351. *Reactions of the Cobaltic Ion. Part IV.* The Oxidation of Olefins by Cobaltic Salts.*

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

The kinetics of the reaction of cobaltic ion with eight unsaturated hydrocarbons (2-methylbut-2-ene, pent-2-ene, hex-1-ene, hept-1-ene, oct-1-ene, 2-ethylbut-1-ene, styrene, and isoprene) in dilute sulphuric acid obey a second-order rate law, and it is shown that the primary reaction is the direct attack of the cobaltic ion at the double bond by electron transfer with the formation of a reactive radical ion :

$$\mathrm{R{\cdot}CH{=}CH_2 + Co^{3+} \longrightarrow R{\cdot}\dot{C}H{-}\overset{+}{C}H_2 + Co^{2+}}$$

The secondary reaction to give the observed products (aldehydes, ketones, acids, and small amounts of diene) results from a series of reactions in which the carbonium ion reacts with water to give hydroxylic compounds which are then rapidly oxidised by the cobaltic ion in successive stages until stable products are formed. The energetics of the primary process are discussed.

Cobalt salts are extensively used as catalysts in the autoxidation of aldehydes and saturated and unsaturated hydrocarbons and in these reactions the cobalt is usually used in the form of the salt of an organic acid which is soluble in the organic substrate. Studies of the oxidation by molecular oxygen of aldehydes and unsaturated hydrocarbons in glacial acetic acid with cobaltous acetate as catalyst have established that the activity of the catalyst resides in the higher-valency cobaltic state which is formed during the oxidation.[1] Other studies have shown that the cobaltic ion readily undergoes electron-transfer with a wide variety of organic molecules forming a free radical[2] and it is the latter reaction which is the initial stage in the oxidation processes. In order to elucidate the catalytic effect of cobalt salts in autoxidation the kinetics and mechanism of the reaction between cobaltic ion and olefins in dilute acid solution have been studied. In the following papers results are reported for the corresponding measurements in glacial acetic–sulphuric acid mixtures and for the reaction of cobaltic salts with hydroperoxides.

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* Part III, *J.*, 1951, 344.

[1] Bawn, Tipper, and Pennington, *Discuss. Faraday Soc.*, 1951, **10**, 282; Bawn, *ibid.*, 1953, **14**, 181; Bawn and Williamson, *Trans. Faraday Soc.*, 1951, **47**, 721, 735.

[2] Bawn and White, *J.*, 1951, 311, 339, 344; Hargreaves and Sutcliffe, *Trans. Faraday Soc.*, 1955, **51**, 786.

EXPERIMENTAL

Cobaltic sulphate was prepared by the method of Swann and Xanthakos [3] and stored in a dark bottle at 0°.

2-Methylbut-2-ene was obtained by dehydration of *n*-pentyl alcohol with its own volume of 48% sulphuric acid at 80°; the hydrocarbon which distilled off was dried ($CaCl_2$), fractionated (b. p. 38·4° ± 0·1°/760 mm.), and stored at −78° under nitrogen.

Pent-2-ene was isolated from technical pentene by stirring it with its own volume of 50% sulphuric acid for 5 hr. at 0° to dissolve 2-methylbut-1- and -2-ene. The insoluble hydrocarbon was washed with a saturated solution of sodium hydrogen carbonate, dried ($CaCl_2$), and fractionated; the fraction boiling at 36·4° ± 0·5°/760 mm. was collected and stored under nitrogen at −78°.

2-Ethylbut-1-ene (from Messrs. Light) was washed with a saturated solution of sodium hydroxide, dried ($CaCl_2$), and fractionated. The hydrocarbon distilling over at 66·6° ± 0·2° was collected.

Styrene and isoprene were purified from stabiliser by washing them with a saturated solution of potassium hydroxide, followed by distillation under reduced pressure.

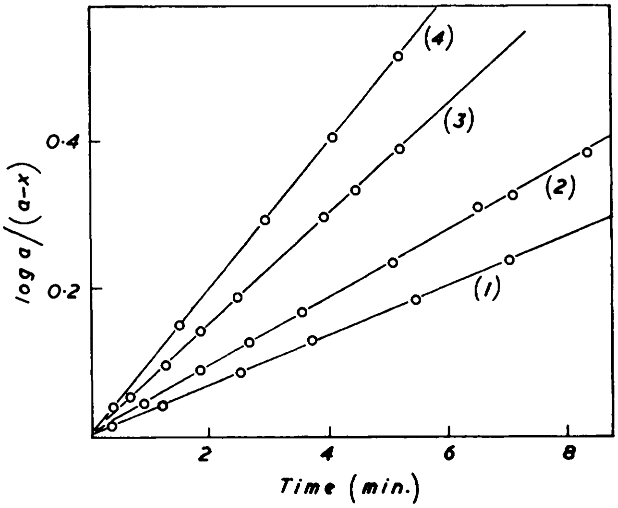

FIG. 1. *First-order plot for reduction of cobaltic sulphate by 2-methylbut-2-ene in 0·09M-sulphuric acid at 23·2°.*

μ = 0·112, $a = 10^{-4}$M. Concentrations of olefin: (1) 0·76 × 10^{-3}M, (2) 1·04 × 10^{-3}M, (3) 1·71 × 10^{-3}M, (4) 2·27 × 10^{-3}M.

Hex-1-ene, hept-1-ene, oct-1-ene, and 2 : 4 : 4-trimethylpent-2-ene, presented by Imperial Chemical Industries Limited, Billingham Division, had been fractionated with high-precision stills. They were freed from hydroperoxide impurity by shaking them either with a saturated solution of sodium hydroxide or by passage through alumina.

Other materials used in this work were " AnalaR," not further purified.

Apparatus.—The reaction vessel consisted of a cylindrical quartz cell, length 10 cm. and diameter 1·5 cm., encased in a brass jacket through which water at a controlled temperature (within ±0·03° for temperatures from 12° to 45°) was pumped at a rate of 2 l. per min. The cell could be fixed into supports between the cell housing and photocell box of the Unicam spectrophotometer.

