mm)]; ir $\nu_{C=O}$ 1680, ν_{NCS} 1980 cm^{-1}. In a similar way **1a** gave benzoyl isothiocyanate: bp 130 °C (12 mm) [lit.[8,9] 115 °C (2.2 mm), 133–137 °C (18 mm)]; ir $\nu_{C=O}$ 1685, ν_{NCS} 1970 cm^{-1}; yield 30%.

Registry No.—1a, 41118-54-1; **1b,** 59318-25-1; **5a,** 59318-26-2; thionyl chloride, 7719-09-7; *p*-chlorothiobenzoic acid, 31143-03-0; *p*-chlorobenzoyl *p*-chlorophenyl disulfide, 59318-27-3; bis-*p*-chlorobenzoyl trisulfide, 59318-28-4; bisethoxythiocarbonyl disulfide, 502-55-6; dimethylammonium dimethyldithiocarbamate, 598-64-1; *N*-dimethyl-*p*-chlorobenzamide, 14062-80-7; diethylammonium diethyldithiocarbamate, 1518-58-7; *N*-diethyl-*p*-chlorobenzamide, 7461-38-3; potassium thiocyanate, 333-20-0; *p*-chlorobenzoyl isothiocyanate, 16794-67-5; benzoyl isothiocyanate, 532-55-8; thiophenol, 108-98-5.

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Acid Catalysis in Dimethyl Sulfoxide Reactions. A Generally Unrecognized Factor[1a]

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Strong acids, generated in situ, are effective catalysts for the oxidation of epoxides and benzyl alcohol, the dehydration of tertiary alcohols, and the conversion of acetamide to bis(acetamido)methane in Me$_2$SO at elevated temperatures (100–190 °C). The reactions are completely inhibited if excess sodium carbonate or other freshly prepared bases (sodium *n*-octoxide or potassium *tert*-butoxide) are present. The acids, the presence of which has usually gone unrecognized, form either by thermolysis of refluxing Me$_2$SO in air or oxygen or by interaction of free radicals derived from decomposing hydroperoxides or peroxides with Me$_2$SO. If an efficient radical trapping agent (acrylonitrile) is present during reaction, acid formation is drastically reduced. The acids formed have been isolated by extraction with a solvent-soluble basic ion-exchange resin and identified as sulfuric and methanesulfonic acids.

In many reactions involving dimethyl sulfoxide (Me$_2$SO) as a reactant and/or solvent without added acid catalysts, the nature of the reactants and products, the experimental conditions, and the obvious analogies to related reactions that normally require strong acids when carried out in other media suggested to us that strong acid catalysis must be playing a critical role. When the present work was initiated in 1966 acid catalysis had neither been demonstrated nor apparently even considered. Since then it has been reported that acid formation may occur in the oxidation of amine salts on prolonged heating in Me$_2$SO[2] and acid catalysis is involved in the thermolysis of Me$_2$SO.[3] Beginning with the putative free-radical oxidation of epoxides by Me$_2$SO,[4] we reinvestigated several of these reactions to attempt to resolve the following questions: (1) Are strong acids formed in situ during these reactions? (2) If acids are formed, how do they originate and can they be isolated and identified? (3) Are the reactions in fact acid catalyzed, failing in the absence of the acids and proceeding normally when the acids are deliberately added?

Results and Discussion

Unrecognized Strong Acid Catalysis in the Me$_2$SO Oxidation of Epoxides. The reaction of Me$_2$SO with styrene oxide at 100 °C (molar ratio 6:1) in the presence of a dry air stream was repeated as originally described.[4] The epoxide was consumed and phenacyl alcohol (25%) was formed as reported. Titration of the aqueous extract of the reaction mixture with base, however, revealed the presence of a small quantity of strong acids (2.5×10^{-2} equiv per mole of epoxide originally present). Addition of barium chloride solution showed the presence of sulfate ion. The reaction was then repeated in the presence of *tert*-butyl hydroperoxide (air absent). Again, oxidation of styrene oxide to phenacyl alcohol occurred and strong acids were shown to be formed (ca. 4–6 $\times 10^{-2}$ equiv per mole of hydroperoxide). When both reactions were repeated in the presence of an excess of sodium carbonate, *no* phenacyl alcohol was formed; sulfate ion was shown to be present in the aqueous phases.

We[5] and others[6] have shown that the Me$_2$SO oxidation of epoxides to α-ketols is catalyzed by strong acids. Since we have now demonstrated that strong acids are formed during the Me$_2$SO oxidation reaction in air and with hydroperoxide, and the oxidation of the epoxide is completely inhibited in the presence of sodium carbonate, we conclude that it is the strong acids formed in these reactions that are the oxidation catalysts and not oxygen or *tert*-butyl hydroperoxide. The mechanism of the acid-catalyzed Me$_2$SO oxidation of epoxides, therefore, can be assumed to be that proposed earlier by us;[5] the overall process does not involve free radicals except as intermediates in the formation of the acid catalysts, in contrast to an earlier conclusion.[4] We have also demonstrated that the well-known free-radical source, di-*tert*-butyl peroxide, which decomposes in Me$_2$SO at 100–120 °C, does not produce strong acids in an inert atmosphere and it is not a catalyst for the oxidation of epoxides at that temperature. (At 155 °C, however, even in an inert atmosphere, strong acids do form but that temperature is well above that required in epoxide oxidations.)

Origin of Strong Acids in Epoxide–Me$_2$SO Reactions. In air, all three components of the reaction mixture (Me$_2$SO, epoxide, air) are necessary for the formation of the strong acid catalyst. Thus, when styrene oxide is heated in air under the usual reaction conditions but in the *absence* of Me$_2$SO, no strong acids are produced.[7] When Me$_2$SO is added to this preoxidized styrene oxide and the reaction is then continued in the *absence* of air, little if any oxidation of epoxide to phenacyl alcohol occurs. Similarly, when air is bubbled through Me_2SO alone under the usual reaction conditions (100 °C), no acids are produced; addition of styrene oxide to the pretreated Me_2SO and continuation of the reaction in the *absence* of air yields only traces of oxidation products.

In the reaction of styrene oxide with Me_2SO and *tert*-butyl hydroperoxide at 100 °C, the strong acid catalysts form by interaction of Me_2SO with the hydroperoxide.[8] Thermal decomposition of *tert*-butyl hydroperoxide in Me_2SO for 16 h at 100 °C yields 0.4–0.5 equiv of strong acid per mole of hydroperoxide used, a substantial quantity of acid. Addition of styrene oxide to the acidic Me_2SO solution and continuation of the reaction at 100 °C yields phenacyl alcohol, as expected. Benzoquinone, a known radical scavenger, added at this point, has no effect on the epoxide oxidation. All of the observations just discussed support the conclusion that the strong acids resulting from the hydroperoxide–Me_2SO reaction are the catalysts for the epoxide oxidation and not the hydroperoxide.

