*Kinetic Studies of the Oxidation of Aromatic Compounds by Potassium Permanganate. Part IV.** n- *and* iso-*Propylbenzene.*

By C. F. Cullis and J. W. Ladbury.

[Reprint Order No. 6306.]

The kinetics of the oxidation by potassium permanganate of *n*- and *iso*-propylbenzene have been investigated and compared with those of the lower homologues. With both isomers, analysis of oxidation products shows that initial attack occurs at the α-carbon atom. *n*-Propylbenzene yields propiophenone, which is rapidly further oxidised to benzoic and acetic acid; *iso*propylbenzene gives acetophenone which is slowly converted into benzoic acid and carbon dioxide. Practically all the carbon dioxide evolved arises from attack of the β- and γ-carbon atoms of the alkyl chain, and not from disruption of the aromatic ring.

The effect of added salts shows that the importance of intermediate manganese ions as oxidising entities depends on whether the group adjacent to the aromatic ring is primary, secondary, or tertiary; susceptibility to direct attack by permanganate, and overall reactivity, both increase in the order, $CH > CH_2 > CH_3$.

EARLIER studies of the oxidation of some monoalkylbenzenes (Parts I—III, *J.*, 1955, 555, 1407, 2850) have been extended to *n*- and *iso*-propylbenzene.

EXPERIMENTAL

The experimental methods were similar to those described in Part I (*loc. cit.*). The solvent was 54·2% w/v aqueous acetic acid.

Products of the Oxidation.—Ether extracts containing the neutral and acidic constituents were obtained by a method similar to that outlined in Part I.

(a) n-*Propylbenzene.* The ether and unchanged *n*-propylbenzene were distilled from the neutral extract. The residue contained a small amount of propiophenone (m. p. of 2 : 4-dinitrophenylhydrazone 188°; lit., 188°); no alcohols could be detected and the iodoform test for the acetyl group was negative.

Some ether was distilled from the extract containing the acid constituents, and on further concentration a large yield of benzoic acid (m. p. 121°; lit., 121°) was obtained. No evidence was found for the presence of ketonic acids or phenols.

Since the only detectable products are propiophenone (in very small yield) and benzoic acid, it appears that oxidation takes place initially at the α-carbon atom to give propiophenone, which is rapidly further oxidised to benzoic acid.

(b) iso*Propylbenzene.* After the ether and unchanged *iso*propylbenzene had been removed from the neutral extract, the remainder distilled completely between 195° and 208° and contained a considerable amount of acetophenone (b. p. 201°; lit., 202°; m. p. of 2 : 4-dinitrophenylhydrazone 249°; lit., 249°). No alcohols could be detected.

On evaporation of the ether from the acid extract, a residue of benzoic acid was obtained. Tests for ketonic acids and phenols were negative.

As with *n*-propylbenzene, the initial point of attack appears to be the α-carbon atom (cf. Stephens, *J. Amer. Chem. Soc.*, 1926, **48**, 1824, 2920). Acetophenone is the first isolable product and this is slowly further oxidised to benzoic acid.

RESULTS AND DISCUSSION

Evolution of Carbon Dioxide.—The results in Table 1 show that the amount of carbon dioxide evolved during the oxidation of *n*-propylbenzene corresponds to complete oxidation of only 5·4% of the combined carbon in this compound. Since almost quantitative yields of benzoic acid are obtained, the small amounts of carbon dioxide must be formed by

---

* Part III, *J.*, 1955, 2850.

processes which do not involve appreciable disruption of the aromatic ring. The two most likely overall reactions are :

$$\mathrm{Ph{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3 + 5O \longrightarrow Ph{\cdot}CO_2H + CH_3{\cdot}CO_2H + H_2O} \quad . \quad . \quad . \quad . \quad (1)$$

$$\mathrm{Ph{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3 + 9O \longrightarrow Ph{\cdot}CO_2H + 2CO_2 + 3H_2O} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

According to (2) the percentage of combined carbon completely oxidised is 22·2%. It is evident therefore that (1) is the predominant reaction and that only 5·4/22·2 × 100%, *i.e.*, 24·3%, of the organic compound is oxidised *via* reaction (2).

With *iso*propylbenzene, the carbon dioxide evolved must come from the two β-carbon atoms. If the overall reaction is :

$$\mathrm{Ph{\cdot}CH(CH_3)_2 + 5O \longrightarrow Ph{\cdot}CO{\cdot}CH_3 + CO_2 + 2H_2O} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

the percentage of combined carbon completely oxidised is 11·1%.

TABLE 1.

Temp. : 50°. Solvent : 54·2% w/v aqueous acetic acid.
[Organic compound] = 0·0103M ; [KMnO$_4$] = 0·103M.

