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A KINETIC STUDY OF THE CATALYTIC DECOMPOSITION OF CYCLOHEXENYL HYDROPEROXIDE BY $RhCl(PPh_3)_3$ *

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Summary

The study of the catalytic decomposition of cyclohexenyl hydroperoxide shows that the reaction occurs by a free-radical process which can be described by a monoelectronic Haber—Weiss mechanism involving rhodium(I), rhodium(II) and rhodium(III) species. The validity of the proposed mechanism was tested by simulating it on a digital computer and comparing the observed and calculated rate constants. Good agreement between kinetic results obtained from the decomposition study and a previously performed autoxidation study was also verified.

Introduction

The chemistry of hydroperoxides in the presence of transition metal ions has received intensive attention over the last decade. The reason for this increased interest no doubt lies in the numerous decomposition paths which may have synthetic applications, such as in autoxidative and polymerisation processes [1-3].

It was in the course of a study on the mechanism of autoxidation of cyclohexene catalysed by rhodium complexes [4] that we found it necessary to investigate in more detail the decomposition reaction of cyclohexenyl hydroperoxide in the presence of these complexes. Although several mechanistic proposals for this reaction had already been made, none was backed by kinetic studies [5-9]. This report presents the results we have obtained in such a study.

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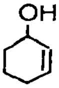
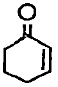
* Dedicated to Professor Eugen Müller on the occasion of his 70th birthday.

TABLE 1

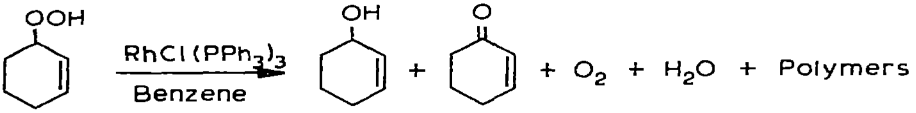
DECOMPOSITION OF CYCLOHEXENYL HYDROPEROXIDE IN BENZENE IN THE PRESENCE OF $RhCl(PPh_3)_3$[a]

			Products (%)[c]				
Unreacted ROOH(%)[b]	Temp. (°C)	Reaction time (h)			O_2	H_2O	Polymers
45.6	50	4	18	33	8	6	35

[a] $[RhCl(PPh_3)_3] = 3.62 \times 10^{-3}$ mol/l. [b] $[ROOH]_0 = 1.822$ mol/l (95% pure). [c] Percent weight.

Results and discussion

In the presence of $RhCl(PPh_3)_3$, cyclohexenyl hydroperoxide in benzene solution is decomposed to give the products shown in eqn. 1.



(1)

A typical experiment is summarized in Table 1. The curves shown in Fig. 1 for decomposition reactions under various conditions indicate in all cases a fast initial period followed by a slower one. The shape of the curves also indicates that the decomposition does not correspond to a simple kinetic law.

These preliminary results led us to reconsider what we had assumed to be the rate law of hydroperoxide decomposition in a previous study [4]. Thus

