Translated from *Uspekhi Khimii*, **44**, 1748 - 1774 (1975) U.D.C. 541.144.8

Short-lived Phenoxy- and Semiquinone Radicals

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The results of the principal studies of the absorption spectra and the kinetics of the destruction of short-lived phenoxy- and semiquinone radicals in the liquid phase are examined. A systematic account is given of the results of investigations of their interaction with metal compounds. Much attention is devoted to the photochemical method of generating phenoxy- and semiquinone radicals from phenolic and quinonoid compounds.
The bibliography includes 205 references.

CONTENTS

I.	Introduction	801
II.	Methods for the investigation of the physicochemical properties of short-lived radicals	801
III.	The involvement of phenoxy- and semiquinone radicals in chemical and biological processes in the dark	802
IV.	Fundamental photochemical processes occurring on photoexcitation of phenols and quinones	802
V.	Sensitised photochemical oxidation of phenols and photochemical reduction of quinones	804
VI.	Absorption spectra and acid-base properties of phenoxy- and semiquinone radicals	804
VII.	Kinetics of the destruction of radicals	807
VIII.	Interaction with metal compounds	809
IX.	Some quantum-chemical calculations on phenoxy- and semiquinone radicals	811

I. INTRODUCTION

In the vast majority of cases the reactions of phenolic compounds in chemical and biological processes have free-radical mechanisms. The phenoxy- and semiquinone radicals formed under these conditions as intermediates and the related flavosemiquinone radicals are π radicals and belong to the class of aromatic radicals. The study of the characteristics of phenoxy-radicals is an important task in connection with the extensive use of phenols as inhibitor-stabilisers in various branches of theoretical and applied chemistry[1-3] and recently also in experimental biology and medicine[4]. There has been an immense growth of interest in the last decade and a half in this field of research in connection with studies by Emanuel' and his coworkers[4-11].

A number of monographs and reviews are devoted to stable phenoxy- and semiquinone radicals[3,12-16]. As a result of the development of pulse methods, extensive data on the physicochemical properties of short-lived phenoxy- and semiquinone radicals have accumulated during the last 10–15 years.

It is therefore desirable to survey the available literature data for the fundamental reactions of phenoxy- and semiquinone radicals and their physicochemical properties.

II. METHODS FOR THE INVESTIGATION OF THE PHYSICOCHEMICAL PROPERTIES OF SHORT-LIVED RADICALS

Almost all the techniques for the investigation of reactivity can be applied to phenoxy- and semiquinone radicals. In this review the term "unstable" or "short-lived" is applied to a radical whose lifetime is shorter than one second in the absence of oxygen at room temperature in a non-viscous solvent at concentrations in the range 10^{-7} to 10^{-5} M.

For a time the ESR method (in its usual version) was the main procedure for the investigation of the properties of radicals. Its use in the study of short-lived radicals is extremely difficult. In such cases one employs a flow system or the radical precursor is irradiated directly in the cavity of the spectrometer. In certain cases the radicals can be stabilised owing to the characteristics of the solvent—a highly alkaline medium (in the case of semiquinone radicals) or the formation of a complex with the solvent[13]. The method of low-temperature stabilisation[17], in which the radicals are stabilised in a solid matrix and their spectra are recorded, has been widely used. In recent years the absorption spectra of aromatic and other radicals, stabilised in a solid poly(methyl methacrylate) (PMMA) or adamantane matrix, have been recorded at room temperature[18-20].

Pulse methods (flash photolysis and pulse radiolysis) have a considerable scope in the study of the properties of short-lived radicals. The use of flash photolysis with detection of intermediates from their ESR spectra is extremely promising.

The absorption of light by an aromatic molecule, for example phenol, leads to the formation of an unstable excited state, which is deactivated either as a result of a photophysical process, for example fluorescence or phosphorescence, or photochemically, i.e. via dissociation into radicals or ionisation. The radicals or radical-ions thus formed can be detected, for example, from their absorption spectra. The method of pulse radiolysis has been also widely used to study aromatic radicals; it differs from flash photolysis by the fact that the excitation is achieved by a short pulse of high-energy electrons†.

