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OXIDATION OF TETRALIN, α TETRALOL AND α TETRALONE

DEPENDENCE OF ALCOHOL TO KETONE RATIO ON CONVERSION

M. MARTAN,* J. MANASSEN and D. VOFSI

Plastics Research Laboratory, The Weizmann Institute of Science, Rehovot, Israel

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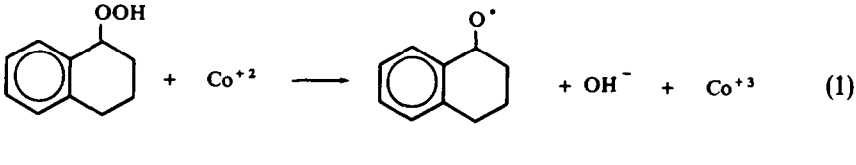
Abstract—Analysis of the products formed during oxidation of tetralin in acetic acid has clarified the course of the reaction. The primarily formed hydroperoxide decomposes to an equimolar mixture of α-tetralol and α-tetralone. α-Tetralol is further oxidized (to α-tetralone) at a higher rate than the rate of tetralin oxidation. Thus, it is found that the ketone to alcohol product ratio increases with increasing degree of conversion. This ratio, however, is essentially independent of the concentration, composition or even physical state of the catalyst. α-Tetralol is also oxidized at the 4-position, and the previously undescribed 1,4-disubstituted naphthalene derivatives, 1,2,3,4-tetrahydro-1,4-dihydroxynaphthalene and 1,2,3,4-tetrahydro-1-keto-4-hydroxynaphthalene, have been isolated and identified. The products, α-naphthol and dihydronaphthoquinone, which were also isolated, explain the autoinhibition observed at high conversion.

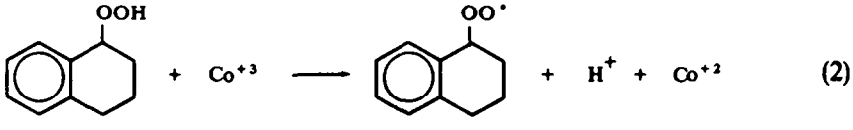
The ketone to alcohol product ratio obtained on decomposition of the hydroperoxide in the absence of air was also shown to depend on the degree of conversion. α-Tetralone is the main product formed at temperatures exceeding 100°. Separate oxidation studies of α-tetralol and α-tetralone support the above conclusions on the course of tetralin oxidation.

INTRODUCTION

THE oxidation of tetralin has been widely studied in the presence as well as absence of catalysts, Several aspects of this reaction have, nevertheless, remained unclear. Previous workers[1–3] were mainly concerned with the kinetic aspect and have, therefore, carried the reaction to low conversions in order to avoid complications. The aim in these studies was to establish the initial rate dependence on catalyst and substrate concentrations. The mechanism of reaction at its early stages was essentially based on the Haber–Weiss catalytic chain decomposition of hydroperoxide:

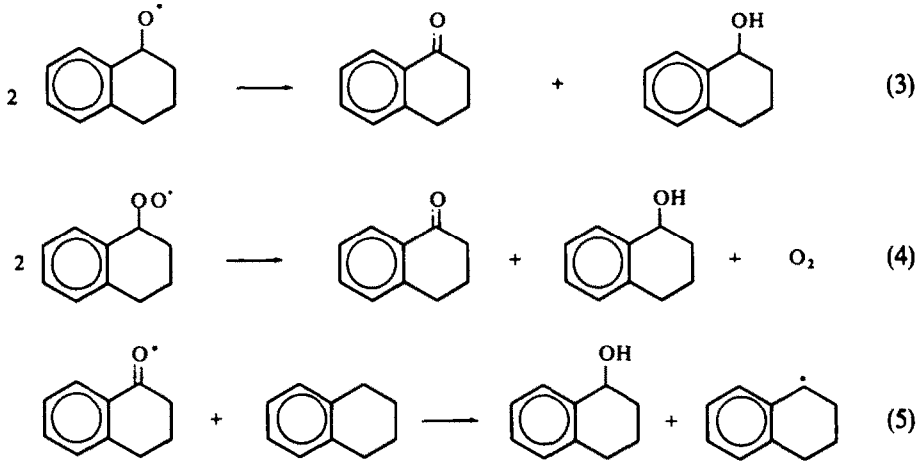


(1)

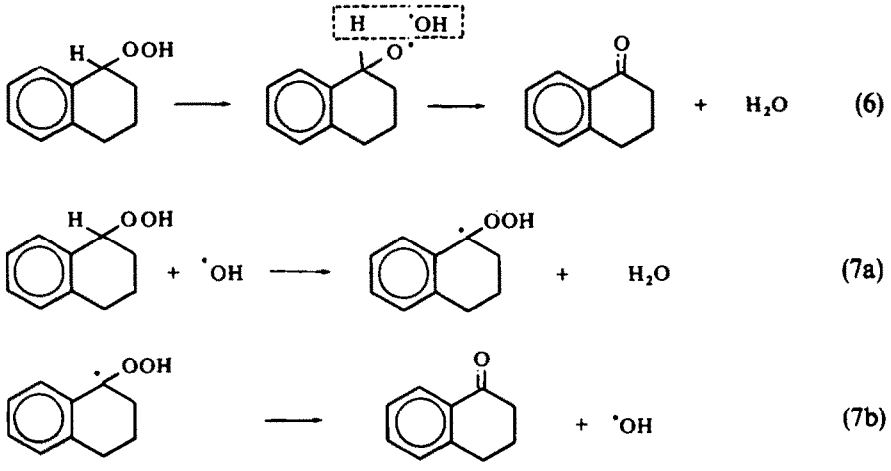


(2)

