Kinetic Studies of the Oxidation of Aromatic Compounds by Potassium Permanganate. Part II. Substituted Toluenes.*

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A kinetic study has been made of the oxidation by potassium permanganate of some substituted toluenes. Oxidation is usually confined mainly to the methyl group which is converted into a carboxyl group, though with the xylenes and toluic acids considerable disruption of the aromatic ring also takes place. In general, the introduction of $+I$ substituents into toluene facilitates oxidation, while the presence of $-I$ groups decreases the ease of reaction.

Some of the compounds studied differ from toluene as regards the development of oxidation rate with time and the influence of reactant concentrations on the rate of reaction; possible explanations of the observed behaviour are discussed.

In Part I (Cullis and Ladbury, *J.*, 1955, 555) the results were presented of a kinetic study of the oxidation of toluene and related compounds by potassium permanganate. The present investigation deals with the oxidation of some substituted toluenes, and the behaviour of the nitro- and chloro-toluenes and of the toluic acids and xylenes is discussed.

Experimental

The experimental methods were similar to those described for toluene in Part I. The solvent was 54·2% w/v aqueous acetic acid in all cases.

Products of the Oxidation.—Full analyses were carried out with the xylenes (cf. Part I).

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* Part I, *J.*, 1955, 555.

The only isolable products were the tolualdehydes and the toluic and phthalic acids corresponding to the original xylene. The acidic extracts gave, however, a faint red colour with diazotised *p*-nitroaniline; a side reaction involving hydroxyl radicals may evidently cause the production of small amounts of phenols (cf. Baxendale and Magee, *Discuss. Faraday Soc.*, 1953, **14**, 160).

o-Tolualdehyde gave a 2 : 4-dinitrophenylhydrazone of m. p. 193° (lit. 194°) which was shown not to be 2 : 4-dinitrophenylhydrazine (m. p. 198°) by mixed-m. p. depression (to 179°). *o*-Toluic acid and phthalic acid were separated by extraction of the former into chloroform. The recrystallised *o*-toluic acid had m. p. 104° and gave an amide of m. p. 141° (lit. 104°, 142°). Phthalic acid was identified by the fluorescein and the phenolphthalein colour reaction. *m*- and *p*-Tolualdehydes were converted into their 2 : 4-dinitrophenylhydrazones, m. p.s 90° and 233° (lit. 91°, 234°), respectively. *m*- and *p*-Toluic acids were separated from *iso*phthalic and terephthalic acids by extraction of the former compounds into benzene and ether, respectively. The toluic acids were identified by their m. p.s: *m*-toluic acid, 110° (lit. 110°); *p*-toluic acid, 179° (lit. 178°); and by conversion into their amides: *m*-toluamide, m. p. 96° (lit. 97°); *p*-toluamide, m. p. 157° (lit. 157°). *iso*Phthalic acid yielded an amide, m. p. 278° (lit. 280°), and terephthalic acid gave a dimethyl ester, m. p. 140° (lit. 140°).

RESULTS AND DISCUSSION

Evolution of Carbon Dioxide.—During the oxidation of all the compounds studied carbon dioxide is evolved; this indicates that some disruption of the aromatic ring occurs simultaneously with side-chain oxidation. Some results of quantitative experiments with the isomeric xylenes and toluic acids are shown in Table 1.

TABLE 1

Temp.: 50°. [Organic compound] = 0·0103M; [$KMnO_4$] = 0·103M.

Compound	Compound completely oxidised (%)	Compound	Compound completely oxidised (%)
Toluene	7·0	*o*-Toluic acid	14·5
o-Xylene	26·9	*m*-Toluic acid	19·2
m-Xylene	41·8	*p*-Toluic acid	9·2
p-Xylene	57·0		

More ring rupture occurs with the xylenes than with the corresponding toluic acids and it is evident that fission of the ring must occur before the monocarboxylic acid is formed. This conclusion is in agreement with that reached with toluene, where it was shown that ring fission probably occurs at the alcohol and aldehyde stages (Cullis and Ladbury, *loc. cit.*).

