

908. *An Exceptionally Powerful Oxidant: the Ion H_3O_2^+ .*

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Solutions of 85% hydrogen peroxide, hydrogen fluoride, and boron trifluoride in tetrahydrothiophen 1,1-dioxide ("sulpholane") probably contain, in significant concentration, the conjugate cation of hydrogen peroxide. They are powerful but unselective oxidants, reacting with, for example, benzene and cyclohexane at room temperature, and effecting extensive or total breakdown of the substrate.

LIKE other families of electrophiles, the peracids, HOX, form a graded series, becoming more reactive and (necessarily) less discriminating as X^- becomes a progressively better leaving group. The limiting member, HO^+ , has probably never been prepared in solution, and the evidence presented below suggests that it would be an oxidant of unparalleled energy and lack of specificity.* We have now examined what we believe to be the case where $\text{X} = \text{H}_2\text{O}^+$, which we expected to obtain by treating hydrogen peroxide with an excess of a solution of hydrogen fluoride and boron trifluoride in tetrahydrothiophen 1,1-dioxide (afterwards referred to as "sulpholane"). These solutions have been shown to be extremely acidic, yet free from alternative electrophiles and reactive nucleophiles.² Experimentally, 85% hydrogen peroxide was added to a solution about 4M in hydrogen fluoride and boron trifluoride in sulpholane. Although always prepared cautiously and on a small scale, this mixture never caught fire or exploded (a mixture of 85% hydrogen peroxide, sulpholane, and phosphorus pentoxide did deflagrate, however). Its stoichiometry was made consistent † with the formation of $\text{H}_3\text{O}^+\cdot\text{BF}_4^- + \text{H}_3\text{O}_2^+\cdot\text{BF}_4^-$. When, to a solution nominally *ca.* 2M in the oxidant, benzene was added, a vigorous reaction occurred and the mixture boiled. More dilute (~ 0.1 — 0.3 M) solutions reacted smoothly but exothermally with aromatic hydrocarbons, much gas being evolved, and detailed investigations seemed worth while. Initially we measured only the uptake of (hydrogen peroxide + peracids), iodometrically with a molybdate catalyst.

The reagent proved to be reasonably stable, typically losing half its activity in one day, providing the sulpholane used was freed from oxidisable impurities present in some commercial samples. Its loss of activity appeared to follow a second-order law, and slow evolution of a gas, probably oxygen, was observed; but no serious study of this reaction was necessary, as most of the oxidations examined were much faster, or profitable, as its rate was obviously affected by the acidity of the solution which would be altered by the formation of water in the oxidations, and possibly by trace-metal catalysis. Reaction with tetralin was negligible when the tetrafluoroboric acid content was less than equivalent to the water introduced in the "85% peroxide," and when intermediate quantities of acid were used the reaction ended with some hydrogen peroxide and hydrocarbon still present, so we usually employed enough acid (*ca.* 0.5M) to protonate any water that could be formed during the oxidation. Typically the solution was 0.13M in peroxide. With differing ratios of acid, peroxide, and hydrocarbon "final" uptake values (moles/mole; after 30—120 minutes, when the change between successive time-intervals was smaller than the

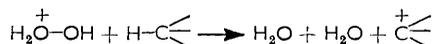
* It is perhaps unfortunate that HO^+ was mentioned, possibly as a formal shorthand expression for the whole family HOX, in an important Paper¹ on the biogenesis of triterpenes and steroids; this has created an impression that HO^+ itself is a possible oxidant under biological conditions. In fact the specificity and the probable need for anchimeric assistance in the attack on squalene implies that the actual oxidant is more likely to be an unusually *weak* member of the family.