Analysis.—*Olefin.* Standard solutions of olefin were prepared by dissolving known volumes in water. To obtain the limits of solubility and to check the concentration of the solution the two following methods were used: (1) Olefins in aqueous solution absorb strongly in the range 180—210 mμ and the absorption was found to be proportional to the olefin concentration. Addition of 20% of ethyl alcohol enabled olefin concentrations greater than the maximum solubility in water to be determined. In these determinations the spectrum was measured against a corresponding alcohol–water blank. (2) The olefin was extracted from a known volume of aqueous solution by shaking it with a weighed quantity of Nujol (ratio Nujol : olefin *ca.* 15 : 1) and the refractive index of the solution measured with an Abbé refractometer. This

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[3] Swann and Xanthakos, *J. Amer. Chem. Soc.*, 1931, **53**, 400.

method gave results accurate to ±3% for aqueous solutions and was used largely to check the much more accurate absorption method.

Cobaltic salts. In the absence of olefins, cobaltic ion was determined by addition of excess of standard ferrous ion and back titration either with potassium permangante, the end point being determined potentiometrically by the differential titration method of Garman and Droz,[4] or with ceric sulphate, the indicator being *o*-phenanthroline. In the presence of the olefin and its oxidation products the permanganate method could not be used and the cobaltic-ion concentration was determined by light absorption. The absorption spectra of cobaltic sulphate solutions whose concentration had been determined by the above analytical procedures were measured from 200 mμ to 1000 mμ and shown to obey Beer's law. By use of this method solutions containing 10^{-5}—10^{-1}M-cobaltic ion could be determined within ±0·5% in the presence of olefins and the oxidation products. This method was used for all solutions whose extinction curves were known.

Procedure.—A standard aqueous solution of sulphuric acid–sodium hydrogen sulphate was shaken with sufficient olefin to saturate the solution. The solution was syphoned free from undissolved olefin and the olefin estimated. A known small volume of standard cobaltic sulphate in dilute sulphuric acid was shaken with a known volume of standard olefin solution, the mixture poured into the reaction cell, the cell placed in position, and the optical density measured within 10 sec. of mixing the two solutions and subsequently at ten-second intervals.

Reaction-rate Measurements.—In the presence of a large excess of olefin, the rate of disappearance of cobaltic ion was found to be accurately of the first order (Figs. 1 and 2), the first-order constants, $k_{\text{obs.}}$, being a linear function of the olefin concentration (Fig. 3) ($a = [\text{Co}^{3+}]_{\text{initial}}$, $x = [\text{Co}^{3+}]$ at time t). All the olefins investigated obeyed these relations. The plot of rate constant against olefin concentration intercepted the rate axis at the value corresponding to the reduction of cobaltic sulphate by the water. In sufficiently acid solutions the latter reaction was negligible.

The reaction rate may therefore be expressed

$$-\text{d}[\text{Co}^{3+}]\text{d}t = k[\text{Co}^{3+}][\text{olefin}] + k'[\text{Co}^{3+}][\text{water}]$$

Thus the velocity constant, $k_{\text{obs.}}$, for the consumption of cobaltic ion at a fixed olefin concentration will be given by $k_{\text{obs.}} = k[\text{olefin}] + k'[\text{water}]$. Since $k'[\text{water}]$ is constant for any temperature and sulphuric acid concentration the second-order rate constant k can be obtained from the slope of the plot of $k_{\text{obs.}}$ against olefin concentration as shown in Fig. 3.

Effect of ionic strength. In 0·09M-sulphuric acid increase of the ionic strength μ from 0·11 to 2·0 by addition of potassium hydrogen sulphate (the salt being assumed to exist entirely as K^+ and HSO_4^- ions) reduced the bimolecular rate constant by 17%, showing that primary salt effects were absent. The rate constants for the different olefins were compared at a constant value of $\mu = 2·0$.

Effect of oxygen and cobaltous sulphate. In view of the catalysis of the autoxidation of olefins by cobalt salts experiments were carried out both with carefully de-aerated solutions and in the presence of air. These showed that the presence of atmospheric oxygen in the solutions did not affect the kinetics. Cobaltous sulphate—the product of the oxidation—also had no influence on the reaction. An increase in the concentration of added cobaltous sulphate from zero to 0·1 mole/l. (*i.e.*, 10^3 × initial cobaltic concentration) did not affect the rate constant.

TABLE 1.

Temp. = 23·20°. Ionic strength = 2·0. $a = 10^{-4}$ g.-ion/l.

$[H_2SO_4]$	0·09	0·31	0·45	0·825	1·75	2·0
10^3[2-methylbut-2-ene]	$1·08 \times 10^{-3}$	0·926	1·03	0·97	0·48	0·71
k (l. mole^{-1} sec.$^{-1}$)	1·34	1·29	1·19	1·56	1·29	1·42

Variation of hydrogen-ion concentration. For a series of sulphuric acid solutions of both oct-1-ene and 2-methylbut-2-ene, variation of the acid concentration from 0·09M to 2M at constant ionic strength 2 had no effect on the rate (Table 1). The rate of reduction of the cobaltic sulphate was therefore not affected by the change in hydrogen-ion concentration.

Variation of rate with olefin structure. The values of the second-order rate constants for the

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[4] Garman and Droz, *Analyt. Chem.*, 1939, **11**, 398.

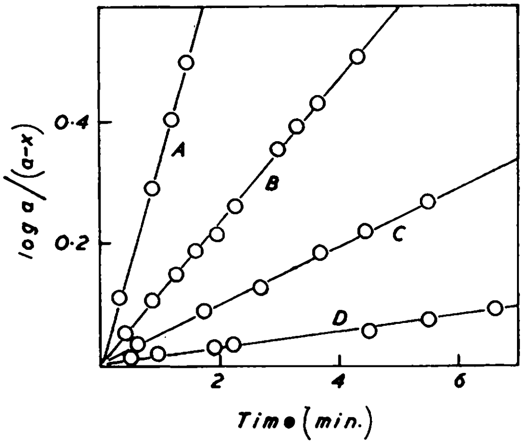

FIG. 2. *Variation of rate of reduction of cobaltic sulphate by hexene with temperature in* 0·09M-*sulphuric acid.*

μ = 0·112, a = 10^{-4}M. *A*, 44·1°; *B*, 37·4°; *C*, 30·60°; *D*, 24·85°.