The chain is propagated by the radicals abstracting H atoms from the substrate the stable products being formed mainly as a result of radical disproportionation (Eqs 4, 5):



Thus, at low conversions, the expected ratio of ketone to alcohol (the On/Ol-ratio) should be equal or smaller than one, depending on the importance of the reaction (Eq 5). Examination of previous studies revealed that this conclusion was not confirmed. In the work of Robertson and Waters[6] excess ketone over alcohol was found. They attributed this to O—O fission in the hydroperoxide, followed by either "cage elimination" or by a chain reaction: (Eq 7)



Denisov *et al.*[7] found that autoxidation of cyclohexane at 140° produced excess of the ketone, while in the cobalt–salt catalyzed oxidation of this substrate at 110° an excess of the alcohol was formed. To explain these results an interaction of the Co-species with peroxy-radicals was invoked.

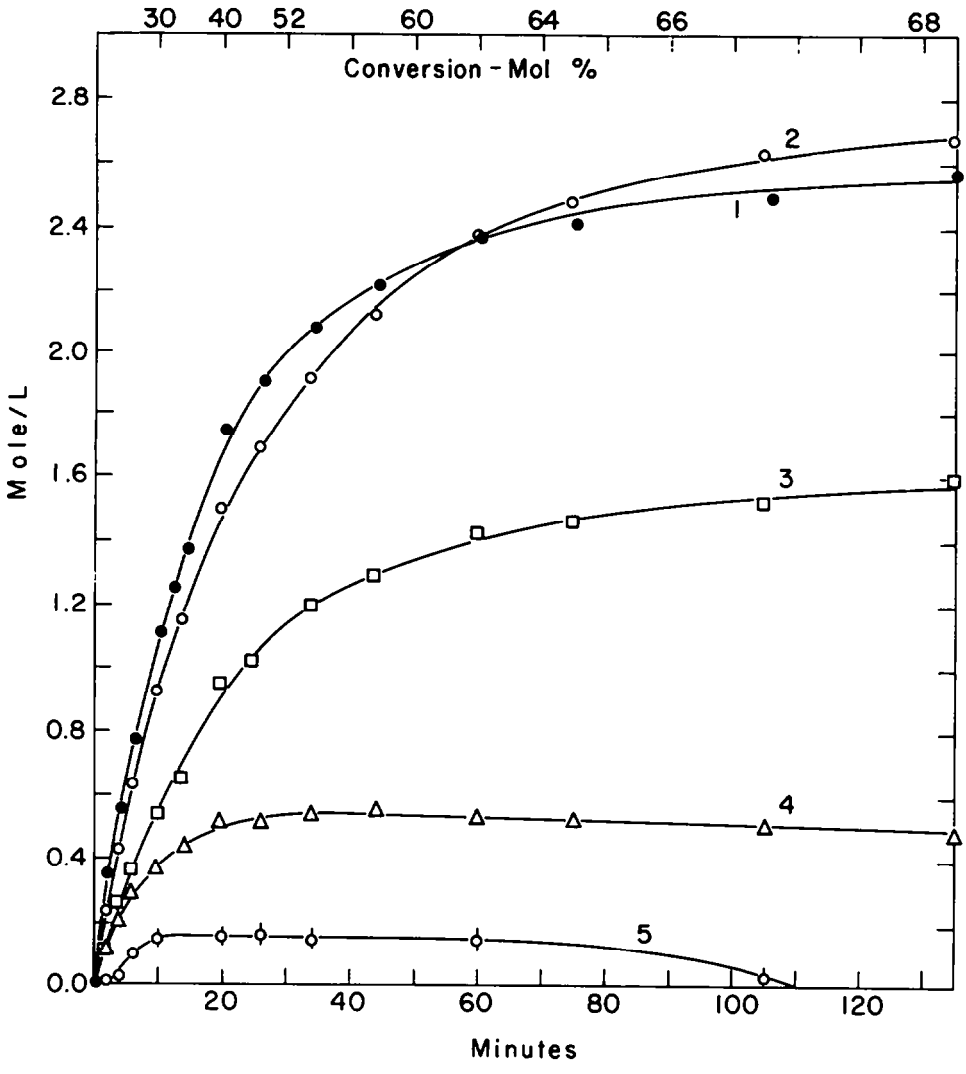


FIG 1. Oxidation of tetralin in acetic acid at 80°.
[Tetralin] = 3·79 M/L. [$Co(OAc)_2$]-0·006 M/L. 1. Tetralin disappearance. 2. Oxygen absorption. 3. Formation of α-tetralone. 4. Formation of α-tetralol. 5. Formation of tetralylhydroperoxide.

More recently, the oxidation of tetralin was carried out in the presence of various heterogeneous catalysts.[8] In this work a product analysis was given and activities of the different catalysts were correlated with the semiconducting properties of the metal oxide catalysts.

