

COMPARATIVE STUDY OF THE REDOX REACTIONS BETWEEN IODINE AND PHENOL DERIVATIVES, THROUGH CORRELATION BETWEEN THERMAL ANALYSIS AND THERMODYNAMIC CALCULATIONS FROM KINETIC DATA

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ABSTRACT

Comparison between reactions of iodine with various phenol derivatives was performed by using data obtained from thermal analysis of the redox products and thermodynamic activation parameters obtained from the study of the kinetics of these reactions under various conditions. This comparative study identifies the fast and slow reactions, and explains the rates of these reactions. In addition, correlation is achieved between the velocity or the rate of these reactions and the Hammett constants of the substituents or the electronegativities of the phenolic ring halogens.

INTRODUCTION

The reaction of halogens with aromatic compounds may lead to nucleophilic and/or electrophilic interaction with the aromatic ring [1,2]. In this laboratory, the products obtained by oxidation of phenol derivatives with iodine in aqueous iodide solution under various conditions [3,4], were separated and investigated through the use of microanalysis, spectrophotometric studies and thermal analysis. The mechanisms of such redox reactions between iodine and phenols have been suggested and explained satisfactorily by using potentiometric and kinetic studies [5–7]. The identification of the solid redox products obtained by thermal analysis and microanalysis leads to information that can be used to confirm the suggested schemes of these redox reactions. The aim of this work is to compare the results obtained by us with those described previously. This study compares the rates of the redox reactions and correlates the Hammett constants and electronegativities of the substituents with these reaction rates. This is made possible by using the data obtained previously from the kinetic studies of the reactions and by thermal analysis of the redox products.

EXPERIMENTAL

Materials

These included iodine as oxidant and phenol derivatives, *ortho* bromophenol (*o*-BP), *p*-bromophenol (*p*-BP), *p*-chlorophenol (*p*-CP), *p*-nitrophenol (*p*-NP), *o*-, *p*- and *m*-aminophenols (*o*-, *p*- and *m*-AP) (BDH).

Instrumentation

A pH/potentiometer Orion Research Model 701 A digital Ionanalyser was used for pH and millivolt measurements. A Pye Unicam SP 1750 UV/visible spectrophotometer was used for all spectrometric measurements. Thermal analyses (thermogravimetric analysis (TGA) and differential thermal analysis (DTA)) were made by using a conventional thermal analyser (Shimadzu system, Shimadzu 30 series thermal analysis instrument).

Procedures

The kinetic measurements and the determination of the overall order and the rate constants of the reactions under various conditions have been described previously [6,7]. The procedure for the potentiometric microdetermination of various monohydric phenols with iodine has been described in detail elsewhere [5]. TGA and DTA were carried out on the redox products of various phenol derivatives and the methods have been described in detail elsewhere [3,4]. All calculations were made by applying previously reported relations [8,9] using a Spectravideo 328 home computer.

RESULTS AND DISCUSSION

Correlation between the Hammett constants of the substituents and the rates of reaction

In recent years the data collected on rates and equilibria of reactions have led to the formulation of a number of empirical correlations [10]. Rates of reactions may be changed by the introduction of substituents. It has been found possible to derive an empirical linear relationship between the logarithms of the rate or the equilibrium constants for one reaction and those of another reaction which has been subjected to some variation in reactant structure. The logarithm of a rate constant, according to the transition-state theory, is proportional to the standard free energy of activation. The linear

free-energy relationship describing the effect of polar factors (I and R) on reactivity in aromatic compounds is known as the Hammett equation,

$$\log_{10} k/k_o = \sigma\rho$$

or

$$\log_{10} K/K_o = \sigma\rho$$

where K and K_o are rate constants, k and k_o are equilibrium constants and σ is the substituent constant. σ is independent of the nature of the reaction and is a quantitative measure of the polar effect relative to hydrogen of a given *m*- or *p*-substituent in the reaction. It represents the electron attracting (withdrawing) or electron-repelling (releasing) power of a substituent. The more positive σ is, the more electron-withdrawing ($-I$ and $-R$) is the substituent, and the more negative σ is, the more electron-releasing ($+I$ and/or $+R$) is the substituent. The constant ρ is called the reaction constant. It is a measure of the sensitivity of a given reaction series to the polar effects of the ring substituents, i.e. to changes in the values of the substituents. It is important to note that this equation deals only with substituents *meta* and *para* to the reaction site in monosubstituted benzene. In these positions steric effects are absent, and hence the correlation of polar factors is satisfactory, since other factors are essentially unchanged.