† In order to obtain high non-equilibrium concentrations of phenoxy- and semiquinone radicals, water was subjected to pulse radiolysis in the presence of the initial phenolic or quinonoid compound. The aqueous solutions contained 0.1–10% of organic additives (alcohol, acetone, formate, etc.) and could be saturated with N_2O to remove undesirable water radiolysis products from the reaction mixture. All the experiments were performed at room temperature.

III. THE INVOLVEMENT OF PHENOXY- AND SEMIQUINONE RADICALS IN CHEMICAL AND BIOLOGICAL PROCESSES IN THE DARK

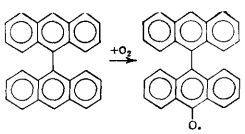
1. Phenoxy-radicals

Phenoxy-radicals are intermediates in various reactions where phenol is oxidised—by inorganic oxidants, oxygen, alkoxy- and peroxy-radicals, oxidation enzymes, anodically, etc. They are formed in hydrocarbon oxidation reactions inhibited by phenol. The mechanism of the action of phenolic inhibitors in free-radical reactions reduces to chain termination owing to the interaction of the phenol (RhOH) with the chain-propagating radicals R$^{\cdot}$ or RO$_2^{\cdot}$:[1]

$$R^{\cdot}\,(RO_2^{\cdot}) + PhOH \rightarrow RH\,(ROOH) + Ph\dot{O}.$$

Aromatic radicals RO$^{\cdot}$ are as a rule incapable of propagating the chain process further and are destroyed by interacting with one another or with the chain-propagating radicals[1,2,21].

Aryloxy-radicals are also formed when condensed aromatic compounds without OH groups are oxidised by oxygen. The oxidation of anthracene leads to the formation of the corresponding aryloxy-radical[22], while the oxidation of bianthryl proceeds via the substitution of its most reactive hydrogen atom by oxygen[23]:



Phenolic compounds are extremely widely distributed in nature. It has been suggested that phenolic substances are involved in the growth, development, immunity, resistance to cold and harmful radiation, respiration, and photosynthesis in plants, i.e. in almost all their vital processes[24,25]. It has been established that certain biologically important phenolic substances are capable of reversible oxidation with formation of the corresponding phenoxy-radicals as intermediates and it has been suggested that these properties constitute the basis of the pharmacological activity of such compounds[25]. Phenolic compounds are incapable of participating in various enzymatic and photochemical oxidation-reduction processes which are of great biological importance[25]. It is nowadays regarded as proved that oxidative coupling of phenols is one of the principal stages in the biosynthesis of natural products[26].

2. Semiquinone Radicals

o- and *p*-Hydroxyphenoxy-radicals and their anions as well as their derivatives constitute the group of semiquinone radicals. As early as the 1930s, Michaelis and coworkers[27] showed that the two-electron oxidation of hydroquinone or the reduction of quinone proceeds via a stage involving the formation of an intermediate containing an odd number of electrons—a semiquinone radical. The existence of semiquinone radicals in quinone reduction or hydroquinone oxidation processes was demonstrated for the first time in measurements of magnetic susceptibility and in potentiometric measurements[27]. *o*- and *p*-Benzosemiquinone radical-anions are relatively stable in an alkaline medium, which makes it possible to record their intense ESR signals in aqueous or alcoholic media at room temperature[28,29].

Like phenoxy-radicals, semiquinone radicals are the primary products of the oxidation of various hydroquinones by inorganic oxidants, by atmospheric oxygen, by enzymes[30], etc. They can probably be formed also in the catalytic oxidation of phenol by oxygen, as shown by the formation of hydroquinone and catechol as the final products of such a reaction[31]. Quinones are well known in organic chemistry as electron acceptors which are reduced to dihydroquinone via the intermediate formation of a semiquinone radical.

A wide variety of numerous quinonoid compounds are encountered in nature and are involved in oxidation-reduction reactions[32,33]. Semiquinone radicals play an important role in biological systems as active agents in electron transfer reactions in living organisms, plants, and microorganisms[34,35]. The simplest quinones (*p*-benzoquinone, chloranil, duroquinone, and naphthoquinone) have aroused interest, because they can be regarded as models for more complex quinones—coenzyme Q, vitamins K, plastoquinones, flavin-adenine dinucleotide, etc. Studies on reversible oxidation reduction reactions of riboflavin (vitamin B$_2$), which also proceed via the formation of flavosemiquinone radicals, are of great interest from the biological point of view.

