The Influence of Solvation on Mesitylene Oxidation by Oxygen in Polar Media

Roumen A. Tarkalanov,* Antoaneta D. Stephanova, and Dimscho I. Dimitrov
Department of the Foundation of Chemical Technology, Higher Institute of Chemical Technology, Darvenitza, 1156 Sofia, Bulgaria

The oxidation of mesitylene by oxygen in acetic anhydride in the presence of cobalt(II) acetate and potassium bromide is reported and some characteristic kinetic quantities are presented. The higher polarity of acetic anhydride compared with acetic acid is one of the reasons for the higher oxidation rate in this medium. Another reason may be the formation of a π-complex between mesitylene and its peroxide radical. The oxidation rate in acetic acid is lower, due to blocking of the peroxide radicals by hydrogen bonds.

Systematic investigations are carried out to throw light on the influence of the medium on the catalytic liquid-phase oxidation of alkylaromatic hydrocarbons by oxygen and on the nature of the oxygen-containing products.[1-6] The influence of acetic acid and its anhydride on the kinetics of oxidation of mesitylene is reported here. We initiated the work in connection with an exploration of the possibilities of a single-stage preparation of benzene-1,3,5-tricarboxylic acid in high yield.

Experimental

The kinetics of the oxidation of mesitylene were studied with a manometer. This allowed an investigation of the initial step of the chain-radical oxidation process with no by-products to complicate the study. The experiments were carried out at constant oxygen pressure of 9.81×10^4 Pa and a temperature of 100 °C. The reaction volume was 5 ml. The oxidation kinetics were monitored by measuring the mol O_2 absorbed in 1 mol mesitylene during the reaction. A detailed description of the experimental method is given in ref. 7.

Mesitylene (99.8%) [other trimethylbenzenes (0.2%)] had b.p. 164.8 °C, d_4^{20} 0.864, n_d^{20} 1.495. Glacial acetic acid (0.8—1% H_2O) had m.p. 14.8 °C, d_4^{20} 1.051, n_d^{20} 1.369. Acetic anhydride (2% H_2O) had b.p. 137—141 °C, d_4^{20} 1.079—1.081, n_d^{20} 1.398. The catalytic system comprised cobalt(II) acetate and potassium bromide in a 1 : 1 ratio. For working out the ratio $k_2/k_6^{0.5}$ an initiator with known rate constant of decomposition was used (azobisisobutyronitrile, k 4.84×10^{-4} s^{-1} at 80 °C).

Results and Discussion

The medium used and the degree of hydrocarbon dilution are factors influencing the course of oxidation. Dilution could favour the process from a kinetic point of view but it could also lead to complications resulting from diffusion. On the other hand, high dilution is not economically desirable. The oxidation kinetics was studied at various volume ratios of mesitylene and medium. For acetic acid it was in the range 4 : 1—1 : 4 and for acetic anhydride 4 : 1—1 : 9. In acetic acid the oxidation rate w passes through a maximum at a ratio of 1 : 1, while for the anhydride the peak is at 1 : 7 (Figure 1). Thus, the rate of mesitylene oxidation increases up to 50 vol % acid in the mixture, which is kinetically justifiable. At high dilution a greater proportion of peroxide radicals are blocked by hydrogen bonds from the acid molecules, *i.e.* there is a specific influence of solvation on the kinetics.

It may be assumed that reactions involving $MO_2^{\cdot}$ radicals as well as solvated $MO^{2\cdot} \cdots HOOCCH_3$ radicals occur in the oxidation in acetic acid [reactions (1)—(6)].

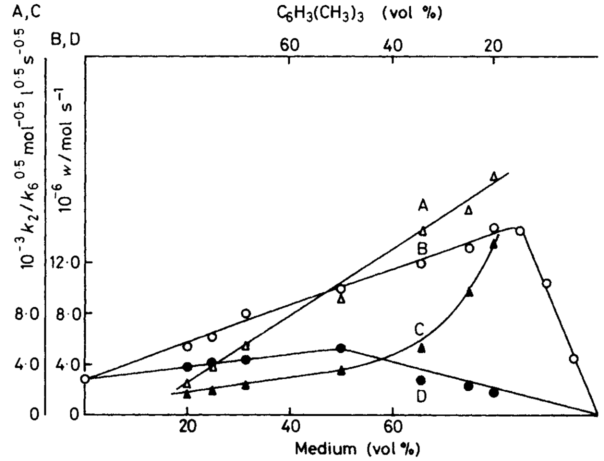
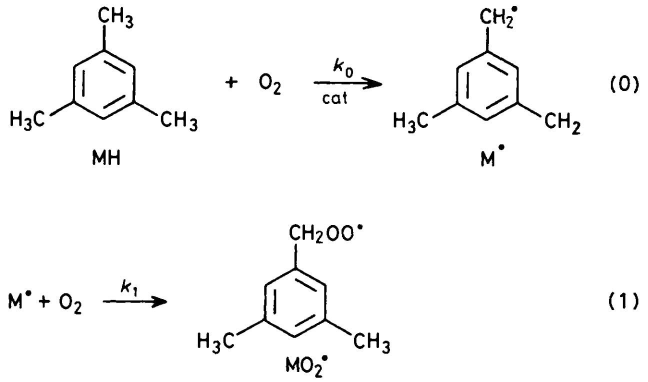


