

## Low-temperature Oxidation of n-Alkanes by Cobaltic Acetate activated by Strong Acids

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The oxidizing activity of cobaltic acetate in acetic acid is enhanced by strong organic or inorganic acids to such an extent that n-alkanes can be significantly oxidized at low temperature. The kinetics of cobalt(III) consumption in the presence of n-heptane as substrate and trifluoroacetic acid as activator under a nitrogen atmosphere has been studied: the process appears to be of the second order with respect to cobalt(III) and it is markedly retarded by cobalt(II). The products of the oxidation of n-alkanes by acid-activated cobaltic acetate in acetic acid are different according to whether oxygen is present or not. Acetic esters of alcohols are formed under nitrogen while ketones are mainly produced if oxygen is present; when trichloroacetic acid is used as activator under nitrogen, alkyl chlorides are the principal products. In each case, the products consist of a mixture of position isomers with a marked predominance of the isomer resulting from attack of the alkane on the second carbon atom of the chain. These results are consistent with a mechanism wherein the n-alkanes are attacked by cobalt(III) to afford reversibly cobalt(II) and an alkyl free radical. The selectivities observed are discussed.

THE oxidation of organic compounds by cobaltic salts at low temperature, *i.e.*, 10–40 °C, has been extensively investigated. Most of these studies, however, have used inorganic cobaltic salts, *e.g.*, perchlorate or sulphate, in aqueous media and, probably for this reason, they have been generally restricted to the oxidation of oxygen-containing<sup>1</sup> or sulphur-containing<sup>2</sup> substrates which are relatively soluble in water. The oxidation of benzene by cobaltic perchlorate was studied by Wells<sup>3</sup> but problems arose from the low solubility of benzene in aqueous solutions. Similar difficulties were experienced by Waters and his co-workers with toluene as substrate, although water-methyl cyanide mixtures were used as solvent.<sup>4,5</sup>

In an attempt to overcome this solubility limitation, Bawn and Sharp used cobaltic acetate in acetic acid for studying the oxidation of olefins. However, no detectable reaction took place during several days unless sulphuric acid was added to the system but the nature of the kinetics determined in these conditions was not clear.<sup>6</sup> More recently, the oxidation of toluene by cobaltic acetate in acetic acid was studied by Heiba *et al.*<sup>7</sup> The addition of acetate ions was shown to enhance the reaction rate but even in these conditions the reduction of cobaltic acetate required several days at 65 °C for completion. Saturated hydrocarbons such as n-alkanes are still less reactive. Thus, according to the same authors, n-nonane at 90 °C is ten times less reactive than toluene.

Recently we observed that the activity of metal oxidants and particularly cobaltic acetate in acetic acid is considerably enhanced by strong organic or inorganic acids to such an extent that aromatic<sup>8</sup> and even aliphatic<sup>9</sup> hydrocarbons can be oxidized at temperatures as low as 20–40 °C. The present paper deals with the results so obtained for n-alkanes.

### RESULTS

*Effect of Strong Acids.*—The effect of different acids on the reduction of cobaltic acetate in the presence and absence of n-heptane is shown in Table I. In pure acetic acid, the reduction of cobalt(III) at 25–40 °C is a very slow

TABLE I

Effect of strong acids on the reduction of cobaltic acetate<sup>a</sup> in acetic acid in the presence of n-heptane. Atmosphere: nitrogen.  $[\text{Co}^{\text{III}}]_0 = 0.18\text{M}$

Acid concn./M	t/°C	Time/h	Co <sup>III</sup> reduced (%)	
			With 0.50M-n-heptane	Without n-heptane
	25	1	0	0
	25	6	5	5
	25	18	13	13
	40	6	10	8
H <sub>2</sub> SO <sub>4</sub>	0.5	25	½	96
H <sub>3</sub> PO <sub>4</sub>	1.0	25	1	46
HClO <sub>4</sub>	1.0	25	1	43
BF <sub>3</sub>	1.5	25	24	37
CCl <sub>3</sub> ·CO <sub>2</sub> H	1.5	25	6	57
CCl <sub>2</sub> ·CO <sub>2</sub> H	1.5	25	18	81
CCl·CO <sub>2</sub> H	1.5	40	6	74
CHCl <sub>2</sub> ·CO <sub>2</sub> H	1.5	40	6	40
CH <sub>2</sub> Cl·CO <sub>2</sub> H	1.5	40	6	14
CF <sub>3</sub> ·CO <sub>2</sub> H	1.5	25	18	71
MeSO <sub>3</sub> H	1.0	25	½	72
PhSO <sub>3</sub> H	1.0	25	¼	97

<sup>a</sup> Preparation: powder (see Experimental section).

process even when n-heptane is present. In fact, the extent of reduction is practically the same whether the hydrocarbon is present or not. This shows that the latter is not significantly oxidized in these conditions which confirms Bawn's conclusions that cobaltic acetate itself is a weak oxidant.<sup>6</sup> However, as soon as an acid of enough strength is added to the system, rapid reduction of cobalt(III) takes place which indicates that some more reactive species has

<sup>4</sup> T. A. Cooper, A. A. Clifford, D. J. Mills, and W. A. Waters, *J. Chem. Soc. (B)*, 1966, 793.

