

### 388. Reactions of the Cobaltic Ion. Part VI.<sup>1</sup> Decomposition of Hydroperoxides in Aqueous Solution and in Glacial Acetic Acid.

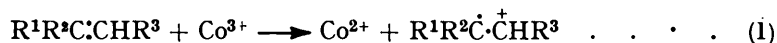
By J. A. SHARP.

The kinetics of the reaction of cobaltic ion with (a) *tert.*-butyl hydroperoxide in dilute sulphuric acid, glacial acetic acid, and acetic-sulphuric acid mixture; and (b) the hydroperoxide of 2-methylbut-2-ene in dilute sulphuric acid have been measured. The reaction in all the solvents obeys a bimolecular rate relation.

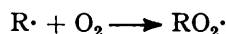
$$-d[\text{Co}^{3+}]/dt = k[\text{Co}^{3+}][\text{RO}\cdot\text{OH}]$$

and  $k$  for *tert.*-butyl hydroperoxide was 8.52, 0.78, and 0.0255 min.<sup>-1</sup> for 0.09N-H<sub>2</sub>SO<sub>4</sub>, 87½% acetic acid-12½% 10N-sulphuric acid (v/v), and glacial acetic acid respectively. This change in reactivity of the cobalt salt is a result of complex formation in solution. The bearing of the results on the autoxidation of olefins by the cobalt salt is discussed.

THE cobaltic ion interacts with the double bond of a series of unsaturated hydrocarbons



[scheme (1)] forming a very reactive radical ion.<sup>1</sup> This radical (R) could initiate the typical autoxidation chain reaction



where RH represents the hydrocarbon. On the other hand, the kinetic measurements of the autoxidation of some olefins<sup>2</sup> show that the initiating process is the reaction of the cobaltic ion with a hydroperoxide, invariably present in minute amounts in the olefin or readily formed by a thermal reaction



Which of these reactions initiates the chain is determined by the relative rates of schemes (1) and (2) Part IV. We measured the rates of reaction of cobaltic ion with hydroperoxides in dilute acid and in glacial acetic acid and compared the results with measurements of the direct reaction with the olefin. The results indicate that in acetic acid the decomposition of hydroperoxide is probably the chain-initiating reaction in olefinic oxidation.

*Decomposition of Hydroperoxide of 2-Methylbut-2-ene in Sulphuric Acid Solution.*—A solution of the hydroperoxide of 2-methylbut-2-ene was obtained by aqueous extraction of the hydroperoxide from the olefin which had been oxidised by air for two months. The aqueous solution also contained 2-methylbut-2-ene at its saturation value. The concentration of hydroperoxide was determined by adding an excess of a solution of ferrous sulphate in dilute sulphuric acid and determining the concentration of ferric ion by its absorption at 300 mμ with the Unicam spectrophotometer. The extinction coefficient of ferric sulphate in the same media was previously determined for calibration purposes.

In a solution of excess of the hydroperoxide the rate of disappearance of cobaltic ion followed a first-order relation as shown in Fig. 1. The rate was markedly dependent on hydrogen-ion concentration, in direct contrast to the results observed with the olefin alone (Part IV). Plots of the first-order rate constant,  $k_{\text{obs}}$ , against the reciprocal of the hydrogen-ion concentration for initial hydroperoxide concentrations of (1)  $2.86 \times 10^{-3}\text{M}$  and (2)  $0.60 \times 10^{-3}\text{M}$  are given in Fig. 2. These results show that at high hydrogen-ion concentration the hydroperoxide reaction becomes slow and of the same order as that of the direct olefin oxidation as indicated by the intercept on the ordinate. At hydrogen-ion concentrations above 0.1N the rate constant

<sup>1</sup> Parts IV and V, *J.*, 1957, 1854, 1866.

<sup>2</sup> Bawn, Pennington, and Tipper, *Discuss. Faraday Soc.*, 1951, 10, 282; Bawn, *ibid.*, 1953, 14, 181.

FIG. 1. First-order plot for decomposition of the hydroperoxide of 2-methylbut-2-ene by cobaltic sulphate at 20°

$a = 10^{-4}M$ ; Hydroperoxide concn. =  $2.86 \times 10^{-3}M$ .  
Hydrogen-ion concn.: (1) 3.30, (2) 1.67, (3) 0.67N.

