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The Reactivities of .OH, $.O^-$, and HO_2. Radicals and Oxygen Atoms in Aqueous Solutions of Aromatic Compounds

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This review considers the results of studies on the reactivities of hydroxy- and perhydroxy-radicals and oxygen atoms with respect to aromatic derivatives of benzene, pyridine, and furan. The rate constants for the reactions investigated have been compared and a relation between them and the structure of compounds oxidised has been demonstrated.
The bibliography includes 60 references.

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I. INTRODUCTION

The ·OH, $\cdot O^-$ and $HO_2\cdot$ radicals and atomic oxygen are formed in many oxidation-reduction processes used in the manufacture of important organic products, biochemical oxidation, and purification of sewage. Owing to their high reactivity, these radicals react rapidly with substances in solution and with one another and therefore their concentration in solutions is very low, which makes it difficult to investigate reactions involving them. Competitive methods, which make it possible to determine by comparatively simple procedures the relative rate constants for these reactions, and also pulse radiolytic methods, whereby the absolute rates may be determined, have been extensively applied to the study of processes of this kind.

The review presents the data obtained in recent years on the kinetics of reactions of ·OH and $\cdot O^-$ radicals with aromatic compounds; this makes it possible to revise many generally accepted hypotheses concerning the mechanisms of these reactions and the properties of the radicals themselves. The results of kinetic studies on the reactions of $HO_2\cdot$ radicals and atomic oxygen in the $O(^3P)$ state, which are as yet very few, have been examined.

II. REACTIONS OF ·OH RADICALS

Catalytic and photochemical decomposition of hydrogen peroxide or the radiolysis of water are used to generate ·OH radicals in aqueous solutions.

It was established in recent years that the active oxidising species formed in the decomposition of H_2O_2 by the above procedures and in the radiolysis of water are identical. This conclusion is based on a comparison of the relative rates of oxidation of the same substrates (benzene and many of its derivatives, methyl and ethyl alcohols, and certain other compounds) in the radiolysis of water and in the catalytic or photochemical decomposition of hydrogen peroxide in the presence of the same ·OH radical traps. *NN*-Dimethyl-*p*-nitrosoaniline (DMNA),[1,2] thymine[3], or H_2O_2 (Armstrong[4]) were used as the ·OH radical traps. The absolute rate constants listed in Table 1 were calculated from the ratios found.

Table 1 shows that the rate constants for the oxidation of substrates by products of the photochemical and catalytic decomposition of hydrogen peroxide are very close to the values obtained for the radiation-induced oxidation. This is consistent with the formation of free hydroxy-radicals in the photochemical and catalytic decomposition of hydrogen peroxide, since the generation of ·OH radicals in the radiolysis of water is not in doubt[6]. In $H_2O_2 + M^{+n}$ systems in the absence of organic additives, the hydroxy-radicals formed are captured by metal ions or their complexes with H_2O_2, which leads to the appearance of new paramagnetic complexes as shown by ESR spectroscopic data[7-10]. The results presented extend the scope of studies on the reactions of ·OH radicals.

Table 1. Comparison of the rate constants for the oxidation of various substrates by products of the photochemical or catalytic decomposition of H_2O_2 and the radiolysis of water.

Substrate	$10^{-9}k$, litre mole^{-1} s^{-1}			
	$H_2O_2 + h\nu$	$H_2O_2 + Fe^{2+}$	$H_2O_2 + Ti^{3+}$	$H_2O \xrightarrow{\gamma^{60}Co}$
Benzene	4.2[5]	4.1[5]	—	4.3[3], 3.8[1]
Benzyl alcohol	2.8[5]	—	—	4.1[1]
Benzoate ion	3.8[5]	—	—	4.1[1]
Anisole	5.0[5]	—	—	4.9[1]
Phenol	8.3[5]			7.5[1]
Methanol	—	0.8[5]; 0.89[4]	0.77[4]	0.75[3] 0.69[4]
Ethanol	—	1.1[5]; 1.7[4]	1.5[4]	1.6[3]
Formic acid	—	0.12[4]	0.12[4]	0.14[4]
Oxalic acid	—	0.016[4]	0.015[4]	0.02[4]

A number of studies were made recently on the interaction of these radicals with various organic acceptors[1-3,11-14]. The kinetics of these reactions with benzene and pyridine derivatives were investigated in detail by Shevchuk et al.[1] and with benzene also by Neta and coworkers[14,15]. Shevchuk et al.[1] and Neta and coworkers[14] employed the method of competitive kinetics using DMNA as the hydroxy-radical acceptor[2]. The systems

were irradiated with cobalt-60 γ-rays. The concentrations of DMNA before and after irradiation were determined spectrophotometrically.