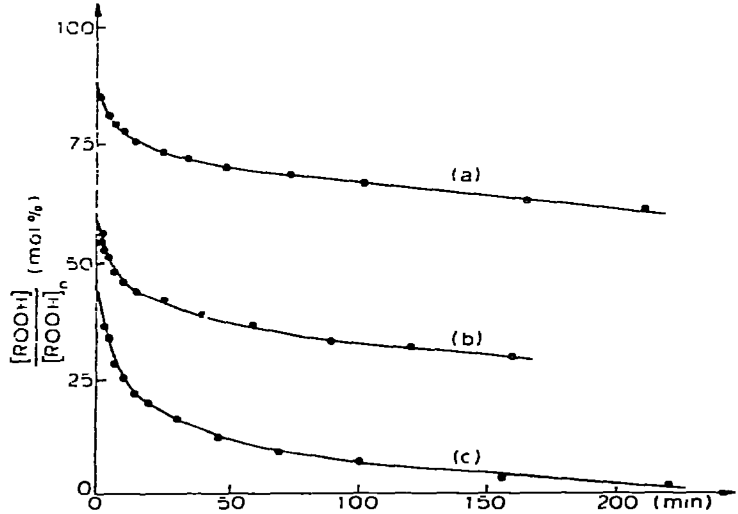


Fig. 1. Decomposition of cyclohexenyl hydroperoxide in benzene catalysed by $RhCl(PPh_3)_3$: $[RhCl(PPh)_3] = 2.42 \times 10^{-3}$ mol/l, (a) $[ROOH] = 0.350$ mol/l, $T = 40°$; (b) $[ROOH] = 0.035$ mol/l, $T = 15°$; (c) $[ROOH] = 0.035$ mol/l, $T = 40°$.

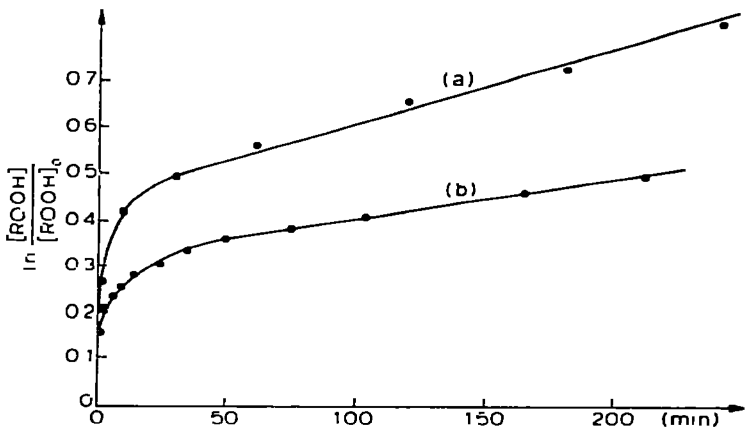


Fig. 2. A plot of $\ln[ROOH]/[ROOH]_0$ against time for the catalytic decomposition of cyclohexenyl hydroperoxide under various conditions. (a) $[RhCl(PPh_3)_3] = 3.62 \times 10^{-3}$ mol/l, $[ROOH]_0 = 0.182$ mol/l, $T = 50°$; (b) $[RhCl(PPh_3)_3] = 2.42 \times 10^{-3}$ mol/l, $[ROOH]_0 = 0.350$ mol/l, $T = 10°$.

kinetic results of the autoxidation of cyclohexene had suggested that the rate of cyclohexenyl hydroperoxide (ROOH) decomposition was given by eqn. 2.

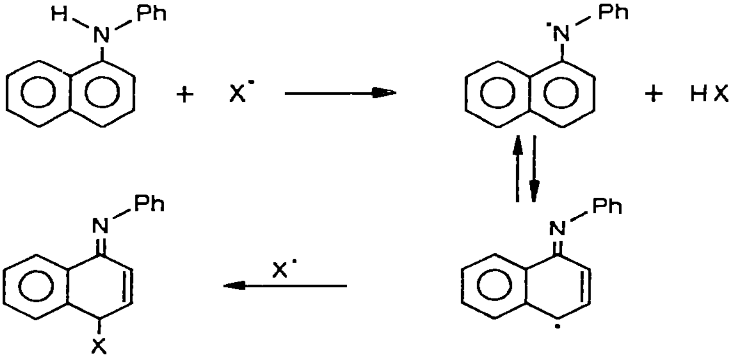
$$v_t = -\frac{d[ROOH]}{dt} = k''_{aut} \cdot [ROOH] \cdot [cat] \qquad (2)$$

Taking the catalyst concentration as constant, it implied that the logarithm of the hydroperoxide concentration should be a linear function of time but the present work indicates that this assumption is not totally valid (Fig. 2), and this led us to check the validity of the Haber—Weiss type mechanism that had been proposed for the autoxidation reaction [4, 6, 7].