<sup>5</sup> T. A. Cooper and W. A. Waters, *J. Chem. Soc., (B)* 1967, 687.

<sup>6</sup> C. E. H. Bawn and J. A. Sharp, *J. Chem. Soc.*, 1957, 1866.

<sup>7</sup> E. I. Heiba, R. M. Dessau, and W. J. Koehl, jun., *J. Amer. Chem. Soc.*, 1969, **91**, 6830.

<sup>8</sup> Belg.P. 727,874/1969; B.P. 1,206,268/1970.

<sup>9</sup> Belg.P. 719,094 and 727,873/1969; B.P. 1,214,417/1970.

<sup>1</sup> For a review, see W. A. Waters and J. S. Littler, in 'Oxidation in Organic Chemistry,' ed. K. B. Wiberg, Academic Press, New York, 1965, p. 186.

<sup>2</sup> A. McAuley and U. D. Gomwalk, *J. Chem. Soc. (A)*, 1969, 977.

<sup>3</sup> C. F. Wells, *Trans. Faraday Soc.*, 1957, **63**, 156.

been produced by interaction of cobaltic acetate and the added acid. As shown in Table I, extensive reduction of cobalt(III) also occurs in the absence of hydrocarbon substrate. This suggests that the activity of the incipient

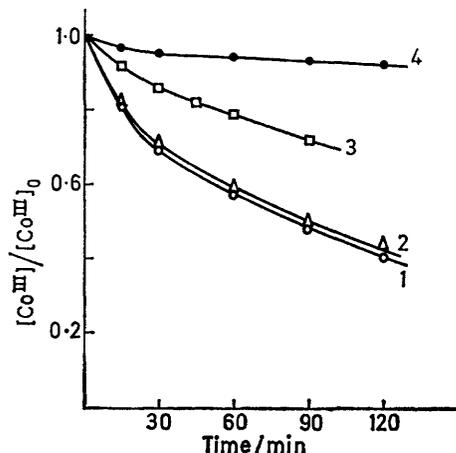


FIGURE 1 Rate of reduction of cobaltic acetate in acetic acid in the presence of n-heptane and 1.03M-trifluoroacetic acid at 40 °C under nitrogen. 1, [n-heptane] 0.50M,  $[\text{Co}^{\text{III}}]_0$  0.16M,  $[\text{Co}^{\text{II}}]_0$  0.05M; 2, [n-heptane] 0.50M,  $[\text{Co}^{\text{III}}]_0$  0.31M,  $[\text{Co}^{\text{II}}]_0$  0.10M; 3, [n-heptane], 0.50M  $[\text{Co}^{\text{II}}]_0$  0.17M,  $[\text{Co}^{\text{II}}]_0$  0.25M; 4,  $[\text{Co}^{\text{III}}]_0$  0.16M,  $[\text{Co}^{\text{II}}]_0$  0.05M. Cobalt(III) preparation: solution (see Experimental section)

cobalt species is so high that acetic acid used as solvent is also attacked. This concurrent consumption of cobalt(III) is particularly important with strong inorganic acids such as sulphuric or perchloric acids and with strong organic acids such as methanesulphonic or benzenesulphonic acids. With weaker organic acids such as trichloroacetic or trifluoroacetic acids, the reduction of cobalt(III) is 2—3 times faster in the presence than in the absence of n-heptane. With the still weaker dichloroacetic acid, activation of cobalt(III) is less marked and with monochloroacetic acid it is almost negligible.