For the competing reactions,

$$\text{Ac} + {}^{\cdot}\text{OH} \xrightarrow{k_1} \text{product},$$

$$\text{RH} + {}^{\cdot}\text{OH} \xrightarrow{k_2} \text{product},$$

it was shown that

$$\frac{1}{G_{(-\text{Ac})}} = \frac{1}{G_{\text{OH}}}\left[1 + \frac{k_2[\text{RH}]}{k_1[\text{Ac}]}\right].$$

where Ac = DMNA, RH = hydrocarbon and $G_{(\text{Ac})}$ and $G_{(\text{OH})}$ are the radiation-chemical yields for the disappearance of the acceptor and the formation of the ·OH radicals respectively.

This equation makes it possible to find the ratio k_2/k_1. Table 2 lists the relative rate constants for substituted benzenes and pyridines obtained by Shevchuk et al.[1] using this method. The logarithms of the $k_{\text{RH}}/k_{\text{benzene}}$ ratios are correlated with Hammett's σ constants. Shevchuk et al.[1] found a satisfactory correlation for substituted benzenes with $\rho = -0.31$. A similar value $\rho = -0.41$ was found by Neta and coworkers[14] using the same acceptor. Dorfman and Neta[15] determined the absolute rate constants for the hydroxylation of substituted benzenes by pulse radiolysis, from the formation curves for hydroxycyclohexadienyl radicals. The correlation between the logarithms of $k_{\text{RH}}/k_{\text{benzene}}$ and Hammett's σ constants yielded $\rho = -0.5$, which is fairly close to the values of ρ obtained by the method of competitive kinetics.

Table 2. Relative rate constants for the reactions of substituted benzenes, furans, and pyridines with hydroxy-radicals.

Substrate		$k_{\text{substrate}}/k_{\text{acceptor}}$
Substituted benzenes		
NHC_6H_5		1.04±0.04
OH (O^-)		0.68±0.02
OCH_3		0.45±0.04
I		0.40±0.02
CH_2OH		0.37±0.02
COO^-		0.37±0.01
Cl		0.36±0.05
H		0.35±0.01
CHO		0.35±0.03
NO_2		0.25±0.01
Substitute pyridines		
COO^-	α	0.13±0.01
Cl	α	0.14±0.01
H	α	0.16±0.01
Br	α	0.19±0.01
CH_3	α	0.20±0.01
O^-	α	0.38±0.01
NH_2	α	0.67±0.12
CN	β	0.06±0.01
$CONH_2$	β	0.08±0.01
Br	β	0.09±0.01
COO^-	β	0.18±0.02
CH_3	β	0.19±0.01
O^-	β	0.43±0.02
$CONH_2$	γ	0.12±0.01
COO^-	γ	0.21±0.01
O^-	γ	0.23±0.01
Cl	γ	0.25±0.01
NH_2	γ	0.40±0.01
2,6-CH_3		0.24±0.01
2,4-CH_3		0.25±0.01
α-Substituted furans		
CH_2OH		1.19±0.10
H		1.16±0.05
COO^-		0.92±0.16
CHO		0.62±0.04

Mention must be made of the discrepancies between the absolute rate constants obtained by pulse radiolysis and the values calculated from the relative constants obtained by the method of competitive kinetics. The former are as a rule higher by a factor of 2—3. The reason for the discrepancy is so far obscure. It may be related to the use of defective techniques in the first or second case[16] and possibly in both. However, comparison of the coefficients for the linear correlations of the rate constants obtained by different methods for series of identical derivatives shows a fairly satisfactory agreement between them.

The negative sign of ρ shows that the hydroxylation reactions are electrophilic; this is in turn consistent with data on the relative amounts of isomers formed[17] and demonstrates the electrophilic properties of the ·OH radicals. The low value of ρ, lower than in the usual electrophilic substitution reaction, suggests a high reactivity of the hydroxy-radicals as a result of which they are less sensitive to the polar influences of the substituents. Table 2 shows that the rate constants for the reactions of substituted pyridines are several times smaller than for benzene, in agreement with the lower reactivity of the pyridine ring in relation to attack by the electrophilic hydroxy-radicals. Accordingly, the absolute value of ρ is higher than for the series of benzenes and reaches 0.73. However, these reactions are also accelerated by electron-donating substituents and are retarded by electron-accepting substituents. A satisfactory correlation has been found only for β-substituted pyridines ($\rho = -0.73$).

