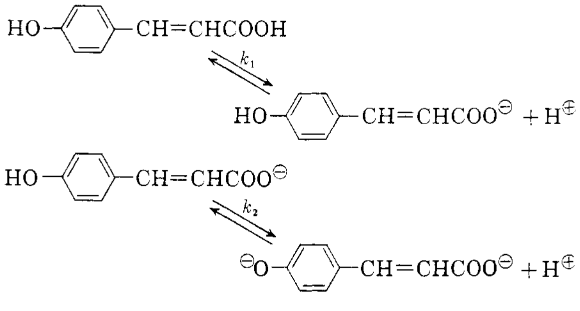
Concentration of the three species at each hydrogen ion concentration was calculated by use of the relationships

$$\alpha_1 = H^2/M; \ \alpha_2 = K_1H/M; \ \alpha_3 = K_1K_2/M$$

where $M = H^2 + K_1H + K_1K_2$ and $\alpha_1$ = concentration of undissociated acid, $\alpha_2$ = concentration of monoanion, $\alpha_3$ = concentration of dianion, $H$ = hydrogen ion concentration and $K_1$ and $K_2$ are constants based on the consecutive equilibria



Dissociation constants at 100° were determined experimentally. The first dissociation of *p*-hydroxycinnamic acid at 25° has been measured as $2.34 \times 10^{-5}$.[21] A solution of the acid (0.02 *M*) was adjusted to *p*H 4.80 and heated to 100°, whereupon the *p*H decreased to 4.63. From the apparent ionization at 25°, $K_1$ at 100° was calculated to be $3.41 \times 10^{-5}$ and $\Delta H_{\text{ion}}$ = 1390 cal./mole. From titration data at 25°,[22] the second dissociation constant (apparent) for *p*-hydroxycinnamic acid was found to be $3.1 \times 10^{-10}$. A solution, adjusted to *p*H 9.50 at 25°, was observed to drop to *p*H 8.57 at 100°. By calculation, $K_2$ at 100° was found to be $2.70 \times 10^{-9}$ and $\Delta H_{\text{ion}}$ = 6530 cal./mole. Calculated rate constants then were obtained as described by equations 1 and 3 (see Discussion).

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[21] W. A. Roth and R. Stoermer, *Ber.*, **46**, 260 (1913).

[22] The procedure described by T. V. Parke and W. W. Davis, *Anal. Chem.*, **26**, 642 (1954), for apparent *pK* values was used.

BETHESDA, MD.

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[CONTRIBUTION FROM CALIFORNIA RESEARCH CORPORATION]

# Oxidation of Organic Compounds with Aqueous Sulfate

BY WILLIAM G. TOLAND

RECEIVED AUGUST 14, 1959

A new oxidizing agent, inorganic sulfate, has been found to have wide utility in organic chemistry. It is most useful for the conversion of methyl groups to carboxylates. Somewhat related to the use of sulfur and a base and the Willgerodt reaction, it is superior in terms of oxidizing capacity per unit weight, simplicity of handling, economy and ease of product isolation. A singular requirement in its application is the presence of a lower valence state of sulfur to initiate the reaction.

## Introduction

Previously it was shown that by the use of sulfur and an aqueous base many organic compounds can be oxidized to carboxylic acids.[1] One of the simplest systems for study is the oxidation of toluic acid with sodium polysulfide, ammonium polysulfide or sodium hydroxide plus sulfur.[2] There are several drawbacks to such systems. Either polysulfide must be specially prepared, or a heterogeneous system must be used involving a separate sulfur phase. The quantities of sulfur required may outweigh the compound to be oxidized; for instance, to oxidize one mole of xylene (106 g.) requires 6 moles of sulfur (192 g.). In turn, 6 moles of $H_2S$ are generated which, if not neutralized, limit the capacity of any reaction vessel owing to the large gas volume or the high pressure generated.

A solution is suggested by the behavior of the sodium hydroxide–sulfur mixtures on heating. Disproportionation occurs to dissolve the sulfur completely. Yields of oxidation products indicate that all of this sulfur can be consumed to give $H_2S$. Thus, whatever disproportionation occurs must be reversible under certain conditions, or the disproportionated products must be equally effective oxidants. The literature gives many examples of such disproportionations of sulfur in basic solutions.[3] Products contain not only sulfide and polysulfide but sulfite and thiosulfate in varying proportion as a function of the ratio of reactants and temperature. It would thus appear reasonable to utilize sulfite or thiosulfate as homogeneous oxidant with greater oxidizing capacity than free sulfur and possibly with greater reactivity. This is in contrast to the use of thiosulfate as a catalyst, described by Pattison and Carmack[4]

$$\text{ArCH}_3 + 3\text{S} + \text{NH}_4\text{OH} + \text{H}_2\text{O} \longrightarrow \text{ArCO}_2\text{NH}_4 + 3\text{H}_2\text{S} \quad (1)$$

$$\text{ArCH}_3 + (\text{NH}_4)_2\text{SO}_3 \longrightarrow \text{ArCO}_2\text{NH}_4 + \text{H}_2\text{O} + \text{NH}_4\text{SH} \quad (2)$$

$$\text{ArCH}_3 + {}^3/_4(\text{NH}_4)_2\text{S}_2\text{O}_3 \longrightarrow \text{ArCO}_2\text{NH}_4 + {}^1/_4\text{H}_2\text{O} + \text{H}_2\text{S} + {}^1/_2\text{NH}_4\text{SH} \quad (3)$$

## Results

Experimental results with the various valence states of sulfur as oxidants are shown in Table I. One of the puzzling features of the oxidations with sulfur is the variation of conversions. In the study of variables, a correlation was found between conversions and the ratio of base to oxidant. The fate of the sulfur finally was established as its disproportionation to sulfate, a reaction not heretofore recognized, although Priestley, in 1775, noted

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[1] W. G. Toland, D. L. Hagmann, J. B. Wilkes and F. J. Brutschy, THIS JOURNAL, **80**, 5423 (1958).

