Radiolysis of Aqueous Toluene Solutions

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Aqueous toluene solutions have been irradiated with [60]Co γ-rays. In unbuffered solutions the various cresol isomers are formed in a total yield of 0.45, 0.87, and 0.94 molecules/100 eV absorbed energy in argon-, N_2O-, and air-saturated solutions, respectively. The yields are reduced in acid (pH 3) solutions ($G = 0.14$, 0.14, and 0.52, respectively) but the reduction is compensated by the formation of 1,2-diphenylethane in yields of 0.49 and 1.60 in argon- and N_2O-saturated solutions, respectively. Benzyl radicals are formed through an acid catalysed water elimination reaction from the initially formed hydroxymethylcyclohexadienyl radical. Phenyltolylmethanes, dimethylbiphenyls, and partly reduced dimers are also formed during the radiolysis. Hydrogen is formed in the same yield as the molecular yield, $g(H_2)$. Xylene isomers and benzene are formed in trace quantities. The most remarkable effects of the addition of Fe(III) ions to deaerated acid toluene solutions are the formation of benzyl alcohol and benzaldehyde and an increase in the yield of 1,2-diphenylethane.

1. INTRODUCTION

The oxidation of toluene in aqueous solutions by OH radicals produced by ionizing radiation or by Fenton's reagent has been studied previously.[1-6] Khenokh and Lapinskaia [1] reported the formation of formaldehyde ($G = 0.17$) and phenols ($G = 0.56$) after γ-irradiation of aerated aqueous toluene solutions. Mancitti *et al.*[2] found 1,2-diphenylethane as the main product, but phenyltolylmethanes, 4,4'-dimethylbiphenyl and *o*- and *m*-cresols were also found after irradiation with γ-rays in oxygen-free solutions. The investigations of Hotta *et al.*[3-5] were mainly concerned with the autoxidation of toluene in aerated aqueous solutions catalysed by iron(II) ions at elevated temperatures ($\geq 70°C$). The pH of the solution was found by Jefcoate *et al.*[6] to have a marked effect on the product distribution when toluene was oxidized by Fenton's reagent. The effect was explained as an acid catalysed water elimination reaction from the initially formed OH adduct, resulting in the formation of benzyl radicals.

In pulse radiolysis studies the initial radicals formed by reaction of OH radicals [7] and H atoms [8] with toluene in aqueous solutions have been studied and the radicals were interpreted as the OH and H adducts, respectively.

In the present investigation we have attempted a more complete product analysis both of the oxygen containing products and of the complex dimer group. We have also made an effort to find some of the reduced products formed, such as partly hydrated toluene and toluene dimers with the purpose of improving the balance between oxidized and reduced products.

2. EXPERIMENTAL

2.1 Material. Toluene (Merck, *p.a.*) was further purified by recrystallisation twice. The water used for irradiations was quadruply distilled. For identification purposes the three isomers of phenyltolylmethane, which were not commercially available, were synthetized by a Friedel-Crafts reaction described by Errede and Cassidy.[9]

2.2 Preparation of samples and irradiation. Quadruply distilled water was deaerated, saturated with purified argon or nitrous oxide, transferred into carefully rinsed 50 ml syringes and subsequently saturated with toluene by procedures previously described.[10] The samples were irradiated in the syringes at ambient temperature with ^{60}Co γ-rays at a dose rate of 11 800 rad/min and with a total dose normally within the range 20 000 – 220 000 rad.

