

Kinetic description of cumene hydroperoxide decomposition catalyzed by cobalt(II) naphthenate

L. MATISOVÁ-RYCHLÁ, J. RYCHLÝ, I. CHODÁK, and M. LAZÁR

*Polymer Institute, Slovak Academy of Sciences,
809 34 Bratislava*

Received 5 May 1976

The empirical equation $I_0 = \mu \cdot [\text{Co}]_0^{0.55} \cdot [\text{ROOH}]_0^{0.75}$ (I_0 is initial intensity of chemiluminescence) for oxidation of *n*-heptane initiated by the system of cumene hydroperoxide and cobalt(II) naphthenate has been found by chemiluminescence method. The kinetic orders lower than one with respect to the initial concentrations of both Co(II) naphthenate and hydroperoxide have been accounted for by association of naphthenate molecules and by formation of bicentric complexes of cobalt which precede the proper decomposition process. An attempt has been made to elucidate the elementary reaction steps leading to the catalyst deactivation.

При окислении *n*-гептана инициированном кумилгидроперекисью и нафтенатом Co(II) было хемилюминесцентным методом установлено уравнение эмпирическое $I_0 = \mu \cdot [\text{Co}]_0^{0.55} \cdot [\text{ROOH}]_0^{0.75}$, где I_0 является начальной интенсивностью хемилюминесцентного излучения. Более низкие кинетические ряды как 1 с учетом начальной концентрации катализатора и гидроперекиси были интерпретированы ассоциацией молекул катализатора и образованием многоядерных комплексов, которые предшествуют собственному процессу разложения. Одновременно был сделан опыт объяснить элементарную стадию реакции, приводящую к дезактивированию катализатора.

Complexes and ions of transition metals are frequently used as catalysts in oxidation of hydrocarbons. Their effect consists in the acceleration of the process by the decomposition of intermediately formed hydroperoxides and, thus, in initiation of the new oxidation chains.

In the present paper we have studied the chemiluminescence of the system of cumene hydroperoxide and Co(II) naphthenate in *n*-heptane where intensities of the light emission observed are much higher when compared with benzene. This fact may be explained by transfer reaction of primary radicals formed in decomposition of hydroperoxide to *n*-heptane, luminescence being emitted in disproportionation reactions of *n*-heptyl peroxy radicals.

Decomposition of tertiary hydroperoxides catalyzed by transition metal ions in non-polar solvents is characterized by a remarkable autoretardation of the process

due to the change of catalyst quality in the course of the reaction. By analysis of the time dependence of chemiluminescence observed as well as by considering some properties of the catalyst precipitated at the final stage of a decomposition process we have attempted to elucidate the mechanism of autoretardation.

Experimental

Chemicals

Cumene hydroperoxide was purified according to *Solomon* [1]. The content of hydroperoxide determined iodometrically was higher than 98 weight %.

Cobalt(II) naphthenate — a mixture of cobaltous salts of cyclopentane carboxylic acids — was commercial product Fluka AG containing 10.9% of Co. The compound was used without any further purification. The molecular weight 540 was taken into account to specify the concentration of catalyst.

n-Heptane was of anal. grade.

Procedures

The kinetics of cumene hydroperoxide decomposition catalyzed by Co(II) naphthenate were measured iodometrically in our previous work [2]. The chemiluminescence measurements were performed on a spectrometer PU SNK 7M made at the Institute of Chemical Physics, Academy of Sciences, Moscow, USSR. The instrument is equipped with photomultiplier FEU-38 of the maximum spectral sensitivity at 460 nm.

The samples were measured immediately after mixing thermostated solutions of cumene hydroperoxide and Co(II) naphthenate in *n*-heptane. The average time interval necessary for manipulation with samples was 10 s. The solutions of individual components of the reacting system were saturated by oxygen.

The chemiluminescence intensity was expressed in relative units (cm) which at the maximum sensitivity of spectrometer correspond to the voltage input of 1.8 mV on the recorder EZ 4 (Metra, Blansko).