The finding that acids are formed from Me_2SO and *tert*-butyl hydroperoxide suggests that the acids formed in the Me_2SO–styrene oxide–air reaction at 100 °C arise by reaction of Me_2SO with hydroperoxides derived from the epoxide. Epoxides, in common with other ethers, are autoxidized to hydroperoxides. The original report[4] that no oxygen is consumed in the Me_2SO–epoxide–air reaction presumably did not take into account the relatively insignificant amount of oxygen that would be required to produce sufficient acid via hydroperoxide to effect catalysis.[9]

Identity of the Strong Acids. When Me_2SO–epoxide–air or *tert*-butyl hydroperoxide oxidation reaction mixtures are diluted with water and treated with aqueous barium chloride, water-insoluble precipitates form suggesting the presence of sulfur acids. These acids were separated by modifying an earlier described analytical technique for the spectroscopic (ir, uv) identification of acids produced in base-catalyzed autoxidations in Me_2SO.[10,11] In the modified method, the acids are directly extracted into a water-immiscible solvent from an aqueous Me_2SO solution by the basic ion-exchange resin, Amberlite LA-2, reportedly a mixture of long-chain aliphatic amines, which forms weakly bonded salts with strong acids.[12a] The success of our modification lies in the discovery that, after separation of the acid-containing resin solution from the aqueous phase, the acids can be easily separated from the resin as phenylhydrazinium salts. On addition of phenylhydrazine, these salts either precipitate or are extracted from the resin solution with water. Further separation and identification of the salts is then carried out using conventional techniques. (Blank runs with the resin, solvents, Me_2SO, and water show no strong acid.)

The strong acids formed by reaction of Me_2SO with *tert*-butyl hydroperoxide are sulfuric and methanesulfonic acids.[12b] Other reaction products identified are *tert*-butyl alcohol, isobutene, acetone, and dimethyl sulfone, the last being the major product isolated (60–65%, based on hydroperoxide consumed). Other pertinent observations are (a) strong acid formation in the reaction of Me_2SO with *tert*-butyl hydroperoxide occurs both in the presence and absence of oxygen, although considerably more acid forms when oxygen is present, suggesting that autoxidation may be one but not the only reaction responsible for acid formation; (b) the yield of acids is reduced by a factor of 25 when the Me_2SO–hydroperoxide reaction is carried out in the presence of acrylonitrile, an effective radical scavenger (molar ratio of acrylonitrile to hydroperoxide 9:1), that forms polyacrylonitrile; and (c) the reaction of dimethyl sulfone with hydroperoxide yields less than one-tenth the acid formed from Me_2SO–hydroperoxide, indicating that the sulfone is not a necessary intermediate in the conversion of sulfoxide to acid.

Unrecognized Strong Acid Catalysis in the Me_2SO Oxidation of Benzyl Alcohol. The similarity between the presumed free-radical oxidation of epoxides by Me_2SO and the free-radical mechanism suggested for the related Me_2SO oxidation of benzyl alcohols to aldehydes[13–16] prompted us to reexamine the latter reaction at 175–190 °C, the temperature range ordinarily used for that oxidation. When a solution of benzyl alcohol in Me_2SO (molar ratio 1:7.6) is saturated with oxygen by flushing with a rapid dry air stream for several minutes and then heated at 190 °C in an NMR tube for 2 h, a 30–35% yield of benzaldehyde is observed, in essential agreement with the original report. However, repetition of the experiment but with sodium carbonate present from the start (molar ratio to benzyl alcohol 1:1) produces no detectable benzaldehyde (NMR).

Repetition of the latter experiment (excess sodium carbonate present) on a small preparative scale at 175 °C for 24 h while a continuous air stream is passed through the mixture produces no benzaldehyde (ir, NMR). Workup of the reaction mixture yields a product whose ir is virtually identical with that of pure benzyl alcohol with only trace absorption at 1700 cm^{-1}. Distillation gives fractions containing only traces of benzaldehyde (ir, NMR); benzaldehyde 2,4-dinitrophenylhydrazone is obtained in a yield of <0.01%. Omission of the sodium carbonate but retention of the air stream produces a steady increase in benzaldehyde, and titration of the reaction mixture indicates that about 2×10^{-3} equiv of strong acid are formed per mole of alcohol originally employed.

As originally reported[13–16] and verified by us,[5] refluxing a solution of benzyl alcohol in Me_2SO containing di-*tert*-butyl peroxide (molar ratio 1:7:0.2) under dry nitrogen for 19 h yields appreciable benzaldehyde (30–35%). After only 3 h, however, the reaction mixture already contains strong acids (3.6×10^{-3} equiv per mole of alcohol and 3.7×10^{-2} equiv per mole of peroxide). Repetition of the experiment with sodium carbonate present (ratio to benzyl alcohol 1:1) produces no detectable benzaldehyde (ir).

As with *tert*-butyl hydroperoxide, it was found that strong acids form when a mixture of Me_2SO and di-*tert*-butyl peroxide (molar ratio 5:1) is heated (155 °C) in an inert atmosphere. As before, the acids were identified as sulfuric and methanesulfonic acids. Other products formed are *tert*-butyl alcohol, isobutene, and dimethyl sulfone (9×10^{-3} mol/mol peroxide). Acrylonitrile (molar ratio to peroxide 12:1), as in the *tert*-butyl hydroperoxide reaction, inhibits acid formation by a factor of 13 and is converted to polymer. Thus, reaction of Me_2SO with peroxide or hydroperoxide yields the same strong acids via a process that most probably involves free radicals.

In the light of these experiments, we conclude that the acids formed in situ in the benzyl alcohol oxidations are responsible for the observed catalysis, as in the epoxide oxidations already discussed. Unlike the epoxide reactions, however, it had not been shown that known strong acids deliberately added are effective catalysts for the alcohol oxidation. Consequently, solutions of benzyl alcohol in Me_2SO (molar ratio 1:7.7) were added to a series of NMR tubes containing no acid, sulfuric or methanesulfonic acids, or "prereacted" Me_2SO-di-*tert*-butyl peroxide (molar ratio 5:1) that had been heated at 155–160 °C for 4 h in an argon atmosphere. All the solutions were purged with argon for 15 min and then heated at 190 °C for up to 7 h, with periodic NMR monitoring of benzaldehyde formation. Results are summarized in Table I.

As Table I shows, sulfuric and methanesulfonic acids are catalysts for the benzyl alcohol oxidation, as are the acids formed by the reaction of Me_2SO with di-*tert*-butyl peroxide at 155 °C. Sulfuric acid is the most efficient catalyst studied. Benzaldehyde is stable on heating in Me_2SO[14] even with oxygen present.

