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Kinetic Investigation of the Oxidation of Bromide Ions by Cobalt(III)

Part 2.—The Influence of Pyridine and Hydrocarbon on the Reaction in Acetic Acid Solvent

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The kinetics of cobalt(III) acetate reduction in acetic acid have been studied under nitrogen at 60–93 °C in the presence of bromide, *p*-xylene and pyridine. At high *p*-xylene concentration the initial rate of reaction obeys the rate law

$$-\left(\frac{d[Co^{III}]}{dt}\right)_0 = k_c\frac{[Co^{III}]^2[HBr]^2}{[Co^{II}][Py]^2}$$

with $k_c = 0.057\ s^{-1}$ at 80 °C and an apparent activation enthalpy of 59.8 ± 5.0 kJ mol^{-1}. The value of the apparent reaction order with respect to hydrocarbon tends to one at low concentrations. The overall stoichiometry of reduced Co^{III} and oxidized Br^- ions, $\Delta Co^{III}/\Delta Br^-$, is close to two. The mechanism of reaction involves attack of hydrocarbon by bromine species coordinated to cobalt.

We previously reported[1] that the reduction of Co^{III} acetate by bromide ions in acetic acid solvent proceeds through the formation of bromine anion radicals as intermediate. The initial rates of reaction increase with the square of concentration of both reagents, but are retarded by cobalt(II) ions and the presence of amines. For different amines the ratio of converted Co^{III} and Br^- ions ($\Delta Co^{III}/\Delta Br^-$) is *ca.* one and the overall reaction follows the equation

$$Co^{III} + Br^- \rightarrow Co^{II} + \tfrac{1}{2}Br_2.$$

Molecular bromine is the final product; however, with pyridine it forms adducts capable of further oxidation by Co^{III} ions.

Since the reaction system mentioned is used for catalysing auto-oxidation of methylbenzenes,[2] many papers have been devoted to elucidate the mechanism of hydrocarbon oxidation. The role of bromide and cobalt ions in auto-oxidation processes has been studied extensively; however, the data concerning the oxidation of hydrocarbons by the Co^{III}–Br system in an inert atmosphere are missing, probably caused by difficulties connected with measurement of this very rapid reaction at lower temperatures. Digurov and coworkers[3] described that in the first 1–2 min of reaction at 60 °C the conversion of Co^{III} ions is almost 50% and, therefore, the kinetics of toluene oxidation by Co^{III} in the presence of NaBr measured by them belong to the second stage of reaction.

This paper reports results of a kinetic study of the reaction of Co^{III} and Br^- ions in the presence of *p*-xylene (PX) and pyridine (Py) in acetic acid solvent under an inert atmosphere. An advantage of the system containing pyridine is that the reaction rates are lower and easily measurable in the initial stage.

Table 1. Initial reduction rates, r_0, of cobalt(III) in acetic acid at 80 °C in the presence of *p*-xylene and different substrates[a]

system	mole ratio	$r_0/10^{-4}$ mol dm^{-3} s^{-1}
Co^{III}	—	0.05
Co^{III}:Py	1:3.75	0.06
Co^{III}:Br_2	1:1.13	0.29
Co^{III}:HBr[b]	1:2.00	70±10
Co^{III}:HBr[b]:Py	1:2:3.75	6.48
Co^{III}:HBr[b]:Py	1:2:3.75	1.85[c]

[a] $[Co^{III}]_0 = 0.0278$ mol dm^{-3}, $[Co^{II}]_0 = 0.0195$ mol dm^{-3}, $[Co^{III}]_0:[PX]_0 = 1:30$. [b] In the form of *ca.* 47% aqueous HBr. [c] In the absence of *p*-xylene.

Table 2. Effect of alkylbenzenes on the initial reduction rate of Co^{III} in acetic acid at 80 °C[a]

hydrocarbon	$r_0{}^b/10^{-4}$ mol dm^{-3} s^{-1}	$r_0{}^c$/mol dm^{-3} s^{-1}
toluene	0.02	5.42
p-xylene	0.05	16.37
ethylenebenzene	0.06	18.16
cumene	0.09	71.33

[a] $[Co^{III}]_0 = 0.0278$ mol dm^{-3}. [b] $[Co^{III}]_0:[Co^{II}]_0:[RH]_0 = 1:0.7:30$ (mol). [c] $[Co^{III}]_0:[Co^{II}]_0:[RH]_0:[HBr]_0:[Py]_0 = 1:0.7:30:2:4$.