† The ion-pair $\text{H}_3\text{O}_2^+\cdot\text{BF}_4^-$ would be expected to equilibrate with $\text{H}_2\text{O}_2 + \text{HF} + \text{BF}_3$, whilst H_2O_2 and BF_3 should form an (ionisable) complex $\text{H}_2\text{O}_2\cdot\text{BF}_3$. All these species will of course be solvated; and HF and BF_3 in particular react exothermally with sulpholane, the latter giving a solid adduct which no doubt contains a covalent O—B bond. We do not claim to know the approximate position of these equilibria.

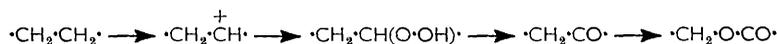
¹ Eschenmoser, Ruzicka, Jeger, and Arigoni, *Helv. Chim. Acta*, 1955, **38**, 1890.

² Powell and Whiting, *Proc. Chem. Soc.*, 1960, 412.

experimental scatter) of 12.4 and 12.8 were obtained for tetralin, and 9.7 and 9.4 for mesitylene, uncorrected for decomposition of the reagent. These suggested that the oxidation was (at least predominantly) converting aromatic nuclei into carbon dioxide and water, alkyl residues remaining with carboxyl groups, a reaction with theoretical uptake values of 13 and 12 moles, respectively. This result would have been consistent with the behaviour of benzene, which gave no evident yield of benzoquinone or muconic acid (detectable in *ca.* 1% yield) or maleic or fumaric acid (detectable in 10% yield); it seemed possible *a priori* as successive hydroxylation, oxidation to a quinone, and further breakdown seemed unlikely to give any intermediate nearly as resistant to oxidation as the aromatic hydrocarbon itself; and would have implied a considerable value for the method in degradative work. We therefore measured the uptake of the reagent by a variety of substrates. Benzoic acid was unaffected (<0.6 mole difference in loss between the solution and a blank after 22 hours) whilst aniline and pyridine appeared to retard the decomposition of the reagent slightly, no doubt by neutralising some of the tetrafluoroboric acid present. Cyclohexanone rapidly consumed 1 mole, presumably in a Baeyer-Villiger reaction, but then continued to oxidise slowly. Oxalic acid rapidly consumed 1 mol., and therefore need not be suspected as an end-product in the oxidation of aromatic compounds. Methanol was quite unreactive, and cyclohexanol consumed the reagent only slowly. To ascertain whether useful aliphatic fragments survived, we oxidised *n*-butylbenzene on a larger scale, isolated the monocarboxylic acids formed, esterified with diazomethane with the addition of an internal standard, and estimated yields by gas chromatography. These were disappointing; 32%, 5%, and <5% for the C₅, C₄, and C₃ acids, plus, presumably, some acetic acid. Tetralin, despite the promising uptake figures, gave even worse results; C₆, C₅, and C₄ dicarboxylic acids were obtained in yields of 4%, 5%, and 1%, respectively. We conclude that much non-specific oxidation, presumably with some tendency to form benzyl cations, takes place, and also, perhaps, various C-acylation processes catalysed by the intensely acidic solvent. Our reagent is thus unlikely to rival ozone, which is already a fairly efficient oxidant of the type envisaged; possibly it might be useful in cases where the formation of a cationic centre would modify relative reactivities. But conversely, it might be capable of attacking *s-sp*³ H-C bonds, in a process so far known only for chromic acid:³



and its reactivity toward cyclohexane, methylcyclohexane, and *trans*- and *cis*-decalin was, therefore, examined. Analysis for unchanged peroxide was supplemented by gas-chromatographic analysis for unchanged hydrocarbon; the ratio of the two rates should then indicate the stoichiometry of the initial oxidation process. This amounted to 1.7–3.5 moles/mole for all the substrates; perhaps the most probable reaction sequences are



which would require a value of 3, and the variant



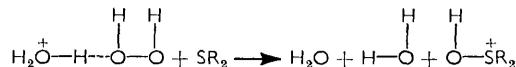
which would require only 1 mole/mole (no direct investigation of products has been attempted). Relative rates for the four hydrocarbons were approximately 1 : 20 : 20 : 40; clearly the hydrocarbons capable of giving a tertiary carbonium ion are thereby able to react much more readily than cyclohexane. Comparison with analogous relative rates for the four hydrocarbons obtained by Mareš, Roček, and Sicher³ (1 : 10 : 8 : 80) for the reagent present in mixtures of chromic, acetic, and sulphuric acids (HCrO₃⁺ or H₃CrO₄⁺) suggests that the species H₃O₂⁺ is less demanding sterically, as might have been expected. The