[2] W. A. Pryor, *ibid.*, **80**, 6481 (1958).

[3] (a) H. V. Tartar and C. Z. Graves, *ibid.*, **46**, 574 (1924); (b) E. R. Bertozzi, U. S. Patent 2,796,325, June 18, 1957; (c) E. Schulek and E. Koros, *Acta Chim. Acad. Sci. Hung.*, **3**, 125 (1953).

[4] D. B. Pattison and M. Carmack, THIS JOURNAL, **68**, 2033 (1946).

TABLE I

SULFUR COMPOUNDS OF INTERMEDIATE VALENCES AS OXIDANTS

| Run | Oxidant[a] | Compound oxidized | Other[a] | Water[a] | Temp., °C. | Time, min. | Conversion, % | Yield of acid, % | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | Toluic | Phthalic |
| 1 | 4.0 S | Sodium toluate[b] | None | 56 | 288 | 360 | 100 | .. | 87.1[c] |
| 2 | 3.0 S | | 1.0 NaOH | 53 | 293 | 270 | 72 | .. | 92.0 |
| 3 | 6.0 S | | 3.0 NaOH | 56 | 288 | 230 | 100 | .. | 90.5 |
| 4 | 2.7 S | | 5.5 NaOH | 56 | 282 | 240 | 7.5 | .. | 95 |
| 5 | 1.0 $Na_2SO_3$ | Sodium *p*-toluate | 0.7 $H_2S$ | 100 | 315 | 60 | 13.6 | .. | 87.1 |
| 6 | 1.0 $Na_2SO_3$ | | 2.0 AcOH<br>0.7 $H_2S$ | 100 | 315 | 60 | 23.3 | .. | 80+ |
| 7 | 2.2 $(NH_4)_2SO_3$ | Xylene[d] | 2.2 $NH_4SH$ | 56 | 315 | 60 | 96.7 | 4.2 | 87.2 |
| 8 | 2.0 $NH_4HSO_3$ | | 2.4 $NH_4SH$ | 56 | 315 | 60 | 96.1 | 5.9 | 76.4 |
| 9 | 2.0 $(NH_4)_2SO_3$ | | 0.4 $NH_4OH$ | 70 | 315 | 60 | 69.5 | 38.5 | 25.9 |
| 10 | 1.0 $Na_2S_2O_3$ | Sodium *p*-toluate | None | 100 | 315 | 60 | 40.6 | .. | 93.2 |
| 11 | 1.5 $Na_2S_2O_3$ | *m*-Xylene | None | 53 | 315 | 90 | 34.0 | 42.2 | 37.9 |
| 12 | 1.5 $(NH_4)_2S_2O_3$ | | None | 53 | 315 | 90 | 100 | 0 | 94.8 |

[a] Moles/mole compound to be oxidized. [b] 85% *m*-toluate, 15% *p*-toluate. [c] Also found 10.3% yield benzoic acid. [d] 85% *m*-xylene, 15% *p*-xylene.

that sulfur dioxide in water at 150° yielded some sulfur and sulfuric acid.[5] It is apparently highly favored at temperatures above about 300°. Equations for such disproportionations are demonstrated for sulfur (4), sulfite (5) and thiosulfate (6)

$$4S + 8NaOH \longrightarrow Na_2SO_4 + 3Na_2S + 4H_2O \quad (4)$$

$$4Na_2SO_3 \longrightarrow 3Na_2SO_4 + Na_2S \quad (5)$$

$$Na_2S_2O_3 \longrightarrow Na_2SO_4 + S \quad (6)$$

It is realized, of course, that relationships not shown here exist between all these species. Once sulfate is formed by these competing reactions, it becomes unavailable as an oxidant under the conditions of experiments in Table I. To the extent they did occur, conversions of toluic acids and xylene were reduced.

By proper combinations and simplifications of equations for the equilibrium constants for these reactions and those for the ionization of water and $H_2S$, it can be shown that

$$K = (H_2S)^3(SO_4^{=})(H^+)^2 \quad (7)$$

which corresponds to the reaction

$$4S + 4H_2O = 3H_2S + H_2SO_4 \quad (8)$$

This demonstrates that sulfate formation is *p*H dependent, and that too high a ratio of base to sulfur species is undesirable. It also explains why conversions with ammonia or ammonium salts are less sensitive to the proportions of reagents. Ammonia, being a much weaker base than sodium hydroxide, gives solutions with higher hydrogen ion concentrations (lower hydroxyl ion concentration). The high dependence upon $H_2S$ pressure is also evident.

