SOLVENT EFFECTS ON THE DECOMPOSITION OF 7-CUMYL HYDROPEROXIDE IN THE PRESENCE OF THE PHTHALOCYANINES OF COBALT AND NICKEL

Heinz KROPF[a], Slavi K. IVANOV[b], Jochen SPANGENBERG[a], Ute TIMMERMANN[a] and Wolfgang UNGER[a]

[a] *Institute of Organic Chemistry and Biochemistry,*
University of Hamburg, D 2000 Hamburg, German Federal Republic, and
[b]*Institute of Organic Chemistry,*
Bulgarian Academy of Sciences, Sofia 13, Bulgary

The decomposition of 7-cumyl hydroperoxide catalyzed by cobalt phthalocyanine in the solvent system decalin–3-chlorotoluene (40°C) follows the 2nd order kinetics in the absence of N-(2-naphthyl)aniline and that of the 1st order in the presence of the inhibitor. The effect of composition of the solvent system on the rate constants and on the quotient of the initial rates in presence and in absence of inhibitor and the mechanism of the decomposition are discussed. Nickel phthalocyanine has an inhibiting effect on the decomposition of 7-cumyl hydroperoxide in the solvent systems decalin–1-chloronaphthalene and 3-chlorotoluene–1-chloronaphthalene (120°C). Decomposition starts after addition of N-(2-naphthyl)aniline. After an autocatalytical phase the reaction follows 1st order kinetics. The rate constants depend on the composition of the solvent system. The temperature dependence of the decomposition on 1-chloronaphthalene was determined. The anomalous slope of the Arrhenius plot is discussed.

In several foregoing papers of these series we reported the decomposition of 7-cumyl hydroperoxide and 2-benzyl-2-propyl hydroperoxide catalyzed by cobalt and copper phthalocyanines[2–6]. It was shown in the solvent systems decalin–1-chloronaphthalene and 3-chlorotoluene–1-chloronaphthalene that besides the polarity and viscosity of the solvent also its structure influences the rate of decomposition [5,6]. In this paper we are reporting the decomposition catalyzed by cobalt phthalocyanine (Co—PC) in the solvent system decalin–3-chlorotoluene, and by nickel phthalocyanine (Ni—PC) in decalin–1-chloronaphthalene and 3-chlorotoluene–1-chloronaphthalene. The purpose of this work was to elucidate the effect of the simultaneous change of polarity and viscosity of the solvent system on the reaction rate and the catalytic activity of Ni—PC because preliminary studies have not given clear results[7].

---

* Part XXV in the series Catalysis by Phthalocyanines; Part XXIV: ref.[1]. Part V in the series Solvent Effects in Radical Reactions, Part IV: ref.[2].

EXPERIMENTAL

Chemicals and Solvents

Cobalt phthalocyanine (Co—PC), nickel phthalocyanine (Ni—PC) and 7-cumyl hydroperoxide were purified in the usual manner[8,9]. N-(2-Naphthyl)aniline (NA) was recrystallized from ethanol (m.p. 108°C). Purification of decalin, 3-chlorotoluene and 1-chloronaphthalene see ref.[5]. The viscosity of the system decalin–3-chlorotoluene determined by a capillar viscosimeter (Schott, Mainz) is shown in Fig. 1.

Decomposition of 7-Cumyl Hydroperoxide

Co—PC catalyzed decomposition was followed as in the previously described manner[5] at 40°C under nitrogen atmosphere in the presence and absence of NA. Starting concentrations: 7-cumyl hydroperoxide 10^{-1} mol/l, Co—PC 10^{-3} mol/l, NA $3 . 10^{-2}$ mol/l. Ni—PC catalyzed decomposition was performed in the manner previously described[6] at 120°C under nitrogen atmosphere. Ni—PC was applied in its α-modification. Starting concentrations: 7-cumyl hydroperoxide 10^{-1} mol/l, α-Ni—PC 10^{-3} mol/l, NA $3 . 10^{-2}$ mol/l. The decomposition of hydroperoxide was followed by iodometric titration.