The results obtained for the effect of substituents in the α-position are probably distorted by the adjacent electronegative nitrogen atom. The rate constants for the reactions of pyridine derivatives with electron-donating substituents in the α-position are higher than for the γ-substituted pyridines (Table 2). For compounds with electron-accepting substituents, the opposite relation between the rate constants for the oxidation of α- and γ-derivatives is observed. This may be because, as shown by Cercek and Ebert[18], hydroxy-radicals add not only to the ring but also partly to the pyridine nitrogen atom. In this process, the inductive effect of α-substituents at the nitrogen atom leads to the observed behaviour of the overall reaction rate constants and is of primary importance.

In contrast to the pyridine ring, furan derivatives readily undergo electrophilic substitution reactions and do not exhibit a tendency towards reactions with nucleophilic species. The relative rate constants for the reactions of furan and some of its derivatives[19] have been obtained by a method of competitive kinetics analogous to that employed by Shevchuk et al.[1] using the DMNA acceptor and were found to be higher by a factor of 2—3 than the corresponding constants for benzene derivatives and be a factor of 7 than for substituted pyridines (Table 2). This demonstrates an enhanced sensitivity of furan derivatives to attack by ·OH radicals. A satisfactory correlation has been found between $k_{\text{RH}}/k_{\text{furan}}$ and Hammett's σ constants with $\rho = -0.81$. The absolute value of ρ is relatively small and does not exceed those encountered in homolytic reactions ($1.5 > \rho > 0$). However, it is higher than the values found for reactions of substituted benzenes and pyridines, which may indicate a greater ease of transmission of the electronic effects of substituents in the furan series[20].

The high reactivity of hydroxy-radicals is consistent with the low activation energies for their reactions. The relative rate constants for reactions of ·OH radicals with various organic substrates have been determined[21] in the temperature range 20—70°C. Thymine was employed as the hydroxy-radical acceptor[3]. The observed activation

energies for reactions involving the abstraction of a hydrogen atom by hydroxy-radicals did not exceed 5 kcal mole^{-1} and those for addition reactions did not exceed 2 kcal mole^{-1}. The variations in activation energy in the benzene series relative to DMNA have been determined[19]. They are of the order of 0.08—0.56 kcal mole^{-1} and do not exceed the experimental error. The activation energies for β-substituted pyridines were found to be about ten times larger: 1.7 ± 0.2 kcal mole^{-1} for pyridine, 1.6 ± 0.3 kcal mole^{-1} for β-nicotinic acid, 2.1 ± 0.3 kcal mole^{-1} for β-nicotinamide, and 1.2 ± 0.1 kcal mole^{-1} for β-hydroxypyridine. It is evident from the above results that the activation energies for pyridine derivatives increase with the electron-accepting properties of the substituents and decrease as their electron-donating properties become more pronounced.

The data for the reactions of ·OH radicals with *ortho*-, *meta*-, and *para*-substituted phenols[22] are presented in Table 3. In order to determine the relative rate constants the DMNA acceptor was employed at pH 9 and isopropyl alcohol at higher pH values[23]. The logarithms of the relative rate constants for *para*-substituted phenols at pH 9 are satisfactorily correlated with Hammett's σ constants ($\rho = -0.32$). This value of ρ hardly differs from that obtained for the oxidation of benzene derivatives, which indicates a similarity of the mechanisms of these reactions. The correlation between the rate constants for *meta*-substituted phenols yielded $\rho = -0.18$. For *ortho*-substituted derivatives, there was virtually no correlation at pH 9 but it was observed at pH 13 with $\rho = -0.61$. This finding may be attributed to the influence of the dissociation of phenols at pH 13 on the *ortho*-effect.

Comparison of the relative rate constants for the reactions of substituted phenols with the analogous constants for the corresponding benzene derivatives shows that the former are higher by a factor of 2—3 (see the data in Tables 2 and 3). This is consistent with the powerful activating effect of the hydroxy-group in reactions with ·OH radicals.

Table 3. Relative rate constants for the reactions of substituted phenols with ·OH radicals at pH 9.

	Substituent	$k_{substrate}/k_{acceptor}$
para	$C(CH_3)_3$	1.49±0.26
	OCH_3	1.15±0.23
	CH_3	1.04±0.09
	CHO	0.82±0.2
	COO^-	0.70±0.06
	H	0.68±0.02
	NO_2	0.61±0.08
	OH	0.44±0.12
meta	OH	0.97±0.12
	Cl	0.58±0.05
	NO_2	0.57±0.05
ortho	CH_3	0.90±0.15
	OH	0.89±0.14
	NO_2	0.74±0.06
	CHO	0.69±0.16
	COO^-	0.69±0.09
	Cl	0.66±0.12

The introduction of a second hydroxy-group into the benzene ring activates the latter still further for reaction with ·OH radicals, but the introduction of a third ·OH group deactivates it, as can be seen from a comparison of the following absolute rate constants ($10^{-9}k$, litre mole^{-1} s^{-1}): 3.8 for benzene[1], 7.5 for phenol[1], 10.7 for 1,3-dihydroxybenzene, and 5.7 for 1,3,5-trihydroxybenzene[22].

