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Effects of Ligands in the Cobalt Salt-catalyzed Decomposition of *t*-Butyl Hydroperoxide*

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A kinetic study has been made of the cobalt acetate-catalyzed decomposition of *t*-butyl hydroperoxide in acetic acid at 40.4°C, and the effects of added lithium salts on the decomposition rate have been studied. The observed rate law for the cobalt acetate-catalyzed decomposition is: $v=k_2[\mathrm{Co(II)}][t\text{-}\mathrm{C_4H_9OOH}]+k_3[\mathrm{Co(II)}]^2[t\text{-}\mathrm{C_4H_9OOH}]$. When lithium halides (chloride and bromide) are added to this system, the cobalt acetate is changed to cobaltous halide and the rate of decomposition is markedly decreased. In the case of lithium bromide the hydroperoxide decomposition is accompanied by the generation of molecular bromine. The mechanisms for the bromine formation will be discussed. The role of these cobalt salts in the course of autoxidation in relation to the hydroperoxide decomposition will also be discussed.

Hydroperoxide decomposition by cobalt salts is an important subject in connection with autoxidation. Some kinetic studies(1) have been reported, but not all of them are in agreement. Moreover, though a comprehensive study of the metal ion-catalyzed decomposition of hydroperoxide has recently been made by Richardson,(2-4) the study of the ligands of metal ions is still insufficient. In this paper, as an aid to discussing the difference in reactivity caused by different ligands of cobalt ions, we wish to report on the effects of added lithium salts on the rate of the cobalt acetate-catalyzed decomposition of *t*-butyl hydroperoxide in anhydrous acetic acid at 40.4°C. Cobaltous bromide is known to be very effective in autoxidation reaction, so some discussion of this subject will also be undertaken.

Experimental

Materials. *t*-Butyl hydroperoxide was prepared by adding 35% hydrogen peroxide (2 mol) to a mixture of *t*-butyl alcohol (2 mol) and 70% sulfuric acid (2 mol) at 5°C; it was purified by the method of Milas and Surgenor.(5) The purified hydroperoxide was shown by iodometric titration to be 97.0% pure. The acetic acid was purified, and the remaining trace amount of water was removed by the conventional method. Reagent-grade anhydrous lithium chloride was used without further purification. Cobalt acetate, cobalt bromide, lithium acetate, lithium bromide, and lithium perchlorate were obtained as hydrates. The water was removed *in vacuo* by heating the hydrates at from 120 to 250°C for several days. They were shown by thermano-balance analysis to contain less than 0.5% water.

Procedure. The required amount of metal salts and acetic acid were introduced into a 100 m*l* reaction flask under a nitrogen atmosphere. The mixture was then stirred for about 30 min at the reaction temperature, during which time the salts dissolved completely. The reaction was initiated by adding *t*-butyl hydroperoxide to the flask. All the runs were carried out at 40.4±0.1°C in a thermostated bath.

Analysis. The rate of hydroperoxide disappearance was determined by iodometric titration. To a flask containing 1.5 g of sodium hydrogen carbonate, 2 m*l* of a saturated potassium iodide solution, and 25 m*l* of acetic acid, there were added 5 m*l* of an aliquot which had been withdrawn from the reaction vessel; then the flask was stoppered. After it had stood for 5 min in the dark, the solution was titrated with a standard sodium thiosulfate solution.(6) The first-order-rate plots were linear up to about a half-life, but after a half-life they showed upward drifts. The thermal decomposition of *t*-butyl hydroperoxide at the same temperature (40.4°C) was also measured; its rate was found to be very small compared with that of the cobalt-catalyzed decomposition (less than 1/100). When molecular bromine is liberated during the reaction, the iodometric method described above shows the total amounts of undecomposed hydroperoxide and liberated molecular bromine. In that case, therefore, before potassium iodide was added the aliquot was introduced into an acetic acid solution of phenol in order to remove any bromine by reacting with phenol.

For the visible and ultraviolet spectra, an Hitachi ESP-2 spectrophotometer was used. Product analysis

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* Oxidation-Reduction Reactions by Transition Metal Complexes. II.

1) For example, a) M. H. Dean and G. Skirrow, *Trans. Faraday Soc.*, **54**, 849 (1958); b) J. A. Bigot, *Rec. Trav. Chim.*, **80**, 825 (1961); c) M. S. Kharasch and A. Fono, *J. Org. Chem.*, **24**, 72 (1959).

2) W. H. Richardson, *J. Am. Chem. Soc.*, **87**, 247 (1965).

3) W. H. Richardson, *ibid.*, **87**, 1096 (1965).

