acid in 200 ml. of dry acetone was added a solution of 14.2 a. (0.2 mole) of pyrrolidine in 200 ml. of dry acetone at 25-35° over a 1-hour period. The clear yellow reaction mixture was heated to the reflux temperature for one hour and the acetone was removed under reduced pressure. The residual yellow oil was dissolved in chloroform (A) and washed with ice-water (B), ice-cold dilute sulfuric acid, and water. The aqueous wash (B), on acidification yielded 8.9 g. of salicylic acid, m.p. 160-162°. A mixed melting point with salicylic acid was not depressed and the infrared spectrum was identical to that of an authentic sample. The chloroform solution (A) was washed with ice-cold sodium carbonate solution which removed an additional 1.2 g. of salicylic acid. The total salicylic acid recovered was 10.1 g. (0.073 mole, 73%). Extraction with ice-cold 0.3 N sodium hydroxide yielded 3.25 g. (13%) of 1-pyrrolidinyl-carbonylmethyl salicylate (XII), identical by mixed melting point and infrared spectrum to the samples of XII prepared by other methods cited in this paper. The chloroform solution containing neutral material yielded 5.6 g. (38%) of chloroacetylpyrrolidine, m.p. 39-45°. Recrystallization several times from *n*-butyl ether yielded an analytical sample, m.p. 44-46° (Kofler block). The low recovery of chloroacetylpyrrolidine is not too surprising since it has an appreciable solubility in water and continuous extraction of all aqueous phases was not used in its recovery.

Anal. Caled. for C. H10CINO: C, 48.82; H, 6.83. Found: C, 48.65; H, 6.41.

Hydrogenolysis of Carbobenzyloxy- β -aminopropionylsalicylic Acid.—A mixture of 22.1 g. (64.5 millimoles) of carbobenzyloxy- β -aminopropionylsalicylic acid, 200 ml. of methanol and 2.0 g. of 5% palladium-on-charcoal was hydrogenated at room temperature at 50–20 p.s.i. The theoretical amount of hydrogen was absorbed in 45 minutes. The amber oil (14.3 g.) was dissolved in ether-ethanol and treated with ethereal hydrogen chloride. A white solid separated from solution, m.p. $104-106^{\circ}$ (6.5 g., 72% based on methyl β -aminopropionate hydrochloride). An analytical sample was prepared by recrystallization from ethanol-ethyl acetate, m.p. $106-107^{\circ}$.

Anal. Calcd. for $C_4H_{10}CINO_2$: C, 34.42; H, 7.22; Cl, 25.40; N, 10.04. Found: C, 34.88; H, 6.94; Cl, 25.38; N, 10.16.

An authentic sample of methyl β -aminopropionate melted at 106–107° and did not depress a mixed melting point with the above compound. The infrared spectra were identical. The filtrate, after collection of the methyl β -aminopropionate, was concentrated to dryness yielding a white solid which after recrystallization from ethyl acetate melted at 155–158°. The infrared spectrum of this inaterial was identical to that of an authentic sample of salicylic acid.

Reaction of Aspirin with Ethyl Alcohol in the Presence of Triethylamine.—Acetylsalicylic acid (90 g., 0.5 mole) and triethylamine (50.5 g., 0.5 mole) were dissolved in 500 ml. of absolute ethyl alcohol and the solution was stored at 25° for 20 hours. The solvent was removed under reduced pressure below 25° and the distillate was collected in a receiver cooled in Dry Ice-acetone. The residue in the distillation flask was dried under reduced pressure yielding 120.4 g. of triethylammonium salicylate (100.5% of theory). The distillate, 500 ml., was analyzed by vapor phase chromatography using helium as the carrier over an "Octoil 5-Celite" column (80" \times 0.25") at 75°. This analysis showed that the distillate contained 44 g. or 9.8% by volume of ethyl acetate (quantitative yield).

