ISSN 1070-3632, Russian Journal of General Chemistry, 2009, Vol. 79, No. 7, pp. 1425–1429. © Pleiades Publishing, Ltd., 2009.
Original Russian Text © A.P. Pokutsa, R.G. Makitra, D.S. Maksim, E.Ya. Pal'chikova, 2009, published in Zhurnal Obshchei Khimii, 2009, Vol. 79, No. 7, pp. 1069–1073.

Quantitative Accounting for the Medium Effect at the Catalytic Decomposition of H_2O_2 in Hydrophilic Solvents

A. P. Pokutsa[a], R. G. Makitra[b], D. S. Maksim[a], and E. Ya. Pal'chikova[b]

[a] *Physics and Chemistry of Combustible Fossil Division, Litvinenko Institute of Physical Organic Chemistry and Coal Chemistry, National Academy of Sciences of Ukraine, ul. Nauchnaya, 3A, Lviv, 79053, Ukraine e-mail: pocutsa@org.lviv.net*

[b] *Institute of Geology and Geochemistry of Combustible Fossils, National Academy of Sciences of Ukraine, ul. Nauchnaya, 3A, Lviv, 79053, Ukraine e-mail: pocutsa@org.lviv.net*

Received April 17, 2007

Abstract—The experimental data on the effect of physicochemical properties of solvent on the rate of hydrogen peroxide decomposition catalyzed by cobalt ions were obtained using a method of adding inhibitors and were generalized quantitatively by the application of multiparametric linear equations.

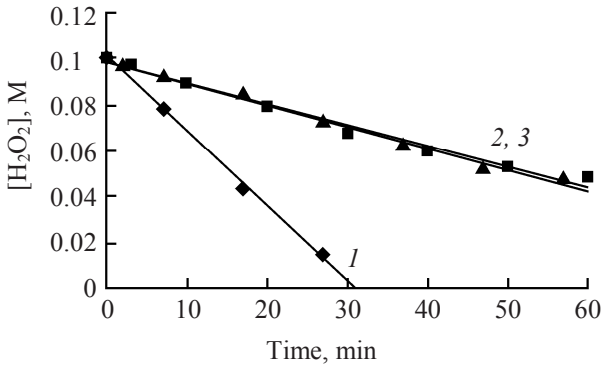
DOI: 10.1134/S1070363209070032

The nature of solvent can affect noticeably both overall rate of radical processes and the kinetics of their separate steps [1, 2]. This effect can be generalized on the basis of the principle of linear free energy relationship (LFE) by application of multiparametric equations. This statement relates in particular to oxidation reactions whose rate to a great extent is defined by the rate of an initiator decomposition, that is in its turn sensitive to the medium nature [3–5]. Similarly the medium effect on the decomposition of peroxy compounds can be generalized when kinetics of induced and molecular decompositions are considered separately [6].

The topic of this investigation is establishing quantitative relations between the rate of H_2O_2 catalytic decomposition catalyzed by soluble cobalt compounds [cobalt(II) acetylacetonate] and physicochemical characteristics of hydrophilic solvents.

The reaction was studied with solvents as media, therefore $[Solvent]_0 >> [H_2O_2]_0$, and the rate of H_2O_2 decomposition to the extent of ~50% could be described by the first order equation (see figure). The maximal values of decomposition rate were observed in alcohols (Table 1). It can be assumed that H_2O_2 forms hydrogen bonds with the solvent facilitating the hydroperoxide decomposition [7]. However the equally high rate of decomposition in the electron-donor tetrahydrofuran and low rates in water and acetic acid (Table 1) are not consistent with such assumption. Therefore for the elucidation of the medium parameters that have the key effect on this process we attempted to generalize our experimental data by application of six-parametric Eq. (1):

$$\log W = a_0 + a_1\frac{n^2-1}{n^2+2} + a_2\frac{\varepsilon-1}{2\varepsilon+1} + a_3\mathrm{B} + a_4E_T + a_5\delta^2 + a_6V_\mathrm{M}. \quad (1)$$



Kinetics of H_2O_2 consumption in (*1*) isopropyl alcohol, (*2*) acetic acid, and (*3*) acetonitrile in the presence of $Co(acac)_2$, 35°C.