The differences observed between the effects of mono-, di-, and tri-chloroacetic acids suggest that activation of cobaltic acetate by strong acids is primarily related to their ability to release protons, a conclusion which is also supported by the fact that activation is effected by quite a large range of both organic and inorganic acids. However, the differences observed between the effects of acids of similar strength might well indicate that the oxidizing power of the resulting species is influenced by the anion of the acid, probably through modification of the environment of cobalt. The particularly high reactivity of the species produced by interaction of cobaltic acetate with sulphuric, methanesulphonic, and benzenesulphonic acids compared with other strong acids such as perchloric acid might be ascribed to co-ordination of cobalt with  $\text{SO}_3^-$  groups.\*

\* Sharp has shown that the addition of dilute sulphuric acid to aqueous solutions of cobaltic acetate causes a rapid initial decrease in the optical density of the solutions at 300 nm followed by a slower decrease.<sup>10</sup> The rapid initial decrease has been interpreted as corresponding to a change in the anions surrounding the cobaltic ions with production of a more reactive species, the decomposition of which would be reflected by the slower decrease. It is noteworthy that the latter process obeys the kinetic law  $-\text{d}[\text{Co}^{\text{III}}]/\text{d}t = k[\text{Co}^{\text{III}}]^2[\text{H}^+]/[\text{Co}^{\text{II}}]_0$  which is similar to the kinetics we have determined for the acid-activated oxidation of hydrocarbons by cobaltic acetate in acetic acid (see below).

*Kinetic Studies.*—The important self-decomposition of cobalt(III) observed when sulphuric acid is used as activator and ascribed above to solvent oxidation makes quantitative kinetics difficult to establish for the oxidation of n-heptane. However, more significant data can be obtained with trifluoroacetic acid which has been shown above to activate more selectively the oxidation of the alkane. This is further illustrated by the results shown in Figure 1: in the conditions used the reduction of cobalt(III) in the presence of n-heptane was seven times faster than self-decomposition (cf. curves 1 and 4). In such cases, the oxidation of the alkane substrate can be considered as contributing for the major part to the process.

Figure 1 also shows that the variation with time of  $[\text{Co}^{\text{II}}]/[\text{Co}^{\text{III}}]_0$  ratio is not dependent on the initial concentration of the oxidant (see curves 1 and 2). This suggests first-order kinetics with respect to the latter, in accordance with most previous work on hydrocarbon oxidation by cobalt(III).<sup>3-6</sup> This is not the case, however, as demonstrated in Figure 1 by the important retarding effect of cobalt(II) (cf. curves 1 and 3). A similar retarding effect of cobalt(II) on the oxidation of toluene by cobaltic acetate in acetic acid has been pointed out by Heiba *et al.*<sup>7</sup> and kinetically demonstrated by Sakota *et al.*<sup>11</sup> This effect can therefore be considered as a general feature of the oxidations by cobaltic acetate in acetic acid medium, whether an acidic activator is present or not.

According to Sakota *et al.* the oxidation of toluene by cobaltic acetate in acetic acid is of the second order with

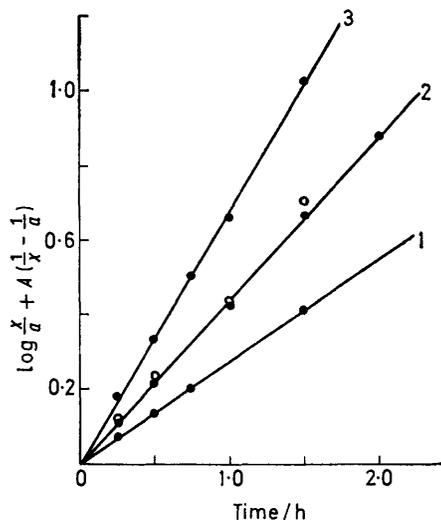


FIGURE 2 Kinetics of the reduction of cobaltic acetate in acetic acid at 40 °C under nitrogen in the presence of n-heptane and 1.03M-trifluoroacetic acid;  $x = [\text{Co}^{\text{II}}]$ ,  $a = [\text{Co}^{\text{III}}]_0$ ,  $A = [\text{Co}^{\text{III}}] + [\text{Co}^{\text{II}}]$ . [n-Heptane] 1, 0.25M; 2, 0.50M; 3, 1.00M. ●  $[\text{Co}^{\text{III}}]_0$  0.31M,  $[\text{Co}^{\text{II}}]_0$  0.10M; ○  $[\text{Co}^{\text{III}}]_0$  0.16M,  $[\text{Co}^{\text{II}}]_0$  0.05M. Cobalt(III) preparation: solution (see Experimental section)

respect to the cobalt(III) and the reaction rate varies inversely with the concentration of cobalt(II) [equation (1)].

$$-\text{d}[\text{Co}^{\text{III}}]/\text{d}t = k_{\text{obs}}[\text{Co}^{\text{III}}]^2/[\text{Co}^{\text{II}}] \quad (1)$$

By integration of equation (1), expression (2) is derived,

<sup>10</sup> J. A. Sharp, *J. Chem. Soc.*, 1957, 2030.

