352. *Reactions of the Cobaltic Ion. Part V.* Oxidation of Olefins by Cobaltic Salts in Acetic Acid–Sulphuric Acid Mixtures.*

C. E. H. Bawn and J. A. Sharp.

In contrast to the oxidation of olefins by cobaltic salts dissolved in dilute sulphuric acid, similar olefins are not oxidised by a cobaltic acetate solution in glacial acetic acid. We have measured the rate of oxidation of 2-methylbut-2-ene, oct-1-ene, and 2 : 4 : 4-trimethylpent-2-ene in mixed acetic–sulphuric acids. The rate of reaction depends on the solvent used for the cobaltic salt. With cobaltic sulphate initially dissolved in sulphuric acid and the olefin in glacial acetic the second-order reaction between Co^{3+} and the olefin agrees very closely with measurements in dilute sulphuric acid (Part IV*). On the other hand, the oxidation of olefins dissolved in acetic acid by cobaltic sulphate dissolved in acetic acid–sulphuric acid obeys a first-order relation for the rate of reduction of the cobaltic complex, independent of the olefin concentration. The drastic change in kinetics is interpreted as being due to the formation of a stable complex cobaltic sulphate–acetate ion.

In Part IV* it was shown that olefins are readily oxidised by solutions of cobaltic salts in dilute sulphuric acid, the rate-determining step being the abstraction of an electron from the double bond by the cobaltic ion. Glacial acetic acid is commonly used as solvent for non-aqueous oxidations and, in contrast with the previous results in aqueous acid, it is observed that neither the straight-chain nor the branched olefins were oxidised by cobaltic acetate in this solvent. Solutions of the olefins in glacial acetic acid containing cobaltic acetate (prepared both by electrolytic oxidation and by dissolution of dry cobaltic sulphate in acetic acid) showed no change in absorption over several days. It is shown in Part VI (in the press) that cobaltic acetate dissolved in glacial acetic acid decomposes hydroperoxides and that the cobaltic complex in acetic–sulphuric acid mixtures is a much stronger oxidising agent than cobaltic acetate alone. We now report measurements of the oxidation of olefins in mixed acids; it is observed that the cobaltic complex formed by the addition of the cobaltic salt to acetic acid containing added sulphuric acid oxidised the olefin more slowly than in sulphuric acid alone. The rate of reduction of the cobaltic complex by the olefin also obeyed a different kinetic relation from that found with aqueous sulphuric acid solution although the products of the reactions were unaltered.

Experimental

The transformation of the cobaltic complex to the cobaltous state was followed by light-absorption measurements with the Unicam spectrophotometer and temperature-controlled cell described in the preceding paper.

The solution of the oxidising agent in acetic–sulphuric acid mixtures was prepared by adding the cobaltic sulphate solution in sulphuric acid to glacial acetic acid before the commencement of measurement. The olefin was dissolved in glacial acetic acid.

I. *Oxidation of Olefins dissolved in Glacial Acetic Acid by Cobaltic Sulphate Solution in Acetic Acid–Sulphuric Acid.*—*2-Methylbut-2-ene.* The rate of change of cobaltic into cobaltous ion was of the first order with respect to the cobaltic complex concentration as is shown by a series of typical plots given in Fig. 1 (a = initial molar concentration of cobaltic ion). Variation of the olefin concentration over a very wide range with all other variables of concentration fixed had no marked influence on the rate of reduction of the cobaltic complex as shown by the summarised results of Table 1. A similar series of rate measurements carried out for a range of sulphuric and acetic acid concentrations also summarised in Table 1 show that the composition of the acid mixture, and thus the hydrogen-ion concentration, had no influence on the rate of reaction. The value of the first-order constants ($k_{obs.} = -d \log_{10} x/dt$) for the region in which cobaltic concentration is similar to or less than that of the olefin could not be measured very

---

* Part IV, preceding paper.

accurately since the concentration of the olefin decreased appreciably during the course of the reaction. However, even these results demonstrated the small effect of change of the initial olefin concentration.

The effect of temperature on the rate of oxidation of 2-methylbut-2-ene was measured for the solution of composition acetic acid 14·8N, sulphuric acid 1·33N, and olefin 0·0125M. The logarithms of the observed first-order constants plotted against the reciprocal of the temperature were linear and the slope corresponds to an activation energy for the reaction of 30·8 kcal./mole.

TABLE 1. *Oxidation of* 2-*methylbut*-2-*ene dissolved in glacial acetic acid by cobaltic sulphate dissolved in acetic acid–sulphuric acid mixtures.*

$a = 1{\cdot}92 \times 10^{-4}$M. Temp. = 24·9°.

