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The Stringent Requirement for Electrophiles in the Facile Solvolytic Hydrolysis of Neutral Sulfate Ester Salts[1]

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The facile desulfation of neutral sulfate ester salts in boiling moist dioxane is well known. The present studies provide evidence that the solvolysis requires initiation by traces of impurities presumably behaving as electrophiles. The surface of a glass containing vessel is adequate to initiate a reaction which is precipitously catalyzed to completion by the acidic products produced. In clean *Teflon* vessels but *not in glass*, 2-octanol (potassium sulfate) (I) and the cholestan-3β-ol analog (II) are stable for prolonged periods in hot moist dioxane, but are almost instantly solvolyzed following addition of almost any trivial potentially acidic contaminant encountered in a laboratory environment. At ambient temperature, dioxane solutions–suspensions of I and II are solvolyzed in less than 1 hr after addition of a trace of H_2SO_4 or other electrophilic reagents.

Sulfate esters of steroids,[2,3] many carbohydrates,[4,5] and simple alcohols[6,7] are notably resistant to hydrolysis in neutral or acidic aqueous systems; however, under appropriate conditions many of these are rapidly solvolyzed in relatively nonpolar, nucleophilic solvents, especially moist (<1% H_2O) ether, dioxane, and tetrahydrofuran. In these solvents, the *free acid esters* desulfate easily at *ambient temperature* while neutral alkali metal salts, with modest exceptions,[2,8] are ordinarily stable.[9]

Ammonium salts (but not sodium salts) of specific sulfatides elaborated by *Mycobacterium tuberculosis* also undergo facile solvolytic hydrolysis at ambient temperature in reagent-grade "anhydrous" ether (H_2O content ~0.005%).[10,11] The principal mycobacterial sulfatide (SL-I) is a complex tetraacyl trehalose-2-sulfate.[12] Studies with these sulfatides led us to the inference that alkali metal sulfate ester or sulfatide salts in general should ordinarily be stable in ether solvents, that a trace of mineral acid or appropriate electrophile should *initiate* solvolysis, and that the reaction would accelerate to completion, since each desulfation event generates a strongly acidic anion (HSO_4^-). For various salts of the mycobacterial SL-I, these deductions were verified.[11]

In earlier studies of steroid sulfate esters Burstein and Lieberman concluded that the species undergoing reaction is the free steroid hydrogen sulfate, and offered a probable mechanism as reproduced in Figure 1.[3] Conclusions of Batts[7] also implicate the zwitterion (of Figure 1) as the reactive species. The proposed mechanisms of our own studies and of Figure 1 have in common the requirement of an intermediate in which the sulfate ester oxygen has accepted a proton (*cf.* also Benkovic[13] and Benkovic and Dunikoski[14]).

It is well known, however, that alkali metal salts of even simple sulfate esters undergo rapid solvolysis in apparently *neutral* ether solvents at elevated temperature, as, for example, in boiling moist dioxane.[8,15,16] In the Haines' group's studies of the sulfatides of *Ochromonas danica*, the solvolysis of (+)-2-octanol (potassium sulfate) as a model compound was examined. Like many steroid sulfatides, it hydrolyzed in minutes in boiling dioxane–1% H_2O (with retention of optical configuration).[16,17] In their interpretation of the reaction, Haines, *et al.*, proposed a quite different mechanistic model in which the water participating in the reaction was assigned a prominent role in hydrating the sulfate core to generate a species proposed as reactive for the nucleophilic solvent (Figure 2). In this interpretation,[18] the intervention of electrophiles or protons is not required—a concept in contradiction with earlier conclusions. The "neutral" conditions of the solvolysis were implicitly advocated as a means of avoiding complications of acidic hydrolysis.[17]

However, reference to this high-temperature transformation as a solvolysis in *neutral* moist dioxane becomes untenable after the initial few desulfation events. The intermediate dioxane–SO_3 complex must be considered

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[1] This investigation was supported by Grant No. AI-08401 of the U. S.–Japan Cooperative Medical Science Program administered by the National Institute of Allergy and Infectious Diseases of the National Institutes of Health, Department of Health, Education and Welfare.

