

Kinetics and mechanism of oxidation of anisole and substituted anisoles by acid bromate in acetic acid–water mixture

T VEERAI AH and S SONDU*

Department of Chemistry, University College of Technology, Osmania University, Hyderabad 500 007, India

MS received 16 January 1992; revised 15 May 1992

Abstract. Oxidation of anisoles by acid bromate has been studied in acetic acid–water system in the presence of sulphuric acid. The reaction is first order each in [anisole] and [Br(V)]. The rate of reaction increased with increase in $[H^+]$ and percentage of acetic acid. The products of oxidation have been identified as ortho and para hydroxyanisoles. From the effect of $[H^+]$ and [acetic acid] on rate, $H_2^+ BrO_3$ has been established as the reactive species. Anisoles having electron-donating substituents in the benzene ring accelerate the rates and vice versa with a Hammett ρ value of -0.6 . A mechanism involving the attack of $H_2^+ BrO_3$ on ortho/para position of the anisole in the rate-determining step has been proposed.

Keywords. Anisole; bromate oxidation; kinetics; mechanism.

1. Introduction

The oxidation of anisoles by several oxidants has been studied from the synthetic point of view; very few kinetic studies have been reported with this substrate (Heiba *et al* 1969; Jefcoate *et al* 1969; Ichikawa *et al* 1971; Akhrem *et al* 1975; Radhakrishna Murthy and Sasmal 1978). Srinivasan and Chellamani (1980) reported the kinetics and mechanism of the reaction of anisole with potassium peroxodiphosphate. However, potassium bromate which has been extensively used for the oxidation of a number of organic compounds in acid medium (Natarajan and Venkatasubramanian 1970; Vijayalaxmi and Sundaram 1977; Radhakrishna Murthy and Sarangi 1980) has not been used as an oxidant for anisoles. Preliminary studies have shown that anisoles undergo oxidation by acid bromate. It is interesting to know whether the methoxy group in anisole, supposed to be resistant to metal ion oxidants, is oxidised by Br(V) or not. In the present study, an attempt has been made to understand the mechanism of oxidation of anisoles by acid bromate from a kinetic study of the reaction in a H_2SO_4 –HOAc mixture.

2. Experimental

All the chemicals used were either of AR(BDH) grade or were purified by standard procedures. Anisole (BDH) was purified to remove the acidic and basic impurities,

*For correspondence

dried and distilled. Substituted anisoles were prepared from the corresponding substituted phenols by the literature procedure (Vogel 1971). Acetic acid was purified by the procedure of Orton and Bradfield (1927). The reaction was followed by estimating the unreacted bromate iodometrically. All the experiments were conducted under pseudo-first-order conditions using ten-fold excess of substrate over oxidant in the presence of mercuric acetate.

The reaction mixture from actual kinetic runs was analysed by TLC (silica gel) and IR spectra and the products were identified as ortho- and para-hydroxyanisoles.

3. Results and discussion

Under the condition $[\text{BrO}_3^-] \ll [\text{anisole}]$, the order in $[\text{BrO}_3^-]$ was unity as revealed by the linear plots of $\log(a/a-x)$ versus time, where a is the initial [oxidant] and $(a-x)$ is the concentration at any time (figure 1A). The pseudo-first-order rate constants (k_{obs}) were obtained from the slopes of such plots. The observed rate constants increased with increase in [anisole] and the plot of $\log k_{\text{obs}}$ versus $\log [\text{anisole}]$ (figure 1B) was linear with unit slope indicating the order in [anisole] also to be unity.

The rate increased with increase in $[\text{H}_2\text{SO}_4]$ and the order in $[\text{H}^+]$ was two (figure 1C) indicating that the reactive oxidant species is probably $\text{H}_2^+ \text{BrO}_3$ formed in the equilibrium