Table 1. Rates of H_2O_2 consumption obtained experimentally and caculated with Eq. (3)

Solvent	log W, mol s^{-1}		Δlog W, mol s^{-1}
	experiment	calculated	
Isopropyl alcohol	0.7160	0.7363	0.023
t-Butyl alcohol	0.7324	0.8038	0.0714
Acetic acid	0.1761	0.1483	–0.0278
Water	–0.3979	–0.4024	–0.0044
1,4-Dioxane	–1.0000	–0.9559	0.0441
Morpholine	–0.5229	–0.5934	–0.0705
Acetonitrile	–0.0969	–0.0207	0.0762
Tetrahydrofuran	0.7324	0.6231	–0.1092

(The parameters notification corresponds to the rules accepted in [8–10], the calculations were carried out along the procedure recommended by the International Group for Correlation Analysis in Chemistry, an Associated Organization of IUPAC [11].)

Generalization of the data for all 8 studied solvents (Table 1) results in relation (2) with the value of multiple correlation coefficient $R = 0.999$.

$$\log W = 9.812 - (35.65\pm0.22)f(n^2) + (8.25\pm0.06)f(\varepsilon) + (0.610\pm0.065)\times10^{-3}B - (7.81\pm0.11)\times10^{-2}E_T - (0.856\pm0.008)\times10^{-3}\delta^2 - (7.48\pm0.32)\times10^{-3}V_M, \quad (2)$$

$$N = 8;\ R = 0.999;\ S = \pm5.76\times10^{-3}.$$

However, the values of paired correlation coefficients r between log W and the selected parameters that are equal respectively to 0.272; 0.532; 0.048; 0.028; 0.280 and 0.156 give no possibility to elucidate their significance (contribution to the effect on the process rate). Therefore in correspondence with [11] this characteristic was determined by the method of alternate exclusion of each term in (2) followed by finding R for the relations with the less number of terms. By this method we established that without accounting for the solvent basicity and molar volume the R values are 0.999 and 0.995 respectively. Further exclusion of the terms of Eq. (1) leads to unacceptably low correlation coefficients (exclusion of E_T or δ^2 gives $R = 0.936$ and 0.915 respectively) or to total distortion of correlation (exclusion of $f(n^2)$ or $f(\varepsilon)$ results in $R = 0.772$ and 0.656, respectively).

Hence, effect of medium properties on the rate of H_2O_2 decomposition catalyzed by Co^{2+} can be adequately described by four-parametric Eq. (3):

$$\log W = 9.416 - (36.80\pm2.24)f(n^2) + (7.72\pm0.39)f(\varepsilon) - (6.96\pm0.79)\times10^{-2}E_T - (0.718\pm0.070)\times10^{-3}\delta^2, \quad (3)$$

$$R = 0.995;\ S = \pm0.067.$$

Consideration of the signs at the terms of Eq. (3) leads to rather unexpected conclusions. First, although the basicity factor has a plus sign, its weak effect on the process rate excludes formation of hydrogen bonds between H_2O_2 and the basic solvent. This conclusion concerns not only the hydroxyl-containing solvents (alcohols and water) but also the electron-donor ones (THF, dioxane). At the same time, the minus at the electrophilicity parameter E_T points to the domination of the peroxide molecule solvation, leading to its relative stabilization. Second, increase in the density of the medium cohesion energy does not promote the peroxide decomposition (due to cell effect) and even retards it. Probably in this case the approach of Co^{2+} ions to H_2O_2 molecules is restricted. As follows from the obtained results, the only property of solvent that favors H_2O_2 decomposition is its polarity. Increase in this parameter promotes dissociation of cobalt compound with the formation of Co^{2+} ions. In Table 1 are listed log W values calculated with Eq. (2) and their differences with the experimental values Δlog W that mostly are less than least-mean-square errors $\delta = \pm0.007$.

