This mechanism is similar to that proposed for the hydration of styrenes,[22] and the same conclusion was reached by Hellin, Gaillard, and Coussemant from their study of the Prins reaction with α-methylstyrene.[16] A mechanism specifically involving a dimer of formaldehyde is not indicated by any of the data.

Experimental Section

Materials.—Chemicals were stored under refrigeration and used without further purification except where otherwise noted. *p*-Methyl-, *p*-chloro-, and *p*-bromostyrene were purchased from Aldrich Chemical Co. Reagent grade styrene and trioxane (>99%) were obtained from Matheson Coleman and Bell. *p*-Methoxystyrene was prepared from 1-(*p*-methoxyphenyl)-ethanol by the method of Brooks.[25]

Solvents were distilled water and 99.85 atom % deuterium oxide (Calbiochem), while the acids were reagent grade sulfuric (>98%) or 99 atom % deuterated sulfuric acid (Stohler Isotope Chemicals).

Apparatus.—The ultraviolet spectral measurements were obtained with a thermally regulated Cary 15 spectrophotometer; the temperature was read (±0.2°) at the sample cell. The sample cell consisted of the usual 10-mm quartz cuvette to which was fused a Teflon stopcock.

The nmr spectral measurements were made in sealed tubes using a Varian A-60 spectrometer in analogy with earlier work.[19−21]

Preparation of Formaldehyde Solutions.—The aqueous and deuterium oxide solutions of formaldehyde were prepared by dilution of a standard formaldehyde–sulfuric acid–water solution or a standard formaldehyde–deuteriosulfuric acid–deuterium oxide solution. These standard solutions were prepared by the depolymerization of trioxane.

All solutions were analyzed for total formaldehyde content using the iodometric method cited by Walker.[26] The acid content was determined by titration with standard base. The densities of the aqueous solutions were taken as equivalent to those presented by Natta and Baccaredda[27] while those of the deuterium

oxide solutions were obtained by extrapolation from the density measurements of Hellin, *et al.*[19]

All solutions were allowed to equilibrate at least 1 week prior to use. Solutions above 20% w/w formaldehyde were maintained above room temperature to prevent precipitation.

Kinetic Measurements.—The reactions were followed by observing the decrease in the π–π* absorption for the styrene and substituted styrene solutions. A typical run was performed as follows: To 10 ml of formaldehyde solution was added 0.1 to 0.2 μl of styrene, and the solution was agitated. Approximately 5 ml of the solution was then transferred to a 13 × 100 mm Pyrex test tube which was sealed and placed in an oil bath for later use as an infinity point sample. The uv sample cell was then filled to a mark with the remaining solution.

The Cary 15 spectrophotometer which had equilibrated for 2 hr at 60.5° ± 0.2° was adjusted using two matched water-filled 10-mm quartz cells to provide a base line of zero at 248 mμ. The instrument was set to a "sync" operation of 50 sec/div. The sample cell was preheated for 2–3 min in a 55–60° oil bath, then cleaned, and immediately transferred to the cell compartment. The disappearance of styrene was followed for at least 1 half-life. The base line was checked with the matched cells at the completion of the run to ascertain instrument stability. After at least 10 half-lives, the contents of the test tube which had been previously placed in the oil bath were cooled, transferred to the sample cell, and allowed to temperature equilibrate. The infinity value was recorded.

The rate constants were calculated using a linear least-squares fit of the integrated form of the first-order rate equation. The rate *vs.* concentration plots and the log rate *vs.* σ+ plots were similarly calculated using a linear least-squares method, assuming variance in the rate constants only. All calculations were performed with an IBM 360, Model 50, computer.

Registry No.—Styrene, 100-42-5; *p*-bromostyrene, 2039-82-9; *p*-chlorostyrene, 1073-67-2; *p*-methylstyrene, 622-97-9; *p*-methoxystyrene, 637-69-4.

(25) L. A. Brooks, *J. Amer. Chem. Soc.*, **66**, 1295 (1944).

(26) J. F. Walker, "Formaldehyde," 3rd ed, Reinhold Publishing Corp., New York, N. Y., 1964, p 480.

(27) G. Natta and M. B. Baccaredda, *Giorn. Chim. Appl.*, **15**, 273 (1933), as cited in ref 26, p 110.

Alkanesulfonate Synthesis. I.
Ion Catalysis of Sulfite Radical-Ion Addition to Olefins

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Certain nitrate salts have unusual, significant, and practical catalytic effects on the selective addition of the sulfite radical ion in the presence of oxygen to unsaturated bonds. Specific cations and anions have selective coinitiation catalytic effects with oxygen on the conversions of olefins into alkanesulfonates. The relative reactivities of homologous 1-alkenes, mixed 1-alkenes, internal *n*-alkenes, branched olefins, monocyclic olefins, bicyclic olefins, dienes, and acetylenes with potassium nitrate catalysis are compared. The competition conversion of hexene isomers indicates a *cis* effect inherent in the olefin activation for addition. The mechanism of the potassium nitrate catalysis and the stereochemistry of the sulfite radical-ion addition are discussed. A mechanism involving (1) the production of sulfite radical ion, directly or indirectly, by nitrate-ion oxidation of sulfite ion, (2) bisulfite ion in the chain-transfer reaction, and (3) termination by sulfite radical-ion oxidation and radical coupling is proposed. The product mixtures containing predominantly 1-alkanesulfonates have been analyzed and characterized. The presence of nitrogen in the organic sulfonate product indicates the incorporation of nitrogen-containing radical species.

Olefin-derived 1-alkanesulfonates have excellent biodegradability and also good surfactant properties[1−4]

and hold promise of new markets for 1 olefins from cracked paraffin wax. They may directly reduce pollution problems and indirectly make more natural fats and oils available for human nutrition. These social and economic considerations, as well as organic chemical interests, make the bisulfite addition to olefins

(1) J. Rubinfeld and H. D. Cross, III, *Soap Chem. Spec.*, **43** (3), 41 (1967).

(2) "Chevron Alpha-Olefins for—Primary Paraffin Sulfonates—Secondary Alkyl Sulfates," Technical Bulletin, Oronite Division, California Chemical Co., Richmond, Calif., 1963.

(3) "Alkane Sulfonate Surfactants," Technical Bulletin 2-4-0664, Esso Research and Engineering Co., Linden, N. J. (about 1964).

(4) M. C. Fuerstenau and J. D. Miller, *Trans. Mining Soc. AIME*, **153** (1967).
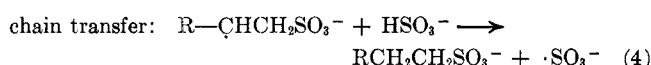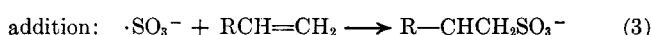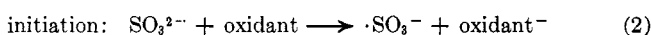
a challenging and attractive reaction for review and research investigation.

