THE PEROXIDE EFFECT IN THE ADDITION OF REAGENTS TO UNSATURATED COMPOUNDS. XVIII. THE ADDITION AND SUBSTITUTION OF BISULFITE*

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INTRODUCTION

The addition of bisulfite in aqueous solution to unsaturated compounds has been investigated by many workers with varying degrees of success.¹ Table I lists the unsaturated compounds studied, and summarizes the results of the investigations.

ADDITION OF BISULFITE TO UNSATURATED COMPOUNDS

Evidence has now been obtained which indicates that the reaction of bisulfite with ethylene compounds is best interpreted on the basis of a freeradical mechanism. In harmony with this hypothesis, we find that oxidizing agents such as oxygen, which are capable of producing free radicals from bisulfite, are essential for the reaction, and that in the absence of such a reagent no addition occurs. Of especial interest is the fact that small amounts of nitrite and nitrate cause the addition of bisulfite to propylene in the absence of oxygen. In the light of these observations, the discordant results exhibited in Table I (viz., those relating to pinene, cinnamyl alcohol, allyl alcohol, and styrene) can readily be explained. Table II summarizes the results obtained in the present research.

In the investigation of those substances which are gases at room temperature, the oxygen effect was easily demonstrated, and was very striking. The reactions were carried out in an apparatus similar to that often used

*This paper records preliminary work on the reactions of sodium and ammonium bisulfites with ethylene derivatives. Further work on addition and substitution reactions of ethylene and acetylene derivatives, and on substitution reactions of saturated aromatic compounds is in progress. For contribution XVII see Kharasch, May, and Mayo, *Chemistry and Industry*, 57, 774-5 (1938).

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¹ (a) MILLER, Ann., **189**, 338 (1877); (b) MUELLER, Ber., **6**, 1442 (1873); (c) ROSEN-THAL, Ann., **233**, 38 (1886); (d) MARCKWALD AND FRAHNE, Ber., **31**, 1864 (1898); (e) LABBE, Bull. soc. chim., [3], **21**, 1077 (1899); (f) DUPONT, Sci. Ind. Bull. Roure-Bertrand Fils, [3], **7**, 3 (1913); (g) KOLKER AND LAPWORTH, J. Chem. Soc., **1925**, 307; (h) ASHWORTH AND BURKHARDT, *ibid.*, **1928**, 1791; (i) HEDÉN AND HOLMBERG, Chem. Zentr., **1937**, I, 1156.

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for catalytic hydrogenation, the reservoir being filled with the olefin. In each case there was an initial rapid pressure drop, but absorption of the olefine by the aqueous bisulfite solution practically ceased after twenty to thirty minutes. When the pressure bottle was opened, flushed out with air, and refilled with olefin, this phenomenon was repeated.

COMPOUND	CONDITIONS	RESULT	REFERENCE
Ethylene Cyclohexene Trimethylethylene Pinene Dipentene Styrene Styrene Pinene Allyl alcohol Allyl alcohol Cinnamyl alcohol Cinnamyl alcohol	0.25 N bisulfite and kieselguhr at 25° for 10 days 25-130°; S. T.ª 25°; S. T.ª Reflux 10-20 hours 100°; S. T.ª Reflux 25°: S. T.ª	Addition Addition Addition Addition Addition Addition Negative ^b Negative Addition Allyl sulfate ^c Addition	1g 1g 1g 1g 1g 1h 1a, e, f, i 1f 1b, d 1c 1e 1f
Cinnamyi alconol	25°; S. 1.ª	Addition	17
Cinnamyl alcohol Limonene Geraniol Linaloöl Rhodinol Esters and ethers of geraniol, linaloöl and cinnamyl al-	130°; S. T.«	Negative Negative Addition Addition Addition	li lf lf lf lf
cohol	ļ) (ļ	Negative	1 <i>f</i>

TABLE I

PREVIOUS WORK ON THE ADDITION OF BISULFITE TO UNSATURATED COMPOUNDS

^a Sealed tube.

^b These workers obtained traces of a water-soluble organic product which was not characterized. Miller¹⁴ obtained sufficient material for analysis.

^c A possible explanation of this result is that the hydroxyl group of allyl alcohol is acted upon by bisulfite at higher temperatures. This, we believe, should be a characteristic reaction of carbinols of weakly electronegative radicals¹.

As in the autoxidation of bisulfite, hydrogen-ion concentration has a profound effect on the rate of the reaction. The effect of pH was studied with propylene and 2N ammonium bisulfite buffered with ammonia to the desired pH value. The reaction proceeded at the maximum rate in the pH range of 5.1 to 6.1. In the case of ethylene no addition took place at a pH of 4.8, while at a pH of 5.9, a 12 per cent yield was obtained. Whether or not this was the optimum was not determined.

In every case in which the rule elaborated by Kharasch, Engelmann, and

Mayo² could be tested, the addition product was found to have the structure predicted for the free radical chain reaction:



TABLE II

		PER CENT RECOV- ERED		TIPLD ⁴ OF	
UNSATURATED COMPOUND	CONDITIONS	Unsatu- rated Com- pound	Bisulfite	ORGANIC SULFONATE	
Ethylene	Evac. to 10 mm.		98	0	
Ethylene	Oxygen present			12	
Propylene	Antioxidant		100	0	
Propylene	Nitrite present ^c			30	
Propylene	Oxygen present		21	55	
Isobutylene	Oxygen present	1		62	
Styrene	Evac. to 1 mm.	100	95	0	
Styrene ^b	Oxygen present	27		55	
Allyl alcohol	Antioxidant	90	95	0	
Allyl alcohol	Oxygen present		5	65	
Cinnamyl alcohol	Evac. to 15 mm.	95	95	3	
Cinnamyl alcohol	Oxygen present	30		90	

Addition of Bisulfite to Unsaturated Compounds

^a The yields represent crude organic sulfonates actually isolated, and were calculated on the basis of the amount of bisulfite or unsaturated compound consumed in the reaction. They were checked at least once.

^b The main yield in the case of styrene was the substitution product (vide infra). ^c In the absence of oxygen.

