Kinetic Studies of the Oxidation of Aromatic Compounds by Potassium Permanganate. Part III. Ethylbenzene.*

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A kinetic study of the oxidation of ethylbenzene and some related compounds is described. Initial attack of ethylbenzene occurs predominantly at the α-carbon atom to yield acetophenone as the first isolable product, which is slowly further oxidised to benzoic acid; measurements of carbon dioxide evolution suggest that there is little, if any, disruption of the aromatic ring.

Studies of the influence of added salts suggest that the Mn^{3+} ion, which is believed to be the principal oxidising entity in the oxidation of toluene, plays a less important rôle in the reactions of ethylbenzene and other compounds containing a β-carbon atom in the side-chain.

The form of the reaction–time curves exhibited by some oxygenated derivatives of ethylbenzene, and the influence of structure on ease of oxidation, are discussed.

PART I of this series (Cullis and Ladbury, *J.*, 1955, 555) described a kinetic investigation of the oxidation of toluene by potassium permanganate. This has now been extended to the next higher homologue, ethylbenzene.

EXPERIMENTAL

The experimental methods were similar to those described in Part I. The solvent was 54·2% w/v aqueous acetic acid. Solutions of 2-phenylethanol and phenylacetaldehyde were stored in an atmosphere of carbon dioxide.

Products of the Oxidation of Ethylbenzene.—Ether-extracts containing the neutral and the acidic constituents of the oxidation products were obtained by a method similar to that outlined in Part I. The neutral extract was dried (Na_2SO_4) and the ether was evaporated under reduced pressure. The residue was cooled to 5°, and the supernatant liquid decanted. Both phases were fractionally distilled. The solid contained a small amount of unchanged ethylbenzene (b. p. 136°; lit., 136°) but mainly acetophenone [b. p. 201° (lit., 202°); 2 : 4-dinitrophenylhydrazone, m. p. 249° (lit., 249°)]. The liquid decanted from the crystals was largely ethylbenzene, with smaller amounts of acetophenone. Tests with α-naphthyl *iso*cyanate showed that no appreciable quantity of 1-phenylethanol (lit., b. p. 205°) was present in the residues of the two distillates.

The ether from the acidic extract was evaporated, leaving colourless crystals soluble in hot, but insoluble in cold water. Recrystallisation from water yielded benzoic acid, m. p. and mixed m. p. 121° (lit., m. p. 121°). The mother-liquor was acidified and washed with ether. This extract was dried (Na_2SO_4); it gave no precipitate when 2 : 4-dinitrophenylhydrazine in aqueous alcohol was added, thus indicating the absence of ketonic acids. The ether extract and the mother-liquor gave negative tests for phenols with diazotised *p*-nitroaniline.

The only products found are thus acetophenone (about 50% yield), benzoic acid, and carbon dioxide. Thus oxidation probably occurs predominantly at the α-carbon atom (cf Cavill and Solomon, *J.*, 1954, 3943). The absence of β-oxygenated intermediates might be due to their being further rapidly oxidised as fast as they are formed. The observed rates of oxidation of β-oxygenated compounds (Table 3) show, however, that, if the β-carbon atom in ethylbenzene suffers appreciable oxidative attack, it should be possible to isolate 2-phenylethanol and phenylacetic acid. Yet they were not found.

RESULTS AND DISCUSSION

Evolution of Carbon Dioxide.—The amount of carbon dioxide evolved during the oxidation of ethylbenzene corresponded to complete oxidation of 7·8% of the combined carbon in this molecule (Table 1). Oxidation to carbon dioxide of one carbon atom per

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* Part II, *J.*, 1955, 1407.

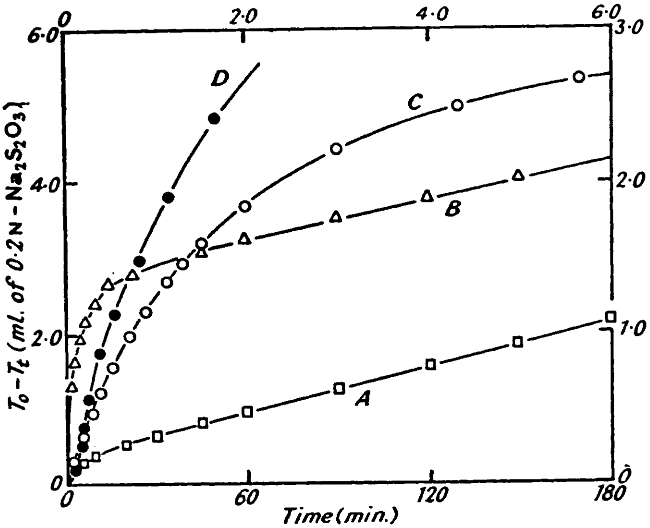
molecule, as would occur if ethylbenzene was oxidised completely to benzoic acid, would, on the other hand, correspond to a value of 12·5%. The difference is no doubt due to incomplete oxidation of acetophenone to benzoic acid.