In the present work *all* the reaction products and intermediates were analyzed in the course of the reaction, at regular intervals and up to a high conversion and a more detailed picture of the mechanism could, therefore, be obtained. It appears that the On/O1 ratio does not depend on the type of catalyst or its concentration,

but is mainly a function of conversion, provided the reaction takes place at temperatures below 100° where O—O fission is relatively unimportant.

While initially the On/O1 ratio is close to one, it increases with conversion, reaching a value of about five, when 70% of the substrate has been converted. In addition, some previously unidentified products of tetralin oxidation were isolated from the reaction mixture.

RESULTS

Oxidation of tetralin. The product distribution as a function of time in the $Co(OAc)_2$ catalyzed oxidation of tetralin in acetic acid at 80° (tetralin conc: 3·79 mol/lit, catalyst conc: 0·006M) is shown in Fig. 1.

The following features are evident:

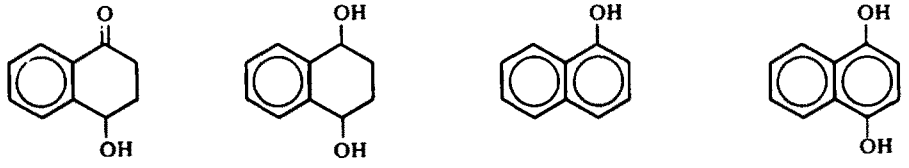
1. Tetralin disappearance is faster than oxygen consumption up to about 60%. At higher conversion, however, consumption of oxygen overtakes the disappearance of substrate.

2. Hydroperoxide is first built up, reaching a stationary state at about 30% conversion, then decreasing slowly.

3. Similar behaviour is seen in the case of the α-tetralol curve. The behaviour of both these products is characteristic of an intermediate in a consecutive reaction.

4. Tetralone formation follows a pattern, different from that of its co-product α-tetralol. Its concentration builds up steadily and shows no decline up to a conversion as high as 70%.

5. The build-up of higher products of oxidation is not shown in Fig. 1, but they were isolated from the distillation residue and identified as:



I II III IV

Compounds I and II have not been isolated previously.[9]

Oxidation of α-tetralol. Fig. 2 the results of a co-oxidation experiment of tetralin and α-tetralol are plotted, the molar ratio of the reactants being 3:23. This ratio was chosen to minimize the concentration effect of the α-tetralol, which is formed from tetralin oxidation. This experiment shows, that α-tetralol is oxidized at a rate at least 50% higher than that of tetralin. This was somewhat unexpected, because steric hindrance was supposed to impair the oxidation of this compound.[10]

The product analysis of α-tetralol oxidation is summarized in Table 1.

It can be seen, that water formation roughly parallels the formation of α-tetralone. It is of interest, that the ketone concentration accounts for only 75% of the tetralol consumed, independent of conversion. This shows that 25% of the consumed tetralol ends up in other products in parallel reactions. It should also be noted, that oxygen

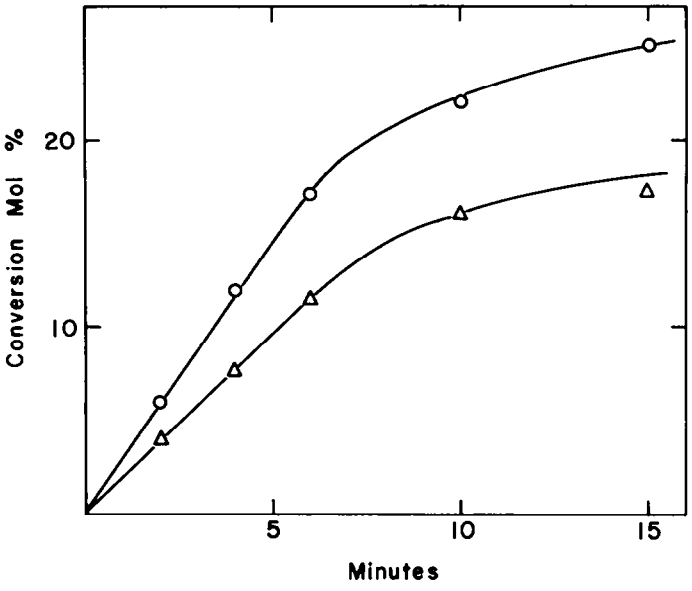


FIG 2. Cooxidation of tetralin and α-teralol in acetic acid at 80°.
[Tetralin] 0·45 M/L, [α-Tetralol] 3·44 M/L, [$Co(OAc)_2$] 0·001 M/L.
△—Tetralin, ○—α-Tetralol.

consumption lags behind the disappearance of tetralol, as can be seen from Fig. 3. Several of the side products could be isolated and were identified as: I, II and III.

The tetralone to tetralol ratio. The dependence of the On/O1 ratio on tetralin conversion for the $Co(OAc)_2$ catalyzed oxidation in acetic acid solution is shown in Fig. 4. Initially this ratio is somewhat smaller than one, but it steadily increases up to a value of about 5 at 70% conversion. Catalyst concentration has no effect on this dependence.