Results and discussion

Curves illustrating the time dependence of chemiluminescence intensity at 28.7°C for the system of cumene hydroperoxide and Co(II) naphthenate in *n*-heptane and for different initial concentrations of Co(II) naphthenate are demonstrated in Fig. 1. Immediately after mixing both reacting components the intensity of chemiluminescence is rising to its maximum value I_0 and then it decreases. Its time dependence cannot be linearized in coordinates of $\log I$ vs. time

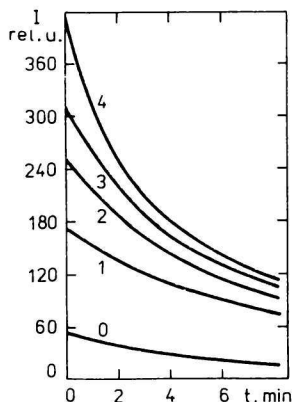


Fig. 1. Decrease of chemiluminescence intensity with time for cumene hydroperoxide and Co(II) naphthenate in *n*-heptane at 28.7°C.

Initial concentration of cumene hydroperoxide:
66 mmol dm⁻³.

Initial concentrations of Co(II) naphthenate:
0.09 (1), 0.18 (2), 0.27 (3), and 0.44 (4) mmol
dm⁻³.

Curve 0 illustrates [Co(II) naphthenate]₀ = 0.44
and [ROOH]₀ = 66 mmol dm⁻³ in benzene.

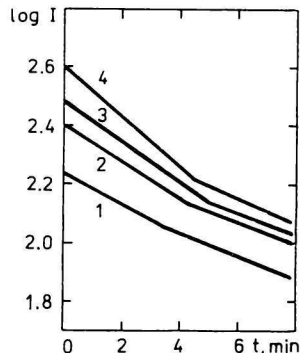


Fig. 2. Semilogarithmic coordinates for curves 1—4 from Fig. 1.

even for relatively short time interval of 8 min from the start of reaction (Fig. 2), which may be due to a relatively fast deactivation of catalyst.

Effective activation energy for initial concentration of Co(II) naphthenate (0.4 mmol dm⁻³) and cumene hydroperoxide (67 mmol dm⁻³) determined from the temperature dependence of the maximum value of chemiluminescence I_0 is 60 kJ mol⁻¹. Kinetic orders m and n with respect to the initial concentration of either Co(II) naphthenate or cumene hydroperoxide allotted as a slope of the dependence of $\log I_0$ on $\log P_0$, where P_0 denotes the initial concentration of reacting component, are 0.55 and 0.75, respectively (Table 1).

In *n*-heptane, as it follows from increased values of chemiluminescence intensities, the latter will depend on the sum of rates of termination reactions of *n*-heptyl peroxy radicals. Provided that the rate of termination is equal to the rate of initiation the chemiluminescence intensity should reflect the rate of hydroperoxide decomposition [3].

It seems to be well-founded that the primary step in reaction of hydroperoxide with catalyst is represented by Haber—Weiss catalytic redox cycle according to which alkoxy and peroxy radicals are formed in an equimolar ratio. Consequently, the orders with respect to the both reaction components should be equal to 1.

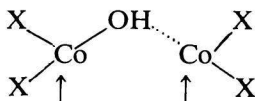
Table 1

Kinetic orders n and m with respect to individual components of the redox system determined from chemiluminescence measurements