TABLE 1.

Temp. : 50°. Solvent : 54·2% w/v aqueous acetic acid. [PhEt] = 0·0103M ; [$KMnO_4$] = 0·103M.

	$BaCO_3$ (g.)	CO_2 (g.)	PhEt completely
PhEt taken (g.)	(corrected for oxidn.	of solvent)	oxidised (%)
0·106	0·1212	0·0270	7·7
0·106	0·1242	0·0276	7·9

FIG. 1. *Reaction–time curves for the oxidation of ethylbenzene and related compounds.*



Temp. : 50°. Solvent : 54·2% w/v aqueous acetic acid.
[Organic compound] = 0·0103M ; [$KMnO_4$] = 0·0206M.

A, Acetophenone. *B*, Phenylacetaldehyde. *C*, Ethylbenzene. *D*, 2-Phenylethanol.

(The left-hand ordinates refer to ethylbenzene, 2-phenylethanol, and phenylacetaldehyde, and the right-hand ordinates to acetophenone. The lower abscissæ refer to ethylbenzene, acetophenone, and 2-phenylethanol, and the upper abscissæ to phenylacetaldehyde. The ordinate values may be converted into " moles of $KMnO_4$ per litre " by multiplication by the factor : $3{\cdot}442 \times 10^{-3}$.)

The number of moles of carbon dioxide produced is approximately equal to the number of moles of benzoic acid formed at any stage. This suggests that the carbon dioxide evolved is derived from the β-carbon atom in ethylbenzene, and that ring fission occurs, if at all, only to a comparatively small extent.

The Development of Reaction with Time.—Reaction–time curves for the oxidation of ethylbenzene and some associated compounds are shown in Fig. 1. With ethylbenzene, as with toluene, autocatalysis is not observed. The reaction–time curves for 2-phenylethanol show slight sigmoid character. With acetophenone and phenylacetaldehyde, a high initial oxidation rate is found, which falls off rapidly to give an almost linear curve. When the permanganate concentration alone is varied, the linear portions of the curves are almost parallel (Fig. 2), suggesting that the oxidation eventually becomes controlled largely by the rate of some internal rearrangement, such as enolisation, of the molecule of the organic compound (cf. Lejeune, *Compt. rend.*, 1926, **182**, 694 ; Drummond and Waters, *J.*, 1953, 440 ; 1955, 497).

With acetophenone, the observed behaviour may be accounted for if, in the system .

$$\mathrm{Ph{\cdot}CO{\cdot}CH_3} \underset{k_1}{\overset{k_1}{\rightleftharpoons}} \mathrm{Ph{\cdot}C(OH){:}CH_2} \qquad . \ . \ . \ . \ (1)$$

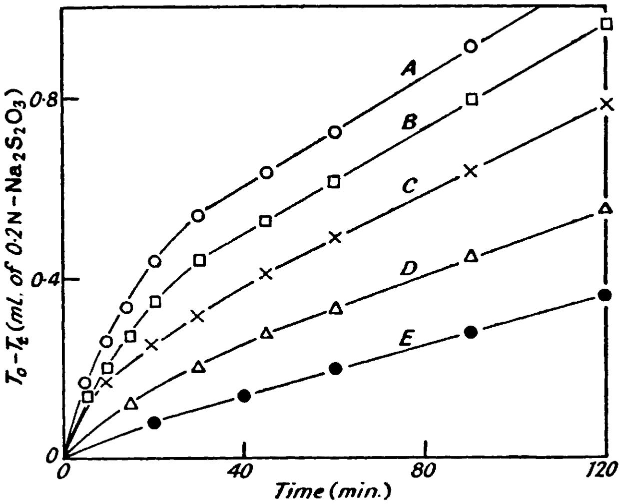
$$\mathrm{Ph{\cdot}CO{\cdot}CH_3 + KMnO_4} \xrightarrow{k_2} \text{Oxidation products} \qquad . \ . \ . \ . \ (2)$$

