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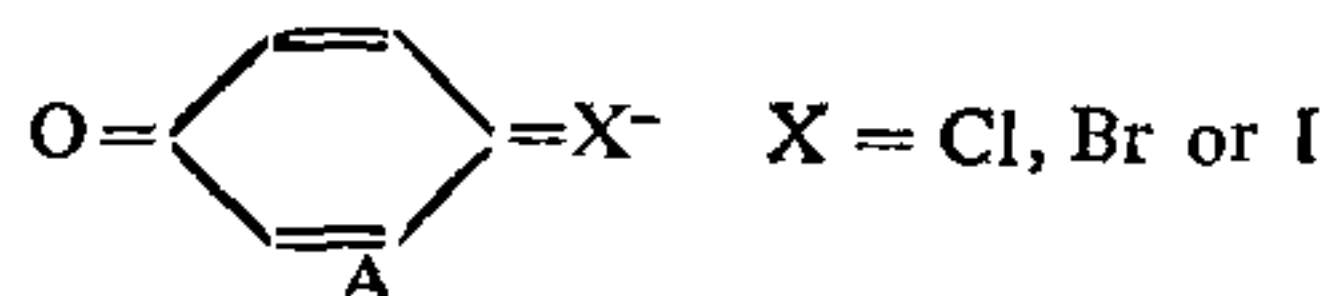
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ON THE MECHANISM OF THE ELBS PEROXYDISULPHATE OXIDATION

The kinetics of the Elbs oxidation of phenols by peroxydisulphate in alkaline medium has been investigated by Behrman^{1,2} and it has been concluded² that it is difficult to decide whether the rate limiting attack by

the peroxydisulphate ion on the phenoxide is at the oxygen or carbon atom. Behrman also concluded that the evidence from the Hammet plots² is not of great value in distinguishing the above two possible electrophilic attacks. We wish to report here the possible attack by a careful analysis of the kinetic data.

In the case of *p*-halogenophenols, the rate of oxidation of *p*-fluorophenol is almost twice than that observed for phenol and the rates of oxidation of *p*-bromo- and *p*-iodophenols are lower. *p*-Chlorophenol has the same rate constant as that of phenol (Table I). The observed rate constants cannot be explained on the basis of +M effect of the halogen atoms though this effect is in the order *p*-F > *p*-Cl > *p*-Br > *p*-I. If this effect is important, then the rate constants of all the *p*-halogenophenols should be higher than phenol. A clue as to the possible site of attack as well as an explanation for the observed reactivities may be obtained if we take into account the possible *d*-orbital resonance in the case of *p*-chloro-, *p*-bromo and *p*-iodophenols. It has been well established by Baliah and co-workers³⁻⁵ that chlorine, bromine and iodine can expand their valence shells by the utilization of their vacant *d*-orbitals. Such a *d*-orbital resonance becomes significant when electron-donating groups are present para to the halogen atom (Cl, Br, or I). In the Elbs oxidation, phenoxide ion is present and due to the *d*-orbital participation *p*-bromo- and *p*-iodophenoxides receive a significant contribution from structure A, which will reduce the



electron density at oxygen. In *p*-fluorophenoxide such a *dπ*-bonding is not possible and due to the +M

TABLE I
The effect of substituents on the rate of oxidation of phenol^a

Phenol	$k_2, 1/\text{mol}\cdot\text{min}$	Phenol	$k_2, 1/\text{mol}\cdot\text{min}$
Phenol	1.16 ± 0.00	<i>m</i> -Fluorophenol	0.752 ± 0.003
<i>p</i> -Fluorophenol	2.42 ± 0.01	<i>m</i> -Chlorophenol	0.350 ± 0.004
<i>p</i> -Chlorophenol	1.17 ± 0.04	<i>m</i> -Bromophenol	0.383
<i>p</i> -Bromophenol	0.970 ± 0.04	<i>m</i> -Iodophenol	0.398
<i>p</i> -Iodophenol	1.05 ± 0.00	<i>m</i> -Methoxyphenol	2.55 ± 0.1
<i>p</i> -Methoxyphenol	20.6 ± 1.0	<i>m</i> -Methylphenol	1.44 ± 0.06
<i>p</i> -Methylphenol	5.62 ± 0.05	<i>m</i> -Cyanophenol	0.225 ± 0.003
<i>p</i> -Cyanophenol	0.140	<i>m</i> -Carboxyphenol	0.327 ± 0.009
<i>p</i> -Carboxyphenol	0.155 ± 0.005	2, 6-di- <i>t</i> -Butylphenol*	31.0 ± 0.5

^a General conditions; Phenol-peroxydisulphate ratio = 10; 1.7 M KOH Temperature 30°.