[2] S. L. Cohen and I. B. Oneson, *J. Biol. Chem.*, **204**, 245 (1953).

[3] S. Burstein and S. Lieberman, *J. Amer. Chem. Soc.*, **80**, 5235 (1958).

[4] J. R. Turvey, *Advan. Carbohyd. Chem.*, **20**, 183 (1965).

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[7] B. D. Batts, *J. Chem. Soc. B*, 547 (1966).

[8] J. McKenna and J. K. Norymberski, *J. Chem. Soc.*, 3889 (1957).

[9] The reported ambient-temperature solvolysis of certain apparently neutral steroid sulfates[2,8] may result as a consequence of anchimeric participation of unsaturated functions in appropriate positions, although such participation is contradicted from studies of Burstein and Lieberman.[3] It cannot yet be ruled out that infinitesimal acidic impurities may account for the instability.

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[11] M. B. Goren, *Lipids*, **6**, 40 (1971).

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[14] S. J. Benkovic and L. K. Dunikoski, Jr., *Biochemistry*, **9**, 1390 (1970).

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[16] T. H. Haines, *Progr. Chem. Fats Other Lipids*, **11**, 299 (1971).

[17] G. L. Mayers, M. Pousada, and T. H. Haines, *Biochemistry*, **8**, 2981 (1969).

[18] Respecting Figure 2, Mayers, *et al.*,[17] and Haines[16] suggest that a hydrated complex in which the water molecule is bonded to two negatively charged oxygens (rather than as in the reactive complex postulated) would have greater stability. However, this would not lead to the desired products on attack by the solvent. It was suggested therefore that the "heat required for the reaction is necessary to provide the initial reacting species" as formulated in Figure 2.

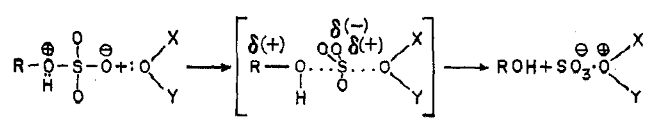

Figure 1.—Mechanism of Burstein and Lieberman for solvolysis of hydrogen sulfate esters.

an electrophile, and hydrolyzes with facility in the moist reaction medium to yield the strongly acidic $KHSO_4$. The reaction mixture therefore quickly assumes the (predictable) character of the acidic low-temperature reaction with the possible disadvantages conferred by the now unnecessary high temperature. Nevertheless, the reaction unquestionably is *initiated* in an apparently neutral system—a seeming paradox which we have sought to resolve in the present study. Beyond this we wished to test in simpler systems our earlier observations that salts of mycobacterial sulfatides which are stable in ether solvents may be gently and completely solvolyzed at ambient temperature following the addition to the stable system of minute amounts of electrophilic reagents.[11]

Results and Discussion

We prepared purified K salts of 2-octanol sulfate (I) and cholestan-3β-ol sulfate (II) for the present studies. These were entirely stable at ambient temperature in moist (<1% H_2O), purified dioxane; however, a gentle, rapid low-temperature desulfation could be initiated with minute traces of appropriate electrophiles—iodine, H_2SO_4, $ZnCl_2$, NH_4Cl, hydrazine sulfate. With precise amounts of H_2SO_4 (0.0025–0.005 equiv relative to sulfate salt) the solvolysis was complete in less than 1 hr (Figure 3). The salt need not be dissolved in the solvent; suspensions are easily desulfated. We conclude that a host of organic sulfate esters, including natural sulfatides, may be effectively hydrolyzed under these gentle conditions without significant degradation such as racemization or inversions, hydrolysis of glycosidic linkages, etc. (*cf.* ref 10, 11, 19–21). The methodology therefore recommends itself for synthesis and for structural investigations.