4) W. H. Richardson, *J. Org. Chem.*, **30**, 2804 (1965).

5) N. A. Milas and D. M. Surgenor, *J. Am. Chem. Soc.*, **68**, 205 (1946).

6) H. A. Liebhafsky and W. H. Sharkey, *ibid.*, **62**, 190 (1940).

was also made. *t*-Butyl alcohol, methyl alcohol, di-*t*-butyl peroxide, and acetone were identified by gas chromatography. Acetone was also identified as 2, 4-dinitrophenylhydrazone.[7]

Results and Discussion

Cobalt Acetate-catalyzed Decomposition of *t*-Butyl Hydroperoxide. The anhydrous cobalt acetate-catalyzed decomposition of *t*-butyl hydroperoxide was investigated. The first-order-rate plots in *t*-butyl hydroperoxide were linear, and from Table 1 it may be seen that the initial concentration of *t*-butyl hydroperoxide does not affect the rate constant. The order in the hydroperoxide, therefore, was determined to be unity.[8] The rates were measured in various cobalt concentrations; the data are tabulated in Table 2. Neither the first-order-rate plot nor the second-order-rate plot in cobalt acetate was linear. Dean and Skirrow[1a] reported a 1.4 order at 55°C, and Richardson[3] found that the order in cobalt acetate is dependent on the temperature. These findings suggest that the rate law may be expressed best as the sum of the first and second-order terms in cobalt. In fact the plot of the apparent second-order rate constant, $k_{\mathrm{II}}(k/[\mathrm{Co(II)}])$, *vs.* the cobalt(II) concentration is linear (Fig. (1)). This corresponds to the rate law given by Eq. (1):

$$-\mathrm{d}[t\text{-}\mathrm{C_4H_9OOH}]/\mathrm{d}t = k_2[\mathrm{Co(II)}][t\text{-}\mathrm{C_4H_9OOH}] + k_3[\mathrm{Co(II)}]^2[t\text{-}\mathrm{C_4H_9OOH}] \qquad (1)$$

The slope of the line is $k_3(2.9\times10^{-1}\ l^2/\mathrm{mol}^2\,\mathrm{sec})$, and the intercept is $k_2(6.1\times10^{-3}\ l/\mathrm{mol\,sec})$.

TABLE 1. THE EFFECT OF INITIAL CONCENTRATION OF *t*-BUTYL HYDROPEROXIDE ON THE RATE CONSTANT[a)]

$[\mathrm{Co(OAc)_2}]$ $\times10^2$ mol/l	$[t\text{-}\mathrm{C_4H_9OOH}]_0$ $\times10$ mol/l	k $\times10^4$ sec^{-1}
1.82	1.64	2.05
1.80	3.16	2.07
1.80	1.01	2.04

a) at 40.4°C in acetic acid.

TABLE 2. DATA FOR ORDER IN COBALT ACETATE

$[\mathrm{Co(OAc)_2}]$ $\times10^2$ mol/l	$[t\text{-}\mathrm{C_4H_9OOH}]_0$ $\times10$ mol/l	k $\times10^4$ sec^{-1}
3.96	1.34	6.82
2.86	1.65	4.26
1.82	1.64	2.05
1.02	1.63	0.918

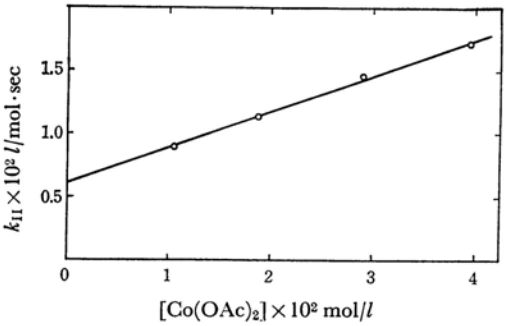

Fig. 1. Order of cobalt acetate at 40.4°C.

From a spectral investigation it was found that the absorption at 535 mμ did not change throughout the reaction. This indicates that the cobalt ion exists almost as divalent; in other words, the concentration of Co(III) is very small. *t*-Butyl alcohol (41% yield), acetone (28% yield), some di-*t*-butyl peroxide, and methyl alcohol were identified and measured by means of product analysis.