² KHARASCH, ENGELMANN, AND MAYO, J. Org. Chem., 2, 299 (1937).

Briefly stated, this rule declares that under antioxidant conditions the bromide ion of hydrogen bromide attaches itself to the carbon atom of the double bond having the lesser electron density, (*i.e.*, in general, the carbon atom possessing the smaller number of hydrogen atoms); whereas under peroxide conditions, the bromine atom becomes linked to the carbon atom about which there is the greater electron density, through a free radical chain mechanism. Thus, propylene yielded the propane-1-sulfonate, isobutylene the 2-methylpropane-1-sulfonate, allyl alcohol the 1-hydroxypropane-3-sulfonate and styrene the 1-phenylethane-2-sulfonate.

The structures of all these products were established by comparison of the physical properties of their derivatives with those of synthetic samples of known structure. These had all been previously prepared, except in the case of allyl alcohol. In this instance a new crystalline derivative, namely the 1-chloropropane-3-sulfonamide, was synthesized. This type of derivative should prove useful for the characterization of hydroxyalkanesulfonic acids in general.

INTERACTION OF BISULFITE AND STYRENE IN THE PRESENCE OF OXYGEN

By analogy with the other bisulfite addition reactions studied, the styrene addition product to be expected is 1-phenylethane-2-sulfonic acid. However, while a small amount of this compound was formed in the reaction, the product under all conditions, including those employed by Ashworth and Burkhardt¹, consisted chiefly of 1-phenylethylene-2-sulfonic acid. The latter compound was first prepared by Quilico and Fleischner³ from styrene and aminosulfonic acid. Their assignment of structure was made on the basis of the facts that cold permanganate oxidation yields benzoic acid, and that fusion with sodium formate yields cinnamic acid. We have further confirmed the structure by catalytic hydrogenation and conversion to 1-phenylethane-2-sulfonamide, in conjunction with the syntheses outlined in Figure I.

The hypothesis that this product was formed by dehydrogenation of the addition product is not tenable, for it was found that sodium 1-phenylcthane-2-sulfonate is not affected by bisulfite and oxygen. The unsaturated sulfonic acid must therefore have been formed by substitution.

The presence of the addition product in the reaction between styrene, bisulfite, and oxygen was proven by treating a solution of the sulfonamide obtained from the crude reaction product with potassium permanganate. The unsaturated sulfonamide was destroyed, permitting the isolation of a pure saturated sulfonamide which was shown to be identical with 1-phenylcthane-2-sulfonamide.

It is to be noted that these results are not in accord with the conclusions of Ashworth and Burkhardt¹, who reported that the styrene-bisulfite addition product is the 1-phenylethane-1-sulfonate.

$C_6H_5CH = CH_2 \xrightarrow{NH_4HSO_3}$	$(C_6H_5C_2H_4)SO_3NH_4 \rightarrow$	$(C_6H_5C_2H_4)SO_2NH_2$	(I)
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 $C_{6}H_{5}CHBrCH_{3} \xrightarrow{(NH_{4})_{2}SO_{4}})C_{6}H_{5}C_{2}H_{4})SO_{3}NH_{4} \rightarrow (C_{6}H_{5}C_{2}H_{4})SO_{2}NH_{2}$ (II)

 $C_{6}H_{5}CH_{2}CH_{2}Br \xrightarrow{(NH_{4})_{5}SO_{3}} (C_{6}H_{5}C_{2}H_{4})SO_{3}NH_{4} \rightarrow (C_{6}H_{5}C_{2}H_{4})SO_{2}NH_{2}$ (III)

³ QUILICO AND FLEISCHNER, Atti. accad. Lincei, [6], 7, 1050 (1929).



Their assignment of structure was made upon the basis of the identity of the sulfonamide derived from the addition product (I) with that derived from the sulfonate obtained by refluxing secondary phenylethyl bromide with concentrated aqueous ammonium sulfite (II), together with the supposed non-identity of sulfonamides I and II with the sulfonamide derived from phenethyl bromide (III). For sulfonamides I and II and for their mixtures a melting point of 121° was reported; for sulfonamide III, a melting point of 124°. The melting-point behavior of mixtures including the latter product was not reported. Other workers record for the melting point of the sulfonamide derived from phenethyl halide $121.5 - 122.5^{\circ 4}$ and $119^{\circ.5}$

However, repetition of these syntheses in our laboratories yielded three apparently identical sulfonamides, all melting, together with their respective mixtures, at 121°. A thorough re-investigation of the structures and properties of the isomeric phenylethanesulfonic acids was therefore undertaken.

Authentic 1-phenylethane-1-sulfonic and 1-phenylethane-2-sulfonic acids were prepared by oxidation of the respective mercaptans. The structures of these substances were established beyond reasonable doubt by the preparation of a series of corresponding derivatives, the non-identity of which is apparent from their melting points and those of their mixtures (Figure I). No sulfonyl chloride or sulfonamide could be prepared from 1-phenylethane-1-sulfonic acid, the compound which Ashworth and Burkhardt believed they had obtained through bisulfite addition to styrene and from the secondary bromide. On treatment with phosphorus pentachloride, sodium 1-phenylethane-1-sulfonate was rapidly converted into secondary phenylethyl chloride, with the evolution of sulfur dioxide. 1-Phenylethane-2-sulfonic acid, prepared either from the mercaptan or the bromide. gave the sulfonamide of melting point 121°. It can readily be seen on the basis of this evidence that the sulfonamide of melting point 121° is actually 1-phenylethyl-2-sulfonamide and that, therefore, the structure of the addition product of styrene and bisulfite corresponds to 1-phenylethane-2sulfonic acid.

It remains to be shown how secondary phenylethyl bromide could yield 1-phenylethane-2-sulfonic acid on refluxing with aqueous ammonium sulfite. It was observed by Evans and his co-workers⁵ and also in this laboratory^{*} that on refluxing such a mixture the following reaction took place:

⁴ JOHNSON AND SPRAGUE, J. Am. Chem. Soc., 58, 1348 (1936).