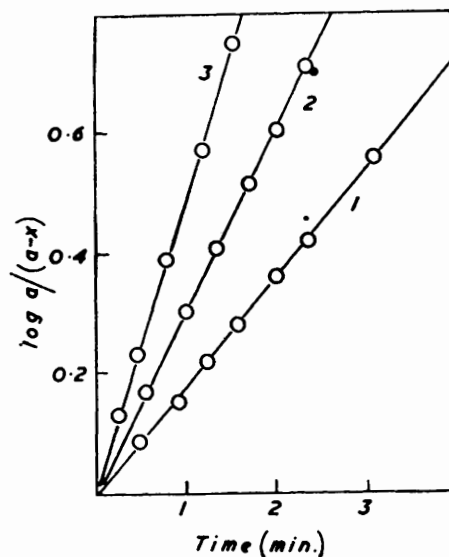


FIG. 2.

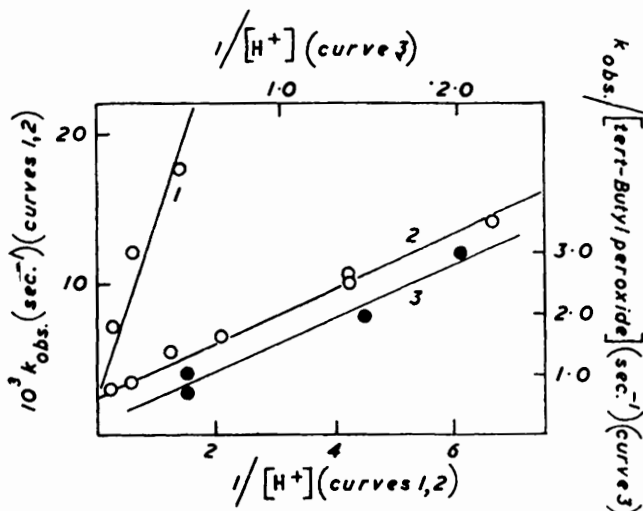
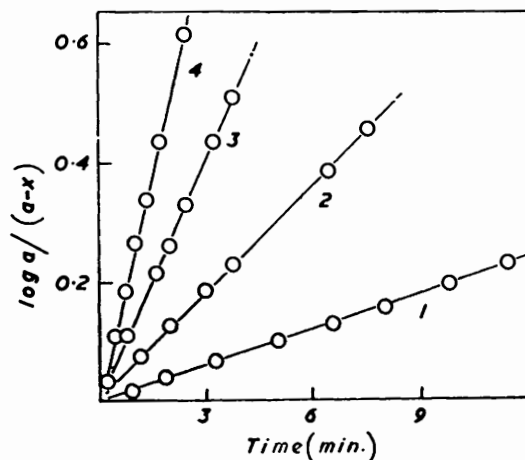


FIG. 3. First-order plot for decomposition of tert.-butyl hydroperoxide at 20°.

$a = 10^{-4}M$ . Curve (1):  $[RO\cdot OH] = 0.69 \times 10^{-3}M$ ;  $[H^+] = 2.0N$ ; Curve (2):  $[RO\cdot OH] = 2.76 \times 10^{-3}M$ ;  $[H^+] = 2.0N$ ; Curve (3):  $[RO\cdot OH] = 2.76M$ ;  $[H^+] = 0.67N$ ; Curve (4):  $[RO\cdot OH] = 3.28 \times 10^{-3}M$ ;  $[H^+] = 0.48N$ .



$k_{\text{obs}}$  was a linear function of  $1/[\text{H}^+]$  but at lower ones this relation is modified by the occurrence of the cobaltic ion-water reaction.

The general expression for the rate of loss of cobaltic ion may be written

$$-d[\text{Co}^{3+}]/dt = k[\text{Co}^{3+}][\text{RH}] + k'[\text{Co}^{3+}][\text{RO}\cdot\text{OH}] + k''[\text{Co}^{3+}][\text{RO}\cdot\text{OH}]/[\text{H}^+]$$

or 
$$-d \log [\text{Co}^{3+}]/dt = k_{\text{obs.}} = k[\text{RH}] + k'[\text{RO}\cdot\text{OH}] + k''[\text{RO}\cdot\text{OH}]/[\text{H}^+]$$

At large  $[\text{H}^+]$  the last term becomes negligible and the results in Fig. 2 show that under these conditions  $k_{\text{obs.}}$  (for constant 2-methylbut-2-ene concentration) was not appreciably changed for a 4.8-fold increase in hydroperoxide concentration. It is evident therefore that  $k' \ll k''$  and that the measured reaction is predominantly that between the cobaltic and hydroperoxide ions.