The addition of bisulfite to unsaturated bonds is very old[5] in the art, but the reaction is still not well understood.

$$R\text{—}CH\text{=}CH_2 + NaHSO_3 \xrightarrow{\text{radical initiation}} R\text{—}CH_2CH_2SO_3Na \quad (1)$$
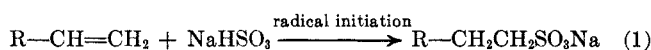
This reaction was reviewed by Kharasch, Mayo, and coworkers[6-8] who established (1) that the reaction requires an "oxidizing agent" for initiation, (2) that the reaction goes anti-Markovnikov giving 1-alkanesulfonate as the major product from 1 olefin, and (3) that the reaction is susceptible to radical-inhibiting reagents.

Mayo and Walling[9] proposed the reaction mechanism outlined below.

initiation: $SO_3^{2-} + \text{oxidant} \longrightarrow \cdot SO_3^- + \text{oxidant}^-$ (2)

addition: $\cdot SO_3^- + RCH\text{=}CH_2 \longrightarrow R\text{—}\overset{\cdot}{C}HCH_2SO_3^-$ (3)

chain transfer: $R\text{—}\overset{\cdot}{C}HCH_2SO_3^- + HSO_3^- \longrightarrow$
$$RCH_2CH_2SO_3^- + \cdot SO_3^- \quad (4)$$

This reaction has received little critical study since the works cited above. The exact nature of the chain-carrying species has not been established since a bisulfite radical could also be involved.[10] Subsequent research has been largely reported in the patent literature.[11-19] Little attention has been given this reaction in subsequent reviews.[20,21]

Investigations in this area have been recently restimulated by the interest in converting readily available commercial 1 olefins into 1-alkanesulfonates, which have good detergent properties[1] and superior biodegradability properties,[2,3] but to date no one has carried this reaction to commercial production.

For practical purposes, the major problem has been to produce the organic sulfonates selectively under conditions which use close to stoichiometric amounts of sodium bisulfite reagent so as to obtain both good sulfonate yields and high sulfonate concentrations (*i.e.*, high activities) in the product mixtures. Initiations with peroxide reagents have been prohibitively expensive and have not been commercialized. Air initiation is often slow and wasteful of bisulfite owing to its by-product oxidation to sulfate. Efforts have been made to improve the rate of reaction, yield, and economics by cosolvents, surfactants, and slow dilute

addition, but these modifications have not been entirely satisfactory.

It is not surprising that the reaction shows some improvement with solvent manipulation since the postulated addition species is a polar radical ion. Russell's[22] investigations of polar effects on radical reactions suggested to us that there might be some promise for specific salt catalysis on the reaction. With this purpose in mind, we undertook an extensive catalyst screening program.

Experimental Section

Reagents.—The sodium bisulfite used was Mallinckrodt reagent grade. 1 olefins were obtained from several sources, but primarily as follows. Propene, 2-methylpentene-1, 2-ethylbutene-1, 2,3-dimethylbutene-2, a mixture of *cis*-hexene-2 and *trans*-hexene-2, cyclohexene, and octene-2 (all of >98% purity) were obtained from the Phillips Petroleum Co. Octene-1, nonene-1, decene-1, undecene-1, dodecene-1, tetradecene-1, hexadecene-1, octadecene-1, eicosene-1, and docosene-1 (all of 95-99% purity) were obtained from the Humphrey Chemical Co.

The norbornene was synthesized from dicyclopentadiene and ethylene by the Diels–Alder addition reaction and fractionally distilled to obtain a cut of >95% purity.

Commercial mixtures of 1 olefins of 85-90% purity were obtained from The California Chemical Co.[23,24]

Reagent grade salts were investigated as catalysts.

Parr Autoclave Reaction Procedure.—The reactions of olefins were carried out in a Parr rocking autoclave apparatus. The 500-ml reaction vessel stopper was equipped with an oxygen inlet line and a glass thermocouple well. A typical procedure given below was used throughout the study.

Sodium bisulfite (21.0 g, 0.20 mol), potassium nitrate (2.2 g, 0.020 mol), 50.0 ml of distilled water, 50.0 ml of 2-propanol, and 1-hexadecene (24.4 g, 0.10 mol, 24.0 ml) were placed in a 500-ml Parr reaction vessel and assembled in the rocking apparatus. All valves were closed and a thermocouple was inserted into the thermocouple well in the rubber stopper which sealed the vessel. The apparatus heater and auxiliary heating jacket were turned on and allowed to warm for approximately 1 hr to 110° and 40-42-psig vessel pressure at equilibrium. The oxygen line pressure was adjusted to equal the equilibrium pressure. The vessel inlet valve was opened, and the applied oxygen pressure was increased to 1.0-2.0 psig in excess of the vessel pressure. The reaction was continued for 3 hr, then cooled.

The following procedure was used for the work-up: (1) the cooled vessel was depressurized by closing the oxygen valve and slowly opening the exhaust tank valve; (2) the cooled reaction mixture was transferred to a separatory funnel and the pH noted, 500 ml of distilled water was added, and the phase was allowed to separate; (3) a measured volume of standardized sodium hydroxide solution was added to adjust the pH to 8 in the aqueous phase; (4) the separated and neutralized aqueous phase was evaporated carefully to near dryness on a hot plate using a controlled air stream; (5) complete drying of the product was effected in a vacuum oven at partial vacuum at 80°; (6) the dried product was deoiled in a Soxhlet extraction thimble in which ether or acetone was refluxed for 4 hr; (7) dried products from steps 5 and/or 6 were submitted for sulfonate analyses, carbon, hydrogen, sulfur, and sodium, and in some cases nitrogen; and (8) recovered hydrocarbons from extraction and phase separation were analyzed by gas–liquid partition chromatography (glpc).

Analytical Procedures.—Glpc analyses confirmed the purity of the olefin reagents used and were used to check the composition of recovered oils.

In our early work ir spectra were used to characterize the alkanesulfonates and to estimate the amounts of sodium sulfate in the alkanesulfonate samples. Spectroscopic analyses for alkanesulfonate by the methylene blue complex absorption in

(5) I. Kolker and A. Lapworth, *J. Chem. Soc.*, **127**, 307 (1925).

(6) M. S. Kharasch, R. T. E. Schenck, and F. R. Mayo, *J. Amer. Chem. Soc.*, **61**, 3092 (1939).

(7) M. S. Kharasch, E. M. May, and F. R. Mayo, *J. Org. Chem.*, **3**, 175 (1939).

(8) R. T. E. Schenck, Ph.D. Thesis, University of Chicago, Chicago, Ill., 1940.

(9) F. R. Mayo and C. Walling, *Chem. Rev.*, **27**, 394 (1940).

