Kinetic Studies of the Oxidation of Aromatic Compounds by Potassium Permanganate. Part I. Toluene.

By C. F. CULLIS and J. W. LADBURY.

[Reprint Order No. 5477.]

A kinetic investigation of the oxidation of toluene by potassium permanganate is described. Under the conditions used, attack occurs mainly at the methyl group, resulting in stepwise oxidation of toluene to benzoic acid. Simultaneously, some disruption of the aromatic ring takes place, but this does not appear to occur during the initial oxidation of toluene itself, being associated only with the further oxidation of certain intermediate products formed.

The dependence of initial oxidation rate on hydrogen-ion concentration is complex, but the reaction is of the first order with respect to both potassium permanganate and toluene. Nevertheless, studies of the effect of complex-forming agents and other added salts show that the greater part of the oxidation is done by Mn^{3+} or associated ions, and that the reaction does not involve to any great extent direct oxidation by the MnO_4^- ion.

A CHARACTERISTIC reaction of the monoalkylbenzenes is their oxidation to benzoic acid. In preparative work, alkaline permanganate is often used to oxidise the alkyl side-chains. A kinetic investigation must, however, be made in acid solution, since aqueous acetic acid is the only suitable solvent. The present paper deals with the reaction of toluene with potassium permanganate; the oxidation of related compounds will be discussed in subsequent papers.

In an early kinetic investigation of the oxidation of aromatic compounds by permanganate, Hinshelwood (*J.*, 1919, 1180) studied the effect of substitution on the oxidation of phenols. Hinshelwood and Winkler (*J.*, 1936, 368, 371) showed that the simple second-order behaviour observed could only be explained on the basis of a reaction between a phenol molecule and the permanganate ion. No simple relation was found between the activation energies and velocity constants. Alexander and Tompkins (*Trans. Faraday Soc.*, 1939, **35**, 1156) found sigmoid reaction–time curves at low acidities for the oxidation of 2 : 6-dinitrophenol in presence of sulphuric acid, the sigmoid character being ascribed to catalysis by the Mn^{2+} ion. These authors suggested that intermediate manganese ions are involved, and that the principal oxidising species is the hydroxyl radical produced by the reaction, $Mn^{3+} + H_2O \rightleftharpoons Mn^{4+} + OH + H^+$. Tompkins (*ibid.*, 1943, **39**, 280) outlined the distinguishing features of oxidations involving on the one hand the permanganate ion and on the other intermediate manganese ions.

With the phenols, the aromatic ring is completely oxidised to carbon dioxide. With toluene and its homologues oxidation of the side chain takes place preferentially, although some ring rupture often occurs concurrently. The only previous kinetic study of the reaction of the toluenes with permanganate is that of chlorotoluenes by Speroni and Barchielli (*Gazzetta*, 1941, **71**, 765), who found that the oxidations are of the second order and are not autocatalytic : no carbon dioxide was evolved, which implies that the aromatic ring remains intact.

Ions derived from every valency state of manganese from 7 to 3, as well as the hydroxyl radical, have been suggested as responsible for the oxidising action of potassium permanganate. In this investigation, the oxidation cannot be attributed to any single species, but the Mn^{3+} ion is believed to be one of the most important entities involved.

EXPERIMENTAL

Materials.—All the organic compounds used, with the exception of acetic acid, were purified by conventional methods. The acetic acid was of "AnalaR" grade and was not specially purified. The inorganic compounds were "AnalaR" materials or of comparable purity. Solutions of benzyl alcohol and benzaldehyde were stored in an atmosphere of carbon dioxide.

Kinetic Measurements.—In the majority of experiments, reaction was followed iodometrically. Manganese dioxide is the end product of permanganate reduction, and is deposited during the reaction. It was therefore necessary to use separate vessels for each determination, and Y-vessels with a total capacity of about 60 ml., in which the solutions of the two reactants could be brought separately to the required temperature and then mixed, were used throughout.

If a is the initial concentration of permanganate in moles/l., x is the number of moles of permanganate per l. consumed in time t, $1/p$ is the normality of the thiosulphate used to titrate the iodine liberated by the residual permanganate and manganese dioxide formed, v is the volume of reacting solutions, and N' and N are the number of ml. of thiosulphate required after respectively zero time and time t, then $x = (N' - N)/3vp$, and $(a - x) = (5N - 2N')/15\,vp$.