<sup>11</sup> K. Sakota, Y. Kamiya, and N. Ohta, *Canad. J. Chem.*, 1969, 47, 387.

where  $x = [\text{Co}^{\text{III}}]$ ,  $a = [\text{Co}^{\text{III}}]_0$ , and  $A = [\text{Co}^{\text{III}}] + [\text{Co}^{\text{II}}]$ . Figure 2 shows a plot of the left-hand side of equation (2) against time for experiments in which n-heptane at different

$$\ln \frac{x}{a} + A \left( \frac{1}{x} - \frac{1}{a} \right) = k_{\text{obs}} t \quad (2)$$

concentrations was oxidized at 40 °C by cobaltic acetate in the presence of trifluoroacetic acid. The agreement with expression (2) may be considered as satisfactory and, in fact, no simple kinetic law other than (1) better fits the experimental results.

The rate constants  $k_{\text{obs}}$  thus determined reasonably fit expression (3) which has an intercept markedly higher than

$$k_{\text{obs}}/\text{h}^{-1} = 0.158 + 0.525[\text{n-heptane}] \quad (3)$$

expected from the rate of the self-decomposition of cobalt(III) observed in the absence of hydrocarbon substrate.\* This might indicate that the self-decomposition of cobalt(III) is enhanced by the presence of the substrate, a conclusion which is also confirmed by the fact that the constants  $k_{\text{obs}}$  lie rather on a slight curve whose tangents have an intercept increasing with the concentration of n-heptane. The same observation has been made by Waters and his co-workers for the oxidation of toluene by cobaltic perchlorate.<sup>5</sup> However, in spite of that minor deviation from linearity, the reaction is clearly of the first order with respect to the hydrocarbon substrate, *i.e.*, by neglecting the self-decomposition term we obtain equation (4).

$$-\frac{d[\text{Co}^{\text{III}}]}{dt} = \frac{k[\text{RH}][\text{Co}^{\text{III}}]^2}{[\text{Co}^{\text{II}}]} \quad (4)$$

The experiments reported above were all made under a nitrogen atmosphere in order to avoid any disturbing effect of oxygen. Often, oxygen has no influence on electron-transfer oxidations by cobaltic salts,<sup>3-5</sup> but here it has a definite retarding effect on the reduction of cobalt(III). Thus, in the oxidation at 40 °C of 0.5M-n-heptane by 0.2M-cobaltic acetate activated by 1.5M-trichloroacetic acid, the consumption of the oxidant in the presence of oxygen is, throughout the reaction, *ca.* 70% of the consumption taking place in the same conditions under nitrogen.

**Product Studies.**—The analysis by v.p.c. of ether extracts of mixtures obtained from the reaction of n-heptane with cobaltic acetate in the presence of trichloroacetic acid reveals that different products are formed according to whether oxygen is present or not. The evolution of these products in both cases is shown in Figure 3. Under nitrogen the main products are heptyl chlorides and heptyl acetates while in the presence of oxygen they are heptanones. About the same distribution is observed when sulphuric acid or trifluoroacetic acid is substituted for trichloroacetic acid except that no chlorides are formed, heptyl acetates being the predominant products under nitrogen. Under oxygen, heptanols are also formed together with heptanones but as the reaction proceeds their concentration tends to decrease which suggests that they are further converted into hept-

anones. Chlorides are never detected when the reaction is carried out under oxygen.

Those different products consist of a mixture of position isomers resulting from attack on the different methylene groups within the carbon chain. Table 2 quotes typical distributions of isomers in each family of products obtained from n-heptane, n-decane, and n-dodecane. In most cases, the isomer substituted on position 2 of the carbon chain is in excess over the proportion which would result from

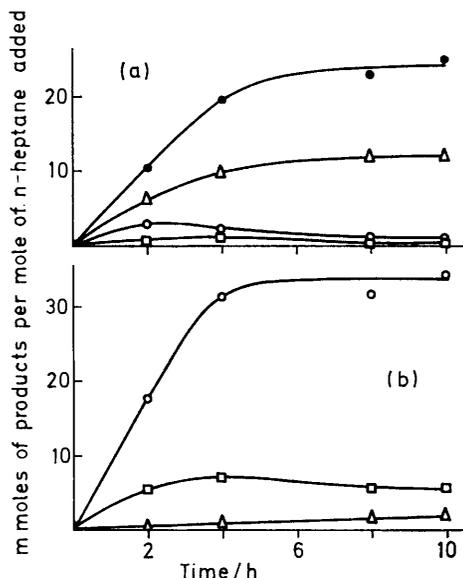


FIGURE 3 Formation of neutral products in the oxidation of n-heptane at 40 °C by cobaltic acetate in acetic acid in the presence of 1.5M-trichloroacetic acid (a) under nitrogen and (b) under oxygen. ○, Heptanones; ●, heptyl chlorides; □, heptanols; △, heptyl acetates. [n-Heptane] 0.50M,  $[\text{Co}^{\text{III}}]_0$  0.18M. Cobalt(III) preparation: solution (see Experimental section)