This effect may be attributed to a change in the hydroxylation mechanism, for example, the site of attack by ·OH radicals changing from the benzene ring to the hydrogen atom of the phenolic hydroxyl.

The relative rate constants (with DMNA as the acceptor) for the reactions of ·OH radicals with carbohydrates, polysaccharides, and certain aromatic compounds have been determined[24,25]. The authors believe that the protective properties of radioprotectors (inositol, propyl gallate, trihydroxypyridine derivatives) can be accounted for by the high rate of their interaction with ·OH radicals.

III. REACTIONS OF ·O$^-$ RADICAL-IONS

The ·OH radicals are known to dissociate at high pH according to the mechanism

$$\dot{O}H + OH^- \underset{k_2}{\overset{k_1}{\rightleftarrows}} \dot{O}^- + H_2O \ ;$$

the pK_a for the dissociation is 11.8 ± 0.2 (Rabani and Matheson)[11] and the rate of the forward reaction is a thousand times higher than that of the reverse reaction[26]:

$$k_1 = (1.2 \pm 0.3) \cdot 10^{10}\ M^{-1}\ s^{-1},$$
$$k_2 = (9.2 \pm 0.2) \cdot 10^{7}\ s^{-1},$$

The study of the kinetics of the hydroxylation of organic substances in alkaline media at increasing pH values yielded information about the relative reactivity of the ·OH radical and its conjugate base ·O$^-$. It was found for reactions with phenols[22] that the relative rates of hydroxylation decrease with increase of pH (Tables 4 and 5). The following changes in the relative rate constants for the reactions of ·OH radicals with phenols have been found: 0.68 ± 0.02 at pH 9, 0.46 ± 0.10 at pH 12, and 0.28 ± 0.04 at pH 13. The constants at pH 13 are more than a factor of 2 lower than those at pH 9 (Table 4).

Table 4. Comparison of the relative rate constants for *ortho*-substituted phenols at pH 9 and 13.

Substituent	$k_{phenol}/k_{acceptor}$(pH 9)	$k_{phenol}/k_{acceptor}$(pH 13)
$-COO^-$	0.69±0.09	0.32±0.05
—CHO	0.69±0.16	0.27±0.06
$-CH_3$	0.90±0.15	0.33±0.03
$-OCH_3$	1.18±0.15	0.46±0.09

This is not related to the dissociation of the *ortho*-substituted phenols themselves, since, firstly, the formation of phenoxide ions would accelerate the addition of ·OH radicals because phenoxide anions are more powerful electron donors than the undissociated phenols and, secondly, at pH 12 and 13 phenols are completely ionised, while the ·OH radical is hardly dissociated at pH 9, at pH 12 the degree of dissociation is 50%, and at pH 13 the dissociation is almost complete. Consequently the decrease of the rate constants can be accounted for only by a lower reactivity of the radical-ions ·O$^-$ radicals compared with ·OH radicals. The data obtained for phenols agree with the conclusion[23] (Table 5) that ·O$^-$ is

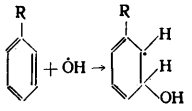
much less reactive in both addition and electron transfer reactions, while reactions involving the abstraction of a hydrogen atom take place with equal efficiency when either of the two species is involved.

Table 5. Comparison of the relative rate constants for the reaction of ·OH radicals in acid, neutral, and alkaline media[23].

Substrate	0.05 *M* H_2SO_4	pH 6.98	0.1 *M* NaOH	1.0 *M* NaOH	Substrate	0.05 *M* H_2SO_4	pH 6.98	0.1 *M* NaOH	1.0 *M* NaOH
$(CH_3)_2CHOH$	1.00	1.00	1.00	1.00	$(C_2H_5)_2O$	1.15	1.20	0.79	—
CH_3OH	0.29	0.36	0.39	0.47	I^-	6.9	8.0	1.82	1.70
CH_3CH_2OH	0.63	0.61	0.64	0.70	Br^-	1.97	1.95	0.03	—
$HCOO^-$	—	1.34	0.60	0.68	C_6H_6	2.2	2.3	0.05	—
HCOOH	0.06	—	—	—	C_6H_5OH	4.4	5.2	0.75	—