During the course of an oxidation, the formation of carboxyl groups will have the desirable effect of lowering the *p*H and reducing sulfate formation. In the case of run 9 a complete accounting of materials was made showing that essentially all sulfur can be accounted for as either sulfide from the oxidation of xylene or sulfate from the disproportionation reaction. Conversion of xylene was incomplete due to the increase in *p*H as reaction 2 proceeded, which in turn permitted the *p*H-dependent reaction 5 to compete more strongly, withdrawing sulfate.

An analysis of the disproportionation reaction was made on the oxidant mixture used in run 7 by exposing it to reaction conditions in the absence of xylene and determining the sulfur species produced. It showed more sulfate formation than would be expected on the basis of the amount of oxidation which had occurred. One of two possible conclusions must be drawn. The formation of carboxyl groups during the oxidation lowered the *p*H of the system sufficiently so that less sulfate formed, or sulfate which had formed was reduced under reaction conditions and thus could serve as an oxidant.

**Use of Sulfate.**—The hypothesis that aqueous sulfate under relatively mild conditions might be a potential oxidizing agent is new. It is known that dry calcium sulfate will oxidize coke and be reduced to sulfide, sulfur or sulfur dioxide above about 900°.[6] Sulfuric acid in concentrated form will oxidize even saturated aliphatic hydrocarbon gases, being itself reduced to sulfur dioxide.[7] To verify the hypothesis, xylene was heated with aqueous ammonium sulfate under oxidizing conditions. No reaction occurred other than severe corrosion of the autoclave. This is in agreement with Lewis and Randall,[5] who observed no reduction of sulfate alone after two days at 180°. Apparently then, sulfate itself does not attack these organic species under such conditions. On the other hand, sulfate reduction is strongly dependent on hydrogen sulfide concentration, according to eq. 7, and can be shown to be similarly related to the concentration of any other dissolved form of inorganic sulfur species in which sulfur has a valence below +6.

Repetition of the above experiment with hydrogen sulfide present established the point dramatically. *p*-Xylene was oxidized to a mixture of terephthalic amides and ammonium salts in over 96% yield. No corrosion was observed in this case.

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(5) (a) G. N. Lewis, M. Randall and F. R. v. Bichowsky, THIS JOURNAL, **40**, 356 (1918); (b) G. N. Lewis and M. Randall, *ibid.*, **40**, 362 (1918).

(6) W. Q. Hull, F. Schon and H. Zirngibl, *Ind. Eng. Chem.*, **49**, 1204 (1957).

(7) British Patent 606,554 to Clark Bros. Co., Inc., issued August 17, 1948.

TABLE II

COMPOUNDS OXIDIZED WITH AQUEOUS AMMONIUM SULFATE

| Compound | Moles | $(NH_4)_2SO_4$, moles | $H_2S$, moles | Water, moles | Temp., °C. | Pressure, atm. | Time, min. | Feed conversion, % | Major products | Yield, mole % |
|---|---|---|---|---|---|---|---|---|---|---|
| Methane[a] | 3.0 | 3.03 | 1.0 | 83 | 325-350 | 23.1 | 70 | (Partial) | CO | 8 |
| | | | | | | | | | $CO_2$ | 92 |
| Cyclohexane[a] | 3.0 | 2.0 | 1.0 | 90 | 315 | 19.5 | 120 | 51.3 | Phenol | .. |
| Methylcyclohexane[a] | 3.0 | 2.0 | 1.0 | 90 | 315 | 19.1 | 60 | 36.7 | Benzoic acid | .. |
| | | | | | | | | | Phenol | .. |
| Ethylene[a] | 4.0 | 2.0 | 7.0 | 90 | 325 | 24.7 | 15 | 100 | Acetic acid | 63.5 |
| Propylene[b] | 3.3 | 1.51 | 3.9 | 60 | 315 | 26.8 | 60 | 81.8 | Propionic acid | .. |
| Isobutene[b] | 2.9 | 1.67 | 3.9 | 60 | 315 | 32.2 | 45 | 83.0 | Isobutyric acid | .. |
| Cycloöctatetraene[b] | 0.5 | 0.8 | 0.2[c] | 50 | 330 | 16.1 | 90 | 100 | Benzoic acid | .. |
| Tetrahydrofurfuryl alcohol[a] | 1.0 | 1.0 | 0.6 | 90 | 315 | 15.8 | 90 | 100 | Glutaric acid | .. |
| | | | | | | | | | Acetic acid | .. |
| *m*-Xylene[b] | 2.12 | 3.5 | 1.0[d] | 53 | 325 | 19.7 | 60 | 100 | Isophthalic acid | 89 |
| *p*-Xylene[a] | 1.5 | 2.3 | 4.6[e] | 100 | 315 | 20.7 | 60 | 56.8 | *p*-Toluic acid | 42.4 |
| | | | | | | | | | Terephthalic acid | 37.6 |
| *p*-Xylene[a] | 1.5 | 2.3 | 4.6[c] | 100 | 315 | 20.7 | 360 | 100 | Terephthalic acid | 96.2 |
| *o*-Xylene[b] | 1.86 | 3.5 | 1.0 | 50 | 325 | 20.4 | 40 | 90 | Benzoic acid | 27.2 |
| | | | | | | | | | *o*-Toluic acid | 6.0 |
| | | | | | | | | | *o*-Phthalic acid | 35.1 |
| *m*-*p*-Toluic acid[b] (85/15) | 2.12 | 1.73 | 1.1 | 53 | 325 | 18.0 | 30 | 100 | Isophthalic acid | 99.7 |
| | | | | | | | | | Terephthalic acid | |
| *p*-Toluenesulfonic acid[b,f] | 1.0 | 0.76 | 1.0 | 60 | 332 | 18.2 | 90 | 100 | *p*-Sulfobenzoic acid | 59.3 |

[a] In 4.5-liter autoclave. [b] In 2.5-liter autoclave. [c] Aq. $(NH_4)_2S$ was used in place of $H_2S$. [d] Sulfur was used in place of $H_2S$. [e] Aq. $NH_4HS$ used in place of $H_2S$. [f] As $NH_4$ salt.