	Compound taken (g.)	Wt. (g.), corr. for oxidn. of solvent, of		Organic compound completely oxidised (%)
		BaCO$_3$	CO$_2$	
PhPr^n	0·1202	0·0956	0·0212	5·4
	0·1202	0·0960	0·0214	5·4
PhPr^i	0·1202	0·3221	0·0719	18·1
	0·1202	0·3264	0·0727	18·4

If, on the other hand, oxidation proceeds according to the equation :

$$\mathrm{Ph{\cdot}CH(CH_3)_2 + 9O \longrightarrow Ph{\cdot}CO_2H + 2CO_2 + 3H_2O} \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

the corresponding value is 22·2%. The observed extent of carbon dioxide evolution (Table 1) lies between these two values, no doubt owing to the slow but appreciable further oxidation of acetophenone to benzoic acid. Measurements of the amounts of benzoic acid and carbon dioxide formed at various stages of reaction suggest that, with this compound too, little disruption of the aromatic ring occurs.

It is thus found in general that, as the size of the alkyl group is increased in the mono-alkylbenzenes, the extent of ring rupture diminishes (cf. Parts I and III).

Stoicheiometry.—The amount of permanganate needed in practice to oxidise *n*-propylbenzene was found by allowing the organic compound to react with an excess of oxidising agent, until the residual oxidising power of the solution showed only a slight decrease with time characteristic of the rate of oxidation of benzoic acid and of the solvent. The results in Table 2 confirm the conclusion, reached from measurements of carbon dioxide evolution, that the predominant reaction is (1), involving conversion of *n*-propylbenzene into benzoic acid and acetic acid. If x is the percentage of reaction which proceeds via (2), it follows from the figures given in Table 2, that $[6{\cdot}0x + 3{\cdot}3(100 - x)]/100 = 4{\cdot}0$, whence $x = 26{\cdot}0\%$. This value of x is in good agreement with that (24·3%) obtained from measurements of carbon dioxide evolution.

The corresponding measurements of the stoicheiometry of the reaction cannot be made with *iso*propylbenzene, owing to the formation of a moderately stable intermediate compound, acetophenone, which is only slowly further oxidised to benzoic acid.

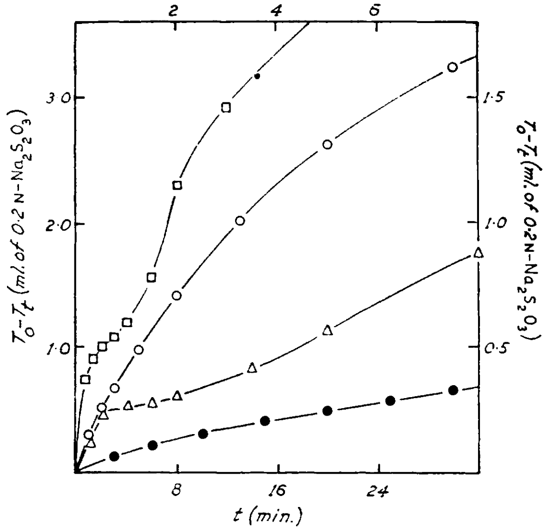
TABLE 2.

Temp. : 50°. Solvent : 54·2% w/v aqueous acetic acid.
[Ph·Pr^n] = 0·00517M ; [KMnO$_4$] = 0·0413M.

	Found	Theor. [reaction (1)]	Theor. [reaction (2)]
Moles of KMnO$_4$ reqd. to oxidise 1 mole of PhPr^n	4·01, 4·05, 3·94 Average : 4·0	3·3	6·0

The Development of Reaction with Time.—The reaction–time curves for the oxidation of *n*-propylbenzene (Fig. 1) are of similar form to those obtained with toluene and ethylbenzene (Cullis and Ladbury, *J.*, 1955, 555, 2850). Those for *iso*propylbenzene, on the other hand, exhibit a very high initial rate followed by a slower reaction which develops autocatalytically with time, particularly when the oxidising agent is in excess, as shown by the typical reaction-time curves in Fig. 1. The amount of permanganate which has been taken up when the initial fast reaction ceases does not correspond to the formation of any likely intermediate compound. The observed behaviour suggests that the *iso*propylbenzene may contain a small amount of an easily oxidisable impurity, such as α-methylstyrene, which rapidly consumes permanganate in the early stages of reaction. The *iso*propylbenzene used was carefully purified and its measured b. p. and refractive index agreed very well with recorded values. Nevertheless, several samples of the compound were subjected to different degrees of purification, and one sample was shaken twice with 60% w/v sulphuric acid to remove unsaturated compounds. No differences in reactivity were, however, detected for any of the samples investigated. It was therefore concluded that the characteristic shape of the reaction-time curves was an integral part of the behaviour of the pure compound.