IV. THE MECHANISM OF HYDROXYLATION BY ·OH RADICALS

One may regard it as established that in the first stage hydroxy-radicals add to aromatic rings with the intermediate formation of hydroxycyclohexadienyl radicals[27-33] according to the mechanism



and do not abstract hydrogen from then with formation of phenyl radicals as suggested previously[34-38]. This is supported by the results of studies on the radiolysis of solutions of benzene in heavy water (D_2O) [29,30] and also by the direct observation of the spectra of hydroxycyclohexadienyl radicals in studies by pulse radiolysis[33] or by ESR in flow systems[32]. Hydroxy-radicals can also add initially to the substituent with a subsequent rearrangement involving a shift to the ring. It has been shown by pulse radiolysis[39] that ·OH radicals react with *p*-nitrophenol, adding to the nitro-group via the mechanism

$$\dot{O}H + OHC_6H_4NO_2 \rightarrow OHC_6H_4\dot{N}O_2 + H^+$$

with $k = (3.8 \pm 0.6) \times 10^9$ litre mole^{-1} s^{-1} and subsequent isomerisation of the resulting radical-ion into a hydroxycyclohexadienyl radical via the reaction

$$OH—C_6H_4\dot{N}O_2 + H^+ \rightarrow OH(OH)\dot{C}_6H_4NO_2 \quad ,$$

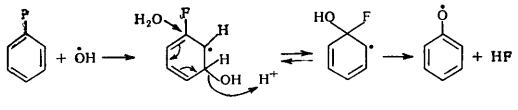
the pK_a of which is 14 ± 2 s^{-1}.

Hydroxy-radicals can also displace a ring substituent. For example, in the reaction between ·OH radicals and anisole, the methoxy-group is substituted with retention in the resulting phenol of the oxygen from anisole[40], in agreement with the following mechanism[41]:

$$C_6H_5OCH_3 + \dot{O}H \rightarrow C_6H_5\dot{O}CH_2 + H_2O \quad ,$$

$$C_6H_5\dot{O}CH_2 \xrightarrow{\dot{O}H} C_6H_5OCH_2OH \rightarrow C_6H_5OH + HCHO \quad .$$

However, such substitution also can occur with incorporation in the resulting phenolic hydroxyl of oxygen from water, for example via the acid fragmentation of the hydroxycyclohexadienyl radical formed[7] at low pH:



with subsequent conversion of the resulting phenoxy-radical into phenol containing oxygen from water.

A similar reaction can probably occur with benzene and many of its derivatives. For some of these, the incorporation of oxygen from water into the product of their oxidation by Fenton's reagent has been established[40,42]. The transfer of oxygen from water is not associated with a rapid exchange of hydroxy-radicals with water, as frequently suggested in the literature[43-45]. Indeed, calculation of the upper limit of the rate of exchange of hydroxy-radicals with water showed that it is slower by 3—4 powers of ten than the rate of reaction of these radicals with organic substances[46]: $0 \leq k < 7 \times 10^6$ litre mole^{-1} s^{-1}.

V. REACTIONS OF HO_2· RADICALS

The participation of HO_2· radicals in the hydroxylation of an aromatic ring has been postulated in a number of studies[47,48]. It has also been suggested that they do not possess electrophilic properties[47] and therefore yield different proportions of the isomeric products in the hydroxylation of the aromatic ring as compared with ·OH radicals and are less reactive than ·OH radicals towards aromatic compounds[49]. The reactivity of HO_2· radicals in aqueous solutions of aromatic compounds has been little investigated quantitatively. This is due to the difficulty of determining the rate constants for their reactions in the presence of the more reactive hydroxy-radicals, the mode of reaction of which is similar. There are only data for the oxidation of the sulphonates of indigo and certain other dyes, which have been obtained by the method of competing acceptors[50,51]. The relative rate constants for reactions of the dyes with HO_2· radicals generated by the γ-radiolysis of water were determined in such studies.

These reactions were carried out in the presence of oxygen in order to convert all the reducing species into HO_2· radicals; the pH was kept at 0.4 to avoid the dissociation of the HO_2· radicals ($pK = 4$):

$$H\dot{O}_2 \rightleftarrows H^+ + \dot{O}_2^-$$

and the reaction was carried out in the presence of added 2,5-dichlorohydroquinone which trapped quantitatively the ·OH radicals.