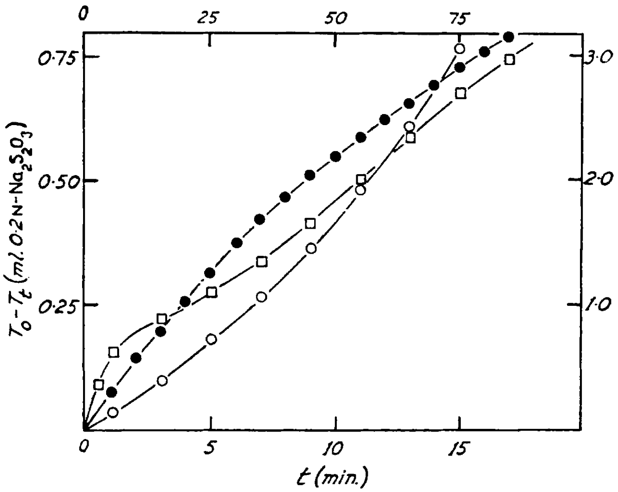
The fact that introduction of a methyl group into toluene increases the extent of disruption of the aromatic ring suggests that $+I$ substituents favour nuclear attack, and it might be expected that $-I$ substituents would exert a stabilising influence in this respect. This is in general true, though with the toluic acids the extent of nuclear attack is greater than with toluene itself. With nitro- and chloro-toluenes, nuclear attack is much reduced; quantitative estimates are difficult to obtain, since oxidation of these compounds is very slow and evolution of carbon dioxide from oxidative attack of the solvent and carboxylic acid " end-product " becomes appreciable.

The work of Speroni and Barchielli (*Gazzetta*, 1941, **71**, 765) suggests that with the chlorotoluenes no oxidative disruption of the aromatic ring takes place at any stage of the reaction unless sulphuric acid is present. The present results indicate that nuclear oxidation, though small, is not inappreciable; not only is carbon dioxide evolved during the oxidation, but chloride ions are formed.

The Development of Reaction with Time.—The course of the oxidation of the nitro- and chloro-toluenes and of *m*- and *p*-toluic acids is similar to that found with toluene. With some of the other compounds studied, *e.g.*, *m*- and *p*-xylene, the reaction–time curves are sigmoid in form, but with others, *e.g.*, *o*-xylene and *o*-toluic acid, oxidation takes place at an initially high rate and this is followed by a slow autocatalytic reaction (Fig. 1). The behaviour exhibited is thus similar to, but less pronounced than, that observed by Hinshelwood with *p*-nitrophenol (*J.*, 1919, 1180).

Study of the oxidation rates of *m*- and *p*-nitro- and of *m*- and *p*-chloro-benzoic acids and of *iso*phthalic acid (terephthalic acid could not be studied since it is almost insoluble in acetic acid) showed that the oxidation of these compounds is very slow. The oxidation

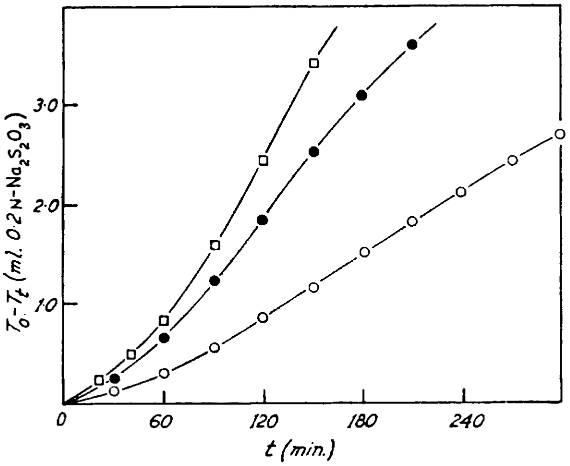
FIG. 1. *Reaction–time curves for the oxidation of* o- *and* p-*xylene and of* m-*toluic acid.*



○ Temp. 50°. [*p*-Xylene] = 0·0103M; [$KMnO_4$] = 0·00516M.
● Temp. 60°. [*m*-Toluic acid] = 0·0103M; [$KMnO_4$] = 0·0206M.
☐ Temp. 50°. [*o*-Xylene] = 0·0103M; [$KMnO_4$] = 0·00516M.

The left-hand ordinates and lower abscissæ refer to *o*- and *p*-xylene; the right-hand ordinates and upper abscissæ to *m*-toluic acid. The ordinate values may be converted into "moles of $KMnO_4$ per litre" by multiplication by the factor 3·442 × 10^{-3}.

FIG. 2. *Reaction–time curves for the oxidation of* o-*substituted benzoic acids.*



Temp. 50°. [Organic compound] = 0·0103M.; [$KMnO_4$] = 0·0206M.
○ *o*-Nitrobenzoic acid; ● *o*-chlorobenzoic acid; ☐ phthalic acid.