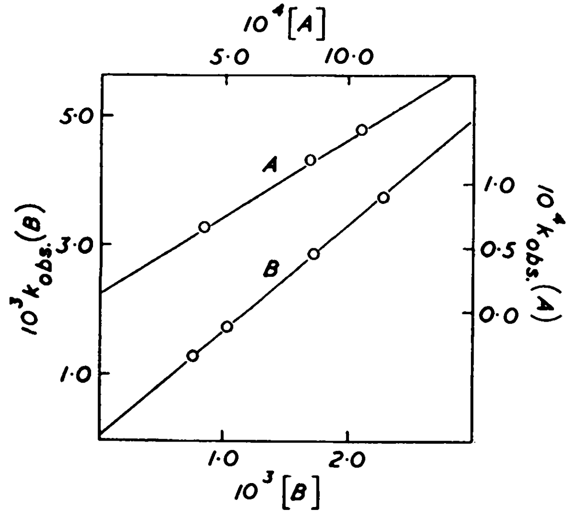

FIG. 3. *Dependence of rate of reduction of cobaltic ion on olefin concentration in* 0·09M-*sulphuric acid.*

A, Oct-1-ene at 19·8°; *B*, 2-methylbut-2-ene at 23·2°. $10^3k_{obs.}$ = − d ln x/dt (sec.$^{-1}$).

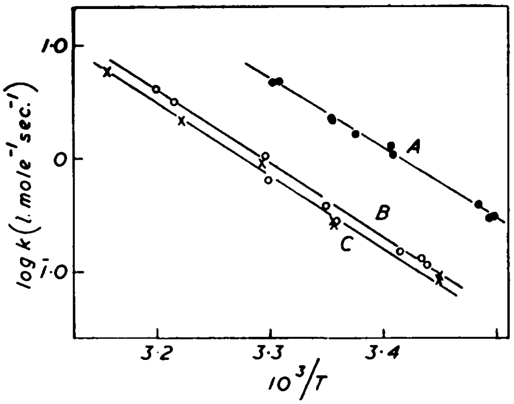

FIG. 4. *Temperature variation of rate of reduction of cobaltic ion by three olefins in* 0·09M-*sulphuric acid* (μ = 0·112).

A, 2-Methylbut-2-ene; *B*, oct-1-ene; *C*, hex-1-ene.

reduction of cobaltic sulphate by eight olefins were measured in 0·09M-sulphuric acid at 25°; the values of the constants are given in Table 2 ($\mu = 2{\cdot}0$).

TABLE 2.

Olefin	k (l. mole^{-1} sec.$^{-1}$)	Type of olefin	Olefin	k (l. mole^{-1} sec.$^{-1}$)	Type of olefin
2-Methylbut-2-ene	2·19	Trialkyl-ethylene	Hept-1-ene	0·368	Monoalkyl-ethylene
Pent-2-ene	0·903	Dialkyl-ethylene	Oct-1-ene	0·369	,, ,,
2-Ethylbut-1-ene	0·751	,, ,,	Styrene	7·38	Phenyl-ethylene
Hex-1-ene	0·321	Monoalkyl-ethylene	Isoprene	6·20	Conjugated diene

These results show that increase in reactivity of the olefin occurs (*a*) on increasing the number of alkyl substituents on the double-bonded carbon atoms, (*b*) by introduction of an aromatic grouping, and (*c*) by conjugation. It was not possible to determine directly the influence of groupings such as carboxyl, hydroxyl, etc., on the reactivity of the double bond since preferential reaction occurred with the substituent grouping. Thus oxidation of crotonic acid by cobaltic sulphate in dilute sulphuric acid obeyed the rate relationship

$$-\mathrm{d}[\mathrm{Co}^{3+}]/\mathrm{d}t = 0{\cdot}0108[\mathrm{Co}^{3+}][\mathrm{CH_3{\cdot}CH{=}CH{\cdot}CO_2H}]/[\mathrm{H}^+]$$

at 25° showing that the crotonate ion was attacked by the cobaltic ion; by comparison, the oxidation at the double bond occurs at a negligible rate. Substitution of the dissociation constant of crotonic acid in the above equation gives

$$\mathrm{d}[\mathrm{Co}^{3+}]/\mathrm{d}t = 494[\mathrm{Co}^{3+}][\mathrm{CH_3{\cdot}CH{=}CH{\cdot}CO_2}^-]$$

The corresponding value of k for the formate ion [3] reaction was 161.

Temperature coefficient. The second-order rate constants for the oxidation of 2-methylbut-2-ene, oct-1-ene, and hex-1-ene were measured over the range 16—36° and the three Arrhenius plots are shown in Fig. 4. The values of the activation energies and the frequency factors are summarised in Table 3.

Products of Olefin Oxidation.—On account of the low solubility ($\sim 2{\cdot}0 \times 10^{-3}$M) of the olefins in aqueous solution it was not possible to isolate and characterise the products of the oxidation under the conditions of the kinetic measurements. In order to obtain sufficient product the cobaltic sulphate solution in 2—10N-sulphuric acid was shaken with an excess of (insoluble) olefin (progressive solution of the olefin occurring as the reaction proceeded) until all the cobaltic ion had reacted. The products from 200 ml. of aqueous solution and any dissolved in the relatively small volume of unoxidised olefin film were analysed.

TABLE 3.

