Kinetics of the Oxidation of Ethylbenzene by Cobaltic Acetate in Acetic Acid

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Under nitrogen and in the absence of strong acid, the reduction of cobaltic acetate by oxidation of ethylbenzene in acetic acid obeys kinetics that can be explained by assuming that cobalt atoms are associated in the dinuclear species Co^{III}–Co^{III} and Co^{III}–Co^{II}, only the former being active for oxidation. In the presence of trichloroacetic acid, similar kinetics are observed except that no inactivation of Co^{III} by Co^{II} apparently takes place. In both cases, the experimental data are consistent with a mechanism whereby ethylbenzene is attacked by the cobaltic species to yield reversibly a benzylic radical. This scheme is further confirmed by the kinetics of oxygen uptake determined when the reaction is carried out in air.

In a previous paper it was shown that when ethylbenzene is treated in acetic acid with relatively concentrated cobaltic acetate the reduction of the latter does not proceed beyond the stage where Co^{III} and Co^{II} become equimolecular.[1] This result had been ascribed to the inactivation of Co^{III} by formation of a mixed complex with Co^{II}. Such an association could also provide an explanation for the retarding effect of Co^{II} on the reduction of Co^{III} as observed in previous studies.[2,3] However, a more direct effect of Co^{II} on the reaction mechanism as postulated in these studies could not be excluded. In the presence of strong acids, the reduction of cobaltic acetate has been shown to proceed well beyond the 50% stage even in concentrated solutions.[1] This system thus appeared to be better suited for studying the effect of Co^{II}. To provide further insight into the processes taking place in both cases, a kinetic study was undertaken, the results of which are reported in this paper.

RESULTS AND DISCUSSION

Under Nitrogen in the Absence of Strong Acid.—The fact that in the absence of strong acid, the reduction of Co^{III} does not take place when $[Co^{III}] = [Co^{II}]$ requires the kinetic equation of the process to be of the type (1).

$$-d[Co^{III}]/dt = k_{obs}\,([Co^{III}] - [Co^{II}])^m \qquad (1)$$

If $x = [Co^{III}]$ and $A = [Co^{III}] + [Co^{II}]$, we have $[Co^{III}] - [Co^{II}] = x - (A - x)$ and equation (1) becomes (2). Equation (2) was checked for different

$$-dx/dt = k_{obs}(2x - A)^m \qquad (2)$$

values of m, *i.e.* 1, 3/2, and 2. It is only for $m = 2$ that the function of x derived by integration of equation (2) follows a reasonable linear dependence on t, *i.e.* expression (3) is obeyed. However, the values of k_{obs} thus

$$1/2(2x - A) = k_{obs}t + \text{constant} \qquad (3)$$

determined show systematic variation with A. This is illustrated in Table 1 which also shows that reasonable consistency is obtained for $k_{obs}A$/[Ethylbenzene] over a wide range of conditions. Accordingly, the process obeys the rate equation (4):

$$-dx/dt = k(2x - A)^2[\text{Ethylbenzene}]/A \qquad (4)$$

Table 1

Kinetics of the reduction of cobaltic acetate by oxidation of ethylbenzene (RH) in acetic acid in the absence of strong acid at 25 °C under nitrogen

[RH]/M	A/M	Co^{III} (%)	10^3k_{obs}/ l mol^{-1} min^{-1} [a]	$10^3k_{obs}A[RH]^{-1}$/ l mol^{-1} min^{-1}
0·49	0·109 [b]	59	123	27
0·49	0·163 [b]	59	61	20
0·77	0·309	81	68	27
1·00	0·098	93	173	17
1·00	0·197	93	98	19
1·05	0·309	81	82	24
1·00	0·512	68	50	26
0·97	0·684	69	41	29
1·00	0·769	66	34	26
0·97	0·954	64	22	22
1·49	0·309	81	99	21
2·47	0·489	90	132	26
2·47	0·645 [b]	61	107	28
2·47	0·774 [b]	61	70	22
2·47	0·903 [b]	61	72	26
2·47	0·978	90	53	21

[a] k_{obs} Determined by the least-squares method from equation (3). [b] Co^{III} preparation, powder; for other experiments, solution (see ref. 12).

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[1] J. Hanotier, M. Hanotier-Bridoux, and P. de Radzitzky, *J.C.S. Perkin II*, 1973, 381.

[2] E. I. Heiba, R. M. Dessau, and W. J. Koehl, jun., *J. Amer. Chem. Soc.*, 1969, **91**, 6830.