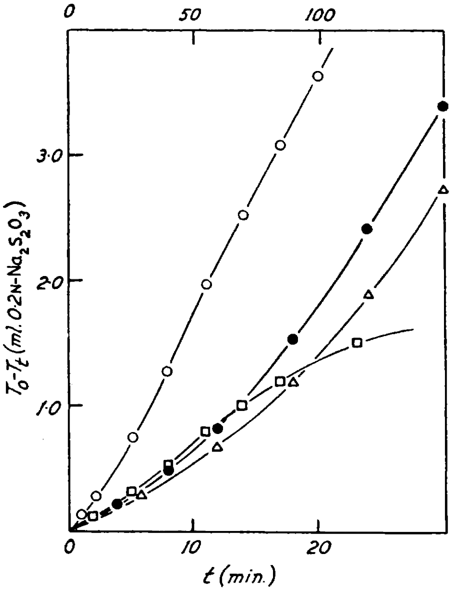
of the three *ortho*-substituted benzoic acids, on the other hand, although initially slow, soon becomes appreciable (Fig. 2).

Sigmoid reaction–time curves are a common feature of reactions involving potassium permanganate, and may be due either to autocatalysis by Mn^{2+} ions (Bradley and van Praagh, *J.*, 1938, **1624**; Alexander and Tompkins, *Trans. Faraday Soc.*, 1939, **35**, 1156) or to fission of the compound undergoing oxidation (Hinshelwood and Winkler, *J.*, **1936**, 368). Although the rate of reaction is reduced, the general form of such curves is not altered by allowing oxidation to proceed in presence of pyrophosphate ions (Fig. 3); these form a comparatively stable complex with the Mn^{3+} ion (Merz, Stafford, and Waters, *J.*, **1951**, 638). If the sigmoid form of the reaction–time curves is due to autocatalysis by the Mn^{2+} ion as a result of the Guyard reaction:

$$MnO_4^- + 4Mn^{2+} + 8H^+ \longrightarrow 5Mn^{3+} + 4H_2O$$

(Guyard, *Bull. Soc. chim. France*, 1864, **1**, 89), then suppression of the above reaction as a source of oxidising entities should diminish the autocatalytic character of the curves. Since the ratio of the maximum oxidation rate to the initial oxidation rate is more or less unaffected by the presence of pyrophosphate ions (Fig. 3), it may be concluded that the intervention of Mn^{2+} ions is not responsible for the characteristic development of rate with time, as is the case, for example, in the oxidation of oxalic acid (Harcourt and Esson, *Phil. Trans.*, 1866, **156**, 193; Bradley and Van Praagh, *loc. cit.*). The sigmoid form of the curves in these reactions is therefore probably due to fission of the ring and formation of labile open-chain fragments.

FIG. 3. *Reaction–time curves for the oxidation of* p-*xylene and of phthalic acid in absence and in presence of pyrophosphate ions.*



Temp. 50° [Organic compound] = 0·0103M.; [$KMnO_4$] = 0·0206M.
○ *p*-Xylene, no $K_4P_2O_7$ added; □ *p*-Xylene, [$K_4P_2O_7$] = 0·0206M; ● Phthalic acid, no $K_4P_2O_7$ added; △ Phthalic acid, [$K_4P_2O_7$] = 0·0206M.

The lower abscissæ refer to *p*-xylene, and the upper abscissæ to phthalic acid.

It is interesting that the maximum diminution in oxidation rate in presence of pyrophosphate ions is about 70% for *m*-xylene and about 50% for the *o*- and *p*-compounds; this suggests that the different oxidising species present effect a variable amount of oxidation depending on the substrate.

Influence of Reactant Concentrations.—With the chlorotoluenes (Speroni and Barchielli, *loc. cit.*), as with toluene itself (Cullis and Ladbury, *loc. cit.*), the initial rate of reaction is proportional to the first power of the concentrations of potassium permanganate and of the organic compound. With some of the substituted toluenes, second-order kinetics are no longer obeyed. The initial rates of oxidation of *m*- and *p*-xylene, for example, though of the first order with respect to the oxidising agent, are somewhat less dependent on the xylene concentration.

Changes of the initial order with respect to the organic compound from unity to zero have previously been observed by Duke (*J. Amer. Chem. Soc.*, 1947, **69**, 2885, 3054), who suggests that such behaviour may be explained in certain systems, *e.g.*, manganic ions–oxalic acid, periodic acid–ethylene glycol, in terms of a rapidly established equilibrium between the initial reactants and a co-ordination complex, the latter undergoing a subsequent slow reaction to yield the oxidation products.