In view of the literature,[1-3] it seems that the reaction mechanism given by Eqs. (2)—(8) (where R is *t*-butyl) is most probable:

$$\mathrm{ROOH+Co(II)} \rightleftharpoons \mathrm{Co(II)\cdot ROOH} \qquad (2)$$

$$\mathrm{Co(II)\cdot ROOH} \rightarrow \mathrm{Co(III)+RO\cdot+OH^-} \qquad (3)$$

$$\mathrm{ROOH+Co(III)} \rightarrow \mathrm{Co(II)+ROO\cdot+H^+} \qquad (4)$$

$$\mathrm{2ROO\cdot} \rightarrow \mathrm{ROOR+O_2} \qquad (5)$$

$$\mathrm{ROO\cdot+Co(II)\cdot ROOH} \rightarrow \mathrm{RO^-+ROH+O_2+Co(III)} \qquad (6)$$

$$\mathrm{RO\cdot+Co(II)} \rightarrow \mathrm{RO^-+Co(III)} \qquad (7)$$

$$\mathrm{RO\cdot} \rightarrow \mathrm{CH_3COCH_3+CH_3\cdot} \qquad (8)$$

Product distribution can be interpreted adequately by this mechanism. This mechanism, however, failed to explain the rate law obtained experimentally (Eq. (1)), because the rate law derived from Eqs. (2)—(8) should show the same order in hydroperoxide and in cobalt. Although the mechanism proposed by Richardson,[3] who assumes that cobalt exists as a dimer in acetic acid, agrees with the experimental rate law, the structure of cobalt in acetic acid is still uncertain; therefore, further investigation concerning the structure of cobalt is needed before we can reach a decision on the mechanism.

Effects of Lithium Perchlorate, Lithium Acetate and Water on the Rate. The effects of lithium perchlorate, lithium acetate, and cobalt acetate tetrahydrate on the rate of cobalt-catalyzed decomposition were investigated; the data are tabulated in Table 3. As can be seen from Table 3, the rate is decreased a little (except No. 1). Though these results may be explained in terms of a change in the redox potential or by the occupation of ligand sites by added anions, the decrease in the rate is too small for a detailed discussion.

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[7] H. A. Iddles and C. E. Jacksman, *Ind. Eng. Chem., Anal. Ed.*, **6**, 454 (1934).

[8] Previously, in a more detailed study with anhydrous cobalt acetate, the order in *t*-butyl hydroperoxide was reported to be 1.1 (at 55°C).[1a] Richardson[3] has reported a similar finding.

TABLE 3. THE EFFECT OF ADDED SALTS ON THE RATE
$[t\text{-}C_4H_9OOH]_0 = 1.65 \times 10^{-1}$ mol/l

No.		[Added Salt] $\times 10^2$ mol/l	[$Co(OAc)_2$] $\times 10^2$ mol/l	k $\times 10^4$ sec^{-1}
		—	1.82	2.05
1	LiOAc	1.68	1.79	2.05
2	LiOAc	5.24	1.83	1.83
3	$LiClO_4$	2.59	1.80	1.78
4	$Co(OAc)_2 \cdot 4H_2O$	1.81	—	1.61

Effects of Lithium Halide. Figure 2 shows the effect of lithium chloride on the decomposition rate. The addition of lithium chloride decreased the rate significantly, but the deep blue color of the reaction mixture did not change throughout the reaction and the linearity of the first-order plot in the hydroperoxide was retained. The addition of lithium bromide produced an unusual phenomenon; that is, an apparent induction period was recognized in the reaction if it was measured by the usual iodometric titration. Figures 3 and 4 show the plots of the apparent induction period and rate constant *vs.* the concentration of added lithium bromide. Under comparable conditions, the combination of cobaltous bromide and lithium acetate gave the same results as that of cobaltous acetate and lithium bromide, as seen from Figs. 3 and 4. The color of the reaction mixture was deep green during the apparent induction period; then it turned dark orange. This again became deep green when additional bromide ions were added to the mixture. From all of these facts it is obvious that the bromide ions are completely consumed during the reaction and that molecular bromine is liberated; these observations were verified spectrometrically. Figure 5 was obtained by a iodometric determination after the liberated

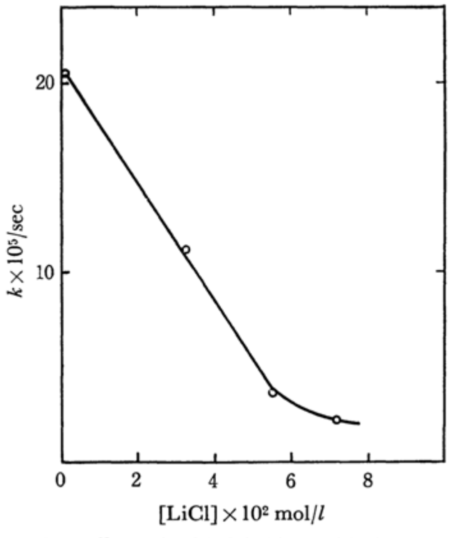

Fig. 2. Effect of added lithium chloride on the rate; initial concentrations: $[t\text{-}C_4H_9OOH]_0 = 1.64 \times 10^{-1}$ mol/l, $[Co(OAc)_2] = 1.82 \times 10^{-2}$ mol/l.