2.3 Analysis. Hydrogen peroxide was determined by the method of Ghormley[11] and hydrogen by use of a van Slyke apparatus for the measurement of the gas-phase and subsequent analysis on a gas chromatograph using a column filled with molecular sieve. The yield of iron(II) ions was determined by the method of Hummel and Spinks.[12] The organic products were extracted from a 50 ml aqueous solution with 3×8 ml hexane and then with 3×3 ml ether and analysed on a Perkin Elmer 880 gas chromatograph equipped with 5 m long 1/8″ OD columns filled with 5 % of either Emulphor O or Silicone DC 710 on 80 – 100 mesh Chromosorb W. These columns are the same as those used by Hoigné and Gäumann in their study of the radiolysis of toluene in liquid phase.[13] The ether phase, which contained cresols and benzyl alcohol, was analysed on a 2 m long column filled with 5 % tri-(2,4-xylenyl) phosphate on 60 – 100 mesh Embacel. Analysis was also carried out on a combined gas chromatograph-mass spectrometer (LKB 9000)
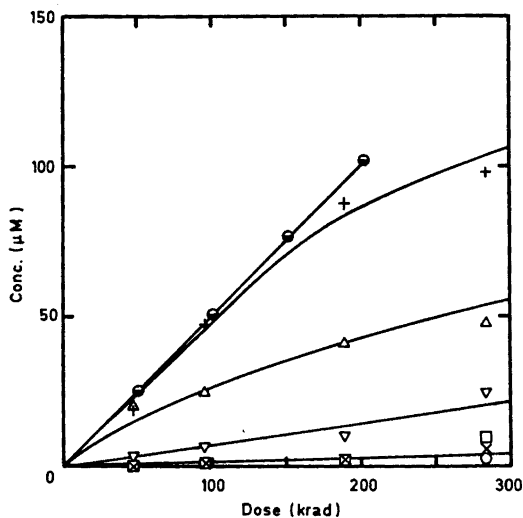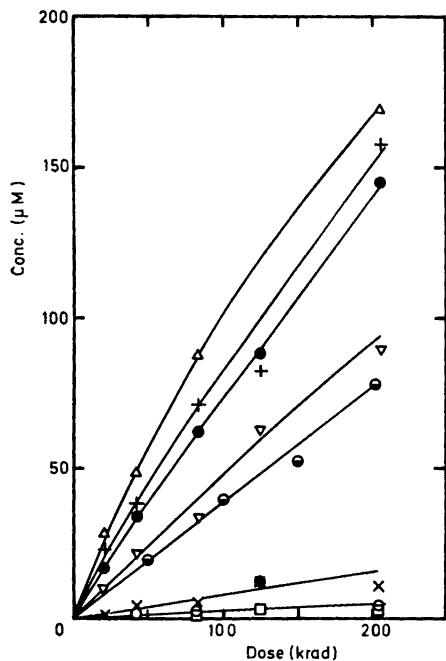

Fig. 1. Yields in unbuffered argon-saturated solutions. $+$, Cresols; $\times$, benzyl alcohol; $\bigcirc$, 1,2-diphenylethane; $\triangledown$, phenyltolylmethanes; $\triangle$, dimethylbiphenyls; $\square$, reduced dimers; $\bullet$, H_2.

Table 1. G values from radiolysis of aqueous toluene solutions. The results after the slant are the yields after the break point of the curves (*i.e.* the yields after consumption of the dissolved oxygen).

	Unbuff. solution sat. with		Acid solution sat. with		Acid solution 1 mM Fe(III) sat. with		Aerated solution	
	Ar	N_2O	Ar	N_2O	Ar	N_2O	Unbuff.	Acid
H_2O_2	0	0.76	0.55	0.33	0	0	2.3/neg.	3.0/0.16
H_2	0.48	0.38	0.49	0.36	0.41	0.36	0.44	0.48
Acid	0	0	0	0			1.1/0.03	1.7/0
Benzaldehyde	0	0	0	0	0.14	0.16	0	0.33/0.03
o-Cresol	0.22	0.48	0.08	0.08	0.09	0.22	0.35/	0.22/
p-Cresol	0.14	0.26	0.03	0.04	0.05	0.11	0.34/	0.17/
m-Cresol	0.09	0.13	0.03	0.02	0.01	0.03	0.25/	0.13/
$\sum$ Cresols	0.45	0.87	0.14	0.14	0.15	0.36	0.94/0.20	0.52/0.03
Benzyl alcohol	0.02	0.06	0.03	0.05	0.56	0.51	0.03	0.03
1,2-Diphenyl-ethane	0.02	0.02	0.49	1.60	1.03	2.07	0/0.17	0/0.54
Phenyltolyl-methanes	0.08	0.46	0.18	0.36	0.06	0.23	0/0.41	0/0.15
Dimethyl-biphenyls	0.29	1.10	0.14	0.06	0	0	0/0.26	0/0.10
Reduced dimers	0.05	0.01	0.57	0.22	0	0	0/0.11	0/0.40
$\sum$ Dimers	0.44	1.59	1.38	2.24	1.09	2.30	0/0.95	0/1.19
$2\sum$ Dimers+ other organic products	1.35	4.11	2.93	4.67	3.03	5.62	2.07/2.16	2.58/2.47
Decomp. of toluene	3.0	5.8	3.9	5.9	3.30	5.7	3.0	3.1

