Benzophenone azine was found not to react with lead tetraacetate under the conditions used in the previous cases. Starting material was quantitatively recovered in all attempted oxidations even though all the lead tetraacetate had been consumed. It is believed that at 80° the lead tetraacetate would form radicals which could decompose if they did not react with the azine. No obvious reason suggests itself for the lack of reaction of benzophenone azine with lead tetraacetate other than the disruption of the conjugated system.

It is believed that the oxidation of azines **1** and **3** with lead tetraacetate proceed *via* a free-radical mechanism. First, no reaction occurs with either azine **1** or **3** at room temperature but the reaction does proceed nicely at 80°; secondly, the formation of the α-acetoxyazine **5** is consistent with a free-radical mechanism since abstraction of the tertiary hydrogen atom would give rise to a rather stable free radical. Such a type reaction would not likely occur in the case of dicyclopropylketazine. It should also be noted that no allylic acetate was isolated in the oxidation of azine **1**. It was also noted that the oxidations of these azines required somewhat more than 1 equiv of lead tetraacetate indicating that some decomposition of the oxidant probably occurs during the course of the reaction.

Experimental Section[4]

Oxidation of Dicyclopropylketazine (1) with Lead Tetraacetate.—To a solution of 20.0 g (0.092 mol) of dicyclopropylketazine[5] in 300 ml of reagent grade benzene was added 85 g (0.163 mol) of lead tetraacetate (85% active). The reaction mixture was heated to reflux for 24 hr. The lead diacetate was then filtered and the excess lead tetraacetate was destroyed by addition of water. The solution was washed several times with water and saturated sodium bicarbonate solution. The benzene solution was then dried over anhydrous sodium sulfate and the solvent was removed with the aid of an aspirator. The residual oil was allowed to sit in the refrigerator overnight. The crystals which formed were washed with cold ethanol to give 12.0 g (42%) of **2**, mp 83–84°. An analytical sample of **2** was prepared by recrystallization from a minimal amount of hot 95% ethanol. The ultraviolet spectrum of **2** had λ_{max}^{EtOH} 360 mμ (ε 34).[6] The infrared spectrum of **2** had strong acetate peaks at 1750 and 1250 cm^{-1} but no azine band at 1610 cm^{-1}. The nmr spectrum of **2** had a sharp singlet at 2.0 ppm, a multiplet of peaks at 1.65–1.20 ppm, and a multiplet at 0.9–0.3 ppm. The relative intensities were 6:4:16, respectively.

Anal. Calcd for $C_{18}H_{26}N_2O_4$: C, 64.65; H, 7.84; N, 8.38. Found: C, 64.47; H, 7.82; N, 8.46.

Oxidation of Diisopropylketazine (3) with Lead Tetraacetate.—To a solution of 20.0 g (0.09 mol) of diisopropylketazine[7] in 300 ml of reagent grade benzene was added 84 g (0.16 mol) of lead tetraacetate (85% active). The solution was heated to reflux for 24 hr. Work-up similar to that previously described afforded a residual liquid which upon cooling in the refrigerator overnight gave 11.0 g (36%) of the bisacetoxyazo compound (**4**), mp 100–101.5°. An analytical sample of **4** was obtained by recrystallization from hot 95% ethanol. The ultraviolet spectrum of **4** had λ_{max}^{EtOH} 355 mμ (ε 21).[6] Its infrared spectrum had strong acetate peaks at 1750 and 1240 cm^{-1} and no azine peak at 1625 cm^{-1}. The nmr spectrum had a septet at 3.1–2.4 ppm, a singlet at 2.05 ppm, and two distorted doublets at 1.3–0.8 ppm. The relative intensities were 4:6:24, respectively.

Anal. Calcd for $C_{18}H_{34}N_2O_4$: C, 63.13; H, 10.01; N, 8.18. Found: C, 63.26; H, 10.14; N, 8.36.

Distillation of the mother liquor obtained in the filtration of **4** afforded 4.1 g (16%) of a yellow liquid (**5**), bp 82–84° (0.25 mm). The infrared spectrum of α-acetoxydiisopropylketazine (**5**) had strong acetate peaks at 1750 and 1245 cm^{-1} in addition to an azine band at 1625 cm^{-1}. The nmr spectrum showed two septets at 3.5–2.4 ppm (due to the two conformations of the azine), an acetate singlet at 2.0 ppm, and a multiplet of peaks at 1.6–0.9 ppm. The relative intensities were 4:3:24, respectively.