Method of obtaining Initial Rates.—In most cases, no simple kinetic law is obeyed throughout the reaction, and the velocity constants cannot be determined by application of an integrated rate equation to the experimental results. Only initial rates were therefore considered. A convenient method of finding these is to plot x/t against x and to extrapolate to $x = 0$ (Hinshelwood, *loc. cit.*; Fudge and Sykes, *J.*, 1952, 119); where this method was used, satisfactory linear plots were obtained for about the first 20% of reaction. Not all the results were amenable to this procedure and in some cases resort had to be made to measurement of initial tangents to the reaction–time curves.

Small corrections were made for oxidation of the acetic acid, which is appreciable in certain cases. Since the solvent is present in large excess, its oxidation is effectively of the first order with respect to the permanganate only. A correction may thus be applied by subtraction from the initial total rate of reaction of the product of the previously determined first-order rate constant and the initial permanganate concentration.

Estimation of Evolved Carbon Dioxide.—Measurements were made of the fraction of aromatic compound oxidised to carbon dioxide during the reaction. "Oxygen-free" nitrogen was passed first through soda-lime and then into the reacting solutions. It was then bubbled into saturated aqueous barium hydroxide contained in three wash-bottles connected in series. After reaction was complete, the barium carbonate was filtered off, dried, and weighed. Blank experiments were performed to allow for oxidation of the acetic acid.

Sources of Error.—(i) Autoxidation of benzaldehyde and other intermediates may cause the rates of reaction in presence of air to differ from those in absence of oxygen. However, when the reaction was carried out in an atmosphere of carbon dioxide, no differences in rates could be detected. No precautions were therefore taken to exclude air from the reaction solutions in subsequent experiments.

(ii) No allowance was found to be necessary for the very slow oxidation caused by manganese dioxide.

(iii) Correction was made for the contraction in volume which occurs when glacial acetic acid and water are mixed.

Products of the Oxidation of Toluene.—An equimolar mixture of toluene and potassium permanganate in 54·2% w/v acetic acid was allowed to react with vigorous stirring for 4 hr. at 50°. After the manganese dioxide had been deposited from the solution, the clear supernatant liquid was decanted off and extracted repeatedly with ether. The manganese dioxide sludge was also treated with ether in a Soxhlet apparatus. The ether extracts were combined and washed with water, and the water washings were found to contain only acetic acid. The ether was next washed with 10% sodium hydroxide solution and then contained only neutral compounds. The alkaline extract was acidified and extracted with ether; the latter then contained the acidic products. The neutral extract was shown to contain only benzaldehyde (m. p. of 2 : 4-dinitrophenylhydrazone 236°, lit. 237°) and unchanged toluene (b. p. 110°, lit. 110°). No benzyl alcohol, dibenzyl, or benzyl acetate could be detected. When the ether extract containing the acid constituents was evaporated, white crystals were obtained, insoluble in cold water and soluble in hot water. These were recrystallised from water and had m. p. 121° which was unaltered on admixture with authentic benzoic acid (lit., m. p. 121°). The mother-liquor from these crystals was tested for the presence of phenols with diazotised *p*-nitroaniline; only a very faint coloration was observed.

RESULTS AND DISCUSSION

Evolution of Carbon Dioxide.—The extent of complete disruption of the aromatic ring, as disclosed by the evolved carbon dioxide, is illustrated in Table 1.

TABLE 1.

Temp.: 50°. Solvent: 54·2% w/v aqueous acetic acid. [$PhCH_3$] = 0·0103M; [$KMnO_4$] = 0·103M.

	Weight (g.), corrected for oxidation of solvent, of		
$PhCH_3$ taken (g.)	$BaCO_3$	CO_2	$Ph{\cdot}CH_3$ completely oxidised (%)
0·0921	0·0981	0·0219	7·1
0·0921	0·0961	0·0214	6·9

Stoicheiometry.—The oxidation of toluene by permanganate probably proceeds through the stages: $Ph{\cdot}CH_3 \longrightarrow (Ph{\cdot}CH_2{\cdot}OH) \longrightarrow Ph{\cdot}CHO \longrightarrow Ph{\cdot}CO_2H$, each of which involves one atom of oxygen (or two-thirds of a molecule of permanganate) provided no side reaction occurs. Inability to detect benzyl alcohol in the product is not readily explicable, though it may be due, at least partially, to the insensitivity of the α-naphthyl *iso*cyanate test. It is interesting that Slack and Waters (*J.*, 1948, 1666) could not isolate diphenylmethanol after oxidation of diphenylmethane by chromic acid.