The rate constant for the reaction of HO_2· with the dye was calculated by considering the competition between the reactions

$$D + H\dot{O}_2 \xrightarrow{k_1} \text{colourless product} \quad ,$$

$$H\dot{O}_2 + H\dot{O}_2 \xrightarrow{k_2} H_2O_2 + O_2 \quad ,$$

where D is the dye, using the equation

$$k_1 = \frac{0.693}{D^0_{1/2}} \sqrt{\frac{2k_2 I}{\alpha G_{HO_2}}} \quad ,$$

where $k_2 = 2.2 \times 10^6$ litre mole^{-1} s^{-1},[52] I the dose rate, $G_{HO_2} = 3.6$ the radiation yield in the formation of HO_2· radicals,[53] $\alpha = 1.66 \times 10^{-23}$ mole ml mol.$^{-1}$ litre^{-1} a conversion factor, and $D^0_{1/2}$ the dose at which the concentration of the dye diminished by 50%.

Table 6 lists the rate constants obtained in this way. They are approximately a million times smaller than the rate constants for the reactions of ·OH radicals with aromatic compounds, which indicates a much lower reactivity of HO_2· radicals compared with hydroxy-radicals.

VI. REACTIONS OF ATOMIC OXYGEN

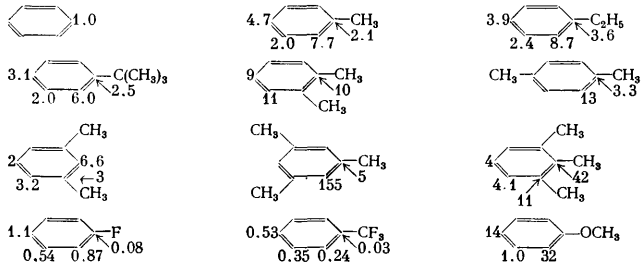
The hypothesis of the intermediate formation and involvement of atomic oxygen in the ground $O(^3P)$ state in chemical and radiation-chemical processes in aqueous solutions has already been put forward in the literature[47,54]. Certain studies have also been made on the reactivity of $O(^1D)$ atoms in solutions. These atoms were generated by the photolysis of ozone at 2537 Å.[55,56] However, since the reaction of $O(^1D)$ with water is very rapid, high concentrations of the corresponding traps are required.

Table 6. Rate constants for the reactions of $HO_2^{\cdot}$ radicals with indigo sulphonates.

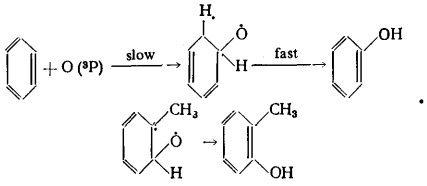
Dye	k_1, litre mole^{-1} s^{-1}
Indigo tetrasulphonate	$7.7 \cdot 10^2$
Indigo trisulphonate	$4.5 \cdot 10^3$
Indigo disulphonate	$8.5 \cdot 10^3$

The reactions of $O(^3P)$ oxygen in the ground state with aqueous solutions of aromatic compounds have been studied by the method of competing acceptors[57] developed by Amichai and Treinin[58]. $O(^3P)$ atoms were generated by the flash photolysis of BrO_3^- ions in the presence of molecular oxygen playing the role of the trap for $O(^3P)$. The partial rate factors for the formation of phenols in the reactions of $O(^3P)$ with substituted benzene were determined in the same study. The results are presented in Table 7.

Table 7. Partial rate factors for the formation of phenols in reactions of substituted benzenes with $O(^3P)$ at 30°C.



These data show that $O(^3P)$ atomic oxygen is electrophilic. The *ortho*-position is more reactive than the *para*-position, which is characteristic of radical reactions, for example those of ·OH radicals. A satisfactory correlation has been obtained ($r = 0.95$) with the logarithms of the partial rate factors for the *meta*- and *para*-positions and Hammett's σ^+ constant for $\rho = -1.15$. The negative sign of ρ indicates the electrophilic nature of $O(^3P)$, while the fairly high absolute value of ρ compared with the corresponding value for ·OH radicals is evidence of a greater selectivity of atomic oxygen compared with hydroxy-radicals. The following mechanism, analogous to that for hydroxylation by ·OH radicals, has been proposed for hydroxylation by atomic oxygen:



The low isotope effect found in the oxidation of an equimolar mixture of benzene and deuteriobenzene ($k_H/k_D = 1.14 \pm 0.04$) shows that the C—H bond is not dissociated in the rate-determining step of the reaction, in agreement with the proposed mechanism.

The absolute rate constant for the oxidation of benzene by atomic oxygen, determined by Grovenstein et al.[57], is $k_{25°} = 1.2 \times 10^7$ litre mole^{-1} s^{-1}.