FIG. 1. *Reaction-time curves for the oxidation of* n- *and* iso-*propylbenzene.*

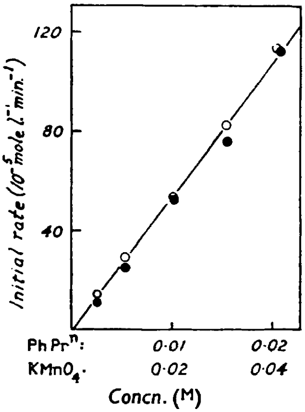


Temp.: 50°. Solvent: 54·2% w/v aqueous acetic acid.

○ [PhPr^n] = 0·02M; [$KMnO_4$] = 0·02M.
● [PhPr^n] = 0·01M; [$KMnO_4$] = 0·005M.
□ [PhPr^i] = 0·01M; [$KMnO_4$] = 0·04M.
△ [PhPr^i] = 0·005M; [$KMnO_4$] = 0·02M.

The left-hand ordinates and lower abscissæ refer to *n*-propylbenzene, and the right-hand ordinates and upper abscissæ to *iso*propylbenzene. The ordinate values may be converted into "moles of $KMnO_4$ per litre" by multiplication by the factor: 3·442 × 10^{-3}.)

FIG. 2. *The dependence of initial oxidation rate on reactant concentration.*



Temp.: 50°. Solvent: 54·2% w/v aqueous acetic acid.

○ [PhPr^n] = 0·01M; [$KMnO_4$] varied.
● [$KMnO_4$] = 0·02M; [PhPr^n] varied.

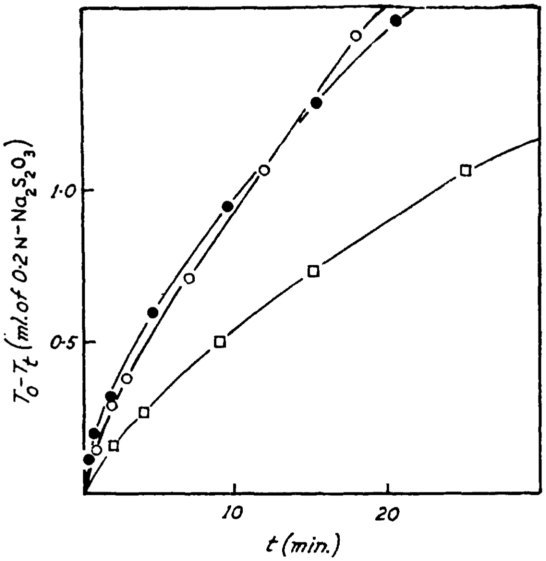
The curves for *iso*propylbenzene are of the same form as, though more pronounced than, those for *o*-xylene and *o*-toluic acid (Cullis and Ladbury, *J.*, 1955, 1407). Similar behaviour is found in the oxidation of *p*-nitrophenol (Hinshelwood, *J.*, 1919, 1180).

Influence of Reactant Concentrations.—As with the lower monoalkylbenzenes, the initial rate of oxidation of *n*-propylbenzene is of the first order with respect to both the organic compound and the oxidising agent (Fig. 2). The very rapid initial reaction of *iso*propylbenzene does not allow the rate to be determined accurately, and no reliable conclusions can be drawn as to the influence of reactant concentrations on the initial rate of oxidation of this compound.

Influence of Added Salts.—With *n*-propylbenzene, the effect of additions of manganous and pyrophosphate ions follows closely that found with toluene (Cullis and Ladbury, *J.*, 1955, 555). Mn^{2+} ions cause the initial oxidation rate to increase (Fig. 3), owing to formation of reactive intermediate manganese ions; the subsequent reaction is retarded owing to reduction of MnO_4^- ions by Mn^{2+} ions to give manganese dioxide. Addition of sufficient pyrophosphate ions, which remove intermediate manganese ions, reduces the rate to a limiting value; in presence of 0·02M-$K_4P_2O_7$, the maximum depression is obtained, which amounts to about one-half of the original rate (Fig. 3).