Experimental

Apparatus, rate measurement, analysis and reagents were the same as described in Part 1.[1] Hydrocarbons were purified by distillation. Reaction products were identified and determined by g.c./m.s. using a Varian MAT 111 GNOM mass spectrometer and Hewlett–Packard 5830 A gas chromatograph.[4]

Results

Kinetics

The reduction rate of Co^{III} acetate in a solution of acetic acid and *p*-xylene at 80 °C is low, but increases markedly in the presence of bromide ions (table 1). The initial reaction rates, estimated from conversion curves of Co^{III} and Br^- ions, decrease in the presence of pyridine; however, they are also influenced by the presence of *p*-xylene and other hydrocarbons (tables 1 and 2).

The effect of concentration of reactants on the initial reaction rates was studied in different concentration ranges. The values of apparent orders of reaction with respect to each component were found from 6 to 9 runs by keeping initial concentrations of all but one reactant constant. Table 3, which gives the data of apparent reaction orders,

Table 3. Apparent reaction orders for the rate of Co^{III} and Br^- consumption and stoichiometry of overall reaction ($\Delta Co^{III}/\Delta Br$)

reactant	concentration range $/10^{-2}$ mol dm^{-3}	reaction order n_{Co}	n_{Br}	$\Delta Co^{III}/\Delta Br^-$
Co^{III} acetate	1.39–5.56	1.98 ± 0.06	2.11 ± 0.09	1.95–2.75
Co^{II} acetate	1.95–8.34	-0.82 ± 0.12	-0.84 ± 0.08	2.01–2.64
HBr[a]	1.39–8.34	2.21 ± 0.09	2.15 ± 0.06	2.59–1.90
PX	4.17–62.55	0.72 ± 0.04	0.56 ± 0.09	0.97–2.38
	62.55–389.2	0.05 ± 0.04	0.08 ± 0.03	2.38–4.20
Py	2.78–26.05	-1.99 ± 0.06	-1.58 ± 0.09	1.97–2.50
	26.05–41.70	-3.64 ± 0.09	-4.02 ± 0.05	1.77–2.30

[a] In the form of *ca.* 47% aqueous HBr.

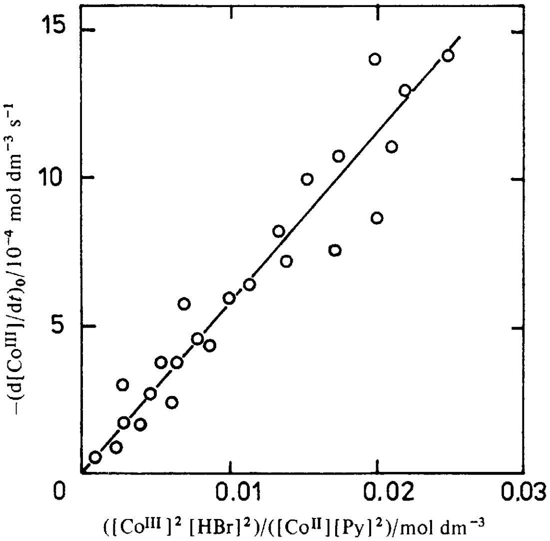


Fig. 1. Plot of $-d[Co^{III}]/dt_0$ against $(k_c[Co^{III}]^2[HBr]^2)/([Co^{II}][Py]^2)$.

shows that at high *p*-xylene and low pyridine concentrations a crude approximation of the rate expression is

$$-\left(\frac{d[Co^{III}]}{dt}\right)_0 = k_c \frac{[Co^{III}]^2[HBr]^2}{[Co^{II}][Py]^2}$$

$$-\left(\frac{d[Br^-]}{dt}\right)_0 = k_b \frac{[Co^{III}]^2[HBr]^2}{[Co^{II}][Py]^2}.$$

A test was made to see whether these equations fit a first-order dependence. From the data of fig. 1 and 2 it was estimated that at 80 °C the initial rate constants k_c and k_b are 0.057 s^{-1} and 0.041 s^{-1}, respectively. The apparent activation enthalpies found in the temperature region 60–93 °C for the oxidation of Br^- and reduction of Co^{III} are the same, 59.8 ± 5.0 kJ mol^{-1} (fig. 3).

