

CATALYTIC EFFECT OF CETYLTRIMETHYLAMMONIUM BROMIDE ON THE RADICAL DESTRUCTION OXIDATION OF PYROCATECHOL VIOLET

Jan LASOVSKÝ, František BŘEZINA and Ladislav NEKL

*Department of Inorganic and Physical Chemistry,
Palacký University, 771 46 Olomouc*

Received February 22nd, 1979

The effect of cetyltrimethylammonium bromide (*I*) on the radical oxidation of pyrocatechol violet by hydrogen peroxide was studied in the presence of *N,N'*-ethylenediamine-bis(*o*-aminobenzaldimine)cobalt(II) bromide and cobalt dichloride. After a short, faster period the reaction obeys the 1st order formalism. In the presence of *I* the experimental rate constants are as much as 42 times higher than in "pure" solutions. In optimum conditions (dye concentration $1.75 \cdot 10^{-4} \text{ mol l}^{-1}$) the reaction can be described in terms of the usual formalism of micellar catalysis. In solutions containing *I* the effect of cobalt compounds can be traced down to cobalt concentration levels of $10^{-8} \text{ mol l}^{-1}$. The dependences of the experimental rate constants on the concentrations of hydrogen peroxide and cobalt compounds and on the temperature and pH are discussed.

Surface active substances affect appreciably the reactivity of molecules¹. In analytical chemistry, use is often made of their effect on chemical equilibria to enhance the sensitivity and selectivity of detection and determination of inorganic ions². Micellar catalysis has been extensively studied in hydrolytic, solvolytic, and in part also radical reactions^{1,3,4}. Cationoid surfactants accelerate the decomposition of crystal violet in alkaline solutions^{5,6}, oxidation of thiophenols⁷, oxidation of the reduced form of nicotinamideadeninedinucleotide⁸, and formation of duroquinone radicals⁹, and have a favourable effect on the yield of electrooxidation of benzhydrol^{10,11}.

The aim of the present work was to study the radical destruction oxidation of pyrocatechol violet by hydrogen peroxide, catalyzed by *N,N'*-ethylenediamine-bis(*o*-aminobenzaldimine)cobalt(II) bromide $[\text{Co}(\text{H}_2\text{enb}_2)]\text{Br}_2$ or cobalt dichloride and cetyltrimethylammonium bromide.

EXPERIMENTAL

Chemicals and Apparatus

Stock solution of *I* was prepared in 10^{-2} M concentration, the tenside surfactant was determined with 10^{-2} M solution of tetraphenylboronnatrium^{12,13}. Pyrocatechol violet was twice recrystallized from ethanol, and its content was determined by alkalimetric titration (as a dibasic acid)¹⁴.

The preparation and purity checking of the $[\text{Co}(\text{H}_2\text{enz}_2)]\text{Br}_2$ complex have been reported^{1,5}. Solutions of CoCl_2 were obtained by diluting the stock solution, in which the cobalt content was determined chelatometrically using murexide as the indicator^{1,6}. The concentration of hydrogen peroxide was determined manganometrically^{1,7}. The pH was adjusted with a triethanolamine buffer (pH 8.00) and differently concentrated sodium hydroxide solutions. The ionic strength was given by the concentration of the buffer; at pH 8.00, I was 0.017. All chemicals used (except the dye) were reagent grade purity.

The reaction was studied at $25 \pm 0.1^\circ\text{C}$ in thermostatted cells of a Unicam SP 8 100 spectrophotometer (Pye Unicam, Cambridge). The pH values were measured on a PHM 64 instrument (Radiometer, Copenhagen) with the precision of ± 0.02 H units.

Experimental Data Evaluation

In neutral or alkaline solutions, pyrocatechol violet is oxidized by hydrogen peroxide in the presence of trace quantities of cobalt compounds to give colourless products. Thus the absorbance of a reaction mixture in 1 cm cells in the time t is

$$A_t = \varepsilon(c_L - x), \quad (1)$$

where ε is the molar absorptivity of the dye and c_L and $(c_L - x)$ are its initial and actual concentrations, respectively. The absorbances were measured at the wavelength of the first long-wavelength band of the H_2L species (595 nm for "pure" solutions, 609 nm for solutions containing I). The experimental rate constants k_{exp} were then calculated numerically according to the relation

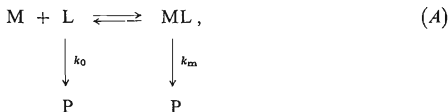
$$\ln(A_0/A_t) = k_{\text{exp}}t, \quad (2)$$

where A_0 and A_t are the initial and actual absorbances of the solution, respectively.

The tabulated values are averages of 7 to 30 measurements; the relative standard deviation of the rate constants did not exceed 5%.