RESULTS AND DISCUSSION

Cobalt Phthalocyanine Catalyzed Decomposition

The decomposition of hydroperoxide started immediately after mixing of reactants. After a period of fast decomposition, a second phase of a slower reaction was observed. In the first phase the colour of the reaction mixture changed from blue to red-brown, whereby the Co—PC dissolved similarly as in the solvent systems decalin–1-chloronaphthalene and 3-chlorotoluene–1-chloronaphthalene[5]. The decomposition followed the 2nd order kinetics, in the presence of NA that of the 1st order. The rate constants (k_2, k_1 for the 1st phase, k'_2, k'_1 for the second phase) are summarized in Table I. The relation between the rate constants k_2 and k_1 and the composition of the solvent system is shown in Fig. 2. The rate constants k'_1 and k'_2 were not evaluated

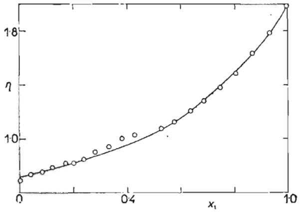


FIG. 1

Viscosity (cP) of the System Decalin–3-Chlorotoluene

$x_1 = n_1/(n_1 + n_2)$, n_1 = decalin, n_2 = 3-chlorotoluene.

because the decomposition in the second phase was catalyzed by the addition product of Co—PC and hydroperoxide and not by Co—PC itself. The k_2 values increase with the mole fraction of 3-chlorotoluene to ~0·25, then they remain constant; the k_1 values rise steadily. Because of the nonlinear relationship between the viscosity and the composition of the solvent system we have moreover evaluated the rate constants using the equation (*1*) (ref.[2,5,6])

$$k = b\varepsilon^2/\eta \,. \tag{1}$$

TABLE I

Rate Constants[a] of the Decomposition of 7-Cumyl Hydroperoxide Catalyzed by Cobalt Phthalocyanine at 40°C in the Solvent System Decalin–3-Chlorotoluene in the Presence of N-(2-Naphthyl)-aniline

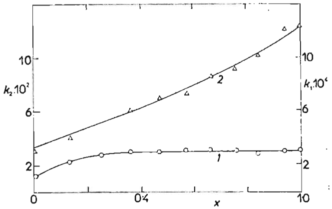
3-Chlorotoluene mole fraction	k_2	k'_2	k_1	k'_1
	$1 . mol^{-1} . s^{-1} . 10^2$		$s^{-1} . 10^4$	
0·000	1·2	1·0	3·03	2·76
0·129	2·2	0·9	4·01	2·76
0·248	2·7	1·4	—	—
0·363	3·0	1·2	6·10	1·84
0·470	2·9	1·2	7·06	3·22
0·570	3·0	1·3	7·37	3·99
0·666	3·0	1·2	8·60	4·30
0·756	3·0	0·9	9·21	4·61
0·842	2·8	0·9	10·20	3·84
0·942	2·9	0·9	12·02	4·45
1·000	2·8	0·6	12·30	4·61

[a] k_1, k_2 holds for the first phase of decomposition, k'_1, k'_2 for the second phase.

FIG. 2

Cobalt Phthalocyanine Catalyzed Decomposition of 7-Cumyl Hydroperoxide

Relation between the rate constants k_2 (*1*, $1\,mol^{-1}\,s^{-1}$) and k_1 (*2*, $1\,s^{-1}$), and the composition of the solvent system; $x = n_1/(n_1 + n_2)$, n_1 = 3-chlorotoluene, n_2 = decalin.



The relation for k_2 values corresponds that for the mole fraction. The k_1 values increase first steeply, then more slowly but linearly in both phases (Fig. 3).

The dependence of the quotient RG_0^1/RG_0^2 of the calculated initial rates in the presence and the absence of NA on ε^2/η is shown in Fig. 4. Starting from value 4 in decalin, there is firstly an increase to 5·2 and then a decrease to ~2 in 3-chlorotoluene. Obtained results confirm our previous data[5]. We were able to show the same differences of the reaction order in absence and presence of NA and the process can be discussed using reaction paths *A* or *B* and *C* resp.

$$\text{Co—PC}\cdots\text{RO}_2\text{H} + \text{RO}_2\text{H} \rightarrow \text{Co—PC} + \text{Products} \tag{A}$$

$$\text{Co—PC}\cdots\text{RO}_2\text{H} \rightleftarrows [\text{Co—PC}\cdots\text{OR}]^{(+)}\,\text{OH}^{(-)} \tag{B}$$

$$[\text{Co—PC}\cdots\text{OR}]^{(+)}\,\text{OH}^{(-)} + \text{NA} \rightarrow \text{Co—PC} + \text{Products} \tag{C}$$