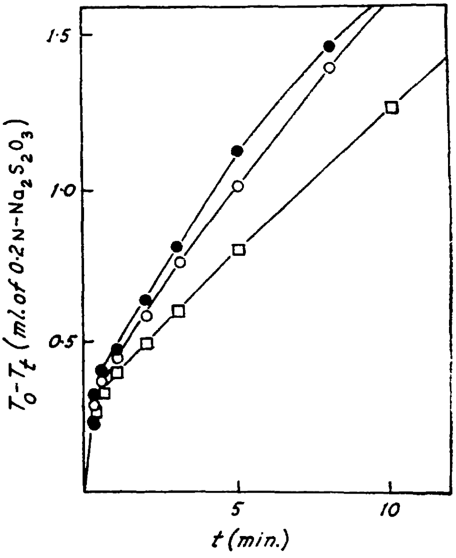
Manganous and pyrophosphate ions, on the other hand, do not appear to affect the initial high oxidation rate of *iso*propylbenzene (Fig. 4), though they alter the rate of the second stage of reaction. The results in Table 3 suggest that the importance of the rôle of intermediate manganese ions, as measured by the limiting reduction in rate on addition of excess of pyrophosphate ions, depends to a marked extent on the nature of the group in the α-position to the aromatic ring. The fact that pyrophosphate ions are without influence on the initial rate of oxidation of *iso*propylbenzene suggests that, in the early stages of reaction, the MnO_4^- ion is the sole active oxidising entity. The importance of intermediate manganese ions evidently decreases, and hence presumably the importance of MnO_4^- ions increases, according to whether the α-carbon atom is primary, secondary, or tertiary.

FIG. 3. *Reaction–time curves for the oxidation of* n-*propylbenzene in absence and in presence of added salts.*



Temp. 50° : Solvent : 54·2% w/v aqueous acetic acid.
[PhPrⁿ] = 0·01M; [$KMnO_4$] = 0·02M.
○ No added salt.
● [$MnSO_4$] = 0·005M.
□ [$K_4P_2O_7$] = 0·02M.

FIG. 4. *Reaction–time curves for the oxidation of* iso*propylbenzene in absence and in presence of added salts.*



Temp. : 50°. Solvent : 54·2% w/v aqueous acetic acid.
[PhPrⁱ] = 0·01M; [$KMnO_4$] = 0·02M.
○ No added salt.
● [$MnSO_4$] = 0·005M.
□ [$K_4P_2O_7$] = 0·02M.

TABLE 3.

Temp. : 50°. Solvent : 54·2% w/v aqueous acetic acid.
[Organic compound] = 0·01M; [$KMnO_4$] = 0·02M; [$K_4P_2O_7$] = 0·02M.

Compound	PhMe	PhEt	PhPrⁿ	PhPrⁱ
$\frac{\text{Inhibited rate in presence of } K_4P_2O_7}{\text{Uninhibited rate}}$	0·30	0·62	0·56	1·00

Influence of Temperature.—The initial rates of reaction of permanganate with *n*- and *iso*-propylbenzene at 50° and the Arrhenius parameters for the oxidation of the former compound (calculated from rate measurements in the temperature range, 40—60°) are shown in Table 4, together with the corresponding data for the lower monoalkylbenzenes. The values of A exhibit a similarity for *n*-propylbenzene and ethylbenzene but an appreciable difference for these two compounds as compared with toluene. This difference between the first and higher members of the homologous series is no doubt due to the change from a CH_3 to a CH_2 group in the α-position to the aromatic ring, which, it has already been seen, also affects the relative amounts of oxidation performed by the different oxidising species present (Table 3).

TABLE 4.

Solvent: 54·2% w/v aqueous acetic acid. [Organic compound] = 0·01M; [$KMnO_4$] = 0·02M.

Compound	10^5 × Initial oxidation rate (at 50°) (mole l.$^{-1}$ min.$^{-1}$)	E (kcal. mole^{-1})	A (l. mole^{-1} min.$^{-1}$)
Toluene	16·6	13·2	6·45 × 10^8
Ethylbenzene	34·7	14·8	1·87 × 10^{10}
n-Propylbenzene	50·8	14·4	1·50 × 10^{10}
*iso*Propylbenzene	*ca.* 520	—	—

The order of reactivity of the four compounds follows that of the inductive effects of the groups attached to the α-carbon atom, *i.e.* $(CH_3)_2 > CH_3{\cdot}CH_2 > CH_3 > H$; this is, of course, the usual order of increasing ease of electrophilic attack.

Influence of Structure.—No functional correlation exists between $\log_{10} k_{50}$ and E for the oxidation of the alkylbenzenes studied in this and earlier parts of the present series of papers, and the considerable changes in reactivity which occur with structure are therefore not primarily dependent on either one or other of the Arrhenius parameters. A similar conclusion was reached by Hinshelwood and Winkler (*J.*, 1936, 368, 371) as the result of an analysis of kinetic data on the oxidation of a number of phenols.

One of the authors (J. W. L.) thanks the East Ham Education Committee for a Senior Award and the Courtaulds' Scientific and Educational Trust Fund for a Postgraduate Scholarship.

INORGANIC AND PHYSICAL CHEMISTRY DEPARTMENT,
IMPERIAL COLLEGE, LONDON, S.W.7.

[*Received, April 6th,* 1955.]