IV. FUNDAMENTAL PHOTOCHEMICAL PROCESSES OCCURRING ON PHOTOEXCITATION OF PHENOLS AND QUINONES

1. Photolysis of Phenols

The majority of the reactions leading to the formation of phenoxy-radicals are associated with the abstraction of hydrogen from the hydroxy-group of phenol under the influence of oxidising agents. The dissociation of the O–H bonds in phenols (as well as PhO–CH$_3$, PhO–C$_2$H$_5$, and PhO–COR bonds) with formation of phenoxy-radicals can occur also under the influence of ionising and ultraviolet radiation or ultrasonic waves[36–56]. The simplest phenols are photolysed in the gas phase via the reaction[45]

$$PhOH + h\nu \rightarrow PhO^{\cdot} + H^{\cdot}.$$

An energy diagram has been plotted for this decomposition pathway of the phenol molecule[45], according to which the absorption of a photon by the phenol results in its transition from the ground state to the first singlet excited state $^1\pi_1$. This level intersects the dissociative level $^3\sigma_0$, and the system can pass to the $^3\sigma_0$ state, which entails the dissociation of the O–H bond and the formation of the radicals PhO$^{\cdot}$ and hydrogen atoms H$^{\cdot}$.

In the pulse photolysis of phenoxide ions in the liquid phase a phenoxy-radical is formed, as in the photolysis of phenol, which indicates the photoionisation of the anion via the reaction[54,55]

$$PhO^- + h\nu \rightarrow PhO^{\cdot} + e^-_{hydr.}$$

The photoionisation of phenols and their anions in a solid matrix at low temperatures proceeds via a two-photon pathway with participation of the triplet excited state[56–62]. The nature of this process in liquid media, particularly in polar liquids, is less clear. The earlier attempts to observe a non-linear relation between the initial yield of solvated electrons, obtained in the photolysis of *p*-cresol, and light intensity were unsuccessful[50].

It was suggested[64] that in certain cases a one-photon process may proceed via an intermediate semi-ionised state, which is produced directly from the unrelaxed excited singlet state. As a result of the energy gain on solvation, photoionisation can be induced by light the energy of whose quanta is less by 3–4 eV than the ionisation potential in the gas phase[65]. It has been shown[18] that the corresponding naphthoxy-radicals are formed from the molecules of α- and β-naphthols in the excited singlet state in a PMMA matrix.

In the liquid-phase photoexcitation of phenols, phenoxy-radicals are formed via the reactions[51,66,67]

$$\mathrm{PhOH} + h\nu \rightarrow \mathrm{PhOH}^* \begin{cases} \xrightarrow[-\mathrm{H}^+]{(a)} (\mathrm{PhO}^-)^* \rightarrow [\mathrm{PhO}^\cdot + e_{solv}] \rightarrow \mathrm{PhO}^\cdot + e_{solv} \\ \xrightarrow{(b)} [\mathrm{PhO}^\cdot + \mathrm{H}^\cdot] \rightarrow \mathrm{PhO}^\cdot + \mathrm{H}^\cdot \end{cases} , \quad (1)$$

where the solvent "cage" is represented by square brackets.

In the flash photolysis of phenol and cresols the relative yield of hydrated electrons falls when the pH becomes less than the pK of the corresponding unexcited phenol molecule[50]. After the dissociation of the phenol molecule in the singlet excited state (pathway a), the electron is "ejected" with formation of a phenoxy-radical. Subsequent studies confirmed that the pK of phenol and cresols in the first singlet state are smaller by 5–6 units than in the ground state[68,69]. The relative contributions of the decomposition pathways of the excited phenol molecule, a or b, are independent of many factors, primarily temperature, solution pH, and the polarity of the medium[51,66]. A detailed mechanism of the photoionisation of aromatic molecules in liquids has been discussed[64,70].

According to Feitelson and Hayon[51], more than 70% of the radicals generated from phenols are obtained via photoionisation (pH 7.0; 25°C) and the remainder via the dissociation of the O–H bonds. (The quantum yield in the dissociation of the O–H bond amounts to about 0.01 for various media[53].) On the other hand, the photoionisation is much less effective with the phenol than that with the corresponding anion[71]. The photoionisation of phenols and their anions in alkaline media proceeds via two-photon and one-photon processes respectively[65]. The concentration of phenoxy-radicals formed under the influence of the flash is proportional to the light intensity I^n, where n varies from 2 to 1 over a relatively narrow pH range. Absorption due to phenoxy-radicals is observed in air-saturated solutions, the radicals being formed in a somewhat lower yield and $n = 1.5$.