Decomposition in the presence of free-radical inhibitors

As many observations were indicative of a free-radical process, we studied the decomposition reaction in the presence of free-radical inhibitors. Such a study can indicate whether the reaction is a free-radical or a molecular process and also, in the case of a free-radical reaction, whether or not it occurs by a chain mechanism. Thus, a lower decomposition reaction rate would indicate a free-radical chain mechanism, and a consumption of inhibitor would exclude a molecular process. The free-radical inhibitor we chose was *N*-phenyl-α-naphthylamine which has been well studied and shown to react with two free-radicals as shown in Scheme 1 [10-12].

SCHEME 1



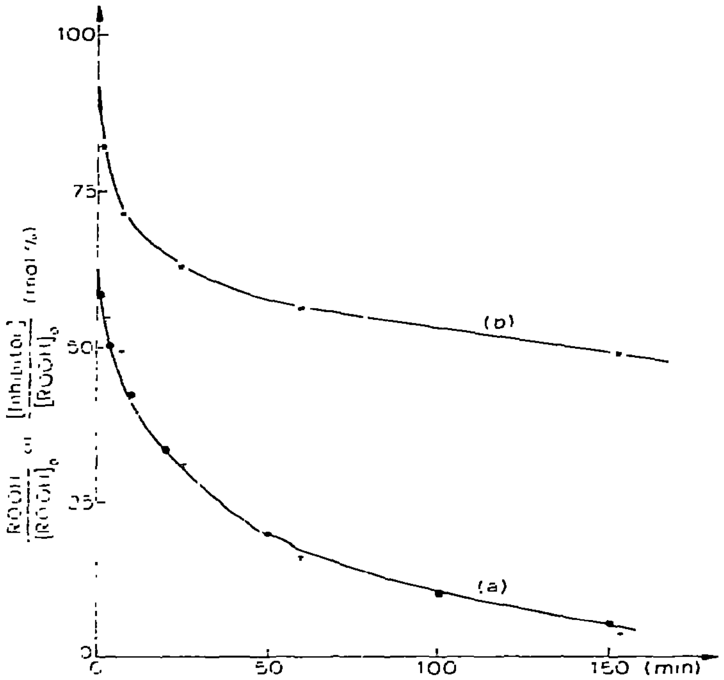
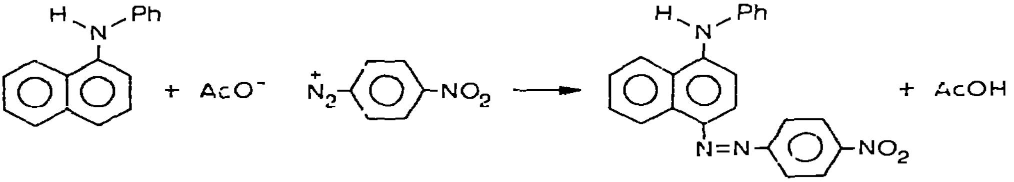


Fig. 3. Influence of N-phenyl-α-naphthylamine on the catalytic decomposition of cyclohexenyl hydroperoxide. Conditions. $[RhCl(PPh_3)_3] = 2.4 \times 10^{-3}$ mol/l, $[ROOH]_0 = 0.032$ mol/l, $T = 40°$, solvent = benzene. (a) Decomposition curve with (+) and without (•) inhibitor. (b) Inhibitor consumption curve (•)

The unreacted inhibitor can then be back-titrated spectrophotometrically with *p*-nitrophenyldiazonium acetate [12] (eqn. 3).

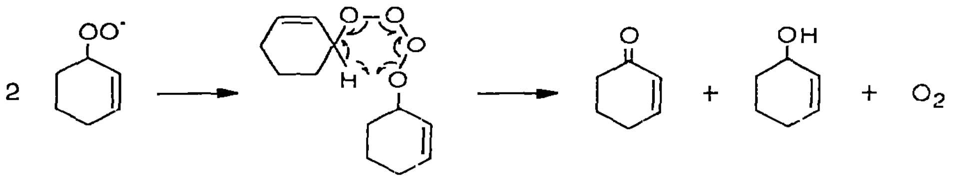


(3)

The results illustrated in Fig. 3 show that the consumption of inhibitor is half that of hydroperoxide indicating that no molecular decomposition occurs. Furthermore, the superposition of decomposition curves with and without inhibitor is a clear indication that the process is not a free-radical chain mechanism, but rather that each hydroperoxide molecule is catalytically decomposed to give one free radical.