The amounts of permanganate needed in practice to oxidise toluene, benzyl alcohol, and benzaldehyde were determined by allowing the compounds to react with an eight-fold 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 are given in Table 2, together with the theoretical quantities needed for oxidation of the side chain only. The differences may be ascribed to concurrent ring rupture, and show that, with toluene, 8·9% is completely oxidised to carbon dioxide; this value may be compared with 7·0% obtained from direct measurement of the carbon dioxide evolved (Table 1). The amounts of benzyl alcohol and benzaldehyde oxidised to carbon dioxide are 9·0% and 6·1% respectively. The fact that the extent of ring rupture of toluene as determined by measurement of the carbon dioxide evolved agrees quite well with the value obtained from the stoicheiometry measurements suggests that the carbon dioxide arises principally from nuclear oxidation of the aromatic compound, and not, for example, from induced oxidation of the acetic acid.

TABLE 2.

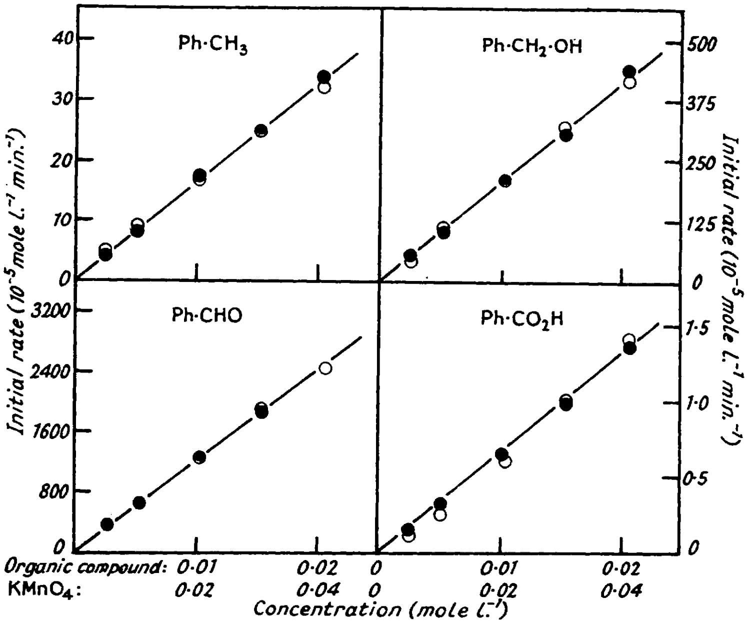
Temp.: 50°. Solvent: 54·2% w/v aqueous acetic acid. [Organic compound] = 0·00517M; [$KMnO_4$] = 0·0413M.

		$PhCH_3$	$Ph{\cdot}CH_2{\cdot}OH$	$Ph{\cdot}CHO$
Moles of $KMnO_4$ reqd. to oxidise 1 mole:	Found ...	2·89	2·23	1·28
	Theor. ...	2·00	1·33	0·67

The difference between the experimental values of the stoicheiometry for toluene and benzyl alcohol (Table 2) is 0·66, and corresponds exactly with the theoretical difference. This implies that no appreciable ring rupture takes place in the first stage of reaction. Attack of the ring does occur, however, in the later stages and the carbon dioxide evolved is evidently derived entirely from ring fission during the oxidation of benzyl alcohol and benzaldehyde.

Influence of Reactant Concentrations.—The initial rates of reaction of permanganate with toluene, benzyl alcohol, benzaldehyde, and benzoic acid are all of the first order with respect to each reactant (Fig. 1). Second-order kinetics are not, however, maintained throughout

FIG. 1. *The dependence of initial oxidation rate on reactant concentrations.*

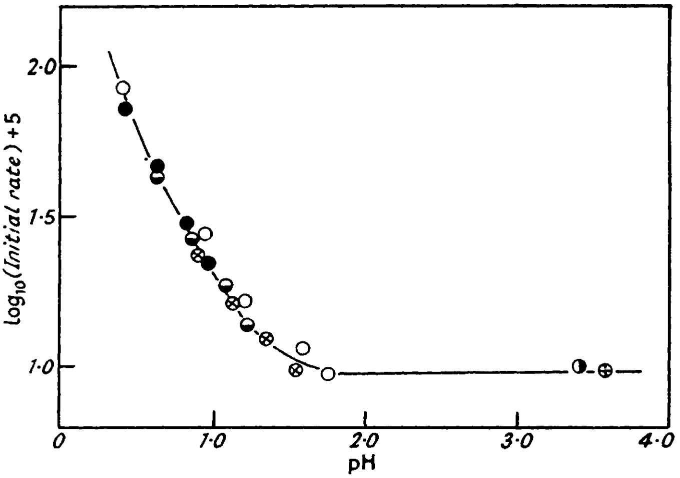


Temp.: 50°. Solvent: 54·2% w/v (9·03 moles $l.^{-1}$) aqueous acetic acid.