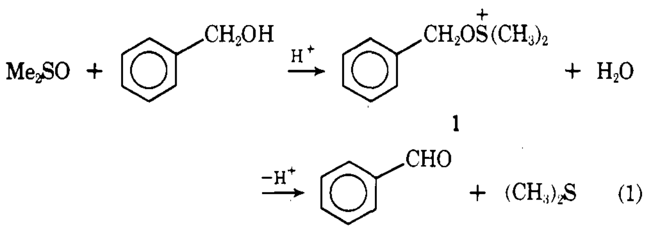
From the above evidence and by analogy with similar oxy-

Table I. Benzyl Alcohol Oxidation to Benzaldehyde by Me_2SO

Acid catalyst	Equiv acid/mol alcohol	Yield of benzaldehyde, %[a]
None		2[b]
Methanesulfonic	3.1×10^{-2}	18
Prereacted Me_2SO-t-Bu_2O_2	4.3×10^{-2}[c]	33
Sulfuric acid	5.5×10^{-3}	43
	7.5×10^{-2}	67

[a] Molar ratio benzyl alcohol to Me_2SO 1:7.7. Reaction time 4 h at 190 °C. Benzaldehyde yields determined by NMR. [b] Yield is 3% after 7 h. [c] Acid content determined by titration. Molar ratio Me_2SO-t-Bu_2O_2 5:1, heated for 4 h at 155–160 °C.

gen transfer reactions involving Me_2SO, the oxidation of benzyl alcohol probably involves acid-catalyzed formation of the benzyloxydimethylsulfonium cation (**1**) followed by redox decomposition (eq 1). It is unlikely that free radicals are directly involved in the oxidation of benzyl alcohol although they play a role in the formation of the acid catalyst. The inhibiting effect of antioxidants on this oxidation observed previously[17a] can now be explained in terms of the ability of the antioxidants to prevent formation of the acid catalyst, as opposed to interruption of a free-radical chain oxidation of the alcohol suggested previously.



"Thermal" Decomposition of Me_2SO. The so-called "thermal" decomposition of Me_2SO is characterized by initial formation of formaldehyde and methanethiol.[18,19] Since the most obvious source of these materials is an acid-catalyzed Pummerer rearrangement of Me_2SO we suspected that strong acids are formed in situ under conditions of "thermolysis". Repetition of the "thermolysis" as originally reported (72-h reflux in air[18]) yields a strongly acidic aqueous solution on workup, a result recently confirmed by others,[3] but the small amount of acid formed precluded identification. In the presence of sodium carbonate, decomposition of Me_2SO is negligible. From these results we conclude that the "thermal" decomposition of Me_2SO is in fact the result of strong acid-catalyzed Pummerer rearrangement.

Repetition of the experiment with oxygen bubbling through the Me_2SO yields 3.9×10^{-3} equiv of acid/mol Me_2SO identified as sulfuric acid by isolation of barium sulfate. When oxygen is excluded either by carrying out the thermolysis in an inert atmosphere (argon) or on a degassed sample, the yield of acid decreases significantly (2.4×10^{-4} equiv/mol Me_2SO in argon; 1.6×10^{-4} equiv/mol Me_2SO in the degassed sample). These results indicate that the major pathway for acid formation in refluxing Me_2SO is an autoxidative one, as has been suggested elsewhere.[3]

To investigate this point further, a low-temperature autoxidation of Me_2SO was carried out by decomposition of AIBN at 80 °C in Me_2SO in an oxygen atmosphere. A mixture of methanesulfonic and sulfuric acids (4.4×10^{-1} equiv total acids/mol AIBN) is produced. No acids form in the absence of oxygen. (It was also found that the sulfuric acid is not derived from methanesulfonic acid by direct autoxidation, as none of the former is produced by decomposition of AIBN in methanesulfonic acid under oxygen.)

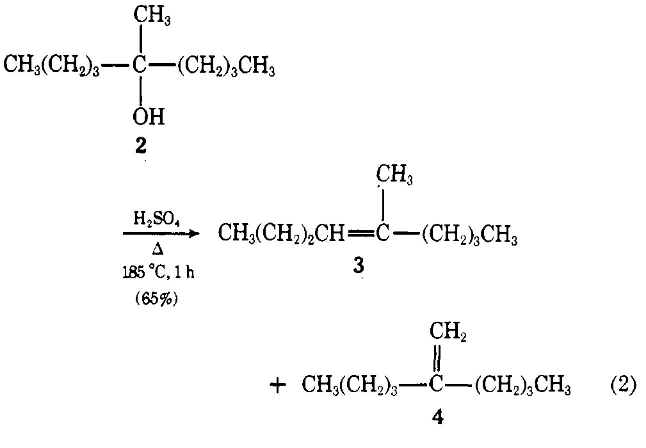
Our conclusion, therefore, is that the acids found on thermolysis of Me_2SO arise from Me_2SO autoxidation, at least in part. A likely pathway involves initial formation of hydroperoxides, either from Me_2SO itself, from minor impurities initially present, or from other components of a reaction mixture (see below). The formation of acid could then proceed as in the case of added hydroperoxide or epoxide-derived hydroperoxide.

Whether the small amount of acid found on thermolysis under nominally oxygen-free conditions arises as a result of the adventitious presence of oxygen or other impurities, e.g., hydroperoxides, or whether another distinct mechanism of acid formation is operative is undetermined. It is now clear from our studies, however, that strong acids are formed when Me_2SO is vigorously heated (160–190 °C) even in supposedly inert atmospheres and more form when oxygen is present. Consequently, inadvertent acid catalysis should be suspected in any reaction carried out in Me_2SO at high temperatures. To test this conclusion further, we reinvestigated two such reactions, namely, the dehydration of a tertiary alcohol and the conversion of acetamide to bis(acetamido)methane.

Dehydration of Tertiary Alcohols in Me_2SO.[14–16,20,21] This reaction is especially interesting because it is reported that acid catalysis can be ruled out as a factor inasmuch as the yield of olefins from two alcohols is little affected by the presence of the bases sodium n-octoxide or aniline.[15]

We reinvestigated the alcohol dehydration reaction but chose 5-methyl-5-nonanol (**2**) rather than 5-n-butyl-5-nonanol originally employed because the former, although structurally similar to the latter, is unsymmetrical and offers the possibility of formation of isomeric olefins which might provide additional insight into the nature of the dehydration process. Although not specified in the original publication, a nominally inert atmosphere (argon) was employed in all of the current experiments.