TABLE 1. OXIDATION OF α-TETRALOL AT 80°
[α-tetralol] = 3·79 Mol/L in acetic acid in the presence of $Co(OAc)_2$–0·006M

Time min.	Oxygen uptake Mol/L	Conversion* in Mol-%	α-tetralol reacted Mol/L	α-tetralone produced Mol/L	Ratio α-tetralone produced/ α-tetralol reacted	H_2O produced Mol/L
5	0·09	4·16	0·158	0·118	0·75	0·13
8	0·32	16·3	0·62	0·475	0·77	0·55
11	0·42	21·5	0·815	0·61	0·75	0·7
14	0·49	25·7	0·935	0·71	0·76	0·83
17	0·55	28	1·06	0·785	0·77	0·9
22	0·613	30·2	1·15	0·862	0·74	0·96
32	0·672	35	1·33	1·0	0·75	1·1
52	0·682	37·5	1·42	1·065	0·75	1·23
67	0·682	38	1·44	1·08	0·75	1·25

* Calculated from GLC analysis as C_0 tetralol/C_0 tetralol

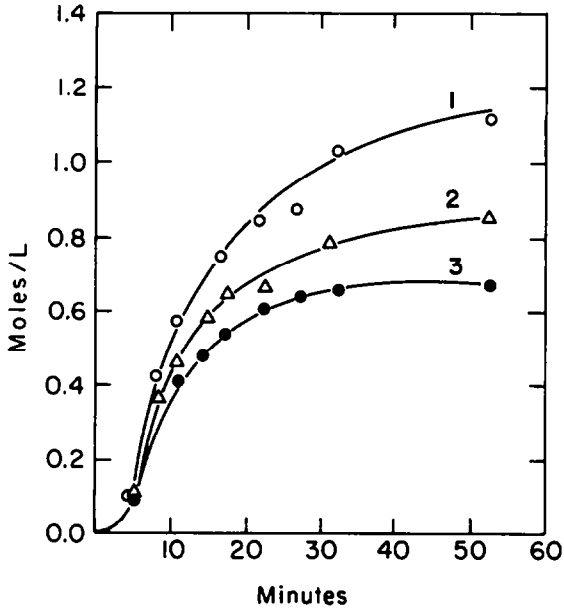


FIG 3. Oxidation of α-tetralol in acetic acid at 80°.
[α-Tetralol] 3·79 M/L, [$Co(OAc)_2$] 0·006 M/L. 1. α-Tetralol disappearance. 2. α-Tetralone formation. 3. Oxygen absorption.

The same pattern emerges in the case of the heterogeneously catalyzed reaction, as may be seen from the data of Table 2.

Oxidation of α tetralone. Contrary to the case of α-tetralol, the oxidation of the ketone has been studied previously.[6, 11] Robertson and Waters[6] identified *o*-carboxyphenylpropionic acid in the reaction mixture, while Kameneva *et al.* also isolated *o*-hydroxymethylphenylpropionic acid.[11] The appearance of both products can be explained

TABLE 2. Mn_2O_4 CATALYZED OXIDATION OF TETRALIN AT 80°
Tetralin concentration: 7·4 moles/lit; Mn_2O_3–0·1 gr/ml tetralin; oxygen absorption—5×10^{-2} moles/lit/min.

Conversion mole %	Hydroperoxide mole %	α-Tetralone mole %	α-Tetralol mole %	Tetralone/tetralol
40	5·2	20	10·0	2
50	4·5	25	10·5	2·4
60	4	33	11·1	3
77	3·6	45	10·4	4·3

by oxidative cleavage of the ketone. In the present work we isolated several products, which are formed without ringopening, namely I, III and IV.

It can be seen from the oxygen absorption data in Table 3 that the oxidation of α-tetralone shows a strong autoinhibition.