equipped with a 2.7 m long column filled with 1 % Silicone SE 30, in order to identify some of the partly hydrated products. For the quantitative analysis phenol and 4,4′-dimethylbiphenyl were used as internal standards.

Ultraviolet spectra of irradiated solutions were also recorded.

3. RESULTS AND DISCUSSION

3.1 Deaerated solutions. Deaerated, unbuffered aqueous toluene solutions saturated with argon or nitrous oxide were irradiated and the resulting yields are shown as a function of dose in Figs. 1 and 2. In Figs. 3 and 4 are shown the yields obtained in solutions acidified with perchloric acid to pH 3. The *G* values of the products of radiolysis under various conditions are given in Table 1, which gives the values for the various isomers, whereas the figures only give the total amount of isomers within a group.

Fig. 2. Yields in unbuffered N_2O-saturated solutions. +, Cresols; ×, benzyl alcohol; ○, 1,2-diphenylethane; ▽, phenyltolylmethanes; △, dimethylbiphenyls; □, reduced dimers, ◓, H_2; ●, H_2O_2.
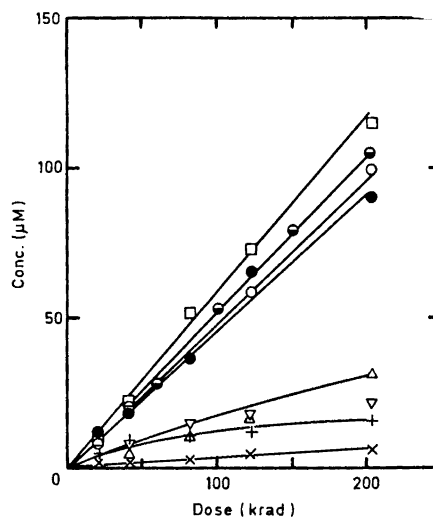
Fig. 3. Yields in acid argon-saturated solutions (pH 3). +, Cresols; ×, benzyl alcohol; ○, 1,2-diphenylethane; ▽, phenyltolylmethanes; △, dimethylbiphenyls; □, reduced dimers; ◓, H_2; ●, H_2O_2.

From Table 1 and the figures it may be observed that in unbuffered solutions the N_2O saturated solutions give a two times higher yield of hydroxytoluenes than the argon-saturated solutions, whereas in acid solutions the yield is unaffected by the presence of N_2O and also considerably lower than in unbuffered solutions. The lower yield of cresols in acid solutions is compensated by a considerably higher yield of dimers, especially 1,2-diphenylethane. The yield of benzyl alcohol is low in all cases (~ 0.05). The yield of the various isomers of cresol was in the order *ortho > para > meta*. It may also