The rate constants obtained in the absence of NA are only little influenced by the composition of the used solvent system. On contrary, the rate constants obtained in the presence of NA are solvent dependent. That means that the reaction rate is in the absence of NA influenced by ε^2 and η in opposite manner. In the presence of NA, the influence of the polarity preponderates correspondingly to the formation of the intermediary complex $[\text{Co—PC}\cdots\text{OR}]^{(+)}\,\text{OH}^{(-)}$. Irregularities found in the

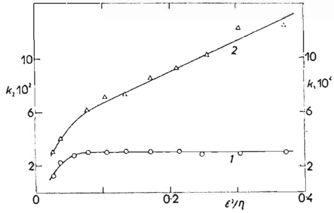


FIG. 3

Cobalt Phthalocyanine Catalyzed Decomposition of 7-Cumyl Hydroperoxide

Relation between the rate constants k_2 (*1*, $\text{l mol}^{-1}\,\text{s}^{-1}$) and k_1 (*2*, l s^{-1}), and ε^2/η.

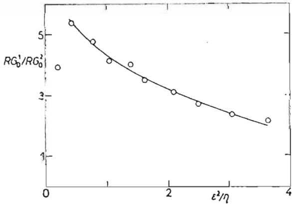


FIG. 4

Cobalt Phthalocyanine Catalyzed Decomposition of 7-Cumyl Hydroperoxide

Relation between the quotient RG_0^1/RG_0^2 and ε^2/η.

system decalin–1-chloronaphthalene and 3-chlorotoluene–1-chloronaphthalene[5,6] were not observed. This confirms the specific effect of 1-chloronaphthalene. For the dependence of the quotient RG_0^1/RG_0^2 of the solvent system two possibilities regarded as border cases can be outlined: *1*) A largery induced decomposition of 7-cumyl hydroperoxide takes place in the absence of NA in decalin, but not in 3-chlorotoluene. *2*) The decomposition is inhibited in the presence of NA in decalin, but not in 3-chlorotoluene. The second case fits better with the previously discussed mechanism[5].

Nickel Phthalocyanine Catalyzed Decomposition

The course of the reaction was similar to that with α-copper phthalocyanine. That means the decomposition started not until NA was added. Exceptions were the reactions either in pure decalin or 3-chlorotoluene in which practically no decomposition was observed. After a phase of an autocatalytical reaction the decomposition followed the 1st order kinetics. The rate constants for the range of the maximum rate k_1 are summarized in Table II. In all cases we could show a quick α → β change of the Ni—PC modification by X-ray measurements. However, also β-Ni—PC was catalytically inactive.

TABLE II

Rate Constants $k_1(\mathrm{s}^{-1} \cdot 10^4)$ of the Decomposition of 7-Cumyl Hydroperoxide in the Presence of Nickel Phthalocyanine and N-(2-Naphthyl)aniline at 120°C in the Solvent Systems Decalin–1-Chloronaphthalene (A) and 3-Chlorotoluene–1-Chloronaphthalene (B)

System A		System B	
1-Chloronaphthalene mole fraction	k_1	1-Chloronaphthalene mole fraction	k_1
0·000	0·000	0·000	0·000
0·274	1·150	0·223	2·300
0·532	1·530	0·463	5·750
0·678	1·535	0·514	6·140
0·725	1·535	0·590	6·900
0·749	7·888	0·639	7·670
0·773	7·984	0·668	7·870
1·000	8·061	0·843	7·670
		0·869	7·680
		1·000	8·060

The relations between the rate constants and the composition of the solvent mixtures are shown in Fig. 5. In the system decalin–1-chloronaphthalene the k values increase only slightly with increasing mole fraction of 1-chloronaphthalene to $x = 0{\cdot}725$. Between $x = 0{\cdot}725$ and $0{\cdot}749$ it is observed a jump practically to the value obtained in pure 1-chloronaphthalene. In the system 3-chlorotoluene–1-chloronaphthalene the k values increase linearly with the mole fraction of 1-chloronaphthalene and approaches to that in 1-chloronaphthalene at $x = 0{\cdot}672$.

Further we have examined the temperature dependence of the decomposition in 1-chloronaphthalene (Table III and Fig. 6). In the Arrhenius plot it is observed a very steep slope up to 123°C. Beyond it the k values increase, surprisingly, more slowly with the temperature. The brutto activation energy in the higher temperature range was calculated to 29 kJ mol^{-1}. The activation energy of the thermal decomposition of 7-cumyl hydroperoxide was determined with 129·8 kJ mol^{-1} and 127·3 kJ mol^{-1} resp. (ref.[10,11]).