As a control and to calibrate the NMR analytical method, dehydration of neat **2** was conducted at 185 °C for 1 h with sulfuric acid catalysis. A 65% yield of a mixture of *cis*- + *trans*-5-methyl-4-nonene (**3**) and 2-n-butyl-1-hexene (**4**) was obtained in a ratio of 19:1 (eq 2). As expected the more highly substituted olefin predominates.



$$CH_3(CH_2)_3-\underset{\underset{\textbf{2}}{OH}}{\overset{CH_3}{\overset{|}{C}}}-(CH_2)_3CH_3 \xrightarrow[\substack{\Delta \\ 185\ °C,\ 1\ h \\ (65\%)}]{H_2SO_4} \underset{\textbf{3}}{CH_3(CH_2)_2CH=\overset{CH_3}{\overset{|}{C}}-(CH_2)_3CH_3} + \underset{\textbf{4}}{CH_3(CH_2)_3-\overset{CH_2}{\overset{\|}{C}}-(CH_2)_3CH_3} \quad (2)$$

Dehydration in refluxing Me_2SO (mole ratio Me_2SO:**2** 10:1) in the absence of added catalyst, carried out for 17 h as originally reported but under argon,[15] gives an approximately 40% conversion to a mixture of olefins **3** and **4** in a molar ratio of 6:1. The aqueous phase obtained during the workup procedure is strongly acidic and gives a positive test for sulfate ($BaCl_2$ solution). Titration of the aqueous phase shows that 1.6×10^{-3} equiv of acid form per mole of **2**. No attempt was made to establish whether the products are kinetically or thermodynamically controlled in either reaction. In both cases, internal olefin predominates even though the ratios of **3** to **4** are not the same.

Repetition of the alcohol–Me_2SO reaction for 30 h but with freshly distilled aniline present (molar ratio **2**:aniline:Me_2SO 1.1:1:10) yields some **3** and **4**, as the literature states,[15,16] but considerable alcohol remains intact. Titration of the aqueous phase obtained in the workup indicates the formation of 8×10^{-3} equiv of strong acid per mole of alcohol; the aqueous phase gives a positive test for sulfate.

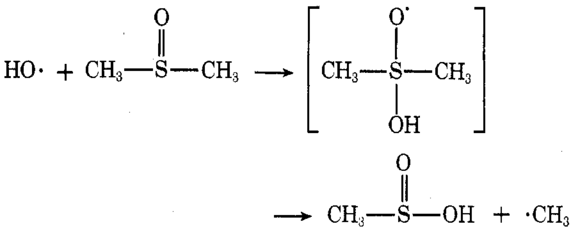
The problem in using aniline as an acid acceptor is that it is a weak base whose presence would not completely inhibit acid catalysis. The use of bases which irreversibly neutralize strong acids is not open to such an objection; therefore, the report that sodium *n*-octoxide does not prevent dehydration is most significant.[15] Repetition of the refluxing Me_2SO–alcohol reaction for 17 h in the presence of freshly prepared sodium *n*-octoxide (mole ratio of alcohol to base varied from 1:1 to 1:0.1) yields no detectable olefins (NMR) and reaction workup yields only a mixture of **2** and 1-octanol, whether the reactions are conducted in air or argon. For confirmation of the role of bases in preventing dehydration, the reactions were repeated using sodium carbonate or potassium *tert*-butoxide; in both cases no olefins could be detected.

We are unable to explain the discrepancy between our results and the earlier literature but our results clearly indicate that the dehydration of tertiary alcohols in refluxing Me_2SO is acid catalyzed; the acid is formed in situ and is comprised, at least in part, of sulfuric acid.

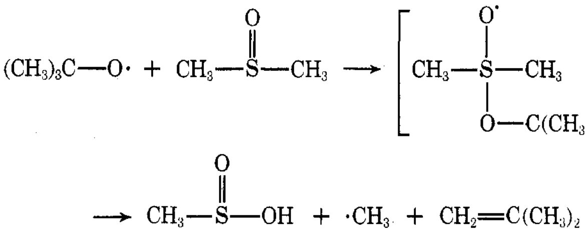
Conversion of Acetamide (5) to Bis(acetamido)methane (6). When **5** is refluxed in Me_2SO in air for 15–20 h, a 50–60% conversion to **6** is obtained (NMR), confirming a literature report in which the atmosphere was not specified.[18] Multiple degassing and freeze–thawing of the Me_2SO–acetamide solution in an argon atmosphere before reaction reduces the conversion to about 15% but does not completely prevent it from taking place. When the reaction is conducted in an oxygen atmosphere, all of the **5** is consumed but a complex product mixture is obtained that could not be analyzed by NMR owing to overlapping signals. However, when the experiment in oxygen is repeated in the presence of sodium carbonate as acid acceptor, only unreacted acetamide is present in the reaction mixture even after extended reaction times (40 h at 185–190 °C). We conclude, therefore, that the conversion of **5** to **6** is acid catalyzed; the acids probably include sulfuric acid although in this case no attempt was made to identify them. The simplest pathway for the overall reaction of **5** to **6** involves formation of formaldehyde by acid-catalyzed decomposition of Me_2SO[18,19] followed by direct condensation of **5** with formaldehyde, although other more complex reaction pathways can be envisioned.[22]

Pathways of Acid Formation in Me_2SO. Numerous free-radical and/or ionic pathways can be written for the formation of sulfuric and methanesulfonic acids from Me_2SO on thermolysis in the presence or absence of oxygen and peroxides or other radical sources. Studies designed to sort out the possibilities unequivocally are outside the scope of this investigation but some data are available.[22]

Our observations on the reaction of Me_2SO with hydroperoxides, either added initially or produced in situ by autoxidation, support a mechanism involving initial homolysis of the hydroperoxide to form hydroxyl radical, followed by its addition to Me_2SO and subsequent decomposition of the adduct (eq 3). This is the sequence that has been observed spectrally (EPR) by other workers.[12b] The inhibitory effect of acrylonitrile on acid formation favors this pathway as opposed to nucleophilic attack of the undissociated hydroperoxide on Me_2SO.[12b] A similar pathway can be written for the reaction of *tert*-butoxy radical (from homolysis of either *tert*-butyl peroxide or *tert*-butyl hydroperoxide) on Me_2SO (eq 4).



$$HO\cdot + CH_3-\overset{\overset{\Large O}{\|}}{S}-CH_3 \longrightarrow \left[CH_3-\underset{\underset{\Large OH}{|}}{\overset{\overset{\Large O^{\cdot}}{|}}{S}}-CH_3 \right] \longrightarrow CH_3-\overset{\overset{\Large O}{\|}}{S}-OH + \cdot CH_3 \quad (3)$$