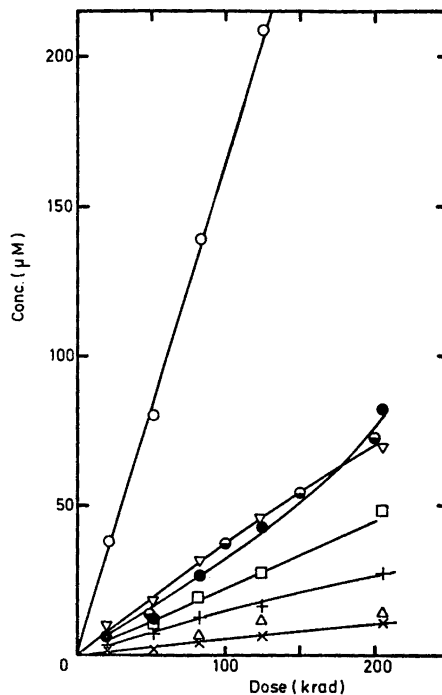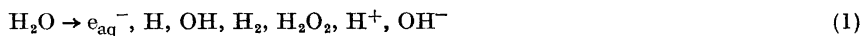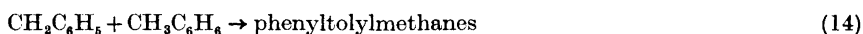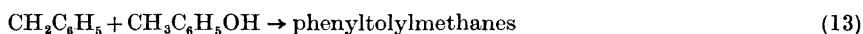*Fig. 4.* Yields in acid N_2O-saturated solutions (pH 3). $+$, Cresols; $\times$, benzyl alcohol; O, 1,2-diphenylethane; $\bigtriangledown$, phenyltolyl-methanes; $\triangle$, dimethylbiphenyls; $\square$, reduced dimers; ◐, H_2; ●, H_2O_2.

be observed that the reduced dimers are formed preferentially in acid solutions, probably due to the reaction of H atoms.
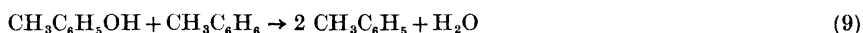
The order of the yield of isomers of phenyltolylmethane was *ortho* > *meta* > *para* with a *para* isomer yield of $15-20$ % of the total yield. The separation of the *ortho* and *meta* isomers on the gas chromatograph column was poor, so only the total yield was determined together with the yield of the *para* isomer. Of the possible dimethylbiphenyl isomers the 4,4' isomer was not produced and the 2,2' isomer only in trace quantities (~ 5 % of the total yield of the isomer), while the 2,3' and 3,3' isomers were formed in equal amounts and with a yield of about 80 % of the total yield of isomers in unbuffered solutions. In acid solutions the 2,2' and 2,3' isomers predominated.

The following reaction scheme may account for the products:

$$H_2O \rightarrow e_{aq}^-, H, OH, H_2, H_2O_2, H^+, OH^- \tag{1}$$

$$e_{aq}^- + H^+ \rightarrow H \tag{2}$$

$$e_{aq}^- + N_2O \rightarrow N_2 + OH + OH^- \tag{3}$$

$$H + CH_3C_6H_5 = CH_3C_6H_6 \tag{4}$$

$$OH + CH_3C_6H_5 \begin{cases} CH_3C_6H_5OH & \tag{5} \\ OHCH_3C_6H_5 & \tag{5a} \end{cases}$$

$$2 \ CH_3C_6H_5OH \rightarrow CH_3C_6H_4OH + \text{other products} \tag{6}$$

$$2 \ CH_3C_6H_5OH \rightarrow \text{unstable dimers} \rightarrow \text{dimethylbiphenyls} \\ \text{and phenyltolylmethanes} \tag{7}$$

$$CH_3C_6H_5OH + CH_3C_6H_6 \rightarrow \text{unstable dimers} \rightarrow \text{dimethylbiphenyls and} \\ \text{phenyltolylmethanes} \tag{8}$$