Figure 1. Dependence of oxidation rate and the $k_2/k_6^{0.5}$ ratio on the degree of dilution of mesitylene: ○, △, $(CH_3CO)_2O$; ●, ▲, CH_3COOH

The rate increases continuously up to 85 vol % acetic anhydride and the subsequent decrease is due to diffusion factors. Acetic anhydride cannot block the peroxide radicals by hydrogen bonds, which is why this is not a case of specific solvation. To establish the different behaviour of acetic and anhydride media, the dependence of lg$w$ on $(\varepsilon - 1)/(2\varepsilon + 1)$ was studied. According to the electrostatic theory of the influence of the medium on reaction kinetics, the character of that dependence determines the type of solvation.[8] The polarity ε increases upon diluting mesitylene with acetic acid as well as with the anhydride. The oxidation rate should then increase but this was not observed in acid medium. Figure 2 shows that the above mentioned dependence is not linear, and therefore the polarity is not the main factor influencing the oxidation kinetics in acetic acid. Conversely, the linear dependence observed in the case of acetic anhydride (Figure 2) does point out the influence of polarity.

Analogous conclusions may be made from studying the dependence of lg$(k_2/k_6^{0.5})$ on $(\varepsilon - 1)/(2\varepsilon + 1)$. A plot is non-linear for the oxidation in acetic acid (Figure 2). But the ratio $k_2/k_6^{0.5}$ increases in spite of a decrease in the rate (Figure 1). The peroxide radical concentration decreases at high acid concentration because of blocking in radical-complexes. Therefore, the oxidation rate, determined by equation (7), will decrease. On the other hand at higher dilutions the probability of reaction (2), or of blocking of $MO_2^{\cdot}$ by CH_3COOH, is considerably greater in comparison to that



$$MO_2^{\bullet} + MH \xrightarrow{k_2} MOOH + M^{\bullet}$$

$$MO_2^{\bullet}\cdots HOOCCH_3 + MH \xrightarrow{k_{2s}} MOOH + M^{\bullet} + CH_3COOH \quad (2)$$

$$MOOH \xrightarrow{k_3} MO^{\bullet} + {}^{\bullet}OH \quad (3)$$

$$M^{\bullet} + M^{\bullet} \xrightarrow{k_4} \text{products} \quad (4)$$

$$M^{\bullet} + MO_2^{\bullet} \xrightarrow{k_5} MO_2M$$

$$M^{\bullet} + MO_2^{\bullet}\cdots HOOCCH_3 \xrightarrow{k_{5s}} MO_2M + CH_3COOH \quad (5)$$

$$MO_2^{\bullet} + MO_2^{\bullet} \xrightarrow{k_6} \text{products}$$

$$MO_2^{\bullet} + MO_2^{\bullet}\cdots HOOCCH_3 \xrightarrow{k'_{6s}} \text{products} + CH_3COOH$$

$$MO_2^{\bullet}\cdots HOOCCH_3 + MO_2^{\bullet}\cdots HOOCCH_3 \xrightarrow{k''_{6s}} \text{products} + 2CH_3COOH \quad (6)$$

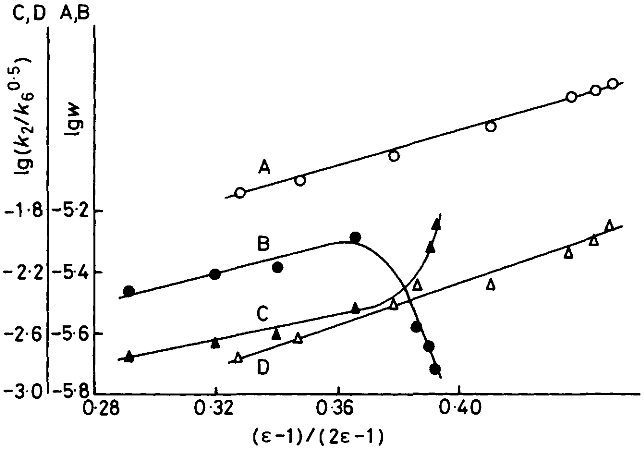


Figure 2. Dependence of lg$w$ and lg$(k_2/k_6^{0.5})$ on $(\varepsilon - 1)/(2\varepsilon + 1)$ for mesitylene oxidation: ○, △, $(CH_3CO)_2O$; ●, ▲, CH_3COOH

$$w = k_2[MH][MO_2^{\bullet}] \quad (7)$$

for $MO_2^{\bullet}$ recombination by reaction (6). As a probability factor is involved in the expression for the rate constant, k_6 decreases quicker than k_2. The total effect will be an increase in $k_2/k_6^{0.5}$.

