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THE KINETICS AND THERMOCHEMISTRY OF THE REDOX REACTION BETWEEN IODINE AND PHENOL DERIVATIVES.
I. WITH *ORTHO*-BROMOPHENOL

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ABSTRACT

In this investigation kinetic studies of the redox reaction between iodine and *o*-bromophenol (*o*-BP)—aiming to throw more light on the mechanism and the nature of this reaction—involve determination of the overall reaction order and the order of the reaction in the presence of excess iodine. It also involves determination of the rate constants and thermodynamic parameters at variable equal concentrations of both reactants, and at different temperature and pH values. The overall order of the reaction was determined from half-life times and was found to be 4. The reaction was found to be first order with respect to the substrate. The thermodynamic parameters E_a^*, ΔS^* and ΔH^* of activation were calculated at various conditions for this redox reaction. A mechanism for the reaction was suggested by considering the results obtained. This reaction involves oxidation of *o*-BP by a 2e mechanism, followed by the formation of an inner ionic complex (intermediate), which is hydrolyzed to give the final solid product. This product was separated, purified and investigated confirming the suggested mechanism for the reaction. The stability and sensitivity of the intermediate to the variation of temperature and pH were explained by considering the values obtained for the thermodynamic parameters.

INTRODUCTION

Kinetic investigation of the oxidation of several substrates by iodine in aqueous media and the gas phase have been published, but nothing has been reported on the oxidation of phenols by iodine. This directed our attention to investigate the nature of such redox reactions [1].

The reaction in sulphuric acid solutions between the tri-iodine cation and deactivated aromatic compounds [2] follows second order kinetics, first order relative to each reagent. These results are consistent with the occurrence of a two-stage reaction in which the loss of the proton is catalyzed by the hydrogen sulphate ion.

The fast reaction between amylose, iodine and iodide ions was studied [3] in aqueous solution by a rapid-mixing technique. The concentration of the free and bound iodine could be calculated based on simultaneous potentiometric and spectrophotometric titrations.

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The kinetics and mechanism of iodine oxidation of coordinated formate in formatopentamminecobalt(III) perchlorate have been investigated [4]. The order of the reaction, both with respect to the oxidant and the substrate is unity. The reaction is catalyzed by iodide ion.

The gas phase reaction of benzaldehyde and iodine has been studied spectrophotometrically [5], over the temperature range 216–308 K. The kinetics of the gas phase reaction of 1,1-difluoroethane with iodine have been determined over the temperature range 609 to 649 K [6]. The kinetics of oxidation of several phenols with other oxidants such as cobalt(III) complexes [7] and periodates [8,9] have been thoroughly examined.

In the present investigation the kinetic studies of the redox reaction of I_2 and *o*-bromophenol involve determination of the overall order and calculation of thermodynamic parameters. The obtained data are considered in order to suggest a suitable mechanism for this redox reaction.

EXPERIMENTAL

Materials

These included iodine as oxidant and *o*-bromophenol (*o*-BP) as reductant (BDH), cerium(IV) sulphate (Merck), potassium iodide, sodium thiosulphate dihydrate, starch and sodium carbonate (BDH). The water used was bidistilled from all-glass equipment.

Solutions

A stock solution of 0.025 M iodine (6.35 g l^{-1}) in aqueous potassium iodide solution (10 g l^{-1}) was prepared (kept in a dark flask) and standardized against standard 0.05 M sodium thiosulphate solution using a starch indicator. The 0.01 M sodium thiosulphate solution was obtained by accurate dilution from 0.05 M stock solution.

o-Bromophenol stock solution (0.02 M) was prepared and standardized against standard cerium(IV) solution potentiometrically using a recommended procedure [10]. The starch indicator (1%) was prepared as usual in bidistilled water.

Chemical microanalysis for the separated solid product of the redox reaction of I_2 and *o*-BP for C, H, I and molecular weight measurements were kindly performed by microanalysts at Cairo University.

Apparatus

A pH/potentiometer Orion research Model 701 A digital Ionalyzer was used for pH measurements using a combined glass electrode.

Procedures

Determination of the overall order and the rate constant K

Equal concentrations of varying strength (4–10 × 10^{-3} M) of both aqueous iodine solution and *o*-BP were mixed well in sodium carbonate media (6 × 10^{-3} M) in a thermostatted stoppered bottle (painted black to avoid the action of light, if any) at 301 K. Measurement of the reacted iodine which is equivalent to the consumed *o*-BP is followed volumetrically versus time by titration of the unconsumed iodine with standard thiosulphate (0.01 M) using a starch end point. The precipitate obtained as a final product of this redox reaction was separated, purified, dried and investigated by IR and microanalysis.