$$CH_3C_6H_5OH + CH_3C_6H_6 \rightarrow 2 \ CH_3C_6H_5 + H_2O \tag{9}$$

$$2 \ CH_3C_6H_6 \rightarrow \text{reduced dimers} \tag{10}$$

$$CH_3C_6H_5OH \xrightarrow{H^+} CH_2C_6H_5 + H_2O \tag{11}$$

$$2 \ CH_2C_6H_5 \rightarrow \text{1,2-diphenylethane} \tag{12}$$

$$CH_2C_6H_5 + CH_3C_6H_5OH \rightarrow \text{phenyltolylmethanes} \tag{13}$$

$$CH_2C_6H_5 + CH_3C_6H_6 \rightarrow \text{phenyltolylmethanes} \tag{14}$$

$$e_{aq}^- + H_2O_2 \rightarrow OH + OH^- \tag{15}$$

In pulse radiolysis investigations of aqueous toluene solutions Dorfman *et al.* [7] and Sauer and Ward [8] have shown that OH radicals and H atoms react with toluene to form the cyclohexadienyl radicals and they excluded any major contribution of the benzyl radical to their transient spectra. However, the presence of 1,2-diphenylethane among the radiolysis products, especially in acid solution, is a strong indication that the benzyl radical is formed. From the table can be seen that the yield of 1,2-diphenylethane in nitrous oxide-saturated solutions is increased much more than the yield of H atoms when the solution is acidified. (At pH 3 about 80 % of the electrons react with N_2O in reaction 3, and only 20 % in reaction 2 to form H atoms.[10]) So the increase in the yield of 1,2-diphenylethane is probably caused by an acid catalysed process such as reaction 11, as proposed by Jefcoate *et al.*[6] in a study of the oxidation of toluene by Fenton's reagent. The reason why such a first order decay of the hydroxymethylcyclohexadienyl radical was not observed by Sauer and Ward could be the much higher dose rate used by them, favouring the bimolecular decay.

The benzyl radical is probably not formed through the reaction of H atoms, as seen by comparison of the yield of 1,2-diphenylethane, $G(B_2)$, in nitrous oxide-saturated $(G(B_2) = 1.60)$ and in argon-saturated $(G(B_2) = 0.49)$ solutions, the yield of H atoms in the latter case being 3 times higher than in the first case.

The observed yield of reduced dimers (with mol. weight 184) is too low to balance the sum of oxidized products, indicating the presence of non-observed reduced products, *e.g.* reduced monomers analogous to the formation of cyclohexadiene, cyclohexene, and cyclohexane by irradiation of aqueous benzene solution.[14] An analysis using a 50 m capillary column in a gas chromatograph did not reveal any hydrogenated toluenes, but showed the formation of xylene isomers in trace quantities.

3.2 The effect of iron(III) ions. Deaerated aqueous toluene saturated with argon or nitrous oxide and containing 10^{-3} M iron(III) ions at pH 3 were irradiated, and the results are shown in Table 1 and in Figs. 5 and 6. The
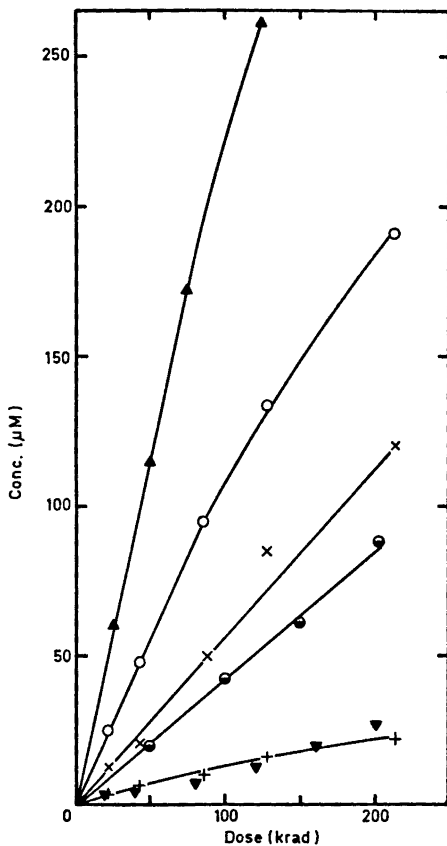
Fig. 5. Yields in acid argon-saturated solutions in the presence of 10^{-3} M Fe(III) ions (pH 3). +, Cresols; ×, benzyl alcohol; ○, 1,2-diphenylethane; ◓, H_2; ▼, benzaldehyde; ▲, Fe(II) ions.
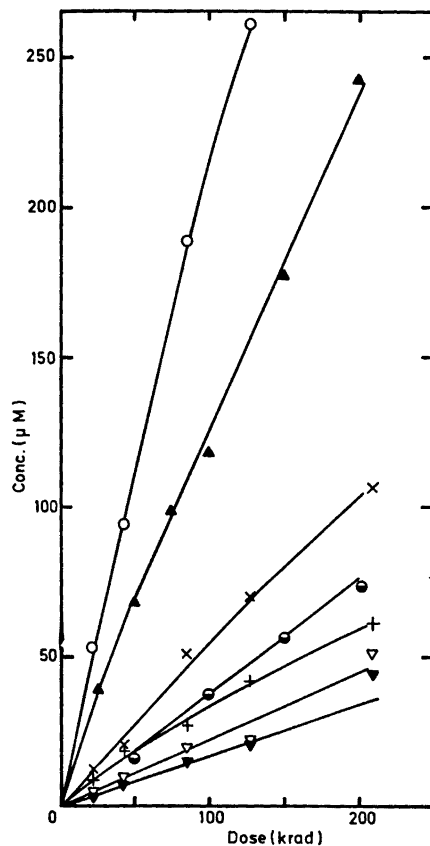
Fig. 6. Yields in acid N_2O-saturated solutions in the presence of 10^{-3} M Fe(III) ions (pH 3). +, Cresols; ×, benzyl alcohol; ○, 1,2-diphenylethane; ◓, H_2; ▽, phenyltolylmethanes; ▼, benzaldehyde; ▲, Fe(II) ions.
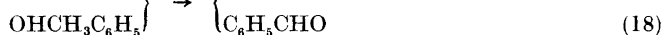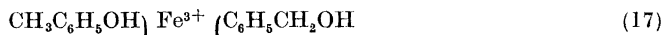
most remarkable effects of iron(III) are the tenfold increase in the yield of benzyl alcohol, the formation of benzaldehyde, the increase of the yield of 1,2-diphenylethane and the decrease to zero of the yield of reduced dimers.