Acknowledgments.—The authors are grateful to Mrs. G. S. Fonken and M. Grostic for infrared spectra and to Mr. W. A. Struck and associates for microanalyses.

KALAMAZGO, MICH.

[CONTRIBUTION FROM THE DEPARTMENT OF BIOLOGICAL CHEMISTRY, WASHINGTON UNIVERSITY, SCHOOL OF MEDICINE]

Oxidation-Reduction Potentials, Ionization Constants and Semiquinone Formation of Indigo Sulfonates and their Reduction Products

By PAUL W. PREISLER, EDGAR S. HILL,¹ ROBERT G. LOEFFEL AND PHILIP A. SHAFFER Received October 27, 1958

The oxidation-reduction potentials of indigo di-, tri- and tetra-sulfonates in alkaline buffers have been reinvestigated. The ionization constants of these compounds and their corresponding fully reduced derivatives have been estimated from spectrophotometric measurements. The potentials indicate pronounced semiquinone formation in alkaline solutions of about pH 10.5 to 12.5. The ionization constants derived from the oxidation-reduction potentials are consistent with those estimated from the spectrophotometric data. The results are of importance in the use of the indigosulfonates as indicates in alkaline solutions.

When indigo^{2,3} in alkaline alcoholic solution or indigo disulfonate⁴ in aqueous buffers of about pH 11to 12.5 are reduced by the gradual addition of reducing agent, a red intermediate color appears between the initial blue (or green) of the fully oxidized and the yellow of the reduced compound; on reoxidation the red color appears in the reverse color sequence. Outside this pH zone, the red color is not observed; in less alkaline solutions of the sulfonates,⁴ the color changes from blue, through the green of the mixture, to yellow; in more strongly alkaline solutions, the initial color is a yellow, which on reduction changes to a lighter yellow. As part of their pioneer work on the oxidationreduction potentials of organic substances, W. M. Clark,⁵ and Sullivan, Cohen and Clark⁶ determined the potentials of the indigo systems in various buffers from pH 1.2 to 12.6. Above pH 9, only a single ratio of oxidant to reductant was measured for each buffer and certain discrepancies noted were ascribed to an effect caused by the borate buffers used rather than to some unique property of the substances themselves.

Our reinvestigation of the oxidation-reduction potentials of the indigo sulfonates and their reduced forms and their absorption coefficients, in alkaline buffers of pH 10 to 15, was conducted to find an explanation for the formation of the red intermediate substances.

(5) W. M. Clark, J. Wash. Acad. Sci., 10, 255 (1920).

(6) M. X. Suilivan, B. Cohen and W. M. Clark, U. S. Pub. Health Rep., 38, 1669 (1923).

⁽¹⁾ Deceased.

⁽²⁾ J. Fritzche, J. prakt. Chem., 28, 193 (1843).

⁽³⁾ W. Vaubel, Z. angew. Chem., 14, 892 (1901); A. Farben Textilchem., 1, 229 (1902).

⁽⁴⁾ P. A. Shaffer and P. W. Preisler, Ind. Eng. Chem., News Ed., 11, 236 (1933).

