Since pure boric oxide is white, these dark brown globules must contain additional boron in some form other than B_2O_3 and B [probably as $(BO)_x$]. Quantitative measurements of the condensed phase reactions between B and B_2O_3 at temperatures in excess of 1000° would be of great value for further elucidating the origin and energetics of the gaseous suboxide of boron.

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THE STABILITY OF ORGANIC SULFONIC ACIDS IN DILUTE AQUEOUS HYDROGEN PEROXIDE

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In a recent communication,[1] Wood has drawn attention to the degradation of sulfonated cross-linked ion-exchange resins with hydrogen peroxide. Some years ago we commenced a study of the stability of sulfonic acids toward hydrogen peroxide[2] but the work was not completed. The results obtained are however of interest in confirming and extending Wood's observations.

The reactions of the following acids with hydrogen peroxide were studied: methanesulfonic-, benzenesulfonic-, *m*-nitrobenzenesulfonic-, toluene-*p*-sulfonic-, polyvinyl sulfonic-, polystyrene sulfonic-, and two sulfonated styrenedivinylbenzene copolymers. In all cases extensive decomposition of the sulfonic acids occurred at 60° with 2.94 molar aqueous hydrogen peroxide solutions. Sulfuric acid, carboxylic acids and carbon dioxide were produced. The results are summarized in Table I and Figs. 1, 2 and 3.

Experimental

Since oxidations involving hydrogen peroxide are catalyzed to varying extents by metallic ions, care was taken in purifying the sulfonic acids. The water soluble materials were freed from traces of copper and iron by passing 0.1 *N* aqueous solutions slowly through a column of sulfonated cross-linked polystyrene (10% divinylbenzene; resin in the hydrogen form). Spectrographic examination of materials treated in this way showed that copper and iron were no longer present. The cross-linked materials were laboratory prepared samples and it is unlikely that they contained even trace amounts of copper or iron.

The oxidations were carried out in the presence of a large excess of hydrogen peroxide. Small samples of the reaction mixtures were withdrawn from time to time and titrated against 0.05 *N* sodium hydroxide. Hydrogen peroxide was estimated in other small samples by titration with 0.1 *N* potassium permanganate. Sulfuric acid was determined as barium sulfate; consistent results were obtained by following Rudy's procedure.[3]

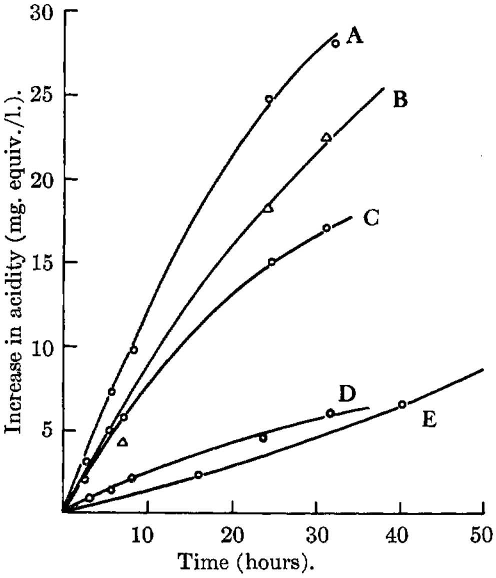

Fig. 1.—Oxidation of sulfonic acids with hydrogen peroxide at 60°: A, 5×10^{-2} *M* toluene-*p*-sulfonic acid + 2.94 *M* H_2O_2; B, 5×10^{-2} *M* *m*-nitrobenzenesulfonic acid + 2.94 *M* H_2O_2; C, 5×10^{-2} *M* benzenesulfonic acid + 2.94 *M* H_2O_2; D, 5×10^{-2} toluene-*p*-sulfonic acid + 0.29 *M* H_2O_2; E, 5×10^{-2} *M* methanesulfonic acid + 2.94 *M* H_2O_2.