In order to confirm the nature of the reactive species the effect of added $[\text{K}_2\text{SO}_4]$ on rate was studied. The pseudo-first-order rate constants ($k_{\text{obs}} \times 10^2 \text{ min}^{-1}$) increased marginally (from 3.68 to 4.14) with increase in $[\text{K}_2\text{SO}_4]$ (from 0.01 to 0.018 mol dm^{-3} under the conditions $[\text{BrO}_3^-] = 5 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{anisole}] = 5 \times 10^{-2} \text{ mol dm}^{-3}$, $[\text{H}_2\text{SO}_4] = 5 \times 10^{-1} \text{ mol dm}^{-3}$, $\text{Hg}(\text{OAc})_2 = 1 \times 10^{-2} \text{ mol dm}^{-3}$, $\text{AcOH} = 40\%(\text{v/v})$ and temperature = 300 K), hence, the reaction may be either ion-dipole or dipole-dipole type. The rate increased with increase in % of AcOH and a plot of \log_{obs} vs $1/D$ (figure 1D) was linear with a positive slope indicating the participation of a positive ion and a dipole in the slow step. The cation here could be $\text{H}_2^+ \text{BrO}_3$. Such reactive species have also been postulated during the oxidation of several organic compounds by acid bromate (Natarajan and Venkatasubramanian 1970). The rate was not affected by the presence of acrylonitrile, indicating the absence of free radicals in the reaction system.

An important point to be considered here is the site of attack of oxidant on anisole. The products of oxidation identified were ortho- and para-hydroxyanisoles indicating that the methoxy group is not attacked by the oxidant in the rate-determining step; instead the ortho- and para-positions of anisole, having high electron densities, were attacked by $\text{H}_2^+ \text{BrO}_3$. Based on these experimental observations and product analysis, the mechanism for the reaction can be deduced as shown in scheme 1.

A similar mechanism can be proposed for the formation of *p*-hydroxy anisole. HBrO_2 , thus formed, participates in further oxidation, finally forming Br^- . Br^- is removed by $\text{Hg}(\text{OAc})_2$ as soon as it is formed in the solution. Scheme 1 leads to the rate law

$$\begin{aligned} \text{rate} &= k'' [\text{anisole}] [\text{H}_2^+ \text{BrO}_3] \\ &= K_1 k'' [\text{anisole}] [\text{H}^+]^2 [\text{BrO}_3^-], \end{aligned} \quad (2)$$

where k'' is the bimolecular rate constant for the slow step.

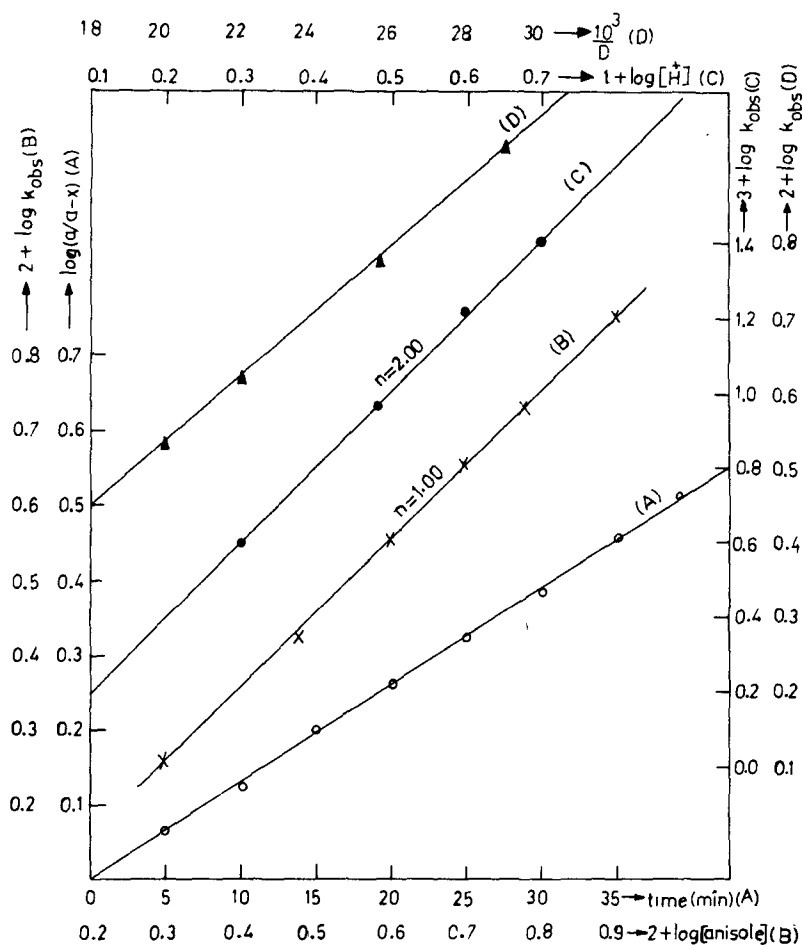
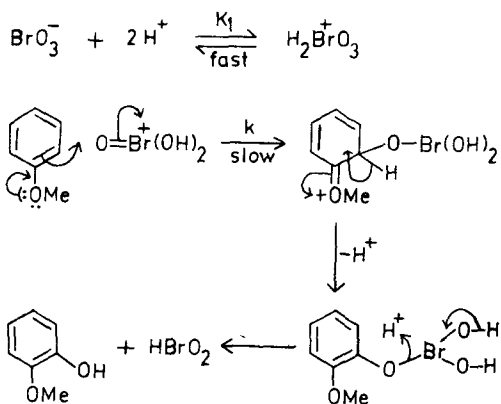