TABLE III

OXIDATIONS WITH VARIOUS SULFATES

| Oxidant | Compound oxidized | Initiator[a] | Water[a] | Temp., °C. | Time, min. | Conversion, % | Acid product | Yield, % |
|---|---|---|---|---|---|---|---|---|
| 1.53 $(NH_4)_2SO_4$ | *p*-Xylene | 3.1 $NH_4SH$ | 80 | 315 | 360 | 100 | Terephthalic | 96.2 |
| 0.67 $Al_2(SO_4)_3$ | *p*-Xylene | 1.0 $H_2S$ | 50 | 335 | 60 | 100 | Benzoic | 13.1 |
| | | | | | | | *p*-Toluic | 12.3 |
| | | | | | | | Terephthalic | 27.5 |
| 0.5 $K_2SO_4$ | *p*-Xylene | 0.66 $H_2S$ | 100 | 329 | 60 | 98.6 | Benzoic | 1.0 |
| 1.5 $KHSO_4$ | | | | | | | Terephthalic | 73.0 |
| 0.29 $Al_2(SO_4)_3$ | Toluic acids[b] | 0.2 S | 40 | 327 | 30 | 61.9 | Isoterephthalic | 63.8 |
| 1.65 $FeSO_4$ | Xylene[c] | 1.0 $H_2S$ | 53 | 327 | 60 | 59.6 | Benzoic<br>Toluic | 7 |
| 1.65 $Li_2SO_4$ | Xylene[c] | 1.0 $H_2S$ | 53 | 329 | 60 | 15.3 | Toluic | 26.2 |
| 3.1 $Na_2SO_4$ | *p*-Xylene | 2.2 $(NH_4)_2S$ | 74 | 315 | 60 | 6.9 | *p*-Toluic | 34.8 |
| | | | | | | | Terephthalic | 14.6 |
| 1.0 $K_2SO_4$ | Toluene | 0.5 $H_2S$ | 50 | 343 | 120 | 45.0 | Benzoic | 24.5 |

[a] Moles/mole compound to be oxidized. [b] 85% *m*-, 15% *p*-toluic acid. [c] 85% *m*-, 15% *p*-xylene.

$$C_6H_4(CH_3)_2 + {}^3/_2(NH_4)_2SO_4 \longrightarrow C_6H_4(CO_2NH_4)_2 + 2H_2O + NH_3 + {}^3/_2H_2S \quad (9)$$

The general utility of aqueous sulfate as an oxidant for a wide variety of organic compounds when triggered by a lower valence state of sulfur then was demonstrated. Table II summarizes the results. Emphasis was placed on the alkyl aromatics, particularly the xylenes, where the method appears admirably suited to the preparation of the phthalic acid isomers. Non-aromatics were screened qualitatively to determine the scope of the oxidation reaction, but no attempt was made to find optimum conditions. Yields found with these compounds therefore have little significance.

It was found desirable to increase temperatures to about 300–350° to obtain faster reaction rates. Below about 300° sulfate reduction becomes extremely slow, even though the organic compound may be capable of oxidation by other forms of sulfur under milder conditions. In general this agent appears capable of oxidizing any organic compound that contains at least one carbon–hydrogen bond. Paraffins and olefins are oxidized to carboxylic acids, yields falling off rapidly above about $C_8$. A wide variety of alkylated aromatic hydrocarbons are oxidizable in high yields to their respective carboxylic acids. Partially oxygenated compounds are also effectively converted to carboxylates. The ring of many heterocyclics will be destroyed, leading to oxygenated products. Dehydrogenating activity typical of sulfur is found in cyclic compounds, such as cyclohexane, to give the benzene ring as well as oxidation to phenolic compounds.

Of the various sulfates, the ammonium salt is a particularly useful oxidant. Its high water solubility and that of the resultant carboxylates and sulfides, the built-in *p*H control possible with a volatile base, and its relatively low molecular weight are all advantages. However, other sulfates do function. Some are listed in Table III.

Amphoteric salts are next in utility, since they come from weak bases, followed by potassium, then sodium, then lithium sulfate. Alkaline earth sulfates are least satisfactory. Sulfuric acid itself is of limited value owing to its corrosive nature.

Of the lower valence states of sulfur suitable for initiating sulfate reduction, hydrogen or ammonium sulfide are the most convenient. They are ultimately formed in the oxidation reaction anyway so that no new components need be introduced. Free hydrogen sulfide has the advantage of maintaining a lower *p*H in the system. It might be considered as a catalyst in the sense that it is regenerated during the oxidation reaction, and only relatively small proportions are necessary. Approximately 0.1 mole of sulfide per mole of sulfate is adequate. Use of the other valence states of sulfur is shown in Table IV.