Studies of the photolysis of aqueous solutions of phenols in the absence of oxygen (at 25°C) with added hexa-2,4-diene, a typical quenching agent for the triplet state, showed that in the photolysis of many phenols the electron is also ejected from a long-lived excited state, possibly the triplet state[51].

Either halogenophenoxy-radicals or hydroxyphenyl radicals may be formed in the photolysis of halogenophenols. The photolysis of iodophenols results in the formation of hydroxyphenyl radicals[18,146], as in the photolysis of p-chlorophenol and monobromophenols[48,73].

The photolysis of 2,4-dibromophenol and 2,4,6-tribromophenol yields the corresponding phenoxy-radicals[72,45]. The absorption recorded in the flash photolysis of certain chlorophenols is due to the formation of chlorophenoxy-radicals[45].

2. Photochemical Reactions Leading to the Formation of Semiquinones

Semiquinone radicals may be obtained by the photochemical oxidation of the corresponding hydroquinones or by the photochemical reduction of quinones. The photochemical oxidation of hydroquinones proceeds partly in the same way as the photolysis of phenols [see Eqn. (1)]. Thus the formation of the corresponding semiquinone radicals and hydrated electrons was observed in the flash photolysis of hydroquinone and catechol in water[59].

The photochemistry of quinones has been vigorously investigated in connection with the elucidation at the molecular level of the destructive effect of light on certain biological objects[33] and also the possible initiation of electron transfer in biological systems following the absorption of light by a quinone[74]. It has been shown that certain alkylquinones are bound to chlorophyll in leaf chloroplasts[33,34]. It has been suggested, that, apart from their function as acceptors in the electron-transport chain, these quinones can play a definite role in photophosphorylation[75].

The damaging influence of ultraviolet light on living organisms is associated with photochemical reactions of quinones, which are the most likely targets for radiation[76]. Semiquinone radicals are frequently the primary products of the photochemical excitation reactions of quinones under these conditions[76–78].

The photochemical reduction processes involving quinones have been studied in fair detail. In an excited state quinone molecules abstract a hydrogen atom (or electron) from the solvent molecule or from another hydrogen (or electron) donor present in solution with formation of a semiquinone radical. Depending on the pH, an acid–base equilibrium involving the half-reduced forms of quinones is then rapidly established. The problem arises as to the nature of this excited state of the quinone. Studies on the kinetics of the destruction of the triplet state of duroquinone DQ(T) and the semiquinone radical DQH$^\cdot$ in liquid paraffin[79,80] showed that DQH$^\cdot$ is formed mainly via the reaction

$$\mathrm{DQ}(\mathrm{S}^*) + \mathrm{RH} \rightarrow \mathrm{DQH}^\cdot + \mathrm{R}^\cdot .$$

However, experiments on energy transfer established that DQH$^\cdot$ is formed also by a path involving the triplet state[81]. It was subsequently shown by laser photolysis that the durosemiquinone radical is indeed formed from the triplet state in ethanol[82].

The fact that DQ(T) is destroyed in liquid paraffin, giving rise to DQH$^\cdot$, has not been rigorously demonstrated[82]. Studies of the photochemical reduction of chloranil have also demonstrated that the photoexcited triplet state of chloranil is quenched by ethanol with direct formation of a semiquinone radical-anion[83]. The lifetime of the triplet state of p-benzoquinone in ethanol is 10 ns and therefore the rate constant for the abstraction of a hydrogen atom from the solvent $k > 10^8$ s^{-1}.[83,84]

The mechanism of the photochemical reduction of p-benzoquinone in ethanol at low temperatures has been considered[85,86]. The photochemical reduction of 1,4-naphthoquinone proceeds with the intermediate formation of the neutral naphthosemiquinone radical[87].

In certain cases the formation of semiquinone radicals on photochemical reduction of quinones is accompanied by electronic polarisation[84,87]. Immediately after the flash, an emission signal appears in the ESR spectrum, is converted into an absorption signal, and then diminishes owing to the destruction of the radicals[84,87].