* In the case of 2, 6 di-*t*-butylphenol, 0.85 M KOH, 40% dioxane under nitrogen. All the values are taken from reference 2.

effect of the fluorine atom the electron density at oxygen will increase during the course of the reaction. The different reactivities of the *p*-halogenophenols now become understandable if the site of attack is oxygen and not the ortho-carbon atom. The rate constants for *p*-chloro-, *p*-bromo- and *p*-iodophenols are either equal to or lower than phenol since the *d*-orbital resonance reduces the electron density at oxygen. The singular behaviour of *p*-fluorophenol, that is its higher rate constant, results due to the +M effect of fluorine. If the above explanation is correct one should expect all the *m*-halogenophenols to behave in a similar manner since contributions from structure A is not possible. In fact the experimental results indicate that all the four *m*-halogenophenols have lower rate constants than phenol (see Table I).

If the attack is at oxygen one should expect that when an electron-releasing group is present in a para-substituted phenol then it will have a higher rate constant than phenol and the rate constant will be lower if the substituent is electron-withdrawing. The results in Table I substantiate this prediction. *p*-Methoxyphenol is oxidised about 20 times faster than phenol and *p*-cyanophenol about 10 times lower than phenol. It appears, therefore, that in the absence of steric effects the electrophilic attack is at oxygen.

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1, 3-ADDITION REACTIONS OF BENZONITRILE OXIDES TO BENZIMIDAZOLES: SYNTHESIS OF 1-[(HYDROXYIMINO)ARYLMETHYL]-1H-BENZIMIDAZOLES AND THEIR 2-METHYL ANALOGS

PRIMARY and secondary amines undergo 1, 3-addition reactions with benzonitrile oxides to give the corresponding benzamide oximes^{1,2}. Such reactions have not been investigated so far using heterocyclic bases containing N-H function. The 1, 3-addition of benzonitrile oxides with benzimidazoles have now been carried out to know the course of the reaction and the nature of the products formed.

When benzhydroxamic acid chloride³ (0.01 mole) was allowed to react with benzimidazole (0.02 mole) in methanol at room temperature, a colourless crystalline compound, m.p. 181° C (M+237) separated out from the reaction mixture. Its i.r. spectrum (KBr) showed an intense, broad absorption at 3100–2500 cm⁻¹ (oxime O-H) and another absorption of medium intensity at 1600 cm⁻¹ (C=N). On the basis of this evidence and analytical data, the compound has been assigned the 1-[(hydroxyimino) phenyl methyl]-1H-benzimidazole (I, R = H, Ar = Ph) structure. Similarly, 2-methyl-benzimidazole also reacted with benzhydroxamic acid chloride to give I (R = CH₃, Ar = Ph). This reaction has been extended to differently substituted benzhydroxamic acid chlorides and the products obtained have been characterised as I (Table I) by analogy. That the reaction is proceeding through the intermediacy of benzonitrile oxide is confirmed by reacting the latter, freshly generated from benzhydroxamic acid chloride and triethylamine, with benzimidazole (R = H), when I (R = H, Ar = Ph) is obtained in almost quantitative yield.

TABLE I

1-[(Hydroxyimino) arylmethyl]-1H-benzimidazoles, I¹

Sl. No.	Ar	R=H		R=CH ₃	
		Yield (%)	M.P. ² (°C)	yield (%)	M.P. ² (°C)
1.	Phenyl	75	181	73	218
2.	4'-methylphenyl	87	201	80	210
3.	2'-chlorophenyl	70	196	88	221
4.	4'-chlorophenyl	72	199	72	233
5.	3'-nitrophenyl	96	221	70	231
6.	4'-nitrophenyl	75	227	72	247
7.	4'-methoxyphenyl	78	210
8.	3', 5'-dichloro-4'-methoxyphenyl	75	221

- All the compounds are recrystallised from methanol and gave satisfactory analytical values for carbon, hydrogen and nitrogen.
- Melting points are uncorrected.