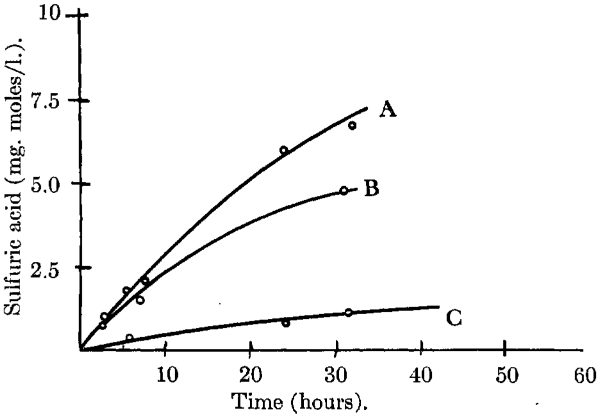

Fig. 2.—Sulfuric acid produced during oxidation of sulfonic acids: A, conditions as for Fig. 1, curve A; B, conditions as for Fig. 1, curve C; C, conditions as for Fig. 1, curve D.

The reaction flasks were connected to absorption trains consisting of two traps containing sulfuric acid, a calcium chloride–soda lime tube and, finally, another trap containing sulfuric acid. In all experiments a slow stream of nitrogen was bubbled first through a hydrogen peroxide "saturator" and then through reaction flask and absorption train. It was found that under these conditions all the carbon dioxide formed during the reactions was swept into the absorption train and that changes in volume of the reaction mixtures due to evaporation were negligible. The weight of carbon dioxide evolved was determined by weighing the soda lime trap. Corrections were applied to allow for changes in volume of the reaction mixtures due to removal of samples for titration.

Table I

Oxidation of Polyvinyl Sulfonic Acid at 60°

2.94 *M* H_2O_2, 4.2×10^{-2} *M* Acid

Time (hr.)	10.5	24.5	31.5	48.0	55.0	72.0	80.0
Increase in acidity (mg. equiv./l.)	14.0	18.5	19.5	24.0	28.0	38.0	42.5
H_2SO_4 (mg. moles/l.)	16.5	18.5	20.0	..	25.5	..	29.5
CO_2 (mg. moles/l.)	0.5	1.5	1.5	6.5	9.0	16.0	17.5

Discussion

It is evident that even in the absence of catalytic

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[1] W. Wood, This Journal, **61**, 832 (1957).

[2] Chemistry Research 1952, Her Majesty's Stationery Office, London, 1953.

[3] R. B. Rudy, *J. Res. Natl. Bur. Standards*, **16**, 555 (1936).

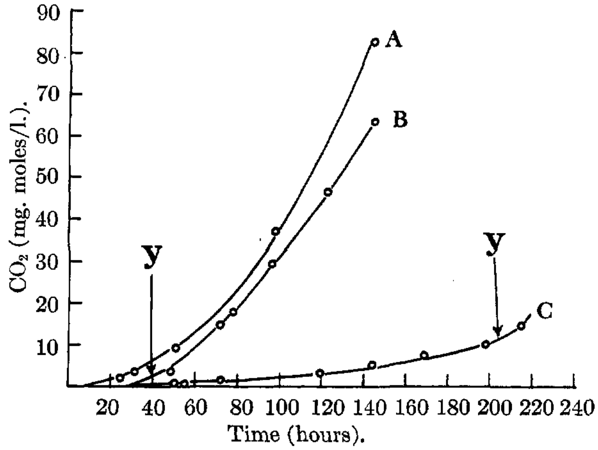

Fig. 3.—Decomposition of polymeric arylsulfonic acids: A, polystyrenesulfonic acid (sulfonated styrene–divinylbenzene copolymer); B, 0.5% divinylbenzene; C, 10% divinylbenzene; all 5 × 10^{-2} *M* with respect to reaction mixture; Y, polymer in solution.

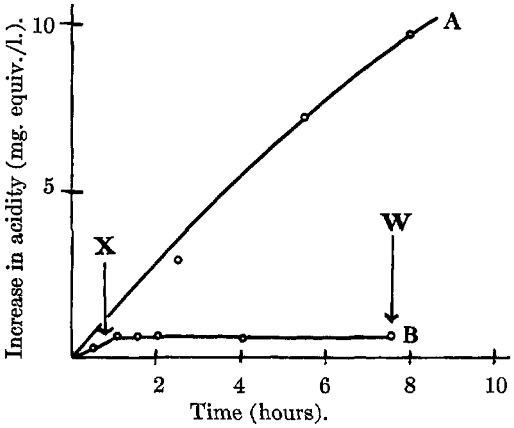

Fig. 4.—Effect of added acrylonitrile on the oxidation: A, 2.94 *M* H_2O_2, 5 × 10^{-2} *M* $C_7H_7SO_3H$; B, as above but 1 *M* with respect to acrylonitrile; X, polymer pptd.; W, 90% yield of polymer.