The pK values of semiquinone radicals in water are fairly well known (Table 2). The assignment of the observed absorption in an organic solvent to a neutral semiquinone radical or radical-anion is usually based on an analysis of ESR spectra [87,88], but here too certain difficulties arise. The photoexcitation of chloranil in ethanol or methanol leads to the formation of the chloranil radical-anion [88], while in another study [89] it is suggested that the primary product of such photochemical reduction in isopropyl alcohol (or dioxan) is a nuetral radical.

The photochemical reduction of anthraquinone derivatives in alcoholic media has been studied in greatest detail, since this process simulates the photochemical degradation of cellulose sensitised by anthraquinone dyes and is of great practical importance [90-96].

Anthraquinone derivatives are reduced photochemically in alcoholic solutions via the reaction

$$AQ\,(T) + RCH_2OH \rightarrow AQH^{\cdot} + R\dot{C}HOH$$

and in alkaline media via the reaction

$$AQ\,(T) + OH^{-} \rightarrow AQ^{\cdot-} + OH^{\cdot}.$$

The resulting semiquinone radical-anion is fairly stable in alkaline solution in the absence of oxygen.

The quinones involved in photochemical biological processes (plastoquinones, tocoquinones, and α-tocopheryl-quinones) also give rise to the corresponding semiquinone radicals on photoexcitation. The final photochemical reduction products from certain plastoquinones and tocoquinones are o-quinone methides [76-78]. The photochemical reduction of many quinones with ring substituents proceeds via an intramolecular mechanism [97-99].

The triplet state responsible for the formation of the semiquinone radical from 1,4-benzoquinone, 1,4-naphthoquinone, and anthraquinone is probably of the $n-\pi$ type [100-103], while the triplet states of duroquinone and chloranil are of the $\pi-\pi^*$ type [82,101,104]. The precursor of the radical is probably the lowest triplet state of the corresponding quinone in all cases where semiquinones are formed [63,87].

The formation of flavosemiquinone radicals, particularly those derived from riboflavin, has been observed in the photochemical reduction of flavins or in their reduction by electrons [105-108,110-115].

It was initially suggested that dihydroriboflavin is formed via the abstraction of two hydrogen atoms from the water molecule [116-118]. Objections were raised to this mechanism [119] on the basis of the process energetics and it was postulated that the decolorisation of riboflavin proceeds via the photochemical oxidation of its own ribityl chain. There is evidence for an intramolecular decolorisation mechanism, obtained in a series of kinetic and polarographic studies by pulse photolysis and theoretical calculations [108,109,120-127]. It has been shown that the lowest long-lived triplet state is photochemically reactive in the anaerobic photochemical decolorisation of riboflavin and flavin mononucleotide [107-110,119]

It has been shown [109,127] that the singlet state of riboflavin can also be involved in photochemical reduction and that this pathway is probably the only one giving rise to the formation of the flavosemiquinone radical in air-saturated solutions.

V. SENSITISED PHOTOCHEMICAL OXIDATION OF PHENOLS AND PHOTOCHEMICAL REDUCTION OF QUINONES

In a study of the photochemical oxidation of a number of sterically hindered phenols by molecular oxygen it was observed that, on irradiation without a sensitiser, the initial phenols remain unchanged [128]. Sensitised photochemical oxidation of sterically hindered phenols proceeds via the following mechanism: a complex is formed by the excited molecule of the sensitiser and oxygen and abstracts the hydrogen atom from the hydroxy-group of the phenol with formation of the phenoxy-radical [128]. (In the photochemical oxidation of unsubstituted phenol and cresol under the influence of light with $\lambda = 253.7$ nm, it was established [73] that the presence of oxygen or other oxidants is not essential for the formation of the phenoxy-radical.)

According to another mechanism of the sensitised photochemical oxidation of phenols [129-135], the phenol is attacked by an excited sensitiser molecule, which leads to the abstraction of the hydrogen atom from the phenolic hydroxyl or to the loss of an electron by the phenoxide ion. Reactions proceeding via this mechanism have been observed [130-136] in the sensitised photochemical oxidation of phenol and its derivatives by eosin (E) and related dyes.