Solvolysis at High Temperature.—Respecting solvolysis at elevated temperatures we confirmed that I and II solvolyzed in minutes in moist dioxane when heated in glass vessels near the boiling point (as little as 2 min for I). However, our evidence suggests that, under these vigorous conditions, a multiplicity of contaminants can function to *initiate* the desulfation, which then progresses precipitously to completion (in seconds) owing to the acidic product(s) generated: $KHSO_4$, a protonated dioxane–SO_3 complex (?); a dioxane–H_2SO_4 complex (?).[22] Trace contaminants on the surface of even diligently cleaned glass containing vessels (or perhaps the glass surface itself) seem the most notable culprits. On the other hand, both I and II may be held near reflux in moist dioxane for prolonged periods (as long as 2 hr for I under ideal circumstances) in clean Teflon vessels and recovered unchanged: the reaction mixture remains neutral, and the salt merely recrystallizes from the cooled solvent.[23]

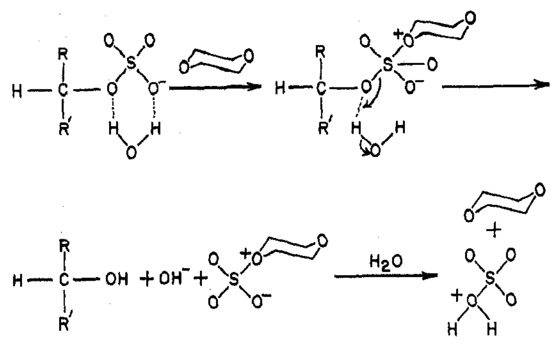

Figure 2.—Proposed mechanism of Haines for solvolysis in neutral dioxane.

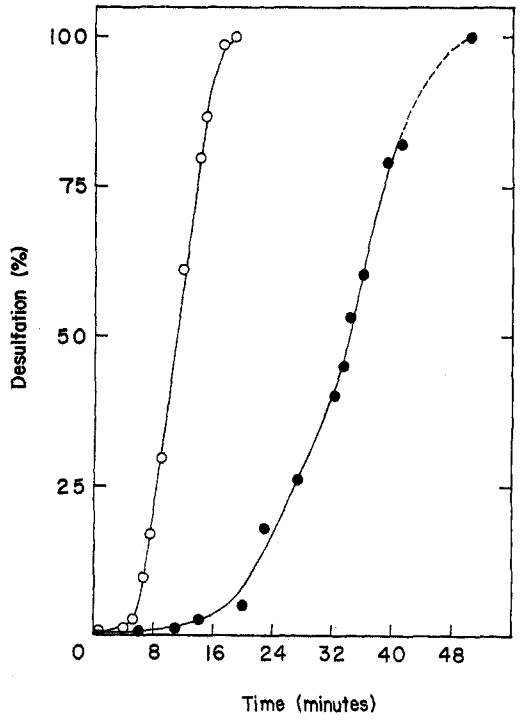

Figure 3.—Solvolysis of potassium sulfate esters in dioxane under acid catalysis: open circles, potassium 2-octyl sulfate ($H^+ \cong 0.25$ mol % with respect to salt); closed circles, potassium β-cholestanyl sulfate ($H^+ \cong 0.5$ mol %).

The rationale for the experimental approach anticipated that, if the sulfate salt is contaminated by even undetectable quantities of sufficiently acidic material, these would detrimentally affect the prolonged stability of the sulfate esters even at ambient temperatures.

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(19) A. J. Hancock and M. Kates, *J. Lipid Res*, in press.

(20) T. G. Kantor and M. Schubert, *J. Amer. Chem. Soc.*, **79**, 152 (1957).

(21) P. Stoffyn and A. Stoffyn, *Biochim. Biophys. Acta*, **70**, 218 (1963).