Olefin	k at 25° (l. mole^{-1} sec.$^{-1}$)	E (kcal./mole)	A	S^* (cal./deg.)
2-Methylbut-2-ene	2·19	27·1 ($\pm 0{\cdot}4$)	$1{\cdot}6 \times 10^{20}$	32·2
Oct-1-ene	0·369	28·5 ($\pm 0{\cdot}9$)	$3{\cdot}1 \times 10^{20}$	33·6
Hex-1-ene	0·321	29·0 ($\pm 0{\cdot}4$)	$5{\cdot}9 \times 10^{20}$	34·8

With most of the olefins all the products were volatile. The aqueous solution was distilled in a small fractionating column, the products being collected at 0°. Each successive 10% of the distillate was analysed independently. Glycols, which would not distil under these conditions, were sought both by the periodate–arsenite method [5] and by periodate oxidation followed by aldehyde determination [6] and shown to be absent. Formaldehyde was determined before distillation by use of chromotropic acid [7] since heating in the presence of olefin and sulphuric acid may lead to its partial removal by the Prins condensation. Individual fractions of the distillate were analysed for organic acids, aldehydes, and ketones as follows: (*a*) Acids (total) were estimated from the difference between the sulphuric acid as determined by titration against sodium hydroxide (bromophenol blue) and the total acid concentration (phenolphthalein). Formic acid was determined by reduction to formaldehyde (with magnesium and dilute hydrochloric acid) which was estimated by the chromotropic acid method. The reduction is not complete and the method was calibrated for the formic acid concentrations in

[5] Reinke and Luce, *Ind. Eng. Chem.* (*Anal.*), 1946, **18**, 244.

[6] Feigl, "Spot Tests," Elsevier, New York, 3rd edn., 1947, p. 326.

[7] Bricker and Johnson, *Ind. Eng. Chem.* (*Anal.*), 1945, **17**, 400.

the range $5{\cdot}0 \times 10^{-4}$M to 10^{-3}M. Under fixed conditions of reduction the ratios of formic acid reduced to formaldehyde produced was reproducible within ±5%. (*b*) Acetaldehyde was detected in the presence of formaldehyde by the red colour produced and by its reaction with diazobenzenesulphonic acid. Measurement by absorption was accurate only to within ±25% owing to the low extinction coefficient of the product. A semiquantitative method dependent on the coloration in Schiff's reaction in neutral solution followed by light absorption determination agreed with results of the first method in that acetaldehyde accounted for less than 0·5% of the products. (*c*) Ketones were identified by isolation as 2 : 4-dinitrophenylhydrazones. Quantitative determination of ketone was effected by measuring the acid liberated when the ketone reacted with hydroxylamine hydrochloride.[8]

These general analytical procedures were supplemented by specific methods of identification and estimation as described below.

Analytical Results.—*2-Methylbut-2-ene.* A series of product determinations are summarised in Table 4. The ketone was identified as acetone; its 2 : 4-dinitrophenylhydrazone whose spectrum and m. p. agreed with the literature data. The absorption spectrum of one of the distillates showed a strong absorption maximum at 230 mμ characteristic of a conjugated system. This product was not formed by the interaction of 2N-sulphuric acid and the hydrocarbon, nor was it initially present as an impurity. Its identity as isoprene was established by (*a*) comparison of its absorption spectra with that of isoprene in water and ether, (*b*) determination of the partition between water and ether, and (*c*) the rate of polymerisation in aqueous solution as determined by the rate of decrease of maximum optical density. The formation of formaldehyde and formic acid also provided indirect evidence for the formation of isoprene since the latter is readily oxidised to these products by cobaltic sulphate.

The analyses indicate that the following simultaneous oxidations occur in the presence of excess of olefin :

$$\mathrm{Me_2C{:}CHMe} + \mathrm{Co^{3+}} \longrightarrow \mathrm{Me_2CO} + \mathrm{Me{\cdot}CHO} + \mathrm{Me{\cdot}CO_2H} \quad \text{. . . . . . . (i)}$$

or

$$\mathrm{Me_2C{:}CHMe} + \mathrm{Co^{3+}} \longrightarrow \mathrm{CH_2{:}CMe{\cdot}CH{:}CH_2} \quad \text{. . . . . (ii)}$$

$$\mathrm{CH_2{:}CMe{\cdot}CH{:}CH_2} + \mathrm{Co^{3+}} \longrightarrow \mathrm{H{\cdot}CHO} + \mathrm{H{\cdot}CO_2H} + \text{other products in small amounts} \quad \text{. (iii)}$$

The concentration of isoprene in solution increased to a stationary value determined by the condition that the rate of production equals the rate of oxidation of isoprene. Since the concentration of the 2-methylbut-2-ene was fixed at its saturation limit the amount of isoprene in solution should be proportional to the total volume of the solution and this is in

TABLE 4. *2-Methylbut-2-ene.*

Series :	1	2	3	4	5
Reaction conditions	Continuous shaking until complete reduction of Co^{3+}				Distillation of product prior to complete reduction
Vol. and concn. of Co$_2$(SO$_4$)$_3$ taken originally	153 ml. of 0·169N	258 ml. of 0·176N	163 ml. of 0·032N	1150 ml. of 0·016N	96 ml. of 0·136N
∴ Co^{3+} (g.-ions) taken	0·0259	0·0459	0·00523	0·0186	0·013
2-Methylbut-2-ene (moles) consumed	0·0127	0·0192	0·0019	0·0079	0·0029
Ratio of Co^{3+} reduced to olefin consumed	2·01	2·36	2·75	2·35	4·46
Ratio of acetone produced to olefin consumed	0·271	0·29	0·40	—	0·55
Ratio of carboxylic acid produced to olefin consumed	0·315	0·35	0·396	0·51	0·57
Ratio of acetaldehyde produced to olefin consumed	0·024	0·040	0·036	0·080	trace
Ratio of formaldehyde produced to olefin consumed	0·0008	0·0008	0·0004	0·0011	,,
Ratio of diene produced to olefin consumed	0·00138	0·00133	0·00835	0·0202	negligible
Diene concn. in product (M)	0·00012	0·000098	0·000093	0·00014	,,
Formic acid in carboxylic acid (%)	13·9	16·0	17·3	7·0	15·1
Ratio of Co^{3+} reduced to Co^{3+} reqd. to yield product	0·875	1·02	0·99	—	1·20

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[8] Milton and Waters, "Quantitative Microanalysis," Arnold, London, 1949, p. 124.

agreement with the results of series 1—4, Table 4. In series 5 the shaking was stopped before the cobaltic sulphate had been consumed. Under these conditions the 2-methylbut-2-ene in solution is rapidly consumed and thus the rate of isoprene formation decreased whilst any isoprene in solution is further oxidised. The stationary concentration of isoprene therefore rapidly falls to zero as observed experimentally.