○ [Organic compound] = 0·01M; [$KMnO_4$] varied.

● [$KMnO_4$] = 0·02M; [Organic compound] varied.

FIG. 2. *The dependence of initial oxidation rate on* pH.



Temp.: 50°. [$Ph{\cdot}CH_3$] = 0·01M; [$KMnO_4$] = 0·02M.

○ $CH_3{\cdot}CO_2H$.

◑ 1·24M-$CH_3{\cdot}CO_2Na$ in 9·0M-$CH_3{\cdot}CO_2H$.

⊕ 1·24M-$CH_3{\cdot}CO_2Na$ in 7·3M-$CH_3{\cdot}CO_2H$.

● H_2SO_4 in 9·0M-$CH_3{\cdot}CO_2H$.

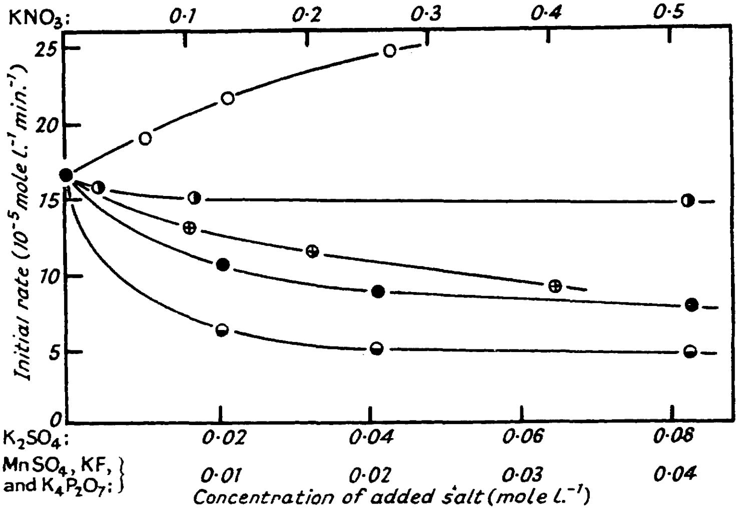
◒ H_2SO_4 in 7·3M-$CH_3{\cdot}CO_2H$.

⊗ H_2SO_4 in 4·4M-$CH_3{\cdot}CO_2H$.

the reactions, and with benzyl alcohol and benzaldehyde the reaction–time curves are sigmoid. Second-order kinetics are a common feature of permanganate oxidations (Hinshelwood, *loc. cit.*; Hinshelwood and Winkler, *loc. cit.*; Alexander and Tompkins, *loc. cit.*; Mann and Tompkins, *Trans. Faraday Soc.*, 1941, **37**, 201; Speroni and Barchielli, *loc. cit.*; Hill and Tompkins, *Trans. Roy. Soc. S. Africa*, 1942, 29, 309; Tompkins, *loc. cit.*), but the simple conclusion that reaction results from a bimolecular interaction between an organic molecule and the permanganate ion is thought not to be correct in the present case.

Hydrogen-ion concentration has a more complex effect on the reaction, and the influence of pH (as measured by a glass electrode) is shown in Fig. 2. Variations in the concentration of acetic acid cause a marked change in rate of oxidation, and it is clear that the principal influence of the solvent lies in its provision of a source of hydrogen ions. The small differences in rate when sulphuric acid and acetic acid are used to produce the same pH may be due to the weak complexing effect of the sulphate ion (cf. Fig. 3).

FIG. 3. *The dependence of initial oxidation rate on added salts.*



Temp.: 50°. Solvent: 54·2% w/v aqueous acetic acid. $[Ph{\cdot}CH_3] = 0{\cdot}01$M; $[KMnO_4] = 0{\cdot}02$M.

○ $MnSO_4$; ◑ KNO_3; ⊕ K_2SO_4; ● KF; ◒ $K_4P_2O_7$.