amounts of copper or iron, extensive decomposition of both aliphatic and aromatic sulfonic acids occurs under the reaction conditions described. The course of the breakdown of the aromatic sulfonic acids is undoubtedly complex, and the marked increases in total acidity and sulfuric acid in the reaction mixtures support the view that ring-breaking must be an early consequence of the oxidation. The rates of decomposition of benzenesulfonic, *m*-nitrobenzenesulfonic and toluene-*p*-sulfonic acids are remarkably similar (Fig. 1, curves A, B and C), and it is tempting to suggest that the first step at least of their decomposition involves a radical, rather than an ionic mechanism. Some support for this view has been obtained by observing the effect of adding a 1 molar aqueous solution of acrylonitrile to a toluene-*p*-sulfonic acid–hydrogen peroxide substrate at 60°. The results are shown in Fig. 4. It will be seen that the oxidation reaction is virtually completely suppressed, but that rapid polymerization of the acrylonitrile takes place. Experiments with methanesulfonic acid and benzenesulfonic acid gave similar results.

Polystyrenesulfonic acid and its cross-linked analogs may be attacked both in the polymer chain and the aromatic ring system. Figure 3 shows the carbon dioxide evolution from typical reaction mixtures. The material containing 0.5% divinylbenzene as cross-linking agent behaved very similarly to polystyrenesulfonic acid. The rate of evolution of carbon dioxide with both the 0.5% and 10% cross-linked materials increased markedly when complete solution was achieved. This increase in rate of decomposition might be expected as a result of the transition from a heterogeneous to a homogeneous reaction.

It will be observed from Table I that the oxidation of polyvinylsulfonic acid showed features which had not previously been encountered. Until rather less than half the sulfonic acid groupings had disappeared virtually no carbon dioxide was evolved and the increase in acidity of the reaction mixture was due entirely to the presence of sulfuric acid. There was a marked increase in the total acidity of the reaction mixture after half the sulfonic groups had formed sulfuric acid. This increase in acidity was greater than the increase in sulfuric acid and was accompanied by a sharp rise in the amount of carbon dioxide evolved. Thus, in contrast to the other sulfonic acids, polyvinylsulfonic acid does not undergo appreciable degradation of the molecule until roughly half the sulfonic acid groupings have disappeared.

Acknowledgment.—This note is published with the approval of the Director, Chemical Research Laboratory.

THE SUBLIMATION PRESSURE OF KRYPTON BELOW 80°K.

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In connection with a study[1] of transitions in absorbed monolayers of krypton it became necessary to know the vapor pressure of solid krytpon in a range considerably below those previously recorded in the literature. In the absorption apparatus employed[2] the vapor pressure of the krypton could be measured directly by condensation of a large excess into the adsorption chamber. Temperatures were measured with an argon vapor pressure thermometer, using the tables of Hoge[3] for conversion to degrees Kelvin. Krypton, of spectroscopic grade (Linde Air Products Company), was used directly without further purification. The argon employed in the vapor pressure thermometer, originally "99.6%" grade (Ohio Chemical and Manufacturing Company), was passed through a charcoal trap at liquid nitrogen temperature to remove adsorbable impurities.

The solid triangles of Fig. 1 show how our data overlap and extend those of previous investigators.[4-7] (The experimental points above 80°K. of

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(1) B. B. Fisher and W. G. McMillan, *J. Am. Chem. Soc.*, **79**, 2969 (1957); *J. Chem. Phys.*, to be published.

(2) Ref. 1, Part I.

(3) H. J. Hoge, Table 19.50, NBS-NACA, Tables of Thermal Properties of Gases, July, 1950.

(4) K. Peters and K. Weil, *Z. physik. Chem.*, **A148**, 27 (1930).

(5) E. Justi, *Physik. Z.*, **36**, 571 (1935).