The reduction of the yield of reduced dimers cannot be caused by the removal of H atoms by Fe(III) ions according to

$$H + Fe^{3+} \rightarrow Fe^{2+} + H^+ \tag{16}$$
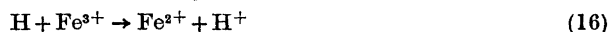
because toluene [$c = 6 \times 10^{-3}$M, $k_4 = 3.9 \times 10^9$ (Ref. 8)] competes favourably with iron(III) ions [$c = 10^{-3}$ M, $k_{16} = 10^8$ (Ref. 15)] for the reaction of H atoms. The formation of iron(II) ions in a yield of 1.3 and 2.3 in nitrous oxide- and argon-saturated solutions, respectively, is therefore probably caused

by reaction of Fe(III) ions with toluene radicals, resulting in the formation of benzyl alcohol and benzaldehyde according to

$$CH_3C_6H_5OH \Big\} \xrightarrow{Fe^{3+}} \Big\{ \begin{array}{l} C_6H_5CH_2OH \quad (17) \\ OHCH_3C_6H_5 \quad\quad\quad C_6H_5CHO \quad (18) \end{array}$$

if the $OHCH_3C_6H_5$ radical is formed. However, as the iron(III) ions increased the yield of 1,2-diphenylmethane and also eliminated the reduced dimers, the oxidation of $C\dot{H}_3C_6H_6$ radicals by iron(III) ions may be possible:

$$CH_3C_6H_6 \xrightarrow{Fe^{3+}} \Big\langle \begin{array}{l} CH_2C_6H_5 \\ CH_3C_6H_5 \end{array} \quad\quad (19)$$

As, according to the reaction mechanism, the hydroxymethylcyclohexadienyl radical causes the formation of cresols (Cr), benzyl alcohol (BA), benzaldehyde (BAld), 1,2-diphenylethane (B_2) and phenyltolymethanes (BT), the total yield, $\sum$, of these products was calculated, counting the yield of B_2 and Cr twice. The total yield together with the yields of H and OH in argon- and nitrous oxide-saturated solutions are shown in Table 2.

Table 2. Yields in the radiolysis of aqueous toluene solutions ($\sum = 2G(Cr) + G(Ba) + G(BAld) + G(BT) + 2G(B_2)$).