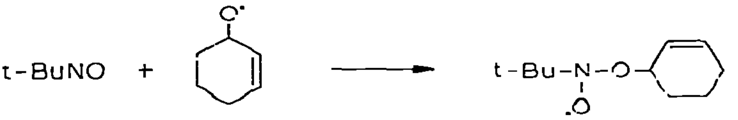
Identification of free-radicals

Two free-radical species were identified in the reaction medium. The identification of the cyclohexenylperoxy radical was based upon two observations; first, that oxygen was present in the reaction products, and second that its formation could not be due to any molecular or catalytic decomposition since the results in the presence of free-radical inhibitors showed clearly that no such process was operative. The formation of oxygen was then rationalized in terms of a known mechanism where two peroxy radicals dimerize to give an unstable tetroxyde intermediate which in turn decomposes with hydrogen transfer to give oxygen, ketone and alcohol [13] (eqn. 4).



(4)

The other free-radical species was shown by ESR spectroscopy to be the cyclohexenyloxy radical. This radical is not stable enough at room temperature to be directly observed; it was trapped by 2-methyl-2-nitrosopropane and identified as the nitroxide derivative (eqn. 5).



(5)

This trapping technique permits one to differentiate easily between an alkyl radical and an alkoxy radical since the coupling constants (a_N) of the unpaired electrons with the nitrogen nucleus are widely different for both species (13-16 G and 27-30 G respectively) [14, 15]. The ESR spectrum of a decomposition mixture carried out in the presence of 2-methyl-2-nitrosopropane showed a triplet with a coupling constant a_N = 27.4 G, well in accord with an alkoxy radical species.

Kinetic model and mechanism for the decomposition

Although the plausibility of the Haber—Weiss type of mechanism had been initially questioned, the results described in the two preceeding sections indicate that a priori it is still valid since both conditions necessary for this kind of process are fulfilled. First, the decomposition occurs by a free-radical path, due only to an interaction with the catalyst, and second, the free-radical species are those found ordinarily in this type of mechanism.

The mechanism previously proposed for the catalytic decomposition of cyclohexenyl hydroperoxide involved a bielectronic transfer mechanism via an oxidative addition of the hydroperoxide upon the d^8-rhodium(I) complex to give directly a rhodium(III) species [7]. Although quite attractive, this model did not fit our kinetic results.

We were able to show that the shape of the decomposition curve, characterized by a fast initial period followed by a less active one, was not due to a partial precipitation of the catalyst since throughout the reaction the solution remained clear. It was also shown that the lowering of the rate was not due to a partial catalyst deactivation by an interaction with the reaction products; this was done by adding, during the course of a decomposition reaction, a fresh amount of catalyst and observing a new fast period followed by a slower one, as is illustrated in Fig. 4.

All these results led us to propose and test Scheme 2 for the catalytic decomposition of cyclohexenyl hydroperoxide (ROOH).

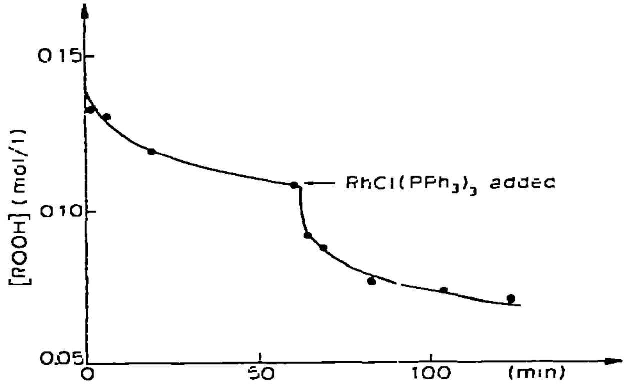


Fig. 4. Effect of fresh catalyst addition during the catalytic decomposition of cyclohexenyl hydroperoxide. Conditions: $[\mathrm{RhCl(PPh_3)_3}]_0 = 1.95 \times 10^{-3}$ mol/l, $[\mathrm{ROOH}]_0 = 0.148$ mol/l, $T = 40°$, solvent = benzene. Added $[\mathrm{RhCl(PPh_3)_3}] = 2.14 \times 10^{-3}$ mol/l.

