drogen bridging between the two equatorial and vicinal amino groups is not optimal.

The inability to detect, in general, intramolecular general-base-catalyzed aminolysis in the case of I[5] finds a possible explanation in the lessened efficiency of catalysis in this system as compared to IVa. Inspection of Figures 9 and 10 reveals that the efficiency of intramolecular general-base-catalysis over simple nucleophilic attack increases as the basicity of the nucleophile decreases. This of course is as expected. The lines of Figure 10 intersect at pK_a of the base $\cong$ 12 so that for primary and secondary amines of pK_a greater than *ca.* 12 intramolecular general-base catalysis should give way to simple unassisted nucleophilic attack. The data of St. Pierre and Jencks[5] reveal that no significant catalysis is present in the reaction of I with basic amines including hydroxylamine (pK_a = 6). Thus, in terms of Figure 9 a similar plot for I (and *p*-carboxyaspirin) would require that the line correlating intramolecular general-base catalysis intersect the line correlating unassisted nucleophilic attack at about a pK_a (of attacking amine) of 5–6 or lower (the point of intersection is not clearly definable due to the fact that relatively few amines were studied). This represents an unusual situation since in I and IVa the base strengths of the intramolecular bases are similar, yet ester IVa appears to be a great deal more efficient than I in catalyzing its reaction with amines. A possible explanation may lie in the nature of the solvation shells of the amine and carboxylate groups. The greater water solvation of the anionic carboxylate group in I could presumably result in the enhanced reaction with H_2O due to intramolecular general-base hydrolysis, and could also inhibit the intramolecular carboxylate-catalyzed reaction of I with nucleophiles that must first penetrate the aqueous solvation shell as in aminolysis. Alternatively, the difference in the susceptability of primary and secondary amines to intramolecular general-base-catalyzed aminolysis of I and IVa may reside in the fact that the mechanism for IVa is actually that of path b of Scheme III. We may only state that this alternative does not appear to be supported by presently existing experimental data.

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Solvolysis of Five-Membered Sultones. Methods for Determining the Intermediacy of Carbanions in the Hydrolysis of Esters with Labile α-Protons

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Abstract: We have examined the question whether carbanions and/or sulfenes are reactive intermediates in the alkaline hydrolysis of labile five-membered sultones which have readily ionizable α-protons. The pK_a values for the ionization of these protons in the compounds studied are above 14. We have developed several general methods for carbon acids with pK values greater than 14 which enable us to conclude that mechanisms involving carbanion intermediates do not appear to be the predominant pathways by which five-membered cyclic sulfonates hydrolyze. We believe therefore that the large rate enhancements we have observed for the alkaline hydrolyses of these compounds relative to their open-chain analogs reflect the differences in the rates of attack of hydroxide ion at the sulfur atoms in the cyclic and acylic systems.

The hydrolysis of catechol cyclic sulfate (I) shows an enormous rate acceleration in alkaline solution compared to that of the acyclic analog, diphenyl sulfate (II).[3] From measurements in oxygen-18-enriched media it has been demonstrated that the observed rate acceleration reflects the difference in the rates of attack of hydroxide ion at the sulfur atoms in a five-membered cyclic sulfate and an open-chain sulfate.[4] A large rate enhancement for the hydroxide-catalyzed hydrolysis of the five-membered sultone, *o*-hydroxy-α-toluenesulfonic acid sultone (III), relative to that of the open-chain compound, phenyl α-toluenesulfonate (IV), also has been found.[5,6] However, in the case of the sulfonate esters, III and IV, hydrolytic mechanisms which do not involve the direct attack of hydroxide ion at sulfur must be considered. Specifically, the mechanisms outlined in eq 1 and 2 where carbanions and/or sulfenes may be reactive intermediates in the hydrolytic pathway can be proposed.[7] Recently, mechanisms analogous to eq 1, involving either isocyanate[8] or ketene[9] intermediates, have been suggested as the pathways for the alkaline hydrolysis of certain esters pos-