(10) C. Walling, "Free Radicals in Solution," John Wiley & Sons, Inc., New York, N. Y., 1957, pp 326–328.

(11) J. H. Werntz, U. S. Patent 2,318,036 (1943).

(12) D. Harman, U. S. Patent 2,504,411 (1950).

(13) C. van Bylandtlaan, British Patent 682,207 (1952).

(14) W. A. Fessler, U. S. Patent 2,653,970 (1953).

(15) E. Clippinger, U. S. Patent 3,084,186 (1963).

(16) E. E. Johnson, U. S. Patent 3,150,169 (1964).

(17) E. Clippinger and R. G. McKee, U. S. Patent 3,168,555 (1965).

(18) W. A. Fessler, U. S. Patent 3,231,606 (1966).

(19) R. T. Adams, E. E. Johnson, and J. M. Salmela, U. S. Patent 3,306,931 (1967).

(20) G. Sosnovsky, "Free Radical Reactions in Preparative Organic Chemistry," The Macmillan Co., New York, N. Y., 1964, pp 89–91.

(21) E. Clippinger, *Ind. Eng. Chem. Prod. Res. Develop.*, **3**, 3 (1964).

(22) G. A. Russell and R. C. Williamson, *J. Amer. Chem. Soc.*, **86**, 2357 (1964).

(23) "Chevron Alpha-Olefins," Technical Bulletin, Oronite Division, California Chemical Co., Richmond, Calif., 1963.
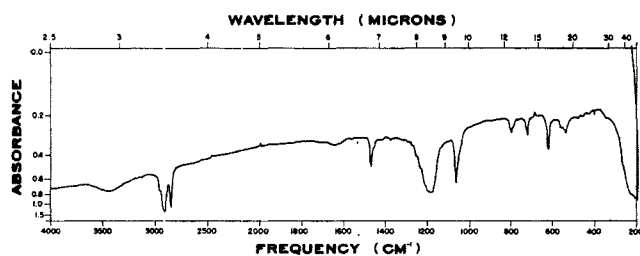
(24) *Oil Gas J.*, **63**, 102 (1965).

Figure 1.—Infrared spectrum of 1-hexadecanesulfonate.

the uv region and by ir absorption were often inconsistent with each other and elemental analyses. A barium alkanesulfonate precipitation procedure or inorganic salt precipitation procedure with methanol, followed by elemental analysis, was developed to characterize better the reaction products.

Calculations.—Olefin conversion based upon unrecovered olefins gives an estimate of the conversion (eq 5). Although

Conversion =

$$\frac{[\text{input olefin vol.} - \text{recovered olefin vol.}]}{[\text{input olefin vol.}]} \times 100\% \quad (5)$$

often given in the literature, this conversion value is subject to errors due to olefin solubilization in the product surfactant solution at high conversion levels and some olefin loss on evaporation in the work-up. Conversions calculated on the basis of weight increase in the dried solid is more reliable, but the vacuum oven-dried sulfonates may contain 1–5 wt % oil. To get precise olefin conversion values, it is necessary to extract the dried product and correct the recovered oil therefrom.

The yield of deoiled alkanesulfonate is calculated from the eq 6.

sulfonate yield =

$$\frac{\begin{bmatrix}\text{total weight of product mixture after drying} \\ \text{and extraction to constant weight} - \text{weight of sodium bisulfite} \\ \text{input (no correction for oxidation to sodium sulfate)}\end{bmatrix}}{\begin{bmatrix}\text{theoretical alkanesulfonate weight calculated for the un-} \\ \text{recovered oil on reaction with the stoichiometric amount of} \\ \text{sodium bisulfite}\end{bmatrix}}$$
$$\times 100\% \quad (6)$$

The sodium sulfate formation would cause only a 5 wt % error in the sulfite weight if all of the bisulfite were oxidized to sulfate at 0% olefin conversion. The error is less at significant conversion levels.

Results

Results of screening a wide range of nitrate salts are summarized in Table I. The estimates of conversions based on the olefin recovery are contrasted with the more reliable conversions calculated by the weight increase of the recovered solid in the third and fourth columns. Theoretical yields were calculated based upon the unrecovered olefin and are valid for relative comparisons.

Table II summarizes results from a study of a variety of potassium salts. These screening conditions of Table II are different from those used for the data of Table I. In the column headed "Product composition," an analysis for the added potassium salt, the unused sodium sulfite, by-product sodium sulfate, and sodium alkanesulfonate is given for several of the products. (The alkanesulfonates are calculated from the organic carbon incorporated in the deoiled solid product. This carbon is assumed to be alkanesulfonate, although small amounts of the carbon may be present as organic by-products.) It is apparent that potassium nitrate gives the highest conversion and yield for production of alkanesulfonate and these results are confirmed by the product analysis.

TABLE I
SALTS SCREENED FOR CATALYSIS OF THE ADDITION OF SODIUM BISULFITE TO 1-DODECENE[a]

Run	Salt added	pH_0/pH_f[b]	Conversion Based on unrecovered olefin, wt %	Based on dried product,[c] wt %	Selectivity, theor yield based on unrecovered olefin,[d] mol
	None	5.4/3.4	24	22.5	86
	A. Cation Effect with Various Nitrates				
1	$Zn(NO_3)_2$, repeated	4.8/3.3, 1.6	55, 54	66.5, 58.4	100, 99
2	$Be(NO_3)_2$	4.9/5.3	48	50.0	95
3	$Bi(NO_3)_3$	4.2/3.0	54	54.8	93
4	$Hg_2(NO_3)_2$	5.4/6.0	49	49.6	92
5	$[Ce(NH_4)_2](NO_3)_6$	2.9/2.2	56	54.0	88
6	NH_4NO_3	5.5/9.6	56	54.0	88
7	$LiNO_3$	5.7/4.7	56	52.4	86
8	KNO_3	5.8/3.6	64	59.9	86
9	$Hg(NO_3)_2$	4.4/1.0	46	43.2	86
10	$Cd(NO_3)_2$	4.9/4.6	61	56.0	85
11	$Fe(NO_3)_3$	4.0/2.0	56	51.8	85
12	$Cr(NO_3)_3$	4.2/1.6	60	54.5	83
13	$Mg(NO_3)_2$	5.0/1.4	52	44.1	78
14	$Pb(NO_3)_2$	5.0/1.4	44	37.4	78
15	$Ni(NO_3)_2$	5.1/1.6	55	46.5	77
16	$AgNO_3$	5.8/3.6	44	35.9	75
17	Arqua[e] 12–50	5.2/1.3	40	32.0	75
18	$NaNO_3$	5.6/8.4	54	43.2	73
19	$Co(NO_3)_2$	5.0/1.9	58	43.5	69
20	$Al(NO_3)_3$, repeated	5.0/3.3, 3.0	Emulsion	51.6, 53.6	50, 61
21	$Cu(NO_3)_2$	4.5/1.0	11	0.0	0
	B. Anion Effects				
22	AgOAc	5.5/5.0	33	29.4	81
23	$AgNO_3$	5.8/3.6	44	35.9	75
24	$Zn(NO_3)_2$	4.8/3.3	55	66.5	100
25	ZnF_2	5.4/2.1	42	40.4	88
26	$Zn(OAc)_2$	5.2/5.7	53	48.3	83
27	$ZnBr_2$	4.9/3.0	50	43.2	79
28	$ZnSO_3$	5.4/5.2	14	11.4	74
29	$ZnSO_4$	5.0/3.1	45	34.5	70
30	$ZnCl_2$	4.8/3.9	20	14.3	66
31	ZnO	5.6/4.4	57	34.1	55
32	ZnI_2	4.8/1.7	6	0.3	5