The effect of temperature on the rate of the reaction

Determination of the rate constant in the temperature range 301–323 K was performed by mixing equal variable concentrations of I_2 and *o*-BP (5 × 10^{-3} M) in 6 × 10^{-3} M sodium carbonate medium and titrating the unreacted iodine with standard 0.01 M thiosulphate solution; thus calculating consumed iodine equivalent to the reacted *o*-BP versus time.

The effect of pH on the reaction rate

Varying equivalent concentrations of both iodine and substrate (5 × 10^{-3} M) at different molarities of Na_2CO_3 (2–10 × 10^{-3} M) were well mixed in a stoppered painted black flask, thermostatted at constant temperature (301 K). The unreacted iodine was determined versus time with 0.01 M thiosulphate solution using starch as indicator and thus calculating the amount of *o*-BP equivalent to consumed iodine.

Test of the redox reaction as first order with respect to the substrate

The reaction order with respect to a single component (substrate) was determined by measurement of a decrease in *o*-BP concentration (4–8 × 10^{-3} M) well mixed with a constant excess of I_2 (12.5 × 10^{-3} M). This was followed by titration of the unconsumed iodine and thus iodine equivalent to the reacted *o*-BP versus time.

RESULTS

Stoichiometry

ortho-Bromophenol as reducing agent was mixed with equal or excess iodine concentration at suitable pH and temperature. The concentration of the unreacted iodine was determined volumetrically against standard thiosulphate using a starch end point; from this the amount of reacted *o*-BP is easily found and thus all kinetic data may be calculated. In all measurements the stoichiometric ratio of [o-BP]/[I_2] is varied from 1 : 1 to 1 : 2.

Kinetics

Determination of the overall order

The overall reaction order was determined from the half-life times. For equivalent initial iodine and o-BP concentrations, the relationship [11] $\log \tau_{1/2} = \log \text{const} - (n-1)\log a$ is valid, where a is the initial concentration of the reactants ($a = [I_2] = [o\text{-BP}]$), $\tau_{1/2}$ is the time required for the reaction of one half of a, and n is the reaction order. The order of the reaction can be determined not only from the half-life time, but also from the time needed for any fraction of a reactant to react, for example one-fourth of the original amount ($\tau_{1/4}$), one-third ($\tau_{1/3}$)...etc., or even from the ratio of the half-life to the time needed for transformation of a definite fraction [12]. On plotting $\log \tau_{1/2}$ against $\log a$, a straight line with a slope equal to $(n-1)$ should be obtained for a constant reaction order. The slope of the straight line (Fig. 1) was found to be 3.0 and consequently the overall order of the reaction is 4.0. The overall rate constant (K_{over}) at varying equal concentrations of both reactants (Table 1) was calculated by computer applying the least squares method for the data obtained from the following modified relationship [12]

$$K_t = \left(\frac{1}{n}\right)\left(\frac{a^{n-1} - (a-x)^{n-1}}{a^{n-1}(1-x)^{n-1}}\right) + C$$

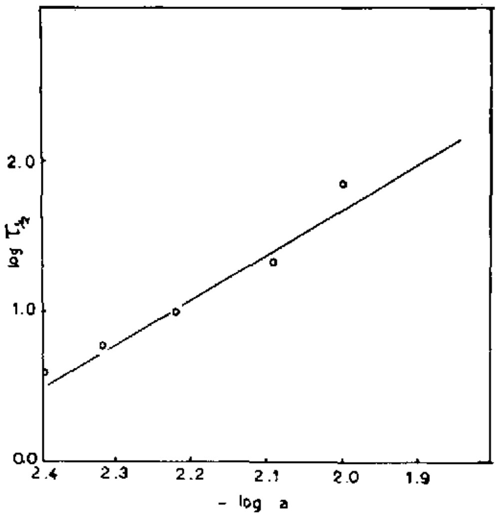


Fig. 1. The determination of overall order of the redox reaction between I_2 and o-BP.

TABLE 1

The obtained overall rate constant (K_{over}) and thermodynamic parameters for the redox reaction between *o*-BP and I_2 at varying equal concentrations of the reactants at temperature 301 K and in 5×10^{-3} M Na_2CO_3 solution

$a \times 10^3$ (mol l^{-1})	$K_{\text{over}} \times 10^{-8}$ (l^3 mol^{-3} s^{-1})	Correlation coefficient	ΔS^* (cal mol^{-1} deg^{-1})	ΔH^* (k cal mol^{-1})
10.0	0.197	0.63	166.00	54.36
8.0	53.50	0.67	177.39	51.01
6.0	110.50	0.41	178.83	50.58
4.8	321.20	0.65	180.95	49.94
4.0	1358.10	0.75	183.81	49.08

where C is a constant dependent upon the nature of the redox reaction. This relation can be reduced to

$$Y = KX + C$$

where

$$Y = \left(\frac{1}{n-1}\right)\left(\frac{a^{n-1} - (a-x)^{n-1}}{a^{n-1}(a-x)^{n-1}}\right)$$

and X = time, a = initial concentration of reactants, X is the concentration of reacted material, and n is the order of the reaction.