The relative amounts of formic acid and acetic acid (or acetone) in the products (Table 4) show that approximately 8% of the 2-methylbut-2-ene is oxidised *via* isoprene. The analytical results may be expressed as

$$\begin{aligned}1{\cdot}00\ \text{2-Methylbut-2-ene} + 2{\cdot}01\ \mathrm{Co^{3+}} &\longrightarrow 0{\cdot}271\ \text{Acetone} + 0{\cdot}315\ \text{Acetic acid} + 0{\cdot}021\ \text{Acetaldehyde}\\ 0{\cdot}00138\ \text{Isoprene} &\longrightarrow 0{\cdot}051\ \text{Formic acid} + 0{\cdot}0008\ \text{Formaldehyde}\end{aligned}$$

Calculation of the amount of cobaltic ion required to oxidise 2-methylbut-2-ene to these products gives the value of 2·30, compared with the average experimental value of 2·01. The agreement is satisfactory and it may be concluded that all the main products of the oxidation have been characterised and estimated. The detailed mechanism of the reaction will be discussed later in this paper.

2-*Ethylbut*-1-*ene*. The oxidation products in dilute sulphuric acid were determined in the same manner as those from 2-methylbut-2-ene; the main ones were formic acid and diethyl ketone. No diene was formed. Summation of the products gave the stoicheiometric relation

$$\begin{aligned}3{\cdot}34\ \text{2-Ethylbutene} + 9{\cdot}3\ \mathrm{Co^{3+}} \longrightarrow 1{\cdot}38\ \text{Formic acid} + 1{\cdot}42\ \text{Diethyl ketone}&\\ + \text{ unchanged 2-ethylbutene}&\end{aligned}$$

showing that the reaction occurred mainly by the rupture of the double bond to yield the two products isolated.

Pent-2-*ene*. The analyses from three experiments summarised in Table 5 show that the course of the oxidation is very similar to that of 2-methylbut-2-ene. The main reaction is the rupture of the olefin double bond to give aldehydes which are rapidly oxidised to acids while a secondary reaction leads to diene formation. The diene formed was not completely characterised but was most probably penta-1 : 3-diene. As in the case of 2-methylbut-2-ene the concentration of the diene reaches a stationary value when its rate of formation is equal to its rate of loss by oxidation and therefore

$$k_1F[\mathrm{Co^{3+}}][\text{pent-2-ene}] = k_2[\mathrm{Co^{3+}}][\text{diene}]$$

where F is the fraction of the pent-2-ene which is oxidised *via* the diene and k_2 is the bimolecular rate constant for the oxidation by cobaltic sulphate. The latter value has not been measured and so in deriving F from the above equation the corresponding value of k_2 for isoprene was used. The value of F so derived indicated that 14—15% of the hydrocarbon was oxidised *via* the diene. This should give a percentage yield of formic acid of 7·3%. The agreement with the experimental values (Table 5) of 6·9, 8·0, and 8·1% is somewhat fortuitous in view of

TABLE 5. *Pent-2-ene.*

Reaction conditions	Continuous shaking until all $\mathrm{Co^{3+}}$ reduced		
Vol. and concn. of $\mathrm{Co_2(SO_4)_3}$ taken originally	163 ml. of 0·15N	2400 ml. of 0·0095N	180 ml. of 0·014N
∴ $\mathrm{Co^{3+}}$ (g.-ions) taken	$2{\cdot}35 \times 10^{-2}$	$2{\cdot}28 \times 10^{-2}$	$2{\cdot}5 \times 10^{-3}$
Vol. of pent-2-ene (ml.) consumed	1·5	0·98	0·148
Pent-2-ene (moles) consumed	$1{\cdot}5 \times 10^{-2}$	$9{\cdot}8 \times 10^{-3}$	$1{\cdot}48 \times 10^{-3}$
Ratio of $\mathrm{Co^{3+}}$ reduced to pent-2-ene consumed	1·57	2·32	1·69
Ratio of carboxylic acids produced to pent-2-ene consumed	0·352	0·60	0·41
Formic acid in carboxylic acid (%)	8·1	8·0	6·9
Ratio of formaldehyde produced to pent-2-ene consumed	$1{\cdot}3 \times 10^{-4}$	—	—
Ratio of other aldehydes produced to pent-2-ene consumed	$1{\cdot}1 \times 10^{-2}$	—	—
Diene concn. in product (M)	2·9	1·03	2·0
Ratio of diene produced to pent-2-ene consumed	$1{\cdot}31 \times 10^{-4}$	$1{\cdot}05 \times 10^{-3}$	$1{\cdot}01 \times 10^{-2}$
Absorption max. (mμ)	225	224	224
Calculated ratio of $\mathrm{Co^{3+}}$ reduced to pent-2-ene consumed	1·41	2·40	1·64
Ratio of $\mathrm{Co^{3+}}$ reduced to $\mathrm{Co^{3+}}$ reqd. to yield products	1·11	0·97	1·03

the approximations employed. However, the result does show that the formation of diene and its further oxidation can be treated quantitatively.

The results of the three analyses show that the mechanism of oxidation is

$$\mathrm{Et{\cdot}CH{:}CHMe + Co^{3+}} \xrightarrow{86\%} \mathrm{Et{\cdot}CHO + Me{\cdot}CHO} \longrightarrow \mathrm{Et{\cdot}CO_2H + MeCO_2H}$$

$$\mathrm{Me{\cdot}CH{:}CH{\cdot}CH{:}CH_2} \xrightarrow{14\%} \mathrm{H{\cdot}CO_2H} + \text{other products}$$

*Oct-*1*-ene.* Oxidation showed that reaction occurred at the double bond to give formic acid and heptanoic acid. No diene or ketone was formed, indicating the absence of secondary mechanisms :

$$\mathrm{C_6H_{13}{\cdot}CH{=}CH_2 + Co^{3+}} \longrightarrow \mathrm{C_6H_{13}{\cdot}CO_2H + H{\cdot}CO_2H}$$

Summary of Product Analyses.—All the results show that oxidation of the olefins with terminal double bonds by cobaltic sulphate splits the olefin at the double bond to give saturated aldehydes, which are rapidly oxidised to acids. With olefins in which the double bond is not in the terminal position, oxidative disruption of the olefin at the double bond is the main reaction, but a small fraction of olefin is oxidised to the diene by a secondary mechanism. The diene is itself oxidised by cobaltic sulphate, oxidative disruption again occurring at the double bonds.