Comparison of the reactivities of the radicals ·OH, $\cdot O^-$, and $HO_2^{\cdot}$ and the $O(^3P)$ oxygen atoms has shown that the hydroxy-radicals are the most reactive among them (Table 8). The reactivity of their dissociated form $\cdot O^-$ is somewhat lower (by a factor of 3—4). The oxygen atoms are less reactive than ·OH radicals approximately by a factor of 300 and the reactivity of the $HO_2^{\cdot}$ radicals is lower still—by 5—6 powers of ten.

In conclusion, we may mention that the rate constants for the reactions of hydroxy-radicals with organic compounds in aqueous solutions have been compiled by Metelitsa[48], Denisov[59], and Anbar and Neta[60].

Table 8. Comparison of the rate constants for the reactions of ·OH, $\cdot O^-$ and $HO_2^{\cdot}$ radicals and $O(^3P)$ oxygen atoms.

Species	k, litre mole^{-1} s^{-1} Compound oxidised		
	benzene	phenol	indigo disulphate
·OH	$3.8 \cdot 10^9$ [1]	$7.5 \cdot 10^9$ [1]	—
$\cdot O^-$	—	$2.1 \cdot 10^9$ [22]	—
$O(^3P)$	$1.2 \cdot 10^7$ [57]	—	—
$HO_2^{\cdot}$	—	—	$8.5 \cdot 10^3$ [51]

REFERENCES

1. L.G. Shevchuk, V.S. Zhikharev, and N.A. Vysotskaya, Zhur. Org. Khim., 5, 1655 (1969).
2. J. Kraljic and C.N. Trumbore, J. Amer. Chem. Soc., 87, 2547 (1965).
3. G. Scholes and R.L. Willson, Trans. Faraday Soc., 63, 2983 (1967).
4. W.A. Armstrong, Canad. J. Chem., 47, 3737 (1969).
5. L.G. Shevchuk and N.A. Vysotskaya, Dokl. Akad. Nauk SSSR, 191, 1099 (1970).
6. A.K. Pikaev, "Impul'snyi Radioliz Vody i Vodnykh Rastvorov" (Flash Radiolysis of Water and Aqueous Solutions), Izd. Nauka, Moscow, 1965.
7. C.R.E. Lefcoate and R.O.C. Norman, J. Chem. Soc. (B), 45 (1968).
8. J.S. Chiang, J. Croddock, et al., J. Phys. Chem., 70, 3509 (1966).
9. F. Sicilio, R.E. Florin, and L.A. Wall, J. Phys. Chem., 70, 47 (1966).