$$\mathrm{Ph{\cdot}C(OH){:}CH_2 + KMnO_4} \xrightarrow{k_3} \text{Oxidation products} \qquad . \ . \ . \ . \ (3)$$

it is assumed that $k_3 > k_1 > k_2$. In the early stages, the rate of oxidation will be given by :

$$k_2[\mathrm{Ph{\cdot}CO{\cdot}CH_3}][\mathrm{KMnO_4}] + k_3[\mathrm{Ph{\cdot}C(OH){:}CH_2}][\mathrm{KMnO_4}]$$

FIG. 2. *Reaction-time curves for the oxidation of acetophenone.*



Temp. : 50°. Solvent : 54·2% w/v aqueous acetic acid. [Ph·CO·CH$_3$] = 0·0103M. [KMnO$_4$] varied : *A*, 0·0410M; *B*, 0·0311M; *C*, 0·0206M; *D*, 0·0103M; *E*, 0·0052M.

As reaction proceeds, the concentration of the enol form will be reduced until (1) becomes rate-controlling with respect to (3). In these circumstances, the overall rate is equal to :

$$k_2[\mathrm{Ph{\cdot}CO{\cdot}CH_3}][\mathrm{KMnO_4}] + k_1[\mathrm{Ph{\cdot}CO{\cdot}CH_3}]$$

and since $k_1 > k_2$, the rate of oxidation depends only to a small extent on the permanganate concentration, as shown by the slight divergency of the almost parallel reaction–time curves in Fig. 2.

If the rates of oxidation, following the initial rapid stage of reaction, are plotted against the permanganate concentration, extrapolation to zero concentration of oxidising agent should, according to the mechanism outlined, give a rate equal to $k_1[\mathrm{Ph{\cdot}CO{\cdot}CH_3}]$, the rate of enolisation of the ketone. The extrapolated oxidation rate, calculated on the assumption that reaction takes place according to the equation

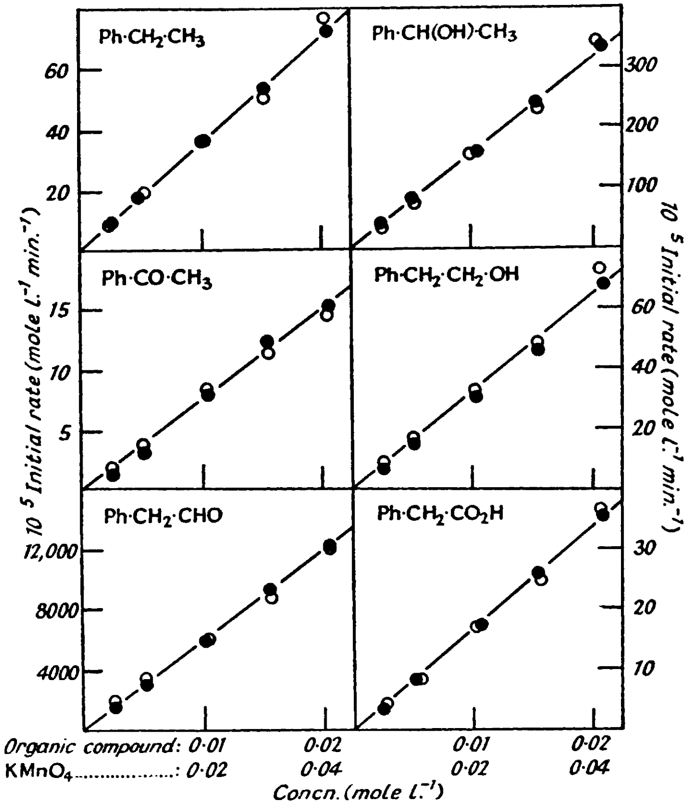
$$\mathrm{3Ph{\cdot}CO{\cdot}CH_3 + 8KMnO_4 + H_2O \longrightarrow 3Ph{\cdot}CO_2H + 3CO_2 + 8KOH + 8MnO_2}$$

is found to have the value $1{\cdot}40 \times 10^{-6}$ mole of acetophenone l.$^{-1}$ min.$^{-1}$. The rate of enolisation of acetophenone, recently determined in this laboratory by Mr. M. H. Hashmi, by means of iodine uptake is $1{\cdot}22 \times 10^{-6}$ mole l.$^{-1}$ min.$^{-1}$ under conditions identical with those in the oxidation experiments. The satisfactory agreement between the two values supports the suggestion that enolisation is an important factor controlling the rate of oxidation of acetophenone.