A study of overall stoichiometry for the initial stage of the reaction shows that the ratio of the average amounts of reduced Co^{III} and consumed Br^- ions $\Delta Co^{III}/\Delta Br^-$

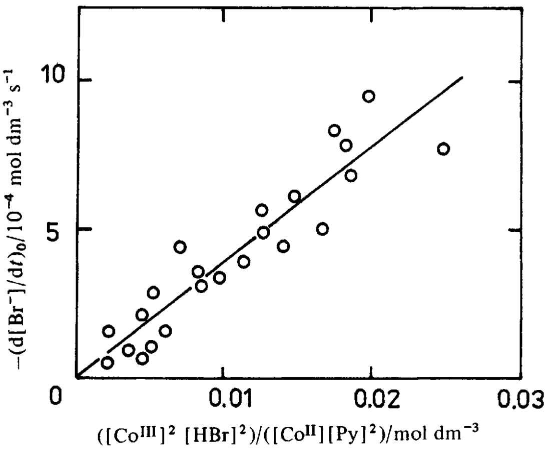


Fig. 2. Plot of $-d[Br^-]/dt$ against $(k_b[Co^{III}]^2[HBr]^2)/([Co^{II}][Py]^2)$.

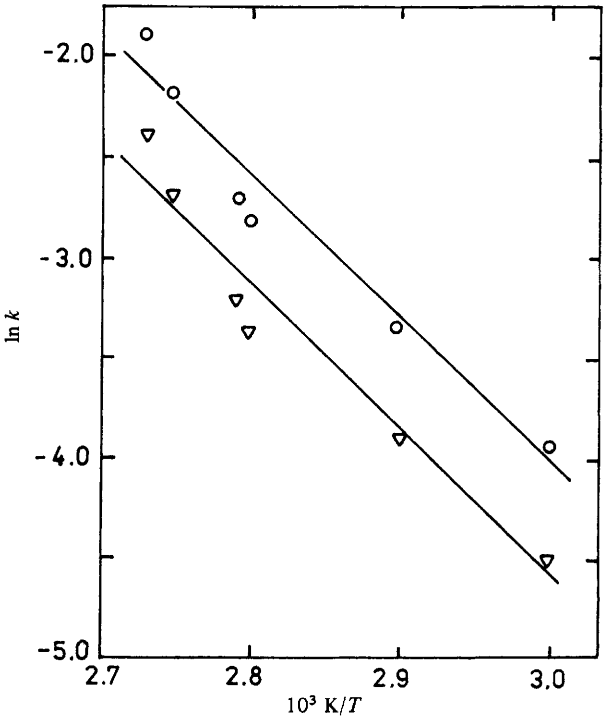


Fig. 3. Effect of temperature on the rate of Co^{III} (○) and bromide (▽) consumption.

changes usually from 2.0 to 2.6 (table 3). The value is similar for different alkylbenzenes; however, it is dependent on the concentration of reactants and reaction temperature. Thus, an increase of temperature from 60 to 93 °C changes this ratio from 2.0 to 2.5. The strongest influence on this ratio is the concentration of *p*-xylene which can be oxidized by Co^{III} ions. In its absence, or at low concentration, this ratio is close to 1, corresponding only to the reaction between Co^{III} and bromide ions.