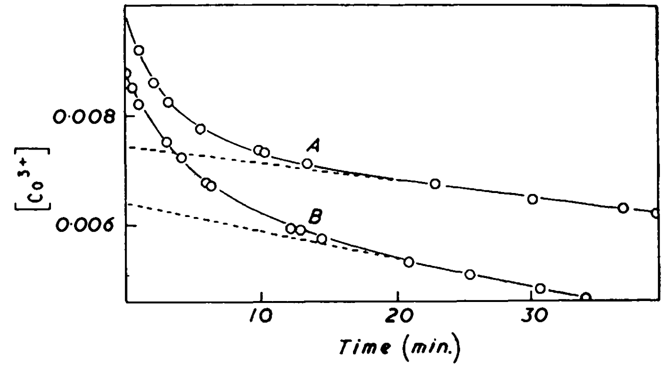

FIG. 5. *Rate of change of cobaltic ion concentration.*

When one of the doubly bonded carbon atoms is dialkyl-substituted, one of the main products formed on disruption of the double bond is a ketone. The ketone formed was relatively stable to cobaltic sulphate and was not further oxidised in the presence of excess of olefin.

Stoicheiometry.—The stoicheiometric ratio of cobaltic ion to 2-methylbut-2-ene reacting was determined by carrying out the reaction in the presence of an excess of cobaltic ion. Measurements of the change of cobaltic-ion concentration by light absorption showed that the rate of reduction to Co^{2+} was initially rapid, becoming slow when 4—5 cobaltic ions per molecule of 2-methylbut-2-ene had been reduced. Typical plots of the change of cobaltic ion concentration with time are shown in Fig. 5. The amount of cobaltic sulphate reduced in the initial fast reaction was determined by extrapolation of the slow reaction to zero time as indicated by the broken line. The values for the stoicheiometric ratio (Table 6) show that 4—5 equivalents of Co^{3+} are consumed per molecule of olefin in the faster reaction. The slower reaction corresponds to the further oxidation of the initial products and the significance of these results will be discussed later.

TABLE 6.

Run	10^3 × Concn. of 2-methylbut-2-ene (M)	10^3 × Concn. of cobaltic ion used (g.-ion/l.)	Stoicheiometric ratio Co^{3+}/2 methylbut-2-ene
41	0·33	1·77	5·36
42	0·66	2·80	4·24
43	0·40	2·17	5·43

DISCUSSION

The kinetics of the acid-catalysed hydration of olefins in aqueous solution have been studied by Lucas and his co-workers [9] who showed that the effective catalyst was the hydroxonium ion. The addition occurs by the two-stage process

$$\mathrm{R{\cdot}CH{=}CH_2 + H{\cdot}OH_2^+ \longrightarrow R{\cdot}\overset{+}{C}H{-}CH_3 + OH_2}$$

$$\mathrm{R{\cdot}\overset{+}{C}H{-}CH_3 + OH_2 \longrightarrow R(CH{\cdot}OH_2^+){\cdot}CH_3}$$

The evidence now summarised indicates that this is not the primary step in the reaction of the olefins with cobaltic ions: (1) The reaction in all cases was found to be independent of the hydrogen-ion concentration, which is not in agreement with the possibility of the olefin's reacting as an alkoxonium ion. A study of the kinetics of the oxidation of *tert.*-amyl alcohol by cobaltic ion (the product of the hydration of 2-methylbut-2-ene) showed that the rate depended very markedly on the hydrogen-ion concentration and was similar to that found by Bawn and White [2] for the lower primary alcohols. (2) The absorption spectrum of the olefin solution showed the absence of hydration under the experimental conditions. (3) The reported rate of hydration of olefins under similar conditions to those used by us were much slower than the rate of oxidation by cobaltic sulphate. (4) The second-order rate kinetics observed show that the initiation reaction is a direct attack of the cobaltic ion at the double bond. The evidence presented indicates that this reaction is an electron extraction with the formation of a reactive radical ion, *viz.*:

$$\mathrm{R{\cdot}CH{=}CH_2 + Co^{3+} \longrightarrow R{\cdot}\dot{C}H{-}\overset{+}{C}H_2 + Co^{2+}}$$

The small change in velocity constant caused by a 20-fold change in ionic strength also supports the view that the measured reaction is that between the cobaltic ion and an uncharged molecule. The independence of the reaction rate on hydrogen-ion concentration also indicates that the reactive species is the hydrated cobaltic ion rather than the ion pair $(\mathrm{Co,OH})^{2+}$. It would be expected that the rate of oxidation by $(\mathrm{Co,OH})^{2+}$ would be slower than that by Co^{3+} and in the oxidation of benzene by cobaltic perchlorate Baxendale and Wells [10] observed that the activation energy of the ion-pair reaction was 17 kcal. greater than that of the hydrated ion. Both the last reactions were, however, measurable owing to the favourable entropy of activation of the ion-pair reaction.