[3] K. Sakota, Y. Kamiya, and N. Ohta, *Canad. J. Chem.*, 1969, **47**, 387.

As pointed out earlier, the dependence of the rate on $2x - A$ cannot be explained except by assuming that Co^{II} is associated with Co^{III} in dinuclear species inactive for oxidation. In this case, indeed, the concentration of the cobalt atoms involved in such valence-mixed species is $2(A - x)$ and therefore the concentration of active Co^{III} is $A - 2(A - x) = 2x - A$. The tendency of cobaltic acetate to form dimers is well established[4-6] and the same has been shown for cobaltous acetate.[7] It is likely therefore that in the concentrated systems under consideration most of the cobalt atoms are present as dinuclear species Co^{III}–Co^{III} and Co^{III}–Co^{II}. And if the latter is inactive, the main attacking species should be dimeric Co^{III}.

The inverse dependence of the reaction rate on A can be accounted for by assuming that the attack of the hydrocarbon substrate RH yields reversibly an intermediate species X according to equations (5) and (6).

$$RH + Co^{III}\text{–}Co^{III} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} X + Co^{III}\text{–}Co^{II} \qquad (5)$$

$$X + Co^{III}\text{–}Co^{III} \xrightarrow{k_2} \text{products} \qquad (6)$$

By application of the steady state principle to X, it is easy to demonstrate that this scheme should result in the rate equation (7). If it is assumed that dinuclear species

$$-\frac{d[Co^{III}\text{–}Co^{III}]}{dt} = \frac{2k_1k_2[Co^{III}\text{–}Co^{III}]^2[RH]}{k_2[Co^{III}\text{–}Co^{III}] + k_{-1}[Co^{III}\text{–}Co^{II}]} \qquad (7)$$

are largely predominant, we have approximately $[Co^{III}\text{–}Co^{II}] = A - x$ and $[Co^{III}\text{–}Co^{III}] = (2x - A)/2$. Hence, equation (7) becomes (8). And if it is further assumed

$$-\frac{dx}{dt} = \frac{k_1k_2(2x - A)^2[RH]}{2(k_2 - k_{-1})x + (2k_{-1} - k_2)A} \qquad (8)$$

that k_{-1} and k_2 are of similar magnitude, this expression becomes identical with the empirical equation (4) wherein $k \simeq k_1$. From the data of Table 1 it can thus be estimated that k_1 amounts roughly to 0·024 l mol^{-1} min^{-1}.

Under Nitrogen in the Presence of Trichloroacetic Acid.—When a relatively strong acid such as trichloroacetic acid is present in sufficiently high concentration, the inactivation of Co^{III} by Co^{II} does not take place as evidenced by the fact that the reduction of Co^{III} proceeds well beyond the 50% stage.[1] In this case, therefore, the concentration of active Co^{III} is simply the analytical concentration x. Different orders with respect to Co^{III}, *i.e.* $m = 1, 3/2$, and 2, and to Co^{II}, *i.e.* $n = 0, -1/2, -1$, were checked. Here again, it is for $m = 2$ and $n = 0$ that the best linear dependences were found. In each case, equation (9) was obeyed. But, as shown in Figure 1, the values thus

$$1/x = k_{obs}t + \text{constant} \qquad (9)$$

determined for k_{obs} are again inversely dependent on A, the concentration of total cobalt.* The intercept of the line may be accounted for by a rate law comprising two terms, one of which being independent of A^{-1}. But the results of Figure 1 are also consistent with the kinetic equation (10).

$$-dx/dt = kx^2/[k'x + k''(A - x)] \qquad (10)$$

Figure 2 shows a plot of observed values of x *versus* time for different A values. The curves were drawn

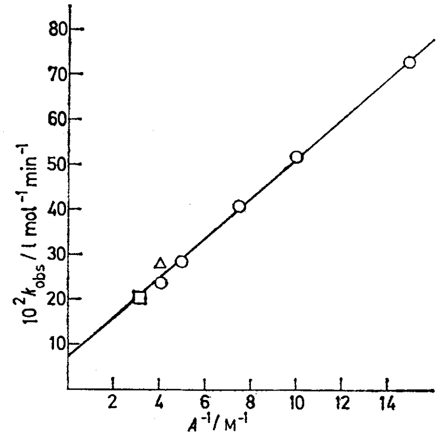

FIGURE 1 Dependence of k_{obs} [equation (9)] on the concentration of total cobalt (A). Initial % Co^{III}: ○ 86; □ 52; △ 42. [Trichloroacetic acid] 1·50M. [Ethylbenzene] 1·00M. Temperature 25 °C. Atmosphere nitrogen