The main products of *p*-xylene oxidation in the absence of oxygen are 4-methylbenzylacetate, 4-methylbenzaldehyde, 4-methylbenzyl alcohol, 4-methylbenzyl bromide and 2-bromo-1,4-dimethylbenzene. The relative proportions of these products, and hence reaction stoichiometry vary with the reaction temperature, concentration of pyridine, bromide, cobalt and duration of the reaction.[4]

Discussion

Reaction Mechanism

In Part 1 it was shown that in acetic acid solvent and absence of *p*-xylene the reduction of $\mathrm{Co^{III}}$ proceeds with consumption of an equimolar amount of $\mathrm{Br^-}$. When *p*-xylene is also present in the system, the stoichiometry of this reaction changes and the consumption of bromide ions is roughly half that of $\mathrm{Co^{III}}$. Since, under reaction conditions, a direct attack of hydrocarbon by $\mathrm{Co^{III}}$ ions is many times lower than in the system with bromide ions (table 1), it suggests that cobalt(III) acetate reacts with bromide as well as with intermediate products formed by oxidation of hydrocarbon with bromine species. A reaction scheme which describes the kinetics of oxidation and observed effects is presented by the following:

$$\mathrm{Co_D^{III} + Br^- \rightleftharpoons Co_D^{III}\,Br^-} \tag{1}$$

$$\mathrm{Co_D^{III}\,Br^- + 2Py \rightarrow Co_D^{III}\,Py + PyHBr} \tag{2}$$

$$\mathrm{Co_D^{III}\,Br^- + Br^- \rightleftharpoons Co^{III}\,Br_2^- + Co^{II}} \tag{3}$$

$$\mathrm{Co^{III}\,Br_2^- \rightarrow Co^{II} + Br_2} \tag{4}$$

$$\mathrm{Co_D^{III} \rightleftharpoons 2Co^{III}} \tag{5}$$

$$\mathrm{Co^{III}\,Br_2^- + RCH_3 \rightleftharpoons [Co^{III}\,Br_2^- \cdots RCH_3]} \tag{6}$$

$$\mathrm{[Co^{III}\,Br_2^- \cdots RCH_3] \rightarrow Co^{II}-HBr + RCH_2^{\bullet} + Br^{\bullet}} \tag{7}$$

$$\mathrm{[Co^{III}\,Br_2^- \cdots RCH_3] + 2Py \rightarrow Co^{II}\,Py + PyBr_2 + RCH_3} \tag{8}$$

$$\mathrm{RCH_2^{\bullet} + Br^{\bullet} \rightarrow RCH_2Br} \tag{9}$$

$$\mathrm{RCH_2^{\bullet} + Co^{III} \rightarrow RCH_2^{+} + Co^{II}} \tag{10}$$

$$\mathrm{RCH_2^{+} + OAc^- \rightarrow RCH_2OAc} \tag{11}$$

$$\mathrm{Br^{\bullet} + Br^{\bullet} \rightarrow Br_2} \tag{12}$$

$$\mathrm{RCH_3 + Br_2 \rightarrow BrRCH_3 \text{ and } RCH_2Br + HBr} \tag{13}$$

where $\mathrm{Co_D^{III}}$ denotes a dimer of cobaltic acetate, $\mathrm{RCH_3}$ denotes *p*-xylene and $\mathrm{BrRCH_3}$ denotes nuclear brominated *p*-xylene.

Some steps of this mechanism and the role of pyridine were discussed in Part 1. Reaction steps involve intermediate complexes formed in rapid pre-equilibria. To simplify the treatment, the following assumptions were made: reactions (4) and (7) are the rate-determining steps, $k_6 \gg k_7$ or k_3'; $k_1' \gg k_3$ and at sufficiently high pyridine concentration $k_2[\mathrm{Py}]^2 \gg k_1'$. Using the steady-state approximation for intermediate complexes and products, the initial rates of $\mathrm{Co^{III}}$ and $\mathrm{Br^-}$ consumption for the mechanism presented above lead to the expression

$$-\left(\frac{\mathrm{d[Co^{III}]}}{\mathrm{d}t}\right)_0 = -\left(\frac{\mathrm{d[Br^-]}}{\mathrm{d}t}\right)_0 = k_{\mathrm{obs}}\frac{[\mathrm{Co^{III}}]^2[\mathrm{Br^-}]^2[\mathrm{RCH_3}]}{[\mathrm{Co^{II}}][\mathrm{Py}]^2(k_4+k_6[\mathrm{RCH_3}])(k_6'+k_8[\mathrm{Py}]^2)} \tag{14}$$