| T °C | $[\text{ROOH}]_0$ mmol dm^{-3} | $[\text{Co(II) naphthenate}]_0$ mmol dm^{-3} | I_0 rel. u. | $m_{[\text{ROOH}]_0}$ | $n_{[\text{Co}]_0}$ |
|-----------|--|--|------------------|-----------------------|---------------------|
| 19.6 | 110 | 0.07 | 102 | | 0.50 |
| | | 0.15 | 174 | | |
| | | 0.22 | 198 | | |
| | | 0.37 | 279 | | |
| | | 0.52 | 360 | | |
| | | 0.67 | 375 | | |
| 19.6 | 28 | 0.37 | 105 | 0.75 | |
| | 55 | | 162 | | |
| | 83 | | 237 | | |
| | 110 | | 275 | | |
| 28.7 | 66 | 0.09 | 174 | | 0.55 |
| | | 0.18 | 252 | | |
| | | 0.27 | 309 | | |
| | | 0.35 | 387 | | |
| | | 0.44 | 420 | | |
| 28.7 | 33 | 0.44 | 276 | 0.70 | |
| | 47 | | 330 | | |
| | 66 | | 429 | | |
| | 99 | | 581 | | |
| | | | 357 | | |
| 33.5 | 66 | 0.09 | 506 | | 0.55 |
| | | 0.18 | 603 | | |
| | | 0.27 | 732 | | |
| | | 0.35 | 861 | | |
| | | 0.44 | 87 | | |
| 33.5 | 7 | 0.18 | 201 | 0.80 | |
| | 20 | | 297 | | |
| | 34 | | 375 | | |
| | 48 | | 741 | | |
| | 102 | | 489 | | |
| 51.4 | 66 | 0.018 | 759 | | 0.60 |
| | | 0.036 | 987 | | |
| | | 0.054 | 1128 | | |
| | | 0.071 | 1311 | | |
| | | 0.089 | | | |

Possible conception explaining the lowering of reaction orders should consist in a significant deactivation of catalyst even at the reaction time close to zero. As it was shown in [2] only 10% of catalyst was deactivated at 33°C after 1 min of reaction. This may in no case explain such a considerable decrease of reaction order with respect to $[\text{Co}]_0$.

Taking into consideration literature data, the marked decrease of both reaction orders below one may have a simple interpretation in assumption of the association of catalyst into larger complexes and in the formation of catalyst micelles [4—6]. At higher concentrations of catalyst in the system the concentration of active particles does not change in a linear way but above a certain critical concentration there increase the sizes of micelles rather than the overall number of particles. At the same time, the activity of catalyst in micelles is obviously lower than that in the true solution. At a certain concentration should, thus, the rate of oxidation attain its optimum. Moreover, in the case of cobaltous or cobaltic catalyst the association of the catalyst molecules is likely to be connected with the formation of bicentric complexes [7] of the type



which consist of molecules CoX_2OH and CoX_2 .

Provided that the decomposition of hydroperoxide takes place on the active centres of such complexes K (marked by arrows), bivalent ion is formed from trivalent ion and *vice versa* and the quality of the complex remains unchanged. The overall reaction may then be described by the equation



Accepting this conception the reaction orders determined from chemiluminescence measurements should depend on conditions of blocking active centres of catalyst by reaction components (*i.e.* hydroperoxide or reaction products).

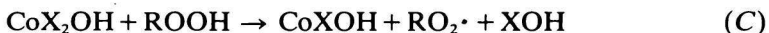
As it necessitates from Fig. 2 the decomposition reaction of hydroperoxide catalyzed by Co(II) naphthenate is successively slowed down and after a sufficiently long time interval there is formed a precipitate from the catalyst in the reaction medium which has a markedly lower content of carbon determined by elemental analysis when compared to the original compound.

One may also assume [8] that the decomposition products of hydroperoxide (formic acid) react with the catalyst under the formation of Co(III) formiate which is sparingly soluble in non-polar medium.

Anionic ligands of catalyst may be replaced even in elementary reaction steps of Haber—Weiss cycle by competition reactions



and



by which the catalyst is transformed by turns into Co(III) hydroxide [2].