The photochemical oxidation reactions sensitised by eosin are of great interest for photobiology, since it has been shown that eosin causes photodynamic inactivation of proteins [136]. The experiments performed by flash photolysis (kinetic and spectrophotometric) have shown that the attack on phenol by a dye molecule in the triplet state results in the formation of a phenoxy-radical and a semiquinone radical derived from the dye [136]:

$$E\,(T) + PhOH \rightarrow EH^{\cdot} + PhO^{\cdot}.$$

It has been established that excited states of 9,10-anthraquinone-2-sulphonic, 9,10-anthraquinone-2,6-disulphonic, and 9,10-anthraquinone-2,7-disulphonic acids are quenched chemically by phenol and hydroquinone with formation of the corresponding phenoxy- (p-benzosemiquinone) and anthrasemiquinone radicals [72,90]. Various α-diketones in an excited state are also capable of oxidising phenols with formation of ketyl and phenoxy-radicals [137,138]. In the quenching of the luminescence of diacetyl by phenols there is a reversible abstraction of a hydrogen atom with formation of phenoxy-radicals [139].

Certain dyes and pigments in an excited state are capable of reducing quinones to semiquinone radicals. Thus the following reaction takes place in the photoexcitation of chlorophyll in alcohols in the presence of p-benzoquinone (duroquinone, vitamin K, and α-tocopheryl-quinone) [132,140-143]:

$$Chl^{*} + Q \rightarrow Chl^{+} + Q^{\cdot-}, \qquad (2)$$

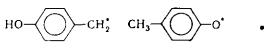
where Chl* is the excited chlorophyll molecule (most probably in the triplet state) and $Q^{\cdot-}$ the semiquinone radical. Eosin in the excited triplet state reduces p-benzoquinone via a type (2) reaction, being oxidised itself to a radical-cation [144].

VI. ABSORPTION SPECTRA AND ACID–BASE PROPERTIES OF PHENOXY- AND SEMIQUINONE RADICALS

The absorption spectra of a number of phenoxy- and semiquinone radicals were recorded in the flash photolysis and pulse radiolysis of phenolic and quinonoid compounds.

The problem of the assignment of the observed absorption in the flash photolysis of aromatic compounds to any specific structural formula is solved individually in most cases[42,43]. Either the triplet state of the molecule or a radical are responsible for the absorption. This problem can be solved by an additional study of the kinetics of the reaction with oxygen, the application of the method of $T-T$ energy transfer, the study of the interaction of the intermediates with various additives, a comparison of the absorption spectra in the liquid and solid phases, etc. Investigation of the dependence of the absorption on the polarity of the medium, pH, ionic strength, and other parameters makes it possible to determine the charge on the transient species.

A study of substituted phenols by flash photolysis showed that, in principle, different radicals can be formed. For example, benzyl and phenoxy-radicals may be formed in the photolysis of *p*-cresol:



In such cases one has to decide to which radical the observed spectrum should be assigned. The spectra of benzyl and phenoxy-radicals differ appreciably in the shape of the bands and in the relative intensities of the long-wavelength and short-wavelength transitions. Flash photolysis of *p*-cresol yielded a spectrum almost identical in form and intensity to that of the phenoxy-radical. On this basis, it was concluded that the primary photochemical process is the formation of a *p*-methylphenoxy-radical[42].

In general the identification of the spectra of aromatic radicals has been based on the study of a series of related substituted compounds[43,145]: the method is particularly convenient and reliable for aromatic compounds, since there are many such compounds and in most cases there is a possibility of cross checks.

1. Phenoxy-radicals

The spectra of phenoxy-radicals are characterised by a system of bands in the region of 300 and 400 nm.[42] The absorption spectrum of the unsubstituted phenoxy-radical was recorded for the first time in the flash photolysis of phenol and anisole vapours in the gas phase[36]. The spectrum consists of a single diffuse band with a maximum at 292 nm. The long-wavelength band in the region of 400 nm has been observed[37,38] in the flash photolysis of phenol in various solvents. Low-temperature studies confirmed the validity of the band assignment[40,42].

The formation of phenoxy-radicals has also been established[44] in the photolysis of phenol, anisole and phenetole in a nitrogen matrix at 4.2 K. In addition to the earlier data[40], bands were found at 295 and 396.5 nm together with a broad band at 240 nm, which correspond to the absorption by the phenoxy-radical. Further photolysis by light in the wavelength range 225–345 nm led to the degradation of the phenoxy-radical itself. Subsequently, a long-wavelength band system with maxima at 395 and 382 nm was observed in the flash photolysis of phenol vapour in the presence of argon[42,46].