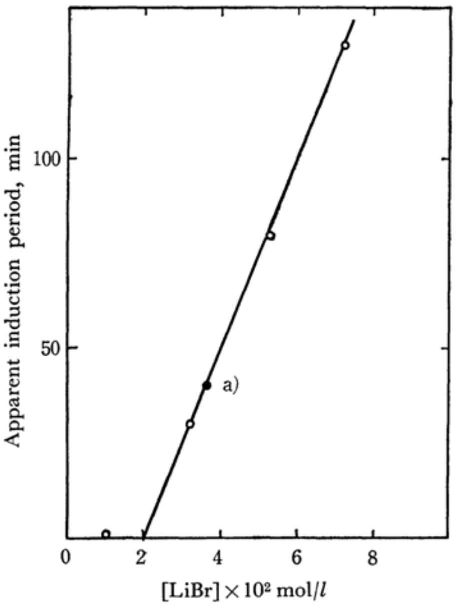

Fig. 3. Effect of added lithium bromide; initial concentrations: $[t\text{-}C_4H_9OOH]_0 = 1.60 \times 10^{-1}$ mol/l, $[Co(OAc)_2] = 1.80 \times 10^{-2}$ mol/l.
a) $[CoBr_2] = 1.82 \times 10^{-2}$ mol/l, $[LiOAc] = 3.61 \times 10^{-2}$ mol/l

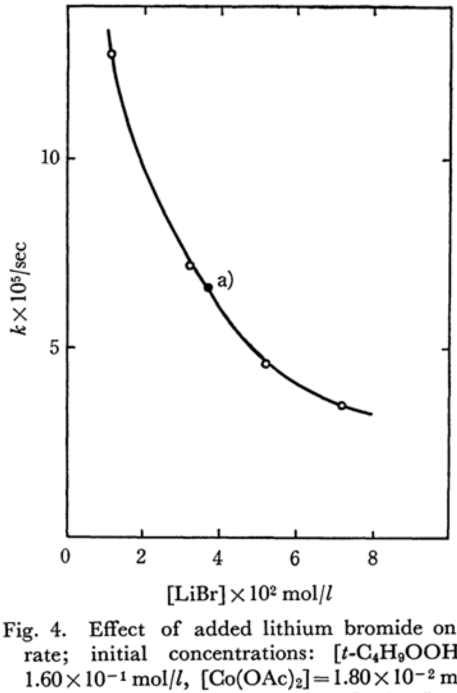

Fig. 4. Effect of added lithium bromide on the rate; initial concentrations: $[t\text{-}C_4H_9OOH]_0 = 1.60 \times 10^{-1}$ mol/l, $[Co(OAc)_2] = 1.80 \times 10^{-2}$ mol/l.
a) $[CoBr_2] = 1.82 \times 10^{-2}$ mol/l, $[LiOAc] = 3.61 \times 10^{-2}$ mol/l

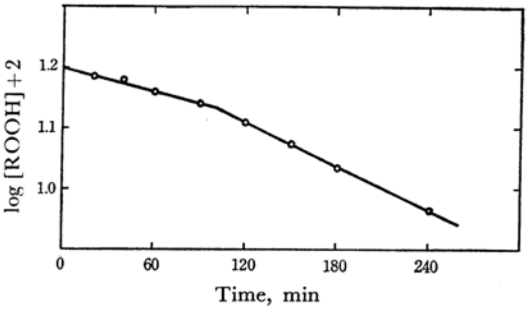

Fig. 5. First order rate plot when phenol is used for analysis; initial concentrations: $[t\text{-}C_4H_9OOH]_0=1.65\times10^{-1}$ mol/*l*, $[Co(OAc)_2]=1.82\times10^{-2}$ mol/*l*, $[LiBr]=7.10\times10^{-2}$ mol/*l*.

bromine had been removed with phenol, as has been described in the experimental section. In the figure it may be seen that, even during the apparent induction period, the decomposition of *t*-butyl hydroperoxide proceeds. Therefore, during this apparent induction period the amount of molecular bromine formed is equivalent to the amount of hydroperoxide decomposed.