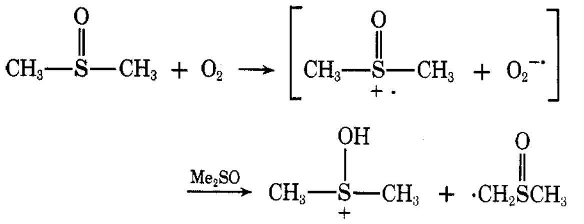


$$(CH_3)_3C-O\cdot + CH_3-\overset{\overset{\Large O}{\|}}{S}-CH_3 \longrightarrow \left[CH_3-\underset{\underset{\Large O-C(CH_3)_3}{|}}{\overset{\overset{\Large O^{\cdot}}{|}}{S}}-CH_3 \right] \longrightarrow CH_3-\overset{\overset{\Large O}{\|}}{S}-OH + \cdot CH_3 + CH_2{=}C(CH_3)_2 \quad (4)$$

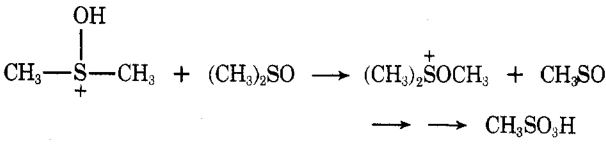
The methanesulfonic acid isolated presumably arises from the subsequent oxidation (in situ or during workup) of the initially produced methanesulfinic acid.

The sulfuric acid produced could be formed by oxidation of methanesulfinic and/or methanesulfonic acids in processes analogous to the oxidation to the sulfoxide (eq 3 and 4). In support of this concept, it had been shown previously that aqueous hydrogen peroxide and methanesulfonic acid yield sulfuric acid on heating, probably via a free-radical reaction.[17b] We found that heating an aqueous mixture of *tert*-butyl hydroperoxide and methanesulfonic acid in an oxygen-free atmosphere also produces sulfuric acid.

An alternate mechanism for autoxidation of Me_2SO not involving hydroperoxides has been proposed[3] (eq 5 and 6).



$$CH_3-\overset{\overset{\Large O}{\|}}{S}-CH_3 + O_2 \longrightarrow \left[CH_3-\underset{+\,\cdot}{\overset{\overset{\Large O}{\|}}{S}}-CH_3 + O_2^{-\cdot} \right] \xrightarrow{Me_2SO} CH_3-\underset{+}{\overset{\overset{\Large OH}{|}}{S}}-CH_3 + \cdot CH_2\overset{\overset{\Large O}{\|}}{S}CH_3 \quad (5)$$



$$CH_3-\underset{+}{\overset{\overset{\Large OH}{|}}{S}}-CH_3 + (CH_3)_2SO \longrightarrow (CH_3)_2\overset{+}{S}OCH_3 + CH_3SOH \longrightarrow \longrightarrow CH_3SO_3H \quad (6)$$

The formation of methanesulfenic acid from protonated Me_2SO (eq 6) was first postulated to account for the formation of methanesulfonic acid from the reaction of Me_2SO, halide salts, and added acids.[17c] We reinvestigated the Me_2SO–halide–acid reaction using fumaric acid and potassium bromide. When carried out as originally described, the procedure does indeed result in the formation of appreciable quantities of additional acid, as determined by titration of the reaction mixture, and the mixture gives a positive test for sulfate. However, when the halide was omitted we find that no additional acid is produced. Since the reaction indicated in eq 6 requires only the presence of protonated sulfoxide for further acid formation, this negative result makes it unlikely that the pathway shown in eq 6 is operative, either in the Me_2SO–halide–acid reaction or in Me_2SO autoxidation. Since the redox reactions of sulfoxides and halides in acidic media are well known, it is much more likely that the methanesulfonic acid found in the Me_2SO–halide–acid reaction is formed by nucleophilic attack of halide on a methyl group of protonated

Me_2SO rather than by attack by Me_2SO (eq 6). Therefore, we tend to favor a mechanism involving in situ hydroperoxide formation to explain the acid products of Me_2SO autoxidation.

The usually easily autoxidized benzaldehyde is stable on heating in Me_2SO even with oxygen present.[14] This stability may be attributable to the scavenging of peroxy radicals by Me_2SO and/or the immediate destruction by Me_2SO or strong acids derived from it of any peroxy acid or other organic peroxides which catalyze the autoxidation of benzaldehyde.

Whatever the details of the mechanism of acid formation, however, what is clear from our studies is that strong acid catalysis, frequently unrecognized by earlier investigators, is responsible for the success of certain reactions performed in Me_2SO solution. In the presence of strong acids, these reactions are efficient and give high yields of products whereas when the acids are prevented from forming or building up (base present) the reactions are effectively inhibited. Adventitious acid catalysis may also be a factor in a large number of other previously reported related reactions[22] and should be taken into account whenever Me_2SO or structurally related sulfoxides are employed at high temperatures or in the presence of oxidizing agents.

Experimental Section[23]

Me_2SO Oxidation of Styrene Oxide. A. Freshly distilled styrene oxide, bp 104° (50 Torr) (12 g, 0.1 mol), and dry pure Me_2SO (44 g, 0.56 mol) were heated at 100 °C for 20 h while a stream of dried air was passed through the reaction mixture. Methyl sulfide was collected in a dry ice–acetone trap and identified as its mercuric chloride complex. The reaction mixture was poured into ice water (100 ml) and the precipitate was filtered, dried under vacuum, and recrystallized from aqueous ethanol–heptane. Phenacyl alcohol (**7**), mp 85–87.5 °C (lit.[24] 86 °C) (2.5 g), was obtained; it was spectrally identical (ir, NMR) with an authentic sample. Collection of several more crystal crops and recrystallization resulted in an overall yield of **7** of 25%. Aliquots of the aqueous solution gave the same titer with 0.1 N sodium hydroxide using either phenolphthalein or alizarin red as indicators, indicating that the aqueous phase contained strong acids. Calculation indicated that 2.5×10^{-2} equiv of acid had formed per mole of epoxide.

B. Weighed portions (0.5 g) of stock solution of Me_2SO, styrene oxide, and *tert*-butyl hydroperoxide (molar ratio 5:1:0.1) were heated at 100 °C for up to 20 h in the absence of air. The reaction mixtures exhibited a steady increase in strong acids with time (0.01 N sodium hydroxide titration) and reached a final value of 5.7×10^{-2} equiv of acid per mole of hydroperoxide.

C. Me_2SO (44 g, 0.56 mol) and *tert*-butyl hydroperoxide (0.99 g, 0.01 mol) were mixed at room temperature; no acidic substances formed. After being heated at 100 °C for 16 h, the reaction mixture contained 0.4 equiv of strong acids per mole of hydroperoxide originally present; peroxide content was reduced by 97%. The volatiles collected in a cold trap showed the presence of acetone, *tert*-butyl alcohol, water, and several unidentified minor components (ir, GLC). Styrene oxide (12 g, 0.1 mol) and benzoquinone (0.003 mol) were added at room temperature and the reaction mixture was heated to 100 °C. After only 20 min intense ir absorption (1680 cm^{-1}) characteristic of **7** was observed and it increased with time. The reaction mixture was worked up as in A above and extracted with carbon tetrachloride or chloroform. The solid obtained upon evaporation of solvent was largely **7**. The aqueous layer gave a positive test for sulfate with barium chloride solution.