TABLE IV

INITIATORS FOR SULFATE REDUCTION[a]

| Initiator | | $(NH_4)_2SO_4$ | Hydrocarbon | Carboxylate formed |
|---|---|---|---|---|
| None | | 1.65 | 1.0 *p*-Xylene | 0.0 |
| $H_2S$ | 0.5 | 1.65 | 1.0 *p*-Xylene | 1.9 |
| $(NH_4)_2S$ | 0.2 | 0.8 | 1.0 Toluene | 0.72 |
| S | 1.0 | 3.5 | 2.12 *m*-*p*-Xylene[b] | 3.75 |
| $NH_4HSO_3$ | 0.5 | 3.5 | 2.12 *m*-*p*-Xylene[b] | 3.33 |
| $(NH_4)_2S_2O_3$ | 0.5 | 3.5 | 2.12 *p*-Xylene | 2.8 |
| $H_2Se$ | 0.2 | 0.8 | 1.0 Toluene | 0.51 |

[a] All quantities in moles. [b] 85% *m*-, 15% *p*-xylene.

Other reducing agents were screened as initiators of sulfate reduction. None approach the effectiveness of the lower valence sulfur species, and most are completely ineffective. Among those which failed are benzaldehyde, ethylene, hydroquinone, active carbon and ammonium iodide. Hydrogen selenide proved reasonably successful.

In those instances where oxidation of an organic compound occurs with sulfur and ammonia or ammonium polysulfide below 300°, as in the Willgerodt reaction, it may be detrimental to yields to have to run the reaction at the higher temperatures required to utilize sulfate most effectively. By first reducing sulfate with massive amounts of sulfide at 300–350°, a polysulfide solution is made which then can be used under milder conditions for the oxidation.

Sulfate reduction is also a potentially useful method of making elemental sulfur from many sulfates and from hydrogen sulfide. After establishing equilibrium, the temperature is lowered below that where sulfate is formed or reduced and excess hydrogen sulfide and ammonia vapor are withdrawn from the vessel. A molten sulfur phase and a water phase remain.

$$(NH_4)_2SO_4 + 4H_2S \longrightarrow (NH_4)_2S_5 + 4H_2O \quad (10)$$

$$(NH_4)_2S_5 \longrightarrow 2NH_3\uparrow + H_2S + 4S \quad (11)$$

Some examples of this system are given in Table V.

TABLE V

REDUCTION OF SULFATES WITH SULFIDE[a]

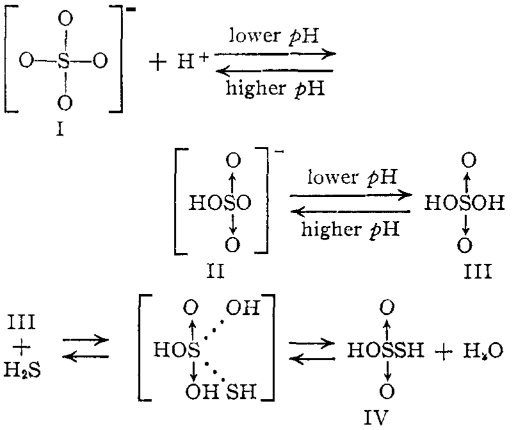
| Sulfate | | $H_2S$ | Water | Reactor, ml. | Temp., °C. | Time, min. | Sulfur |
|---|---|---|---|---|---|---|---|
| $(NH_4)_2SO_4$ | 2.0 | 7.0 | 90 | 4500 | 327 | 60 | 6.2 |
| $Na_2SO_4$ | 1.5 | 6.0 | 53 | 2500 | 327 | 15 | 0.75 |
| $K_2SO_4$ | 2.0 | 8 8 | 50 | 4500 | 335 | 80 | 0.42 |
| $K_2SO_4$[b] | 2.0 | 8.8 | 50 | 4500 | 335 | 80 | 1.21 |
| $MgSO_4 \cdot 7H_2O$ | 2.5 | 10.0 | 90 | 4500 | 327 | 60 | 0.1 |
| $CaSO_4 \cdot 2H_2O$ | 1.5 | 6.0 | 53 | 2500 | 327 | 15 | Trace |

[a] All quantities in moles. [b] 2.0 moles of benzoic acid was also added to this run to demonstrate effect of acidity on sulfate reduction.

The effectiveness of the alkali sulfates can be increased by the addition to the system of hydrogen ions, as predicted from eq. 7. This is illustrated in Table V with $K_2SO_4$, with and without added acid. It can also be enhanced by the use of bisulfate and applied to the oxidation of organic compounds. This is illustrated in Table III by *p*-xylene and $KHSO_4$. Aluminum sulfate has built-in *p*H control. Application of this principle to sulfite, where the anomalous effect of excess alkali and *p*H were first observed, increases its effectiveness also, as would be predicted from the theory (Table I).