⊅H	Buffer type	Oxid. + Red. molar concn.	Type of titration	<i>E</i> 6' , v.	S v. (from grapbs)	$\begin{array}{c} E_2 - E_1, \\ v. \\ (calcd.) \end{array}$
9.04	Carbonate	0.0002	Ox	-0.193	+0.028	-0.100
9.23	Carbonate	.0001	Ox	203	.028	100
9.63	Carbonate	. 0002	Ox	208	.028	080
9.97	Carbonate	.0002	Ox	218	.031	052
10.00	Carbonate	. 0001	Ox	220	. 031	052
10.35	Carbonate	.0002	Ox	230	. 033	034
10.93	Phosphate	. 0001	Red	249	.041	+ .007
11.18	Phosphate	.0002	Ox	253	.045	.019
11.44	Phosphate	. 0001	Red	264	.048	.028
11.54	Phosphate	.0001	Red	270	. 053	.038
11.79	Phosphate	.0002	Ox	273	.057	.045
11.79	Phosphate	. 0002	Ox	273	. 054	.040
12.14	Phosphate	. 0001	Ox	284	.054	.040
12.20	Phosphate	.0001	Red	287	.058	.046
12.20	Phosphate	.0004	Ox	282	.057	. 045
12.20	Phosphate	.002	Ox	284	.057	.045
12.41	NaOH	.0001	Red	3()()	.066	.050
12.60	NaOH	.0002	Red	← .303	.054	.040
12.68	NaOH	.0001	Red	311	.056	.044
12.97	NaOH	.000 2	Red	327	.042	.010
13.13	NaOH	.0001	Red	333	.041	. 007
13.34	NaOH	. 0001	Red	345	.034	023
13.64	NaOH	.0001	Red	← .361	. 03 3	046
13.68	NaOH	.0001	Red	360	.031	046
13.98	NaOH	.0001	Red	380	.030	063
14.10	NaOH	. 0001	Red	387	.030	063
14.29	NaOH	.0001	Red	397	.030	058

TABLE I EXPERIMENTAL RESULTS AND CALCULATIONS FOR INDIGO DISULFONATE AT 30°

The experimental results of our potential measurements of the indigo disulfonate system (Table I) were subjected to the mathematical analysis developed for the two-step (one equivalent per step) two-equivalent change systems by Elema.⁷

From theoretical considerations, it is evident that the limitation of detectable amounts of red intermediate to within a certain pH zone must be dependent upon the relative ionization constants of the oxidant, reductant and semiquinone. The effect of pH upon the potentials cannot be satisfactorily explained on the basis of the heretofore reported single ionization constant of the oxidant^{8,9} and single constant of the reductant.6

Spectrophotometric measurements have established additional constants (Table II) to those previously estimated.^{5,6,8,9} The intersection of the theoretical slopes of the curves of $E_m - pH$, E_1 pH and $E_2 \rightarrow pH$, for the various ionic species, also located and confirmed these constants (Table II). $(E_m \text{ is also termed } E_0' \text{ in the literature.})$

The data establish conclusively that the red intermediate color is due to semiquinone formation and that neither dimer formation nor the splitting of the indigo molecule into two free radicals can be explanations for the results obtained. Dimer formation is excluded, because the potentials at a particular ρH do not change significantly as the total concentration is changed (Table I); and

(7) B. Elema. Rec. trav. chim., 50, 807 (1931); 50, 1004 (1931); 52, 569 (1933); 54, 76 (1935); J. Biol. Chem., 100, 149 (1933).

(8) W. C. Holmes, THIS JOURNAL, 46, 208 (1924).
(9) W. M. Clark, "The Determination of Hydrogen Ions," 1928; "Topics in Physical Chemistry," Williams and Wilkins Co., Baltimore, Md., 1948

TABLE II

DISSOCIATION CONSTANTS⁴

_	Reductant		Oxidant		Semi- quinone
Colorimetric	pK'_{R_1}	pK′R₂	<i>pK</i> ′01	<i>pK′</i> ₀₁	¢K's
Monosulfonate	7.5	12.4			
Disulfonate	7.5	12.1	12.3	12.8	
Trisulfonate	7.3	12.1	11.7	12.8	
Tetrasulfon ate	7.2	11.8	11.9	12.9	
Potentiometric					
Disulfonate	(7.5)	12.3	12.3	12.7	13.9
Trisulfonate	(7.3)	11.9	11.8	12.5	13.3
Tetrasulfonate	(7.1)	12.0	11.9	12.7	13.6
^a Estimated acc	uracy of	ϕK val	lues: ±	0.2. V	/alues_ii

() taken from reference 11. Values: ± 0.2 . Values in

splitting of the indigo molecule into two free radicals is excluded because the red intermediate of the tri-sulfonate has a characteristic absorption band of its own rather than both the di- and tetrabands (Table III). The related thioindigo tetrasulfonate was found by Preisler and Hempelmann¹⁰ to behave as a two-step system at alkaline pН.