(22) The "explosive" behavior which characterizes the desulfation in the experiments described, and which was seen in numerous other experiments not reported here, led us to consider the possible intervention of (transient) intermediates generated by the reaction itself, more potent in catalyzing the solvolysis than hydrated or solvated protons. Although we have no evidence in support of its existence, we speculate that a dioxane–SO_3 complex which is protonated on one of the SO_3 oxygens (or a dioxane–H_2SO_4 complex) might have such characteristics—stemming from the combined nucleophilic and electrophilic properties, which may allow participation in a concerted attack on the ester. These species would also regenerate themselves as well. Although the former protonated complex is entirely speculative, a dioxane–H_2SO_4 complex of appropriate structure is firmly established [Y. K. Syrkin and K. M. Anisimova, *Chem. Abstr.*, **42**, 6593 (1948)]. Similar complexes of dioxane with $HClO_4$ and H_3PO_4 are known.

(23) During this stable period we were unable, in numerous experiments, to detect any measurable amount of solvolysis products, *e.g.*, $KHSO_4$ or any released alcohol (by gas chromatography). If heating is prolonged sufficiently, invariably a sudden desulfation occurs, the reaction being completed in a few seconds. Since our studies show that nanogram amounts of, *e.g.*, H_2SO_4 or $HClO_4$ initiate almost instantaneous desulfation when added to such hot stable systems, it is possible that the "stable period" involves an immeasurably slow solvolysis which eventually produces a *critical* concentration of acidic reaction products, with a resultant cataclysmic completion of the reaction. However, we were unable to obtain any data in support of this interpretation.

Accordingly, extraordinary precautions were taken to mitigate as much as possible against such contaminants. As a point of departure we speculated that the initial desulfation events might simply involve a (probably very slow) hydrolysis at the high temperature. To discriminate against the catalytic influence of the bisulfate which this would generate, the initial high-temperature experiments examined the effects of alkali (KOH) on the solvolytic behavior (in glass). Such alkaline systems were indeed found to be stable, but inordinately subject to abrupt destabilization, *e.g.*, during sampling, removal of the condenser, twisting of the condenser in its joint, insertion of a glass pipet—capricious incidents which made us suspect the possible catalytic intervention of the glass equipment. We therefore examined the reaction in Teflon, first with very small amounts of added alkali, and then in the absence of any added reagents. Completely stable systems were obtained.

Finally, we examined a variety of substances as potential initiators. Hot stable systems in Teflon were almost instantly solvolyzed following the addition of traces of mineral or Lewis acids (nanogram amounts of H_2SO_4 or $HClO_4$ as dilute solutions, salts of Zn or Fe; pyridine–SO_3 complex; precipitated $KHSO_4$ from a previous solvolysis) by apparently "neutral" salts such as $MgSO_4$; sulfur dust, $Na_2S_2O_3$, $Na_2S_2O_4$, citrazinic acid; and, *ad absurdum*, dust from laboratory surfaces. Many substances were inactive: Na_2CO_3, KOH, $NaHCO_3$, 2-pyridone, 2-aminopyridine, isonicotinic acid, acetic acid, 2,4-dichlorophenol, quinhydrone, and pyrogallol. Some were selected to assess possible functionality as both electrophile and nucleophile,[22] others simply because of acidic properties. We can only speculate that dichlorophenol and acetic acid were ineffective initiators because they are too weakly acidic under the specific conditions (acetic acid is principally dimeric in hot dioxane[24]).

Many of the initiators are clearly electrophiles. Others may simply provide solid surfaces that act catalytically to initiate the reaction. We infer, however, that the function is merely *initiative*, and that the reaction then progresses almost explosively owing to the catalytic influence of the geometrically increasing acidic product(s) of the hydrolysis. Although water in excess of about 2% dramatically inhibits the solvolysis,[15-17] a sudden initiation, *e.g.*, with traces of citrazinic acid, pyridine–SO_3, or nanogram quantities of H_2SO_4 in dioxane, effects immediate and quantitative desulfation in systems containing as much as 7% H_2O.[22] We hope to incorporate the results and implications of the latter studies in a subsequent, brief communication.