SCHEME 2

$$\begin{aligned}
&\mathrm{Rh^{I}} && + \mathrm{ROOH} \xrightarrow{k_1} \mathrm{Rh^{II}OH} + \mathrm{RO^{\cdot}}\\
&\mathrm{Rh^{II}OH} && + \mathrm{ROOH} \xrightarrow{k_2} \mathrm{Rh^{I}} + \mathrm{ROO^{\cdot}} + \mathrm{H_2O}\\
&\mathrm{Rh^{II}OH} && + \mathrm{ROOH} \xrightarrow{k_3} \mathrm{Rh^{III}(OH)_2} + \mathrm{RO^{\cdot}}\\
&\mathrm{Rh^{III}(OH)_2} && + \mathrm{ROOH} \xrightarrow{k_4} \mathrm{Rh^{II}OH} + \mathrm{ROO^{\cdot}} + \mathrm{H_2O}
\end{aligned}$$

For such a model may be written:

$$\frac{-\mathrm{d}H}{\mathrm{d}t} = \mathrm{H}[k_1C_1 + (k_2 + k_3)C_2 + k_4C_3] \tag{6}$$

$$\frac{\mathrm{d}C_1}{\mathrm{d}t} = \mathrm{H}(k_2C_2 - k_1C_1) \tag{7}$$

$$\frac{\mathrm{d}C_2}{\mathrm{d}t} = \mathrm{H}[k_1C_1 - (k_2 + k_3)C_2 + k_4C_3] \tag{8}$$

$$\frac{\mathrm{d}C_3}{\mathrm{d}t} = \mathrm{H}(k_3C_2 - k_4C_3) \tag{9}$$

(where $C_1 = [\mathrm{Rh^I}]$, $C_2 = [\mathrm{Rh^{II}OH}]$, $C_3 = [\mathrm{Rh^{III}(OH)_2}]$ and $\mathrm{H} = [\mathrm{ROOH}]$)

with a steady state approximation where:

$$\frac{\mathrm{d}C_1}{\mathrm{d}t} = \frac{\mathrm{d}C_2}{\mathrm{d}t} = \frac{\mathrm{d}C_3}{\mathrm{d}t} = 0 \tag{10}$$

one has:

$$k_2 \cdot C_2 = k_1 \cdot C_1;\ k_3 \cdot C_2 = k_4 \cdot C_3 \tag{11}$$

and:

$$\frac{-\mathrm{dH}}{\mathrm{d}t} = 2\,\mathrm{H}(k_2 + k_3)C_2 \qquad (12)$$

If $C = [\mathrm{cat}]_0$ then one can write the following rate law:

$$\frac{-\mathrm{d}[\mathrm{ROOH}]}{\mathrm{d}t} = kC[\mathrm{ROOH}] \qquad (13)$$

where:

$$k = 2\left(\frac{k_2 + k_3}{1 + k_2/k_1 + k_2/k_4}\right) \qquad (14)$$

This model was tested in various ways. First, integration of the rate law gives a linear relationship between the logarithm of hydroperoxide concentration and time. This was indeed shown to be the case after about 30 min, which implies that the different catalytic species have attained the steady state by that time.

Secondly, the model was programmed on a digital computer and yielded nearly superimposed experimental and calculated decomposition curves, as shown in Fig. 5. This allowed us to obtain the various rate constants k_i in l/mol min: $k_1 = 226$, $k_2 = 254$, $k_3 = 60.6$, $k_4 = 0.607$, and thus to calculate the overall reaction constant k: $k_{\mathrm{calcd}} = 6.17$ l/mol min. The comparison with a value of k obtained from experimental points is quite satisfactory: $k_{\mathrm{expt}} = 4.6$ l/mol min. The calculated k_i values permitted also the estimation of the distribution of the catalytic species: $C_1/C = 1.1$; $C_2/C = 1.0$; $C_3/C = 97.9$ %.