Resonance effects are the main causes of the failure of the Hammett equation. In this case, it is possible to get good agreement with the Hammett equation by defining a second substituent constant σ^- (sigma minus, e.g. NO_2 group). The negative sign indicates that the *p*-substituent group is capable of a resonance electron-withdrawal effect. It appears that rates of *m*-substitution may be correlated satisfactorily using σ values, but σ^+ must be used for *p*-substituents.

Effect of substituents on redox reactions of phenol derivatives with iodine

There are two ways of studying the relative reactivities of positions in substituted benzene, one based on charge distribution and the other on the stabilities of the intermediate carbonium ions (σ -complexes). In both approaches, the effects of substituents (described below) apply to kinetically controlled products, but they do not always apply to the thermodynamically controlled products.

The plot of σ values (Table 1) of some *p*-derivatives of phenol vs. $\log_{10} K$ (logarithm of the rate constants of the redox reactions of these derivatives with iodine) using the modified Hammett relation

$$\log_{10} K = \sigma\rho - \log_{10} 1/K$$

leads to a straight line on application of the least-squares method [11]. The slope of this line is the reaction constant and the intercept is $-\log_{10} 1/K_o$, where K_o is the rate of reaction between iodine and phenol calculated from the intercept by computer program.

TABLE 1

Correlation between Hammett constants and rate constants of iodine-phenol redox reactions

Phenol derivative	K ($l^3 \text{ mol}^{-3} \text{ s}^{-1}$)	σ_p^a	$\log_{10} K$
<i>p</i> -BP	$(7.97-23.46) \times 10^4$	+0.23	4.9
<i>p</i> -NP	3.99-19.69	+0.78	0.6
<i>p</i> -AP	$(1.07-331.9) \times 10^5$	-0.66	5.03

^a Reference 11; σ_p , Hammett constant for *p*-substituents.

The ratio K/K_0 of the rate constants of various phenol derivatives (K) and of phenol (K_0) (Table 2) indicates that the fastest reaction is that of *o*-BP with iodine. The order of increasing rate of reaction between iodine and phenol derivative is *o*-BP \gg *p*-AP > *p*-BP > *m*-AP \gg *p*-NP. The low rate of reaction of iodine with the *p*-derivatives can be explained by the stability due to resonance effects of the ring system with the substituent in the *p*-position (e.g. *p*-NO₂ in *p*-NP) [12].

The increased positive charge on the oxygen atom (of the OH group) in *p*-NP facilitates proton release and consequently eases its oxidation with iodine in the first step of the reaction (fast step) to give, e.g. *p*-nitrophenoxonium ion, NP⁺. Resonance increases the stability of the phenoxonium ion against iodination (electrophilic substitution) in the second, slow, rate-determining step. The hydrogen bonding in *o*-BP decreases the rate of oxidation of *o*-BP in the first, slow, rate-determining step of the reaction and iodination of the *o*-BP⁺ in which there is no resonance effect is the fast step. NH₂ in *m*-AP deactivates the ring against both oxidation and iodination, which is confirmed by the fact that the rate of reaction of *p*-AP with iodine, (despite the possible resonance) is faster than *m*-AP with iodine (cf. Table 2). Comparing the rate constants of the reactions of the various phenol derivatives with iodine gives $K_{p\text{-BP}}/K_{p\text{-NP}} = 1.99 \times 10^4$. This is attributed to the high resonance stability of *p*-NP⁺ (due to NO₂) compared with that of

TABLE 2

Comparison of the rate constants of the redox reactions between iodine and phenol derivatives with that of phenol ($K_0 = 6.854 \times 10^3$ at 295 K)

Phenol derivative	K/K_0^a
<i>o</i> -BP	472.7
<i>p</i> -BP	11.628
<i>p</i> -NP	5.82×10^{-4}
<i>p</i> -AP	15.61
<i>m</i> -AP	0.026

^a K_0 calculated by computer plot of $\log_{10} K$ vs. σ_p . K values obtained from kinetic calculations (refs. 3, 6 and 7).