Figure 1. (A) Plot of $\log a/(a-x)$ vs time, $[BrO_3^-] = 5.00 \times 10^{-3} \text{ mol dm}^{-3}$; $[anisole] = 5.00 \times 10^{-2} \text{ mol dm}^{-3}$; $[H^+] = 5.00 \times 10^{-1} \text{ mol dm}^{-3}$; $[HOAc] = 40\%$ (v/v); $[Hg(OAc)_2] = 1.00 \times 10^{-2} \text{ mol dm}^{-3}$; temperature = 300 K. (B) Plot of $\log k_{obs}$ vs $\log [anisole]$; $[anisole] = 2.00 \times 10^{-2}$ to $8.00 \times 10^{-2} \text{ mol dm}^{-3}$; other conditions as in A. (C) Plot of $\log k_{obs}$ vs $\log [H^+]$, $[H^+] = 1.00 \times 10^{-1}$ to $9.00 \times 10^{-1} \text{ mol dm}^{-3}$. (D) Plot of $\log k_{obs}$ vs $1/D$.



Scheme 1.

Table 1. Effect of substituents in anisole on rate constants and activation parameters.

$[\text{BrO}_3^-] = 5.00 \times 10^{-3} \text{ mol dm}^{-3}$; $[\text{anisole}] = 5.00 \times 10^{-2} \text{ mol dm}^{-3}$; $[\text{H}^+] = 5.00 \times 10^{-1} \text{ mol dm}^{-3}$; $[\text{Hg}(\text{OAc})_2] = 1.00 \times 10^{-2} \text{ mol dm}^{-3}$; $[\text{HOAc}] = 40\% \text{ (v/v)}$; temperature = 300 K.

Substituents	$k'' \times 10^{-3}$ ($\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$)	E_a (kJ mol^{-1})	ΔH^* (kJ mol^{-1})	ΔG^* (kJ mol^{-1})	ΔS^* ($\text{J deg}^{-1} \text{ mol}^{-1}$)
-H	10.2	37.9	35.4	84.9	-165
<i>p</i> -CH ₃	14.2	28.5	25.9	84.1	-194
<i>m</i> -CH ₃	11.8	34.6	32.1	84.5	-175
<i>p</i> -Br	7.46	51.2	48.9	85.8	-122
<i>p</i> -Cl	7.12	68.6	66.1	85.1	-65.3
<i>m</i> -Br	5.75	56.7	54.4	86.2	-105.8
<i>m</i> -Cl	6.61	79.1	76.5	86.2	-32.1
<i>m</i> -NO ₂	4.07	85.6	83.7	87.4	-9.75
<i>p</i> -NO ₂	3.83	91.4	89.1	87.0	-6.98