The plot of Y and X is given in Fig. 2. The plot of X and Y without applying the least squares method gives two straight lines (Fig. 3), and from this data stepwise rate constants K_1 and K_2 were calculated (Table 2), which means that the redox reaction passes through two steps.

The temperature dependence of the reaction rate

An attempt was made to obtain a relation between the rate of the reaction and temperature. The redox reaction was carried out at an initial concentration of $a = 5 \times 10^{-3}$ M of both I_2 and *o*-BP, at different temperatures to calculate the activation energy E_a from the relationship [13]

$$\ln K = -\frac{E_a}{RT} + \ln A$$

where A is the Arrhenius factor, T is absolute temperature, and R is the gas constant $= 1.987 \times 10^{-3}$ kcal mol^{-1} deg^{-1}. The plot of ln K against $(1/T)$ gave a straight line with a slope of $-E_a/R$ and intercept of ln A. Applying the least square method to the kinetic data at various temperatures and plotting ln K vs. $(1/T)$ (Fig. 4a) a straight line is obtained, from the slope of which the calculated overall activation energy is $E_{\text{over}} = 57.62$ and intercept is $\ln A = 107.7$. On the other hand plotting ln K vs. $(1/T)$ (Fig. 4b,c)

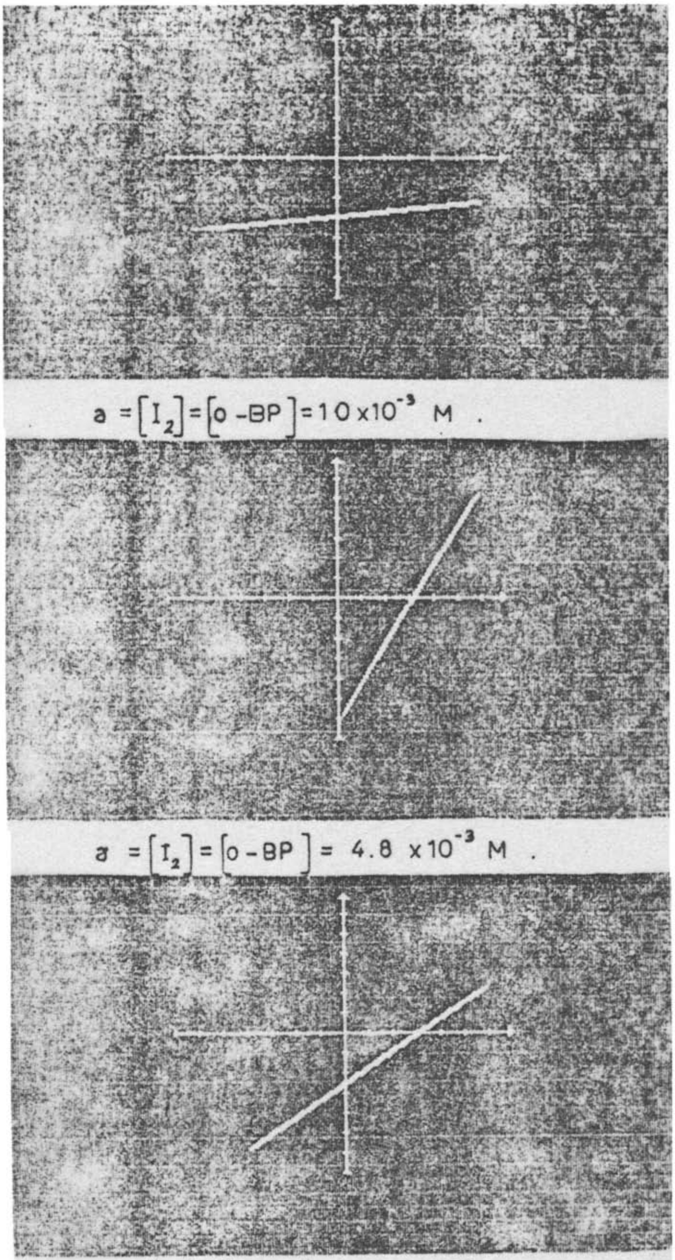


Fig. 2. Graphical representation of the rate data of the redox reaction between I_2 and *o*-BP using a computer technique at 301 K and 5×10^{-3} M Na_2CO_3.

for the kinetic data obtained without applying the least squares method the calculated stepwise activation energies are $E_1 = 27.81$ and $E_2 = 61.59$ and the intercepts are $\ln A_1 = 61.85$ and $\ln A_2 = 115.70$. These values were used