⁶ Evans, Mabbott, and Turner, J. Chem. Soc., 1927, 1159.

* The high yields (40 per cent.) of sulfonic acid reported by Evans and co-workers (*loc. cit.*) for this reaction could not be reproduced. In more than a dozen experiments, we consistently obtained yields of only 5 per cent.

$$\begin{array}{c} \operatorname{Br} \\ \downarrow \\ C_6H_5 \longrightarrow C \longrightarrow C_6H_5CH \longrightarrow CH_2 + \operatorname{HBr} \\ \downarrow \\ H \end{array}$$

The hydrogen bromide formed was absorbed by the aqueous layer, causing the evolution of sulfur dioxide. Under such conditions, the active reagents were styrene and bisulfite, and the reaction, therefore, on the basis of which Ashworth and Burkhardt identified the addition product of styrene and bisulfite, was actually the addition of bisulfite to styrene.

 $C_6H_5CH=CH_2 + NH_4HSO_3 \rightarrow C_6H_5CH_2CH_2SO_3NH_4$

In order to avoid the formation of styrene, with the attendant formation of bisulfite, the reaction was carried out at room temperature, with a strongly ammoniacal solution of ammonium sulfite. An excellent yield (50 per cent) of the sulfonic acid was obtained. This material was identical in its properties with the 1-phenylethane-1-sulfonic acid obtained by the oxidation of the corresponding mercaptan. A poorer yield of the acid was obtained by refluxing secondary phenylethyl chloride with aqueous sodium sulfite containing one-half molar equivalent of sodium hydroxide.

MECHANISM OF THE ADDITION REACTIONS

The end-products of the reaction between bisulfite and unsaturated substances in the presence of oxygen are sulfate ion and alkansulfonate, and the ratio of the two depends on the organic compound in question. The facts outlined point strongly to a chain reaction whereby the free radicals⁶ or free radical ions⁷ postulated in the autoxidation of bisulfite attack the unsaturated compound.[†] It is proposed that this reaction proceeds through a chain similar to that suggested to account for the freeradical addition of hydrogen bromide² and of thioglycollic acid⁸:

⁶ FRANCK AND HABER, Ber. Berl. Akad., 1931, 250.

⁷ BÄCKSTRÖM, Z. physik. Chem., **B25**, 122 (1934).

† Strong evidence for a free radical chain mechanism in the autoxidation of sulfite has been adduced by Bäckström and Haber and their respective co-workers. The literature on this subject is well summarized in the recent publication of Bäckström (*loc. cit.*).

⁸ KHARASCH, READ, AND MAYO, Chem. & Ind., 57, 752 (1938).

[‡]This initial step in the autoxidation of sulfite (thermal reaction) is postulated by both Bäckström and Haber (*loc. cit.*).

b.

$$\mathrm{HSO}_{3}^{-} + \mathrm{O}_{2} \rightarrow \left[\begin{matrix} : \ddot{\mathrm{O}} : \\ : \ddot{\mathrm{O}} : \ddot{\mathrm{S}} : \ddot{\mathrm{O}} : \\ : \ddot{\mathrm{O}} : \ddot{\mathrm{S}} : \ddot{\mathrm{O}} : \end{matrix} \right]^{-} + \mathrm{HO}_{2}$$

2.
$$\begin{bmatrix} :\ddot{O}:\\ :\ddot{O}:\ddot{S}:\ddot{O}:\\ :\ddot{O}:\ddot{S}:\ddot{O}:\end{bmatrix}^{-} + H_2O \rightleftharpoons H:\ddot{O}:\ddot{S}:\ddot{O}: + OH^{-1}$$

3. a.
$$\mathbf{R}_{1}: \mathbf{C}: \ddot{\mathbf{C}}: \mathbf{H} + \begin{bmatrix} \vdots \ddot{\mathbf{O}}: \\ \vdots \ddot{\mathbf{O}}: \vdots \vdots \vdots \\ \vdots \ddot{\mathbf{O}}: \ddot{\mathbf{S}}: \ddot{\mathbf{O}}: \end{bmatrix}^{-} \rightarrow \mathbf{R}_{1}: \ddot{\mathbf{C}}: \ddot{\mathbf{C}}: \mathbf{H} \\ \mathbf{R}_{2} \ddot{\mathbf{H}} \end{bmatrix}$$

or

4.

b.
$$\begin{split} & R_1:C:\ddot{C}:H + H:\ddot{O}:\ddot{S}:\ddot{O}: \rightarrow R_1:\dot{C}:\ddot{C}:H \rightarrow R_1:\dot{C}:\ddot{C}:H + H^+ \\ & \dot{R}_2\dot{H} & \dot{R}_2\dot{H} & \dot{R}_2\dot{H} \\ & & \dot{R}_1:\dot{C}:\ddot{C}:H + HSO_3^- \rightarrow R_1:\ddot{C}:\ddot{C}:H + \left[\begin{array}{c} :\ddot{O}: \\ :\ddot{O}:\ddot{S}:\ddot{O}: \\ :\ddot{O}:\ddot{S}:\ddot{O}: \end{array} \right]^- \\ & & \dot{R}_2\dot{H} & \dot{R}_2\dot{H} \\ \end{split}$$

Various details of the experimental data lend themselves to interpretation on the basis of this mechanism. Thus, when the solubility of unsaturated substance in the bisulfite solution was low, the chains were necessarily short and a rigorous oxygen-exclusion technique was not needed to inhibit the reaction. With allyl alcohol, however, both a high degree of evacuation and the presence of an antioxidant were necessary to inhibit the reaction, as shown in the experimental part, (Table III). This, we believe, is due to the long chains produced by the presence of a high concentration of unsaturated compound.