[a] Conditions: 0.20 mol of $NaHSO_3$; 0.22 mol of 1-dodecene; 0.010 mol of salt; 50.0 ml of H_2O; 50.0 ml of 2-propanol; 1.0 psig of O_2 in Parr vessel at 80° for 2 hr. Product neutralized to pH 8.0. [b] All product mixtures were adjusted to pH 8 with standard base before work-up. [c] According to eq a. [d] According to eq b.

wt % conversion =
$$\frac{\text{solid wt increase, g}}{33.6 \text{ g } (0.2 \text{ mol}) \text{ of } C_{12}H_{24} \text{ theor max wt increase}} \times 100\% \quad (a)$$

mol theor yield =
$$\frac{\text{solid wt increase, g}}{\text{theor wt of } C_{12}H_{25}SO_3Na \text{ for olefin unrecovered}} \times 100\% \quad (b)$$

[e] 50% active solution of dodecyl trimethylammonium chloride.

Superficially, the ir spectra of the recrystallized products obtained by potassium nitrate catalysis with 1 olefins compare closely with spectra of alkanesulfonates in the literature.[25,26] The spectrum of 1-hexadecane sulfonate is given in Figure 1.

Table III summarizes the elemental analysis of a homologous series of alkanesulfonate products obtained using potassium nitrate catalyst.

These alkanesulfonates were isolated from the product mixture by recrystallization from aqueous alcohol solution one or more times. The empirical carbon values are all lower than theory for 1-alkanesulfonates, and the empirical sulfur values and most of the sodium values are higher than theory for 1-alkanesulfonates, suggesting the presence of alkanedisulfonate. This

(25) D. Hummel, "Identification and Analysis of Surface-Active Agents by Infrared and Chemical Methods," E. A. Wulkow, translator, Interscience Publishers, New York, N. Y., 1962.
(26) K. Fujimori, *Bull. Chem. Soc. Jap.*, **32**, 850 (1959).

TABLE II
POTASSIUM SALT CATALYST STUDY[a]

Salt added	pH₀/pH_f	Added salt	Na₂SO₃	Na₂SO₄	RSO₃Na	Conversion based on unrecovered 1-dodecene, wt %	Theor yield based on 1-dodecene input, mol %
			Product composition, wt %				
Blank (none)	4.9/3.8		57.14	30.27	7.0	10	2.9
KNO₃	5.0/2.4	0.58	0.00	26.59	72.12	51	51.3
KNO₂	5.5/3.5	0.00	33.31	52.24	13.15	17	6.2
KNO₂/KNO₃ (50:50)						42 (interpolated 34)	
KBr	4.6/3.4	6.90	10.54	61.86	20.72	25	13.5
KCl	4.8/4.1	5.11	15.37	69.69	9.84	31	4.7
KI	4.4/3.5	11.84	55.86	26.20	4.74	22	1.4
KF	4.8/3.8		43.87	42.65	13.48	13	6.8
K₂SO₄						22	
KOAc						20	
KBrO₃						13	
KSCN						21	
K₂CO₃						34	
K₂HPO₄						19	

[a] Conditions: 0.20 mol of NaHSO₃; 0.20 mol of 1-dodecene; 0.020 mol of salt; 50.0 ml of water; 50.0 ml of 2-propanol; and 2.0 psig of O₂ in Parr vessel with shaking at 110° for 3 hr.

TABLE III
ELEMENTAL ANALYSES OF RECRYSTALLIZED[a] ALKANESULFONATES PREPARED FROM 1-ALKENES[b]

Carbon no.	Conversion, wt %	Yield, mol %		% C	% H	% Na	% S	% N	% O (by difference)
6	100.0	100.0	Calcd	38.29	6.96	12.21	17.04	0.00	25.50
			Found	31.56	5.73	13.19	17.65	0.42	31.45
6 (2-ethyl-1-butyl)	100.0	100.0	Calcd	38.29	6.96	12.21	17.04	0.00	25.50
			Found	37.24	7.05	12.18	17.11	0.26	26.16
8	91.6	92.6	Calcd	44.43	7.92	10.63	14.83	0.00	22.19
			Found	38.75	7.02	11.22	19.82	0.27	22.92
9	95.2	95.7	Calcd	46.94	8.32	9.98	13.92	0.00	20.84
			Found	39.86	7.23	10.84	15.44	0.30	26.33
10	97.8	89.3	Calcd	49.16	8.66	9.41	13.12	0.00	19.65
			Found	47.68	8.51	8.89	12.89	0.39	21.64
10 (repeat)			Calcd	49.16	8.66	9.41	13.12	0.00	19.65
			Found	37.99	7.09	11.99	16.71	0.49	25.73
12	97.7	78.0[c]	Calcd	52.91	9.19	8.46	11.74	0.00	17.70
			Found	52.74	9.09	8.23	11.48	0.50	17.96
14	97.0	97.3	Calcd	55.96	9.75	7.65	10.67	0.00	15.97
			Found	55.36	9.78	7.92	10.95	0.50	15.49
16	95.1	84.2	Calcd	58.50	10.12	7.00	9.76	0.00	14.62
			Found	56.59	9.92	7.68	10.88	0.70	14.23
18	94.8	91.9	Calcd	60.63	10.46	6.45	8.99	0.00	13.47
			Found	58.69	10.07	6.54	9.13	0.50	15.07
20	93.9	96.7	Calcd	62.46	10.74	5.98	8.34	0.00	12.48
			Found	61.03	10.59	6.07	8.84	0.70	12.77
22	72.8	73.8	Calcd	64.03	10.99	5.57	7.77	0.00	11.64
			Found	62.29	10.80	5.48	8.08	0.10	13.25

[a] Recrystallized from aqueous 2-propanol. [b] Conditions: 0.20 mol of NaHSO₃; 0.10 mol of olefin; 0.020 mol of KNO₃; 50.0 ml of H₂O; 50.0 ml of 2-propanol; 2.0 psig of O₂ in Parr vessel with shaking at 110° for 3 hr. [c] Lower yield due to use of 0.10 mol of NaHSO₃ and 0.010 mol of KNO₃.

interpretation has been explicitly confirmed by subsequent analyses.[27]

A variety of olefins of differing molecular weight and structure was reacted using potassium nitrate catalyst. Conditions and results are summarized in Table IV. A more accurate and reliable comparison of molecular weight and structural effects upon reactivity was made under conditions of competitive reaction summarized in Table V and Figure 2.