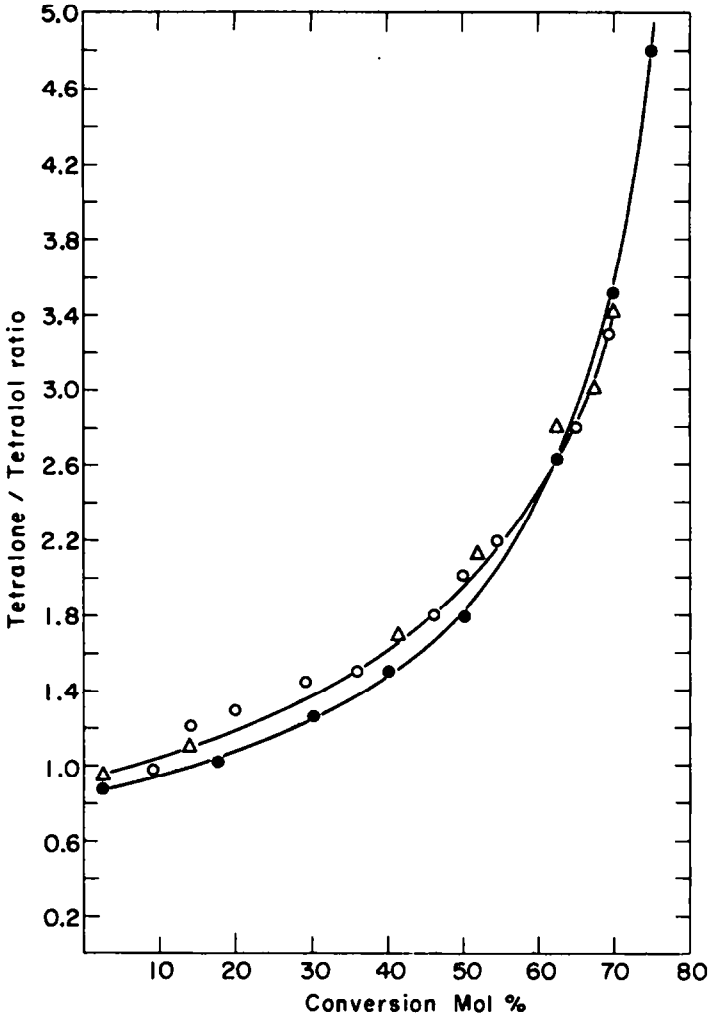


FIG 4. Dependence of the ratio α-tetralone/α-tetralol on tetralin conversion during oxidation in acetic acid at 80°
[Tetralin] 3·79 M/L. [$Co(OAc)_2$]: ●—0·002 M/L, △—0·004 M/L, ○—0·006 M/L.

TABLE 3. OXIDATION OF α-TETRALONE AT 80°
[α-tetralone] = 3·79/mol/l acetic acid
[$Co(OAc)_2$] = 0·006 M

Time/minutes	Conversion* mole %
5	1·2
10	1·75
15	2
30	2·12
60	2·25

* Based on oxygen absorption.

The On/O1 *ratio in hydroperoxide decomposition.* During decomposition of hydroperoxide, oxygen is evolved (Eq. 4), which may cause further *in situ* oxidation, primarily of the alcohol (v.i.). The On/O1 ratio in an uncatalyzed slow decomposition of *pure* hydroperoxide would depend on the relative rates of oxygen evolution versus consumption. If the rate of oxidation of the alcohol is of the same order of magnitude as that of oxygen evolution, one would expect a drift from a ratio of 1 towards a higher On/O1 ratio with time. This was indeed observed upon decomposition of tetralyl hydroperoxide at 80°. On the other hand, when a *catalyzed* decomposition of a 5% hydroperoxide solution in tetralin is effected at this temperature (in presence of 6×10^{-3} M, $Co(OAc)_2$ in acetic acid) reaction is complete in a few seconds, and an On/O1 ratio of 2:3 is found in the products. Under these conditions, the oxygen evolved in step (4) is not consumed for alcohol oxidation, and the predominance of alcohol is due to step (5).

Decomposition of a 5% solution of tetralylhydroperoxide in tetralin at 200° in the absence of catalyst, produced ketone only, which can best be explained by the importance of reaction (6) at this temperature.

Kinetic results. Although the main purpose of this work was product analysis, we found some kinetic features, which supplement those of other workers.

Under the present conditions and at 80° (Fig. 1), the stationary concentration of hydroperoxide is reached after about 30% conversion of tetralin, a value higher than that found by others at a lower temperature.[2] Also the limiting concentration of cobalt acetate, beyond which the rate becomes independent of catalyst concentration, was seen to be lower at the higher temperature. At a tetralin concentration of 3·79 mole/l in acetic acid, the limiting concentration was found to be 0·05M at 50°, 0·02M at 70° and 0·01M at 80°. It has been shown[1] that the stationary concentration of hydroperoxide is proportional to the reciprocal value of the catalyst concentration according to equation

$$[ROOH]_\infty \sim \frac{1}{[Co(OAc)_2]^n} \tag{8}$$

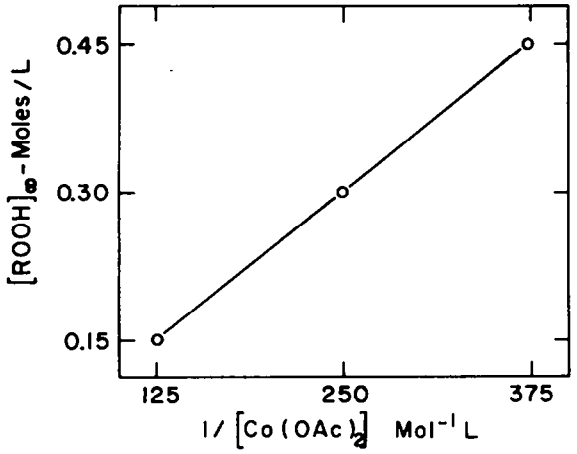


FIG 5. Dependence of the stationary hydroperoxide concentration on the reciprocal of the catalyst concentration during tetralin oxidation in acetic acid at 80° [Tetralin] 3·79 M/L.

From Fig. 5, where this stationary concentration is plotted as a function of the reciprocal value of the catalyst concentration, it can be seen, that at 80° the value of n is approximately one.

DISCUSSION

The results of the present work clearly suggest, that oxidation of tetralin proceeds via a complex series of consecutive and parallel reactions. Since oxygen is formed according to reaction (4) at least part of it being used up *in situ*, it is clear why tetralin consumption is greater than external oxygen absorption during this stage. At a later stage of the reaction, when the oxidation of α-tetralol becomes important due to its build-up, oxygen absorption overtakes consumption of tetralin. Oxygen consumed by oxidation of α-tetralone is not of much importance in this balance, since it is very sluggish and its effect is felt only when conversion of 50% to tetralone has been reached (v.i.).