Franck and Haber⁶ have proposed that neutral bisulfite free radicals $(\cdot \text{HSO}_3)$ are the chain-carriers in the autoxidation of bisulfite, postulating for them such an acid strength that they would exist only in the pH range of autoxidation. Bäckström⁷, on the other hand, considers sulfite ion free radicals $(\cdot \text{SO}_3^-)$ to be the chain-carriers, and claims that the dependence of the rate of autoxidation on pH is due to the fact that bisulfite ion is involved in the chains. He bases his assumption on the fact that the inhibitory action of alcohols (which, in breaking the chains, are dehydrogenated) is lost in more acid solutions in which the concentration of bisulfite ion is high, this latter species then being preferentially dehydrogenated to sulfite ion free radicals.

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Baumgarten⁹ has shown that pyridine, when present in high concentration during the autoxidation of bisulfite, is oxidized in small yield to dipyridyl compounds, whereas in the absence of oxygen no such reaction occurs. We have found that a small amount of styrene or 1-phenylethylene-2-sulfonate is oxidized to benzoic acid during the interaction of styrene and bisulfite in the presence of oxygen.

EXPT. NO.	CONDITIONS	ADDED REAGENTS	PER CENT BISUL- FITE UNREACTED	REMARKS
5	Vacuum	None	10	a
7	Vacuum	Hydroquinone	91	b, g
8	Vacuum	Hydroquinone	100	Ъ
13	Oxygen	Ascaridole	3	c, d
14	Oxygen	None	5	d
15	Oxygen	Hydrogen peroxide	10	d
16	Oxygen	None	100	d, e
36	Oxygen	None		d, f

TABLE III Addition of Bisulfite to Allyl Alcohol

(a) Allyl alcohol not distilled in vacuo.

(b) Allyl alcohol distilled in vacuo.

(c) Ascaridole recovered unchanged.

(d) In the oxygen runs oxygen was bubbled through the solution for two minutes.

(e) No allyl alcohol added. Titrated immediately after oxygen was bubbled through.

(f) Addition product isolated in 65% yield.

(g) Eight cc. of water used. On cooling, ally l alcohol separated and was recovered in 90% yield.

Winstein and Lucas¹⁰ have suggested a mechanism by which one form (V) of a resonating oxygen complex (IV and V) with the double bond is



responsible for the directing influence of oxygen (and peroxides) in the addition of hydrogen bromide to double bonds. Although this mechanism accounts as satisfactorily as our own for the direction of addition of hydrogen bromide, it offers no explanation of the non-reversal of the direction

⁹ BAUMGARTEN, Ber., 69, 229 (1936).

¹⁰ WINSTEIN AND LUCAS, J. Am. Chem. Soc., 60, 843 (1938).

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of addition of such acids as hydrochloric, hydriodic, and sulfuric in the presence of oxygen. If, as we believe, the oxygen-catalyzed hydrogen bromide addition and the bisulfite addition are essentially similar, the fact that nitrate and nitrite ions in the absence of oxygen cause the addition of bisulfite to propylene may be regarded as additional evidence of a freeradical chain mechanism.

MECHANISM OF THE SUBSTITUTION REACTION WITH STYRENE

Two alternative mechanisms present themselves for the formation of the substitution product: the first may be represented by equations 1 and 2.

$$1 \qquad C_{6}H_{5}:C:\ddot{C}:H + \begin{bmatrix} \vdots \ddot{O}:\\ \vdots \ddot{O}:\ddot{S}:\ddot{O}:\\ \vdots \ddot{O}:\ddot{S}:\ddot{O}: \end{bmatrix}^{-} \rightarrow C_{6}H_{5}:\ddot{C}:\ddot{C}:H \\ \dot{H} \ddot{H} \\ 2. \qquad C_{6}H_{5}:C:\ddot{C}:H + \begin{bmatrix} \vdots \ddot{O}:\\ \vdots \ddot{O}:\ddot{S}:\ddot{O}:\\ \vdots \ddot{O}:\ddot{S}:\ddot{O}: \end{bmatrix}^{-} \rightarrow C_{6}H_{5}:C::\ddot{C}:H + HSO_{3}^{-} \\ \dot{H} \ddot{H} \\ \end{array}$$

The alternative mechanism implies a similarity between the complex H_3 described by Eyring and his co-workers¹¹ and the activated complex formed in equation 1. By analogy to the hydrogen atom-hydrogen molecule collision, the mechanism would then be:

3.
$$C_{6}H_{5}:C:\ddot{C}:H + \begin{bmatrix} :\ddot{O}:\\ :\dot{O}:\ddot{S}:\ddot{O}:\\ :\dot{O}:\ddot{S}:\ddot{O}: \end{bmatrix} \rightarrow \begin{bmatrix} SO_{3}\\ C_{6}H_{5}:\dot{C}:\ddot{C}:H\\ H \ddot{H} & H \end{bmatrix} \rightarrow C_{6}H_{5}:C::\ddot{C}:H + H$$

4. $H^{\cdot} + \begin{bmatrix} :\ddot{O}:\\ :\ddot{O}:\ddot{S}:\ddot{O}:\\ :\ddot{O}:\ddot{S}:\ddot{O}: \end{bmatrix} \rightarrow HSO_{3}^{-}$

Thus, the two mechanisms are the same insofar as the overall result is concerned and differ only in the manner in which hydrogen is lost by the hypothetical complex between styrene and the sulfite-ion free radical. In either case the reaction chain is broken and the slowness of the substitution reaction is thus explained.

EXPERIMENTAL*

Materials.—Isobutylene was prepared in the usual manner from tert.-butyl alcohol and hydrated oxalic acid. Cinnamyl alcohol was the Eastman product. Constant-

¹¹ HIRSCHFELDER, EYRING, AND ROSEN, J. Chem. Phys., 4, 121 (1936).

^{*} New compounds are indicated by asterisks.

boiling 60-70% allyl alcohol was redistilled, b.p. 87°. Styrene was obtained through the courtesy of the Bakelite Corporation, from cinnamic acid,¹² and from phenethyl alcohol and solid sodium hydroxide.¹³ It was freshly distilled *in vacuo* before use.