TABLE 3

Activation parameters for redox reactions of iodine and phenol derivatives at different temperatures T

Phenol derivative	T (K)	ΔH^* (kcal mol ⁻¹)	ΔS^* (J K ⁻¹ mol ⁻¹)	E_a (kcal mol ⁻¹)	K (l ³ mol ⁻³ s ⁻¹)
<i>o</i> -BP	301–333	55.44–59.8	+680 to +622	57.62	(3.24–33.35) × 10 ⁶
<i>p</i> -BP	295–323	7.42–7.44	–65.6 to –66.46	7.35	(7.97–23.46) × 10 ⁴
<i>p</i> -NP	296–323	12.62–12.75	–45 to –48.2	22.85	3.99–19.69
<i>p</i> -AP	290–325	26.8–26.3	+299 to +236	26.18	(1.07–331.9) × 10 ⁵ (l mol ⁻¹ s ⁻¹)
<i>m</i> -AP	296–325	6.55–6.9	–28.54 to –29.46	6.78	179.4–259.6

p-BP⁺ (due to Br). $K_{o\text{-BP}}/K_{p\text{-BP}} = 142.12$ and $K_{p\text{-AP}}/K_{p\text{-BP}} = 141.47$. These are of the same order of magnitude. This means that both *o*-BP and *p*-AP react with iodine 142 times faster than *p*-BP. $K_{o\text{-BP}}/K_{m\text{-AP}} = 1.28 \times 10^5$ and $K_{p\text{-AP}}/K_{m\text{-AP}} = 1.28 \times 10^5$. These are of the same order of magnitude. This means that both *o*-BP and *p*-AP react with iodine 1.28×10^5 times faster than *m*-AP. The ratio $K_{p\text{-AP}}/K_{m\text{-AP}}$ indicates that NH₂ in the *p*-position, despite the possible resonance effect, reacts with I₂ $\approx 10^5$ times faster than NH₂ in the *m*-position. This is confirmed by K/K_0 values of 0.026 for *m*-AP and 15.61 for *p*-AP. The fast reactions of *p*-AP and *o*-AP with iodine lead to the formation of polymeric redox products, whereas with *m*-AP only a dimer is formed. This has been investigated in detail by Zayed [3].

The high values of the activation parameters (Table 3) for the redox reactions between iodine and *o*-BP or *p*-AP indicate the high reactivity of these derivatives towards iodine. This result is in good agreement with the high rate constants obtained for the reactions of *o*-BP and *p*-AP with iodine in comparison with those of other derivatives. The low values of the activation parameters of the other redox reactions confirm the slowness (low rate constants) of these reactions.

The temperature dependence of the rates of these redox reactions is shown in detail by the graphical representation of the data in Fig. 1. The curves show peaks at the temperatures 323, 303 and 313 K for *o*-BP, *p*-BP and *m*-AP (Fig. 1, curves 1, 4), after which there is an abrupt decrease in the rate constant with increasing temperature. These peaks may be attributed to the formation of highly active intermediates or free radicals which are abruptly changed into products. In the case of *p*-BP there is a slow decrease in the rate constant with temperature after the peak (Fig. 1, curve 2) and, finally, an increase. This final increase may be attributed to other possible side reactions. For *p*-NP and *p*-AP, K values increase slowly with increasing temperature in the range 290–315 K. This means that in this temperature range the reaction of I₂ with *p*-NP and *p*-AP is affected only slightly by temperature. This is due to the stability of the phenolic ring (by resonance

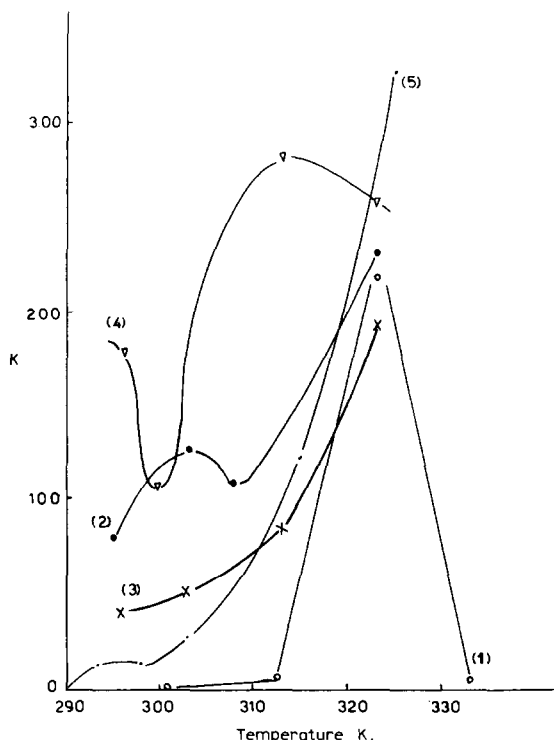


Fig. 1. Dependence of the rate constants of the redox reactions between I_2 and phenols on temperature: (1) K of *o*-BP $\times 10^7$; (2) K of *p*-BP $\times 10^2$; (3) K of *p*-NP; (4) K of *p*-AP; (5) K of *p*-AP $\times 10^5$.

with NO_2 and NH_2 groups) in the rate-determining step [3,12]. This step leads to the formation of active free radicals which react quickly with iodine to give iodinated free radicals or intermediates at temperatures > 315 K, and, finally, monomers, dimers or polymers are formed [7]. This is confirmed by a pronounced increase in K with increase in temperature (Fig. 1, curves 3,5)

The formation of intermediates and active free radicals can also be confirmed by further study of reactions of I_2 with *p*-BP (Fig. 2, curves 1, 2) and *p*-NP (Fig. 2, curves 3, 4).