	10^{-3} M $HClO_4$ + 10^{-3} M Fe(III) ions saturated with		10^{-3} M $HClO_4$ saturated with		Unbuffered saturated with	
	Ar	N_2O	Ar	N_2O	Ar	N_2O
H	3.15	1.07	3.15	1.07	0.55	0.55
OH	2.65	4.73	2.65	4.73	2.65	5.25
$\sum$	3.12	5.76	1.47	3.89	1.04	2.30
$\sum$/OH	1.18	1.22	0.56	0.82	0.39	0.44

The ratio $\sum$/OH is the same in argon- and nitrous oxide-saturated solutions containing iron(III) ions, indicating that H atoms do not contribute to the $\sum$ yield. An effect of iron(III) ions is, hence, to remove the $CH_3C_6H_6$ radicals, a part of which in the absence of iron(III) ions could react with the $CH_3C_6H_5OH$ radicals according to reaction 9.

3.3 Aerated solutions. The effect of oxygen on the radiolysis of aqueous toluene solutions has been studied by irradiation of aerated solutions [$c(O_2) \simeq 0.25$ mM] and the results are shown in Figs. 7 and 8 and in Table 1. A high yield of acid may be noted both in acid and in unbuffered solutions. The increase in the cresol yield, caused by oxygen, is not so large as the corresponding increase in the phenol yield during the radiolysis of aqueous benzene solutions.[16] On the other hand the yield of hydrogen peroxide is increased to the same value as in the benzene system, and the yield of dimers, including reduced dimers, is zero until the oxygen is consumed, in agreement with the
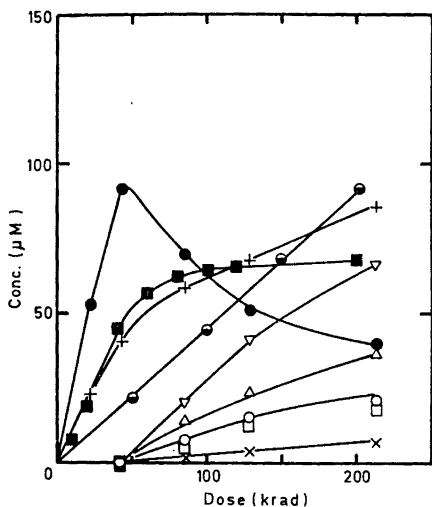
Fig. 7. Yields in unbuffered aerated solutions. +, Cresols; ×, benzyl alcohol; ○, 1,2-diphenylethane; ▽, phenyltolylmethanes; △, dimethylbiphenyls; □, reduced dimers; ◖, H₂; ●, H₂O₂; ▼, benzaldehyde; ■, acids.
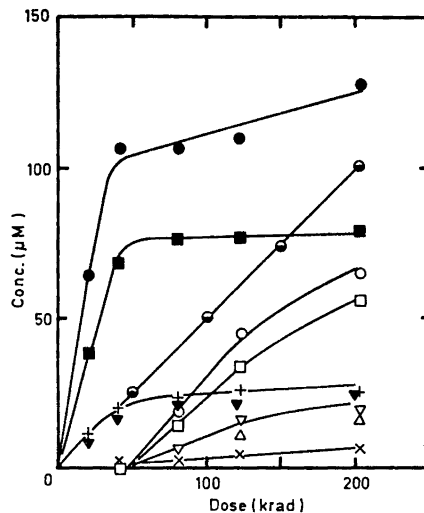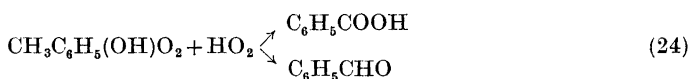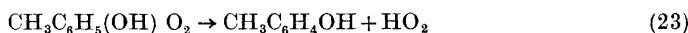
Fig. 8. Yields in acid aerated solutions (pH 3). +, Cresols; ×, benzyl alcohol; ○, 1,2-diphenylethane; ▽, phenyltolylmethanes; △, dimethylbiphenyls; □ reduced dimers; ◖, H₂; ●, H₂O₂; ▼, benzaldehyde; ■, acid.

absence of biphenyl in the benzene system as long as oxygen is present. Consequently, the reaction of oxygen with the hydroxymethylcyclohexadienyl radical (reaction 22) competes favourably with the elimination of water from the same radical (reaction 11).

