

DECOMPOSITION OF α -CUMENE HYDROPEROXIDE CATALYSED BY NAPHTHENATE Co(II) IN SATURATED HYDROCARBON

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In the present study the kinetics of α -cumene hydroperoxide decomposition catalysed by naphthenate Co(II) in heptane is analysed. The sequence of elementary steps of this process is elucidated both from the initial kinetic parameters of the decomposition reactions and from the activity variation of the redox system due to the transformation of both reaction components during the reaction. The results obtained indicate that the decomposition proceeds not only *via* simple complex intermediate products but also via their higher analogue formed by two catalyst molecules. The observed continuous retardation of the hydroperoxide decomposition is ascribed to the cobalt compound activity decrease caused by gradual exchange of ligands which manifest itself by the catalyst transformation to a precipitate.

Peroxide decomposition catalysed by complexes of transition metals has already been applied in practice, *e.g.* in initiation of polymerisation processes. By studying the mechanism of the decomposition reaction it was found that, in principle, the radicals formed are able to initiate chain reaction of a monomer as well as the analogous reaction of an unsaturated polymer¹. In a saturated polymer the formation of macroradicals is based on a relatively slower substitution reaction and therefore, side radical processes become also important which, of course, makes the initiation of polymer transformation more complicated².

With regard to the possibility of gaining some information about the reactivity of radicals at lower temperatures³ as well as of finding a more suitable method of saturated polymers crosslinking², we have investigated the sequence of elementary reactions proceeding during the decomposition of the hydroperoxide in a saturated hydrocarbon. In the present study we analyse the kinetics of α -cumene hydroperoxide decomposition, catalysed by naphthenate Co(II) in a model low-molecular medium — heptane. The mechanism of the process is elucidated on the basis of both the initial kinetic parameters as well as the change of the redox system activity caused by the transformation of both reaction components during the process.

EXPERIMENTAL

α -Cumene hydroperoxide, purified according to (ref.⁴), was 98.7% pure according to iodometric analysis. Naphthenate Co(II) was a commercial product (Fluka AG) containing 10.9% of Co, de-

terminated by gravimetric analysis. α,α' -Cumyl peroxide (Perkadox SB-Noury Van der Lande) was recrystallised from cool ethanol, m.p. 39°C (39.2°C according to ref.⁵). Heptane was of analytical grade.

The procedure for measuring the decrease of the hydroperoxide concentration was the following: α -cumene hydroperoxide solution was flushed with nitrogen and then was heated up to the required temperature ($\pm 0.1^\circ\text{C}$); the initial hydroperoxide concentration was determined and then a measured volume of heptane solution of naphthenate Co(II) was added. An inert atmosphere was kept by blowing nitrogen during the reaction slowly above the solution surface. The content of hydroperoxide in the series of samples was determined iodometrically⁴.

In order to evaluate the effect of α -cumene hydroperoxide decomposition products on the course of its decomposition we have used as an initial medium a mixture of the two main decomposition products, *i.e.* α -cumyl alcohol and acetophenone³, which were prepared by α,α' -cumyl peroxide decomposition at 145°C (4 h). (Under these conditions α,α' -cumyl peroxide gives equimolar amount of α -cumyl alcohol and acetophenone⁶.)

As the cobalt complex precipitates out during the reaction we have compared the precipitate composition at the stage when almost all hydroperoxide was decomposed (after 7 hours at 50°C in the reaction mixture containing 0.12 mol/l of α -cumene hydroperoxide and $6 \cdot 10^{-4}$ mol/l of naphthenate Co(II)) with the composition of the initial compound. The precipitate was filtered off, washed and dried. The amount of the precipitate corresponded to 40% of the initial amount of naphthenate Co(II). Both compounds were analysed for Co (gravimetry) and by elemental analysis.

The course of the precipitate formation during the hydroperoxide decomposition was determined quantitatively by measuring the turbidity change of the reaction solution with the use of a photometer Specol (Zeiss, Jena). The instrument automatically records extinctions at 530 nm. Reaction mixture was prepared according to the above described procedure directly in the measuring cell thermostated to a required temperature. The concentration decrease of the catalyst was calculated from the turbidity increase; the maximum turbidity value obtained at the end of the reaction was considered to correspond to the overall amount of the precipitated cobalt component.

RESULTS AND DISCUSSION

As in this case the process of α -cumene hydroperoxide decomposition catalysed by naphthenate Co(II) is mediated by mutual interaction of both components of the bi-component system, it is not possible to express the kinetics only by the decrease of hydroperoxide concentration because the concentration change of the active catalyst form during the process cannot be ruled out. In view of this obstacle the kinetics of reaction was analysed from the initial rates of hydroperoxide decomposition. The values of initial rates v_0 were determined graphically as the slopes of tangent of the dependence of hydroperoxide concentration *vs* time at the time $t = 0$. Fig. 1a gives the value of the initial rates (v_0) of α -cumene hydroperoxide decomposition (obtained from the experimental data of the hydroperoxide decomposition *vs* time at different initial hydroperoxide concentrations and constant naphthenate Co(II) concentration) in dependence on its initial concentrations ($[\text{ROOH}]_0$) at two different temperatures. The curves also serve for the determination of the reaction order with respect to hydroperoxide component (n). The reaction order follows

from the general relation between the instant rate of the reaction (in this case v_0) and the initial hydroperoxide concentration

$$\log v_0 = \text{const.} + n \log [\text{ROOH}]_0 \quad (1)$$

Even if the method of the initial rates of the hydroperoxide decomposition does not guarantee adequate accuracy for the determination of the value of n it is seen in Fig. 1a, that the value of n is close enough to unity.