## Discussion

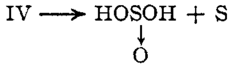
The mechanism by which sulfate functions as an oxidant is still under active study, but several conclusions and hypotheses already can be made. Sulfate itself does not initially attack hydrocarbon. This is demonstrated by the lack of reactivity of such mixtures. Any inorganic-soluble sulfur species of valence below +6 can serve as the initiator. Such species are also capable of disproportionating at reaction temperature to give sulfur of higher and lower valence including sulfide. Some one of these must be the attacking species which leads to sulfate reduction. It is postulated that of the various sulfur species present, the one most capable of such attack will be non-ionized hydrogen sulfide. Anions, such as sulfite, thiosulfate or sulfide, would be repelled from sulfate ion. Hydrogen sulfide and elemental sulfur are the only neutral components present. While both initiate reduction, the former is the only one unable to disproportionate further. Therefore, it must be capable of direct attack. This is, of course, in agreement with eq. 7. The method of attack might be visualized by the scheme



(12)

(13)

Compounds II and I in that order with their negative charges would be less apt to permit the approach of electronegative sulfur, although this is not forbidden. The product IV is thiosulfate, which under acid conditions is known to be unstable, decomposing to free sulfur and sulfite.



$$\text{IV} \longrightarrow \text{HO}\underset{\begin{smallmatrix}\downarrow\\ \text{O}\end{smallmatrix}}{\text{S}}\text{OH} + \text{S} \qquad (14)$$

The further decomposition of these species has been described already. Sulfate formation could occur by the reverse process, being favored at higher *p*H.

There is reason to believe, on the basis of relative reaction rates, that oxidations with sulfate, thiosulfate and possibly sulfite may proceed through more reactive sulfur species than given by polysulfide or free sulfur and base. This could be due to the formation of a "nascent" or energetically richer elemental sulfur by eq. 14. Reduction may well proceed through monatomic sulfur and lower sulfur aggregates not normally present in polysulfide at these temperatures. These could show much higher reactivities than ordinary $S_8$. Such highly reactive forms of a metastable state of sulfur have been reported from the reaction of sulfur dioxide and hydrogen sulfide[8] and from decomposition of $S_2O_3^{=}$.[9]

The ability to reduce sulfates to polysulfides or free sulfur through initiation by sulfur species of lower valence may well have biological and geological significance beyond the immediate scope of this work. While reaction rates must be very slow at lower temperatures, the mechanism of such reductions may apply over a wide range of conditions.

## Experimental

Procedures, equipment and reagents were in general those reported previously[1] unless otherwise specified.

**Oxidations of Table I. Xylene Oxidation with Sulfite (Run 9).**—The objective of this isolation procedure was to obtain a complete accounting for the oxidative capacity of sulfite. When reaction was complete and all gases had been withdrawn through a caustic scrubber, liquid products were steam distilled to *p*H 7 to remove all dissolved $NH_3$ and $H_2S$ and 38.5 g. of unreacted xylene. The remaining light yellow solution was carbon treated and filtered. The colorless filtrate was treated with $SO_2$ to precipitate phthalic and toluic acids and amides which after washing and drying weighed 66.4 g. and analyzed as containing 36.5 g. (0.268 mole) of toluic and 29.9 g. (0.18 mole) of phthalic acids plus amides. Of the total carboxyls formed, 10.5% was present as amides.

An aliquot of the filtrate and washes was analyzed for sulfate after further acidification with HCl and precipitation as $BaSO_4$, indicating the presence of a total of 1.02 moles. On the basis of the ammonium analog of eq. 5 which produced the sulfate, the remaining oxidizing potential of the original oxidant can be calculated. Formation of 1.02 moles of sulfate required 1.36 moles of the 2.0 moles of sulfite charged. This left 0.64 mole of sulfite capable of producing 0.64 mole of carboxyl. Analysis showed 0.268 mole in the form of toluic and 2 × 0.18 mole as phthalics, for a total of 0.628 mole, well within the limits of experimental error.

**Run 7.**—A blank was first run on the oxidant for this run to determine how much free sulfur would be formed under reaction conditions, which could serve as oxidizing agent, and how much disproportionated to "unavailable" sulfate. Using the same reaction conditions, 1.53 moles of $NH_4HSO_3$ and 1.55 moles of $(NH_4)_2S$ were charged to a 2.5-liter autoclave, diluted to 1000 cc. with water. After reaction, products were steamed free of $NH_3$ and $H_2S$, precipitating 0.83 mole of sulfur from polysulfide and leaving a filtrate which by $BaSO_4$ precipitation was shown to contain 0.99 mole of $(NH_4)_2SO_4$. The latter, formed by a disproportionation like eq. 5, consumed 1.32 moles of sulfite leaving 0.21 mole. If this was reduced by sulfide to free sulfur, analogously to Priestley's observation,[5] it would form 0.21 × 4 or 0.84 mole, in good agreement with the 0.83 mole actually found. This could produce a theoretical 0.28 mole of carboxyl groups by eq. 1.

An identical run then was made with 0.707 mole of 85% *m*-, 15% *p*-xylene present, run 7 of Table I. The isolation procedure was as in run 9 and yielded 0.569 mole of mixed phthalics and 0.029 mole of toluics, for a total of 1.167 moles of carboxyl. This is considerably above the 0.28 mole obtainable from the sulfur formed in the blank, and not too far from the 1.53 moles obtainable if all sulfite were available. This experiment led to the hypothesis that sulfate might serve as an oxidant under proper conditions of *p*H and initiation.