At a phenol derivative concentration of 10^{-2} M and an I_2 concentration of 0.02 M maxima are present (Fig. 2, curves 1, 3) which may indicate the formation of activated states. These maxima are followed by minima which may also indicate the formation of intermediates. These activated states and/or intermediates start to decompose to give products as indicated by the re-increase of the rate of reaction with increase in the concentration of phenol derivatives.

On studying the reactions of *p*-BP or *p*-NP with I_2 at different molarities of NaOH (Fig. 2, curves 2, 4), the rate of reaction between *p*-BP and I_2

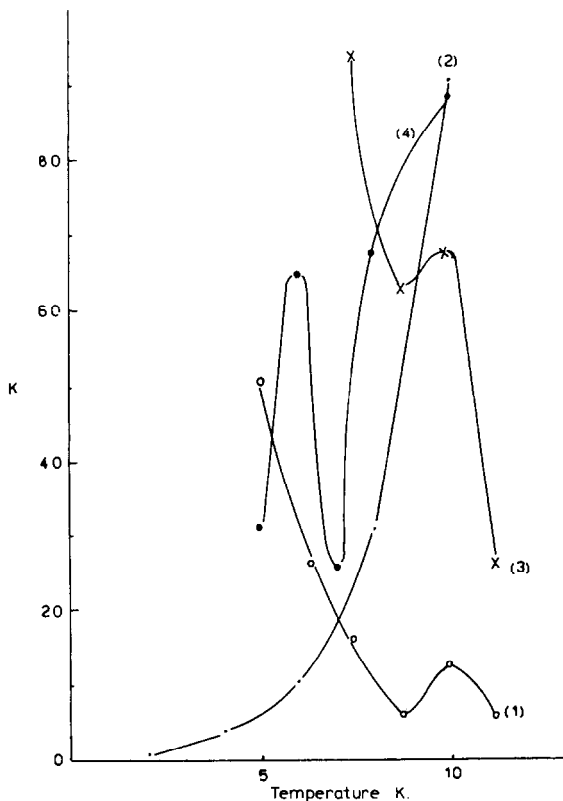


Fig. 2. Dependence of the rate constants of the redox reactions between I_2 and phenol derivatives on phenol concentration (curves 1, 3) and on NaOH concentration (curves 2, 4). (1) K of p -BP $\times 10$; (2) K of p -BP $\times 10^{-4}$; (3) K of p -NP; (4) K of m -NP $\times 10^{-2}$.

increases with an increase in the concentration of NaOH and there is no formation of activated states. In the case of p -NP (Fig. 2) formation of activated states and intermediates is possible, as confirmed by the appearance of a maximum and a minimum. This difference in the behaviours of p -NP and p -BP may be due to the resonance stability in p -NP as a result of the NO_2 group in the p -position.

Correlation between thermal analysis of redox products and rates of redox reactions

The TGA data of some redox products (from the reaction of iodine with phenol derivatives (A–D)) are shown in Table 4 and the DTA data are shown in Fig. 3. The TGA data show that fragmentation of the obtained polymeric redox products of aminophenols starts at low temperatures in the range 66–190°C where loss of N_2 and NH_3 molecules occurs. This may be attributed to the lower stability of the dimer obtained by oxidation of m -AP

TABLE 4

Mass loss of redox products (A-D)

Products ^a	Temperature range (°C)	Wt. loss (%)		Decomposition
		Found	Calculations	
A	220–296	17.2	16.62	2H ₂ O + CO
B	210–293	12.2	11.94	H ₂ O + CO
C	66–180	6.0	5.88	N ₂ + NH ₃
	180–210	4.0	4.0	CO
	237–320	4.0	3.66	CO
D	160–190	4.0	4.44	$\frac{1}{2}$ N ₂ + NH ₃
	196–260	8.0	8.33	2CO

^a A: *o*-BP product, C₆H₄I₂O·2H₂O; B: *p*-BP product, C₆H₄I₂O·H₂O; C: *p*-AP product, C₂₄H₂₁I₂N₃O₂; D: *m*-AP product, C₁₂H₈I₄N₂O₂.