The following reactions, based on analogy with the benzene system, together with reactions 1,2, and 5 can explain the mechanism

$$e_{aq}^- + O_2 \rightarrow O_2^- \rightleftharpoons HO_2 \tag{20}$$

$$H + O_2 \rightarrow HO_2 \rightleftharpoons O_2^- \tag{21}$$

$$CH_3C_6H_5OH + O_2 \rightarrow CH_3C_6H_5(OH) O_2 \tag{22}$$

$$CH_3C_6H_5(OH) O_2 \rightarrow CH_3C_6H_4OH + HO_2 \tag{23}$$

$$CH_3C_6H_5(OH)O_2 + HO_2 \underset{\searrow}{\overset{\nearrow}{}} \begin{matrix} C_6H_5COOH \\ C_6H_5CHO \end{matrix} \tag{24}$$

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \tag{25}$$

Thus the total yield of hydroxytoluenes, benzoic acid and benzaldehyde is 2.1 and 2.6 in unbuffered and acid solutions, respectively, and almost the same as the phenol yield in the benzene system (2.1 and 2.3, respectively).

The formation of benzoic acid and benzaldehyde may occur through intermediates like peroxides and hydroperoxides which may be formed in the toluene system as in the benzene system.[16]

CONCLUSIONS

The reaction mechanism in the aqueous toluene system is analogous with the mechanism in the aqueous benzene system,[16] except that in acid deaerated solutions the methylhydroxycyclohexadienyl radical splits off a water molecule to form the benzyl radical. A similar reaction has not been observed in the benzene system. In aerated solutions acid is formed in the toluene but not in the benzene system and consequently oxygen does not increase the cresol yield as much as the phenol yield in the benzene system.

Addition of iron(III) ions changes the distribution of hydroxytoluenes favouring the formation of benzyl alcohol.

In acid solutions containing Fe(III) ions or oxygen the agreement between the toluene decomposed $G(-To)$ and the total yield of organic products $G(Org)$ was good. In unbuffered argon-saturated solutions $G(-To)$ exceeded $G(Org)$ indicating the formation of non-detected organic products.

REFERENCES

1. Khenokh, M. A. and Lapinskaia, E. M. *J. Gen. Chem. USSR* **28** (1958) 679.
2. Mancitti, M. A. B., Bertolaccini, P. L. and Pucini, L. *Energia Nucl.* **8** (1961) 519.
3. Suzuki, N. and Hotta, H. *Bull. Chem. Soc. Japan* **40** (1967) 1361.
4. Hotta, H. and Suzuki, N. *Bull. Chem. Soc. Japan* **41** (1968) 1537.
5. Hotta, H., Suzuki, N. and Isoda, K. *Bull. Chem. Soc. Japan* **42** (1969) 3056.
6. Jefcoate, C. R. E., Smith, J. R. L. and Norman, R. O. C. *J. Chem. Soc.* **B 1969** 1013.
7. Dorfman, L. M., Taub, I. A. and Bühler, R. E. *J. Chem. Phys.* **36** (1962) 3051.
8. Sauer, M. C., Jr. and Ward, B. *J. Phys. Chem.* **71** (1967) 3971.
9. Errede, L. A. and Cassidy, J. P. *J. Am. Chem. Soc.* **82** (1960) 3653.
10. Christensen, H. C. and Gustafsson, R. *Nukleonik* **12** (1969) 49.
11. Allen, A. O. *et al. Decomposition of Water and Aqueous Solutions Under Pile Radiation*, 1949 (ORNL-130) 9.
12. Hummel, R. W. and Spinks, J. W. T. *Can. J. Chem.* **31** (1953) 250.
13. Hoigné, J. and Gäumann, T. *Helv. Chim. Acta* **44** (1961) 2141.
14. Studier, M. H. and Hart, E. J. *J. Am. Chem. Soc.* **91** (1969) 4068.
15. Anbar, M. and Neta, P. *A Compilation of Specific Bimolecular Rate Constants for the Reactions of Hydrated Electrons, Hydrogen Atoms and Hydroxyl Radicals With Inorganic and Organic Compounds in Aqueous Solution*, 1966 (IA-1079).
16. Christensen, H. C. *Nukleonik* **7** (1965) 1.