Kinetics of the Rapid Reaction $Cl_2 + 2Br^- \rightarrow Br_2 + 2Cl^-$ in Aqueous Solution

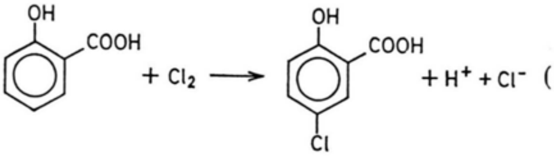
T. S. Rao, S. I. Mali, and V. T. Dangat

Department of Chemistry, University of Poona,
Pune-411 007 (India)

Z. Naturforsch. **33 a**, 391-392 (1978);
received January 8, 1978

A competition technique has been employed to study the kinetics of the rapid reaction $Cl_2 + 2\,Br^- \rightarrow Br_2 + 2\,Cl^-$ in aqueous solution. The specific rate at 25 °C and the energy of activation for the reaction are found to be 88.8 $M^{-1}\,s^{-1}$ and 71.1 kJ $mole^{-1}$, respectively.

The displacement of bromine from aqueous solutions of bromide ions by chlorine is a well-known reaction, but its kinetics has not yet been studied, presumably due to its rapidity. We have studied this kinetics on the basis of a comparison of the rate of this reaction with that of the chlorination of salicylic acid (SA) in aqueous solution. A small, measured amount of Cl_2 is added to a mixture of SA and Br^- of large, known concentrations. Both of these compete for the Cl_2 according to the reactions


(1)

$$Cl_2 + 2\,Br^- \rightarrow Br_2 + 2\,Cl^- . \qquad (2)$$

The Br_2 liberated in reaction (2) reacts with SA, but this does not affect our study. For every mole of Cl_2 reacted, one mole of Cl^- is produced in reaction (1), and two moles in reaction (2). The actual value will lie between one and two, depending upon the rates of the two competing reactions. The kinetics of reaction (1) has been studied [1] in a manner similar to that of the bromination of some substituted anilines [2]. Since the specific rate of reaction (1) is thus known, that of reaction (2) can be evaluated on the basis of the determination of the amount of Cl^- produced in the competition. This involves the prior determination of the order of the reaction.

Experimental

Analytical grade chemicals are used to prepare 0.01 M SA, 0.01 M KBr, 0.50 M KNO_3, 0.004 M $AgNO_3$ and 0.02 M Cl_2 solutions in distilled water. $AgNO_3$ solution is standardized with KCl by potentiometric titration and the Cl_2 solution is standardized iodometrically.

Starting with these solutions 10.0 cm^3 of SA and 1.0 cm^3 of KNO_3 are mixed with 5.0 cm^3 of KBr. The mixture is diluted to 24.7 cm^3. The ionic strength of the mixture is the same as in the study of reaction (1). The mixture is kept vigorously stirred, and 0.30 cm^3 of 0.0167 M Cl_2 is added from a micropipette. The total amount of KCl produced in the experiment is then determined by potentiometric titration with $AgNO_3$. This determination is performed several times and with utmost care since it largely determines the accuracy of the results. The temperature is varied in the range 10 to 30 °C.

For determining the order of the reaction, the above experiment is repeated at 25 °C with the same SA concentration and various KBr concentrations.

The results are presented in Tables 1 and 2.

Table 1. Determination of the order of the reaction $Cl_2 + 2\,Br^- \rightarrow Br_2 + 2\,Cl^-$.

Temperature = 25.0 °C
Specific rate of the chlorination of salicylic acid in aqueous solution at 25.0 °C = 25.0 $M^{-1}\,s^{-1}$
Concentration of salicylic acid = 4.0×10^{-3} M

Concentration of bromide ions/10^{-3} M	1.2	2.0	2.8	4.0	5.0
Cl^- produced per mole of Cl_2 reacted	1.52	1.64	1.71	1.78	1.82
Competition ratio X	1.08	1.78	2.39	3.50	4.46
Third order rate constant $k/10^4\,M^{-2}\,s^{-1}$	7.50	4.44	3.05	2.19	1.78
Second order rate constant $k/M^{-1}\,s^{-1}$	90.0	88.8	85.4	87.5	89.2

Results and Discussion

The rates R_1 and R_2 of the reactions (1) and (2) are, respectively,

$$-\,d[SA]/dt = R_1 = k_2[Cl_2]\,[SA], \qquad (3)$$

$$-\,d[Br^-]/dt = R_2 = k[Cl_2]^x[Br^-]^y, \qquad (4)$$

where k_2 and k are the specific rates.