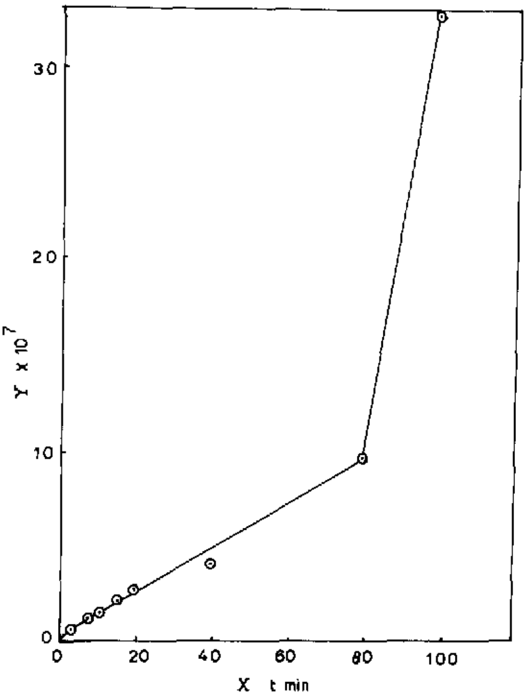


Fig. 3. Graphical representation of the rate data of the redox reaction between I_2 and o-BP at 301 K and 5×10^{-3} M Na_2CO_3; $a = [I_2] = [o\text{-BP}] = 10^{-4}$ M.

for calculation of the overall and stepwise thermodynamic parameters ΔS^* and ΔH^* for various conditions (Tables 1–6 and 8, 9) applying the thermodynamically modified relations [14]

$$\Delta S^* = E_a/T - R\left(\ln\frac{kT}{Kh}\right)$$

TABLE 2

The stepwise rate constants (K_1 and K_2) and thermodynamic parameters obtained for the redox reaction between o-BP and I_2 at varying equal concentrations of the reactants: temperature 301 K and in 5×10^{-3} M Na_2CO_3 solution

$a \times 10^3$ (mol l^{-1})	$K \times 10^{-7}$ (l^3 mol^{-3} s^{-1})		ΔS^* (cal mol^{-1} deg^{-1})		ΔH^* (kcal mol^{-1})	
	K_1	K_2	ΔS_1	ΔS_2	ΔH_1	ΔH_2
10.0	0.002	0.0083	53.55	168.60	31.06	62.42
8.0	0.0445	0.4670	95.71	176.61	29.21	60.01
6.0	1.1167	80.000	66.02	186.83	27.28	56.93
4.8	2.217	23.33	67.38	184.38	26.87	57.67
4.0	8.333	26.67	70.02	184.65	26.08	57.59

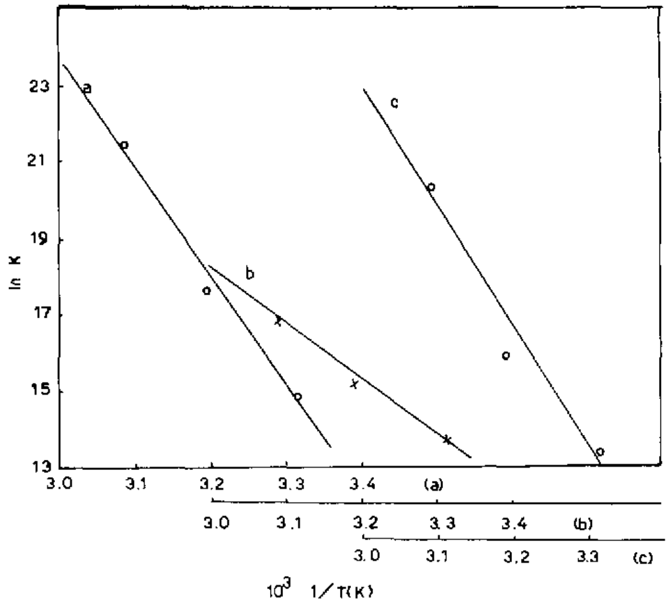


Fig. 4. Plot of ln K against reciprocal of absolute temperature for the oxidation of *o*-BP by I_2 in 6×10^{-3} M Na_2CO_3 medium; $a = [I_2] = [o\text{-BP}] = 5\times10^{-8}$ M. (a) for ln K_{over}; (b) for ln K_1; (c) for ln K_2.

TABLE 3

The dependence of the overall rate constant (K_{over}) and stepwise rate constants (K_1 and K_2) of the redox reaction between *o*-BP and I_2 on temperature at $a = [I_2] = [o\text{-BP}] = 5\times10^{-3}$ M in 6×10^{-3} M Na_2CO_3 solution

T	$1/T\times10^3$	$K_{over}\times10^6$	ln K_{over}	$K_1\times10^{-6}$	ln K_1	$K_2\times10^{-6}$	ln K_2
301	3.32	3.24	14.992	1.00	13.815	0.67	13.415
313	3.19	45.69	17.643	4.16	15.241	8.33	15.935
323	3.09	2227.33	21.524	21.66	16.890	666.0	20.316
333	3.00	33.35	17.322	11.16	16.227	58.33	17.880