Discussion

A radical-ionic character of this reaction is well established.[6] Therefore, in light of the fact that even nonionic radical reactions have been shown by

(27) C. J. Norton, unpublished results.

reinvestigation[22] to be very susceptible to solvent and salt effects, it is not surprising that this reaction should show considerable susceptibility to polar effects as well.

Solvent Effects.—The starting reaction mixture has three liquid phases; a nearly complete conversion gives a single liquid phase at the reaction temperature. So solvent effects are critical, complicated, and vary over the course of the reaction.   Kohler and Lapworth[5] in their early work claim that dilution favors the reaction.   Mayo and Walling[9] state, "The yields of addition products from the less reactive alkenes are decreased by the use of either alcohol or hydrocarbon solvent and slightly increased by the use of ethylenediamine." Clippinger's[21] studies and our investigations of aqueous alcohol solvents, summarized in Table VI, show that 1-propanol is the best alcohol solvent
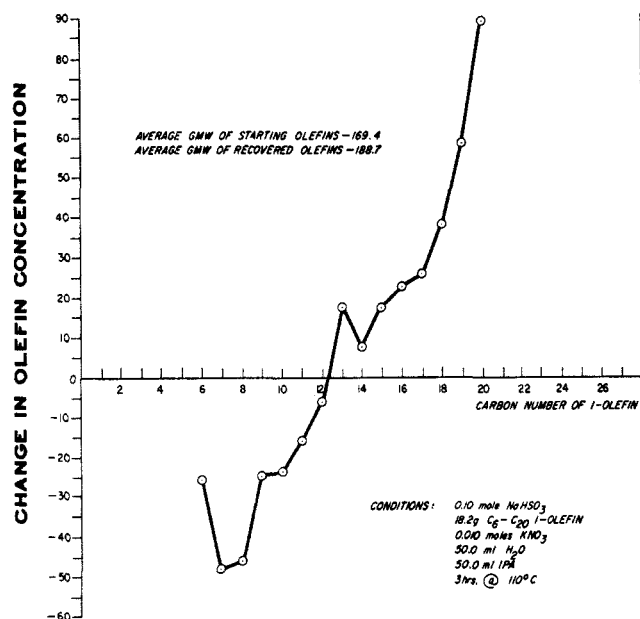
Figure 2.—Competitive reaction of 1-olefin homologs for bisulfite addition.

TABLE IV
THE EFFECTS OF OLEFIN STRUCTURE ON CONVERSIONS INTO ALKANESULFONATE[a]

Hydrocarbon reactant	Conversion, wt%
A. Effect of Isomeric Olefins	
2-Methylpentene-1	99.0
2-Methylpentene-2[b]	88.7
2,3-Dimethylbutene-2[b]	71.0
Hexene-1[b]	52.8
Hexene-2[b] (92.5% cis, 7.5% trans)	38.4
B. Effect of Molecular Weight	
Hexene-1	97.0
Octene-1	92.5
Nonene-1	95.5
Decene-1	97.8
Dodecene-1	94.6
Tetradecene-1	97.3
Hexadecene-1	95.0
Octadecene-1	94.9
Eicosene-1	81.8
Docosene-1	69.6
Equimolar mixture of C_6–C_{16} 1 olefins	54.7
C. Effect of Cyclic Structure	
Cyclohexene	37.1
Cyclododecene[c]	23.7
Norbornene[c]	83.0
D. Miscellaneous Olefins	
1,7-Octadiene[c]	100.0
Styrene[c]	100.0
1-Decyne	22.9

[a] Conditions: 0.20 mol of NaHSO3; 0.10 mol of olefin; 0.02 mol of KNO3; 50.0 ml of 2-propanol; 50.0 ml of water; 2.0 psig of O_2 in Parr vessel with shaking at 3 hr at 110°. [b] Run at 1:1 bisulfite to olefin ratio at 80°. [c] 0.02 mol of KNO3 used.

and is very much superior to water. Ethylenediamine is not a good solvent under our reaction conditions. For practical synthetic reasons most of our work employed the cheaper 2-propanol.

Under conditions of photoinitiation, spectacular solvent effects have been demonstrated,[28] but we find

(28) C. L. Furrow and C. E. Stoops, *Div. Petrol. Chem., Preprints,* **12**, D-107 (1967).

TABLE V
COMPETITIVE ADDITION OF SULFITE TO HEXENE ISOMERS[a]

Hexene isomer	Conversion,[b] wt %
2-Methylpentene-1	95.8
Hexene-1	86.5
2,3-Dimethylbutene-2	72.8
Cyclohexene	69.1
Hexene-2, cis (2.3 g input, 0.39 g recovered)	
Hexene-2, trans (0.19 g input, 1.00 g recovered)	44.2
Total mixture	74.6

[a] Conditions: 0.20 mol of NaHSO3; 0.10 mol of hexene; 0.020 mol of KNO3; 50.0 ml of H_2O; 50.0 ml of 2-propanol; 2.0 psig of O_2 in Parr vessel with shaking at 95° for 3 hr. [b] Determined by weight and gas–liquid partition chromatographic analysis of recovered olefins.

TABLE VI
SOLVENT EFFECTS ON SULFITE ADDITION[a] TO 1-DODECENE

Solvent	Conversion, wt %
Water	7.0
Methanol	51.6
Ethanol	68.5
1-Propanol	85.4
2-Propanol	58.9
1-Butanol	16.8
2-Butanol	2.7
2-Methyl-2-propanol	4.0
1,4-Butanediol	10.3
Ethylenediamine	4.9

[a] Conditions identical with those in Table II except for the variation in solvents. Oxygen partial pressure fixed at 5% over the solvent pressure at 110°. Recovered and washed olefin analyzed by gas–liquid partition chromatography.

solvent effects are not so large in the absence of photoinitiation.

pH Effects.—Reported optimums in the literature range widely from pH 5 to 9. Mayo[9] reports that the optimum pH for the reaction is 5.1–6.1. The more recent literature[19] indicates that the optimum is near pH 7. In our research, we found the reaction proceeds best within the pH range 5–7 where there is a good proportion of both sulfite and bisulfite ions (Table VII). These pH observations suggest that both ions may be involved in the propagation phase of the reaction.