From our observations we conclude that the high-temperature solvolysis has an absolute requirement for an initiator, presumably behaving as an electrophile, the reaction then progressing almost instantaneously owing to the acidic products generated—and that a facile "neutral" solvolysis as proposed earlier[16,17] is untenable.

Experimental Section

Dioxane was employed almost exclusively in the solvolytic experiments. Baker's reagent grade dioxane was purified according to the method of Hess and Frahm[25] (*cf.* Fieser and Fieser[26]), and finally refluxed for several hours with either Na, $LiAlH_4$, or CaH_2 and distilled. The H_2O content as estimated from examination of the infrared band at 1640 cm^{-1} and comparison with standard samples was below 0.1%. Experiments were performed with this solvent and stable systems in Teflon obtained at high temperature; more often small amounts of water (usually about 0.4–0.5%) were added to aid in dissolving the sulfate ester salts.

2-Octanol (potassium sulfate) (I) was prepared by modification of the procedure described by Mayers, *et al.*[17] The product was recrystallized from absolute ethanol or butanol: it sinters at 165°, foams at 175°, and gives a clear melt at 182°. *Anal.*[27] Calcd for $C_8H_{17}SO_4K$: C, 38.71; H, 6.85; K, 15.74. Found: C, 38.55; H, 6.87; K, 15.8.

Cholestan-3-β-yl potassium sulfate (II) was prepared both by reaction of cholestan-3-β-ol with chlorosulfonic acid in dioxane and by reaction with pyridine–SO_3 complex followed by metathesis.[8] The products were recrystallized several times from hot methanol containing about 3% H_2O. Only the first crops of fine needles which crystallized were collected. The melting point of the vacuum-dried potassium salt depends upon the manner in which it is taken: 234–235° dec, 240–240.5° with gas evolution (reported mp 234–235°,[8] 236°[28]). *Anal.* Calcd for $C_{27}H_{47}SO_4K$: C, 63.98; H, 9.35; K, 7.71. Found: C, 64.37; H, 9.25; K, 8.06.

Equipment.—*All* glassware, precleaned in acid dichromate and washed, and washed Teflon ware were heated in 5–10% aqueous alkali for several hours, exhaustively rinsed with deionized water, wrapped in protective Al foil, and dried. For solvolysis studies in Teflon, we employed Nalgene narrow-mouth "Boston Round" Teflon bottles (4-oz capacity) with fluorocarbon closures.

Methods.—Ordinarily 5–6 ml of dioxane was pipetted into the reaction vessel along with 10–20 μl of deionized H_2O or other reagents dissolved to appropriate concentration. The sulfate salt (40–50 mg) was weighed into a small, clean test tube, which was inserted far into the mouth of the container before the contents were emptied. The reaction vessel with cap or condenser was heated for brief periods with gentle shaking until the salt was in solution and droplets of the dioxane (slightly below its boiling point) were condensing. The vessel was then inserted in a boiling water bath and a stopwatch was started. Solvolysis was recognizable by a sudden turbidity in the clear solution and precipitation of $KHSO_4$. Analysis of these turbid reaction mixtures invariably indicated that solvolysis was complete. Maintenance of clarity was examined so many times as a criterion of stability as to be definitive: many such clear samples, quenched and then analyzed for acidity or, when appropriate, for octanol-2 content (by gas chromatography), were entirely free of either product of solvolysis.

Experiments.—Probably more than 100 solvolyses were examined. A few representative experiments are reported here.

A. Low-Temperature Solvolysis. Catalysis by Electrophiles. 1.—I (193 mg) was suspended in 10.0 ml of dioxane to which 25 μl of H_2O was added and the mixture was stirred (magnetic stirrer) at room temperature. In a period of 6 days the mixture remained neutral. A minute crystal of iodine was added. Within 20 min the suspension of sulfate ester was completely solvolyzed as indicated by titration of the released $KHSO_4$ with standard alkali. Other effective initiators included $ZnCl_2$, $FeCl_3$, mineral acids, and hydrazine sulfate.