**Oxidations of Table II. 1. Methane.**—After reaction, analysis of the gas phase by mass spectrograph showed the only components in concentrations above 0.1% to be methane, hydrogen sulfide, carbon dioxide and carbon monoxide. The water phase, *p*H 7–8, liberated 11.5 g. of sulfur on acidification with sulfuric acid. No organic products could be found. The ratio of CO to $CO_2$ then permitted calculation of yields as indicated in Table II.

2. **Cyclohexane.**—Distillation of the organic layer of oxidation products yielded 130 g. of unreacted cyclohexane. Aqueous alkali extraction of the organic sulfide-smelling still residue failed to yield any acidic products. The main water layer was acidified to *p*H 6 and filtered free of sulfur and by-products, acidified to *p*H 2, ether extracted, and evaporated to dryness to recover any dibasic acids or amides. Alcohol and acetone extraction of the residue yielded none. Evaporation of the ether layer left 26.8 g. of residue which was distilled through a 12-inch helices-packed column to give 17 g. boiling 185–210° and containing 7.8 g. of phenol by the bromide–bromate method.

3. **Methylcyclohexane.**—The organic phase of the reaction products was distilled to recover unreacted methylcyclohexane (190 g.). The still residue consisted of 27 g. of organic sulfides. The water phase was saponified in excess NaOH until all $NH_3$ was removed, acidified to *p*H 7, and filtered free of precipitated sulfur and neutral by-products. Acidification of the filtrate to *p*H 2 yielded a precipitate of 19.8 g. of benzoic acid; sublimed, neutral equivalent 121.5 (theory 122.1). Combined ether extracts of the filtrate were treated with aqueous $Pb(OAc)_2$ to extract organic sulfur compounds and were dried and evaporated. The residue was analyzed by ultraviolet spectrograph and found to contain 9.9 g. of phenol.

The presence of phenol here, taken in conjunction with its formation from cyclohexane, suggests the possible intermediate formation of a hydroxybenzoic acid which underwent decarboxylation. Such decarboxylations have been studied.[10]

4. **Ethylene.**—Based on the pressure rise, reaction was complete by the time reaction temperature was reached. Gaseous products were largely $H_2S$, with smaller amounts of methyl and ethyl mercaptans. No unreacted ethylene remained. The reaction mixture was a homogeneous, light colored water phase, which was distilled with no column after strongly acidifying with $H_2SO_4$ to give 1880 ml. of distillate. This was found to contain 2.54 moles of acetic acid by titration and isolation as sodium acetate. Longer reaction times and higher temperatures increase decarboxylation reactions.

In the oxidation of olefins with sulfate initiated with $H_2S$, the initial step appears to be $H_2S$ addition to the olefin, followed by mercaptan addition to any remaining olefin. This withdrawal of the initiator of sulfate reduction can inhibit the oxidation reaction considerably if all $H_2S$ is consumed in this way. In the above example, a molar excess of $H_2S$ over olefin was used to ensure rapid reaction. In a similar example using 2.5 moles of $H_2S$ and 4.6 moles of ethylene, conversion was again essentially complete. But when this ratio was dropped below 1:2, to 0.6 mole of $H_2S$ and 3.0 moles of ethylene, the principal product was diethyl

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(10) B. R. Brown, D. L. Hammick and A. J. B. Scholefield, *J. Chem. Soc.*, 778 (1950).

sulfide with very little oxidation. This problem is easily solved *if olefin is not introduced until after sulfate reduction.*

5. **Propylene.**—Gaseous products were found to contain 0.6 mole of unreacted propylene. Liquid products consisted of two layers. An organic phase of dipropyl sulfides, specific gravity of 0.967, was not further characterized after extracting with base. The water phase was saponified with 160 g. of NaOH, concentrated down, adjusted to *p*H 6 with $H_2SO_4$, carbon treated, acidified to *p*H 2, and ether extracted. The water layer was treated with 700 g. of $CaCl_2$ to precipitate unreacted sulfate and salt out remaining organic acids. A dry cake of 384.7 g. of $CaSO_4 \cdot 2H_2O$ was recovered. Filtrate was re-extracted with ether. Fractional distillation of all ether layers yielded a total of 0.66 mole of propionic acid, b.p. 138–141°, neutral equivalent 75.6.

6. **Isobutene.**—A total of 0.495 mole of isobutene was recovered from the gaseous products. An organic phase of 36.6 g. of crude diisobutyl sulfides, specific gravity 0.882, was separated from the liquid products. Of this, 71.2% distilled between 64 and 160°; 50% boiling 150–160°. The aqueous phase was fractionally distilled through a 3-foot helices packed column. Considerable ammonium sulfide was evolved. Water was removed until 330 cc. remained, consisting of two liquid phases. Crystals separated from both layers on cooling. Ether extraction yielded 81 cc. of an organic liquid which was chloroform extracted to separate any ammonium salts from carboxamide. Evaporation of solvent left 27.5 g. of crude solid amide, saponification equivalent 94.2 (theory for isobutyramide, 87.1). Identity was established by saponification with alkali, acidification, ether extraction, and fractional distillation. Product distilled 150–154°, neutral equivalent 85.8 (isobutyric acid boiling point 154.5°, neutral equivalent 88.1).