The absorption spectra of eighteen different alkylphenoxy-radicals were obtained by Land and Porter in the flash photolysis of the corresponding phenols[45]. They showed that aliphatic substituents have an insignificant influence on the absorption spectrum of the phenoxy-radical, leading to slight shifts of the long-wavelength band system as a function of the position of the substituent in the ring. Phenoxy-radicals are the principal short-lived species detected in the flash photolysis of proteins such as egg albumin, where they are formed from compounds of the type of tyrosine[145].

Phenoxy-radicals with large alkyl substituents have spectra in which the band distribution remains largely the same as in the spectrum of the unsubstituted phenoxy-radical, their intense colour being due to broad bands extending to the visible region. Alkylated phenoxy-radicals are blue and alkoxy- and phenyl groups cause a hypsochromic shift in the visible region, giving rise to radicals with $\lambda_{max} \simeq 530$ nm. On the other hand, electron-accepting substituents (formyl, keto-, and cyano-groups) cause a bathochromic shift and the radicals can be blue or green[12]. A weak diffuse absorption is observed in the region of 600 nm in the spectra of certain trialkylphenoxy-radicals[48]. The existence of such a broad band was also expected for the unsubstituted phenoxy-radical[42]; it was observed in the gas phase under conditions of high resolution[46]. Apart from the 380 and 395 nm bands, which correspond to $\pi-\pi^*$ absorption like the 292 nm band, a broad and weak absorption band was detected in the range 530–610 nm with $\lambda_{max} = 600$ nm; it is probably due to absorption of the $n-\pi^*$ type[43,46].

Studies on the absorption spectra of phenoxy-radicals in PMMA showed that the long-wavelength absorption limit of the radical is 850 nm.[18] However, on the basis of quantum-chemical calculations, the author[18] believes that the long-wavelength absorption in the spectrum of the phenoxy-radical in the region of 600 nm is also of the $\pi-\pi^*$ type. The theory of the absorption spectra of the simplest aromatic radical has been discussed[42].

The absorption spectra of phenoxy-radicals have been recorded in the pulse radiolysis of phenol and *p*-cresol in water[49]. The extinction coefficients of phenoxy-radicals were determined either by pulse radiolysis (when the radiation yields of the radiolysis products are known)[49] or by comparison with the absorption of hydrated electrons formed in the photolysis of phenoxide ions. When the latter method was used, unduly high extinction coefficients were apparently obtained in many instances. This is probably because the hydrated electron has a very short lifetime, comparable to the duration of the flash. A comparatively simple and reliable method for the determination of the extinction coefficient of phenoxy-radicals in experiments on the photochemical oxidation of phenols sensitised by anthraquinone-2,6-disulphonic acid has been proposed[72]. When this method is used, it is possible to obtain the extinction coefficients of halogenophenoxy-radicals[72,146]. (Halogenophenols do not give rise to hydrated electrons on photochemical excitation or effectively quench such electrons[66].) Data for the spectra of the simplest phenoxy-radicals are listed in Table 1.

The differences between the spectra of the radicals at different temperatures and in different solvents are usually small. Small changes in the absorption maxima and shapes of the bands are observed in gas–liquid–solid transitions[42].

In solutions, over the entire range of acidities (up to solutions containing 12 M H_2SO_4), phenoxy-radicals are present as uncharged species[40,43]. Protonation of the radicals usually alters greatly the absorption spectrum and such changes can be readily detected. The protonated phenoxy-radical $Ph\mathring{O}H^+$ is a very powerful acid and cannot be observed with appreciable equilibrium concentrations[40,43]. The pK of certain substituted phenoxy-radicals have been obtained by flash photolysis and all the pK values are less than -1.[43]

Quantum-chemical calculations[147] showed that the existence of unsubstituted phenoxy- and semiquinone radical-cations in an aqueous medium is virtually impossible.

Table 1. The absorption maxima and extinction coefficients of phenoxy-radicals in water at 20°C.