Addition to ethylene and propylene was carried out in a low-pressure hydrogenator, the reservoir tank of which was filled with the olefin to a pressure of 35 to 40 pounds. One hundred cc. of 2N ammonium bisulfite buffered with ammonia to a pH of 5.9 was added to the pressure bottle. The solution was shaken until the rate of absorption of gas by the solution, as indicated by the pressure drop, was negligible. The bottle was then removed, flushed with air, and the procedure was repeated. In general, air was added to the system every half-hour, and after nine to twelve additions the reaction was complete. The product was worked up according to the method of Kolker and Lapworth.¹⁹

Barium ethanesulfonate.—The yield of crude product was 2.8 grams or 12% of the bisulfite used. It was recrystallized once from water.

Anal. Cale'd: C, 13.56; H, 2.83.

Found: C, 13.53; H, 2.93.

Barium propane-1-sulfonate.—The yield of crude product varied from 11.5 to 13.8 grams. The ratio of sulfate to alkanesulfonate formed was approximately 0.8. After one recrystallization from water, the product was analytically pure.

Anal. Calc'd: C, 18.85; H, 3.67.

Found: C, 18.75; H, 3.83.

Vacuum runs with ethylene and propylene were made by evacuating the system to 20 mm. before admitting the olefin. This did not eliminate all oxygen from the system. However, very little gas was absorbed by the solutions after 10 hours' shaking. Ethylene yielded no addition product, while in the case of propylene 0.2 gram was isolated. When a small amount of hydroquinone was added to the bisulfite solution, the reaction with propylene was completely inhibited.

The effect of pH on the rate of the addition of bisulfite to propylene was studied qualitatively by observing the rate of absorption of the gas over the solution as measured by a pressure gauge which recorded the pressure in the pressure bottle when the valve to the reservoir was closed. pH was measured with a Beckman "pHmeter."

Addition of bisulfite to propylene in the presence of nitrite and nitrate.—One hundred cc. of 2N ammonium bisulfite (pH 5.9) containing 1.2 grams each of sodium nitrate and sodium nitrite was shaken under twenty pounds pressure of propylene, the system having been previously evacuated several times to 1 mm. and flushed with propylene. The initial rate of absorption was approximately the same as in the oxygen reaction. After two hours, absorption was negligible, due to the fact that the solution had become alkaline. The product was separated from inorganic sodium salts by extraction with alcohol and evaporation to dryness. The yield was 6 grams. The material was characterized by conversion through the sulfonyl chloride (yield 4.5 grams) to the sulfonamide as described below.

Identification of the propylene addition product.—The two isomeric propanesulfonic acids were prepared from the bromides in the form of their barium salts, according to the method of Hemilian,¹⁴ and converted into the sulfonamides as described by

¹² Organic Syntheses, Coll. Vol. I, p. 430, John Wiley and Sons, New York, 1932.

¹³ SABETAY, Bull. soc. chim., [4], **45**, 69 (1929). This method gives the excellent yields reported by this author, and is far superior to the Organic Syntheses method. Due to an unfortunate mistranslation of alcoholic potassium hydroxide for "potasse a l'alcohol," the editors of Organic Syntheses apparently rejected this method.

¹⁴ HEMILIAN, Ann., 168, 146 (1873).

Duguet.¹⁵ Propane-1-sulfonamide melted at 51-2°, and when mixed in any proportion with the sulfonamide obtained from the addition product, no depression was noted. When either of these amides was mixed with propane-2-sulfonamide (m.p. 63°) melting began at room temperature.

Anal. (Propane-1-sulfonamide, addition product) Calc'd: C, 29,27; H, 7.32.

Found: C, 29.40; H, 7.31.

Isobutylene in excess was poured onto 20.8 grams of sodium bisulfite and 2.0 grams sodium hydroxide in 100 cc. of water in the pressure bottle, which was immersed in a cooling bath at -20° . The pressure bottle was then attached to the evacuated hydrogenator and allowed to warm to room temperature. At this point a pressure of 30 pounds was exerted by the system. The addition was then carried out as in the case of ethylene and propylene, any excess liquid isobutylene condensed in the pressure bottle being allowed to escape before the first flushing with air. The solution was evaporated to dryness at 45° under a stream of air. The residue was extracted first with 250 cc. of boiling 95% alcohol, then with 250 cc. of boiling 50%alcohol. The first alcoholic extract, upon evaporation to dryness yielded 9 grams of the sodium sulfonate free from inorganic material. The second extract, on treatment with an equal volume of 95% alcohol, yielded a precipitate of inorganic material. After this had been removed, the solution on evaporation to dryness yielded a further 10.5 grams of the sodium sulfonate which contained a very small amount of inorganic impurity. Total crude yield was 19.5 grams or 62% theoretical. The product may readily be purified by crystallization from alcohol.

The identification of the addition product of isobutylene and bisulfite was carried out by converting the crude product to 2-methylpropane-1-sulfon- α -naphthylamide according to the method of Duguet.¹⁵ This product melted at 103-5°, and when mixed with an authentic specimen prepared according to the method of this author from isobutyl bromide, no depression in melting point was noted.

Allyl alcohol.—Five grams of sodium bisulfite, 5.0 cc. of constant-boiling allyl alcohol, and 10.0 cc. water were sealed off in bomb tubes with added reagents as noted in Table III. The tubes were heated 3 to 5 hours in a steam bath. The contents were then diluted to 250 cc. and titrated in weakly acid solution with standard iodine. Allyl alcohol was found not to affect the titer. An oxygen run was not so diluted, but drowned in alcohol, and the heavy viscous layer was extracted with alcohol until all the organic material had been removed. The inorganic residue weighed 1.2 grams. The alcoholic extract on evaporation to dryness yielded 6.0 grams of sodium 1-hydroxypropane-3-sulfonate which ash test showed to contain 15% sodium sulfate. The yield of addition product was therefore 65%. In order to prepare larger amounts of material for identification purposes, one part of pure allyl alcohol, 2.2 parts of potassium metabisulfite and ten parts of water were refluxed ten hours and then allowed to stand overnight. A slow stream of air was allowed to bubble through. Alcohol was added to complete precipitation of inorganic salts, which were filtered off, and the solution was evaporated on the steam bath to first signs of crystallization, filtered hot through carbon, and allowed to crystallize in the ice box. The crystals were separated by filtration from the viscous liquid, stirred in 95% alcohol and collected by filtration. In this manner, 260 grams of allyl alcohol yielded 60 grams of fairly pure crystals. The filtrates on evaporation to dryness yielded 300 grams of less pure material. Either sample was satisfactory for identification purposes. Vacuum runs were made according to the technique

¹⁵ DUGUET, Rec. trav. chim., 25, 216 (1906).

described by Kharasch and Mayo.¹⁶ In order to inhibit the reaction completely, it was found necessary not only to distil the allyl alcohol in high vacuum but also to add ten mole per cent. of hydroquinone.