Although in the present system co-ordination between the oxidising agent and substrate is unlikely to occur, an explanation similar to that proposed by Duke may well account for the behaviour observed with *m*- and *p*-xylene. In the oxidation of toluene and other compounds studied here, it is believed that the principal oxidising entity is not the MnO_4^- ion but some species derived from it. Thus we may have :

$$KMnO_4 \underset{k_1'}{\overset{k_1}{\rightleftharpoons}} \text{Intermediate manganese ion} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\text{Intermediate manganese ion} + \text{Organic compound} \xrightarrow{k_2} \text{Products} \quad . \quad (2)$$

When (1) is rapid compared with (2),

$$\text{Initial rate} = k_2\,[\text{Intermediate manganese ion}]\,[\text{Organic compound}]$$

$$= \frac{k_1k_2}{k_1'}\,[KMnO_4]\,[\text{Organic compound}]$$

and second-order kinetics are observed.

With more reactive compounds such as the xylenes (Table 2), reaction (2) may occur at a comparable rate to (1). In suitable circumstances reaction (1) may become rate-determining, and independence of rate on the concentration of the organic compound may be observed. Between the limits of applicability of these two rate laws there will be a range of concentrations where the order with respect to the organic compound lies between zero and unity. This may be, in its simplest terms, the explanation of the behaviour found with *m*- and *p*-xylene. Other special explanations may be advanced to account for the breakdown in second-order kinetics observed with some of the other compounds investigated.

TABLE 2

Temp. : 50°. [Organic compound] = 0·01M. ; $[KMnO_4]$ = 0·02M.

Compound	10^5 × Initial oxidation rate (mole l.$^{-1}$ min.$^{-1}$)	*E* (kcal. mole^{-1})	*A* (l. mole^{-1} min.$^{-1}$)
Toluene	15·7	13·2	$6{\cdot}45 \times 10^8$
o-Xylene	110	10·3	—
m-Xylene	96·6	13·0	—
p-Xylene	49·6	13·2	—
o-Toluic acid	13·9	14·9	$7{\cdot}93 \times 10^9$
m-Toluic acid	8·44	13·9	$9{\cdot}95 \times 10^8$
p-Toluic acid	7·46	13·2	$3{\cdot}24 \times 10^8$
o-Nitrotoluene	0·72	13·8	$7{\cdot}41 \times 10^7$
m-Nitrotoluene	1·15	11·8	$5{\cdot}83 \times 10^6$
p-Nitrotoluene	2·44	14·7	$9{\cdot}61 \times 10^8$
o-Chlorotoluene	2·86	13·8	$2{\cdot}93 \times 10^8$
m-Chlorotoluene	4·96	15·7	$1{\cdot}03 \times 10^{10}$
p-Chlorotoluene	5·16	14·6	$2{\cdot}01 \times 10^9$
o-Nitrobenzoic acid	0·6	—	—
o-Chlorobenzoic acid	1·7	—	—
Phthalic acid	2·8	—	—
Benzoic acid	0·6	11·8	$2{\cdot}76 \times 10^6$

Influence of Structure.—The initial rates of oxidation of the compounds studied are shown in Table 2, together with the Arrhenius parameters in certain cases ; the rates given are corrected for oxidative attack of the solvent.

The order of ease of oxidation of the nitro- and chloro-toluenes is : H > *p* > *m* > *o*, while with the toluic acids the order is : H > *o* > *m* > *p*. For the xylenes, the sequence is : *o* > *m* > *p* > H. The same order of rates of oxidation is found with the *ortho*-substituted benzoic acids as with the *ortho*-substituted toluenes, *i.e.*, $CO_2H > Cl > NO_2$, but *o*-nitrobenzoic acid is oxidised at the same initial rate as benzoic acid, while toluene reacts about twenty times as fast as *o*-nitrotoluene. The results in Table 2 show that such variations in rate as occur when the position of a given substituent is altered are due to changes in both the Arrhenius parameters, *E* and *A*. The general effect of substitution is evidently quite complex and it is not surprising that structural changes affect the values of *E* and *A* to different extents, and hence give different sequences of ease of oxidation according to the nature of the substituent.

In general, however, the introduction of $-I$ substituents into toluene decreases the oxidisability, while $+I$ substituents facilitate oxidation. This suggests that the oxidising agent is a cationic species such as Mn^{3+} and not a free radical, for in reactions involving the attack of aromatic molecules by radicals there is evidence that both $+I$ and $-I$ groups exert an activating influence (Dewar, " Electronic Theories of Organic Chemistry," Oxford University Press, 1949, p. 278; De Tar and Scheifele, *J. Amer. Chem. Soc.*, 1951, **73**, 1442; Hey, *J.*, 1952, 1974).

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