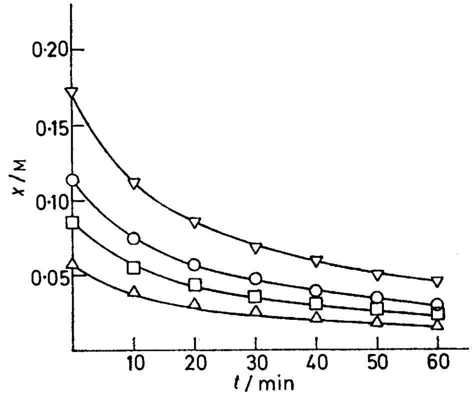

FIGURE 2 Variation with time of the concentration of Co^{III} (x). Total cobalt: ▽ 0·201; ○ 0·134; □ 0·100; △ 0·067M. Initial % Co^{III} 86. [Trichloroacetic acid] 1·50M. [Ethylbenzene] 1·00M. Temperature 25 °C. Atmosphere nitrogen. The curves are calculated from equation (10), assuming k'/k = 13·9 and k''/k = 20·5

on the basis of equation (10), by assuming k'/k and k''/k to be respectively 13·9 and 20·5. It appears clear that expression (10) is a valid way to account for the experimental data.

The kinetics can be explained by equations (11) and

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* Sharp[8] has shown that the decomposition of cobaltic acetate in aqueous sulphuric acid obeys the kinetic law $-d[Co^{III}]/dt = k[Co^{III}]^2[H^+]/[Co^{III}]_0$ which is formally identical with the kinetics determined here. As shown in the next section, the linear dependence on $[H^+]$ is also observed in the present case.

[4] J. A. Sharp and A. G. White, *J. Chem. Soc.*, **1952**, 110.

[5] Y. Wormser and D. Peschanski, *Bull. Soc. chim. France*, **1962**, 876.

[6] E. Koubek and J. O. Edwards, *J. Inorg. Nuclear Chem.*, **1963**, **25**, 1401.

[7] W. P. Tappmeyer and A. W. Davidson, *Inorg. Chem.*, **1963**, **2**, 823.

[8] J. A. Sharp, *J. Chem. Soc.*, 1957, **2030**.

(12) which result in the rate equation (13), which is

$$\mathrm{RH} + \mathrm{Co^{III}} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{X} + \mathrm{Co^{II}} \qquad (11)$$

$$\mathrm{X} + \mathrm{Co^{III}} \xrightarrow{k_2} \text{products} \qquad (12)$$

$$-\frac{\mathrm{d}[\mathrm{Co^{III}}]}{\mathrm{d}t} = \frac{2k_1k_2[\mathrm{Co^{III}}]^2[\mathrm{RH}]}{k_2[\mathrm{Co^{III}}] + k_{-1}[\mathrm{Co^{II}}]} \qquad (13)$$

identical with equation (10) with $k'/k = 1/2k_1[\mathrm{RH}]$ and $k''/k = k_{-1}/2k_1k_2[\mathrm{RH}]$.

As k'/k has been estimated as *ca.* 13·9, k_1 should amount roughly to 0·036 l mol^{-1} min^{-1}. It is noteworthy that this value and that estimated for k_1 in the absence of strong acid (see preceding section) are of similar magnitude.

Thus, in the presence of trichloroacetic acid, the mechanism of Co^{III} reduction appears to be substantially the same as in the absence of strong acid except that no kinetic evidence is found for the occurrence of associated structures.

In Air in the Presence of Trichloroacetic Acid.—In an oxygen-containing atmosphere the reduction of Co^{III} is not a good measure of the reaction rate as extensive regeneration of the oxidant has been shown to take place under these conditions.[1,9] The rate is more validly measured by the consumption of the substrate or, more simply, by the oxygen uptake. Table 2 shows the dependence of the initial rate of oxygen uptake on the concentration of Co^{III}. Clearly, the process is first order with respect to the oxidant.