Sullivan, Cohen and Clark⁶ attempted without success to determine the second ionization constant of the reductant by measurement of the potentials at various *p*H of a solution of reductant containing about 14% oxidant. The deviations from the expected theoretical results can possibly be explained by the change in potentials due to semiquinone formation.

Indigo trisulfonate and tetrasulfonate gave potentials and ionization constants in the same (10) P. W. Preisler and L. H. Hempelmann, THIS JOURNAL. 58, 2307 (1937).

TABLE III					
Absorption Maxima and Coefficients of In	DIGO				
SULFONATES					
	n				

	Semi-				
Wave the iength abso of max., coe m _µ (X		e, be molar ssorption pefficient ζ 10 ⁻⁴) mμ		quinone mµ oH 12.5	
⊅ H 7.	0 buffer	80%	ethanol	buffer	
615	1.59	615	2.14	550	
613	2.22	615	2.37	555	
6 0 5	2.38	6 08	2.36	576	
5 90	2.28	599	2.4 0	591	
	Wave length of max., mµ \$	Oxidat Wave the molar absorption of max., pH 7.0 buffer 615 1.59 613 2.22 605 2.38 590 2.28	Oxidant Wave the molar length absorption of max., coefficient mµ (× 10 ⁻⁴) mµ pH 7.0 buffer 80% 615 1.59 615 613 2.22 615 605 2.38 608 590 2.28 599	$\begin{array}{c ccccc} & & & & & \\ \hline & & & & \\ \hline & & & & \\ length & & & \\ of max., & & & \\ ccefficient & & \\ m\mu & & (\times 10^{-4}) & \\ \hline & pH 7.0 & buffer & 80\% & ethanol \\ \hline & & 615 & 1.59 & 615 & 2.14 \\ \hline & & 613 & 2.22 & 615 & 2.37 \\ \hline & & 605 & 2.38 & 608 & 2.36 \\ \hline & & 590 & 2.28 & 599 & 2.40 \\ \hline \end{array}$	

general region as the disulfonate. From the pK' data (Table II) and the $E_{\rm h}$ of the mid-points found for the potential curves at pH 9, where trisulfonate $E_{\rm h} = -0.152$ and tetrasulfonate $E_{\rm h} = -0.111$ volt, the theoretical $E_{\rm m}(E_0') - pH$, $E_1 - pH$, $E_2 - pH$ curves can be constructed. Both tri- and tetrasulfonate showed a greater tendency to decompose than the disulfonate so that the data are less exact.

Data for the sulfonates indicate that the effect of substitution of sulfonic acid groups into the benzene ring of indigo is to increase the $E_m(E_0)$ values at pH 9 by about 0.040 volt for each group. The pK' in some cases do not differ sufficiently to establish any definite order: in general, the pK'decreases as the number of sulfonic acid groups increases.



Fig. 1.—Shift of the absorption band of indigo disulfonate oxidant with pH change.

Except in the region of pH where semiquinone formation produces a noticeable effect (above pH 10), our data confirm the previous work of Sullivan, Cohen and Clark.⁶ Titrations of 0.0001 Mindigo sulfonate in 0.05 M potassium acid phthalate (pH 4.00) gave for $E_m(E_0')$ values, di +0.051, tri +0.091 and tetra +0.125 volt; the former observations⁶ were, respectively, +0.050, +0.092 and +0.125 volt. Our titrations in carbonate buffer of pH 9.00 gave $E_m(E_0')$ of di -0.193, tri



Fig. 2.—Per cent, of un-ionized and ionic species of indigo disulfonate oxidant present at various *p*H.



Fig. 3.—Variation of spectral absorption of the reductants of indigo sulfonates with pH at the wave lengths indicated.