where

$$k_{\mathrm{obs}} = \frac{k_1 k_4 k_6 k_7 K_3}{k_2 K_5}.$$

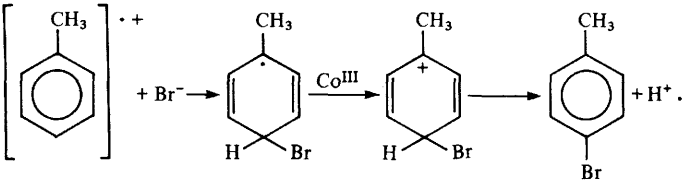
By using the experimental values it was found that the calculated rate constant k_6 is 3.7 times higher than k_4. From eqn (14) it is seen that for a low *p*-xylene concentration k_4 becomes higher than $k_6[RCH_3]$, *i.e.* the reaction order with respect to *p*-xylene will tend to one, but at a high *p*-xylene concentrations, transition to zero order takes place. The inverse dependence of the reaction rate on Co^{II} and pyridine can be accounted for by assuming that these compounds attack active intermediate complexes reversibly. The retarding effect of Co^{II} ascribed to the formation of inactive mixed dinuclear Co^{III}–Co^{II} species[1, 5] is less important in this system since, under experimental conditions, the reduction of Co^{III} proceeds almost completely.

As expected on the basis of the proposed mechanism, the *p*-methylbenzyl radical is formed by the reaction of intermediate bromocobalt complexes with *p*-xylene. In the absence of oxygen this radical is rapidly oxidized by Co^{III} to a carbonium ion to afford an acetate [reaction (10)] rather than recombine with bromine radicals [reaction (9)] formed in reaction (7).[4] This sequence of reactions may lead to $\Delta Co^{III}/\Delta Br^- = 2$. However, this value increases in the latter stages of the reaction and more so at high *p*-xylene concentration. It is probably a consequence of the subsequent oxidation of *p*-methylbenzylacetate which is *ca.* 20 times more reactive than *p*-xylene towards Co^{III}.[6] Moreover, cobalt(II) acetate enhances the regeneration of bromide anions from *p*-methylbenzyl bromide:[2, 4]

$$RCH_2Br + AcOH \xrightleftharpoons{Co(OAc)_2} RCH_2OAc + HBr. \qquad (15)$$

The reactions of Co^{III} with intermediates explain why the estimated value of the rate constant k_c is higher than k_b.

Analysis of reaction products shows that during the reaction, chain and ring brominated compounds are formed.[4] Nucleophilic attack on the aromatic ring is a possible reaction of radical cations derived from alkylaromatics and increases with an increase in the nucleophile concentration:[7]



Since, under the conditions used, direct oxidation of *p*-xylene by Co^{III} leading to cation radicals is substantially less than the reaction of Co^{III} with bromide it suggests that ring brominated products are formed by bromination with molecular bromine produced through reactions (4) and (12). However, reaction (4) is slower than (7), which could explain the findings that the rates of Co^{III} reduction in the presence of *p*-xylene are 1.4 times higher and the apparent activation enthalpy is *ca.* 25 kJ mol^{-1} lower than the values obtained in a similar system but in the absence of *p*-xylene.[1]

In the rate-determining step (7) the formation of active species between the intermediate bromocobalt complex and alkylbenzene is postulated. This is not surprising since the formation of weak complexes of the charge-transfer type between cobalt(III) and aromatic hydrocarbons has been observed.[8] Since the reactivity of such complexes should depend on the nature of the hydrocarbon substrate, the values of the relative rates of Co^{III} reduction obtained for toluene, ethylbenzene and cumene (table 2), which are in the sequence of C—H bond rupture process observed with bromine radicals,[9] support the proposed formation of the active species.

From the kinetics of the reduction of cobalt(III) acetate under nitrogen in the presence of bromide, pyridine and *p*-xylene it follows that the rate expression is similar to that determined for the reaction in the absence of hydrocarbon.[1] The primary step of the reaction involves oxidation of bromide by Co^{III}, and the bromine radical anion thus formed (coordinated to cobalt) attacks the hydrocarbon in the subsequent rate-determining step. Moreover, bromine radical anions in the presence of pyridine also participate in the reoxidation of Co^{II} ions, which is supported by the results of analysis of the reaction products.[4]

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