TABLE VII
EFFECT OF pH ON SULFITE ADDITION[a] TO 1-DODECENE

Reaction time, hr	Initial pH	Final pH	Conversion, wt %
0.5	4.5	3.7	18.2
3.0	4.5	1.3	45.5
3.0	6.1	3.7	74.1
3.0	7.0	10.0	73.5
3.0	7.1	12.1	86.7
3.0	8.0	9.3	32.2

[a] Conditions identical with those in Table II. Initial pH adjusted with 40% aqueous potassium hydroxide and water to give a total water volume of 50.0 ml.

The pH and ionization constants determine the ion species distribution of the sulfite–bisulfite reagent as indicated on Figure 3.[29] The addition of 2-propanol shifts the pH of the reaction solution by only +0.2 of a unit. At an initial pH of 5, the reagent is present as about 30% sulfite and 70% bisulfite; at an initial pH

(29) "Sodium Metabisulfite," Technical Bulletin 1-250, Monsanto Corp., St. Louis, Mo. (about 1965).

CHART I
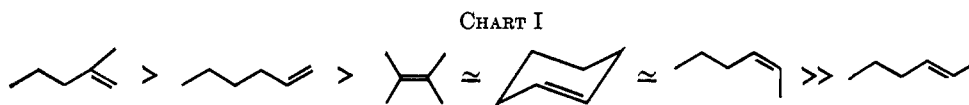
of 6, the reagent is present as about 85% sulfite and 15% bisulfite. The desired reaction (eq 1) has the net effect of removing bisulfite protons from the solution and, therefore, produces a net basic reaction. The undesired side reaction is the two-electron oxidation of bisulfite to bisulfate which produces an acidic reaction. The change of the pH during the course of the reaction can be diagnostic and depends upon the proportions of these two reactions. If the addition reaction predominates, there is generally a drift to higher pH's, whereas if the acid-producing by-product reaction predominates, the drift is to lower pH's. The initial and final pH's of our reaction solutions are recorded in Tables I, II, and VII. Unfortunately, the Parr apparatus was not amendable for recording and controlling the pH during the course of the reaction. Since our screening runs in Table I contain excess sulfite reagent which is ultimately oxidized to sulfate, the reactions usually go acid even under conditions of good conversion into sulfonate; so the over-all changes are of no interpretive value in these screening experiments. When a 1:1 sulfite to olefin ratio is used, as in Table VII, the best conversions are accompanied by drifts to high final pH's. Obviously, a high concentration of sulfite ion favors the reaction, but initial pH's of 8.0 or above are unfavorable for the reaction, presumably because the concentration of bisulfite is too low to sustain the chain-transfer reaction step.

Effect of Olefin Molecular Weight and Structure.— Very high conversions and yields can be obtained with 1 olefin ranging from hexene-1 to docosene-1 under conditions of potassium nitrate catalysis. When an approximately equimolar mixture of olefins reacts competitively, but incompletely, the differences in olefin reactivity are well demonstrated by comparing the analysis of the initial olefin mixture with that of the recovered olefin mixture. The per cent changes for each olefin concentration are plotted against carbon number in Figure 3. The lower molecular weight olefins are more reactive than the higher molecular weight olefins owing to their greater solubility in the aqueous phase of reaction emulsion.

The effects of the olefin structures are compared individually in Table IV and competitively for isomeric hexenes in Table V. The order of hexene reactivities observed is shown in Chart I. The greater reactivity of *cis* over *trans* olefinic structures is indicated by the fact that, when a mixture of 76.5% *cis*- and 23.5% *trans*-hexene-2 reacts, the recovered hexene-2 is greatly enriched in *trans* over its original concentration. Indeed, more *trans*-hexene-2 is recovered than was put into the reaction owing to the rapid isomerization of *cis*-hexene-2 to *trans*-hexene-2 by the reversible addition of sulfite radical ion to the olefin. The *cis* olefins are more reactive than the *trans* olefins owing to higher energy ground states—the so-called *cis* effect. The reactivity order of norbornene, cyclohexene, and cyclododecene is also consistent with increasing *cis*-double-bond strain (Table IV).

The substitution of the terminal double bond with a methyl group at the 1 position reduces reactivity for
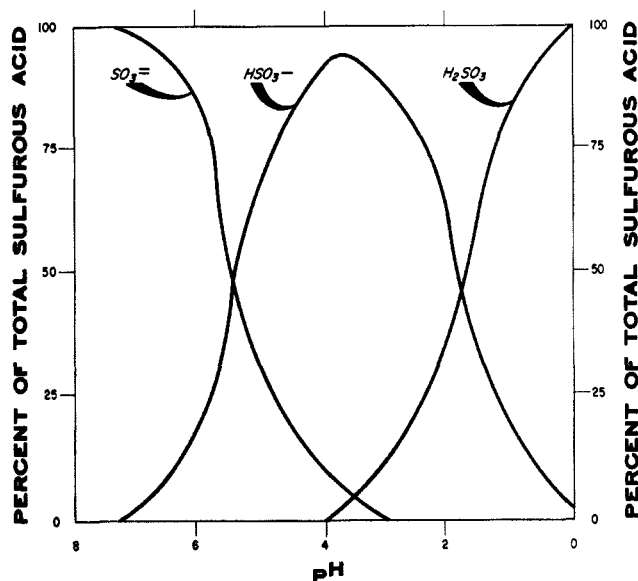
Figure 3.—Effect of pH on distribution of sulfurous acid in solution.[23]

sulfite radical-ion addition for electronic reasons, while, conversely, methyl substitution at the 2 position enhances reactivity, possibly by stabilizing the alkane-sulfonate radical-ion intermediate. Steric inhibition for the addition by one, two, or three methyl group on the double bonds appears to be small relative to the electronic effects. These small steric effects are consistent with the interpretation that the sulfite radical ion approaches in the plane of the π bond rather than in the plane of the σ bond and alkyl groups.

Nitrate Catalysis.—Copper nitrate gives very poor results owing to efficient catalysis of cupric ion for the oxidation of the bisulfite to sulfate. Most of the metal nitrates, which do not accelerate bisulfite oxidation to sulfate,[30] are beneficial to the reaction, largely owing to the nitrate effect. Ammonium, alkali, and alkaline earth nitrates give good catalysis because the cations are not catalytic for the oxidation of sulfite to sulfate.

The over-all catalytic effect of potassium nitrate is due to the nitrate ion. This is demonstrated by varying the anions associated with nitrate in Table II. The product analysis confirms that the nitrate is very selective for high conversions and yields of alkanesulfonate. Lithium and ammonium nitrates are very effective, but potassium is more practical for our synthetic interests.