D. When reactions A and C were repeated for 28–48 h but in the presence of anhydrous sodium carbonate[25] (0.1–1 mol per mole of styrene oxide), the ir and NMR spectra showed essentially no changes. Usual workup (aqueous dilution followed by chloroform extraction) yielded a residue of styrene oxide (ir); no absorbances for **7** could be observed. The aqueous phases were acidified with hydrochloric acid and boiled to destroy carbonate; addition of barium chloride solution yielded an insoluble precipitate indicating that sulfate ion was present.

Origin of Strong Acids in Epoxide–Me_2SO Reactions. A. Air was passed through neat styrene oxide (0.1 mol) for 19 h at 100 °C after which the system was flushed with dry nitrogen for 1 h. Aliquots were titrated with 0.1 N NaOH using phenolphthalein or alizarin red; the titer with the former was almost four times that with the latter indicating the presence of a weak acid. Ir showed very weak bands at 3500 and 1680 cm^{-1} charcacteristic of **7**. Addition of Me_2SO (0.5 mol) followed by heating at 100 °C under nitrogen for an additional 27 h resulted in only slight increases in intensity at 3500 and 1680 cm^{-1}. Volatiles were collected in a cold trap. The contents of the cold trap consisted of Me_2SO and water.

B. Air was passed through Me_2SO (0.2 mol) at 100 °C for 17 h followed by nitrogen flushing for 0.5 h. Less than 0.05 ml of 0.1 N NaOH was consumed by a 2-g aliquot (phenolphthalein indicator). Styrene oxide (0.04 mol) was then added and heating was continued for an additional 27 h and then 26 h more. Only traces of **7** were formed (ir).

Identification of Strong Acids. A. General Procedure. Me_2SO reaction mixtures were cooled to room temperature and poured into ice water (threefold excess v/v). Solids, if formed, were filtered off for separate examination and the filtrate was multiply extracted with ether (ten extractions, each portion 2:1 v/v ether to aqueous phase). The aqueous phase was then extracted successively with freshly prepared ether solutions of Amberlite LA-2 183 (5% v/v in ether) until the aqueous phase was slightly basic (three to five extractions typically). The aqueous phase was further extracted with several portions of ether and these were combined with the initial Amberlite LA-2 ether extracts. The combined LA-2 extracts were dried over Linde 4A molecular sieves and, after filtration, an ether solution of phenylhydrazine (20% v/v in ether) was added dropwise to the filtrate until no further turbidity was produced. The precipitate was filtered and recrystallized from absolute ethanol or absolute ethanol–ether; the crystalline product was identical with authentic phenylhydrazinium sulfate. The ether filtrate from the initial phenylhydrazine salt precipitation was then multiply extracted with water (five times, each portion 1:1 v/v ether to water). The water was evaporated under reduced pressure (30–40 Torr), and the residual red solid or oil was successively recrystallized from a minimum of absolute ethanol and then absolute ethanol–ether. This procedure usually cleanly separated phenylhydrazinium methanesulfate from any residual phenylhydrazinium sulfate.

B. Me_2SO–*tert*-Butyl Hydroperoxide Reactions. Nitrogen Atmosphere (Preparative Experiment). *tert*-Butyl hydroperoxide (17.5 g of 90% commercial material, 0.175 mol) was added dropwise over several hours to Me_2SO (27.5 g, 0.352 mol) at 100 °C while a stream of dry nitrogen was used to sweep volatile products into a dry ice–acetone cold trap. After 43 h at 100 °C only a faint test for hydroperoxide (KCNS–$FeSO_4$) was obtained. The reaction mixture was cooled to room temperature and the resulting precipitate was filtered and purified by sublimation (ca. 50 °C at 0.5 Torr). The sublimate was triturated with cold ether to remove any contaminating Me_2SO, dried, and recrystallized from ethanol. The solid was dimethyl sulfone, mp 106–109 °C, mmp with authentic sample 108–110 °C. The filtrate of the reaction mixture after extraction of the acidic components as described in A precipitated additional sulfone for a total yield after recrystallization of 60–65%, based on hydroperoxide. The acidic components were separated from the filtrate as described in A. Phenylhydrazinium sulfate: mp 226–230 °C dec; mmp with an authentic sample 230–233 °C dec; ir spectra of the isolated and authentic salts were identical; equiv wt calcd 157, found 157. Phenylhydrazinium methanesulfonate: mp 193–195 °C dec; mmp with an authentic sample 193–195 °C dec (lit.[26] 193–194.5 °C); ir and NMR spectra and TLC R_f values of the isolated and authentic salts were identical; equiv wt calcd 204, found 207.

The contents of the cold trap were fractionally distilled and various components of the mixture were identified by conventional means (GLC, ir, NMR) as *tert*-butyl alcohol, acetone, isobutylene, and water, and traces of hydroperoxide, Me_2SO and sulfone, among others.

Oxygen Atmosphere. Me_2SO (44 g, 0.564 mol) and *tert*-butyl hydroperoxide (0.895 g of 90% pure material, 0.0089 mol) were heated for 24 h at 100 °C in an oxygen atmosphere. The reaction mixture was diluted to a known volume with water and an aliquot was titrated with 0.1 N NaOH; 0.50 equiv of acid per mole of hydroperoxide was formed.

Argon Atmosphere. Repetition of the above experiment but under an argon atmosphere yielded only 0.13 equiv of acid per mole of hydroperoxide (molar ratio of reactants, Me_2SO:*tert*-butyl hydroperoxide 45.8:1).

Effect of Acrylonitrile. Repetition of the above experiment in the presence of freshly distilled acrylonitrile gave a 90% yield of polyacrylonitrile but only 0.0053 equiv of acid per mole of hydroperoxide (molar ratio of reactants, Me_2SO:acrylonitrile:*tert*-butyl hydroperoxide 45.8:9.16:1).

Me_2SO Oxidation of Benzyl Alcohol. A. NMR Experiments. A stock solution of benzyl alcohol (1.08 g, 0.01 mol) in Me_2SO (5.93

g, 0.076 mol) containing DSS (0.05 g) was prepared and portions were added to NMR tubes by means of a syringe. Oxygen was bubbled through the solutions for several minutes and the tubes were then immersed in a bath maintained at 190 °C while oxygen was slowly passed over the contents. Periodically, a tube was removed, cooled to room temperature, and the benzaldehyde conversion was determined by NMR (ratio of the integral of the aromatic proton signal to that of the aldehydic proton singlet at δ 10). After 2 h at 190 °C, a 30–35% conversion to benzaldehyde was obtained. Addition of sodium carbonate (equimolar with respect to benzyl alcohol[25]) to the NMR tube prior to heating resulted in no benzaldehyde formation even though a plentiful supply of oxygen was provided.