³ Mareš, Roček, and Sicher, *Coll. Czech. Chem. Comm.*, 1961, **26**, 2355; Mareš and Roček, *ibid.*, p. 2370.

factor for the relative rates of removal of secondary and tertiary hydride ions (CH₂ in cyclohexane versus MeHC< in methylcyclohexane) is about 200, and even if the entire rate of decomposition of the reagent is attributed to attack on the CH₂ groups of sulpholane (which is almost certainly not true; probably most of the peroxide yields oxygen) a minimum factor of 25 can be calculated for the relative rates of attack on ·CH₂· in cyclohexane and sulpholane. These results support the postulated mechanism. The reasonably high selectivity between secondary and tertiary CH groups (compare free-radical reagents) suggests that this reagent, in conjunction with gas-chromatographic examination of products, might be useful in the degradation of branched-chain saturated compounds, *e.g.*, the bacterial lipids.

We have discussed this reagent as, effectively, the cation H₃O₂⁺; Derbyshire and Waters observed⁴ substitution by this entity in 10*N*-sulphuric acid (*H*₀ about 11),⁵ which is comparable with that of our reagent. Hydrogen peroxide has been estimated to be more than a million times less basic than water.⁶ Accepting that the basicity of water varies with the medium,⁷ and assuming that that of hydrogen peroxide varies similarly, we would anticipate *pK* values algebraically below -7.7, -8.5, -9.8, and -11 in water, acetic acid, formic acid, and sulphuric acid from published estimates⁸ of the basicity of water. We have deduced⁹ a value of *ca.* -5.0 for water in sulpholane, which suggests about -11 for the peroxide in that solvent, and *H*₀ about -8 for 0.5*M*-tetrafluoroboric acid. These figures, which require careful definition to be quantitatively meaningful, at least imply that, even in the solutions of Derbyshire and Waters and in our own, the peroxide is probably only partly protonated. It follows that the use of more acidic solutions would give proportionally more rapidly active oxidants. There is, however, still some doubt that all, or most, of the reactions we have described should be attributed to H₃O₂⁺; for, if not fully protonated, the peroxide may well compete with sulpholane, surely not a strong Lewis base, for boron trifluoride and for hydrogen fluoride, giving the species HO-⁺OH-⁻BF₃ and HO-OH···[F-H]_{*n*}. These belong to the family HO-X and are undoubtedly capable of reacting as HO⁺ donors. The second is unlikely to be powerful, but the first should be a formidable oxidant. It is, however, more probably the main effective ingredient in the mixture of hydrogen peroxide and boron trifluoride etherate,¹⁰ a much milder (and probably more useful) oxidant than ours. An attempt to prepare this species in sulpholane gave a solution with much the same properties as that in "tetrafluoroboric acid;" but in its preparation intensely acidic species like HBF₃(OH) and HBF₄ would necessarily be formed from the water introduced with the peroxide, and this experiment need not negate the hypothesis that H₂O₂·BF₃ is a milder reagent than ours.

The cation H₃O₂⁺ has been postulated^{11,12} as the reagent in some very mild oxidations observed in aqueous solutions. In fact it seems more probable that these involve a perhydrated oxonium cation:



(where S is the substrate, typically a sulphide). Such a species must be present in overwhelmingly higher concentration than that of H₃O₂⁺·*n*H₂O in these solutions.