statistical attack (40, 25, and 20% for n-heptane, n-decane, and n-dodecane respectively). The same selectivity has been observed to a lesser extent in the non-catalytic oxidation of n-dodecane<sup>12</sup> and in the cobalt-catalysed oxidation of n-heptane.<sup>13</sup> However, in most cases the distribution of products from the oxidation of n-alkanes has been reported to be purely statistical.<sup>14,15</sup> In this respect, it is noteworthy that the selectivity for 2-isomers is adversely affected by rising temperature above 40 °C so as to become nearly statistical at 100 °C (experiments 8—12). Moreover, at this temperature the composition of the products is completely altered, *i.e.*, under oxygen esters and halides are formed in substantial amounts together with unidentified compounds. Obviously a change in reaction mechanism takes place at the higher temperatures.

In addition to neutral products such as ketones, esters, *etc.*, some acids are also produced by oxidation of n-alkanes with cobaltic acetate. Table 3 gives the composition of the

\* In the conditions used, the self-decomposition of cobalt(III) obeys no simple kinetics: the rate constants determined as above decrease abnormally with time from *ca.* 0.045 h<sup>-1</sup> after 15 min to a steady value of *ca.* 0.015 h<sup>-1</sup> after 2 h. This suggests that the self-decomposition of cobalt(III) in its early stages corresponds mainly to the consumption of some impurity present in the reaction mixture.

<sup>12</sup> A. W. Dawkins, Proc. Symp. Normal Paraffins (Manchester, 1966); *Eur. Chem. News Suppl.*, 1966, Dec. 2, p. 49.

<sup>13</sup> J. A. Bigot, P. L. Kerkhoffs, and T. Theeuwen, *Rec. Trav. chim.*, 1965, **84**, 1243.

<sup>14</sup> J. L. Benton and M. M. Wirth, *Nature*, 1953, **171**, 269.

<sup>15</sup> A. N. Bashkirov and V. V. Kamzolkin, Proc. 5th World Petroleum Congress, New York, 1959, sect. 4, p. 175.

acids obtained from n-heptane in the presence of trichloroacetic acid as activator. Under a nitrogen atmosphere, n-heptanoic acid is mainly formed clearly through further oxidation of the products resulting from attack on a terminal methyl group. [1-Chloroheptane and heptyl acetate are much less resistant to oxidation by cobalt(III) than their secondary isomers.] Under oxygen, there is obtained a mixture of acids from which n-hexanoic acid is virtually absent. These

may be ascribed to further oxidation (5) of the incipient free radical into a carbonium ion and reaction (6) of the



latter with the solvent. Another possibility is that heptyl acetates are formed from radicals through a

TABLE 2

Isomer distribution in the products from the oxidation of n-alkanes by cobaltic acetate<sup>a</sup> in acetic acid in the presence of strong acids. [n-Alkane] = 0.50M. [Co<sup>III</sup>]<sub>0</sub> = 0.18M

No.	Atmosphere	Alkane	Added acid	[Acid]/M	t/°C	Time/h	Principal products (mole % <sup>b</sup> )	Isomer distribution (%)					
								1	2	3	4	5	6
1	N <sub>2</sub>	n-Heptane	H <sub>2</sub> SO <sub>4</sub>	0.5	25	½	Acetates 69	0	64	27	9		
2	N <sub>2</sub>	n-Heptane	HClO <sub>4</sub>	1.0	25	1	Acetates 88	0	70	24	6		
3	N <sub>2</sub>	n-Heptane	CF <sub>3</sub> ·CO <sub>2</sub> H	1.4	25	18	Acetates 85	0	81	16	3		
4	N <sub>2</sub>	n-Heptane	CCl <sub>3</sub> ·CO <sub>2</sub> H	1.5	25	6	Chlorides 76	6	80	9	5		
5	O <sub>2</sub>	n-Heptane	H <sub>2</sub> SO <sub>4</sub>	0.5	25	½	Ketones 69	0	60	27	13		
6	O <sub>2</sub>	n-Heptane	CCl <sub>3</sub> ·CO <sub>2</sub> H	1.5	25	6	Ketones 80	0	83	12	5		
7	O <sub>2</sub>	n-Heptane <sup>c</sup>	CCl <sub>3</sub> ·CO <sub>2</sub> H	1.5	25	18	Ketones 75	0	75	18	7		
8	O <sub>2</sub> <sup>d</sup>	n-Heptane	CCl <sub>3</sub> ·CO <sub>2</sub> H	1.5	25	4	Ketones 80	0	78	15	7		
9	O <sub>2</sub> <sup>d</sup>	n-Heptane	CCl <sub>3</sub> ·CO <sub>2</sub> H	1.5	40	4	Ketones 84	0	76	17	7		
10	O <sub>2</sub> <sup>d</sup>	n-Heptane	CCl <sub>3</sub> ·CO <sub>2</sub> H	1.5	60	4	Ketones 96	0	66	23	11		
11	O <sub>2</sub> <sup>d</sup>	n-Heptane	CCl <sub>3</sub> ·CO <sub>2</sub> H	1.5	80	4	Ketones 84	0	59	28	13		
12	O <sub>2</sub> <sup>d</sup>	n-Heptane	CCl <sub>3</sub> ·CO <sub>2</sub> H	1.5	100	4	Ketones 44	0	47	36	17		
13	O <sub>2</sub>	n-Decane	CCl <sub>3</sub> ·CO <sub>2</sub> H	1.5	40	6	Ketones 81	0	67	13	20		
14	O <sub>2</sub>	n-Dodecane	CCl <sub>3</sub> ·CO <sub>2</sub> H	1.5	40	6	Ketones 78	0	65	13	22		0