TABLE 4

The overall rate constant K_{over} and thermodynamic parameters obtained for the redox reaction between *o*-BP and I_2 at different temperatures; at $a = [o\text{-BP}] = [I_2] = 5\times10^{-3}$ M in 6×10^{-3} M Na_2CO_3 solution

T K	$K_{over}\times10^{-6}$ (l^3 mol^{-3} s^{-1})	Correlation coefficient	ΔS^* (cal mol^{-1} deg^{-1})	ΔH^* (kcal mol^{-1})
301	3.244	0.81	162.69	55.44
313	45.96	0.83	160.55	56.00
323	2227.33	0.71	162.49	55.30
333	33.35	0.62	148.73	59.80

TABLE 5

The overall rate constant (K_{over}) and thermodynamic parameters obtained for the redox reaction between *o*-BP and I_2 at different molarities of Na_2CO_3. Temperature 301 K and $a = [I_2] = [o\text{-BP}] = 5 \times 10^{-3}$ M

M of Na_2CO_3 $\times 10^3$	K_{over} (l^3 mol^{-3} s^{-1})	Correlation coefficient	ΔS^* (cal mol^{-1} deg^{-1})	ΔH^* (kcal mol^{-1})
0	0.0149×10^4	0.927	142.85	61.42
2	0.0764×10^4	0.829	146.10	66.44
4	0.4727×10^4	0.625	149.72	59.35
5	732.53×10^4	0.857	164.32	54.96
6	96.459×10^4	0.990	160.29	56.17
8	1994.9×10^4	0.845	166.31	54.36
10	2107×10^6	0.708	175.57	51.57

TABLE 6

The stepwise rate constants (K_1 and K_2) and thermodynamic parameters obtained for the redox reaction between *o*-BP and I_2 at different molarities of Na_2CO_3; temperature 301 K and $a = [o\text{-BP}] = [I_2] = 5 \times 10^{-3}$ M

$M \times 10^3$ (mol l^{-1})	$K \times 10^{-5}$ (l^3 mol^{-3} s^{-1})		ΔS^* (cal mol^{-1} deg^{-1})		ΔH^* (kcal mol^{-1})	
	K_1	K_2	ΔS_1	ΔS_2	ΔH_1	ΔH_2
0	0.0041	0.0045	45.82	158.23	33.39	65.54
2	0.0166	0.0077	48.60	159.30	32.55	65.22
4	1.1166	0.0710	56.96	163.71	30.04	63.89
6	5.9000	9.500	60.27	173.44	29.04	60.96
8	20.8300	75.000	62.78	177.55	28.28	59.73
10	156.6600	6666.000	66.79	186.47	27.08	57.04

TABLE 7

The dependence of the overall rate constant (K_{over}) and the stepwise rate constants (K_1 and K_2) of the redox reaction between *o*-BP and I_2 on the molarity of the Na_2CO_3 solution at temperature 301 K and $a = [I_2] = [o\text{-BP}] = 5 \times 10^{-3}$ M

M of Na_2CO_3 ($\times 10^3$)	ln K_{over}	ln K_1	ln K_2
0	5.00	6.032	6.109
2	6.638	7.418	6.652
4	8.461	11.623	8.877
5	15.807	13.017	16.628
6	13.779	13.296	13.764
8	16.809	14.549	15.830
10	21.468	16.567	20.317

TABLE 8

The first order overall rate constant K_{over} and the thermodynamic parameters obtained at various concentrations of *o*-BP and excess $[I_2] = 12.5 \times 10^{-3}$ M at temperature 301 **K** and in 5×10^{-3} M Na_2CO_3 solution

$[o\text{-BP}] \times 10^3$ (mol l^{-1})	$K_{\text{over}} \times 10^3$ (l^3 mol^{-3} s^{-1})	Correlation coefficient	ΔS^* (cal mol^{-1} deg^{-1})	ΔH^* (kcal mol^{-1})
11.25	0.020	0.77	111.41	70.885
6.39	0.133	0.85	115.18	69.750
4.79	0.432	0.95	117.51	69.048
4.00	2.405	0.97	120.92	68.020

TABLE 9

The stepwise first order rate constants (K_1 and K_2) and thermodynamic parameters obtained for the redox reaction between *o*-BP and I_2 at various concentrations of *o*-BP and excess $[I_2]$ (12.5×10^{-3} M) at temperature 301 **K** and in 5×10^{-3} M Na_2CO_3 solution

$[o\text{-BP}] \times 10^3$ (mol l^{-1})	$K \times 10^5$ (l^3 mol^{-3} s^{-1})		ΔS^* (cal mol^{-1} deg^{-1})		ΔH^* (kcal mol^{-1})	
8.0	4.667	0.85	14.05	122.90	42.95	76.18
6.4	68.33	8.83	19.39	127.55	41.35	74.78
4.8	115.17	31.17	20.42	130.05	41.03	74.02
4.0	337.83	163.83	22.56	133.35	40.39	73.03