⁴ Derbyshire and Waters, *Nature*, 1950, **165**, 401.

⁵ Jorgenson and Hartter, *J. Amer. Chem. Soc.*, 1963, **85**, 878.

⁶ Mitchell and Wynne-Jones, *Discuss. Faraday Soc.*, 1953, **15**, 161; *Trans. Faraday Soc.*, 1955, **51**, 1690; Wynne-Jones, personal communication.

⁷ Arnett and Wu, *J. Amer. Chem. Soc.*, 1962, **84**, 1680.

⁸ Hammett and Deyrup, *J. Amer. Chem. Soc.*, 1932, **54**, 4239; Lemaire and Lucas, *ibid.*, 1951, **73**, 5198; Wyatt, *Discuss. Faraday Soc.*, 1957, **24**, 162.

⁹ Alder, Chalkley, and Whiting, unpublished results.

¹⁰ McClure and Williams, *J. Org. Chem.*, 1962, **27**, 24.

¹¹ Ross, *J. Amer. Chem. Soc.*, 1946, **68**, 1484.

¹² Overberger and Cummins, *J. Amer. Chem. Soc.*, 1953, **75**, 4783.

EXPERIMENTAL

Purification of Tetrahydrothiophen 1,1-Dioxide (Sulpholane).—The commercial solvent, prepared by addition of sulphur dioxide to butadiene and hydrogenation, may contain oxidisable contaminants, probably including dihydrothiophen 1,1-dioxide, and/or tetrahydrothiophen 1-oxide and tetrahydrothiophen. The procedure described gives a product of high melting-point and stable to hydrogen peroxide-tetrafluoroboric acid; if stability to oxidation is not necessary the preliminary treatment with permanganate may be omitted.

Concentrated sulphuric acid (50 g.) was added to ice (1 kg.), then potassium permanganate (50 g.) and commercial sulpholane (m. p. 20–23°) (1 l.) were added successively. The mixture was set aside for 2 hr. at 20° with occasional swirling, treated with enough sodium pyrosulphite to give a clear solution, and extracted with dichloromethane (3 × 500 c.c.). The extract was evaporated at 760 mm., and the residue was stirred with phosphorus pentoxide (5 × 2 g.; added over 30 min.). The sulpholane was decanted and distilled at 100–105°/0.02 mm. and had m. p. 27.6–28.4°, according to the varying purity of the starting material (Birch and McAllen¹³ give m. p. 28.86°, obtained by extrapolating data from m. p.s in the range 20–25° and certainly not reliable to 0.01°; Burwell and Langford¹⁴ give m. p. 26°).

Hydrogen fluoride. Solutions were prepared by transferring the reagent from the cylinder to a polyethylene container cooled in ice-salt, then redistilling through an ice-salt-cooled spiral of polyethylene to a similar vessel containing a weighed amount of sulpholane. These solutions slowly darkened, and the containers became brittle after several months' storage at 0°; the use of polytetrafluoroethylene bottles was more satisfactory. Direct addition of liquid hydrogen fluoride to solid sulpholane is possible but requires care, as there is an appreciable positive heat of solution.

Boron trifluoride. Solutions were prepared by passing the gas, freed from mechanically-entrained contaminants by a polyethylene trap, into a weighed amount of sulpholane in a polyethylene container which was first gently warmed, then cooled in ice, as the heat of solution is strongly positive. When the solutions were more than 25% w/w they solidified on cooling to room temperature; the adduct had m. p. > 50°.

"Tetrafluoroboric acid." Solutions (ca. 20% w/w) were prepared from weighed amounts of the two components (heat of mixing negligible) and preferably stored in polytetrafluoroethylene containers. They attack glass, although not so rapidly as solutions of hydrogen fluoride alone; much more dilute solutions can be handled in glass without noticeable effects.