-0.152 and tetra -0.114, which values are in substantial agreement with those calculated by the equation of Sullivan, Cohen and Clark.⁶ using their E_0 and pK_{R_1} data, being, respectively, -0.199, -0.152 and -0.111.

The indigo sulfonates must be used with caution as oxidation-reduction indicators above pH 9, because of semiquinone formation and the several ionizations of the components of the systems.

Experimental

Preparations and Analyses.—The degree of sulfonation of indigo depends upon the amount of excess sulfur trioxide in the fuming sulfuric acid, the temperature and the duration of the period of heating. The procedure of Sullivan, Cohen and Clark⁶ was followed for the disulfonate and the tetrasulfonate. In preparing the trisulfonate by their method, tetrasulfonate principally resulted nuless about onehalf of the amount of fuming sulfuric acid recommended by them was used (grams instead of cc.). After several reprecipitations, well crystallized salts resulted which gave the following analyses for potassium, after drying the sample at 135°, weighing and ashing to potassium sulfate. K found (%), di 15.58, 15.49; tri 18.93, 18.87; tetra 21.12, 21.22: K calculated; di 15.69, tri 19.01, tetra 21.28.



Fig. 4.—Oxidation-reduction potentials E_h of the component systems of indigo disulfonate at various pH.

Potentiometric titrations were made at 30° by the technique previously described.¹⁰ The oxidant in Luffer was titrated stepwise with sodium dithionite, Na₂S₂O₄, in the same buffer, or the reductant with ferricyanide. A saturated KCl calomel reference cell was used with a saturated KCl-4% agar bridge. Approximate corrections for the liquid junction potentials between the bridge and the hydroxide solutions were calculated by Urban and Shaffer¹¹; using the equations of Henderson.¹² and applied to the pHand E_b values. All solutions were deoxygenated and stirred with tank nitrogen purified by passage over hot copper. The buffer system components were: for pH 9 to 10.5, bicarbonate and carbonate; for pH 10.5 to 12.2, dibasic phosphate, tribasic phosphate; and for pH 12.4 and above, sodium lydroxide. Relatively stable reproducible potentials were obtained throughout with the disulfonate; potentials for trisulfonate and tetrasulfonate were less stable except in the extreme alkaline range (pH 12.5 to 14.3). Decomposition was apparently the cause of the instability. The two platinum wire electrodes in the same solution usually agreed to within 0.0002 v. Potentials, E_b , refer to the normal hydrogen electrode. The results and calculations are given in Table I.

Mathematical treatment of the potentiometric data was made by the graphical method developed by Elema⁷ for the two-step two-equivalent systems. A tangent was drawn at the mid-point, E_m (sometimes termed E'_0), of the titration curve. The value of E_h at the intersection of this tangent with the potential (drawn at 100% oxidant and 0% reductant) minus E'_0 was designated S (in volts). The semiquinone formation constant K was calculated from K = $(76.63S - 2)^2$. The theoretical separation of the two steps, oxidant-semiquinone (E_2) , and semiquinone-reductant (E_1) , was found from $E_2 - E_1 = 0.06 \log K$. It follows that $E_2 = E_0' + (E_2 - E_1)/2$ and $E_1 = E_0' - (E_2 - E_1)/2$.

 $(76.63S - 2)^2$. The theoretical separation of the two steps, oxidant-semiquinone (E_2) , and semiquinone-reductant (E_1) , was found from $E_2 - E_1 = 0.06 \log K$. It follows that $E_2 = E_0' + (E_2 - E_1)/2$ and $E_1 = E_0' - (E_2 - E_1)/2$. The E_0' , E_1 and E_2 , values of the indigo disulfonate system were then plotted against pH and an attempt was made to fit these points to the standard theoretical slopes of the $E_m(E_0') - p$ H, $E_1 - p$ H and $E_2 - p$ H curves which were possible on the basis of the heretofore determined ionization constants^{5,6,8,9} of $pK_R' = 7.31$ and $pK_0' = 12.8$. It was apparent that additional ionizations would be required to make the data consistent with the mathematical formulations applying to systems involving semiquinones.