It is of interest, that under the conditions of the present work, the steady state concentration of hydroperoxide is attained at a conversion of about 30%. In the work of Mesrobian *et al.*[1] at 50° (but otherwise similar conditions) a steady hydroperoxide concentration appears to be established shortly after commencement of the reaction, which proceeds at a constant rate almost from the start. Ingold *et al.*[2] obtained a different result at the same temperature. $[ROOH]_\infty$ is established after about 11% conversion, while a steady reaction rate is achieved well *before* this concentration is reached. This indicates, that the achievement of a steady reaction rate is not necessarily connected with a stationary hydroperoxide concentration, as was also found by Balaceanu in the case of cyclohexene oxidation in acetic acid.[12]

A feature of the present study which is at variance with results of previous workers[1–3] is the dependence of $[ROOH]_\infty$ on the reciprocal concentration of the catalyst. While in these earlier studies, $[ROOH]_\infty$ was proportional to the square of the reciprocal catalyst conc., we found a dependence on the first power (Fig. 5).

The second power dependence was attributed to a dimeric state of the catalyst in the reaction medium. However, at 80°, and at a catalyst concentration range of 0·008M to 0·0027M (which is lower than the one used in the work of Ingold *et al.*[2]), complete dissociation of the catalyst seems to occur which explains the first power dependence.

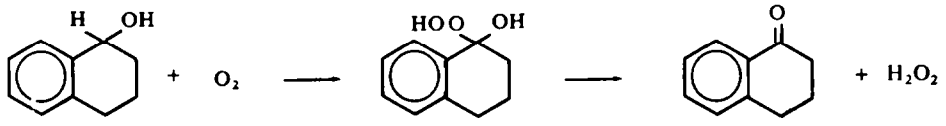
The main conclusion from the present results is that the α-tetralone/α-tetralol ratio depends primarily on the conversion of tetralin. At low conversions, this ratio might even be smaller than one as was found for cyclohexane; this follows from reactions (3), (4) and (5). For higher conversions the On/O1 ratio increases rapidly, because the alcohol is oxidized at a higher rate than tetralin. Therefore, the dependence of this ratio on conversion is only related to the activation of hydrogen by the hydroxyl group, which should be independent of catalyst, catalyst concentration or even its physical state, as was indeed found.

This conclusion is in agreement with the recent work of Gould *et al.*,[13] who found that chromium based catalysts do not fit into this pattern; the On/O1 ratio obtained with chromium catalysts is appreciably higher than with the other transition metals hitherto studied. No explanation has yet been advanced for this anomaly. The higher On/O1 ratios obtained by Mukherjee and Graydon[8] with some catalysts in the

heterogeneous oxidation of tetralin are most probably due to the higher conversions obtained with these catalysts rather than to catalyst specificity (cf. Table 2).

Another factor that influences this ratio is reaction temperature. The decomposition of tetralyl-hydroperoxide at 200° yielded the ketone almost exclusively, which is a result of prevalence of O—O fission at this temperature. This same trend is also observed in autoxidations of secondary hydrocarbons at temperatures above 100°. Thus, the interpretation of the results of Denisov[7] on cyclohexane oxidation do not require the assumption of radical-metal ion interactions.

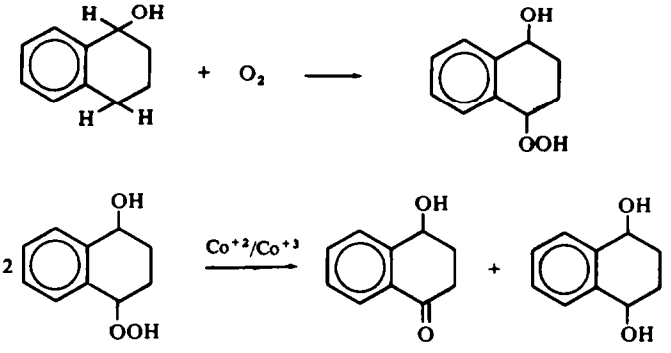
The prevalent site of attack in α-tetralol is evidently the hydrogen at position 1. The fact that substrate disappearance overtakes oxygen consumption (Fig 3) is the outcome of reactions



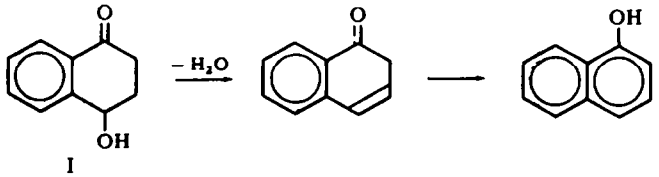
$$H_2O_2 \rightarrow H_2O + 1/2O_2$$

Thus, water formation matches the formation of ketone (Table 2) while the liberated oxygen is at least in part absorbed *in situ*.