<sup>a</sup> Preparation: experiment 1—7, powder; 8—14, solution (see Experimental section). <sup>b</sup> In products determined in ether extract (see Experimental section); minor amounts of unidentified products not taken into account. <sup>c</sup> No solvent is used. <sup>d</sup> Pressure: 10 kg cm<sup>-2</sup>; experiments performed in a 316 stainless-steel autoclave.

acids do not result from further oxidation of heptanones for in this case n-hexanoic acid should be present in a

TABLE 3

Formation of acids in the oxidation of n-heptane by cobaltic acetate<sup>a</sup> in acetic acid in the presence of 1.5M-trichloroacetic acid

Temperature, 40 °C. Time of reaction, 6 h. [n-Heptane] = 0.5M. [Co<sup>III</sup>]<sub>0</sub> = 0.18M.

Atmosphere	Acids in the products <sup>d</sup> (mole %)	Distribution of the acids <sup>c</sup> (mole %)				
		C(3)	C(4)	C(5)	C(6)	C(7)
Nitrogen	12	0	0	6	6	88
Oxygen	27	20	20	42	2	16

<sup>a</sup> Preparation: solution (see Experimental section). <sup>b</sup> Minor amounts of unidentified products not taken into account. <sup>c</sup> Some acetic acid is probably produced but cannot be distinguished from the solvent.

significant amount.\* It appears that another mode of chain-fission is operative.

## DISCUSSION

The results of the product studies can only be explained by assuming that the first species produced from attack on the alkanes by cobalt(III) is a free radical. The formation of heptyl acetates observed when the oxidation of n-heptane is carried out under nitrogen

\* Heptanones are oxidized by cobalt(III) mainly into acids. A typical distribution of the acids obtained from 2-heptanone is the following (in mole %): propionic, 4%; butyric, 10%; pentanoic, 67%; hexanoic, 19%.

concerted process involving the acetate ligands of cobalt(III). From the available data the mechanisms cannot be distinguished.

The extensive formation of heptyl chlorides observed when the reaction is performed in the presence of trichloroacetic acid results undoubtedly from chlorine abstraction (7) by heptyl radicals from trichloroacetic



acid. The same type of reaction is known to occur in the free-radical addition to olefins of halogenomethanes and related compounds including trichloroacetyl chloride and trichloroacetonitrile.<sup>16</sup> It has been shown in this laboratory that alkyl halides are also formed in the reaction of alkanes with cobaltic acetate in the presence of a variety of halogeno-compounds such as carbon tetrachloride, chloroform, trichlorobromomethane, tribromoacetic acid, α-bromoisobutyric acid, and even molecular bromine.<sup>17</sup>

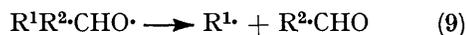
The formation of alkyl halides is however completely precluded when the oxidation of alkanes is performed in the presence of oxygen. This can be easily explained by the greater tendency of alkyl radicals to react with molecular oxygen to give peroxy radicals, as in reaction (8). Ketones, alcohols, and acids formed in these



<sup>16</sup> C. Walling, 'Free Radicals in Solution,' Wiley, New York, 1957, p. 239 *et seq.*

<sup>17</sup> Belg.P. 727,875/1969; B.P. 1,209,140/1970.

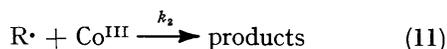
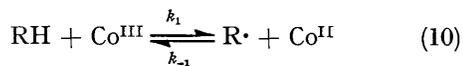
conditions are the expected products from further transformation of these peroxy radicals through reactions known to occur in most catalytic systems. For instance, the formation of acids from n-heptane as observed under oxygen (Table 3) may be partly explained by homolytic fission (9) of intermediate alkoxy radicals.