Hydrogen peroxide. Solutions in the tetrafluoroboric acid reagent were prepared from commercial 80–85% reagent (stabilised aqueous solution) previously standardised iodometrically, to which was added gradually, behind an explosion screen, a 20–30% (w/w) solution of tetrafluoroboric acid. This concentrated solution evolved gas (oxygen?) rather rapidly and was diluted with sulpholane as soon as possible. In one set of experiments a solution 1.2M in "tetrafluoroboric acid" and 0.35M in hydrogen peroxide, in 2 c.c. aliquots, was decomposed at 25.0° and estimated iodometrically; first-order constants drifted downwards from $6-7 \times 10^{-6}$ sec.⁻¹ at 2–20% reaction to $2.5-2.2 \times 10^{-6}$ sec.⁻¹ at 70–90% reaction, whereas second-order constants were steady, with much scatter, at $4.5 \pm 1.5 \times 10^{-5}$ l. mole⁻¹ sec.⁻¹. Hydrogen peroxide (0.237M) in sulpholane alone was completely stable during 2 days.

Titration of unreacted (hydrogen peroxide + peracids) were effected as follows. The solution was diluted with m-sulphuric acid (20 c.c.) and distilled water (10–20 c.c.), an excess of solid potassium iodide, and three drops of a 3% solution of ammonium molybdate were added, and the liberated iodine was at once titrated with 0.1M-sodium thiosulphate solution (10 c.c.; \equiv 17 mg. H₂O₂). Starch was added only when the solutions were coloured; a carbon dioxide atmosphere made no difference; end-points were stable for 10–15 min.

Reactions. These were carried out using stoppered 5 c.c. glass flasks containing 2 c.c. aliquots of a dilute solution of the substrate in sulpholane, plus a 2 c.c. blank of pure sulpholane. Each was placed in a thermostat bath at 25° and treated with 2 c.c. of hydrogen peroxide-tetrafluoroboric acid. After varying times the mixtures were titrated as described above. Thus, aliquots containing initially 3.71 mg. of tetralin in 4 c.c. of sulpholane, 0.564M in tetrafluoroboric acid and 0.128M in hydrogen peroxide, retained after 0, 5, 15, 30, 60, and 120 min., 17.3, 11.4, 8.7, 7.1, 6.0, and 5.1 mg., respectively, of hydrogen peroxide, corresponding to an uptake

¹³ Birch and McAllen, *J.*, 1951, 2556.

¹⁴ Burwell and Langford, *J. Amer. Chem. Soc.*, 1959, **81**, 3799.

of 0, 6.2, 9.0, 10.7, 11.8, and 12.8 moles of the peroxide per mole of tetralin. The blank flask contained 16.4 mg. after 120 min., implying a loss of 1.0 mol.; no attempt was made to apply a correction. In a repetition of this experiment with the acid concentration halved the uptake was 12.4 mol.; on the other hand with the acid concentration down to 0.125M and the peroxide concentration 0.129M (the water introduced inevitably being therefore *ca.* 0.05M) the uptake was only 1.2 mol. after 457 min. and 2.5 mol. after 2798 min., uncorrected.

In similar experiments mesitylene showed an uptake of 9.4 and 9.7 mol. after 30 min.; benzoic acid less than 0.6 mol. after 22 hr. (corrected), pyridine and aniline a negative uptake, in that such solutions at any given time contained more hydrogen peroxide than the blank; methanol, no uptake after 120 min.; and cyclohexanol a slow oxidation, reaching 1.3 mol. after 120 min. Cyclohexanone reacted with 1.26, 1.37, and 1.75 mol. after 6, 22, and 122 min.