For the oxidation in acetic anhydride the dependence of lg$(k_2/k_6^{0.5})$ on $(\varepsilon - 1)/(2\varepsilon + 1)$ is linear (Figure 2). An active transient complex $MO_2^{\bullet}\cdots MH$ is formed in reaction (2). As its polarization determines the reaction rate,[9] it follows that the reaction rate depends on the medium polarity (or the dielectric constant of the medium). If the theoretical value of the dipole moment of this transient complex coincides with the experimental value found from the slope of the curve (Figure 2, curve D), according to Kirkwood's theory this shows that there is an influence of medium polarity over the oxidation kinetics.[10] A linear relationship between lg$(k_2/k_6^{0.5})$ and $(\varepsilon - 1)/(2\varepsilon + 1)$, which should take place in our conditions, was observed. It was assumed for our purposes, that MH and $MO_2^{\bullet}$ interact in their monomeric forms. According to Kirkwood and Martin,[10,11] equation (8) holds where k

$$\lg(k_2/k_6^{0.5}) = [\lg(k_2/k_6^{0.5})]_{\varepsilon=0} + \frac{1}{2.3kT}\frac{\varepsilon - 1}{2\varepsilon + 1}\left(\frac{\mu_{MH}^2}{r_6^3} + 0.5\,\frac{\mu_6^2}{r_6^3} - \frac{\mu_2^2}{r_2^3}\right) \quad (8)$$

is the Boltzman constant, μ the dipole moment, r the atomic (molecular) radius, and the indexes 2 and 6 correspond to the transient complexes of reactions (2) and (6).

For mesitylene $\mu_{MH} = 0.1 \times 10^{-18}$ and $r_{MH}^3 = 2.31 \times 10^{-22}$ cm^3. It was accepted that $r_2^3 = 2r_{MH}^3 = 4.62 \times 10^{-22}$ cm^3 and $\mu_2 = 2.13 \times 10^{-18}$. An extreme case was considered, when the dipole moments in the transient complex met in opposite directions, or $\mu_6 = 0$. Then, the slope of the curve should be given by equation (9), while experimentally it was

$$\frac{\Delta \lg(k_2/k_6^{0.5})}{\Delta(\varepsilon - 1)/(2\varepsilon + 1)} = \frac{1}{2.3kT}\left(\frac{\mu_{MH}^2}{r_{MH}^3} - \frac{\mu_2^2}{r_2^3}\right) = -0.6 \quad (9)$$

found to be −6.2. This difference indicates that the polarity is not the only factor influencing the oxidation kinetics of mesitylene in acetic anhydride. Probably the quicker increase in $k_2/k_6^{0.5}$ than theory assumes is due to the formation of a π-complex between MH and $MO_2^{\bullet}$. It could take place because of the unpaired electron in the $MO_2^{\bullet}$ radical. As a result of the formation of that complex the interaction between MH and $MO_2^{\bullet}$ is facilitated and the rate w_2 increases.

The difference in behaviour of mesitylene peroxide radical in both media was shown by e.s.r. The spectra from the reaction of diphenylamine with peroxide radical were studied in both acetic acid and acetic anhydride. Typical nitroxide signals were not observed in acetic acid, proving that $MO_2^{\bullet}$ radical is blocked in the complex $MO_2^{\bullet}\cdots HOOCCH_3$, which is less reactive and does not react with diphenylamine. Conversely, the signals for diphenyl nitroxide in acetic anhydride were observed, *i.e.* the $MO_2^{\bullet}$ radical is not blocked in that medium and has high reactivity. This may be the reason for the high rate of oxidation of mesitylene with oxygen in acetic anhydride, in addition to the higher polarity.

References

1 C. E. Boozer and G. S. Hammond, *J. Am. Chem. Soc.*, 1954, **76**, 3861.
2 E. A. Bljumberg, A. D. Mallijevskii, and N. M. Emanuell, *Dokl. Akad. Nauk SSSR*, 1961, **136**, 1130.
3 G. E. Zaikov and Z. K. Maizus, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1962, 1175.
4 G. E. Zaikov, L. M. Andronov, Z. K. Maizus, and N. M. Emanuell, *Dokl. Akad. Nauk SSSR*, 1967, **174**, 127.
5 G. E. Zaikov, Z. K. Maizus, and N. M. Emanuell, *Dokl. Akad. Nauk SSSR*, 1967, **173**, 859.

6 G. E. Zaikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1967, No. 8, 1692.
7 J. L. Bolland, *Proc. R. Soc. London, Sect. A*, 1946, **186**, 218.
8 N. M. Emanuell, G. E. Zaikov, and Z. K. Maizus, ' The Role of the Medium in Chain-radical Oxidation Reactions of Organic Compounds,' Nauka, Moscow, 1973.
9 K. J. Laidler and H. Eyring, *Ann. N.Y. Acad. Sci.*, 1940, **39**, 303.
10 J. Kirkwood, *J. Chem. Phys.*, 1934, **2**, 351.
11 A. R. Martin, *Trans. Faraday Soc.*, 1934, **30**, 759; 1937, **33**, 191.

Received 27th April 1981; *Paper* 1/1154