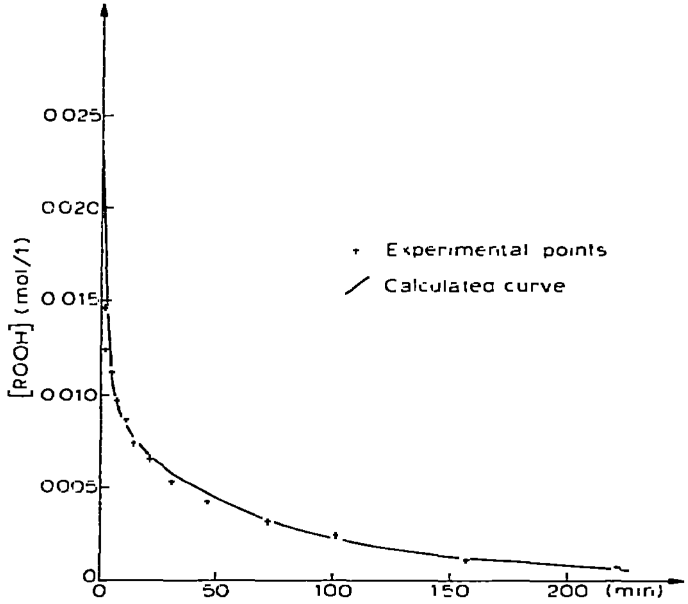


Fig. 5. Comparison between experimental and calculated catalytic decomposition curves of cyclohexenyl hydroperoxide. Conditions: $[\mathrm{RhCl(PPh_3)_3}] = 2.42 \times 10^{-3}$ mol/l, $[\mathrm{ROOH}]_0 = 0.035$ mol/l, $T = 40°$, solvent = benzene.

A high proportion of rhodium(III) is not unexpected if one considers the oxidizing character of the reaction medium; furthermore, the lowering of the catalytic activity could well correspond to the elevation of the rhodium species towards this higher oxidation state. The low proportion of rhodium(II) is also in accord with its relative instability [16]. The presence of this paramagnetic species was confirmed by ESR spectroscopy which showed a signal at $g = 2.036$ attributed to the rhodium(II) species [17-19]. The low proportion or rhodium(I) on the other hand is a priori somewhat surprising due to the high stability of $RhCl(PPh_3)_3$; however, it is most probable that one or two molecules of triphenylphosphine are replaced by solvent leading to a more labile rhodium(I) species, hence its low percentage at equilibrium of the catalytic species [20].

Comparison of decomposition and autoxidation kinetics

This work prompted us to check the validity of the kinetics by comparing the results obtained in the present study with those in the autoxidation of cyclohexene [4].

Since the autoxidation study had been carried out using cyclohexene as solvent, we performed a decomposition reaction in this olefin and obtained, as expected, an overall reaction rate constant somewhat lower than in benzene, $k_{expt} = 2.30$ l/mol min in cyclohexene at 60°.

The kinetic study of the catalytic autoxidation of cyclohexene led to the rate law of eqn. 15:

$$V = \frac{-d[O_2]}{dt} = k_{aut} \cdot [RH] \cdot [cat]^{1/2} \cdot [ROOH]^{1/2} \qquad (15)$$

(R = cyclohexene)

from which one may derive eqn. 16:

$$V = k'_{(aut)} \cdot [RH] \cdot (v_i)^{1/2} \qquad (16)$$

where v_i is given by eqn. 2, and thus may deduce eqn. 17:

$$k_{aut} = k'_{aut} \cdot k''^{1/2}_{aut} \qquad (17)$$

The value of k_{aut} was obtained experimentally (7.0×10^{-2} l/mol min) while the value of k'_{aut}, characteristic for the autoxidation of cyclohexene, was taken from the literature [0.048 (l/mol min)$^{1/2}$] [21]. This gives for the rate constant of free-radical initiation: $k''_{aut} = 2.13$ l/mol min. The good agreement between k''_{aut} and k_{expt} shows clearly that, once the steady state is attained, the rate of free-radical initiation is indeed equal to the rate of hydroperoxide decomposition by a Haber—Weiss type mechanism.