TABLE 2

Dependence of the initial rate of oxygen uptake on the initial concentration of Co^{III} at 25 °C in air. Initial % Co^{III}, 72; [Trichloroacetic acid], 1·00M; [Ethylbenzene], 1·00M

$[\mathrm{Co^{III}}]_0$/M	$10^4(-\mathrm{dO_2}/\mathrm{d}t)_0$/ mol l^{-1} min^{-1}	$10^4(-\mathrm{dO_2}/\mathrm{d}t)_0[\mathrm{Co^{III}}]_0^{-1}$/ min^{-1}
0·137	10	73
0·206	15	73
0·274	18	66
0·343	24	70
0·412	31	75

The effect of Co^{II} was checked by addition of cobaltous acetate prepared by reduction of cobaltic acetate (see Experimental section). No incidence at all of this addition on the oxygen uptake was noticed. This absence of inhibition by Co^{II} contrasts with results recently reported for the cobalt-catalysed autoxidation of toluene in acetic acid.[9,10] However, these results have been obtained with systems with relatively high concentration in cobalt and free from strong acid so that the observed retarding effect of Co^{II} might well result from inactivation of Co^{III} by formation of mixed complexes as evidenced in the present study.

Figure 3 shows the dependence of the initial rate of oxygen uptake on the concentration of trichloroacetic acid. The process is first order with respect to the acid in the range of concentrations used. The intercept is certainly significant as some oxidation is expected to take place in the absence of strong acid. From these data it can be calculated that the presence of 1M-trichloroacetic acid results in a ten-fold increase of the reaction rate. A similar effect by trichloroacetic acid was observed in the reduction of Co^{III} under nitrogen.[1] The mechanism of this activation is not clearly understood as yet. A possibility might be that the dinuclear cobalt complexes apparently predominant in the absence of strong acid (see earlier) are dissociated into monomeric species. This mechanism would explain why Co^{III} is not inactivated by Co^{II} in the presence of strong acids.[1] But another possibility is the formation of more reactive cationic species as suggested by Lande and Kochi[11] [equation (14)]. It is difficult, from the present data,

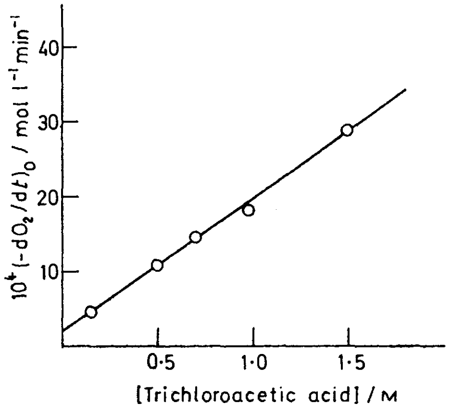

FIGURE 3 Dependence of the initial rate of oxygen uptake on the concentration of trichloroacetic acid. [Total cobalt] 0·384M. Initial % Co^{III} 71. [Ethylbenzene] 1·00M. Temperature 25 °C. Atmosphere air

$$\mathrm{Co_2(OAc)_6} + \mathrm{CCl_3CO_2H} \rightleftharpoons \mathrm{Co_2(OAc)_5^+} + \mathrm{CCl_3CO_2^-} + \mathrm{AcOH} \qquad (14)$$

to distinguish between the possibilities. It would seem, however, that the latter is more consistent with first-order kinetics in Co^{III} as observed.

Another result difficult to explain is the fact that the initial rate of oxygen uptake shows rather little variation when the concentration of ethylbenzene is increased. This variation fits a slight curve with tangents of increasing intercept. A similar dependence has been observed for the rate of reduction of Co^{III} in the presence of n-heptane as substrate and has been tentatively ascribed to an increased contribution of the self-decomposition of the oxidant.[12] In the present case, however, the higher reactivity of ethylbenzene makes the self-decomposition of Co^{III} a minor side-reaction and, in fact, no significant oxygen uptake could be detected in the absence of ethylbenzene. As shown by Figure 4, the dependence of the initial oxygen uptake on the concentration of ethylbenzene reasonably fits a Michaelis–Menten

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[9] Y. Kamiya and M. Kashima, *J. Catalysis*, 1972, **25**, 326.

[10] E. J. Y. Scott and E. W. Chester, *J. Phys. Chem.*, 1972, **76**, 1520.

[11] Sh. S. Lande and J. K. Kochi, *J. Amer. Chem. Soc.*, 1968, **90**, 5196.

