

Kinetics of bromination of *bisphenol-C* and *bisphenol-S* in acetic acid

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Abstract. The kinetics of bromination of *bisphenol-C* and *bisphenol-S* in glacial acetic acid were determined at various temperatures and substrate concentrations. Various kinetic parameters are determined to support reaction mechanism.

Keywords. Kinetics; bromination; *bisphenols*.

1. Introduction

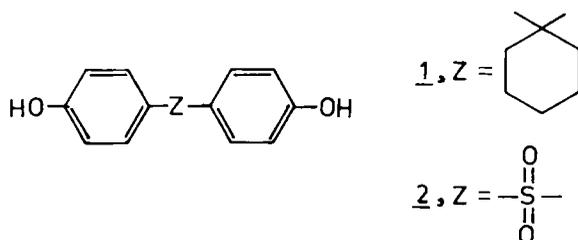
Halogenated derivatives play key roles in industry as well as in synthetic organic chemistry. Several investigators have investigated the kinetics of bromination of phenol in acetic acid (Dela Mare 1964), substituted phenols and anisoles using pyridinium bromide-perbromide (Sharma *et al* 1977), phenols and substituted phenols by N-bromosuccinimide in pure acetic acid-sodium acetate and in aqueous acetic acid-sodium acetate (Radhakrishnamurthi and Rao 1981), *p*-hydroxy biphenyl and *o*-hydroxy biphenyl in glacial acetic acid catalysed by iodine bromide (Joshi and Vibhute 1990) and phenols with molecular bromine in acetic acid (Vibhute and Jagdale 1990). Moreover, data on the kinetics of bromination on *bisphenols* are scanty. The kinetics of bromination of *bisphenols* in acetic acid medium was investigated with a view to further investigate overall order at different concentrations, individual orders and kinetic parameters for *bisphenol-C* and *bisphenol-S*.

2. Experimental

All the chemicals used were of laboratory grade and purified prior to use by appropriate methods. *Bisphenol-C* was synthesized and purified according to literature methods (Parsania 1990; Garchar *et al* 1991; Tokai Electro Chem 1982). The required solutions (*bisphenols* and bromine) were prepared in glacial acetic acid.

The kinetic measurements were carried out by determining the concentration of bromine iodometrically as a function of time. Since the reaction is faster, the batch method (Yeddanapalli and Gnanapragasam 1956) was adopted. Equal volumes of *bisphenols* and bromine (5 ml each) were taken in several stoppered flasks and thermostated at the required temperature. When the solutions attained the bath temperature, the *bisphenol* solution was quickly added to the bromine solution. The mixture was allowed to react for a definite length of time and was then arrested by quick addition of 5 ml of 10% potassium iodide. The reaction mixture was kept for one

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minute after which the liberated iodine was titrated against standard sodium thiosulphate. The stoichiometry of the reaction was confirmed as 1:1 by assuming $[\text{Br}_2] \gg [\text{phenol}]$ (Venkateshwarlu and Jagannadham 1988).

The brominated bisphenols were isolated and purified repeatedly from benzene and methanol and their structures were supported by elemental, TLC, IR, $^1\text{H NMR}$, $^{13}\text{C NMR}$ and MS analyses (Garchar *et al* 1993). It is confirmed that the substitution takes place at the 3 and 5 positions of the benzene rings.

3. Results and discussion

Figure 1 shows the typical experimental data on the bromination of bisphenol-S against time at 5°C . The overall order of the reactions was calculated from the initial rates (figure 2) which are found to be 2.14 and 2.32 for bisphenol-C and bisphenol-S, respectively. The order of the reactions was also determined by the fractional change (10, 15 and 20%) method at three different initial equimolar concentrations (0.01, 0.005 and 0.0025 M). The average overall order of the reactions was found to be 1.7 for both bisphenols. In the above cases, the initial concentrations were different but the extent of the reaction was the same and therefore the relative amounts of hydrogen bromide and

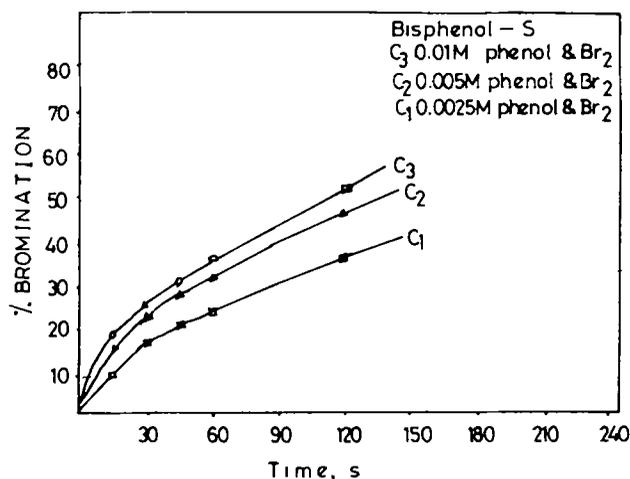


Figure 1. The plots of % bromination vs time at different concentrations of bisphenol-S and bromine at 50°C .