and of the polymer obtained by oxidation of *p*-AP [3]. The instability of these dimers or polymers towards thermal treatment may be attributed to the presence between the rings of the dimers or polymers, of many weak bonds containing nitrogen. The formation of these polymeric products from the interaction of free radicals or intermediates is an indication of the high

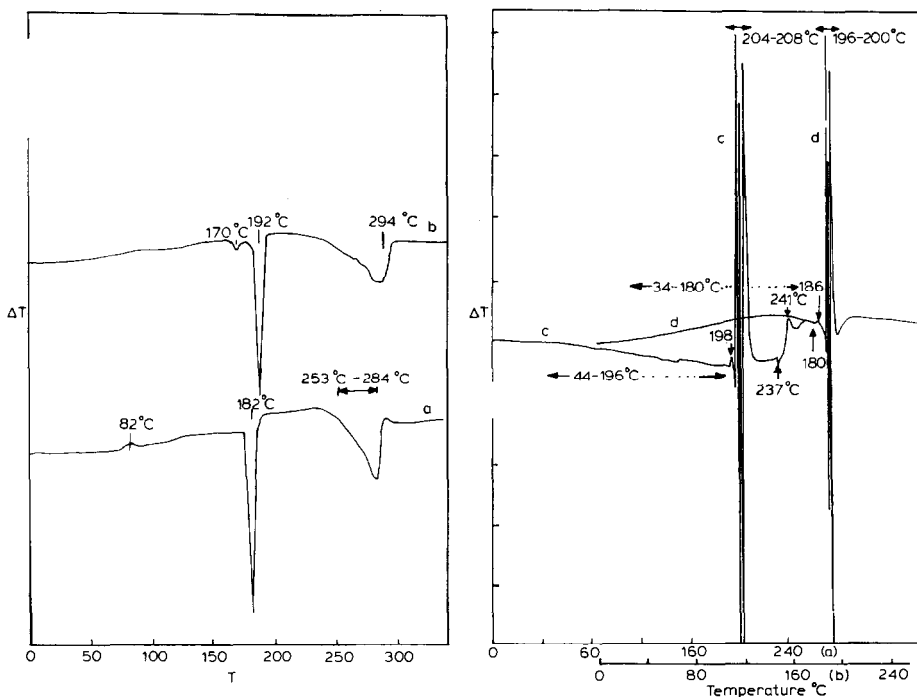


Fig. 3. DTA of the redox products from the reaction of phenol derivatives with iodine: (a) *o*-BP; (b) *p*-BP; (c) *p*-AP; (d) *m*-AP.

values of the rate constants of the reactions leading to these products (*p*-AP, $K = (1.07-331.9) \times 10^5$ and *m*-AP, $K = 179.4-259.6$). Conversely, fragmentation of the redox products of bromophenols (monomers) by a change in temperature starts at a higher temperature ($> 210^\circ\text{C}$). This may be attributed to the electron withdrawing ability of the halogen atoms (their electronegativity) which stabilizes the ring systems in these monomers so that fragmentations do not occur so easily. The stability of these products confirms the high values of the rate constants of the reactions which produce them (*o*-BP, $K = (3.24-33.35) \times 10^6$ and *p*-BP, $K = (7.97-23.46) \times 10^4$).

The greater stability towards thermal treatment of the redox products of BPs compared with those of APs is in good agreement with the abrupt decrease in the rate of formation of the products of BPs with an increase in temperature above 320 K (Fig. 1). The opposite occurs in the case of APs in which K increases with increasing temperature due to dimerization or polymerization of active free radicals or intermediates to form less stable products.

DTA of the BPs and APs are shown in Fig. 3. The heat capacity at any point on the DTA curves is proportional to the displacement from the base line [13]. Figs. 3a,b show an increase in heat capacity of the redox products of BPs with an increase in temperature up to 170°C . A broad endotherm in the temperature range $250-294^\circ\text{C}$ indicates a slow change in the heat capacity of the redox products with an increase in temperature as a result of the stability of the ring systems, due to halogen electronegativity (withdrawing ability). This confirms the conclusion drawn from TGA and the correlation between temperature and rate of reaction.

The DTA curves for aminophenol redox products (Fig. 3, curves c and d) show the decrease in heat capacity of *p*-AP redox products with increase in temperature up to 180°C and of *m*-AP up to 193°C . The narrow exotherms obtained in the temperature range $196-208^\circ\text{C}$ indicate the vigorous decomposition of these unstable compounds and the possibility of chemical reactions following this decomposition. Thus the redox products of APs and the reactions producing them differ greatly from those of BPs.

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