2.—The conditions of experiment 1 were duplicated except that 25 μl of 0.02 *N* H_2SO_4 was added instead of water (to 53 mg of I in 15 ml of dioxane). Aliquots were withdrawn at intervals, quenched into 10 ml H_2O, and titrated to the methyl red end point. (The stability of acidified I in such an aqueous mixture was demonstrated in a separate experiment.) The results given in Figure 3 indicate that complete solvolysis occurred in about 18 min.

3.—II (46 mg, 9.13×10^{-5} mol) was suspended in 5 ml of dioxane and stirred at room temperature. After 12 hr the still *neutral* suspension was acidified with 10 μl of 0.05 *N* H_2SO_4 (0.54 mol % H^+ based on II) and 0.1-ml samples were withdrawn peri-

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[24] S. Fenéant-Eymard, *Chem. Abstr.*, **48**, 7399 (1954).

[25] K. Hess and H. Frahm, *Ber.*, **71**, 2627 (1938).

[26] L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Wiley, New York, N. Y., 1967, p 333.

[27] Analyses by Huffman Laboratories, Lakewood, Colo. We thank Donald Papineau for potassium analysis.

[28] A. E. Sobel and M. J. Rosen, *J. Amer. Chem. Soc.*, **63**, 3536 (1941).

odically, quenched as in the preceding experiment, and analyzed. The solvolysis of the acidified K salt suspension was complete in less than 1 hr (Figure 3).

B. Solvolysis at High Temperature (in Glass Vessels).—I (50 mg), 6 ml of dioxane, and 18 μl of H_2O were mixed in a 10-ml Bantam ware flask fitted with a condenser. The mixture desulfated before it had reached maximum temperature on top of a steam bath. In many such experiments solvolysis occurred within 2–4 min. The solvolysis in glass could be prevented for many hours by 10–20 μl of KOH (8–1 *M*), but only if the reaction mixture was not disturbed (*vide supra*). The aqueous alkali does not dissolve in the dioxane, but merely coats the walls of the flask.

C. Stability at High Temperature in Teflon. 1.—A reaction mixture of 50 mg of I, 5 ml of dioxane, and 20 μl of 8×10^{-3} *M* KOH (<0.001 mol/mol sulfate ester) was heated in a Teflon bottle for intermittent brief periods until the sulfate had dissolved, and thence continuously in a steam cone (96°). This concentration of KOH did not prevent desulfation in glass. After 2 hr, the solution was chilled, sampled, and found not acidic to methyl red; nor was octanol-2 detectable by glc. The solution was transferred to a clean, glass round-bottom flask with condenser and heated on the steam bath. Desulfation occurred in about 3 min.

2.—Experiment C-1 was repeated except that 18 μl of deionized water was substituted for the alkali. The mixture was heated at full steam bath temperature for 1 hr, carefully removed, and allowed to cool and crystallize. The crystalline material was recovered by filtration and washing with cold ethanol, 43 mg, sinters at 165°, begins to foam and melt at 174°, and is complete at 182°, *i.e.*, essentially identical with the starting 2-octanol (potassium sulfate). The mother liquor was neutral.

3.—II (40 mg) in 5 ml of dioxane plus 10 μl of H_2O in a Teflon bottle was heated as above. At 21 min the flask was removed, cooled, and sampled. The material had not dissolved completely and the suspension was not acidic to methyl red. It was reheated for an additional 40 min and now was completely desulfated. The insoluble material was identified as $KHSO_4$ (mp 206–208°); cholestan-3-β-ol (mp 143°) was recovered from the organic phase.

4.—The previous experiment was repeated with 51 mg of II. After 20 min, the flask was removed from the steam bath and chilled. A small sample was tested and found to be not acidic. Water (15 ml) was added to the reaction mixture along with a drop of methyl red. A 30-μl portion of 0.01 *N* H_2SO_4 was more than enough to give an intense red color. Accordingly, solvolysis could not have progressed to even 0.3% of the sulfatide charged. In glass the sulfatide solvolyzed completely in the interval between 6.5 and 7.5 min.