Anal. Calcd for $C_{16}H_{30}N_2O_2$: C, 68.04; H, 10.71; N, 9.92. Found: C, 68.19; H, 10.90; N, 10.13.

Oxidation of Benzophenone Azine with Lead Tetraacetate.—To a solution of 10.0 g (0.028 mol) of benzophenone azine in 250 ml of reagent grade benzene was added 14.6 g (0.028 mol) of lead tetraacetate (85% active). The reaction mixture was heated to reflux for 24 hr. A test for lead tetraacetate was weakly positive. Work-up similar to that previously described afforded 9.8 g (98%) of a yellow solid whose infrared spectrum and melting point were identical with that of benzophenone azine.

Registry No.—Lead tetraacetate, 546-67-8; **1**, 15813-18-0; **2**, 15813-21-5; **3**, 15813-19-1; **4**, 15813-20-4; **5**, 15856-54-9.

Acknowledgment.—The authors wish to acknowledge the assistance of the National Science Foundation in providing for departmental use a Cary 14 spectrophotometer, upon which the ultraviolet spectra contained herein were obtained.

(4) Boiling points and melting points are uncorrected. Microanalyses were performed by A. Bernhardt, Mülheim, Germany, and H. Galbraith, Knoxville, Tenn. The spectra were measured on a Cary Model 14 ultraviolet-visible spectrophotometer and a Perkin-Elmer Model 137 double-beam infrared spectrophotometer. The nmr spectra were measured on a Varian Model A-60 spectrophotometer at 60 MHz with tetramethylsilane as an internal standard.

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The Hydrolysis of Some Sodium N-Substituted Sulfamates in Aqueous Perchloric Acid[1]

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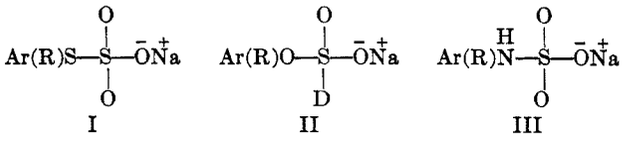
Recently, Kice *et al*,[2] reported that sodium S-alkyl and S-aryl thiosulfates (I) hydrolyze at similar rates in aqueous acid. In contrast, sodium aryl sulfates (II) hydrolyze much faster than sodium alkyl sulfates.[3] This difference has been attributed to increased delocalization of electrons on oxygen into the aryl π system in the transition state for hydrolysis of II compared to its ground state.[4] This effect is presumably absent in hydrolysis of compounds of type I. We wish to report kinetic results that we have obtained on the hydrolysis of the corresponding nitrogen system, the sodium N-substituted sulfamates (III).



I II III

(1) Taken in part from the M.S. Thesis of M. D. Bentley, Auburn University, Auburn, Ala., 1965.

(2) J. L. Kice, J. M. Anderson, and N. E. Pawlowski, *J. Amer. Chem. Soc.*, **88**, 5245 (1966).

(3) S. Burnstein and S. Liberman, *ibid.*, **80**, 5235 (1958).

(4) J. L. Kice and J. M. Anderson, *ibid.*, **88**, 5242 (1966).

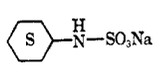
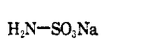
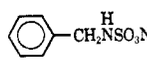
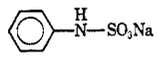
The mechanism of hydrolysis of sulfamic acid proposed by previous workers[5,6] involves rate-determining cleavage of the N–S bond without participation of water (A-1 mechanism). Hydrolysis of the N-substituted sulfamates in aqueous acid by a similar mechanism would then be analogous to the established mechanism[4] for hydrolysis of substituted sulfates and thiosulfates (I and II). On this basis, one might predict that since nitrogen and oxygen are both in period II of the periodic table the reactivity pattern of the sulfamates would more closely resemble that of compounds of type II than type I. This is borne out in the results presented in Table I. The 3100-fold acceleration of sodium N-phenylsulfamate compared with its saturated analog, sodium N-cyclohexylsulfamate, implies a substantial delocalization increase in the transition state for hydrolysis of the former. This is also reflected in the lower (5–6 kcal/mol) activation energy of the aryl sulfamate compared to the alkyl derivatives. The rate acceleration of the sulfamates might be compared with the 500-fold acceleration of $C_6H_5OSO_3^-Na^+$ relative to $CH_3OSO_3^-Na^+$ reported by Kice.[4]

$$\overset{+}{H} + H_2NSO_3^- \rightleftharpoons H_3\overset{+}{N}-SO_3^- \xrightarrow{\text{slow}}$$