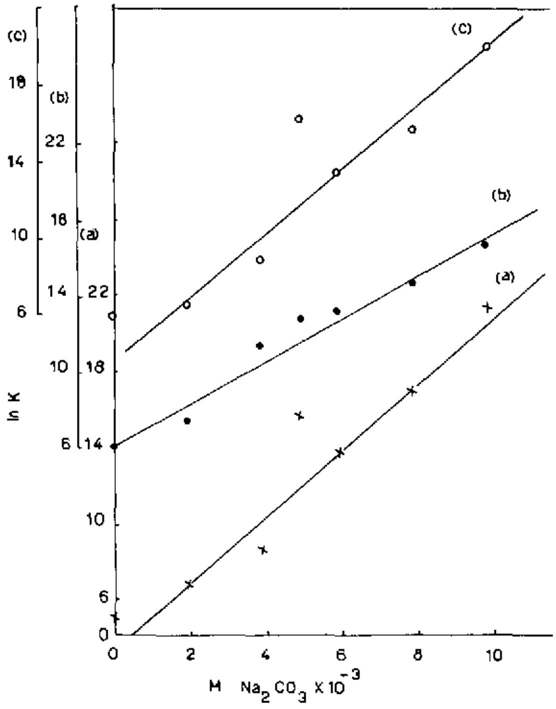


Fig. 5. The dependence of the rate constant on the molarity of Na_2CO_3 at 301 **K** and $a = [I_2] = [o\text{-BP}] = 5 \times 10^{-3}$ M. (a) for ln K_{over}; (b) for ln K_1; (c) for ln K_2.

where E_a is the activation energy, k is Boltzmann's constant, h is Planck's constant and K is the rate constant and

$$\Delta H^* = RT(\ln A - \ln K)$$

The pH dependence of the reaction rate

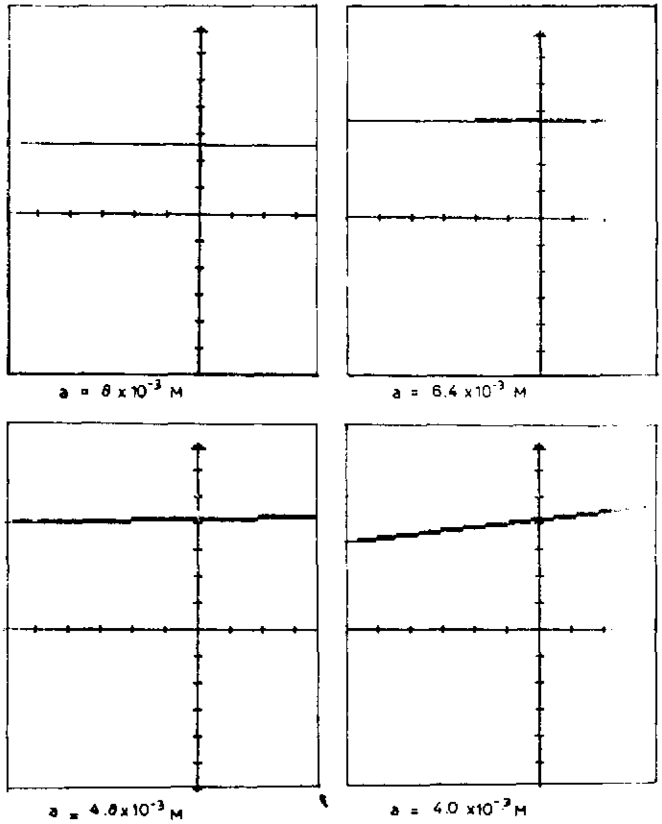
It was found that the reaction rate varies logarithmically with the variation of pH (Fig. 5 and Table 7).

Test for the reaction as first order with respect to the substrate

The first order reaction between variable concentrations of *o*-BP (4–11.25 $\times 10^{-3}$ M) and excess of I_2 (12.5×10^{-3} M) was checked. The reaction was found to be first order with respect to the substrate. A typical first-order plot of $\log(a - x)$ vs. time was obtained by using the relation [12]

$$\log(a - x) = -(K/2.303) + C$$

and a straight line with a slope $-K/2.303$ was obtained applying the least



$a = 8 \times 10^{-3}$ M

$a = 6.4 \times 10^{-3}$ M

$a = 4.8 \times 10^{-3}$ M

$a = 4.0 \times 10^{-3}$ M

Fig. 6. Plot of $-\log(a - x)$ against time t using a computer technique for the oxidation of *o*-BP at 301 K and 5×10^{-3} M Na_2CO_3; $[I_2] = 12.5 \times 10^{-3}$ M.