Oxidation of n-Butylbenzene.—The hydrocarbon was a redistilled commercial specimen which gave a single peak on gas chromatography. Hydrogen peroxide (683 mg.; 85%) and a solution of tetrafluoroboric acid in sulpholane (12.24 g.; 20% w/w) were mixed in a 25 c.c. glass conical flask which was cooled in ice-water and stirred magnetically. Butylbenzene (136 mg.) was added dropwise during 12 min., and stirring was maintained for a further 5 min. The deep brown solution was diluted with water (600 c.c.) and distilled, 500 c.c. being collected. The distillate was made just alkaline and evaporated to dryness and the residue was acidified with the minimum of 30% sulphuric acid and extracted with ether (5 c.c.). The extract was washed with saturated brine (1 c.c.), dried (MgSO_4), and concentrated to 3 c.c. through a fractionating column; the acids therein were converted into their esters by adding ethereal diazomethane. Toluene (29 mg.) was added (2 drops from a calibrated dropper) and the mixture was chromatographed on a 170 cm. column of 20% dinonyl phthalate on Embacel (diatomaceous earth) at 80°, H_2 , 43 c.c./min. Peaks were observed with retention times of 2.6, 5.2, 7.8, and 11.5 min., identified, respectively, as methyl propionate, methyl butyrate, toluene, and methyl valerate. By comparison with mixtures of known weights the yields of the three esters were calculated as 4.4 (4.9%), 5.5 (5.3%), and 37.5 mg. (32%). Methyl acetate under these conditions is inseparable from ether.

Oxidation of Tetralin.—The commercial hydrocarbon was repeatedly shaken with concentrated sulphuric acid, subjected to preparative gas chromatography to remove decalin, and distilled from potassium. The oxidation was carried out as above, with 133 mg. of tetralin added to 571 mg. of 85% hydrogen peroxide in 14.43 g. of 20% tetrafluoroboric acid in sulpholane. Stirring was maintained for 10 min. after addition was complete, 20% aqueous potassium hydroxide solution was added, and the precipitated potassium salt filtered off. The filtrate was extracted with dichloromethane (5×100 c.c.) to remove sulpholane and the aqueous solution was evaporated to dryness; the residue was heated under reflux with a solution (6 c.c.) of concentrated sulphuric acid (5 c.c.) in methanol (20 c.c.) for 16 hr. Anhydrous potassium carbonate (4 g.) was added and the solid residue was washed with hot ether (10 c.c.). The ether and methanol solutions were evaporated to *ca.* 1 c.c., tetralin (52.9 mg.) was added as an internal standard, and the mixture was analysed gas chromatographically on a 200 cm. column of 30% Apiezon L (paraffinic hydrocarbons) on Embacel at 140°. Yields of dicarboxylic acids, based on peaks obtained for the dimethyl esters when the pure acids were subjected to the esterification and chromatography technique, were: C_6 , 4%; C_8 , 5%; and C_4 , 1%.

Oxidations of Alicyclic Hydrocarbons.—The decalins were obtained by preparative gas chromatography of the commercial material on a 12 ft. \times 1 in. column of 30% Apiezon L on Embacel at 150—155°. Each was distilled from potassium; by gas chromatography each contained about 1% of the other, and by ultraviolet absorption about 1% (*trans*) and 0.6% (*cis*) of an aromatic contaminant having an assumed ϵ of 300 at 2540 Å (probably C_9). Cyclohexane was of spectroscopic grade, shown to be pure by ultraviolet spectroscopy and gas chromatography. Methylcyclohexane was prepared by repeated shaking with a nitrating mixture followed by preparative gas chromatography on the above column at 93°; it was then chromatographically pure.

The general procedure was as described for butylbenzene, except that before titrating for unchanged peroxide the contents of each flask were washed into a small separating funnel with 1.3M-sulphuric acid (15 c.c.) and 1 c.c. of a solution of an internal standard in ether or light petroleum was added, plus 1—2 c.c. more solvent for convenience. After equilibration and separation, the organic phase was dried and chromatographed. Each decalin (in light petroleum) was used to label the other, and cyclohexane and methylcyclohexane (in ether) were

4712 *An Exceptionally Powerful Oxidant: the Ion H₃O₂⁺.*

also used reciprocally. Analyses of the decalin mixtures were effected on a 250 cm. column of 10% benzylbiphenyl on Embacel at 100°, H₂, 45 c.c./min.; cyclohexane-methylcyclohexane mixtures were analysed on 200 cm. of 30% Apiezon L on Embacel at 60°, N₂, 22 c.c./min.