Analysis of the data in [12, 13] on the decomposition of benzoyl and furoyl peroxides showed that these reactions proceeded by two parallel pathways, monomolecular and induced, and the character of the solvent effects on these pathways were different. The reaction proceeding by the homolytic route is promoted by the ability of solvent to non-specific solvation of the substrate while the effect of cohesion energy density is insignificant. On the contrary, at the induced decomposition the medium cohesion prevails. This factor appears as the cell effect that promotes an increase in the efficiency of the initiation and chain transfer by radicals [14]. According to [15], the general equation of the rate of decomposition (of benzoyl peroxide) is described as:

$$W_\Sigma = W_{\text{monomolecular}} + W_{\text{induced}} = k_{\text{InH}}[Bz_2O_2] + k_{\text{induced}}[Bz_2O_2]^{3/2}. \quad (4)$$

The reaction proceeding by two pathways can be presumed also in our case. Therefore for establishing the contributions of two pathways into the rate of H_2O_2 decomposition and features of the solvation effect on these reactions we investigated the decomposition of

Table 2. Rates of monomolecular (inhibited, W_{InH}) and induced ($W_{induced}$) pathways of H_2O_2 decomposition calculated with Eq. (4)

Solvent	log W_{InH}, mol s^{-1}			log $W_{induced}$, mol s^{-1}		
	experiment	calculated	$\Delta\log W$	experiment	calculated	$\Delta\log W$
Isopropyl alcohol	–0.1549	–0.1779	–0.0230	0.6532	0.6915	0.0383
t-Butyl alcohol	–0.3010	–0.1533	0.1477	0.6902	0.7591	0.0689
Acetic acid	–0.5229	–0.5542	–0.03013	0.0792	0.0429	–0.0363
Water	–0.6990	–0.7036	–0.0046	–0.6990	–0.7048	–0.0058
1, 4-Dioxane	–1.3010	–1.2689	0.0321	–1.3010	–1.2481	0.0529
Morpholine	–1.0000	–1.0213	–0.0213	–0.6990	–0.7812	–0.0822
Acetonitrile	–0.6990	–0.6696	0.0294	–0.2218	–0.1342	0.0876
Tetrahydrofuran	–0.1549	–0.2838	–0.1289	0.6721	0.5487	–0.1234

hydrogen peroxide in the presence of benzoquinone, the radical reaction inhibitor (Table 2).

The data on the inhibited decomposition of hydrogen peroxide show that the quinone addition decreases sharply (in some solvents almost by an order of magnitude) the rate of H_2O_2 decomposition (Table 2). The generalization of these data using Eq. (1) leads to expression (5):

$$\log W_{InH} = 5.818 - (20.43\pm1.06)f(n^2) + (5.88\pm0.27)f(\varepsilon) - (0.131\pm0.314)\times10^{-3}B - (6.09\pm0.55)\times10^{-2}E_T - (0.502\pm0.037)\times10^{-3}\delta^2 - (1.019\pm0.156)\times10^{-2}V_M, \quad (5)$$

$$R = 0.998; S = \pm0.028.$$

It follows from this expression that the signs at the separate regression terms except B are the same as for the total rate and are close to them by the absolute value. Like in the preceding case, the r values that are equal respectively to 0.401; 0.624; 0.050; 0.186; 0.075, and 0.001 give no possibility to attach a significance to the separate terms. By an alternate exclusion of the terms of correlation equation we established that like in the relation for the overall rate the factors B and V_M show practically no effect on the R value that equals at these exclusions to 0.998 and 0.983, respectively. By this method we obtained a four-parametric Eq. (6) that adequately describes the effect of solvent on the rate of homolytic (inhibited) decomposition of H_2O_2, and that is close in character to Eq. (3):

$$\log W_{InH} = 5.048 - (22.76\pm2.61)f(n^2) + (4.84\pm0.46)f(\varepsilon) - (4.18\pm0.92)\times10^{-2}E_T - (0.353\pm0.082)\times10^{-3}\delta^2, \quad (6)$$

$$R = 0.982; S = \pm0.078.$$

In this case further exclusion of some terms also leads to a sharp decrease in R, therewith the most significant is found to be the factor of non-specific solvation.