Spectrophotometric measurements were made at various pH with a Bausch and Lomb optical spectrophotometer. Additional ionizations found were one for the oxidant (making a total of two) and one for the reductant (total of two) with a second indicated (total of three). These findings established that there were three changes of slope of the theoretical curves $E_m(E_0') - pH$, $E_1 - pH$ and $E_2 - pH$ within the zone pH 9 to 13, the intersections of these slopes (Fig. 4) locate the pK' which are in agreement with those determined spectrophotometrically.

⁽¹¹⁾ F. Urban and P. A. Sbaffer, J. Biol. Chem., 94, 697 (1932).
(12) P. Henderson, Z. physik. Chem., 59, 118 (1907); 63, 325 (1908).

The oxidants of the indigo sulfonates changed color from blue through green to yellow as the pH was gradually changed from pH 12 to 15. Going from pH 10 to 12, the absorption band in the yellow was replaced by a band in the red extending into the infrared and from pH 12 to 14, as the color changed from green to yellow, the absorption band in the rcd was replaced by one in the violet. Three colored species of the indigo group are involved,

the acid or un-ionized group, the first salt or monobasic ion, and the second salt or dibasic ion.

The form of Beer's Law equation used was $-\log P_e/P_i$ = ϵCl where P_{ϵ} is the emergent power per unit cross section, P_i the incident power, ϵ the molar absorption coefficient, C the concn. in moles/liter and l the length in em. The wave length maxima (Table III) were determined

for the potassium salts in aqueous solution and for 80% ethanol.

The absorption coefficients of indigo disulfonate were determined also for buffers of pH 7.0, 12.5 and 14.7. The wave length at the maxima (Fig. 1) were those used in estimating the amount of the various ionic species plotted (Fig. 2). The proportion of monobasic ion could not be accurately estimated directly because pK'_{01} and pK'_{02} were too close.

The reductants were pale yellow in solutions more acid than pH 4 and, as the pH was increased, they became lighter

yellow, until about pH 9. Further increase caused no noticeable change until beyond pH 10.5, when the solutions became more yellow or orange (Fig. 3), indicating ioniza-tions of about $pK'_{R_1} = 7.5$ and $pK'_{R_1} = 12$. If there were but one ionization in the reductant above pH 10, the ab-sorption curves would become parallel to the pH axis at about pH 14. However, from the shape of the curves, a third is indicated. Because of the possible interference of this third ionization pK'_{T_2} may estimated by a trial and this third ionization, $\rho K'_{R_2}$ was estimated by a trial and error method. A trial $\rho K'_{R_2}$ was chosen and the transmittance of a selected characteristic wave length for the dibasic ion at this pH was assumed to be 50%; the fraction of dibasic ion present at other pH were calculated by dividing the transmittance at a pH by twice the transmittance at the assumed pK'; the results were then plotted and compared to the theoretical ionization curve for the pK'; the pK' was varied until the best fit to a particular theoretical pK' curve was obtained. The final pK'_{R_1} so estimated are given in Table II.

The intermediates were bright red in color and had a narrow absorption band in the green which is easily recognized from about pH 11 to 15. The band shifts toward the red with increasing sulfonation (Table III). The pK' were estimated from the electrometric curves; that for the disulfonate from Fig. 4.

ST. LOUIS, MISSOURI

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF NORTHWESTERN UNIVERSITY]

Sulfonation of Olefins. VIII.¹ Formation of Unsaturated Sulfonic Acids

By F. G. Bordwell and C. Edward Osborne

Received October 8, 1958

The sulfonation of olefins with β - and δ -branches was found to give predominantly unsaturated sulfonic acid. The position of the double bond $(\alpha,\beta$ or $\beta,\gamma)$ in these unsaturated sulfonic acids appears to be determined primarily by steric factors. Evidence is presented to show that the unsaturated sulfonic acids are formed from carbonium-sulfonate or β -sultone intermediates rather than by a one-step concerted mechanism.