Influence of Reactant Concentrations.—The reactions of potassium permanganate with ethylbenzene and many associated compounds are initially of the first order with respect to each reactant. This can be seen from plots of initial rate against initial concentration of the two reactants when these are varied separately (Fig. 3). Second-order kinetics are, however, never maintained as reaction proceeds. The exhibition of comparatively simple behaviour initially, followed by a change to more complex kinetics, is frequently observed in studies of oxidation by potassium permanganate (Hinshelwood, *J.*, 1919, **115**, 1180; Musgrave and Moelwyn-Hughes, *Trans. Faraday Soc.*, 1933, **29**, 1162; Hinshelwood and Winkler, *J.*, 1936, 368).

Influence of Added Salts.—In presence of a large concentration of pyrophosphate ions, which form a comparatively stable complex with Mn^{3+} ions (Merz, Stafford, and Waters, *J.*, 1951, 638), the rates of oxidation of ethylbenzene and related compounds are reduced to about 60% of their original values (Table 2). Comparison of these results with those obtained for some other aromatic compounds shows that the proportion of oxidation effected by manganic ions depends quite markedly on the nature of the substrate. It appears that, with compounds containing a β-carbon atom, the Mn^{3+} ion is a less important oxidising entity than with toluene and the xylenes.

FIG. 3. *The dependence of initial oxidation rate on reactant concentrations.*



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

Influence of Structure.—Table 3 gives the values of the second-order velocity constants for the initial reaction at 50°, together with the Arrhenius parameters, for the oxidation of ethylbenzene and some related compounds. The values of ethylbenzene and the β-oxygenated derivatives may be compared with those for toluene, benzyl alcohol, benzaldehyde, and benzoic acid (Table 4).

The greater rate of oxidation of ethylbenzene, as compared with toluene, may be attributed to the increased electron density on the α-carbon atom due to the presence of the adjacent methyl group. The fact that 2-phenylethanol is less readily oxidised than benzyl alcohol must be due to the fact that the inductive effect of the ring is diminished by the presence of an interposed methylene group, which prevents the enhancement of polarisation of the O–H bond. Thus the α-carbon atom in 2-phenylethanol does not suffer to the same extent as that in benzyl alcohol the increased electron density due to the electronegativity of the oxygen atom.

TABLE 2.

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	Inhibited rate in presence of $K_4P_2O_7$ / Uninhibited rate
Ethylbenzene	0·62
(±)-1-Phenylethanol	0·67
Acetophenone	0·61
2-Phenylethanol	0·50
Phenylacetaldehyde	0·68
Phenylacetic acid	0·65
Toluene	0·30
o-Xylene	0·50
m-Xylene	0·36
p-Xylene	0·47

TABLE 3.

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

Compound	k_{50} (l. mole^{-1} min.$^{-1}$)	E (kcal. mole^{-1})	A (l. mole^{-1} min.$^{-1}$)	Compound	k_{50} (l. mole^{-1} min.$^{-1}$)
Ethylbenzene	1·89	14·8	$1·87 \times 10^{10}$	2-Phenylethanol	1·65
(±)-1-Phenylethanol	8·04	14·8	$8·49 \times 10^{10}$	Phenylacetaldehyde	300
Acetophenone	0·355	15·9	$2·07 \times 10^{10}$	Phenylacetic acid	0·675

TABLE 4.

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

R	CH_3	$CH_2·OH$	CHO	CO_2H
$k_{Ph·CH_2R}/k_{PhR}$	2·41	0·17	4·96	23·3

It has already been suggested that, with some of the compounds studied, the enol form may suffer preferential oxidation. If this is the case, the greater reactivity of phenylacetaldehyde than of benzaldehyde may be due to the possibility of enolisation in the former compound, which will be favoured by conjugation. Finally, the high rate of oxidation of phenylacetic acid, relative to that of benzoic acid, is in accord with the fact that side-chain carbon atoms are generally more susceptible to attack than carbon atoms in the aromatic ring, unless the latter positions are activated by the presence of substituents such as hydroxyl (Hinshelwood, *loc. cit.*) or methyl (Cullis and Ladbury, *loc. cit.*).

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