Alternatively, the changes in activity of catalyst may also be due to the radical oxidation of its ligands. It follows from our experiments that a remarkable loss of catalyst activity is to be observed only in the presence of peroxy radicals. At the reaction of azobisisobutyronitrile with Co(II) naphthenate in *n*-heptane or benzene at 60°C the precipitation of the catalyst was observed only in the presence of air whereas in nitrogen the reaction solution remained transparent during all the reaction time. Similarly, in oxidation of *n*-heptane in air at 140°C catalyzed by Co(II) naphthenate the catalyst is turned gradually into the precipitate while under comparable conditions of experiment in nitrogen the deactivation of catalyst does not occur.

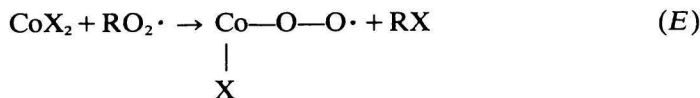
Though formic acid may be formed in a given system only in the presence of oxygen and, consequently, in radical reactions of hydrocarbons the peroxy radicals should be taken into account as reaction intermediates, we assume that the way of catalyst deactivation *via* formic acid is not quite unambiguous. As a matter of fact, the formation of precipitate of catalyst during oxidation of *n*-heptane at 140°C contradicts to this interpretation since there are formed secondary peroxy radicals as active intermediates which do not undergo fragmentation reactions as do *e.g.* cumyloxy radicals. Formic acid, therefore, cannot come into existence as such. Moreover, the catalyst precipitate is not well soluble both in water at 100°C and in acetic acid at room temperature. Such lowered solubility is to a certain extent also in contradiction with mechanism leading simply to Co(OH)₃ [2].

In connection with primary reaction step during the catalyst deactivation and consequently with the gradual exchange of its ligands it is worthy to notice the paper [9] where the formation of RO₂· radicals at the interaction of Co(II) acetylacetonate and *tert*-butyl hydroperoxide has been investigated by e.s.r. method. It was proved that the concentration of RO₂· radicals observed remained unchanged even in the case when the most of hydroperoxide present in the system was removed by distillation. Peroxy radicals produced in interaction of both components of the redox system are thus considered to be complex bound to transition metal ion.

In analogy with HO₂· radicals which in water systems are in equilibrium with ·O₂⁻ ionradicals



we have suggested that the relatively stable e.s.r. singlet spectrum corresponding to peroxy radicals may in non-polar medium be interpreted alternatively by the scheme



in which superoxide ionradicals forming in interaction with the catalyst substitute naphthenate anions in micelles of catalyst. Particles $X-Co-O-O\cdot$ which originate in the system along with $RO_2\cdot$ radicals undergo further reactions and owing to the fixation of a radical centre on central atom there increases the probability of transfer reaction in the framework of one micelle and simultaneously the oxidative degradation of bulky ligands of-catalyst becomes probable, too.

References

1. Solomon, D. H., Swift, J. D., O'Leary, G., and Treeby, I. G., *J. Macromol. Sci., Chem.* **A5**, 995 (1971).
2. Chodák, I., Rado, R., and Rychlý, J., *Collect. Czech. Chem. Commun.* **39**, 3689 (1974).
3. Zakharov, I. V. and Shlyapintokh, V. Yu., *Dokl. Akad. Nauk SSSR* **150**, 1069 (1963).
4. Reich, L. and Stivala, S. S., *Autooxidation of Hydrocarbons and Polyolefins*. M. Dekker, New York, 1969.
5. Denisov, E. T. and Emanuel, N. M., *Usp. Khim.* **29**, 1409 (1960).
6. Brook, J. H. T. and Mathews, J. B., *Discuss. Faraday Soc.* **10**, 298 (1951).
7. Freydin, B. G., *Zh. Prikl. Khim.* **30**, 768 (1957).
8. Hiatt, R., Irwin, K. C., and Gould, C. W., *J. Org. Chem.* **33**, 1430 (1968).
9. Tkáč, A., Veselý, K., Omelka, L., and Přikryl, R., *Collect. Czech. Chem. Commun.* **40**, 117 (1975).

Translated by J. Rychlý