Energetics of Primary Process.—The heat of the reaction

$$\mathrm{(RHC{=}CH_2)_{aq} + Co^{3+} \longrightarrow (RH\overset{+}{C}{-}\dot{C}H_2)_{aq} + Co^{2+}{}_{aq}} \quad \dots\dots \quad (1)$$

can be calculated from the energy of ionisation of cobaltous ion and ΔH_1 as determined by the following cycle:

$$\begin{tikzcd}
\mathrm{(RHC{=}CH_2)_g} \arrow[r, "I_O"] & \mathrm{(RH\overset{+}{C}{-}\dot{C}H_2)_g + e} \arrow[d, "Q_O^+"] \\
\mathrm{Co^{3+} + (RHC{=}CH_2)_{aq}} \arrow[u, "Q_O"] \arrow[r, "\Delta H_1"] & \mathrm{(RH\overset{+}{C}{-}\dot{C}H_2)_{aq} + Co^{2+}}
\end{tikzcd}$$

where I_O is the ionisation potential of the olefin, and Q_O and $Q_O{}^+$ are the heat of solution of olefin and radical ion respectively. $Q_O{}^+$ has not been measured and was assumed to be equal to the heat of hydration of the carbonium ion $\mathrm{Me_2CH^+}$, *ca.* 74 kcal.[12] I_O = 220·2 kcal. for monoalkyl olefins and Q_O was taken as approximately equal to the latent

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[9] Lucas and Liu, *J. Amer. Chem. Soc.*, 1934, **56**, 2138; Lucas and Eberz, 1934, **56**, 460.
[10] Baxendale and Wells, *Discuss. Faraday Soc.*, 1953, **14**, 239.

heat of vaporisation (= 5·0 kcal.). The ionisation potential of the cobaltous ion in aqueous solution (J) can be derived from the following reaction :

$$Co^{2+}{}_{aq} + H^{+}{}_{aq} \xrightarrow{\Delta H_2} Co^{3+}{}_{aq} + \tfrac{1}{2}(H_2)_{aq}$$

$$J = \Delta H_2 + \tfrac{1}{2}D(H_2) + I(H) - Q(H^+)$$

where $D(H_2)$ is the dissociation energy of hydrogen and $Q(H^+)$ is the heat of solution of the proton. The free energy of the cobaltous–cobaltic change referred to the hydrogen electrode is 42·5 cal. and ΔH_2 can be determined from $\Delta H = \Delta G - T\Delta S$ by use of the entropy relation :

$$S_2 = S(Co^{3+}) + \tfrac{1}{2}S(H_2) - S(Co^{2+}) - S(H^+)$$

Now $S(Co^{2+}) = -27$, $\tfrac{1}{2}S(H_2) = 15{\cdot}6$, $S(H^+) = 0$, and $S(Co^{3+}) = -71{\cdot}8$ e.u. and hence $S_2 = -29{\cdot}2$ e.u. The entropy of the cobaltic ion was estimated by comparison with the entropies and ionic radii of Cr^{3+} and Fe^{3+} :

Ion	Ionic radius (Å)	Entropy in aqueous soln. at 25°
Cr^{3+}	0·62	−73·5
Co^{3+}	0·63	—
Fe^{3+}	0·64	−70·1

Hence $\Delta H_2 = 33{\cdot}8$ kcal. and the ionisation potential of the cobaltous ion in solution is 117·3 kcal., as obtained from the above equation by using $D(H_2) = 104{\cdot}1$, $I(H) = 313{\cdot}4$, and $Q(H^+) = 282$ kcal., respectively. The endothermicity of the electron abstraction from a monoalkyl-olefin by the cobaltic ion is given by

$$\Delta H = \Delta H_1 - J = Q_O + I_O - Q_O{}^+ - J = 33{\cdot}9 \text{ kcal.}$$

A similar calculation of the endothermicity of the reaction $(Me_2C{=}CHMe)_{aq} + Co^{3+}{}_{aq} \longrightarrow (Me_2\overset{+}{C}{-}\dot{C}HMe)_{aq} + Co^{2+}{}_{aq}$ gave a value of 21·6 kcals. The heat of solution of the radical ion was assumed to be that of Me_3C^+ (= 69·0 kcal.) and the ionisation potential of trimethylethylene according to Honig [11] is 17·3 kcal. less than that of the monosubstituted ethylene. Within the limits of the accuracy of the thermochemical data the endothermicities approximate closely to the observed activation energies of 29 and 27 kcal. respectively. On energetic grounds therefore it may be concluded that reaction (1) is probable.

Effect of Substitution on Olefin Reactivity.—Comparison of the bimolecular rate constants at 25° shows that trialkylolefins react about 6 times as fast as the monoalkylethylenes and that dialkylethylenes react 2—3 times as fast as the monoalkyl derivatives. Although E (Table 3) cannot be measured with the same accuracy as the rate constant the result shows that the effect of substitution largely affects the activation energy and not the frequency factor. These results may be understood in terms of the energy of the transformation

$$(R{\cdot}CH{=}CH_2)_{aq} \longrightarrow (R{\cdot}\overset{+}{C}H{-}\dot{C}H_2)_{aq} + e \quad . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

since the $Co^{3+}{}_{aq} \longrightarrow Co^{2+}{}_{aq}$ reaction contributes a constant energy term independent of the olefin. The endothermicity of eqn. (2) is given by $\Delta H_2 = S_i{}^+ - S_i - I$ where $(S_i{}^+ - S_i)$ is the difference of solvation energies of the ion-radical and the olefin and I is the ionisation potential of the olefin. We make the reasonable assumption that $S_i{}^+$

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[11] Honig, *J. Chem. Phys.*, 1948, **16**, 105.

[12] Evans, *Trans. Faraday Soc.*, 1946, **42**, 722.

depends on the number of groups attached directly to the positive carbon atom and that substitution farther away has a negligible effect. For the change from a secondary to a tertiary ion Evans [12] showed that $(S_i^+ - S_i)$ was approximately -5 kcal. The ionisation potentials of the olefins and styrene as measured by electron-impact and spectrosopic data are summarised in Table 7 together with the values of ΔH_2.

TABLE 7.

	Ionisation potential			
	Electron impact	Spectroscopic	$\Delta(S_i^+ - S_i)$	ΔH_2
2-Methylbut-2-ene	—	8·75	−0·22	−8·98
Pent-2-ene	9·16	9·16	0	−9·16
2-Ethylbut-1-ene	—	—	0	—
Hex-1-ene	9·59	—	0	−9·59
Hept-1-ene	9·54	—	0	−9·52
Oct-1-ene	9·52	—	0	−9·52
Styrene	8·82	8·81	0	−8·81
Isoprene	9·08	—	0	−9·08

Since the configuration of the transition state will be similar for all the olefins it is to be expected that variation of the energy of activation ΔE with change of substituent attached to the double bond will be related to the endothermicity of the reactions. This conclusion is in agreement with the estimated changes in ΔH_2 for the three cases in which the energy of activation was measured. Moreover, since the main influence of the substitutent is reflected in the change of ΔE and not the entropy of activation ΔS^*, it is justifiable to compare ΔH_2 with changes in the measured rate of reaction. This shows very clearly that changes in k follow closely those in ΔH_2, and the results indicate a relationship between ΔE and ΔH of the form $\Delta E = \alpha\Delta H$ as observed with other systems in which the structure of one of the reactants has been varied.