The value of  $k''$  calculated from  $dk_{\text{obs.}}/d(1/[\text{H}^+]) = k''$  for hydroperoxide concentrations of 0.60 and  $2.80 \times 10^{-3}$  are 1.65 and  $8.3 \times 10^{-3}\text{M}$  respectively and for  $k''/[\text{RO}\cdot\text{OH}]$  are 2.75 and 2.90  $\text{sec.}^{-1}$  respectively. The close agreement of these results justifies the first-order dependence of the rate on hydroperoxide concentration, and the representation of the overall rate by the equation

$$-d[\text{Co}^{3+}]/dt = k[\text{Co}^{3+}][2\text{-methylbut-2-ene}] + 2.8[\text{Co}^{3+}][\text{hydroperoxide}]/[\text{H}^+]$$

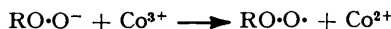
Comparison with the results of the direct reaction with the olefin (Part IV) shows that in 0.09M-sulphuric acid at 20° the bimolecular constant for the decomposition of 2-methylbut-2-ene hydroperoxide is 15.7 times the bimolecular constant of the oxidation of 2-methylbut-2-ene by cobaltic sulphate.

*Decomposition of tert.-Butyl Hydroperoxide in Acid Solution.*—This section records preliminary measurements on the reaction of cobalt ion with *tert.*-butyl hydroperoxide in acid carried out (a) to determine the effect of peroxidic impurities on the rate of the direct reaction with the olefin (Part IV) and (b) for comparison with the rate measurement in acetic acid and mixtures of acetic acid and sulphuric acid recorded in the next section. The rate of disappearance of cobaltic sulphate in the presence of excess of *tert.*-butyl hydroperoxide was observed by a procedure similar to that used to measure the oxidation of olefins (Part IV). The rates were of the first order with respect to cobaltic-ion concentration as shown in Fig. 3, and of first order with respect to hydroperoxide concentration (Table). Under the experimental conditions the decomposition of cobaltic ion by water was negligible, and the reaction with the hydroperoxide fast compared with the direct reaction with the olefin.

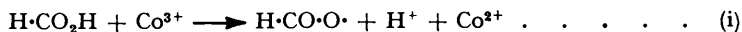
A plot of the bimolecular rate constant  $k$  as given by

$$-d[\text{Co}^{3+}]/dt = k[\text{Co}^{3+}][\text{RO}\cdot\text{OH}]$$

against the reciprocal of the hydrogen-ion concentration was linear (Fig. 2, curve 3) and hence the reaction rate obeys the relation  $-d[\text{Co}^{3+}]/dt = k'[\text{Co}^{3+}][\text{RO}\cdot\text{OH}]/[\text{H}^+]$  where  $k' = 1.42 \text{ sec.}^{-1}$  at 20°. This result indicates that the rate-determining reaction is that of the cobaltic ion with the hydroperoxide ion



The concentration of the hydroperoxide ion is given by  $[\text{RO}\cdot\text{O}^-] = K[\text{RO}\cdot\text{OH}]/[\text{H}^+]$  where  $K$  is the ionisation constant of the hydroperoxide. A similar result was observed for the reaction of formic acid with cobaltic ion:<sup>3</sup>



and it was found that the rate constants of (i) and (ii) were  $6.8 \times 10^{17} \exp(-26.9/RT)$  and  $2.0 \times 10^{18} \exp(-21.7/RT)$  respectively. With *tert.*-butyl hydroperoxide the experimental evidence indicates that reaction between cobaltic ion and the undissociated molecule was negligible compared with that of the hydroperoxide ion over the hydrogen-ion concentration range 0.5—2.0N.

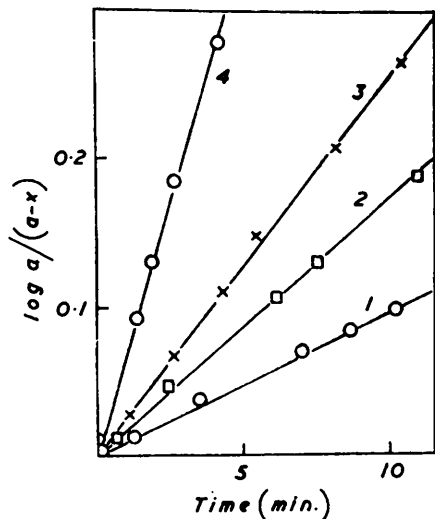
*Decomposition of tert.-Butyl Hydroperoxide in Glacial Acetic Acid and in Acetic-Sulphuric Acid Mixtures.*—On addition of a solution of 2-methylbut-2-ene in acetic acid to a solution of

<sup>3</sup> Bawn and White, *J.*, 1951, 331, 339, 344.

electrolytically prepared cobaltic acetate in glacial acetic acid, the absorption of the solution does not change over a period of days, showing that the olefin is not oxidised by cobaltic acetate. An identical experiment, in which cobalt acetate prepared by dissolving pure dry cobaltic sulphate in acetic acid was used, confirmed this result.