RESULTS AND DISCUSSION

The reaction is of complex nature both in the absence and in the presence of cationoid surfactant. At the beginning, a slightly faster period appears, followed in 20 minutes by a slower course, obeying the first order formalism until the pyrocatechol violet has reacted. The experimentally established rate constants k_{exp} (Eq. (2)) are dependent upon the concentration of the cationoid surfactant (Table I). In case that the reaction rate is proportional to the dye concentration in the micellar phase, it can be described in terms of the usual formalism of micellar catalysis¹,



where L and ML denote the dye in the aqueous and in the micellar phases, respectively,

decomposing to the products P, and M is the "pure" micellar formation. The stability constant of the micellar complex of the dye (with the assumed stoichiometry 1 : 1) is then

$$\beta = [\text{ML}]/([\text{L}][\text{M}]) . \quad (3)$$

The experimental rate constants are related with the rate constants k_0 and k_m through

$$k_{\text{exp}} = k_0 F_0 + k_m F_m , \quad (4)$$

where F_0 and F_m denote the aqueous and micellar fractions of the dye, respectively. Combining Eqs (3) and (4) and rearranging we obtain the relation

$$1/(k_{\text{exp}} - k_0) = 1/(k_m - k_0) + [1/(k_m - k_0)] \{N/[\beta(c_S - C_{\text{mc}})]\} , \quad (5)$$

TABLE I

Dependence of the Rate Constant on the Concentration of Cetyltrimethylammonium Bromide

$c_{\text{H}_2\text{O}_2} = 0.084 \text{ mol l}^{-1}$, pH 8.00, $t = 25^\circ\text{C}$; A: $c_L = 1.75 \cdot 10^{-4} \text{ mol l}^{-1}$, $c_{\text{CoCl}_2} = 2 \cdot 10^{-7} \text{ mol l}^{-1}$; B: $c_L = 3.9 \cdot 10^{-5} \text{ mol l}^{-1}$, $c_{\text{CoCl}_2} = 2 \cdot 10^{-7} \text{ mol l}^{-1}$; C: $c_L = 3.9 \cdot 10^{-5} \text{ mol l}^{-1}$, $c_{\text{Co}(\text{H}_2\text{enbz}_2)} = 2 \cdot 10^{-7} \text{ mol l}^{-1}$.

$c_S \cdot 10^4$ mol l^{-1}	$k_{\text{exp}} \cdot 10^4, \text{s}^{-1}$		
	A	B	C
0	0.26	0.21	0.17
1	0.15	1.53	1.20
2	0.95	2.30	1.94
3	—	2.89	2.82
4	1.60	3.46	3.39
6	2.01	3.88	2.32
8	2.39	2.01	1.64
10	2.87	1.54	1.49
12	2.89	—	—
14	3.20	—	—
16	3.33	—	—
18	3.24	—	—
20	2.95	2.18	—
30	2.69	1.20	—
40	2.64	0.93	1.50
48	2.79	—	—
60	—	0.86	—

in which the concentration of the "pure" micellar formations is approximated as

$$[M] = (c_s - C_{mc})/N; \quad (6)$$

here c_s is the total concentration of I , C_{mc} its critical micellar concentration, and N the aggregation number (for I , N is 61 – refs^{1,2}). The C_{mc} value is difficult to estimate

TABLE II

Dependence of the Experimental Rate Constants on the Concentration of N,N'-Ethylenediamine-bis(*o*-aminobenzaldimine)cobalt(II) Bromide

$c_s = 4 \cdot 10^{-3} \text{ mol l}^{-1}$, $c_L = 1.75 \cdot 10^{-4} \text{ mol l}^{-1}$, $c_{\text{H}_2\text{O}_2} = 0.084 \text{ mol l}^{-1}$, pH 8.00, $t = 25^\circ\text{C}$.

$c_{\text{Co}} \cdot 10^8$ mol l^{-1}	$k_{\text{exp}} \cdot 10^4$ s^{-1}	$c_{\text{Co}} \cdot 10^8$ mol l^{-1}	$k_{\text{exp}} \cdot 10^4$ s^{-1}
2	0.55	30	1.29
4	0.58	40	1.54
8	0.72	50	1.80
10	0.75	100	3.07
20	1.03	150	4.35

TABLE III

Dependence of the Experimental Rate Constants on the pH and on the Hydrogen Peroxide Concentration

$c_L = 1.75 \cdot 10^{-4} \text{ mol l}^{-1}$, $c_s = 4 \cdot 10^{-3} \text{ mol l}^{-1}$, $c_{\text{Co}(\text{H}_2\text{enbz}_2)} = 2 \cdot 10^{-7} \text{ mol l}^{-1}$, $t = 25^\circ\text{C}$

pH ^a	$k_{\text{exp}} \cdot 10^4$ s^{-1}	$c_{\text{H}_2\text{O}_2} \cdot 10^4$ mol l^{-1}	$k_{\text{exp}} \cdot 10^4$ s^{-1}
4.81	0.05	0.99	0.80
7.10	0.67	4.96	0.86
7.32	0.86	10.10	0.91
8.00	1.03	50.30	1.29
8.31	1.29	102	1.32
8.86	1.67	509	1.18
9.20	16.40	848	1.03
9.49	26.60		
10.48	46.90		