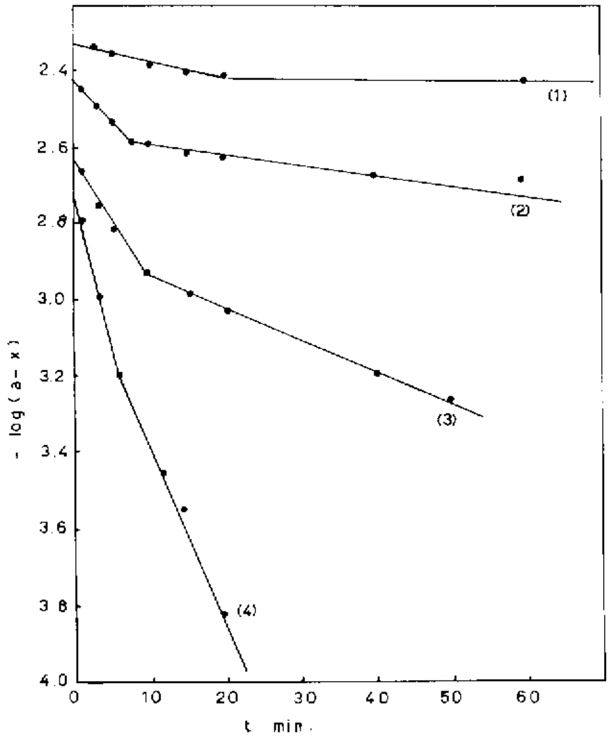


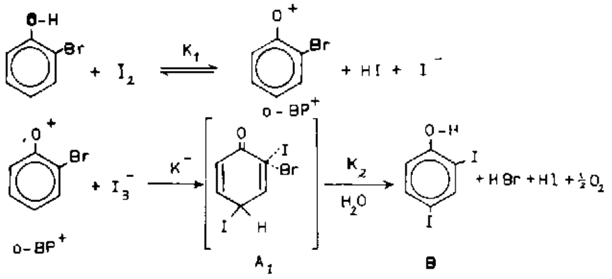
Fig. 7. Plot of $-\log(a-x)$ against time t for the oxidation of *o*-BP at 301 K and 5×10^{-3} M Na_2CO_3; $[I_2]=12.5\times10^{-3}$ M.

squares method [15] by calculation (Fig. 6). From the slope of this line K_{over} (overall first-order rate constant) can be calculated at various concentrations of *o*-BP (Table 8). The stepwise first-order rate constants were obtained from the plot of the kinetic data without applying the least squares method (Fig. 7 and Table 9).

DISCUSSION

Iodine as oxidant in aqueous media in the presence of iodide ions, is known to exist as various species [14–16], e.g. HOI, I_3^-, and I_2. Sahu et al. [4] proved that $[I_3^-]=[I_2]_T$ and [HOI] is very small, whereas $[I_2]_T$ is the total iodine. They assumed that if the iodine molecule is the oxidizing species, the rate constant should increase with increasing iodide concentration, which means that almost all I_2 (in I^- solution) molecules are present in the form of I_3^- ions; this is the case in the present investigation.

In this investigation, kinetics of the redox reaction between I_2 and *o*-BP are thoroughly studied and critically investigated at various conditions with the aim of clarifying the mechanism of these redox reactions.



Scheme 1.

Depending upon the obtained results, this reaction can be explained mechanistically by Scheme 1, which involves oxidation of *o*-BP by a 2e mechanism, followed by the formation of inner ionic complexes which eventually hydrolyze to give the final products. This scheme is dependent upon several factors. Firstly there are two electrons exchanged between *o*-BP and I_2 as shown by potentiometric studies [1]. Secondly I_2 or I_3^- form inner ionic complexes or outer additive complexes [16–18] in their reaction with organic compounds. The formation of inner complex A_1 between I_2 and *o*-BP is usually supported by a polar solvent such as water as a medium. This inner complex is hydrolyzed in neutral or slightly alkaline media to give the solid product B, which is separated, purified and investigated by IR, elemental analysis for C, H, I and molecular weight determination. The product is found to be in good agreement with Scheme 1. Thirdly the calculated entropy and enthalpy of activation refer to the formation of an intermediate A_1 complex at various conditions.

In the oxidation of *o*-BP with I_2 at different equal concentrations the overall or stepwise rate constants obtained (Tables 1, 2) increase with the decrease of concentration of both reactants. This means that the rate constants decrease with the decrease of the liberated iodide, due to the reduced iodine concentration, which catalyzes the redox reaction. This is also confirmed by the general increase of entropy and decrease of enthalpy of activation with the decrease of concentration of both reactants. Consequently the concentration of the intermediate A_1 decreases and the formation of the product B becomes appreciable.