[12] J. Hanotier, Ph. Camerman, M. Hanotier-Bridoux, and P. de Radzitsky, *J.C.S. Perkin II*, 1972, 2247.

reciprocal plot, the validity of which is confirmed by the fact that the same plot holds for the rate of Co^{III} consumption under nitrogen atmosphere. It is interesting to point out that this particular dependence is apparently related to the presence of trichloroacetic acid in the system since the order with respect to ethylbenzene is clearly one in the absence of strong acid (see Table 1).

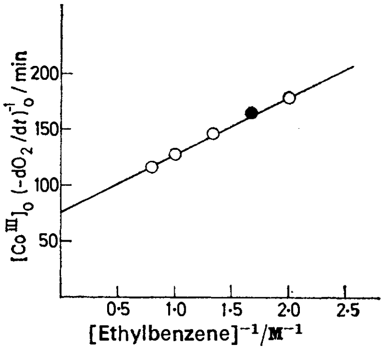

FIGURE 4 Dependence of the initial rate of oxygen uptake on the concentration of ethylbenzene. [Co^{III}]: ○ 0·339; ● 0·170M. Initial % Co^{III} 71. [Trichloroacetic acid] 1·25M. Temperature 25 °C. Atmosphere air

From these different results, it can be concluded that the whole rate equation for the acid-activated process is (15). This equation can be accounted for by equations

$$-dO_2/dt = k[\mathrm{Co^{III}}][\mathrm{CCl_3CO_2H}][\mathrm{RH}]/(k' + k''[\mathrm{RH}]) \quad (15)$$

(16)—(18) wherein the predominant cobaltic species is represented by Co^{III}, irrespectively of its association state, and by Co^{III}, CCl$_3$CO$_2$H the reactive complex produced by interaction with trichloroacetic acid.

$$\mathrm{Co^{III} + CCl_3CO_2H \rightleftharpoons Co^{III}, CCl_3CO_2H} \quad (16)$$

$$\mathrm{RH + Co^{III}, CCl_3CO_2H \longrightarrow R\cdot + Co^{II}, CCl_3CO_2H + H^+} \quad (17)$$

$$\mathrm{R\cdot + O_2 \longrightarrow products} \quad (18)$$

By application of the steady state principle to the reactive cobaltic complex and to the intermediate radical, a rate equation can be derived which is identical to the empirical expression (15).

Conclusion.—From the kinetics of the oxidation of ethylbenzene by cobaltic acetate under nitrogen, it was concluded that an intermediate species X should be formed reversibly by interaction of the substrate with Co^{III}. The same conclusion has been drawn by Andrulis and his co-workers to account for the kinetics of the oxidation of *p*-methoxytoluene by manganic acetate. The intermediate was postulated to be a radical-cation derived by abstraction of a π-electron from the benzene nucleus.[13] More recently, an identical mechanism [equations (19)—(22)] has been proposed by Heiba and his co-workers for the oxidation of toluene by cobaltic acetate.[2]

Reactions (19)—(22) account for the occurrence of a free radical as demonstrated previously by the fact

$$\mathrm{PhMe + Co^{III} \rightleftharpoons (PhMe)^+ + Co^{II}} \quad (19)$$

$$\mathrm{(PhMe)^+ \longrightarrow PhCH_2\cdot + H^+} \quad (20)$$

$$\mathrm{PhCH_2\cdot + Co^{III} \longrightarrow PhCH_2^+ + Co^{II}} \quad (21)$$

$$\mathrm{PhCH_2^+ + AcO^- \longrightarrow PhCH_2OAc} \quad (22)$$

that benzylic acetates are produced in large predominance under nitrogen whereas carbonyl compounds predominate when oxygen is present.[1] The subsequent formation of a carbonium ion as depicted in equation (21) is also consistent with these results. However, this scheme should result in first-order kinetics with respect to Co^{III} and the rate equation should be the same in the presence as in the absence of molecular oxygen. It can therefore be rejected on consideration of the present kinetic data.

To account for the observed second-order dependence of the rate on Co^{III} concentration, Sakota and his co-workers [3] have suggested that the intermediate radical-cation would also react with Co^{III} as in equation (23).

$$\mathrm{(PhMe)^+ + Co^{III} \longrightarrow PhCH_2^+ + Co^{II} + H^+} \quad (23)$$

Although it is satisfactory with respect to the kinetics this modified scheme does not account clearly for the intermediate formation of a benzylic free radical. Recently, the second-order dependence on [Co^{III}] has been explained by assuming the cobaltic species responsible of reactions (19) and (21) to be dimers.[9] In this case, however, the observed kinetics can still only be accounted for by assuming the monomeric species to be predominant and inactive, which is highly questionable.