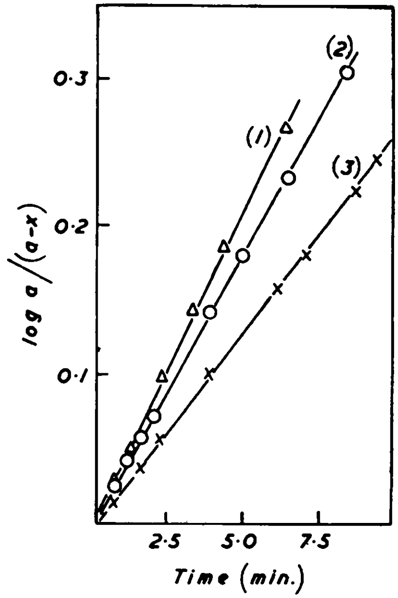
$Me{\cdot}CO_2H$ (M)	H_2SO_4 (N)	Olefin (M)	$k_{obs.}$ (min.$^{-1}$)
14·9	1·25	0·480	0·0362
		0·0283	0·0240
		0·00085	0·0180
13·0	2·1	0·00282	0·020
		0·00048	0·026
		0·00028	0·0229
16·3	0·42	0·302	0·0422
		0·047	0·0265
		0·0094	0·0339

TABLE 2. *Oxidation of oct*-1-*ene by cobaltic complex in acetic acid–sulphuric acid mixture.*

$a = 1{\cdot}92 \times 10^{-4}$M.

$Me{\cdot}CO_2H$ (M)	H_2SO_4 (N)	Olefin (M)	$k_{obs.}$ (min.$^{-1}$)	Temp.
16·3	0·42	0·0554	0·0213	22·0°
		0·0111	0·0162	
		0·277	0·0144	
14·2	1·66	0·0221	0·0145 *	
			0·0163 *	
			0·0120 †	20·0
			0·0116 †	

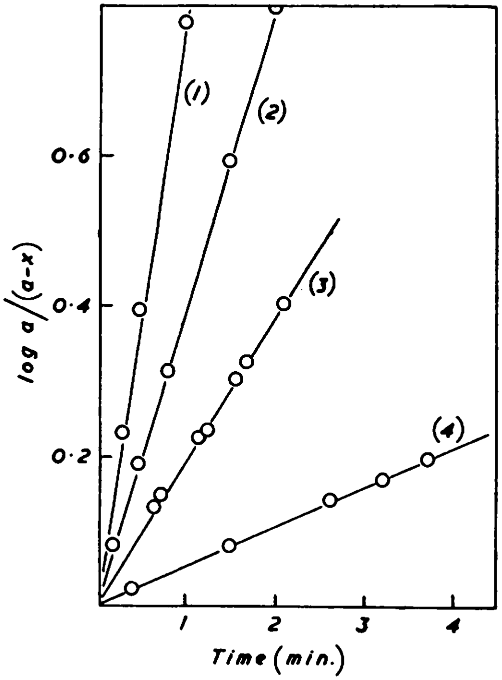
FIG. 1. *First-order plot of the reduction of* Co^{3+}.



Acetic acid–sulphuric acid: (1, 3) 16·3M–0·42M; curve (2) 14·9M–1·25M. $a = 1{\cdot}92 \times 10^{-4}$M.

Concn. of 2-methylbut-2-ene: (1) 0·302M; (2) 0·48M; (3) 0·047M.

FIG. 2. *First-order plots of the reduction of* Co^{3+} *by* 2-*methylbut*-2-*ene.*



$a = 1{\cdot}92 \times 10^{-4}$M. Concn. of 2-methylbut-2-ene: (1) $1{\cdot}44 \times 10^{-2}$M; (2) $0{\cdot}72 \times 10^{-2}$M; (3) $0{\cdot}36 \times 10^{-2}$M; (4) $0{\cdot}12 \times 10^{-2}$M. Temp. = 20·4°.

Oct-1-*ene and* 2 : 4 : 4-*trimethylpent*-2-*ene.* Measurements with these hydrocarbons were carried out as with 2-methylbut-2-ene. The rate of cobaltic-ion consumption was of the first order with both olefins and, as shown by the results presented in Tables 2 and 3, the rate of reaction was only slightly dependent on olefin concentration. Hence the kinetic relations are similar for the three hydrocarbons and the rate constants are also of similar magnitude. The rate of reduction of the cobaltic complex by hex-1-ene and hept-1-ene could not be measured by the light-absorption method since the addition of sulphuric acid to solutions of these olefins in glacial acetic acid produced deep green and blue colours, respectively. That these coloured compounds, which may be addition complexes between the olefins and sulphuric acid, have no influence on the rate of oxidation of the olefin was shown by measurements of rates of reactions in which all reactant concentrations were kept constant and (*a*) the sulphuric acid was added to the solution of olefin in acetic acid several hours before addition of the cobaltic compound or (*b*) the cobaltic ion in the required concentrations of sulphuric and acetic acids was added to the olefin in glacial acetic acid. Two such pairs of experiments with oct-1-ene are denoted by * and † in Table 2 and it may be concluded that addition-compound formation of the olefin and sulphuric acid did not affect the rate of oxidation.

