content of the sulfinates was determined by means of potentiometric titration with sodium nitrite (for **2a** and **2b**) or by oxydimetric titration[18] with potassium permanganate (for **2c** and **2d**). The water used in all experiments was demineralized and distilled twice in an all quartz distillation unit.

Spectroscopic Measurements. Ultraviolet (UV) spectra (25.0 °C) were measured on a Zeis PMQ II spectrophotometer using 2-cm quartz cells (10–12 mL). The sulfinate concentration was kept constant at 10^{-3} M for all series and the CTAB concentration was varied by adding up to 100 μL of a concentrated (0.1 M) solution of CTAB containing 10^{-3} M sulfinate. The NMR spectra were recorded on a Varian XL-100 spectrometer (probe temperature 34.6 °C) locked on the HOD signal. All samples were D_2O solutions (5 mL) containing 10 μL of H_2O in a 12-mm probe. The sulfinate concentration was 2×10^{-2} M in all cases and the CTAB concentration was varied between 0 and 0.1 M.

Kinetic Measurements. The rate of hydrolysis of **1** was determined by monitoring the change in the absorption at 235 nm. The initial pH of the reaction mixtures was brought to ca. 3.5 by addition of HCl. Pseudo-first-order kinetics were observed for at least 2–3 half-lives. The reactions were carried out in 2-cm quartz cells which were placed in the thermostated (±0.05 °C) cell compartment of a Zeiss PMQ II spectrophotometer.[19] Rate constants were reproducible to within 3%. In the presence of the sulfinates **2c** and **2d,** there was no suitable wavelength for monitoring the hydrolytic reaction. Therefore conductivity measurements were employed by means of a Philips PW 9501 conductivity meter. The accuracy of this method was, however, somewhat less satisfactory (see Table I).

Acknowledgment. The investigations were supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO). We thank Professor G. Challa for stimulating discussions.

Registry No.—**1,** 14894-56-5; CTAB, 57-09-0.

References and Notes

(1) Part 1: J. C. Jagt and J. B. F. N. Engberts, *J. Am. Chem. Soc.*, **99,** 916 (1977).
(2) (a) E. H. Cordes and R. B. Dunlap, *Acc. Chem. Res.*, **2,** 329 (1969); (b) E. J. Fendler and J. H. Fendler, *Adv. Phys. Org. Chem.*, **8,** 271 (1970); (c) C. A. Bunton, *Prog. Solid State Chem.*, **8,** 239 (1973); (d) E. J. Fendler and J. H. Fendler, "Catalysis in Micellar and Macromolecular Systems", Academic Press, New York, N.Y., 1975.
(3) A. Bruggink, B. Zwanenburg, and J. B. F. N. Engberts, *Tetrahedron*, **25,** 5655 (1969).
(4) J. B. F. N. Engberts, H. Morssink, and A. Vos, *J. Am. Chem. Soc.*, **100,** 799 (1978).
(5) D. de Filippo and F. Momicchioli, *Tetrahedron*, **25,** 5733 (1969).
(6) R. F. Rekker, "The Hydrophobic Fragmental Constant", Elsevier, Amsterdam, 1977, pp 350–355.
(7) S. Riegelmann, N. A. Allawala, M. K. Hrenoff, and L. A. Strait, *J. Colloid Sci.*, **13,** 208 (1958).
(8) L. Sepulveda, *J. Colloid Sci.*, **46,** 372 (1974).
(9) J. C. Eriksson and G. Gillberg, *Acta Chem. Scand.*, **20,** 2019 (1966).
(10) C. A. Bunton, M. J. Minch, J. Hidalgo, and L. Sepulveda, *J. Am. Chem. Soc.*, **95,** 3262 (1973).
(11) C. A. Bunton and M. J. Minch, *J. Phys. Chem.*, **78,** 1490 (1974).
(12) W. Breemhaar and J. B. F. N. Engberts, *J. Org. Chem.*, **43,** 3618 (1978).
(13) The fact that during our kinetic runs constant values for k_{obsd} are obtained should be rationalized in terms of compensation effects in the second and third term in the expression for k_{obsd} (see ref 1). Moreover, k_{obsd} values were largely obtained for the second half of the reaction, so that [product] is not too different from the final product concentration.
(14) As done before, we assume that the pK_A of the rather hydrophobic sulfinic acids[4] **2a–d** is decreased by 0.5 pK_A unit as a result of binding to CTAB micelles. No correction is applied to the pK_A of formic acid and butyric acid; compare ref 11.
(15) I. V. Berezin, K. Martinek, and A. K. Yatsimirskii, *Russ. Chem. Rev.* (*Engl. Transl.*), **42,** 787 (1973).
(16) C. A. Bunton and M. McAneny, *J. Org. Chem.*, **42,** 475 (1977).
(17) E. F. J. Duynstee and E. Grunwald, *J. Am. Chem. Soc.*, **81,** 4540, 4542 (1959).
(18) B. Lindberg, *Acta Chem. Scand.*, **17,** 383 (1963).
(19) All rate constants in this paper pertain to reactions in unstirred solutions (compare ref 1).

Mechanism of Azo Coupling in Nonpolar Media

Pedro N. Juri and Richard A. Bartsch*

Department of Chemistry, Texas Tech University, Lubbock, Texas 79409

Received July 28, 1978

The coupling of aryldiazonium cations with activated aromatic compounds is one of the most widely studied reactions of organic chemistry.[1] A preponderance of literature on the subject concerns reactions conducted in aqueous or highly polar organic solvents, such as acetonitrile, nitromethane, and nitrobenzene,[2-4] in which arenediazonium salts are soluble. Reports of azo coupling in nonpolar media are rare.[5-7]

Aryldiazonium tetrafluoroborates and hexafluoro phosphates have been solublized in solvents of low polarity by: (1) attaching a lipophilic alkyl group to the aryl ring;[5,6,8] (2) metathetical gegen ion exchange with tetraalkylammonium chlorides to yield the chlorocarbon-soluble aryldiazonium chlorides;[7] and (3) complexation with crown ethers in chlorocarbon solvents.[9,10] The first two methods have been employed to solublize aryldiazonium ions for azo coupling reactions in nonpolar solvents. Thus, Bradley and Thompson[5,6] coupled *p*-decyloxybenzenediazonium tetrafluoroborate with 2-naphthol in benzene in the presence of pyridine. Very recently, Korzeniowski and Gokel[7] treated chloroform-soluble para-substituted benzenediazonium chlorides with *N,N*-dimethylaniline and produced the corresponding azo coupling products.

Mechanistic information concerning azo coupling in sol-

0022-3263/79/1944-0143$01.00/0