However, the benzylic hydrogen at position-4 provides an alternate oxidation pathway



Hydrogen abstraction at position-4 (the rate determining step) is, however, slower by a factor three than that at position-1. This follows from the constant ratio of ketone/other products = 3:1, that was obtained in this reaction. The occurrence of α-naphthol in the oxidation products is most probably due to:

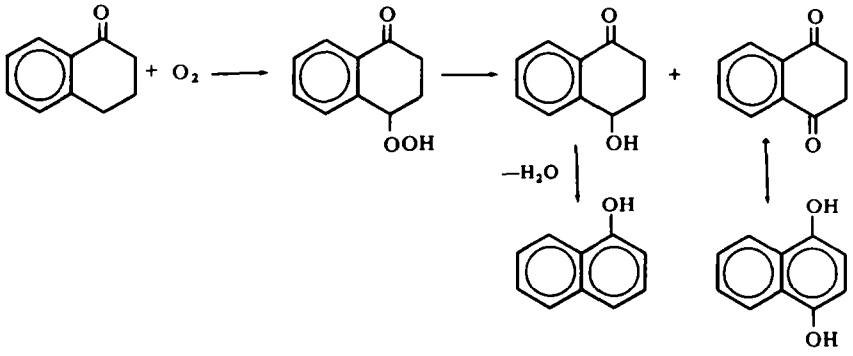


I

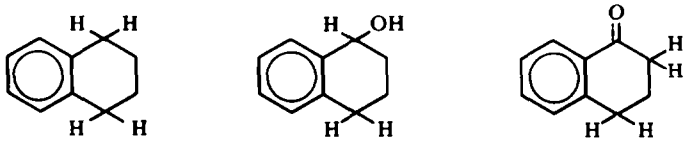
since I was shown to be very easily dehydrated by trace acids. The strong inhibition of tetralol oxidation is apparently caused by the build-up of α-naphthol.

In the oxidation of α-tetralone previous workers have isolated from the reaction mixture products which were the result of attack at position-2, with subsequent C_1—C_2 fission.

It is somewhat surprising that products formed from attack at position-4 (benzylic hydrogen!) were hitherto not detected. In the present work, we were able to show, that these products, namely



are at least as abundant in the oxidation mixture of tetralone as those formed by oxidative cleavage. We conclude, therefore, that attack at position-4 must be at least as important as that at position-2. This behaviour of α-tetralone on oxidation is not surprising. If we consider the three substrates,



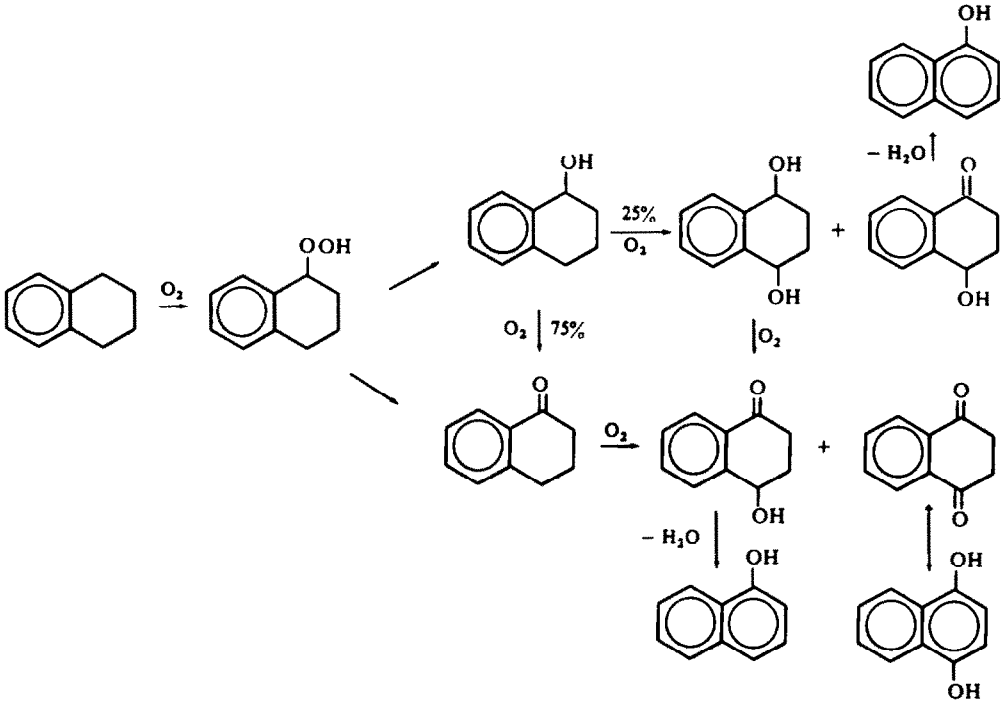
we find in tetralin four benzylic hydrogens; in tetralol there are three such hydrogens, but at position-1 H-atom is activated by the geminal hydroxyl. This activating effect overrides any steric interference from the hydroxyl, since in a cooxidation experiment with tetralin, tetralol is oxidized by a factor 1·5 faster, in spite of the decrease in the number of benzylic hydrogens.

The overriding susceptibility of the hydrogen at position-1 to abstraction is also evidenced from the ratio of products obtained in the oxidation of tetralol, which is 3:1 in favour of those derived from attack at position-1.

In α-tetralone, there are two benzylic H-atoms and two α-carbonyl activated hydrogens. The relative reactivity by various C—H bonds towards abstraction by phenyl radicals has been measured.[14] With those radicals, that are less selective than the chain carrying radicals of the present system—it was shown[14] that benzylic hydrogens are more easily abstracted than secondary hydrogens in a position α to a carbonyl group. It would therefore be expected that attack at position 4 would be at

least as frequent as attack at position-2. The onset of strong autoinhibition with the three substrates is caused by accumulation of higher oxidation products. While tetralin conversion can be carried at a reasonable rate to 70%, and that of α-tetralol to 37%, α-tetralone oxidation practically stops at a very low conversion. In this latter case, the oxidation product IV is an efficient radical scavanger.