From Eq. (4) follows that the rate of induced (radical) decomposition equals to the difference between the overall process rate and the rate of monomolecular (inhibited) reaction pathway. The respective values are listed in Table 2. These data allow an assumption that the process defining the rate of H_2O_2 decomposition is the induced reaction pathway. For the evaluation of the role of solvation effects and for comparison those with the solvent effect on the rate of monomolecular decomposition and the overall rate, the respective $W_{induced}$ values calculated with Eq. (4) (Table 2) were generalized by means of Eq. (7):

$$\log W_{induced} = 10.377 - (38.76\pm0.54)f(n^2) + (9.40\pm0.14)f(\varepsilon) + (0.678\pm0.160)\times10^{-3}B - (0.084\pm0.003)E_T - (1.049\pm0.019)\times10^{-3}\delta^2 - (8.41\pm0.80)\times10^{-3}V_M, \quad (7)$$

$R = 0.999; S = \pm0.014; r = 0.225; 0.517; 0.074; 0.009; 0.074; 0.20$ (r are the pair correlations coefficients).

Note that the signs at the respective terms of this equation are the same as in Eqs. (2) and (5).

After exclusion of terms B and V_M of little significe the simplified equation appears as:

$$\log W_{induced} = 9.930 - (40.06\pm2.54)f(n^2) + (8.81\pm0.45)f(\varepsilon) - (0.074\pm0.009)E_T - (0.894\pm0.080)\times10^{-3}\delta^2, \quad (8)$$

$$R = 0.995; S = \pm0.076.$$

Although the term defining possible electrophilic solvation also contributes insignificantly, its exclusion leads to a three-parametric equation $\log W_{induced} = f(n^2, \varepsilon, \delta^2)$ with a considerably worse correlation (R = 0.945).

Analysis of the obtained equations shows that the character of the solvent effect is the same in the monomolecular and the induced decomposition and the factor defining acceleration of reactions in both paths is the medium polarity. The effect of the solvent ability to specific solvation (basicity and electrophilicity) on the considered process is minor. Due to the low significance of B parameter it is possible to suggest that hydrogen peroxide does not form hydrogen bonds with nucleophilic (dioxane, tetrahydrofuran) solvents. Even assuming the existence of this type bonding, we conclude that it does not affect substantially the peroxide decomposition. Of course, comparing solvation effect on the decomposition of H_2O_2 and benzoyl peroxide it should be accounted for the possibility of solvation in the second case not only at O–O group but also at the aromatic rings that is seen from the effect of the solvent polarizability which favors the decomposition of the latter compound [15].

It is noteworthy that the obtained correlations account for the effect of physicochemical characteristics of the solvents on the overall hydrogen peroxide decomposition rate. The quantitative contribution to the H_2O_2 decomposition of the effects owing to solvation of catalyst we do not consider in this work due to the problems of their experimental measuring; in literature also there are no publications on this problem. Minor effects of B and E_T on the decomposition rate of hydrogen peroxide also can be a consequence not only of an insignificant effect of hydrogen bonds but of an increase in the contribution of specific solvation by alcohol of the catalyst particles. Lower rate of hydrogen peroxide consumption in acetic acid as compared with alcohols can be a consequence of an increased cell effect in the latter solvent. In this case W_{InH} should be higher and W_{induced} lower in the alcohol than in the acid. However, as seen from the experimental findings (Table 2), the real picture is not consistent with this assumption. On the other hand, according to the correlation relations the increase in value of the term δ (responsible for the cell effect) should lead to a decrease in the peroxide decomposition rate. This probably points to a higher degree of catalyst solvation with alcohols than with acetic acid, and as a consequence, to an increase in the negative contribution of the medium cohesion energy to the overall rate of H_2O_2 decomposition. It is interesting that decomposition of H_2O_2 catalyzed with Fe^{2+} in *t*-butyl alcohol and in acetic acid proceeds with almost equal rates [16].

Thus, the process of hydrogen peroxide decomposition in organic solvents catalyzed by cobalt(II) compounds proceeds predominantly by the induced pathway. Effect of physicochemical properties of the solvent on the rate of the decomposition process is complicated and can be generalized by application of multiparametric equations of free energy linearity. The role of cohesion energy in the hydrogen peroxide decomposition is negative, in contrast to the commonly accepted concept: the increase in the cohesion energy leads to a decrease in the rate of the decomposition process. The solvation of catalyst by solvent certainly contributes significantly to the total rate of H_2O_2 consumption, but additional investigations should be carried out for quantitative evaluation of this effect.