From the preceding experiments (1–4) it is evident that the solvolysis occurs only suddenly—there is no evidence of a slow progression.

D. Initiation of Solvolysis by Trace Materials.—In these experiments stable solutions of 2-octanol (potassium sulfate) (50 mg) in 5–6 ml of dioxane plus 10–20 μl of H_2O were maintained in Teflon in a boiling water bath, usually for 20–30 min, at which time minute amounts of test solids or aqueous solutions were dropped in. Quantities of solids were ordinarily those left on the very tip of a microspatula or a needle-pointed capillary tube after insertion into a bottle of reagent and tapping off excess. Liquids were judged to be about 0.5 μl (*cf.* Results and Discussion).

Registry No.—I, 41209-93-2; II, 41209-94-3.

Substituent Effects in Sulfone Carbanions[1a]

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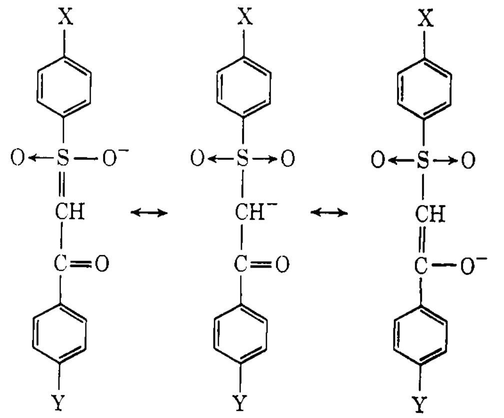
The pK_a's of a series of substituted phenyl phenacyl sulfones (2) were determined. With variation of the phenylsulfonyl substituents, the sulfone acidities followed a linear correlation with σ. The ρ value for this correlation was +2.01, indicating that electron-withdrawing substituents increase sulfone acidity and that this system is very responsive to substituent changes. Since correlation of acidity with σ^+ was not obtained, there is no enhanced resonance interaction between the substituent and the electron-deficient sulfone group. Variation of the phenacyl substituents gave linear correlation of acidity with σ and a ρ value of +2.35. Acidifying effects in the sulfones are considered to be identical with the factors stabilizing the corresponding sulfone carbanions. The large positive ρ indicates that the carbanion is stabilized substantially by pπ–dπ overlap with the sulfur. The magnitude of this stabilization depends upon the electronegativity of the sulfur which, in turn, is determined by the electronic effects of the substituents. The interaction of the substituents through the phenyl ring with the sulfur is principally inductive in nature.

It is well established that the sulfone group can stabilize an adjacent carbanion.[2] Sulfone carbanions have been utilized in numerous syntheses, but there has been no quantitative systematic study of their electronic effects. This study was undertaken to determine the nature and magnitude of such carbanion stabilization. Several resonance structures which can be envisioned for β-carbonyl sulfone carbanions are **1a**, utilizing sulfur d orbitals; **1b**, the carbanion structure; and **1c**, the enolate structure. The magnitude of carbanion stabilization afforded through resonance structures **1a** and **1c** was determined by measuring the acidity of the sulfone precursors. Schwarzenbach and Felder[3] determined the pK_a's (in water) of several sulfones [*i.e.*, $CH_3SO_2CH_2COCH_3$, 10; $(CH_3SO_2)_2CH_2$,



1a **1b** **1c**

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[1] (a) This work was presented in part at the Twenty-third Annual Undergraduate Chemistry Symposium of the Chicago Section of the American Chemical Society, Chicago, Ill., May 1972. (b) Author to whom inquiries should be addressed at Department of Chemistry, Viterbo College, LaCrosse, Wis. 54601. (c) Undergraduate Research Participant.

[2] A. W. Johnson, "Ylid Chemistry," Academic Press, New York, N. Y., 1966, pp 351–352.

[3] G. Schwarzenbach and E. Felder, *Helv. Chim. Acta*, **27**, 1701 (1944).