The same procedure was used for the determination of the reaction order with respect to naphthenate Co(II) at the redox decomposition of α -cumene hydroperoxide. The corresponding initial rates were obtained from the time dependences of the hydroperoxide decomposition at approximately the same hydroperoxide concentrations and at different catalyst concentrations $[\text{C}]_0$. Fig. 1b gives the course of the relationship (1) at two different temperatures, provided that $[\text{ROOH}]_0$ is substituted by $[\text{C}]_0$. The results show, that in this case, the slope of the lines depicted, differs significantly from unity and that its value at both temperatures is higher.

The time dependence of the hydroperoxide decomposition (Fig. 2a) show quite clearly that at higher conversion the kinetic equation, involving the molecularity

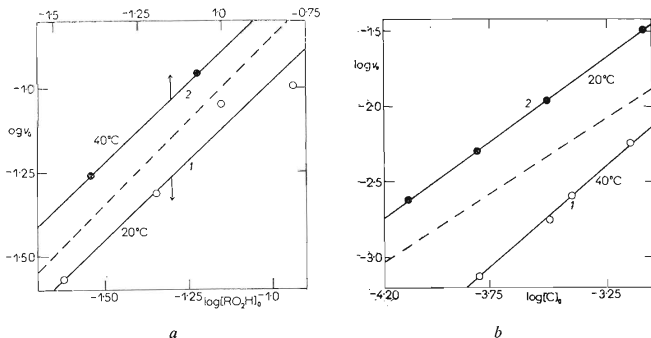


FIG. 1

Initial Rate of Decomposition of α -Cumene Hydroperoxide (v_0 in $\text{mol l}^{-1} \text{min}^{-1}$) Catalysed by Naphthenate $\text{Co}^{\text{II}}(\text{C})$ vs

a) Initial Hydroperoxide Concentration ($[\text{ROOH}]_0$ in mol l^{-1}) at 20°C ($[\text{C}]_0 = 4.0 \cdot 10^{-4} \text{ mol l}^{-1}$) and at 40°C ($[\text{C}]_0 = 3.2 \cdot 10^{-4} \text{ mol l}^{-1}$), b) Initial Catalyst Concentration ($[\text{C}]_0$ in mol l^{-1}) at 20°C ($[\text{ROOH}]_0 = 8.08-8.60 \cdot 10^{-2} \text{ mol l}^{-1}$) and at 40°C ($[\text{ROOH}]_0 = 7.60$ to $8.62 \cdot 10^{-2} \text{ mol l}^{-1}$). Dashed lines represent the courses having the slopes equal to unity.

values determined from the initial rates, would not describe the process adequately, possibly, because of the continuous catalyst deactivation followed by the continuous fall of the decomposition rate. The effect of the decomposition products, which according to the opinion of the authors of the paper⁷, can cause the observed phenomenon, was in fact none, since their presence at the beginning of the reaction in concentration corresponding to a complete hydroperoxide decomposition (Fig. 2a) did not affect the kinetics of the process.

The decrease of the reaction rate can be better explained by the fact that the catalyst precipitates out during the reaction. The determined composition of the cobalt compound before (10.9% Co, 58.8% C, 9.6% H, 20.7% O) and after the reaction (25.6% Co, 30.0% C, 4.2% H, 40.2% O) enables us to evaluate also the mechanism of its deactivation. With respect to a lower carbon and hydrogen content in the resulting cobalt compound whose central atom is even in its higher oxidation state, one can judge that the catalyst deactivation proceeds by a gradual substitution of voluminous naphthenate ligands (cycloalkane acids moieties having different number of C atoms) by hydroxyl anions formed in the first step of the redox process.

In view of these facts, the above discussed controversy between the kinetics at the beginning and at further stages of the reaction is due to a continuous decrease of the catalyst activity followed by the change of the reaction rate. This can be still more clearly demonstrated by the quantitative determination of the soluble catalyst concen-