(1) Predoctoral Fellow of the National Institutes of Health.
(2) Fellow of the Alfred P. Sloan Foundation.
(3) E. T. Kaiser, I. R. Katz, and T. F. Wulfers, *J. Amer. Chem. Soc.*, 87, 3781 (1965).
(4) E. T. Kaiser and O. R. Zaborsky, *ibid.*, 90, 4262 (1968).
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(6) E. T. Kaiser, K. Kudo, and O. R. Zaborsky, *ibid.*, 89, 1393 (1967).
(7) The intermediacy of sulfenes in the solvolyses of some sulfonyl halides has been established by studies done in deuterated solvents; see W. E. Truce, R. W. Campbell, and J. R. Norell, *ibid.*, 86, 288 (1964); 88, 3599 (1966); J. F. King and T. Durst, *ibid.*, 86, 287 (1964); 87, 5684 (1965).
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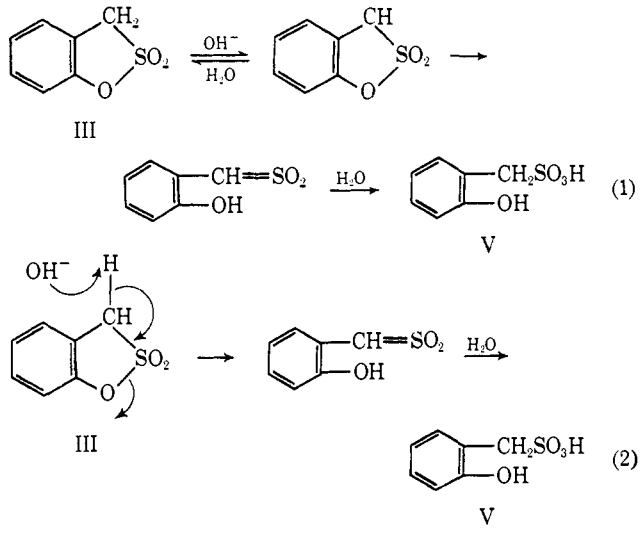


sessing readily ionizable protons adjacent to the carbonyl function.

In a very recent communication[10] Tobias and Kezdy have reported an experimental approach to determining whether a mechanism like that given in eq 1 applies to the alkaline hydrolysis of 5-nitrocoumaranone, a lactone with labile α-protons which undergo ionization with a pK_a of 9.8. This approach is limited to cases in which the carbon acid is fully ionized at an alkalinity accessible in aqueous media. In the present paper several general methods will be described which can be used in those cases where the pK_a of the carbon acid is equal to or greater than 14. In order to test the reliability of these methods we have applied them to reactions where preliminary evidence[6] already indicated that carbanions are not intermediates in the alkaline hydrolysis of an ester. Specifically, we have employed these methods in studying the alkaline hydrolysis of certain sultones.[11]

Experimental Section

Compounds. The preparation of *o*-hydroxy-α-toluenesulfonic acid sultone has been described already.[5] 2-Hydroxy-3,5-dinitro-α-toluenesulfonic acid sultone was obtained as a gift from Dr. K. W. Lo. Reagent grade materials were used in all experiments. 1,4-Dioxane (Baker Analyzed Reagent) used in kinetic experiments was freshly distilled from lithium aluminum hydride.

Physical Measurements. An AEI MS 9 mass spectrometer was used for the mass spectral measurements. Nmr spectra were determined on Varian A-60, A-60A, or A-56/60 spectrometers. Ultraviolet spectra were recorded on a Cary 15 instrument. Some kinetic measurements were made with a Beckman DU spectrophotometer. pH values were measured with a Radiometer Type 4 pH meter equipped with a type C electrode.

Deuterium Exchange Measurements. The measurements were carried out on sultone solutions in 66.6% dioxane–deuterium oxide. Tris buffers were used. Variation in the Tris concentration from 0.033 to 0.10 *M* at constant pH had no effect on the rate of hydrogen–deuterium exchange for III.