Sodium 1-hydroxypropane-3-sulfonate.—Forty-five grams of trimethylene bromohydrin (Eastman Kodak) was refluxed with an equal weight of anhydrous sodium sulfite in a concentrated aqueous solution until the organic layer had disappeared. The solution was then evaporated to a small volume and filtered from sodium bromide. Four hundred cc. of alcohol was added to the filtrate, precipitating 10 grams of the sodium sulfonate containing only a small amount of bromide. Evaporation of the mother liquor to one-half its original volume yielded an additional 9 grams of sodium sulfonate of similar quality.

1-Chloropropane-3-sulfonamide.—Nine grams of the second crop of sodium 1hydroxypropane-3-sulfonate was dried for two hours at 120°, was finely ground, and was added to 12 grams of phosphorus pentachloride in 35 cc. of dry carbon tetrachloride. Violent decomposition occurred when the solvent was not used. After three hours' refluxing, and standing overnight, the suspension was filtered. The filtrate was evaporated at the pressure of the water pump at a temperature not exceeding 40°. Approximately two grams of oil was obtained. This material was taken up in ether, washed with water, and dried over calcium chloride. It was extremely lachrymatory. Conversion to 1-chloropropane-3-sulfonamide was effected by adding the ether solution to a solution of ammonia in ether at 0°. After standing 1 hour, the solution was filtered, evaporated to 25 cc., diluted to faint turbidity with ligroïn, and allowed to stand in the icebox overnight. A precipitate of fine needless contaminated with oily material was obtained. After two further recrystallizations from ether-ligroïn, the melting point was constant at 63°. The material gave a strong Beilstein test.

Anal. Calc'd: N, 8.89; Found: N, 8.91.

Identification of the addition product of allyl alcohol and bisulfite was carried out by conversion to the chloropropanesulfonamide as described above. This material melted at 63°, and gave a strong Beilstein test. When mixed in all proportions with the authentic sample, no depression in melting point was noted.

Anal. Calc'd: N, 8.89.

Found: N, 8.81.

Treatment of cinnamyl alcohol and of styrene with bisulfite.—Equivalent amounts of unsaturated compound and 1 to 2N ammonium bisulfite solution were shaken in a vessel connected to an oxygen reservoir with rubber tubing. The reservoir was refilled with oxygen every 1 to 2 hours. After oxygen absorption ceased, the unsaturated substance was separated and weighed. The aqueous solution was worked up according to the method of Kolker and Lapworth.¹⁹ Vacuum runs were conducted side by side with oxygen runs on the shaker, with identical amounts of material and vessels of the same shape and size.

Styrene.—The yields varied from 30 to 70%, but yields of 50-60% were usual. The time required for reaction varied from 20 to 30 hours with air above the shaken reaction mixture to 10 hours with pure oxygen at 5 to 10 lbs./sq. in. above atmospheric pressure. The effect of alcohol as a common solvent was to decrease the yield and induce the formation of polystyrene, which was never noted in the absence of this solvent. The recovered styrene had the same boiling point as the freshly distilled material. Larger runs were conducted on the hydrogenator, with 25 grams of

¹⁶ KHARASCH AND MAYO, J. Am. Chem. Soc., 55, 2468 (1933).

styrene, 100 cc. of 2N ammonium bisulfite (pH 5.9), and oxygen under five to ten pounds pressure. It was found necessary toward the end of the reaction to add small amounts of ammonia. The substitution product, in the form of the barium sulfonate, was readily purified by a single crystallization. No attempt was made to isolate the addition product, except in the form of the sulfonamide. Benzoic acid was isolated in small quantity from the residues of a number of runs, by acidification, extraction with ether, and recrystallization from water. It was identified by its melting point and that of its mixtures with an authentic sample.

Cinnamyl alcohol.—The reaction was practically complete in 10 hours. The relative proportion of sulfate to organic sulfonate formed in the reaction was 2 to 1. The barium salt of the reaction product was not readily crystallizable. It was therefore converted to the sodium salt, which was crystallized from dilute alcohol.

Anal. Calc'd: Na, 9.63.

Found: Na, 9.62.

Secondary phenylethyl bromide, (b.p. 88° at 15 mm), was prepared by bubbling dry hydrogen bromide through ice-cooled styrene.

Secondary phenylethyl chloride, (b.p. 69-70° at 13 mm.), was prepared by hydrolyzing secondary phenylethyl bromide in cold alcoholic potassium hydroxide, adding water, and shaking the separated phenylmethylcarbinol with concentrated hydrochloric acid.¹⁷

Secondary phenylethyl mercaptan, (b.p. 83° at 15 mm.), was prepared according to Sontag.¹⁸

Potassium 1-phenylethane-1-sulfonate was prepared according to Levene¹⁹ by oxidizing secondary phenylethyl mercaptan with potassium permanganate.

Barium 1-phenylethane-1-sulfonate was prepared by shaking 50 grams of secondary phenylethyl bromide, 100 cc. of 42% ammonium bisulfite solution and 50 cc. of concentrated aqueous ammonia for 10 hours. The oil was removed, an excess of barium hydroxide was added, and the ammonia was boiled out. Sulfuric acid was then added to bring the solution almost to neutrality, and the insoluble barium salts were collected by filtration and washed. The filtrates were then concentrated to crystallization. The yield was 35 grams or 50%.