EXPERIMENTAL

The kinetic experiments were carried out at 35ºC in a glass cell with a magnet stirrer with a Teflon-covered bar at a temperature control. The initial concentrations of H_2O_2 and Co^{2+} were 0.1 M and 5×10^{-4} M, respectively. Analysis on the content of hydrogen peroxide in the samples was carried out by titration with potassium permanganate solution.

Quinone (InH) was synthesized from hydroquinone along the procedure in [17] and purified by a double recrystallization from ethanol.

The solvents (analytical grade) were purified along the commonly applied procedures and distilled just prior to the experiments. Cobalt(II) acetylacetonate (Aldrich) was used without additional purification.

ACKNOWLEDGMENTS

Authors are grateful to Professor Hans-Ullrich Siechl for providing the possibility to report the preliminary results of this investigation on the Seventh European Symposium on Organic Reactivity [18].

REFERENCES

1. Howard, I.A. and Ingold, K.U., *Canad. J. Chem*., 1964, vol. 42, no. 5, p. 1044.
2. Niki, E., Kamiya, Y., and Ohtu, N., *Bull. Chem. Soc. Japan*., 1969, vol. 42, no. 11, p. 3224.
3. Makitra, R.G., Pirig, Ya.M., and Yatchishin, I.I., *Zh. Org. Khim*., 1999, vol. 35, no. 7, p.1073.
4. Makitra, R.G., Polyuzhin, I.P., and Golovata, I.P., *Zh. Obshch. Khim*., 2005, vol. 75, no. 2, p. 197.

5. Midyana, G.G., Makitra, R.G., and Pal'chikova, O.Ya., *Zh. Org. Khim*., 2004, vol. 40, no. 10, p. 1459.
6. Gavryliv, E. M., Makitra, R.G., and Pirig, Ya.M., *Dokl. Akad. Nauk SSSR*, 1991, no. 2, p. 98.
7. Zaikov, G.E., Maizus, Z.K., and Emmanuel', N.M., *Izv. Akad. Nauk SSSR, Ser. Khim*., 1968, p. 256.
8. Pal'm, V.A., *Osnovy kolichestvennoi teorii organicheskikh reaktsii* (Fundamentals of Quantitative Theory of Organic Reactions), Moscow: Khimiya, 1977.
9. Makitra, R.G., Pirig, Ya.M., and Kivelyuk, R.B., Deposited in VINITI, Moscow, 1985, no. 628.
10. Abboud, J.L.M. and Notario, R., *Pure Appl. Chem*., 1999, vol. 71, no. 4, p. 645.
11. *Quant. Struct. Act. Relat*., 1985, vol. 4, p. 29; *Ukr. Khim. Zh*., 1992, vol. 58. no. 3, p. 269.
12. Molnar, S., *Period. Polytechn. Chem. Eng.,* 1973, vol. 17, no. 3, p. 257.
13. Nozaki, K. and Bartlett, P.D., *J. Am. Chem. Soc*., 1946, vol. 68, no. 9, p. 1686.
14. Pirig, Ya.M., Makitra, R.G., and Gavryliv, E.M., Deposited in VINITI, Moscow, 1988, no. 8418–1388.
15. Foster, W.R. and Williams, G.H., *J. Chem. Soc*., 1962, no. 8, p. 2862.
16. Walling, C. and Goosen, A., *J. Amer. Chem. Soc*., 1973, vol. 95, no. 9, p. 2987.
17. *Sintezy organicheskikh preparatov. Sbornik 1* (Synthesis of Organic Preparations. Collection 1), Kazanskii, B.A., Ed., Moscow: Inostrannaya Literatura, 1949, p. 463.
18. Pocutsa, A., Makitra, R., and Maksim–Lutsik, D., Abstracts of Papers, *7th European Symposium on Organic Reactivity*, Ulm, 1999, p. 185.