By following the formation of the differing products during the oxidation of tetralin, up to high conversion, it has thus been possible to explain the complicated events, which occur during this reaction, and the following scheme summarizes the chain of events;



EXPERIMENTAL

Reagents. Tetralin (Fluka, purum) was purified[1] before use. Anhydrous cobalt (II) acetate was made by dehydration of the tetrahydrate (Merck).[1]

α-*Tetralol* was prepared by oxidation of tetralin in AcOH (1:1 by weight) in the presence of cobalt (II) acetate (0·2% on tetralin) at 80° for 2 hr, a cut boiling at 65–70°/0·3 mm (70% conversion) comprising an α-tetralone-α-tetralol mixture—was isolated. The tetralone present was reduced according to Ref. 15, yielding 98% pure α-tetralol (1% 1,2-dihydronaphthalene, 1% tetralin).

α-*Tetralone* was prepared by vapour phase dehydrogenation of the above cut over copper chromite (Harshaw, Cu-1407 catalyst) at 290° (1·5 ml mixture per ml catalyst per hr). Traces of phenolics were removed by an alkaline wash. Chromatographically pure α-tetralone was obtained after distillation.

α-*Tetralyl hydroperoxide* prepared and crystallized as described.[1]

All reagents were kept in cold storage under argon.

Analysis. GLC was used for products analysis (F and M Model 700 gas chromatograph; Diethylene Glycol adipate polyester 20% on chromosorb W, 30–60 mesh; ¼" × 60 cm column; programming 15°/min from 150° to 225°; diphenyl used as internal standard).

Peaks appeared in the order: solvent, tetralin 1,2-dihydronaphthalene, naphthalene, diphenyl: α-tetralone, α-tetralol, α-naphthol, 1,2,3,4-tetrahydro-1 hydroxy-4 keto-naphthalene (I). To prevent de-

hydration of α-tetralol and I during analysis, a glass tube that was cleaned periodically was inserted in the injection port. Quantitative analysis of water was achieved on a Porapak Q 80-100 mesh (Waters Assoc.) ¼" × 40 cm column.

The high boiling products 1,4-dihydronaphthoquinone (IV) and 1,4-dihydroxytetralin (II) were converted to the respective trimethyl-silyl derivatives[16] prior to GLC analysis.

Hydroperoxides were determined by iodometric titration.[17]

Apparatus. Peroxidations were performed in a baffled 3-necked flask, equipped with a teflon stirrer (1200–1300 rpm) and connected to an oxygen containing gas burette; it was thermostated to within ±0·5°. Samples for analysis were withdrawn by syringe through a rubber septum. A part of the sample was used for hydroperoxide titration and in the second part the hydroperoxide was reduced by triphenyl phosphine[18] before the GLC analysis.

Oxidation products of tetralin. At the end of a run, the reaction mixture was extracted with water then taken up in ether. The ethereal extract was washed with a $NaHCO_3$ aq. After the usual work-up the following products were isolated by fractional distillation at 0·3 mm; tetralin (33°)—30%; α-tetralone/α-tetralol (65–70°)—58%; a fraction (120–122°)—8%, containing 30% of α-naphthol and 70% of I. This fraction was washed by NaOH aq after distillation of the organic layer. Compound I was isolated and identified by means of mass spectrometry (m.n. 162 for complete molecule; m.n. 144 for (I-H_2O); m.n. 134 for (I-CO);) and NMR (4H-δ = 8·6–7·5, 1H δ = 5·6–4·8, H-3·8–4·4, 4H-3·2–2·2): m.p. of the dinitrophenyl hydrazone 194°. (Found: C, 56·16; H, 4·17; N, 16·53 Calc.: C, 56·14; H, 4·12; N, 16·4)).

After silanation (16) of the distillation residue trimethyl-silyl derivatives of the enol-form of IV and II were identified by GLC in comparison with authentic samples of these products.

Oxidation products of α-tetralol. The work up procedure was carried out as above. After distilling off the On-Ol fraction naphthalene, α-naphthol and I were identified by GLC in the residue. Naphthalene is most probably produced by dehydration in the GLC apparatus, as otherwise it would have appeared in the distillate prior to the On-Ol fraction. Indeed, upon silanation of the residue, the naphthalene peak disappeared, while the derivatives of I, II and of α-naphthol were identified. Compound II was isolated as follows: the residue was extracted several times with boiling water. Upon cooling, an oil separated from the aqueous extract, and taken up in benzene. After storing the benzene soln in the cold for 24 hr, crystals separated, m.p. 98–100°. Mass-spectrometric analysis produced for this substance the parent peak of 164, as well as 146 (II-H_2O) and 128 (II-$2H_2O$).

Oxidation products of α-tetralone. The products in this case were I, α-naphthol and IV. Upon silanation of the product mixture, the —$Si(CH_3)_3$ derivative of IV was identified. No attempt was made to isolate oxidation products derived from ring opening reactions.

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