Sodium 1-phenylethane-1-sulfonate was prepared by refluxing a mixture of 42 grams of secondary phenylethyl chloride and 300 cc. of a solution containing 45 grams of anhydrous sodium sulfite and 7.2 grams of sodium hydroxide for 20 hours, with stirring. The product was worked up according to Houlton and Tartar.²⁰ The yield was 3.5 grams.

Phenylhydrazinium 1-phenylethane-1-sulfonate* was prepared by the method of Latimer and Bost.²¹ It melted at 115° in a preheated bath. On slow heating it decomposed gradually below its melting point to give a high-melting substance.

 α -Phenylethyl 2,4-dinitrophenyl sulfide* was prepared according to the method of Bost, Turner and Norton.²² Care must be taken to avoid excess alkali. Stout canary-yellow needles; m.p. 109°.

¹⁷ Norris, Watt, and Thomas, *ibid.*, **38**, 1078 (1916).

¹⁸ Sontag, Ann. chim., [11], 1, 428 (1934).

¹⁹ LEVENE, J. Biol. Chem., 70, 365 (1926).

²⁰ HOULTON AND TARTAR, J. Am. Chem. Soc., 60, 544 (1938).

²¹ LATIMER AND BOST, *ibid.*, **59**, 2500 (1937).

²² BOST, TURNER, AND NORTON, *ibid.*, **54**, 1985 (1932).

 α -Phenylethyl 2,4-dinitrophenyl sulfone* was prepared as by Bost, Turner and Norton.²² M.p. 161°, with decomposition.

Anal. Calc'd: N, 8.34.

Found: N, 8.44.

Attempted preparation of 1-phenylethane-1-sulfonyl chloride.—The well-dried and ground sodium, potassium, lead and barium salts of 1-phenylethane-1-sulfonic acid prepared from secondary phenylethyl bromide, chloride or mercaptan as described above, were treated with a 10% excess of phosphorus pentachloride in the presence and absence of carbon tetrachloride. In the absence of the solvent, an instantaneous vigorous reaction took place and the only product isolated was secondary phenylethyl chloride in good yield. In the presence of the solvent, the reaction was less vigorous, with, however, the same result. Phosphorus oxychloride and phosphorus trichloride gave oily products which did not react with ammonia in ether solution; thionyl chloride yielded only polystyrene.

Phenethyl alcohol was obtained through the courtesy of Van Ameringen-Haebler, Inc.

Phenethyl bromide, (b.p. 95.5° at 18 mm.), was prepared by the method of Schroeter, Lichtenstadt, and Irineu.²³

Phenethyl mercaptan (b.p. 93° at 14 mm.) was prepared as by Sontag.¹⁸

Potassium 1-phenylethane-2-sulfonate was prepared by the oxidation of the mercaptan as in the case of the isomeric sulfonate.

Barium 1-phenylethane-2-sulfonate was prepared from phenethyl bromide by the method of Ashworth and Burkhardt.^{1h}

Phenylhydrazinium 1-phenylethane-2-sulfonate* was prepared according to the method of Latimer and Bost;²¹ m.p. 154°.

1-Phenylethane-2-sulfonyl chloride was prepared by mixing the dried and powdered barium or potassium sulfonates with a 10% excess of phosphorus pentachloride. After heating for thirty minutes on the steambath and standing for several hours, the mixture was poured into ice-water, shaken in a separatory funnel and extracted with ether. The ether extract was dried overnight in the refrigerator over calcium chloride. The solution was filtered through carbon, and the ether was removed *in vacuo*. The residual oil was taken up in ligroïn, filtered through carbon if cloudy, and allowed to crystallize in the ice box. A 75% yield of material melting at $34^{\circ 4,5}$ was obtained.

1-Phenylethane-2-sulfonamide, (m.p. 121°) was prepared by passing dry ammonia into an ether solution of the sulfonyl chloride, filtering, evaporating to dryness and recrystallizing the residue twice from water. Carbon must be used on the first recrystallization to remove oily impurity.

Anal. Calc'd: C, 51.89; H, 5.94.

Found: C, 51.93; H, 5.91.

Zinc 1-phenylethane-2-sulfinate.—Ten grams of 1-phenylethane-2-sulfonyl chloride in 200 cc. of 98% alcohol and 10 grams of zinc dust, purified by sludging with diluted ammonia and drying *in vacuo*, were shaken for 10 hours. The mixture was then heated to 60° and allowed to stand overnight. It was filtered hot, and the precipitate was extracted twice with 100-cc. portions of boiling alcohol. From the combined filtrates was obtained on cooling 6.5 grams of white needles, or 65% theoretical. A small sample, on removal of the zinc with sodium carbonate, and acidification, yielded with ferric ion the characteristic orange-yellow insoluble ferric sulfinate.

²³ SCHROETER, LICHTENSTADT, AND IRINEU, Ber., 51, 1599 (1918).

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Phenethyl 2,4-dinitrophenyl sulfone.—Four and four-hundredths grams of zinc 1-phenylethane-2-sulfinate was suspended in 40 cc. of 50% alcohol, and 1.06 grams sodium carbonate in 10 cc. water was added. The zinc carbonate was filtered off, and the filtrate was evaporated to dryness *in vacuo*. The residue was dissolved in 50 cc. of 90% alcohol, and filtered, and 4 grams of 2,4-dinitrochlorobenzene in 15 cc. alcohol was added. The solution was refluxed for thirty minutes, and filtered hot, and the precipitate was washed with boiling alcohol. The yield, after recrystallization, was 4 grams; m.p. 131°.²²

Anal. Calc'd: N, 8.34.

Found: N, 8.12.

Phenethyl 2,4-dinitrophenyl sulfide was prepared by the method of Bost, Turner, and Norton²² from the mercaptan. It melted at 88°, and on oxidation²² yielded a material, m.p. 131°, which showed no depression in melting point when mixed with phenethyl 2,4-dinitrophenyl sulfone prepared from the sulfinate.

Phenethyl carboxymethyl sulfide was obtained through the courtesy of Dr. Read of this laboratory. It was prepared by the addition of thioglycollic acid to styrene, in the presence of ascaridole.