^a $c_{\text{H}_2\text{O}_2} = 0.083 \text{ mol l}^{-1}$; ^b pH 8.00,

The tabulated value^{1,2} is $9.2 \cdot 10^{-4} \text{ mol l}^{-1}$. Extrapolation of conductometric measurements gave¹⁸ the value of $4 \cdot 10^{-4} \text{ mol l}^{-1}$ for I (I 0.5). During the evaluation of the colour changes of the bulky anionic dye Rose Bengal Extra induced by addition of I , the value of $4 \cdot 10^{-6} \text{ mol l}^{-1}$ was established³. Studying the emission spectra of fluorescein¹⁹, we estimated the C_{mc} value to $2 \cdot 10^{-4} \text{ mol l}^{-1}$. With the last value, the linear transformation (5) is obeyed over the cationoid tenside concentration region of $(0.8-1.6) \cdot 10^{-3} \text{ mol l}^{-1}$ ($c_L = 1.75 \cdot 10^{-4} \text{ mol l}^{-1}$, $c_{CO} = 2 \cdot 10^{-7} \text{ mol l}^{-1}$, $c_{H_2O_2} = 0.08 \text{ mol l}^{-1}$, pH 8.00). The rate constant k_m determined graphically is $4.69 \cdot 10^{-4} \text{ s}^{-1}$, the k_m/k_0 ratio is 18. When lower dye concentrations are used ($c_L = 4 \cdot 10^{-5} \text{ mol l}^{-1}$), the dependence of k_{exp} on c_S displays a maximum. This is a common appearance in the case of micellar catalysis, and is explained in terms of saturation of the substrate with the micellar formations^{1,20}. The surfactant concentration at which the rate constants attain their maxima is usually low ($4-6 \cdot 10^{-4} \text{ mol l}^{-1}$) as compared with other nucleophilic reactions. Moreover, the k_{exp} vs c_S plots do not exhibit the usual plateaus for low surfactant concentrations, indicating the formation of kinetically active micellar formations^{1,20}. These facts lead us to suppose that in the reaction under study, kinetically active molecular complexes of the dye with the tenside, or smaller, pre-micellar formations play an important part. The cause of this lies probably in the high affinity of the bulky anion towards the cationoid surfactant; only the decrease in the rate constant at $c_S > 8 \cdot 10^{-4} \text{ mol l}^{-1}$ is presumably associated with micelle formation. An identical shape with a pronounced maximum is observed also for the k_{exp} vs c_S plots in phosphate buffer (pH 6.34, I 0.006). The highest rate, $k_{exp} = 5.73 \cdot 10^{-4} \text{ s}^{-1}$, is attained with the tenside concentration $c_S = 8 \cdot 10^{-4} \text{ mol l}^{-1}$ ($c_L = 4 \cdot 10^{-5} \text{ mol l}^{-1}$, $c_{CO} = 8 \cdot 10^{-7} \text{ mol l}^{-1}$, $c_{H_2O_2} = 0.08 \text{ mol l}^{-1}$); the k_{exp}/k_0 ratio is 42.

The experimental rate constants depend linearly on the concentration of the cobalt compounds, as expected, also in the presence of the cationoid surfactant (Table II). In fact, when all the reaction components except the cobalt compound and the dye are present in a high excess, the rate of the catalyzed reaction can be written²¹ as

$$(dx/dt)' = kc_{Co}(c_L - x). \quad (7)$$

Simultaneously with the catalyzed reaction, the noncatalyzed reaction can proceed as well:

$$(dx/dt)^* = k'(c_L - x). \quad (8)$$

The total rate is then the sum of the two contributions:

$$(dx/dt) = (kc_{Co} + k')(c_L - x). \quad (9)$$

Under these conditions, the experimental rate constant is a linear function of the catalyst concentration²¹:

$$k_{\text{exp}} = kc_{\text{Co}} + k' \quad (10)$$

The slope of this linear dependence of the bulky $[\text{Co}(\text{H}_2\text{enb}_2)]^{2+}$ ion is $258 \text{ l}^3 \cdot \text{mol}^{-1} \text{ s}^{-1}$, and the catalytic effect is apparent at concentrations as low as $10^{-8} \text{ mol} \cdot \text{l}^{-1}$.