The two decalins were oxidised with 0.296M-acid and 0.154M-hydrogen peroxide; *trans*-decalin and methylcyclohexane with 0.462M-acid and 0.145M-H₂O₂, and cyclohexane with 0.427M-acid and 0.139M hydrogen peroxide. The results are given in the Table. Plots of remaining concentrations of peroxide and hydrocarbon against time were made and tangents at $t = 0$ were drawn, giving the following initial rates (l. mole sec.⁻¹):

$$\textit{trans}\text{-decalin: } -d[\text{H}_2\text{O}_2]/dt = 5.1 \times 10^{-6}; \quad -d[\text{RH}]/dt = 2.0 \times 10^{-6}$$

$$\textit{cis}\text{-decalin: } -d[\text{H}_2\text{O}_2]/dt = 8.5 \times 10^{-6}; \quad -d[\text{RH}]/dt = 4.0 \times 10^{-6}$$

$$\textit{trans}\text{-decalin: } -d[\text{H}_2\text{O}_2]/dt = 9.2 \times 10^{-6}; \quad -d[\text{RH}]/dt = 2.6 \times 10^{-6}$$

$$\text{methylcyclohexane: } -d[\text{H}_2\text{O}_2]/dt = 5.3 \times 10^{-6}; \quad -d[\text{RH}]/dt = 3.3 \times 10^{-6}$$

$$\text{cyclohexane: } -d[\text{RH}]/dt = 1.0 \times 10^{-7}$$

The first two experiments and the second two are comparable, the two rates for *trans*-decalin being presumably a function of acid concentration. The rate of loss of peroxide in cyclohexane-sulpholane-acid was only about twice that in sulpholane-acid alone, so that no

Oxidations of olicyclic hydrocarbons.

Time (sec.)	[H ₂ O ₂] in control *	<i>cis</i> -Decalin		<i>trans</i> -Decalin	
		[H ₂ O ₂]	[RH]	[H ₂ O ₂]	[RH]
		0	0.154	0.154	0.0216
600		0.149	0.0183	0.149	0.0205
1800		0.140	0.0159	0.145	0.0216
3600	0.151	0.133	0.0103	0.140	0.0204
14,100	0.144	0.092	0.0063	0.110	0.0167

* The control contained only sulpholane and no hydrocarbon.

Time (sec.)	[H ₂ O ₂] in control	<i>trans</i> -Decalin		Methylcyclohexane	
		[H ₂ O ₂]	[RH]	[H ₂ O ₂]	[RH]
0	0.145	0.145	0.0196	0.145	0.0241
1800		0.129	0.0149	0.135	0.0194
3600		0.114	0.0149	0.128	0.0176
7200		0.094	0.0118	0.115	0.0160
14,400		0.079	0.0109	0.097	0.0157
36,000	0.106	0.030	0.0055	0.049	0.0118

Time (sec.)	[H ₂ O ₂] in control	[H ₂ O ₂] in reaction	[Cyclohexane] in reaction
0	0.139	0.139	0.0139
900		0.138	0.0140
3600		0.132	0.0140
7200	0.130	0.121	0.0132
21,600	0.107	0.101	0.0120
86,400	0.072	0.055	0.0091
259,200	0.034	0.010	0.0080

useful estimate can be given for $-d[\text{H}_2\text{O}_2]/dt$. Relative rates of oxidation were calculated from the above values of $-d[\text{RH}]/dt$ and the initial hydrocarbon concentrations, assuming the reaction to be first-order in hydrocarbon.

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