Products of Oxidation.—The products of the oxidation of 2-methylbut-2-ene by the cobalt complex formed in 90% acetic acid–10% 10N-sulphuric acid were analysed by the methods described in Part IV. The reactants formed a homogeneous solution and reduction of the cobaltic state was complete within 1 hr. The average analysis from several experiments, excluding acids which were difficult to separate from acetic acid, was

$$9{\cdot}5 \text{ 2-Methylbut-2-ene} + 20\ \mathrm{Co}^{3+} \longrightarrow 3{\cdot}12 \text{ carbonyl group (mainly acetone)} + 0{\cdot}04 \text{ diene}$$

In spite of the marked change in kinetic relations these results show that the type and relative distribution of the products were very similar to those observed in aqueous sulphuric acid (Part IV).

TABLE 3. *Oxidation of 2 : 4 : 4-trimethylpent-2-ene by cobaltic complex in acetic acid–sulphuric acid mixture.*

$a = 1{\cdot}92 \times 10^{-4}$M. Temp. = 22·0°.

$Me{\cdot}CO_2H$ (M)	H_2SO_4 (N)	Olefin (M)	$k_{obs.}$ (min.$^{-1}$)
16·3	0·42	0·0111	0·0126
14·9	1·25	0·0332	0·0157
16·3	0·42	0·0554	0·0146
16·3	0·42	0·277	0·0227

TABLE 4. *Oxidation of 2-methylbut-2-ene in acetic acid–sulphuric acid mixtures.*

Temp. = 20·4°. $a = 1{\cdot}92 \times 10^{-4}$M.

$Me{\cdot}CO_2H$ (M)	H_2SO_4 (N)	Olefin (100 × M)	$k_{obs.}$ (min.$^{-1}$)	$\frac{k_{obs.}}{[\text{olefin}]}$
8·5	5·0	1·44	0·74	51
			0·78	54
		0·72	0·404	56
			0·378	53
		0·36	0·191	53
			0·197	55
		0·12	0·055	46

DISCUSSION

The first-order relation for the reduction of the cobaltic complex independent of acid and olefin concentration can be explained by either of the following mechanisms. (1) An intermediate complex is formed between the olefin and the cobaltic salt, the first-order decomposition of which is the rate-determining step. This mechanism is unlikely since it would require immediate and fairly complete complex-formation of the reactants even when the metal ion and olefin were at approximately equal concentration. We have sought the formation of such a complex with cobaltic salts without finding any indication of its existence. (2) The first-order dissociation of the cobaltic acetate complex gives an active cobaltic ion complex which reacts rapidly with the olefin. The rate-determining step here would be the dissociation process which could be imagined to occur by an S_N1 type of mechanism as observed with six other substitution reactions of complex cobalt salts.[1] Although the precise structures cannot as yet be formulated the process may be pictured broadly as

$$\text{Cobaltic acetate complex} \xrightarrow[\text{slow}]{} \text{Active cobaltic complex} \xrightarrow[\text{fast}]{\text{olefin}} \mathrm{Co}^{2+} + \text{Products}$$

II. *Oxidation of 2-Methylbut-2-ene dissolved in Acetic Acid by Cobaltic Sulphate dissolved in Sulphuric Acid.*—When a solution of cobaltic sulphate dissolved in 10N-sulphuric acid instead

---

[1] Ingold, " Kinetics and Mechanism of Inorganic Reactions in Solution," *Chem. Soc. Special Publ. No.* 1, 1954, p. 10.

of acetic–sulphuric acid mixtures was added to an equal volume of a solution of 2-methylbut-2-ene in glacial acetic acid, the rate of reduction of the cobaltic compound was of the first order with respect to the cobaltic-ion concentration as before, as shown by the first-order plot in Fig. 2, and was now also of the first order with respect to the olefin concentration (Table 4). At 20·4° the kinetic relation

$$-d[Co^{3+}]/dt = 2{\cdot}0[Co^{3+}][\text{2-methylbut-2-ene}]\ (\text{moles l.}^{-1}\ \text{sec.}^{-1})$$

was obeyed. This bimolecular rate expression was in very close agreement with that obtained (Part IV) for the oxidation of 2-methylbut-2-ene by cobaltic sulphate in dilute sulphuric acid. Hence under the above experimental conditions the cobaltic ion reacts in the same way as in dilute sulphuric acid solution and is therefore reacting with the olefin before conversion into the more stable cobaltic sulphate–acetate complex. These results indicate that the drastic change in the rate and the kinetic relationships on dissolving cobaltic sulphate in an acetic acid–sulphuric acid mixture is caused by complex-formation of the cobaltic ion and that the reactivity of the olefin is not changed by previous dissolution in acetic acid.

DEPARTMENT OF INORGANIC AND PHYSICAL CHEMISTRY,
THE UNIVERSITY, LIVERPOOL.

[*Received, October* 12*th*, 1956.]