$$NH_3 + SO_3 \xrightarrow[\text{fast}]{H_2O,} \overset{+}{N}H_4 + HSO_4^-$$

TABLE I

HYDROLYSIS RATES OF SODIUM N-SUBSTITUTED SULFAMATES IN AQUEOUS PERCHLORIC ACID

Structure	Temp, °C	k, sec^{-1}	k (rel) 99.96°	E_a, kcal/mol
	89.98	7.44×10^{-6}		
	99.96	2.56×10^{-5}		
	109.75	7.53×10^{-5}	1	32.4
	69.85	9.25×10^{-6}		
	80.01	3.42×10^{-5}		
	89.98	1.20×10^{-4}	13[a]	31.5
	80.01	1.24×10^{-5}		
	89.98	4.56×10^{-5}		
	99.96	1.20×10^{-4}	5	30.8
	30.61	2.65×10^{-5}		
	39.23	8.22×10^{-5}		
	48.97	2.94×10^{-4}	3100[a]	25.8

[a] From extrapolated rate data.

The relative reactivity of sodium sulfamate and the sodium N-alkylsulfamates appears to be in the order expected on the basis of inductive stabilization of the N–S bond. Indeed, the σ^* values[7] for these substituents are linearly related to the corresponding log k value ($\rho^* = 3.5$), although any argument based on those several values is obviously tenuous.

Experimental Section

Sodium sulfamate was prepared by NaOH neutralization of recrystallized sulfamic acid.

Sodium N-cyclohexylsulfamate (Abbott, Food Grade) was recrystallized first from dilute aqueous NaOH, then from ethanol–water.

Sodium N-benzylsulfamate and sodium N-phenylsulfamate were prepared by the method of Audrieth and Sveda[8] from the corresponding amines and chlorosulfonic acid. The preparation of sodium N-benzylsulfamate is presented below as an example.

Sodium N-Benzylsulfamate.—To 65.5 ml (0.6 mol) of benzylamine (Eastman, Practical Grade) dissolved in 250 ml of chloroform was added 13.2 ml (0.2 mol) of chlorosulfonic acid (Eastman, Practical) with stirring over a period of 1.5 hr at 0°. The resulting suspension of white solid was suction filtered and the insoluble material dissolved in 20 g (0.5 mol) of sodium hydroxide in 100 ml of water. After evaporation, the resulting sodium N-benzylsulfamate was thrice recrystallized from 75% ethanol to yield 6.50 g of pure material.

Anal. Calcd for $C_7H_8NSO_3Na$: S, 15.33. Found: S, 15.21.

Kinetic Procedures.—All kinetic runs were made in duplicate with solutions of 0.02 M sulfamate in 1.41 M perchloric acid which was prepared by dilution of 60% perchloric acid (J. T. Baker, Reagent Grade). The reactions were followed by titration of sulfate in aliquots of the reaction mixture using the titrimetric method of Archer.[9] All runs were made using the usual sealed ampoule technique except those on sodium N-phenylsulfamate which were conducted in a volumetric flask from which aliquots were removed. All were thermostated to ±0.05° using an oil bath in conjunction with a Sargent Thermonitor temperature control system.

Registry No.—Perchloric acid, 7601-90-3; sodium N-cyclohexylsulfamate, 139-05-9; sodium sulfamate, 13845-18-6; sodium N-benzylsulfamate, 15790-83-7; sodium N-phenylsulfamate, 15790-84-8.

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Dihydroacridizinium Salts[1]

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Reduction of acridizinium compounds both catalytically[2,3] and by means of sodium borohydride[3] has been previously described. In both cases reduction occurred in the quinolizinium portion of the molecule to produce benzoquinolizidines. It appeared to be of interest to study reduction under different conditions to determine whether a product could be obtained in which reduction was less complete. When a 10% Pd–C catalyst was substituted for the platinum oxide[2,3] previously employed, absorption of hydrogen at atmospheric pressure by acridizinium bromide decreased sharply after the consumption of 1 molar equiv. The colorless product which showed no significant ultraviolet absorption above 262 mμ was assigned the structure of 6,11-dihydroacridizinium (1) bromide. Acridizinium salts with substituents at the 6 and 11

(1) This research was supported by a grant (CA-05509) from the National Cancer Institute of the National Institutes of Health.
(2) C. K. Bradsher and L. E. Beavers, *J. Amer. Chem. Soc.*, **77**, 4812 (1955).
(3) C. K. Bradsher and N. L. Yarrington, *J. Org. Chem.*, **25**, 294 (1960).