The primary alkyl radical  $R^1\cdot$  would then react readily with oxygen to afford ultimately the corresponding acid *via* the aldehyde. In such fissions, alkyl radicals higher than methyl are known to be more easily eliminated,<sup>18,19</sup> which accounts for the negligible formation of hexanoic acid, as actually observed.

The radicals formed from a given n-alkane should have a stability decreasing in the order  $\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CH}_2\text{R} > \cdot\text{CHEt}\cdot\text{CH}_2\text{R} > \cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\text{R}$  as determined by the number of hydrogen atoms that can be concerned in hyperconjugation. This order is consistent with the selectivity observed for isomers oxidized at the  $\alpha$ -position with respect to a terminal methyl group. This selectivity, however, cannot be ascribed only to energetic factors as demonstrated by other results obtained in this laboratory from branched alkanes.<sup>17</sup> For instance, from the reaction of 2-methylpentane with cobaltic acetate in the presence of trichloroacetic acid under nitrogen there are obtained mainly chloride isomers with the following distribution: 1-, 6%; 2-, 5%; 3-, 2%; 4-, 74%; 5-, 13%. We see that in spite of the presence of a tertiary hydrogen atom in the starting alkane, the attack by cobalt(III) takes place mainly on the methylene group  $\alpha$  to the terminal methyl group. The radical  $\cdot\text{CHMeBu}^1$  is thus produced 15 times more rapidly than the radical  $\cdot\text{CMe}_2\text{Pr}^n$  although the latter is more stable than the former by 4 kcal mol<sup>-1</sup>. The only possible explanation for such results is that interaction between hydrocarbons and cobalt(III) depends greatly on steric factors.\*

By taking into account the kinetic results reported above, we conclude that the first step of the oxidation of n-heptane is hydrogen abstraction (10) by cobalt(III) with reversible formation of a free radical and cobalt(II).



Reactions (10) and (11) would lead to the kinetic expres-

\* In their recent work on the hydrogen-deuterium exchange in alkanes catalysed by platinum(II), Hodges and his co-workers observed that the rate of exchange of hydrogen atoms decreases in the order primary > secondary > tertiary.<sup>20</sup> Clearly the same kind of steric effect is operating in this system.

<sup>18</sup> D. G. Hoare and W. A. Waters, *J. Chem. Soc.*, 1964, 2552.

<sup>19</sup> P. Gray and A. Williams, *Chem. Rev.*, 1959, 59, 239.

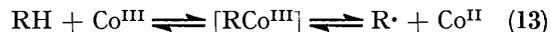
<sup>20</sup> R. J. Hodges, D. E. Webster, and P. B. Wells, *J. Chem. Soc. (A)*, 1971, 3230.

<sup>21</sup> U.S.P. 1,976,757/1934.

sion (12) and if it is assumed that  $k_2[\text{Co}^{\text{III}}]$  is smaller

$$-\frac{d[\text{Co}^{\text{III}}]}{dt} = \frac{2k_1k_2[\text{RH}][\text{Co}^{\text{III}}]^2}{k_2[\text{Co}^{\text{III}}] + k_{-1}[\text{Co}^{\text{II}}]} \quad (12)$$

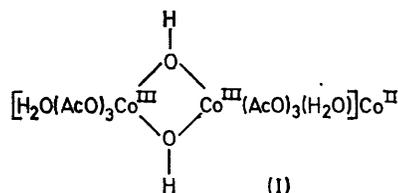
than  $k_{-1}[\text{Co}^{\text{II}}]$  we obtain the experimental equation (4). The actual mode of interaction between cobalt(III) and the substrate has still to be elucidated. It is likely that an intermediate alkylcobalt complex (13) is involved.



Similar complexes have been demonstrated to be formed through interaction of alkyl radicals with chromous species and were shown to be hydrolysed or acetylated to an alkane and a chromic species.<sup>21</sup> The selectivities observed in the present work might thus be explained by steric hindrance to formation of this alkylcobalt complex.