Observation of the effect of temperature on the redox reaction of I_2 and *o*-BP shows that the rate of the reaction increases irregularly with its increase (Tables 3, 4) which can be deduced from the calculated values of the overall or stepwise rate constants, together with the values of the calculated thermodynamic parameters ΔS^* and ΔH^*. This irregularity is attributed to the sensitivity of the intermediate A_1 to the temperature change. At different temperatures $\Delta S_2^* > \Delta S_1^*$ and $K_2 > K_1$ which means that the first step shown in Scheme 1 is the slow rate-determining step. This is in good agreement with Scheme 1. This slowness is also attributed to the hydrogen bonding in *o*-BP which makes its oxidation slow, because it becomes more difficult to obtain the phenoxonium ion *o*-BP$^+$ during the redox reaction course. It is worth mentioning here that, at some temperatures abrupt changes occur. It is noticed that the rate constants K_{over}, K_2 or K_1 and entropy are of very high values at 323 K but decrease again at 333 K (Table 3) which shows that the decomposition of the intermediate A$_1$ to give product B is very fast at 323 K and thus produces the high rate of this redox reaction. Thus from this analysis the rate equation can be given by

$$\text{Rate} = K_1 K_2 [o\text{-BP}]^{-n} [\text{H}^+]^{-n} + \overline{K} [o\text{-BP}^+]^n [\text{I}_3^-]^n$$

where $n = 4$; $\overline{K}$ is the undetermined formation constant of intermediate A$_1$.

This proposed mechanism and the given rate equation are also confirmed by the fact that the overall and stepwise rate constants usually increase with increasing pH (Tables 5, 6). This shows that the rate of hydrolysis of A$_1$ to B becomes faster at higher pH. Therefore, this product was prepared and separated in an alkaline medium for separate investigation. The change of the rate constants of this redox reaction with pH is logarithmic in nature as indicated by the plot of ln K values with pH (Fig. 5), which indicates the high sensitivity of the intermediate A$_1$ to the change of pH and consequently its hydrolysis to give the product B.

The rate of decreasing concentration of *o*-BP when reacting with excess I$_2$ was found to be first order as shown by the linear plot (Fig. 6). The rate equation therefore for this first-order reaction is given by

$$\text{Rate} = K_1 K_2 [o\text{-BP}]^{-1}$$

Investigation of the oxidation product

The solid product B obtained on oxidation of *o*-BP was separated, dried and recrystallized from an ethanol : water mixture (1 : 1). The sharp melting point of this solid product was 118 ± 1°C. This product was microanalyzed for C, H, I and molecular weight was determined. From the microanalysis data the possible general formula is $C_6H_4OI_2 \cdot 2H_2O$ (calculated: C = 18.84, H = 2.09, I = 66.49, M. wt. = 382 and found: C = 18.7, H = 2.05, I = 66.1, M. wt. = 380.8). This is in good agreement with the proposed structural formula B in Scheme 1. This suggested formula was also confirmed by the IR spectrum using the KBr disc technique (Table 10). The IR spectrum [19] shows a band at 3420 cm^{-1} which is due to a weakly hydrogen-bonded OH group attached to I in the *o*-position of the product B, together with other frequencies in the range 3480–3510 cm^{-1} from the water molecules of crystallization. The frequency at 860 cm^{-1} stems from the two adjacent vacant positions in the aromatic ring. The other one at 880 cm^{-1}, which is associated with the isolated positions of I atoms, occurs due to electrophilic attack on the aromatic ring by iodine. This is dependent upon the fact that

TABLE 10

Identification of the important frequencies in the IR spectrum of oxidation products of the reaction of *o*-BP with I_2

Important bands cm^{-1} (solid B from *o*-BP)	Assignment
860 vsh	*p*-Substituted two adjacent
880 vsm	Isolated–H
1150 vsh	C–O (stretching)
1260 sh	O–H bending
1540–1560 sm b	Aromatic ring bands
3390–3420 sm b	Water of crystallization
3780–3740 sm b	Intramolecular and weakly bonded O–H J-bonded –OH in solid

vsh = very sharp, b = broad, sm b = small broad, sh = sharp.

outer and inner complexes are essential intermediates in the electrophilic action of molecular I_2 on aromatic compounds [17,18,20] which thus undergoes a ring substitution reaction assisted by a polar medium (e.g. H_2O or ethanol). Iodination of phenols can also be achieved by the action of hypoiodous acid formed in alkaline solution. The action of HOI is believed to resemble the action of molecular iodine. The electrophilic center of iodine is I^+ formed by the heterolytic fission of I_2. The incipient cation is conveyed to the aromatic nucleus in the form of a unit such as IOH_2^+, I_2, HOI or even perhaps I_3^-. The last species is formed in aqueous solutions of iodine and even in organic solvents such as alcohol. Also iodine can act as a nucleophilic reagent due to its primary σ-acceptor function [16,17]. This amphoteric behavior of I_2 is consistent with its "soft acid" character in its interaction with species having primarily donor functions such as phenols (σ-donors via oxygen or OH), which contain non-bonding electrons.

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