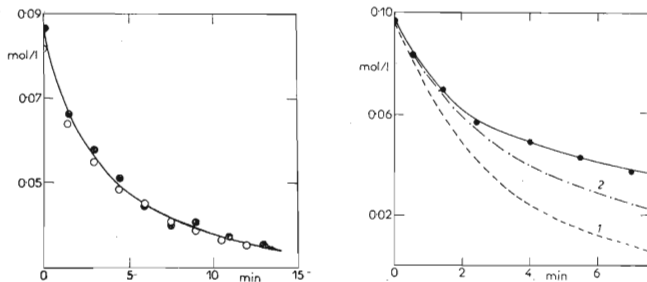


FIG. 2

Decomposition of α -Cumene Hydroperoxide Catalysed by Co(II) Naphthenate (C) in Heptane

a) Experimental data ($[C]_0 = 4.0 \cdot 10^{-4}$ mol/l, 40°C): \circ in heptane, \bullet in heptane solution of α -cumyl alcohol and acetophenone (see Experimental); b) calculated according to Eq. (2) ($[C]_0 = 5.2 \cdot 10^{-4}$ mol/l, 33.5°C): 1 for $[C]_0 = \text{const.}$, 2 for varying $[C]$ in the course of reaction (for results see Results and Discussion).

tration ($[C]_0 = 5 \cdot 10^{-4}$ mol/l) during α -cumene hydroperoxide decomposition ($[ROOH]_0 = 1 \cdot 10^{-1}$ mol l $^{-1}$) in heptane at 33.5°C:

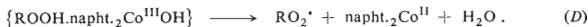
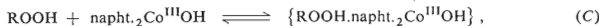
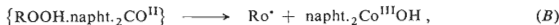
t , min:	0	1	2	3	4	5	6	7	8	9	10	12	15	20
[C], %:	100	91.1	83.6	75.6	79.5	66.4	61.6	57.2	54.8	51.8	50.6	46.4	39.6	35.7

If we take into account this fact when describing quantitatively the kinetics of the hydroperoxide decomposition, we get the equation which describes the experimental course of the reaction (Fig. 2b) more precisely. The ordinates of the theoretical curve in Fig. 2b were calculated from the following kinetic relation

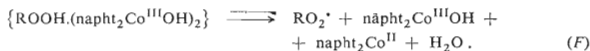
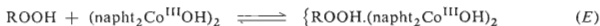
$$[ROOH] = [ROOH]_0 \exp(-[C]^n kt) \quad (2)$$

The values were calculated for each 30 s interval where as the values of $[ROOH]_0$ and $[C]$ were taken the average values of the corresponding time interval t . The rate constant $k = 3.6 \cdot 10^3$ l mol $^{-1}$ min $^{-1}$ was calculated from the initial rate of the experimental reaction course (v_0) 2.7 mol l $^{-1}$ min $^{-1}$ and the value of n 1.25 was obtained as the average value of slopes of the straight lines in Fig. 1b. The difference of the theoretical and the experimental courses of the reaction (Fig. 2b) can possibly be due to the fact that the catalyst activity decreases not only due to the catalyst precipitation but also due to the gradual exchange of the ligands in the cobalt cation coordination sphere, *i.e.* the catalyst is still in its soluble form and the precipitation is the final form of the catalyst deactivation.

The determined first order reaction with respect to α -cumene hydroperoxide, which was also found for other analogous redox systems in nonpolar solvents^{8,9}, indicates that this bimolecular reaction proceeds without any marked participation of a higher order induced decomposition. Considering also other already known facts (primary interstage of the hydroperoxide-catalyst complex formation^{9,10}) we put forward the following reaction scheme for the bimolecular reaction which fulfils the experimentally determined condition of pseudomonomolecularity of the reaction with respect to the hydroperoxide:

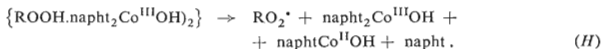


In the case that the hydroperoxide decomposition would be ruled only by the quoted elementary steps, the kinetic pseudomon molecularity would have to be observed also for the second reaction component, *i.e.* for naphthenate Co(II). The experimentally proved higher reaction order with respect to the last mentioned component leads to a supposition that the hydroperoxide decomposition proceeds not only *via* a simple complex intermediate product formed by the reactions (A) and (C), but also via its higher analogue which consists of one molecule of hydroperoxide and two catalyst molecules. From the viewpoint of formal kinetics, it is quite the same whether such a complex is formed by bivalent or trivalent cobalt, it should therefore be sufficient to illustrate the considered case by only one of all analogous possibilities



The exponent value with respect to the catalyst concentration in the kinetic relation describing such decomposition process, is then the measure of the relative rates of the processes involving bi- or trimolecular complexes. If, in contrast to hydroperoxide, the kinetic order with respect to catalyst depends on the catalyst tendency to form both considered types of complexes, then its value will change according to the character of components and reaction conditions⁹; the maximum being $n = 2$ (ref.¹⁰).

With respect to the observed character of catalyst deactivation, one has to admit also such alternatives of the processes (D) and (F) at which proton from the hydroperoxide does not react with hydroxyl but with naphthenate ligand of Co(III) to give an acid



If the product ($\text{naphthCo}^{\text{II}}\text{OH}$) enters the reactions (A)–(B) again a dihydroxide of naphthenate Co(III) is formed and the subsequent reaction cycle leads to cobalt trihydroxide. Even when the above mentioned processes are less probable and therefore less frequent they lead to a gradual retardation of hydroperoxide decomposition, especially at the latter reaction stages, because of the manifold changes of cobalt valency during the reaction.

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