Experimental

All solvents and starting materials were purified by standard methods. Gas chromatographic analyses were carried out for the organic compounds using a 3 m × 4 mm column packed with 15% GE XE60 on 60/80 mesh Chromosorb W AW at 140°; for water using a 1.6 m × 4 mm column packed with 60/80 mesh solid adsorbent Chromosorb 101 at 160° and for oxygen using a 30 cm × 4 mm column pack with 5Å molecular sieves at 25°. Infrared data were obtained on a Perkin—Elmer 337 spectrophotometer. Ultraviolet-visible analyses were carried out using a Perkin—Elmer 137 UV spectrophotometer. ESR spectra were obtained using a Varian E 3 spectrometer. Iodometric titration of peroxidic function was carried out following potentiometric standard procedures.

Tris(triphenylphosphine)chlororhodium

This compound was prepared from hydrated rhodium trichloride by the method of Wilkinson [22].

Cyclohexenyl hydroperoxide

This compound was prepared by autoxidation of large quantities of cyclohexene at 60° to low percent conversion (2.5%). The excess cyclohexene was distilled off under 100 mm reduced pressure, and cyclohexenyl hydroperoxide purified by careful fractional distillation at 39°/0.10 mm. The purity determined by iodometric titration was 95%.

Decomposition of cyclohexenyl hydroperoxide in the presence of $RhCl(PPh_3)_3$

The following procedure is representative. The catalyst (0.168 g, 1.81 $\times 10^{-4}$ mol) was placed under nitrogen in a reaction flask equipped with a reflux condenser connected to a gas burette, a dropping funnel, a thermometer, a magnetic stirrer and a side arm fitted with a rubber septum. Benzene (45 ml) was added through the dropping funnel and the solution thus obtained allowed to reach 50° by immersing the reaction flask in a thermoregulated oil bath. A benzene solution (5 ml) containing 95% pure cyclohexenyl hydroperoxide (1.1 g, 9.1×10^{-3} mol) was then added through the dropping funnel with vigorous stirring while time zero was recorded. Weighed samples (2 × 1 ml) were taken from the reaction mixture by means of a hypodermic syringe and quenched quickly in cold isopropanol (—20°). One sample was then titrated iodometrically for peroxidic function, while the other was treated with excess triphenylphosphine and analysed by GLC using an internal standard. Oxygen evolution was followed volumetrically.

Decomposition of cyclohexenyl hydroperoxide in the presence of $RhCl(PPh_3)_3$ and N-phenyl-α-naphthylamine

The procedure for the decomposition reaction in the presence of free-radical inhibitor was the same as the one described above, with the difference that an equimolecular amount of freshly recrystallized *N*-phenyl-α-napththylamine was added to the 5 ml benzene solution containing the hydroperoxide. Weighed samples (2 × 1 ml) were taken from the reaction mixture and quickly quenched in cold isopropanol. One sample was titrated iodometrically as described above, the other was conveniently diluted with benzene and allowed to react with the diazonium salt as follows. The benzene solution was placed directly in a volumetric flask containing 20 ml of glacial acetic acid, and a known amount of *p*-nitrophenyldiazonium acetate in solution was added, corresponding approximately to 1.5 times the theoretical quantity. The volumetric flask was then filled with glacial acetic acid and titrated iodometrically in the visible at λ 530 nm ($\epsilon \approx 25000$ l/mol cm).

p-Nitrophenyldiazonium acetate

This compound was prepared by slowly adding sodium nitrite (0.105 g, 7.6×10^{-4} mol) to a 50 ml solution of glacial acetic acid containing 0.105 g (15.2×10^{-4} mol) of *p*-nitroaniline at 25°.

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