Kharasch, May, and Mayo[7] reported that the system sodium nitrite–sodium nitrate is an effective "oxidizing agent" in the absence of air for initiating the addition of bisulfite to olefins. We find potassium nitrite with oxygen to be an inferior catalyst when compared with potassium nitrate. Table II shows that a 50:50 mixture of potassium nitrate and potassium nitrite is more effective than anticipated for the average but not so good as potassium nitrate alone. No nitrite could be detected in the product mixture. The

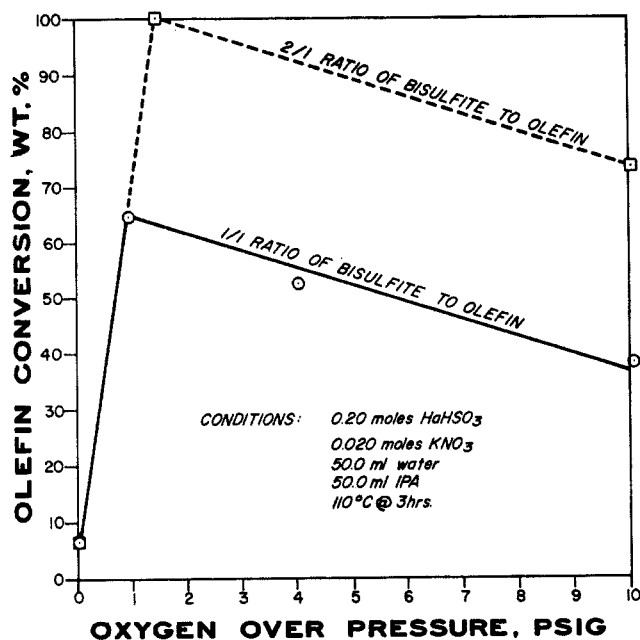(30) M. Gerendas, *Z. Physiol. Chem.*, **254**, 184 (1938).

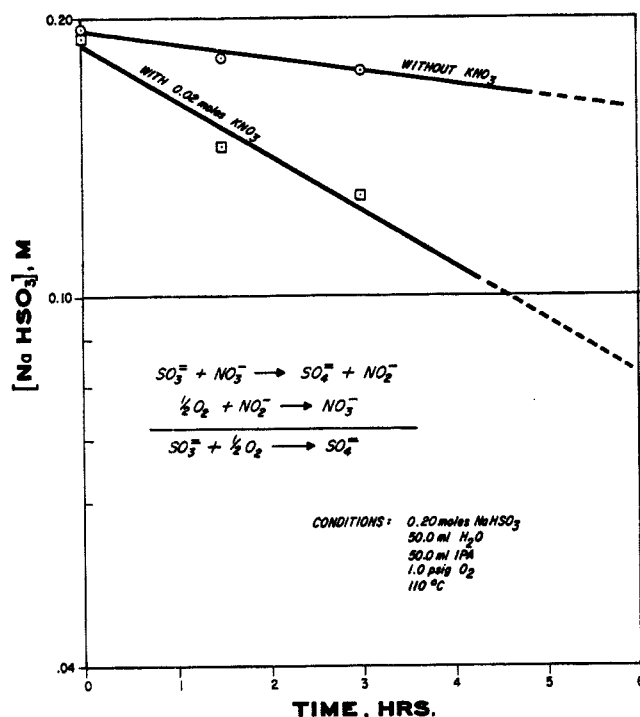Figure 4.—Optimum oxygen pressure depends on bisulfite to olefin ratio.

Figure 5.—Potassium nitrate catalyzes the oxidation of bisulfite.

nitrite ion is oxidized to nitrate under these reaction conditions and the effective anion is the nitrate anion. Nitrite is probably less effective than nitrate, because it consumes oxygen and it takes time to oxidize it to nitrate.
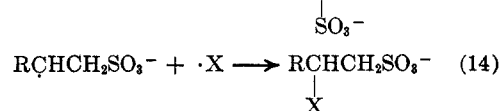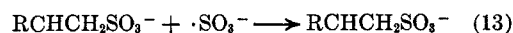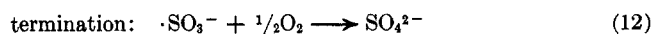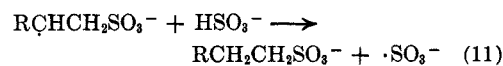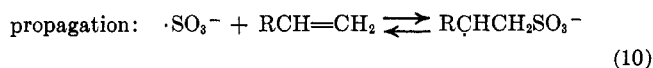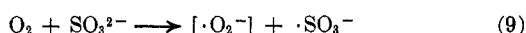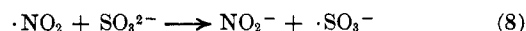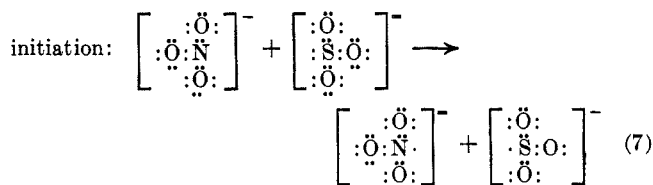
Only about 10% of the potassium nitrate is accounted for by direct analysis of the product mixture. Some nitrogen is incorporated into the organic product (Table III).

The effect of potassium nitrate concentration was also investigated. An adequate relative concentration of the nitrate is about 10 mol % of the bisulfite concentration. The oxygen partial pressure used in conjunction with the nitrate promoters is also important;

1.0 psi is optimum for a 1:1 bisulfite to olefin ratio and 2.0 psi is optimum for a 2:1 bisulfite to olefin ratio (Figure 4). Too much oxygen inhibits formation of alkanesulfonate.

The effect of potassium nitrate on the oxidation of bisulfite in the absence of olefin was investigated, and results are presented in Figure 5, wherein it is demonstrated that potassium nitrate exerts its function by catalyzing the air oxidation of sodium bisulfite. Sulfite is more readily oxidized by air at pH 7.4 than at lower pH's.[30] The nitrate ion is a catalyst for the oxidation of sulfite under acidic conditions.[31] Apparently, it is also more selective in effecting the one-electron transfer oxidation of a sulfite anion to a sulfite radical ion than oxygen alone.