Hydroxylamine-Catalyzed Reaction of III. The rate of disappearance of III was studied as a function of the hydroxylamine concentration in solutions containing 0.5 *M* sodium perchlorate at 25.0°. A second-order rate constant for the attack of hydroxylamine on the sultone of $3.2 \times 10^{-2}\ M^{-1}\ \text{sec}^{-1}$ was found, using a concentration range of hydroxylamine from 0.025 to 0.1 *M*.

(10) P. S. Tobias and F. J. Kezdy, *J. Amer. Chem. Soc.*, **91**, 5171 (1969). We thank these authors for informing us of their results prior to publication.

(11) In the alkaline hydrolysis of III we observe a first-order dependency for solvolysis on the hydroxide ion concentration up to pH 13.5 which indicates that the pK for the ionization of the labile α-protons in this compound must be above 14.

Results and Discussion

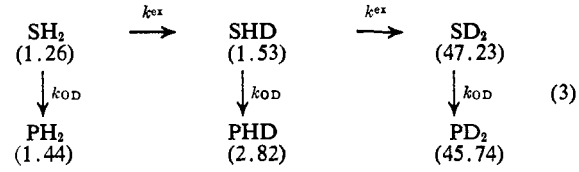
If the exchange of the labile α-protons occurs at a rate which is comparable to the rate of solvolysis of a sultone in deuterated media it is easy to obtain evidence against the mechanism shown in eq 1. For example, mass spectrometric analysis reveals that when 2-hydroxy-3,5-dinitro-α-toluenesulfonic acid sultone is solvolyzed in alkaline 66.6% dioxane–deuterium oxide solutions as much as 50% unlabeled product acid can be isolated. Obviously, for the dinitro-substituted sultone a very substantial portion of the product obtained must be formed without the intervention of a carbanion intermediate.

In instances where the α-protons exchange considerably more rapidly in deuterated media than solvolysis proceeds we have devised two methods to test whether carbanions are formed as reactive intermediates. Both methods have been used in studying the hydrolysis of III.

In one approach we have combined measurements by nmr spectroscopy on the rate of hydrogen–deuterium exchange in III with measurements on the susceptibility of III to nucleophilic attack. We have found that hydrogen–deuterium exchange proceeds 27 times faster than deuterolysis of the sultone in 66.6% dioxane–deuterium oxide at 37°. This observation indicates that if eq 1 applies for the hydrolysis of III, proton abstraction must not be rate limiting. We know that the rate-limiting step for eq 1 cannot be the breakdown of a sulfene species because by stopped-flow spectrophotometric observations over a wide pH range up to pH 13.5 we have not found any evidence for the buildup of such an intermediate. Therefore, if eq 1 operates we must make the hypothesis that the rate-controlling step is the breakdown of the carbanion intermediate to the sulfene. Since the breakdown of the carbanion is a unimolecular step this hypothesis leads to the prediction that the addition of nucleophiles at a given pH will not affect the rate of reaction of the sultone. However, we have found that various nucleophiles such as hydroxylamine greatly accelerate the rate of decomposition of the sultone III. Thus, eq 1 cannot accommodate our experimental results.

The other approach we have used to explore the question, whether it is necessary to postulate the mechanism for the hydrolysis of III illustrated in eq 1, involves a quantitative mass spectrometric analysis of the product and the starting sultone isolated from a partial solvolysis of III in 66.6% dioxane–water. This analysis reveals what appears to be, at first, a complex result. The recovered sultone and the product formed contain undeuterated, monodeuterated, and dideuterated material. We have found that our observations can be readily interpreted by the postulate that a fast equilibration of the methylene protons of the starting sultone with the labeled solvent takes place and that solvolysis occurs only from the nucleophilic attack of the deuterioxide ion at the sulfur atom of a sultone molecule. Equation 3 can be assumed in which SH_2 represents undeuterated starting sultone, PH_2 is the undeuterated product, with the other designations being self-explanatory.[12]

(12) The numbers in parentheses in eq 3 are the experimental percentages of the various isotopic species obtained in a typical experiment involving the hydrolysis of III with 0.5 equiv of sodium deuterioxide in