In the reaction mixture, the concentrations of the competitors are much larger than that of the chlorine reacting with it and hence may be con-

Table 2. Determination of the energy of activation for the reaction $Cl_2 + 2\,Br^- \rightarrow Br_2 + 2\,Cl^-$.

Concentration of salicylic acid				=	4.0×10^{-3} M
Concentration of bromide ions				=	2.0×10^{-3} M
Temperature $t/°C$	10.0	15.0	20.0	25.0	30.0
Cl^- produced per mole of Cl_2 reacted	1.52	1.56	1.60	1.64	1.68
Competition ratio X	1.08	1.29	1.51	1.78	2.13
$k_2/M^{-1}\,s^{-1}$	8.6	12.3	17.6	23.7	33.2
$k/M^{-1}\,s^{-1}$	18.8	31.6	53.2	88.8	140.0
Slope of the curve log k versus T^{-1}			$= -3.8 \times 10^3$ K		
Energy of activation for the reaction			$= 71.1$ kJ $mole^{-1}$		
Entropy of activation for the reaction			$= 21.1$ J K^{-1} $mole^{-1}$		

sidered as virtually unchanged during the competition.

$R_2/R_1 = X$ may be defined as the competition ratio. In the competition, the number of moles of Cl^- produced per mole of Cl_2 reacted is $1/(1+X)$ in reaction (1) and $2\,X(1+X)$ in reaction (2). Hence $(1+2\,X)/(1+X) = C$ is the total Cl^- produced per mole of Cl_2 reacted, and thus

$$X = \frac{C-1}{2-C} \tag{5}$$

can be calculated from the experimentally determined value of C at any particular $[SA]/[Br^-]$ ratio.

From Equations (3) and (4), one obtaines

$$k = \frac{X\,k_2[Cl_2]\,[SA]}{[Cl_2]^x [Br^-]^y} \,. \tag{6}$$

Considering the nature and stoichiometry of reaction (2), the probable values of x and y are 1 and 2, respectively. If, however, one substitutes the various quantities in (6), the values of k show a systematic variation if [SA] in kept constant and $[Br^-]$ is varied (cf. Table 1). On the other hand, if y is considered to be 1, the values of k are constant within the limits of experimental error (±2.5%). Therefore it is concluded that the reaction is of second order.

If one plots X versus C from (5), it is evident that X changes least with C at low values of C. However low values of C are hard to determine experimentally. It is found that $[SA] = 4.0 \times 10^{-3}$ M and $[Br^-] = 2.0 \times 10^{-3}$ M, are the optimal concentrations to determined X accurately. The values are then reproducible to ±1.5%. Hence this condition was maintained for the determination of k and it's temperature dependence.

Mechanism of the reaction: Chlorine hydrolyzes in aqueous solution according to the equilibrium

$$Cl_2 + H_2O \rightleftarrows HOCl + H^+ + Cl^-$$

in which both the forward and reverse reactions are rapid [3]. While the predominant chlorinating species in reaction (1) is known to be Cl_2 [4], that in reaction (2) could be either Cl_2 or HOCl. The following two mechanisms are therefore likely, although a proof is not feasible considering the special technique used in this study.

$$\begin{array}{lll}
\text{I} & Cl_2 + Br^- & \rightarrow BrCl + Cl^- \\
 & BrCl + H_2O & \rightarrow HOBr + H^+ + Cl^- \\
 & HOBr + Br^- & \rightarrow Br_2 + OH^- \\
 & OH^- + H^+ & \rightarrow H_2O \\
\text{II} & Cl_2 + H_2O & \rightleftarrows HOCl + H^+ + Cl^- \\
 & HOCl + Br^- & \rightarrow HOBr + Cl^- \\
 & HOBr + H^+ + Br^- & \rightleftarrows Br_2 + H_2O
\end{array}$$

Mechanism I seems less likely as it involves the formation and the subsequent hydrolysis of the interhalogen compound which is known to be very unstable [5]. In mechanism II, which is more likely, the first step is a first order reaction while the third is a very rapid third order reaction [3]. In view of the observed second order kinetics of the reaction under study, the second step could be the rate determining one.

[1] T. S. Rao, S. I. Mali, and V. T. Dangat, J. Uni. of Poona, Science and Technology Section **52** (1978) (under print).

[2] T. S. Rao and S. I. Mali, Z. Naturforsch. **31 a**, 1735 (1976).

[3] M. Eigen and K. Kustin, J. Amer. Chem. Soc. **84**, 1355 (1962).

[4] E. Berliner, J. Chem. Edu. **43**, 124 (1966).

[5] F. A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, 2nd Ed., Wiley Eastern Private Limited, New Delhi, 1972, p. 585.

Verantwortlich für den Inhalt: A. KLEMM
Satz und Druck: Konrad Triltsch, Würzburg