Aqueous products after the above ether extraction were evaporated to dryness to recover unreacted $(NH_4)_2SO_4$ (42.3 g.) after alcohol extracting the residue. This extract and insolubles from the above $CHCl_3$ extraction were acidified in water solution to liberate organic acid from ammonium salts, extracted into ether, and concentrated to yield 17.5 g. of isobutyric acid.

7. **Cycloöctatetraene** was obtained from Monomer–Polymer, Inc. Products were isolated as for *m*-xylene. Final product proved to be 10.6 g. of benzoic acid, neutral equivalent 121.9. This agrees with the results of Reppe[11] which indicate cycloöctatetraene isomerizes to ethylbenzene at these reaction temperatures with this oxidant, in contrast with its reported low temperature isomerization to *p*-xylene when oxidized with $CrO_3$–AcOH to yield terephthalic acid.

8. **Tetrahydrofurfuryl Alcohol.**—Products were filtered from 2.9 g. of dark cake and steam distilled from *p*H 8 to 6 to remove excess $NH_3$ and $H_2S$. No solids precipitated. The solution was saponified with 150 g. of NaOH and concentrated to 400 ml., before acidifying to *p*H 6 with $H_2SO_4$, filtering from a trace of silicates, and acidifying to *p*H 2. After ether extracting and evaporating the dried ether, 4.5 g. of acetic acid remained. The water layer was evaporated to dryness and acetone extracted to obtain any dibasic acids. Evaporation of the acetone left 9.3 g. of glutaric acid, neutral equivalent 66.1 when recrystallized from benzene (theory 66.0).

9. ***m*-Xylene.**—In this run elemental sulfur was used in place of $H_2S$ to initiate sulfate reduction. The procedure throughout followed that of earlier work.[1] Besides 312 g. of isophthalic acid, there was obtained 58.9 g. of sulfur.

10. ***p*-Xylene.**—Procedures were as with *m*-xylene. *The effect of time on the conversion is demonstrated* by the two runs in Table II. Use of $H_2S$ rather than $(NH_4)_2S$ gives a sufficiently lower *p*H to the system to permit complete reaction in an hour under otherwise similar conditions.

11. ***o*-Xylene.**—All liquid reaction products in this case were withdrawn at reaction temperature from the autoclave into ice to minimize decarboxylation by over reaction. The resultant slurry was filtered to give a damp cake which was steam distilled to give 36.1 g. of organic layer. Distillation through a 1-foot helices packed column yielded 20 g. of unreacted *o*-xylene and 11 g. of *o*-tolunitrile.

Filtration of the non-steam-distillable slurry gave 97.4 g. of crude mixed *o*-phthalic acid and amide, neutral equivalent 261.7, saponification equivalent 85.1. This was saponified with 100 g. of NaOH until free of $NH_3$, acidified to *p*H 6, filtered from a trace of sulfur, and then strongly acidified with $H_2SO_4$. Upon concentrating, successive fractions of crystals of *o*-phthalic acid were recovered. Heating these fractions evolved water, leaving a liquid, b.p. 279–282° uncor. This was sublimed to give needles of phthalic anhydride, neutral equivalent 74.6.

The main filtrate was saponified and concentrated, carbon treated, and then acidified to *p*H 2. Filtration yielded 41.2 g. of benzoic acid, neutral equivalent 124.1 (theory 122.1). Benzene extraction of the filtrate yielded an additional 14.3 g. of benzoic acid.

The more extensive decarboxylation of *o*-phthalic acid than of the other isomers is not surprising for this orientation under these conditions.[12]

12. ***m-p*-Toluic Acids.**—Except for the oxidant, the procedure followed that in earlier work.[1] On the basis of the pressure rise, reaction was complete in about 15 minutes. Products were isolated as before.

13. ***p*-Toluenesulfonic Acid.**—Products were saponified with aqueous alkali and then isolated as in the past[1] to give monosodium *p*-sulfobenzoic acid, neutral equivalent 229.5 (theory 232.7).

**Oxidations in Table III.**—Technique and equipment was as in similar experiments. Where bisulfate was used, reagents were placed in a glass liner which fitted a 4.5-liter autoclave. Small weep holes in the glass above liquid level permitted pressure equalization inside and outside the liner.

Unfortunately the most desirable *p*H range for utilization of sodium and potassium sulfates is also highly conducive to half-salt formation of the phthalic acids. This ionization state has been demonstrated to be decarboxylated most readily.[12] As a result, varying amounts of benzoic acid are formed, as well as phthalic acids. Judicious balancing of temperatures and reaction times is required to keep decarboxylation to a minimum.

Products from metal sulfate oxidations were first steam distilled to remove any hydrogen sulfide, then converted to sodium salts by digestion with aqueous sodium hydroxide, filtered to remove metal sulfides and hydroxides, and then isolated as described previously.[1]

***Oxidations in Table IV.***—*In the study of initiators for sulfate reduction*, all runs were made under similar conditions; 315–350°, 2.5-liter or 4.5-liter autoclaves with 50–100 moles of water per mole of hydrocarbon, and reaction times of one hour. Results are expressed as total moles of carboxyl produced, to demonstrate that the amount of oxidation occurring is greater than can be attributed to the action of the initiator itself.

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[11] W. Reppe, O. Schichting, K. Klager and T. Toepel, *Ann.*, **560**, 1 (1948).

[12] B. R. Brown, *Quart. Revs.*, **5**, 131 (1951).