The complexity of the catalyzed oxidation reaction appears in the dependences of the rate constants on pH, peroxide concentration, and temperature, which do not follow a simple shape. A pronounced oxidation of the dye ($k_{\text{exp}} \geq 10^{-4} \text{ s}^{-1}$) is associated with the occurrence of the H_2L^{2-} and HL^{3-} species (dissociation of the phenolic groups of the dye), $\text{p}K_{\text{a}2} (\text{H}_3\text{L}^- \rightarrow \text{H}_2\text{L}^{2-})$ 7.80, $\text{p}K_{\text{a}3} (\text{H}_2\text{L}^{2-} \rightarrow \text{HL}^{3-})$ 9.76 (ref.¹⁴)*. In the pH 7.1–8.9 region the rate constants are but slightly dependent on the pH, and only at pH > 9 the reaction rate increases considerably (Table III). This can be explained by the higher concentration of the easily oxidizing HL^{3-} or L^{4-} species ($\text{p}K_{\text{a}4} (\text{HL}^{3-} \rightarrow \text{L}^{4-})$ 12.8, ref.¹⁴) or by a greater oxidation ability of hydrogen peroxide activated by cobalt compounds. The reaction order with respect to the peroxide approaches zero, and the k_{exp} vs $c_{\text{H}_2\text{O}_2}$ dependence exhibits a maximum at approximately $10^{-2} \text{ mol l}^{-1}$ (Table III). The temperature dependence of the experimental rate constants does not obey the Arrhenius equation. Rise in the reaction temperature from 25°C to 70°C brings about an increase in the rate constant from $1.03 \cdot 10^{-4} \text{ s}^{-1}$ to $7.37 \cdot 10^{-4} \text{ s}^{-1}$.

It should be noted that *I* by itself has no effect on the decomposition of hydrogen peroxide by cobalt(II) compounds. Its effect is substantial only during oxidation of a bulky anion, where, owing to ionic and hydrophobic interactions, kinetically active molecular complexes, pre-micellar and micellar formations are created.

REFERENCES

1. Fendler J. H., Fendler E. J.: *Catalysis in Micellar and Macromolecular Systems*, p. 104. Academic Press, New York, San Francisco, London 1975.
2. Bailey B. W., Chester J. E., Dagnall R. M., West I. A.: *Talanta* 15, 1359 (1968).
3. Fendler E. J., Fendler J. H.: *Advances in Physical Organic Chemistry*, Vol. 8, p. 271. Academic Press, London, New York 1970.
4. Mikeš O., Vepřek-Šiška J., Štrob P.: *Chem. Listy* 70, 125 (1976).
5. Albrizzio J., Archila J., Rodulfo T., Cordes E. H.: *J. Org. Chem.* 37, 871 (1972).
6. Shirahama Keishiro: *Bull. Chem. Soc. Jap.* 49, 2731 (1976).
7. Shinkai Seiji, Ando Reiko, Yoneda Fumio: *Chem. Phys. Lett.* 1977, 147.

* The published values of the dissociation constants pertain to "pure" solutions, free of surfactants. The presence of *I* can result in an increase in the acidity of the phenolic groups exceeding one order²² of magnitude.

8. Anderson B. M., Anderson C. D.: *Biochim. Biophys. Acta* 205, 161 (1970).
9. Katmazovski N. N., Fomin G. V.: *Zh. Khim.* 46, 2427 (1972).
10. Franklin T., Sidarous L.: *Chem. Soc., Chem. Commun.* 1975, 741.
11. Franklin T., Sidarous L.: *J. Electrochem. Soc.* 124, 65 (1977).
12. Cross J. T.: *Analyst (London)* 90, 315 (1965).
13. Uno T., Miyajima K., Tsukatani H.: *Yakugaku Zasshi* 80, 153 (1960); *Chem. Abstr.* 54, 11 824 (1960).
14. Chiacchierini E., Gocchieri R., Sommer L.: *This Journal* 38, 1478 (1973).
15. Březina F.: Unpublished results.
16. Schwarzenbach G., Flaschka H.: *Kompleksonometricheskoe Titrovanie*, p. 243. Khimiya, Moscow 1970.
17. Tomiček O.: *Kvantitativní analýza*, p. 208. Státní zdravotnické nakladatelství, Prague 1958.
18. Bruice T. C., Katzhendler J., Fedor L. R.: *J. Amer. Chem. Soc.* 90, 1333 (1968).
19. Lasovský J., Grambal F.: *Acta Univ. Palacki. Olomuc., Fac. Rerum Natur.*, in press.
20. Bunton C. A., Robinson L.: *J. Org. Chem.* 34, 773 (1969).
21. Mark H. B., Rechnitz G. A.: *Kinetika v Analiticheskoj Khimii*, p. 34. Mir, Moscow 1972.
22. Lasovský J., Ružička E.: *This Journal* 42, 1941 (1976).

Translated by P. Adámek.