Influence of Added Salts.—Manganous sulphate reacts with potassium permanganate (Guyard, *Bull. Soc. chim.*, 1864, **1**, 89) to produce intermediate manganese ions such as Mn^{3+} (Bassett and Sanderson, *J.*, 1936, 207); the latter are readily removed by pyrophosphate and fluoride ions by complex formation. If MnO_4^- ions are primarily responsible for the oxidation, a reduction in initial rate should be observed in presence of added Mn^{2+} ions which reduce the concentration of MnO_4^-. If, on the other hand, intermediate manganese ions are the active oxidising species, Mn^{2+} ions should cause an acceleration. Similarly addition of pyrophosphate and fluoride ions should retard reaction if intermediate manganese ions are mainly responsible for oxidation, but should cause no significant change if MnO_4^- ions are the principal oxidising entities. Fig. 3 shows the effect of added salts. Manganous sulphate has an accelerating influence, and the complex-forming agents cause retardation. This suggests that Mn^{3+} and associated ions are the principal species responsible for oxidation. The observed effects are much greater than normal salts effects, as shown by the influence of potassium nitrate. Addition of potassium sulphate causes a slight slackening in rate, probably owing to formation of the complex $[Mn(SO_4)_2,2H_2O]^-$ (Ubbelohde, *J.*, 1935, 1605).

Even with a high concentration of pyrophosphate ions, the rate is only reduced to about 30% of the normal value. Ions derived from Mn^{3+} are thus not the sole oxidising entities, though they appear to be the most important species present.

It was found that the presence of the added salts in the concentrations used did not significantly affect the pH of the system, so that the observed changes in oxidation rate cannot be ascribed to a buffering action.

Influence of Temperature.—The initial rates at 50° and the Arrhenius parameters for the reactions of permanganate with toluene, benzyl alcohol, benzaldehyde, and benzoic acid are shown in Table 3 together with data on related compounds.

The closeness of the values of A for the first three compounds is to be expected since in each case attack occurs predominantly at the side-chain; the similar steric factor for benzyl acetate suggests that here too an analogous mode of attack occurs. The lower value for benzoic acid may be attributed to oxidation of this compound only at the aromatic ring.

The comparative ease of oxidation of benzyl alcohol and benzaldehyde (Table 3) may be ascribed to the electro-negative character of the oxygen atom in the side-chain. This and the $-I$ effect of the aromatic ring will both tend to promote ionisation of the hydrogen atoms on the α-carbon atom, so that the excess of negative charge developed can become the centre for oxidative attack. If the charge is dispersed to the ring by the normal tautomeric transfers, then the ring itself becomes susceptible to attack. This would explain why considerable ring rupture occurs with benzyl alcohol and benzaldehyde. An analogous explanation may account for the fact that diphenylmethanol is oxidised by chromic acid much faster than diphenylmethane (Slack and Waters, *loc. cit.*).

The results in Table 2 suggest that, with toluene, oxidation takes place almost exclusively at the methyl group, and the effect of added salts indicates that Mn^{3+} ions are among the principal oxidising entities involved. Initial attack of the organic compound may well occur by hydrogen abstraction according to the reaction :

$$\mathrm{Ph{\cdot}CH_3 + Mn^{3+} \longrightarrow Ph{\cdot}CH_2{\cdot} + Mn^{2+} + H^+}$$

which in turn is followed by other reactions, of the benzyl radical.

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.$^{-1}$)
Toluene	0·785	13·2	$6{\cdot}45 \times 10^8$
Benzyl alcohol	9·60	12·9	$5{\cdot}40 \times 10^9$
Benzaldehyde	60·5	11·8	$9{\cdot}77 \times 10^9$
Benzoic acid	0·029	11·8	$2{\cdot}76 \times 10^6$
Benzyl acetate	0·196	15·7	$7{\cdot}67 \times 10^9$
Dibenzyl	2·82	—	—

After oxidation of diphenylmethane with chromic acid, Slack and Waters (*loc. cit.*) were able to isolate tetraphenylethane and hence to show that hydrogen abstraction from the methylene group takes place to some extent. By analogy, it might be expected that appreciable amounts of dibenzyl would be found among the products from toluene on the basis of the mode of attack proposed. The failure to detect this compound does not, however, form evidence against the reaction postulated, for the dimerisation of benzyl radicals could only occur to a significant extent if subsequent oxidation of such radicals was slow in comparison with their formation.

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, June* 18*th*, 1954.]