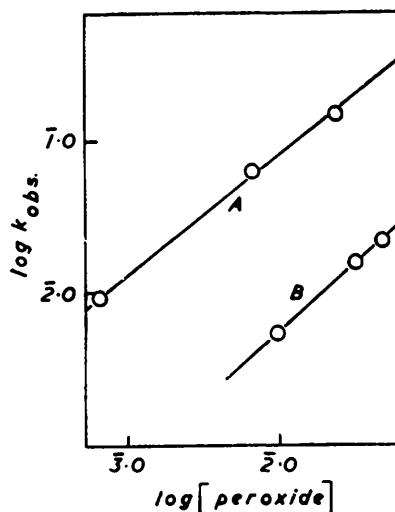
In the autoxidation of 2-methylbut-2-ene in acetic acid in the presence of cobaltic acetate, previous investigations<sup>3</sup> have established the formation of hydroperoxide as the initial product of the oxidation. Thus it is probable that the catalytic effect of cobaltic acetate in these systems depends on an initial reaction between cobaltic acetate and the hydroperoxide molecule formed thermally to yield a free radical which initiates a chain reaction.

FIG. 4. First-order plots of the reaction of cobaltic ion with *tert.*-butyl hydroperoxide in sulphuric acid mixtures at 20°.



$a = 1.92 \times 10^{-4}M$ . Curves (2) and (3), glacial acetic acid,  $[RO\cdot OH] = 5.0 \times 10^{-2}M$  and  $3.3 \times 10^{-2}M$  respectively. Curves (1) and (4), 87½% acetic acid–12½ 10N-sulphuric acid,  $[RO\cdot OH] = 0.066$  and  $0.66M$  respectively.

FIG. 5.



A, 87½% Acetic acid–12½% 10N-sulphuric acid.  
B, Glacial acetic acid.

In order to check this mechanism, the rate of reduction of cobaltic acetate by *tert.*-butyl hydroperoxide in glacial acetic acid was measured by observing the decrease in the absorption intensity of the cobaltic complex with the Unicam spectrophotometer as described in Part IV. The rate of this reaction was of the first order with respect to cobaltic acetate, as shown in Fig. 4.

The slope of the first-order plots was proportional to the concentration of *tert.*-butyl hydroperoxide and the plot of the logarithm of the rate constant so derived against the logarithm of the hydroperoxide concentration was linear and of slope of approximately 1.0 (Fig. 5).

The rate of reduction of cobaltic acetate in glacial acetic acid can therefore be represented by the expression  $-d[Co^{3+}]/dt = k[Co^{3+}][RO\cdot OH]$  where  $k = 0.0225 \text{ min.}^{-1}$  at 25°.

When cobaltic sulphate, dissolved in 87½% acetic acid–12½% 10N-sulphuric acid (v/v) was used in place of cobaltic acetate in glacial acetic acid the rate was still found to be of the first order with respect to cobaltic-ion concentration and approximately of the first order with respect to *tert.*-butyl hydroperoxide (Fig. 5), but now the value of  $k$  was increased by a factor of about 35, showing that the sulphate-acetate complex is a far stronger oxidising agent than pure cobaltic acetate.

The rate of reduction of cobaltic complex in 87½% acetic acid–12½% 10N-sulphuric acid at 25° is given by  $-d[Co^{3+}]/dt = 0.78[Co^{3+}][RO\cdot OH] \text{ min.}^{-1}$ . Therefore, in dilute sulphuric acid solution in which the cobaltic ion is not highly complexed the corresponding rate of reduction is more than 100 times faster than in the dilute mixed acids (Part IV). These comparative measurements emphasise the power of complex-forming groups in defining the oxidative power of the

cobaltic ion. A full discussion of the nature of the reaction which occurred in mixed acetic and sulphuric acid mixture will be given in Part VIII.

It may be concluded that cobaltic acetate in glacial acetic acid reacts immeasurably more quickly with the hydroperoxide than with the olefin, and that the catalysing power of cobaltic acetate in the oxidation of hydrocarbons is due to its reaction with hydroperoxide, present initially as impurity and rapidly produced in small amounts by a thermal chain reaction.

<i>tert.</i> -Butyl hydroperoxide (10 <sup>3</sup> M)	[H <sup>+</sup> ]	10 <sup>3</sup> <i>k</i> <sub>obs.</sub> (sec. <sup>-1</sup> )	<i>k</i> <sub>obs.</sub> [H <sup>+</sup> ]/[RO·OH] (mole l. sec. <sup>-1</sup> )
2.76	2.0	2.16	1.65
2.76	0.70	5.18	1.32
0.69	2.00	0.75	2.16
3.28	0.48	10.1	1.54

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