10. Takeshi Shiga, J. Phys. Chem., 69, 3805 (1965).
11. J. Rabani and M. S. Matheson, J. Amer. Chem. Soc., 86, 3175 (1964).
12. L. M. Dorfman, I. A. Taub, and D. A. Harter, J. Chem. Phys., 41, 2954 (1964).
13. J. R. Lindsay and R. O. Norman, J. Chem. Soc., 2897 (1963).
14. M. Anbar, D. Meyerstein, and P. Neta, J. Phys. Chem., 70, 2660 (1966).
15. P. Neta and L. M. Dorfman, "Radiation Chemistry 1", Advances in Chemistry Series, 1968, Vol. 81, p. 222.
16. F. S. Dainton and B. Wiseal, Trans. Faraday Soc., 64, 694 (1968).
17. R. O. C. Norman and I. K. Radda, Proc. Chem. Soc., 138 (1962).
18. B. Cercek and M. Ebert, Trans. Faraday Soc., 63, 1687 (1967).
19. O. S. Savel'eva, L. G. Shevchuk, and M. A. Vysotskaya, Zhur. Org. Khim., 9, 737 (1973).
20. Yu. A. Zhdanov and E. I. Minkin, "Korrelyatsionnyi Analiz v Organicheskoi Khimii" (Correlation Analysis in Organic Chemistry), Rostov, 1966, p. 257.
21. L. B. Alfassi, H. Reisler, and M. Anbar, Israel Atomic Energy Commission, 91 (1968).
22. O. S. Savel'eva, L. G. Shevchuk, and M. A. Vysotskaya, Zhur. Org. Khim., 8, 283 (1972).
23. G. Hughes and H. A. Makada, Trans. Faraday Soc., 64, 3276 (1968).
24. N. V. Zakatova, N. G. Minkhadzhiddinova, and V. A. Sharpatyi, Izv. Akad. Nauk SSR, Ser. Khim., 1633 (1969).
25. V. A. Sharpatyi, N. V. Zakatova, and G. A. Brodskaya, Khim. Vys. Energii, 2, 473 (1968).
26. G. V. Buxton, Trans. Faraday Soc., 66, 1656 (1970).
27. E. V. Barelko, L. I. Kartasheva, P. D. Novikov, and M. A. Proskurnin, "Trudy I Vsesoyuznogo Soveshchaniya po Radiatsionnoi Khimii" (Proceedings of the First All-Union Conference on Radiation Chemistry), Izd. Akad. Nauk SSSR, Moscow, 1958, p. 89.
28. M. A. Proskurnin and E. G. Barelko, "Sbornik Rabot po Radiatsionnoi Khimii" (Collected Papers on Radiation Chemistry), Izd. Akad. Nauk SSSR, Moscow, 1955, p. 99.
29. L. I. Kartasheva, Z. S. Bulanovskaya, E. V. Barelko, Ya. M. Varshavskii, and M. A. Proskurnin, Dokl. Akad. Nauk SSSR, 136, 143 (1961).
30. I. P. Gragerov, A. F. Levit, Yu. A. Zonov, and M. Ya. Turkina, Dokl. Akad. Nauk SSSR, 150, 109 (1963).
31. J. Loeff and G. Stein, Nature, 184, 901 (1959).
32. W. T. Dixon and R. O. C. Norman, Proc. Chem. Soc., 97 (1963).
33. L. M. Dorfman, J. A. Taub, and R. E. Bühler, J. Chem. Phys., 36, 3051 (1962).
34. G. Stein and J. Weiss, J. Chem. Soc., 3245 (1949).
35. P. V. Phung and M. Burton, Radiation Res., 7, 199 (1957).
36. M. A. B. Manzitti, P. L. Bertolaccini, and L. Puccini, Energia nucleare (Milan), 8, 445 (1961).
37. J. H. Merz and W. A. Waters, J. Chem. Soc., 2427 (1949).
38. J. H. Baxendale and J. Mage, Discuss. Faraday Soc., 14, 160 (1953).
39. B. Cercek and M. Ebert, "Radiation Chemistry I", 1968, vol. 1, p. 210.
40. L. G. Shevchuk and N. A. Vysotskaya, Zhur. Org. Khim., 2, 1229 (1966).
41. B. Fraser-Reid, J. K. Jones, and M. B. Perry, Canad. J. Chem., 39, 555 (1961).
42. L. G. Shevchuk and N. A. Vysotskaya, Zhur. Org. Khim., 4, 1936 (1968).
43. I. A. Kazarnovskii, N. P. Lipikhin, and M. V. Tikhomirov, Dokl. Akad. Nauk SSSR, 120, 1038 (1958).
44. O. L. Forheimer and H. Taube, J. Amer. Chem. Soc., 74, 3705 (1952).
45. O. L. Forheimer and H. Taube, J. Amer. Chem. Soc., 76, 2099 (1954).
46. V. S. Zhikharev, Candidate's Thesis, Institute of Physical Chemistry, Academy of Sciences of Ukrainian SSR Kiev, 1969.
47. Hj. Staudinger and V. Ullrich, Z. Naturforsch., 19b, 877 (1964).
48. D. I. Metelitsa, Uspekhi Khim., 40, 1175 (1971) [Russ. Chem. Rev., No. 7 (1971)].
49. J. R. Smith and R. O. C. Norman, J. Chem. Soc., 2897 (1963).
50. N. T. Rakintzis, Z. phys. Chem., 44, 257 (1965).
51. N. T. Rakintzis, Z. phys. Chem., 57, 99 (1968).
52. G. Czapski and B. H. Bielski, J. phys. Chem., 67, 2180 (1963).
53. E. Hayon, Trans. Faraday Soc., 61, 723 (1965).
54. M. Daniels and E. Wigg, Science, 153, 1533 (1966).
55. H. Taube, Trans. Faraday Soc., 53, 656 (1956).
56. W. B. Demore, J. Phys. Chem., 73, 391 (1969).
57. E. Grovenstein, Jr. Arthrir, and J. Mosher, J. Amer. Chem. Soc., 92, 3810 (1970).
58. O. Amichai and A. Treinin, Chem. Phys. Letters, 3, 611 (1969).
59. E. T. Denisov "Konstanty Skorosti Gomoliticheskikh Zhidkofaznykh Reaktsii" (Rate Constants for Homolytic Liquid-Phase Reactions), Izd. Nauka, Moscow, 1971.
60. M. Anbar and P. Neta, Internat. J. Appl. Radiation Isotopes, 16, 227 (1965).

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