B. Preparative Experiments. Results identical with those in A were obtained on a preparative scale. Only traces of benzaldehyde were formed in the presence of air when sodium carbonate was used; the aldehyde yield was estimated to be less than 0.01% (ir, NMR, and isolation of the 2,4-dinitrophenylhydrazone) and the benzyl alcohol was unchanged. In the absence of base, 2×10^{-3} equiv of acid per mole of benzyl alcohol formed after 6 h reaction at 175 °C.

C. *tert*-Butyl Peroxide–Me$_2$SO–Benzyl Alcohol Reactions. Benzyl alcohol (1.04 g, 0.0096 mol), Me$_2$SO (5 ml, 0.07 mol), and *tert*-butyl peroxide (0.280 g, 0.002 mol) were refluxed under dry nitrogen with periodic removal of samples for ir examination. From previously determined Beer's law plots on solutions of known concentrations of benzyl alcohol and benzaldehyde, conversion of benzyl alcohol to benzaldehyde was calculated to be about 30% after 19 h. Repetition of this experiment but with sodium carbonate present (1.05 g, 0.01 mol[25]) yielded no benzaldehyde (lower limit of detection by ir less than 2%).

D. Acid-Catalyzed Me$_2$SO–Benzyl Alcohol Oxidations. The NMR experiments in A were repeated except that (a) all solutions were carefully purged with argon and maintained in an argon atmosphere and (b) known quantities of strong acids were added to the NMR tubes, as shown in Table I.

Me$_2$SO–*tert*-Butyl Peroxide Reactions. A. Preparative Experiment. *tert*-Butyl peroxide (10.3 g, 0.0704 mol) was added dropwise over a period to Me$_2$SO (27.5 g, 0.352 mol) maintained under argon at 155–160 °C, the Me$_2$SO having been sparged with argon at 160 °C for 1 h before beginning the peroxide addition. Heating was continued for 3 h after peroxide addition was complete. The reaction mixture was allowed to cool and then was poured into water (250 ml). The aqueous mixture was filtered and then treated as already described to separate the acidic components which were identified from their phenylhydrazine salts as methanesulfonic and sulfuric acids. The volatile products collected in a dry ice–acetone trap were identified as methyl sulfide, *tert*-butyl alcohol, isobutylene, and what appeared to be acetaldehyde (NMR); other unidentified products were also present.

B. Effect of Acrylonitrile. *tert*-Butyl peroxide (0.590 g, 0.00404 mol), Me$_2$SO (15.4 g, 0.197 mol), and freshly distilled acrylonitrile (2.64 g, 0.00498 mol) were heated together under argon for 1 h at 155 °C (vigorous refluxing). This resulted in the formation of polyacrylonitrile (2.2 g, 85%); the yield of acid was found by potentiometric titration to be 0.014 equiv per mole of peroxide.

When the experiment was repeated in the absence of acrylonitrile, the yield of acid was 0.181 equiv per mole of peroxide, about 13 times that in the presence of monomer.

C. Effect of Temperature. *tert*-Butyl peroxide (1.46 g, 0.0100 mol) and Me$_2$SO (2.5 ml, 0.035 mol) were allowed to react under nitrogen at 100–120 °C. After 18–42 h, the titre of a 5-ml aliquot with 0.1 N aqueous sodium hydroxide was 0.1 ml. When the reaction was repeated at reflux temperatures (170–180 °C), however, the titre of a 5-ml aliquot after only 2 h was 3.0 ml and the appearance of the solution indicated pronounced decomposition of Me$_2$SO.

Autoxidation of Me$_2$SO Using AIBN. Me$_2$SO (44.0 g, 0.563 mol) and AIBN (2.05 g, 0.0125 mol) were allowed to react under oxygen at 80 °C for 20 h. Another portion of AIBN (2.05 g, 0.0125 mol) was then added, and the reaction was allowed to continue for another 24 h. The reaction mixture was poured into water and the resulting precipitate was collected by filtration. The precipitate was recrystallized from water and sublimed (80 °C at 0.05 Torr) to give tetramethylsuccinonitrile, mp 170–171 °C (lit.[27] 169 °C). The filtrate was treated to separate the acids present, which were identified via their phenylhydrazinium salts as methanesulfonic and sulfuric acids. In a similar experiment, the yield of acids was found by titration to be 0.440 equiv per mole of AIBN. When the reaction was carried out on a degassed sample (in an apparatus fitted with a Bunsen valve which allowed the nitrogen produced by the decomposition of AIBN to escape but which prevented oxygen from entering), no acid could be detected by titration with 0.01 N sodium hydroxide.

Attempted Autoxidation of Methanesulfonic Acid Using AIBN. AIBN (0.820 g, 4.99×10^{-3} mol) was decomposed by heating in methanesulfonic acid (15.0 g, 0.156 mol) at 80 °C for 17 h under oxygen. Treatment of the reaction mixture with aqueous barium chloride (1 ml of a saturated solution) resulted in the formation of lustrous platelets of barium methanesulfonate which redissolved completely on addition of sufficient water, indicating the absence of barium sulfate and hence sulfuric acid. Previous experiments using various dilutions of sulfuric acid had shown that a minimum concentration of 2.0×10^{-3} mol/l. of sulfuric acid could be detected in the presence of 50% aqueous methanesulfonic acid using this method.

"Thermal" Decomposition of Me$_2$SO. Me$_2$SO was vigorously flushed with oxygen at room temperature and then heated to reflux (190 °C) for 72 h while a slow stream of oxygen was passed through it. The internal temperature fell to 160 °C because of the presence of lower boiling decomposition products and a white coating, presumably polyformaldehyde, covered the surface of the container. The bright yellow Me$_2$SO solution was diluted with 1.5 volumes of water and an aliquot was titrated with 0.1 N sodium hydroxide (phenolphthalein). The acids formed amounted to 3.9×10^{-3} equiv per mole of Me$_2$SO. Treatment of the aqueous system with barium chloride solution yielded barium sulfate, identified by x-ray analysis. When the thermolysis was conducted in an argon atmosphere the yield of acid was reduced to 0.24×10^{-3} equiv per mole of Me$_2$SO. Repetition of the thermolysis with a degassed sample yielded 0.16×10^{-3} equiv of acid per mole of Me$_2$SO. In the presence of sodium carbonate, decomposition of Me$_2$SO is negligible as evidenced by the failure to obtain volatile decomposition products and polyformaldehyde.