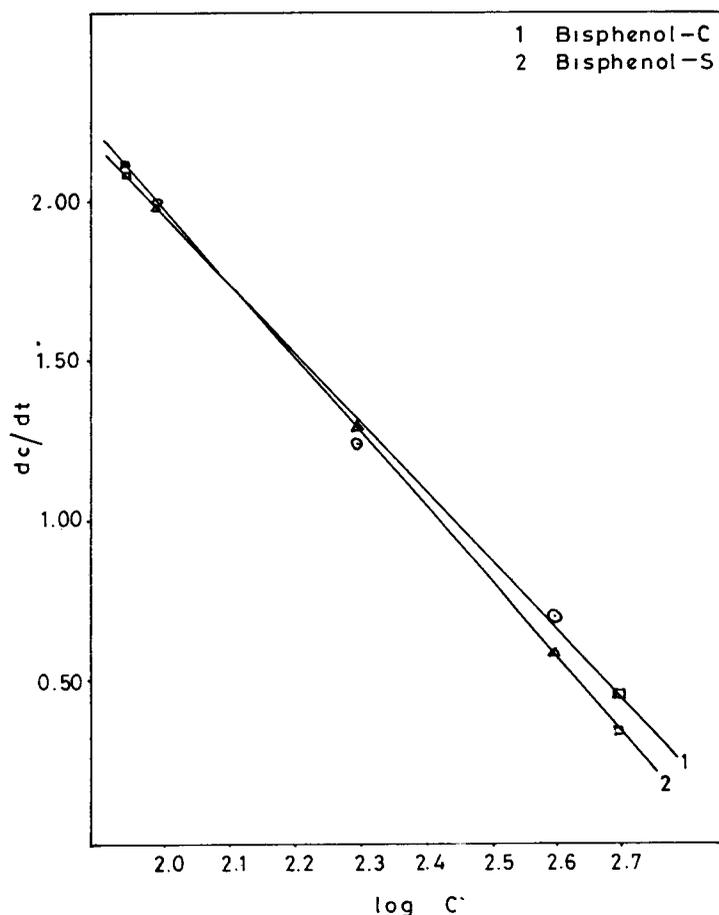


Figure 2. The plots of initial rates dc/dt vs $\log C$ for bisphenol-C (1) and bisphenol-S (2).

hence the relative incidence of side reactions can be expected to be smaller under these conditions. According to Frost and Pearson (1961) the fractional change is always below 50% and therefore, in the present investigation 10–20% fractional conversion was assumed for the estimation of n .

The individual order of reactions for bromine and bisphenols were determined by the method of isolation at 10, 15 and 20% fractional changes which is found to be 1.4. Thus the overall order of the bromination reaction is 2.

In order to estimate several kinetic parameters, the bromination reactions were carried out by taking equimolar concentrations (0.02 M) of reactants at different temperatures. The pseudo second-order rate constants (k_2) at different temperatures are reported in table 1.

It is observed that the bromination reaction of bisphenols-C is about five times faster than that of bisphenol-S. Comparative kinetic parameters such as ΔH^\ddagger , ΔG^\ddagger and ΔS^\ddagger are also reported in table 1.

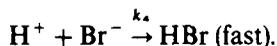
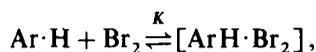
Table 1. The rate constant (k_2), ΔH^\ddagger , ΔG^\ddagger and ΔS^\ddagger of bromination of bisphenol-C (1) and bisphenol-S (2) in acetic acid at five different temperatures.

Temp. (°C)	$k_2 \times 10^{+3}$ (dm ³ ·mol ⁻¹ min ⁻¹)		ΔH^\ddagger (kJ mol ⁻¹)		ΔG^\ddagger (kJ mol ⁻¹)		ΔS^\ddagger (JK ⁻¹ mol ⁻¹)	
	1	2	1	2	1	2	1	2
5	4.20	0.98	21.00	20.54	81.13	84.73	-208.15	-222.21
10	4.60	1.17	20.96	20.50	82.38	85.65	-208.32	-222.34
15	5.89	1.42	20.29	20.46	83.30	86.73	-208.45	-222.51
20	6.50	1.52	20.88	20.42	84.56	88.12	-208.61	-222.63
25	7.81	1.71	20.84	20.38	85.56	89.37	-208.74	-222.79

It is clear from table 1 that ΔH^\ddagger is almost the same at all temperatures for both bisphenols. A similar trend is also observed in case of ΔS^\ddagger which is negative and large in magnitude while ΔG^\ddagger increases with temperature.

It is reported that the bromination of phenols in acetic acid medium is third order at higher concentrations and of second order at low concentrations (Rajaram and Kuriacose 1968; Vibhute and Joshi 1990). The overall second-order reaction at lower concentrations may be pseudo second order with the solvent molecules participating in the reaction (Vibhute *et al* 1976).

On the basis of the experimental observations the following reaction mechanism (Rajaram and Kuriacose 1968) is proposed,



The rate equation can be expressed as

$$\text{rate} = k_2([\text{ArHBr}_2]), \text{ and}$$

$$[\text{ArHBr}_2] = K[\text{ArH}][\text{Br}_2].$$

Therefore,

$$\text{rate} = Kk_2[\text{ArH}][\text{Br}_2].$$

The comparison of the rates of reaction of the two bisphenols clearly emphasizes that the electron-withdrawing sulphone group retards the rate, while the electron-releasing cyclohexyl group enhances the rate of the reaction. Moreover, the large negative values of ΔS^\ddagger and small values of A (91.4 and 17.1 for bisphenol-C and bisphenol-S respectively) indicate that the formation of the intermediate complex compound is the rate-determining step (Sharma *et al* 1977; Radhakrishnamurti and Rao 1981; Rajasekaran *et al* 1984; Venkateswarlu and Jagannadham 1988).

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