We are thus forced to suggest an alternative mechanism wherein the intermediate X is the benzylic free radical itself, *i.e.* equations (24)—(26) with ethylbenzene as substrate. In the presence of oxygen, the incipent

$$\mathrm{PhEt + Co^{III} \rightleftharpoons Ph\dot{C}HMe + Co^{II} + H^+} \quad (24)$$

$$\mathrm{Ph\dot{C}HMe + Co^{III} \longrightarrow Ph\overset{+}{C}HMe + Co^{II}} \quad (25)$$

$$\mathrm{Ph\overset{+}{C}HMe + AcOH \longrightarrow PhCH(OAc)Me + H^+} \quad (26)$$

free radical should readily react according to reaction (27) ultimately to afford acetophenone as observed.[1] This reaction may be expected to prevail over the

$$\mathrm{Ph\dot{C}HMe + O_2 \longrightarrow PhCH(OO\cdot)Me} \quad (27)$$

competitive reaction of the radical with Co^{II} [equation (24)]. It is easy to demonstrate that in this case the oxygen absorption should be virtually independent of [Co^{II}] and first order with respect to Co^{III} as observed (see earlier).

Part of the evidence advanced for supporting the formation of a radical-cation from alkylbenzenes is the fact, also observed in this laboratory, that cumene is markedly less reactive towards Co^{III} than toluene while an inverse order of reactivity should be expected if a

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[13] P. J. Andrulis, M. J. S. Dewar, R. Dietz, and R. L. Hunt, *J. Amer. Chem. Soc.*, 1966, **88**, 5473.

C–H bond rupture was involved.[2,3] However, similar kinetics as established for alkylbenzenes have been reported to hold for n-alkanes for which no possibility of π-electron abstraction exists.[12] In this case also abnormal reactivities have been observed which can only be explained by stringent steric effects similar to those observed in the deuteriation of alkanes by tetrachloroplatinate.[14]

Thus, even if radical-cations may be produced from some alkylaromatic compounds of high ionization potential,[15] it appears that other possibilities need be considered to explain the experimental data now available.

EXPERIMENTAL

Materials.—Ethylbenzene (pure grade) was obtained from Union Chimique Belge. Before use, it was redistilled from sodium under nitrogen and stored under similar conditions. Acetic acid (RPE grade) was from Carlo Erba and trichloroacetic acid (' pro analysi ' grade) from Merck. Cobaltic acetate was prepared as described elsewhere.[12] Unless otherwise stated, it was prepared as a solution in acetic acid (ref. 12, method 1a). The Co^{III} to Co^{II} ratio varied from *ca.* 19 : 1 for freshly prepared solutions down to *ca.* 65 : 35 after storage for several weeks at room temperature. When lower ratios were needed to check the effect of Co^{II}, cobaltous acetate was prepared by heating gently on a water bath a solution of Co^{III} containing trichloroacetic acid until reduction was complete. The resulting solution was then added to a Co^{III} solution prepared by the usual procedure.

Kinetic Measurements.—The procedure used for studying the kinetics of reduction of Co^{III} under nitrogen atmosphere has been described.[12]

For experiments with air as atmosphere, 0·5 to 1·0 ml of reaction mixture was used and the oxygen uptake was determined in a Warburg constant volume respirometer,[16] the measurements being corrected for temperature and pressure changes in each case. Shaking of the flasks was at a rate of 115 oscillations min^{-1}. This rate was shown to be not limiting as a rate of 65 oscillations min^{-1} did not result in a decreased oxygen uptake. The initial rates of oxygen uptake were determined graphically, by plotting measured rates *versus* time and extrapolating to zero time. The standard deviation of the values thus determined can be estimated as *ca.* 10^{-4} mol l^{-1} min^{-1}.

[2/2459 *Received*, 31*st October*, 1972]

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[14] R. J. Hodges, D. E. Webster, and P. B. Wells, *J. Chem. Soc.* (*A*), 1971, 3230.

[15] R. M. Dessau, S. Shih, and E. I. Heiba, *J. Amer. Chem. Soc.*, 1970, **92**, 412.

[16] W. W. Umbreit, R. H. Burris, and J. F. Stauffer, ' Manometric Techniques and Related Methods for the Study of Tissue Metabolism,' Burgess, Minneapolis, 1945.