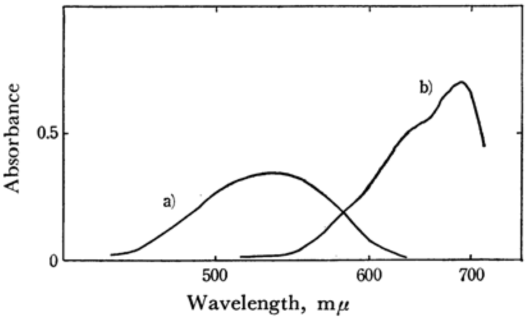

Fig. 6. Absorption spectra of cobalt salts in acetic acid;
a) $[Co(OAc)_2]=1.82\times10^{-2}$ mol/*l*,
b) $[Co(OAc)_2]=3.64\times10^{-3}$ mol/*l*, $[LiBr]=9.54\times10^{-3}$ mol/*l*.

Two subjects remain to be discussed, the marked decrease in the rate of decomposition by the addition of halide ions, and the liberation of molecular bromine. The reddish violet cobaltous acetate in acetic acid turned deep blue on the addition of lithium halide. As is shown in Fig. 6, the absorption of cobaltous acetate at 530 mμ disappeared and new absorptions appeared at 690 mμ in the case of bromide and at 580 mμ and 660 mμ in the case of chloride. In these cases the following equilibria, where X is Cl^- or Br^-, are likely to be operative, in which Co(OAc)X and CoX_2 mainly seem to be present[9,10]:

$$Co(OAc)_2 \rightleftharpoons Co(OAc)X \rightleftharpoons CoX_2 \rightleftharpoons CoX_3^- \rightleftharpoons CoX_4^{2-} \quad (9)$$

Proll and Sutcliffe[9,10] suggested in their study that cobaltous acetate in acetic acid exists in an octahedral form, but that, on the addition of lithium halide, it is converted to tetrahedral cobaltous halide. On the other hand, the trivalent cobaltic ion is known to exist in an octahedral form. On the basis of these facts, it seems that the decrease of the rate on the addition of halide arises from the difference in configuration; that is, the rearrangement from tetrahedral cobaltous halide to octahedral cobaltic halide needs more energy than does the change from octahedral cobaltous acetate to octahedral cobaltic acetate.

As a process of the formation of molecular bromine, a mechanism involving a radical according to Eqs. (10)—(12) may be considered:

$$Br^- + Co(III) \rightarrow Br\cdot + Co(II) \quad (10)$$

$$Br^- + RO\cdot \rightarrow Br\cdot + RO^- \quad (11)$$

$$2Br\cdot \rightarrow Br_2 \quad (12)$$

King and Pandow[11] reported a similar reaction, the oxidation of bromide ions to bromine by cerium(IV). As has been seen above, however, the amount of molecular bromine formed is equivalent to the amount of decomposed hydroperoxide. Therefore, the radical formation mechanism is not likely to be the main process. It may be concluded that the process of bromine formation can well be interpreted by the mechanism given by Eqs. (13)—(15);

$$Co^{II}Br + ROOH \rightarrow Co^{III}Br\cdots RO\cdot + OH^- \quad (13)$$

$$Co^{III}Br\cdots RO\cdot \rightarrow Co^{II} + ROBr \quad (14)$$

$$ROBr \xrightarrow[AcOH]{LiBr} ROH + Br_2 \quad (15)$$

that is, cobalt(II) reduces *t*-butyl hydroperoxide, and the resulting unstable cobalt(III) oxidizes the bromide ions immediately to form *t*-butyl hypobromite, which is then converted to alcohol and molecular bromine.[12]

In autoxidation, as is well known, cobaltous bromide is a very effective catalyst among many metal salts, and Hay and Blanchard[13] and other workers have stated that the real active species is $Co^{II}(OAc)Br$. On the contrary, it has been shown by this experiment (for example, Fig. (4)) that cobaltous bromide is not as effective as cobaltous acetate in the decomposition of the hydroperoxide. These results seem to suggest that the extraordinary activity of cobaltous bromide in autoxidation is connected with steps other than the initiation—hydroperoxide decomposition—step.

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[9] P. J. Proll, L. H. Sutcliffe and J. Walkley, *J. Phys. Chem.*, **65**, 455 (1961).
[10] P. J. Proll and L. H. Sutcliffe, *ibid.*, **65**, 1933 (1961).
[11] E. L. King and M. L. Pandow, *J. Am. Chem. Soc.*, **75**, 3063 (1953).
[12] M. Ambar, I. Dostrovsky, D. Samuel and A. D. Yoffe, *J. Chem. Soc.*, **1954**, 3603.
[13] A. S. Hay and H. S. Blanchard, *Can. J. Chem.*, **43**, 1306 (1965).