Phenylethyl carboxymethyl sulfoxide was prepared as by Holmberg.²⁴ On steam distillation with 1N sulfuric acid it yielded phenethyl mercaptan, which, on treatment with 2,4-dinitrochlorobenzene²² gave the sulfide, m.p. 88°, which mixture melting point determinations showed to be identical with the material prepared from phenethyl bromide.

Phenethylmercuric chloride was prepared by refluxing an alcoholic solution of 1-phenylethane-2-sulfinate with 1.5 molar equivalents of mercuric chloride until no further sulfur dioxide was evolved. The solution was filtered hot, the precipitate was extracted with boiling alcohol, and the filtrates were poured into water. The crude product thus precipitated was recrystallized once from alcohol, and then melted at 165°. Kharasch and Flenner²⁵ give 165° for the melting point of phenethylmercuric chloride.

Proof of structure of barium 1-phenylethylene-2-sulfonate.—Ten grams of barium 1-phenylethylene-2-sulfonate was converted to the sodium salt in 150 cc. of water. One-half gram of platinic oxide monohydrate was added, and the mixture shaken for six hours at room temperature under two atmospheres of hydrogen. The solution was freed of catalyst and evaporated to dryness. The yield was 8 grams of material which did not react with potassium permanganate. On conversion to the sulfonyl chloride as described in the preparation of 1-phenylethane-2-sulfonyl chloride, a crystalline material could not be obtained. The oil was therefore dissolved in ligroïn, and dry ammonia was passed in. The precipitate was filtered, washed with ligroïn and recrystallized several times from water; carbon was used to remove oily impurities. The resulting crystals melted at 118° and were shown to be 1-phenylethane-2-sulfonamide by determination of the melting point of a mixture with an authentic specimen.

Proof of the presence of addition product in the interaction of styrene and bisulfite.— Two runs were made according to the method of Ashworth and Burkhardt,^{1h} one at a pH of 5.0, the other at 5.9. The former yielded 4 grams of crude product in 4 days, the latter yielded in two days 6.5 grams of material of which 2.5 grams was isolated as pure barium 1-phenylethylene-2-sulfonate. The crude residues were

²⁴ HOLMBERG, J. prakt. Chem., [2], 141, 93 (1934).

²⁵ KHARASCH AND FLENNER, J. Am. Chem. Soc., 54, 674 (1932).

treated separately with phosphorus pentachloride, the crude sulfonyl chloride being extracted with ether, dried, and treated with ammonia. The crude product in each case yielded after two recrystallizations a sulfonamide melting at $131-2^{\circ}$ which corresponds to one part of 1-phenylethane-2-sulfonamide with six of 1-phenylethylene-2-sulfonamide (assuming that these are the only components of the system). The mother-liquors from the recrystallizations were then combined and potassium permanganate was added in slight excess. The filtered solution was then extracted with an equal volume of ether. The ether layer was evaporated on the steam bath. The residue was taken up in boiling water and the solution was filtered with carbon. Upon cooling there was a small yield of crystals, m.p. 119°. No depression in melting point was noted when this substance was mixed with 1-phenylethane-2-sulfonamide.

1-Phenylethylene-2-sulfonyl chloride.—Seventeen grams of barium 1-phenylethylene-2-sulfonate and 17 grams of phosphorus pentachloride were mixed in an Erlenmeyer flask fitted with a calcium chloride tube, and the mixture was heated on the steam bath until the mass became viscous; it was then allowed to stand overnight. It was then poured into ice-water and shaken with 250 cc. of ligroïn. The whole mass was filtered; the ligroïn layer was separated, and placed in the ice box. The aqueous layer was discarded. The precipitate on the filter was extracted with 150 cc. of ether, and was dried over calcium chloride. Upon the removal of the ether *in vacuo*, 6.5 grams of the sulfonyl chloride was obtained; m.p. 87° .³ The ligroïn solution yielded an additional 2.3 grams of crystals; m.p. 87° . The total yield was 75% of the theoretical. The ligroïn mother-liquor contained only highly impure material.

Phenylhydrazinium 1-phenylethylene-2-sulfonate* was prepared according to the method of Latimer and Bost;²¹ m.p. 148°.

Zinc 1-phenylethylene-2-sulfinate.*—Six grams of 1-phenylethylene-2-sulfonyl chloride was treated in the same manner as described for 1-phenylethanesulfonyl chloride, yielding 1.2 grams of the zinc salt.

Styryl 2,4-dinitrophenyl sulfone; was prepared in the same manner as phenethyl 2,4-dinitrophenyl sulfone; 1.2 grams of the zinc sulfinate yielded 0.7 grams of sulfone; m.p. 158°.

Anal. Calc'd: N, 8.38.

Found: N, 8.39.

Styrylmercuric chloride* was prepared in the same manner as phenethylmercuric chloride; m.p. 207°.

Anal. Cale'd: Hg, 59.2.

Found: Hg, 59.0.

1-Phenylethylene-2-sulfonamide, m.p. 142°,³ was prepared in the same manner as 1-phenylethane-2-sulfonamide.

Anal. Calc'd: C, 52.46; H, 4.92; N, 7.75.

Found: C, 52.90, 52.77, 52.85; H, 4.93, 4.87, 5.08; N, 7.58, 7.46.

SUMMARY

1. The interaction of bisulfite with ethylene, propylene, styrene, allyl alcohol and cinnamyl alcohol has been shown to proceed only in the presence of oxygen, or such oxidizing agents as nitrite and nitrate ions.

2. The products of addition of bisulfite to propylene, isobutylene, sty

rene, and allyl alcohol are those predicted by the rule for free-radical additions to double bonds.

3. The interaction of bisulfite and styrene yields mainly 1-phenylethy-lene-2-sulfonate.

4. A chain mechanism involving free radicals has been proposed to explain the addition of bisulfite to unsaturated compounds.

5. New derivatives of 1-phenylethane-1-sulfonic acid, 1-phenylethane-2sulfonic acid, 1-phenylethylene-2-sulfonic acid, and 1-hydroxypropane-3sulfonic acid have been prepared.