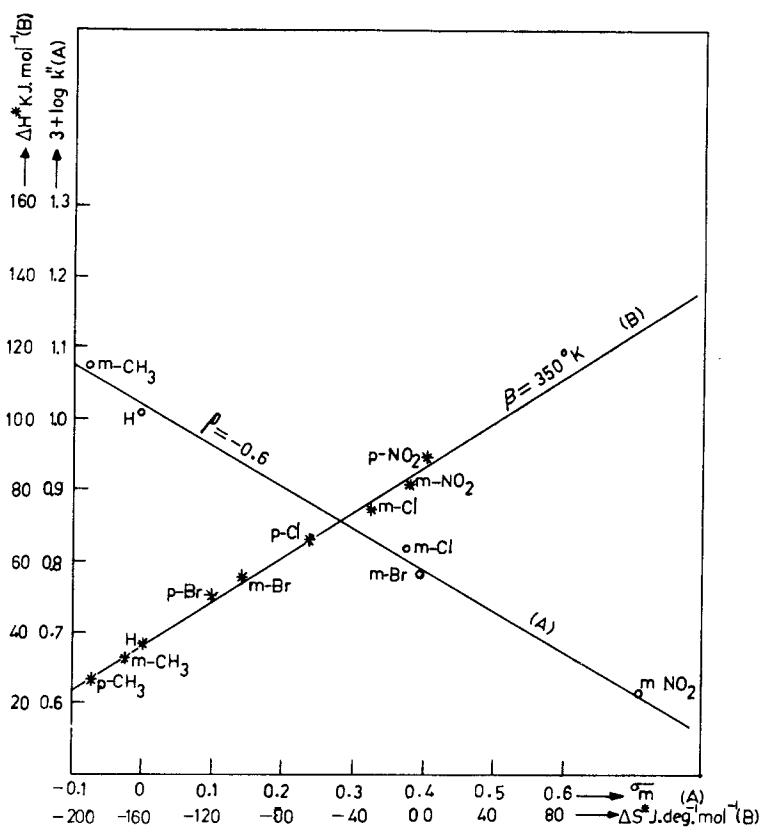


Figure 2. (A) Plot of $\log k''$ vs σ_m , $[\text{BrO}_3^-] = 5.00 \times 10^{-3} \text{ mol dm}^{-3}$; $[\text{anisole}] = 5.00 \times 10^{-2} \text{ mol dm}^{-3}$; $[\text{H}^+] = 5.00 \times 10^{-1} \text{ mol dm}^{-3}$; $[\text{HOAc}] = 40\% \text{ (v/v)}$; $[\text{Hg}(\text{OAc})_2] = 1.00 \times 10^{-2} \text{ mol dm}^{-3}$; temperature = 300 K. (B) Plot of ΔH^* vs ΔS^* .

Oxidation of several substituted anisoles has been studied and the reactivity was found to be in the order $p\text{-CH}_3 > m\text{-CH}_3 > \text{H} > p\text{-Br} > p\text{-Cl} > m\text{-Cl} > m\text{-Br} > m\text{-NO}_2 > p\text{-NO}_2$. Applying the Hammett equation to the present data (table 1) the relation $\log k''$ versus σ_m gave a good straight line plot with a negative slope ($\rho = -0.6$) (figure 2A) ($r = 0.990$) at 300 K. The negative ρ value indicates that the reaction is facilitated by high electron density at the reaction site (Wells 1963). The para-substituents are not well correlated probably due to resonance effects.

The activation parameters are calculated in the usual manner and presented in table 1. From these values it is clear that both the parameters ΔH^* and ΔS^* are important in controlling the rates of reaction, though the enthalpy factor appears to predominate. This point was also verified by calculating the isokinetic temperature (β) from the slope of the plot of ΔH^* versus ΔS^* (figure 2B). This ($\beta = 350$ K) was found to be above the experimental temperature range (300 to 315 K) used in the present work suggesting that the reactions are enthalpy-controlled. Constancy of calculated ΔG^* values for all anisoles indicates that the same mechanism is probably operative in all the cases.

Acknowledgements

The authors wish to thank Professor T Navaneeth Rao and Shir B Yadagiri Reddy for their valuable help and encouragement. Financial assistance to one of the authors (TV) under Minor Research Project from the University Grants Commission is gratefully acknowledged.

References

- Akhrem A A, Kiselev B A and Metalista D I 1975 *React. Kinet. Catal. Lett.* **2** 177
Heiba E I, Dessau R M and Koehl W J Jr 1969 *J. Am. Chem. Soc.* **91** 138
Ichikawa K, Uemura S, Nakano T and Uegaki E 1971 *Bull. Chem. Soc. Jpn.* **44** 545
Jefcoate C R E, Lindsay Smith J R and Norman R O C 1969 *J. Chem. Soc. B* 1013
Natarajan R and Venkatasubramanian N 1970 *Tetrahedron Lett.* **30** 785
Orton K J P and Bradfield A E 1927 *J. Chem. Soc.* 983
Radhakrishna Murthy P S and Sarangi L D 1980 *Indian J. Chem.* **A19** 1124
Radhakrishna Murthy P S and Sasmal B M 1978 *Indian J. Chem.* **A16** 598
Srinivasan C and Chellamani A 1980 *Oxid. Commun.* **1** 339
Vijayalaxmi and Sundaram E V 1977 *Indian J. Chem.* **A15** 612
Vogel A I 1971 *Text book of practical organic chemistry* 3rd edn (London: ELBS and Longman) p. 671
Wells P R 1963 *Chem. Rev.* **63** 171