In summary, a proposed mechanism for this reaction is outlined below.

$$\text{initiation:} \quad \begin{bmatrix} :\ddot{O}: \\ :\ddot{O}:\ddot{N} \\ :\ddot{O}: \end{bmatrix}^{-} + \begin{bmatrix} :\ddot{O}: \\ :\ddot{S}:\ddot{O}: \\ :\ddot{O}: \end{bmatrix}^{-} \longrightarrow$$

$$\begin{bmatrix} :\ddot{O}: \\ :\ddot{O}:\ddot{N}\cdot \\ :\ddot{O}: \end{bmatrix}^{-} + \begin{bmatrix} :\ddot{O}: \\ \cdot\ddot{S}:O: \\ :\ddot{O}: \end{bmatrix}^{-} \quad (7)$$

$$\cdot NO_2 + SO_3^{2-} \longrightarrow NO_2^- + \cdot SO_3^- \quad (8)$$

$$O_2 + SO_3^{2-} \longrightarrow [\cdot O_2^-] + \cdot SO_3^- \quad (9)$$

$$\text{propagation:} \quad \cdot SO_3^- + RCH{=}CH_2 \rightleftarrows R\dot{C}HCH_2SO_3^- \quad (10)$$

$$R\dot{C}HCH_2SO_3^- + HSO_3^- \longrightarrow RCH_2CH_2SO_3^- + \cdot SO_3^- \quad (11)$$

$$\text{termination:} \quad \cdot SO_3^- + {}^1\!/_2O_2 \longrightarrow SO_4^{2-} \quad (12)$$

$$R\dot{C}HCH_2SO_3^- + \cdot SO_3^- \longrightarrow \underset{\underset{SO_3^-}{|}}{RCHCH_2SO_3^-} \quad (13)$$

$$R\dot{C}HCH_2SO_3^- + \cdot X \longrightarrow \underset{\underset{X}{|}}{RCHCH_2SO_3^-} \quad (14)$$

Initiation may be effected by a number of "oxidizing agents." Nitrate is known to initiate the reaction in the absence of oxygen.[7,12] Obviously, under the conditions we studied, nitrate anion is directly or indirectly an initiator. But the precise mechanism by which nitrate manifests its initiation is debatable. Direct reaction of a nitrate anion with a sulfite anion is appealing for the isoelectronic simplicity (eq 7), but unlikely because of the strong electrostatic repulsion between the negatively charged ions. A more likely mechanism of nitrate catalytic initiation is its decomposition to nitrogen dioxide, a stabile free radical, which is present at low concentration in equilibrium with nitric acid[31] under the reaction conditions (eq 8). The nitrite ion is reoxidized slowly by oxygen to nitrate under the reaction conditions. This explains why nitrite is a less effective initiator than nitrate. There is also a significant amount of oxygen coinitiation under these conditions as well (eq 9). The easiest sulfite ion from which to remove an electron would be the divalent sulfite, giving rise to a sulfite radical ion.

Propagation (eq 10 and 11) is effected by the addition of the sulfite radical ion to the olefin to give a radical intermediate which rapidly chain transfers with bisulfite

(31) W. M. Latimer and J. H. Hildebrand, "Reference Book of Inorganic Chemistry," rev ed, The Macmillan Co., New York, N. Y., 1940, pp 195–207, 247–248.

ion in solution, one of the sources of labile hydrogen, to regenerate the sulfite radical ion.

Termination (eq 12–14) of the reaction may result by a number of processes. One is the consumption of the sulfite by oxidation to sulfate or bisulfate ion—an undesirable side reaction which is catalyzed by many transition metals.[30] Several coupling reactions may be postulated from analogy to radical reactions in general. As the concentration of the radical species becomes appreciable, alkanesulfonate radical may couple with sulfite radical ion to produce a disulfonate. We have analytical results that show substantial amounts of disulfonate of these molecular proportions are produced.[27] Conceivably, two of the alkanesulfonate radicals may couple to produce a higher molecular weight disulfonate for which we have no evidence.

Neighboring-Group and Substituent Effects in the Solvolysis of Substituted α-Bromophenylacetate Ions[1]

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A study of the rates of solvolysis of *meta*- and *para*-substituted α-bromophenylacetate ions was made in an attempt to help clarify the nature of the intermediate in the solvolysis of α-halocarboxylate ions. The first-order rate constants were correlated with the Hammett equation and ρ was found to be −2.66 at 25.0° and −2.74 at 35.6°, the solvent being 0.681 *M* aqueous acetone; in 80% methanol, ρ was −2.33 at 25.0°. The reaction does not appear to be very sensitive to base concentration, ionic strength, or solvent effects. A striking similarity is noted between the α-bromophenylacetate and α-bromopropionate ions in terms of salt and solvent effects as well as the values of the activation parameters. It is suggested that the similarities in the ρ value for the solvolysis of the α-bromophenylacetate ions with those for the solvolysis of benzyl derivatives in nucleophilic solvents is a consequence of neighboring carboxylate participation. The value of ρ suggests that the intermediate is an α-lactone with much ionic character.

One of the earliest known examples of the neighboring-group effect is that involving carboxylate participation.[3-6a] The classical work of Cowdrey, Hughes, and Ingold suggested the existence of an α-lactone intermediate during the solvolysis of α-bromopropionate ion. Although β-lactones and larger membered ring lactones have been isolated from the solvolysis of the corresponding halocarboxylate ions,[6a,7] the unstable α-lactone has not, and, as Streitwieser points out, the intermediate has been described as a zwitterion, an α-lactone with much ionic character, and simply an α-lactone. The nature of this intermediate has been thoroughly studied by Grunwald and Winstein[4] in terms of the effects of ionic strength and solvent upon the rate of solvolysis of α-bromopropionate. Their results indicate the creation of a small amount of additional charge in the transition state relative to the ground state.

The present account reports another approach designed to obtain additional information about the

"α-lactone" intermediate. The Hammett reaction constant ρ has been evaluated for the solvolysis of several substituted α-bromophenylacetate ions since ρ can be interpreted as a measure of the change in the electron density between the ground state and the transition state at the reaction site.[8] Moreover, a reasonable extension of the Hammond postulate[9] suggests that a reactive intermediate and the transition state leading to it should closely resemble one another. The magnitude of ρ, according to Swain and Langsdorf,[8] can be interpreted in terms of bond making and bond breaking and should therefore be a measure of the electronic structure of the "α-lactone" intermediate.

The kinetics of the solvolysis of *p*-OCH₃-, *p*-H-, *p*-Cl-, *m*-NO₂-, and *p*-NO₂-α-bromophenylacetates were determined, as well as the activation parameters for several of the compound. Salt and solvent effects were also studied to a limited extent.

Results and Discussion

Kinetics.—First-order rate constants for the hydrolysis of several substituted sodium α-bromophenylacetates in 0.681 *M* aqueous acetone are presented in Table I. The hydrolyses were carried out on the sodium salts of the bromo acids in the presence of an equivalent amount of sodium hydroxide and at

(1) (a) Presented in part at the 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967, Abstract S97. (b) Based in part on the M.S. Thesis of D. Metzger, 1967.

(2) National Science Foundation Cooperative Fellow, 1964–1966.

(3) W. Cowdrey, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 1028 (1937).

(4) E. Grunwald and S. Winstein, *J. Amer. Chem. Soc.*, **70**, 841 (1948).

(5) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp 383–386.

(6) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y.: (a) pp 116–119; (b) pp 75, 76.

(7) B. Capon, *Quart. Rev.* (London), **18**, 45 (1964).

(8) C. G. Swain and W. P. Langsdorf, *J. Amer. Chem. Soc.*, **73**, 2813 (1951).

(9) G. S. Hammond, *ibid.*, **77**, 334 (1955).