#### EXPERIMENTAL

*Preparation of Cobaltic Acetate.*—Cobaltic acetate was prepared from commercial cobaltous acetate tetrahydrate in acetic acid by co-oxidation with acetaldehyde in the presence of molecular oxygen.<sup>22</sup> The resulting solution was further treated according to two different methods: (a) The solution is concentrated to at least 2/3 of its original volume by evaporation under reduced pressure to eliminate most of the water produced in the preparation. The resulting concentrate is eventually diluted with glacial acetic acid to a concentration of 1.0–1.5M. In the solutions thus prepared, generally more than 95% of cobalt is in cobaltic form (*ca.* 75% only when air is substituted for pure oxygen in the co-oxidation step). (b) The solution is evaporated under reduced pressure to a viscous mass which is then triturated with ether until a homogeneous slurry is obtained. By filtration a green powder is separated which, after being dried, can be stored in the cold for long periods without significant loss of activity. This powder is easily soluble in acetic acid and in most polar solvents including water. Its cobalt content is given in Table 4 wherein it is compared with other samples<sup>23,24</sup> of cobaltic acetate described in the literature and for which ionic structures such as (I) have been



suggested.<sup>23</sup> The solutions obtained by dissolving in acetic acid powdered cobaltic acetate prepared by method

<sup>22</sup> J. K. Kochi and J. W. Powers, *J. Amer. Chem. Soc.*, 1970, 92, 137.

<sup>23</sup> Y. Wormser and D. Peschanski, *Bull. Soc. chim. France*, 1962, 876.

<sup>24</sup> J. A. Sharp and A. G. White, *J. Chem. Soc.*, 1952, 110.

(b) have a lower oxidizing activity than the solutions prepared by method (a). This may be ascribed to the retarding effect of cobalt(II) present in the powder. Qualitatively, however, both preparations afford identical results.

TABLE 4

Cobalt content (% w/w) of powdered preparations of cobaltic acetate

Sample	Total Co	Co <sup>III</sup>	$\frac{\text{Co}^{\text{III}}}{\text{Total Co}}$
This work, typical sample	30.9	19.2	0.62
Ref. 24, sample 3	29.4	17.4	0.59
Ref. 23, sample e	31.2	20.6	0.66
Ref. 23, sample f	30.1	20.0	0.66
Calculated for formula (I)	29.4	19.6	0.67

Cobalt(III) was determined by reaction with an excess of aqueous ammonium iron(II) sulphate and back-titration of the ferrous ions with potassium dichromate with sodium biphenylsulphonate as indicator. Total cobalt was determined by first reducing cobalt(III) by heating with dilute sulphuric acid on a water-bath and titrating cobalt(II) with sodium ethylenediaminetetra-acetate with murexide as indicator.

*Kinetic Measurements under Nitrogen Atmosphere.*—The experiments for studying the kinetics of cobalt(III) reduction in an oxygen-free atmosphere were performed on ca. 5 ml of reaction mixture in closed test-tubes immersed, without agitation, in a thermostat. The tubes were first deaerated by flushing with nitrogen and a solution of the substrate and the acidic activator in acetic acid was introduced. The tubes were then allowed to equilibrate in the thermostat for ca. 10 min before the addition of cobaltic acetate dissolved in acetic acid. The resulting mixture was homogenized and maintained for the desired time in the thermostat, the introduction of cobaltic acetate being considered as the zero-time of the reaction.

At the end of the experiment, the mixture was poured

in a vessel containing ferrous ions and unchanged cobalt(III) was determined as described above.

*Determination of Neutral and Acidic Products from Oxidation of n-Alkanes.*—Typically, the experiments for determining the products formed by oxidation of n-alkanes were performed in 100 ml Erlenmeyer flasks containing ca. 10–15 ml of reaction mixture. The flasks were usually closed with a rubber cap and flushed with nitrogen or oxygen through syringe needles before introduction of the reactants. For the experiments carried out under nitrogen the flasks were maintained at a controlled temperature without agitation. For those in the presence of oxygen, they were agitated in a shaking incubator.

At the end of the experiment, unchanged cobalt(III) was reduced with aqueous ammonium iron(II) sulphate, the internal standards (*p*-dichlorobenzene and octanoic acid when n-heptane was the substrate) were added, and the products were extracted exhaustively with ether. The ether extract was neutralized in the cold with aqueous KOH, then washed with water saturated with sodium chloride, dried (Na<sub>2</sub>SO<sub>4</sub>), and concentrated by distillation before being analysed by v.p.c. To determine the acidic products, the alkaline aqueous phase was first washed with ether to remove any neutral product and then it was acidified with sulphuric acid to liberate the acids. These were extracted again with ether in a continuous-extraction apparatus for ca. 4 h. The resulting ether extract was also concentrated by distillation and analysed by v.p.c.

In the experiments where acidic oxidation products have to be determined, care should be taken that the acetic acid used as solvent be free from propionic acid. Acetic acid from Carlo Erba, RP-grade, was shown to fulfil this condition.

We thank the Institut Belge pour l'Encouragement de la Recherche Scientifique dans l'Industrie et l'Agriculture for support and J. Vaerman and J. N. Bertrand for assistance.

[2/383 Received, 21st February, 1972]