(3)

We assume that the secondary isotope effects for hydrogen–deuterium exchange and hydrolysis can be neglected. With this assumption the rate constant ratio k_{ex}/k_{OD} can be calculated to be 34.[13] This value agrees well with the value of 27 which we obtained as described earlier in this article. With the assumption of the lack of a secondary isotope effect we can also calculate predicted percentages of PHD and PD_2 which should be obtained, knowing the ratio k_{ex}/k_{OD} and the percentages of SHD and SD_2 found. The values we calculate are 2.75% for PHD and 45.79% for PD_2. Considering our experimental error and the assumption involved in our calculation these values are in excellent agreement with the experimental data we have. Furthermore, according to the pathway assumed in eq 3 it would be expected that the percentage of PH_2 would exceed the percentage of SH_2 and the percentage of SD_2 should exceed that of PD_2. Even with a relatively small proportion of the hydrolysis reaction occurring by a carbanion mechanism such as that shown in eq 1 these relative percentages would be equal or reversed. The results, of course do show that % PH_2 > % SH_2 and that % SD_2 > % PD_2.

Finally, eq 2 can be ruled out as the mechanism of sultone solvolysis since the rate of deuterolysis of III containing deuterium atoms in the methylene group is somewhat faster under comparable conditions than the rate of hydrolysis of unlabeled III in unlabeled solvent. A substantial primary isotope effect would have been expected if eq 2 were correct with the deuterated compound reacting several times slower than the undeuterated one.[14]

From a variety of experimental approaches we conclude that mechanisms involving carbanion intermediates do not appear to be the predominant pathways by which five-membered cyclic sulfonates hydrolyze, as indicated earlier[6] by indirect evidence. The large rate enhancements we have observed for the hydrolyses of these compounds relative to their open-chain analogs must then reflect the differences in the rates of attack of hydroxide ion at the sulfur atoms in the cyclic and acyclic systems just as we have found for the corresponding sulfates. We have demonstrated thus that our methods provide reliable tools to determine whether or not carbanions lie along the reaction pathway in ester hydrolyses.

Acknowledgment. This investigation was supported in part by grants from the National Institutes of Health.

66.6% dioxane–deuterium oxide. In the presence of a large excess of deuterium oxide the deuterium exchange reactions can be treated as irreversible processes. The extent of deuterium incorporation in the hydrolysis products was determined after they were recyclized to the sultone.

(13) The formula used for the calculation is simply k_{ex}/k_{OD} = [100 − % PH_2 − % SH_2]/2(% PH_2): O. R. Zaborsky, Ph.D. Thesis, University of Chicago, 1968, p 136.

(14) From such measurements a k_{OH}/k_{OD} ratio of about 0.7 was obtained: K. Kudo, unpublished results confirmed by W. Berg.

Vinylic Cations from Solvolysis. II. The Stereochemistry of the SN1 Reaction of 1,2-Dianisyl-2-phenylvinyl Halides[1]

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Abstract: *cis*- and *trans*-1,2-dianisyl-2-phenylvinyl bromide and chloride were prepared and their stereochemistry determined. Solvolysis in the presence of benzylthiolate and *p*-toluenethiolate ions in 80% ethanol, chloride ion in acetic acid and in dimethylformamide, and acetate ion in acetic acid gave *cis* and *trans* products derived from capture of the intermediate cation by the nucleophile, in 1:1 ratios. 1,2-Dianisyl-2-phenylethanone is formed on solvolysis in aqueous ethanol, formic acid, and dimethylformamide. Predictions regarding the stereochemistry of the SN1 vinylic substitution are discussed and it is concluded that the product-forming intermediate is a linear sp hybridized dissociated vinyl cation.

Although the interest in vinyl cations is increasing[2-5] many aspects of their chemistry are unknown. An important example is the structure of the cation formed during the solvolysis of vinyl halides or sulfonates.[5] The vinyl cation may be either linear, sp

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