Dehydration of 5-Methyl-5-nonanol (2). A. Sulfuric Acid Catalyst. Neat **2** (1.6 g, 0.0010 mol) containing a drop of concentrated sulfuric acid was refluxed for 1 h. The reaction mixture was poured into water (30 ml), neutralized with aqueous base, and extracted with *n*-hexane (3 × 20 ml). The hexane solution was washed with water (2 × 10 ml) and dried (Na$_2$SO$_4$). Evaporation of the solvent at 25–30 °C yielded a yellow, oily residue (0.94 g, 65% yield). Based on chemical shifts, multiplicities, and integration,[28] and by comparison with spectra of related olefins,[29] the signals in the olefinic region were assigned to *cis*- and *trans*-5-methyl-4-nonene (δ 5.61) (**3**) and 2-*n*-butyl-1-hexene (δ 4.70) (**4**). The ratio of **3**:**4** was 19:1.

B. In Refluxing Me$_2$SO. A solution of **2** (1.27 g, 0.00807 mol) in Me$_2$SO (6.54 g, 0.0831 mol) was refluxed for 17 h in an argon atmosphere; the reaction mixture separated into two phases. The mixture was poured into water (70 ml) and an aliquot was titrated with 0.1 N NaOH. The yield of acid was 1.6×10^{-3} equiv per mole of alcohol. Further workup as in A gave a light yellow oil (0.33 g, 40% yield) whose NMR spectrum (neat) was qualitatively identical with that of the product from the sulfuric acid catalyzed dehydration; the ratio of **3**:**4** was 6:1, however. The aqueous phase gave a positive test for sulfate ion with barium chloride solution.

C. In Refluxing Me$_2$SO with Aniline. Me$_2$SO (11.2 g, 0.143 mol), **2** (2.17 g, 0.0140 mol), and freshly distilled aniline (1.15 g, 0.0123 mol) were heated at reflux for 30 h in an argon atmosphere. Workup yielded a dark oil which consisted largely of unreacted **2** and aniline with **3** and **4** as minor products (NMR). The aqueous phase gave a positive test for sulfate and was found to contain 8.4×10^{-3} equiv of acid per mole of alcohol. The same qualitative results were obtained when the reaction was conducted in air.

D. In Refluxing Me$_2$SO with Bases. Me$_2$SO (1.82 g, 0.0233 mol), **2** (4.22 g, 0.0267 mol), and freshly prepared sodium *n*-octoxide (4.00 g, 0.0261 mol) were heated under argon for 17 h at 185 °C; olefin formation could not be detected. Workup yielded a yellow oil (5.6 g) which consisted exclusively of **2** and 1-octanol (NMR). The same results (olefins absent) were obtained when the ratio of **2** to base was 10:1; when the ratio of **2** to Me$_2$SO was 1:10 and air was not excluded; and in the presence or absence of oxygen when sodium carbonate or potassium *tert*-butoxide were the bases.

Acetamide (5) Condensations in Me$_2$SO. A. Air. A solution of acetamide (1.03 g, 0.0174 mol) in Me$_2$SO (7.07 g, 0.091 mol) in an NMR tube was heated to 190 °C for 17 h; conversion of **5** to **6** was 50–60%. The percent conversion was calculated from NMR by comparing the integrated value of the methylene protons (t, δ 4.40) with that of the combined values of the methyl signals of **6** (s, δ 1.81) and **5** (s, δ 1.79). The NMR assignments were verified by comparison with the NMR spectra of authentic materials in Me$_2$SO. The yield of acids formed was 0.15 equiv per mole of acetamide.

B. Argon Atmosphere. Merely flushing the reaction mixture of A with argon at room temperature for 6 h prior to heating caused no change in conversion of **5** to **6**. A solution of **5** in Me$_2$SO in an NMR tube capped with a rubber septum was frozen in dry ice–acetone while reducing the pressure through a hollow needle to 0.05 Torr followed by thawing under positive argon pressure. The freeze–thaw process was repeated four times and the solution was then heated to 190 °C for 23 h. NMR indicated a 16% conversion of **5** to **6**.

C. Sodium Carbonate. When an equimolar quantity of sodium carbonate[25] to **5** was present during the heating process (42 h), **6** was not formed either in the presence or absence of oxygen.

Reaction of Methanesulfonic Acid and *tert*-Butyl Hydroperoxide. A mixture of methanesulfonic acid (0.200 g, 0.00208 mol), *tert*-butyl hydroperoxide (0.220 g of 90% material, 0.00220 mol), and water (10 g) was degassed and then allowed to react under helium at 95 °C for 15 h. Treatment of the reaction mixture with aqueous barium chloride (1 ml of a saturated solution) resulted in the formation of a mixture of lustrous platelets of barium methanesulfonate, which dissolved on dilution with water, and a finely divided white precipitate, presumably barium sulfate, which remained insoluble, indicating the presence of sulfuric acid.

Reaction of Me$_2$SO with Fumaric Acid. A. In the Presence of Potassium Bromide. Me$_2$SO (5.05 g, 0.0647 mol), fumaric acid (0.0667 g, 5.74×10^{-4} mol), and potassium bromide (0.116 g, 9.75×10^{-4} mol) were allowed to react in air for 0.5 h at reflux (bath temperature maintained at 195 °C). Refluxing quickly became very vigorous, and pronounced decomposition of the Me$_2$SO was evident. The mixture separated into a liquid upper phase and a gel. The contents of the flask were transferred quantitatively into water (35 ml) and the acid content was determined by titration. The acid formed in excess of the fumaric acid orginally present was found to be 4.31×10^{-2} equiv per mole of Me$_2$SO. The reaction mixture also gave a strong positive test for sulfate with aqueous barium chloride.

B. In the Absence of Potassium Bromide. When the reaction was repeated in the absence of potassium bromide, vigorous refluxing was not evident until the end of the 0.5-h reaction period. The reaction mixture yellowed slightly, but decomposition of the Me$_2$SO was not pronounced. Titration revealed no acid in excess of that originally present. Only a faint opalescence was observed on treatment with aqueous barium chloride. The results were the same whether the reaction was carried out on a degassed sample under argon, in air, or in an oxygen atmosphere.

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Registry No.—**2**, 33933-78-7; **5**, 60-35-5; sodium carbonate, 7542-12-3; methanesulfonic acid, 75-75-2; sulfuric acid, 7664-93-9; Me$_2$SO, 67-68-5; styrene oxide, 96-09-3; *tert*-butyl hydroperoxide, 75-91-2; benzyl alcohol, 100-51-6; *tert*-butyl peroxide, 110-05-4; fumaric acid, 110-17-8.

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