Parallel effects of substituents in influencing reactivity seem to be characteristic of the reaction of olefins with positive groups and similar results have been observed in measurements of the rate of bromination,[13] acid-catalysed hydration,[14] oxidation by peracetic acid,[15] and in the ionic polymerisation of olefins.[16]

The very high values of the entropy of activation of about 30 e.u. are much greater than usually observed in the reaction between an ion and a neutral molecule, and correspond to a considerable increase in the degrees of freedom of the reaction system. Although the combination of an olefin molecule and a cobaltic ion to form the activated complex occurs with a decrease in translational degrees of freedom of the reactants there will be a considerable increase in the degrees of freedom of the water molecules released from the hydration shell of the cobaltic ion. In the transition complex the charge will be distributed on the olefin and the metal ion. The olefin can be regarded as breaking up the symmetry of the hydration shell by displacing some of the water molecules in forming the complex. This large increase in entropy also supports the view that the hydrated cobaltic ion (entropy = −71·3 e.u.) is the reactive species rather than the ion-pair $(Co,OH)^{2+}$ (entropy estimated by analogy with $FeOH^+$ to be −24·0 e.u.) since reactions between ions and molecules usually involve small entropy changes and the increase in entropy is greater for reactions of an ion which has the more negative entropy.

Secondary Oxidation Reactions.—The main course of the oxidation to give the observed products—ketones, aldehydes, acids, etc.—must result from the disruption of the double bond and this occurs by a series of reactions in which the carbonium ion reacts with water to give hydroxylic compounds which are then rapidly oxidised by the cobaltic ion in

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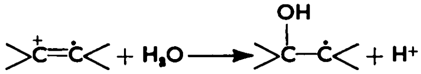
[13] Anantakrishnan and Ingold, *J.*, 1935, 984.

[14] Lucas and co-workers, *J. Amer. Chem. Soc.*, 1934, **56**, 2138; Lucas and Eberz, 1934, **56**, 460.

[15] Swern, *Chem. Rev.*, 1949, **45**, 48.

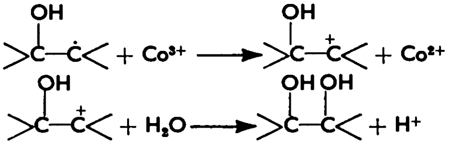
[16] Norris and Halpern, *J. Amer. Chem. Soc.*, 1927, **49**, 873.

successive stages until relatively stable products are formed. Thus, after the rate-determining reaction (1), the radical ion reacts with the aqueous solvent according to



$$>\overset{+}{C}=\dot{C}< + H_2O \longrightarrow >\overset{OH}{\overset{|}{C}}-\dot{C}< + H^+$$

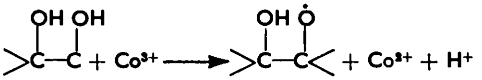
The radical formed is stable to water but reacts rapidly with Co^{3+}, since the ionisation potential of this type of radical (6·5—7·6 e.v.) is very much lower than that of the initial olefin (8·8—9·7 e.v.), to give a carbonium ion which on further reaction with water gives a glycol:



$$>\overset{OH}{\overset{|}{C}}-\dot{C}< + Co^{3+} \longrightarrow >\overset{OH}{\overset{|}{C}}-\overset{+}{C}< + Co^{2+}$$

$$>\overset{OH}{\overset{|}{C}}-\overset{+}{C}< + H_2O \longrightarrow >\overset{OH}{\overset{|}{C}}-\overset{OH}{\overset{|}{C}}< + H^+$$

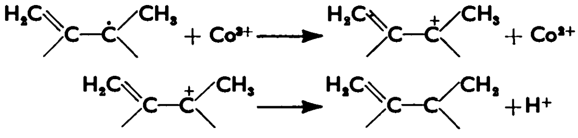
Glycols are readily oxidised by cobaltic salts and glycol fission ensues by a one-electron transfer with the formation of a free radical as in the above reactions, *viz.*,



$$>\overset{OH}{\overset{|}{C}}-\overset{OH}{\overset{|}{C}} + Co^{3+} \longrightarrow >\overset{OH}{\overset{|}{C}}-\overset{\dot{O}}{\overset{|}{C}}< + Co^{2+} + H^+$$

The radical so formed rapidly disrupts into an aldehyde R·CHO or ketone RR′CO and the radical $>\dot{C}\text{-}OH$. The last, by further reaction with Co^{3+}, again gives an aldehyde or ketone. A similar reaction scheme has been postulated by Drummond and Waters [17] and by Duke and his co-workers [18] for the oxidation of pinacol by manganic and ceric salts respectively. The aldehydes formed in these secondary reactions are further oxidised by a similar series of successive single-electron transfer and hydroxylation steps to yield carboxylic acids. This reaction scheme consisting of a series of simple electron-transfer processes of the cobaltic ion not only explains the formation of the products but is in agreement with the observed stoicheiometry of the overall oxidation.

The small amount of diene in the final product indicates that the radical ion $>\overset{+}{C}\text{-}\dot{C}<$ can lose a proton to yield a resonance-stabilised allylic radical. The latter is oxidised by Co^{3+} to a carbonium ion which splits off a hydrogen ion to form the diene, for example



The absence of diene in the oxidation of olefins having terminal double bonds is in conformity with these views.

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[17] Drummond and Waters, *J.*, 1953, 435.

[18] Duke and Bremer, *J. Amer. Chem. Soc.*, 1951, **73**, 5179; Duke and Forist, *ibid.*, 1947, **69**, 2790.