The obtained results can be discussed only in connection with the thermal decomposition of 7-cumyl hydroperoxide. A comparison of the received data with the values of the thermal decomposition performed at the same conditions but at 110°C shows that the decomposition in the presence of α-Ni—PC proceeds more slowly; that means α-Ni—PC acts as an inhibitor of the decomposition.

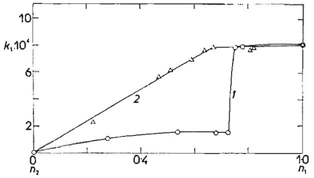


FIG. 5

Decomposition of 7-Cumyl Hydroperoxide in the Presence of Nickel Phthalocyanine and N-(2-Naphthyl)aniline

Relation between the rate constants k_1 (ls^{-1}) and the composition of the solvent system decalin–1-chloronaphthalene *1* and 3-chlorotoluene–1-chloronaphthalene *2* resp. $x_1 = n_1/(n_1 + n_2)$, n_1 = 1-chloronaphthalene, n_2 = decalin and 3-chlorotoluene resp.

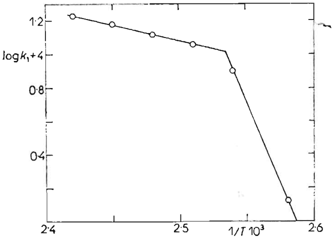


FIG. 6

Temperature Dependance of the Decomposition of 7-Cumyl Hydroperoxide in the Presence of Nickel Phthalocyanine and N-(2-Naphthyl)aniline

TABLE III

Temperature Dependence of the Decomposition of 7-Cumyl Hydroperoxide in the Presence of Nickel Phthalocyanine and N-(2-Naphthyl)aniline in 1-Chloronaphthalene

T, K	k_1 $s^{-1} . 10^4$	T, K	k_1 $s^{-1} . 10^4$
388·16	1·34	403·16	13·43
393·16	8·06	408·16	15·3
398·16	11·51	413·16	17·2

In connection with the surprising course of the temperature dependence of the decomposition we discuss the mechanism of the inhibition as follows. In the low temperature range ($< 123°C$) the thermal activated 7-cumyl hydroperoxide molecules are desactivated on the surface of heterogeneous Ni—PC. With increasing temperature the portion of the desactivated molecules decreases and in the high temperature range ($> 123°C$) the decomposition of hydroperoxide by β-Ni—PC is observed. That means α-Ni—PC does not act as a chemical but as an energetic inhibitor. This mechanism seems possible by that the energy taken up of the Ni—PC is distributed on the whole particle system and delivered on the wall and the solvent. In the first phase of the reaction the $\alpha \rightarrow \beta$ change is accelerated.

The work was done within an agreement on scientific cooperation between the Bulgarian Academy of Sciences and the Deutsche Forschungsgemeinschaft and presented in part at the Symposium on Reactions of Hydroperoxides organized on the basis of Multilateral Cooperation of Academies of Sciences of Socialist Countries hold in Sofia.

REFERENCES

1. Kropf H., Vogel W., Seckel P.: Justus Liebigs Ann. Chem. *1977*, 1125.
2. Kropf H., Ivanov S. K.: Justus Liebigs Ann. Chem. *1975*, 1051.
3. Kropf H., Ivanov S. K., Diercks P.: Justus Liebigs Ann. Chem. *1974*, 2046.
4. Kropf H., Ivanov S. K., Zink I.: Justus Liebigs Ann. Chem. *1974*, 2055.

5. Kropf H., Spangenberg J., Hofer A., Wenck H.: Justus Liebigs Ann. Chem. *1976*, 1242.
6. Kropf H., Spangenberg J., Hofer A.: Justus Liebigs Ann. Chem. *1976*, 1253.
7. Kropf H., Ivanov S. K., Büsch M.: Unpublished results.
8. Kropf H.: Justus Liebigs Ann. Chem. *637*, 73 (1960).
9. Kropf H., Bernert C.-R.: Justus Liebigs Ann. Chem. *751*, 109 (1971).
10. Kropf H.: Justus Liebigs Ann. Chem. *637*, 91 (1960).
11. Fordham J. W. R., Williams H. L.: Can. J. Res. B *27*, 943 (1949).