The reaction of unbranched olefins such as styrene,² 1-hexene³ or cyclopentene⁴ with an equimolar quantity of dioxane-sulfur trioxide is believed to form a dioxane-solvated carbonium ion (Ia) and/or a β -sultone (Ib). Hydrolysis of sulfonation mixtures containing these intermediates gives largely β -hydroxyalkanesulfonic acids, which can be accounted for as hydrolysis products of Ia or Ib.

$$\begin{array}{c} \text{RCH} = \text{CH}_2 \\ + \\ \oplus \\ \text{OC}_4\text{H}_8\text{OSO}_3 \\ \end{array} \xrightarrow{\oplus} \begin{bmatrix} \text{RCHCH}_2\text{SO}_3 \\ \downarrow \\ \text{OC}_4\text{H}_8\text{O} \end{bmatrix} \rightleftharpoons \begin{bmatrix} \text{RCH} - \text{CH}_2 \\ \downarrow \\ \text{O} \\ \text{OC}_4\text{H}_8\text{O} \end{bmatrix}$$

About 10-20% of unsaturated sulfonic acids are also formed in the above sulfonations, and for styrene^{2a} or 1-hexene³ the proportion of unsaturated sulfonic acid may be increased by heating the sulfonation mixture prior to hydrolysis. The proportion of unsaturated product is also increased for styrene by treatment of the sulfonation mixture with bases, such as pyridine, aniline, sodium methoxide or sodium hydroxide.^{2b} These observations are explicable by postulating E1 and E2 type reactions of the solvent and/or added solvents or reagents with Ia or Ib.

- (3) F. G. Bordwell and M. L. Peterson, ibid., 76, 3952 (1954).
- (4) F. G. Bordwell and M. L. Peterson. ibid., 76, 3957 (1954).

Sulfonation of α -olefins with a β -branch such as isobutylene,⁵ methallyl chloride,⁶ α -methylstyrene,⁷ 2-inethyl-3-phenyl-1-propene⁸ and methylenecyclohexane⁹ gives predominantly unsaturated sulfonic acids. While it is clear from the work described $above^{2-4}$ that these unsaturated sulfonic acids may be formed from intermediates Ia or IIa, a concerted one-step mechanism via a quasi six-membered ring transition state, as suggested by Arnold for sulfonation and chlorination,9 is an attractive alternative. As indicated in the equation

this mechanism would predict the formation of β , γ -rather than α , β -unsaturated sulfonic acids, which is in agreement with most of the recorded data.5.6.8.9 On the other hand, one would expect α,β -unsaturated sulfonic acids to be formed from intermediates such as Ia or Ib since this would allow formation of the conjugated compound (E1

- (5) C. M. Suter and J. D. Malkemus, ibid., 63, 978 (1941).
- (6) C. M. Suter and F. G. Bordwell, *ibid.*, 65, 507 (1943).
 (7) C. M. Suter and W. E. Truce, *ibid.*, 66, 1105 (1944).
- (8) F. G. Bordwell, C. M. Suter and A. J. Webber, ibid., 67, 827 (1946).
- (9) R. T. Arnold and J. F. Dowdall, ibid., 70, 2590 (1948).

⁽¹⁾ For Part VII, see F. G. Bordwell and G. W. Crosby, THIS JOUR-NAL, 78, 5367 (1956).

 ^{(2) (}a) F. G. Bordwell and C. S. Rondestvedt, Jr., *ibid.*, 70, 2429
 (1948); (b) F. G. Bordwell, M. L. Peterson and C. S. Rondestvedt, Jr., ibid., 76, 3945 (1954).