Radical	λ_{max}, nm	ϵ, litre mole^{-1} s^{-1}	References
Phenoxy-	402	1 800*	42
	299	5 000	42
	400±5	2200±200	49
	290±5	4000±800	49
	399	11 000	50
	400	2 300	72
o-Methylphenoxy-	395, 380, 363	—	45
	395	8 700	50
	405	3 400	72
m-Methylphenoxy-	412, 381, 372	—	45
	412	4 800	50
	420	3 000	72
p-Methylphenoxy-	405, 385, 368	—	45
	388, 405	—	54
	405	15 000	50
	405±5	2400±400	49
	295±5	5000±1000	49
	410	3200±300	51
	400	2 500	72
m-Nitrophenoxy-	450	490	72
2,4-Dibromophenoxy-	420	3 700	72
Phenoxy-radical from tyrosine	410	2 100	72
	410	2750±200	51
p-Iodophenoxy-	420	2 800	146

*In hexane.

2. The Absorption Spectra and Dissociation Constants of Semiquinone Radicals

The absorption spectra of many short-lived *p*-semiquinone radicals have been recorded by methods of flash photolysis[79,80,147-153] and pulse radiolysis[74,154-166] in studies on hydroquinone and quinones. Pulse radiolysis proved to be a convenient method for the investigation of the properties of semiquinone radicals (the studies were performed mainly in aqueous solutions). When this method is used to generate the radicals, there is no need for the formation of an excited state (which may be readily quenched by impurities or oxygen) and it is possible to determine the extinction coefficients. The study of the dependence of the absorption intensity of the radical on the pH of the solution under otherwise constant conditions makes it possible to obtain "titration curves" of the radicals and to determine the pK values, which for the majority of *p*-semiquinone radicals are in the range 3–6 (Table 2).

The spectra of the majority of semiquinone radical-anions have maxima in the range 400–450 nm (Table 2), while the absorption maxima of the neutral radicals are displaced to the ultraviolet and are located in the range 370–425 nm.[163] This is consistent with the general postulate that the basic forms of free radicals absorb at lower energies than the acid forms[163]. In most cases semiquinone radicals and radical-anions have absorption bands in the ultraviolet and far ultraviolet[165,166] but, with one exception[167], these bands have not been investigated in detail.

The electron combined with an excited quinone molecule converts its quinonoid structure into an aromatic structure and the absorption of light involves transitions of the $\pi-\pi^*$ type in semiquinone radicals[125].

The absorption spectrum of the *p*-benzosemiquinone radical-anion has been investigated thoroughly[167]. The radical-anion was obtained by oxidising hydroquinone with manganese dioxide and its absorption and ESR spectra were recorded; the latter made it possible to determine the concentration of the radical-anions. The results are in Table 2. The absorption spectra of a number of semiquinone and flavosemiquinone radicals have also been published[70,105,106,110,164-166,170,171]. The flavosemiquinone radicals investigated differ only by the substituents in the isoalloxazine ring and have very similar absorption spectra.

Table 2. The absorption maxima, extinction coefficients, and dissociation constants of semiquinone radicals in aqueous, aqueous organic, and organic media at 20°C.

Initial quinone	$Q^{\cdot-}$		$QH^{\cdot}$			References
	λ_{max}, nm	ϵ, litre mole^{-1} cm^{-1}	λ, nm	ϵ, litre mole^{-1} cm^{-1}	pK	
p-Benzoquinone	430	6 100	410	4 300	4.1	164[a]
	425	7 300	415	5 500	4.0	154
	430	5 400	—	—	—	167
	404	4 600	—	—	—	167
	371	3 700	—	—	—	167
	316	40 000	—	—	—	167
	310	33 000	—	—	—	167
	425	7 200	415	4 500	4.0	163[b]
Duroquinone	445	—	430	—	5.1	158[c]
	445	7 100	425	4 000	5.1	163[b]
	—	—	410	3 500	—	168[e]
1,4-Naphthoquinone	390	—	380	—	4.1	158[c]
	390	12 500	370	7 100	4.1	164[a]
	390	13 000	370	7 300	4.1	163
Vitamin K_3	400	10 200	380	9 000	5.5	164[c]
	395	12 000	370	9 500	4.5	165
	300	12 500	290	6 000	—	165
9,10-Anthraquinone	395	7 800	375	11 000	5.3	163[d]
	480	7 300	—	—	—	163
9,10-Anthraquinone-1-sulphonic acid	400	8 000	385	12 000	5.4	74
	500	8 000	—	—	—	74
9,10-Anthraquinone-2-sulphonic acid	500	8 200	—	—	3.25	74
	398	9 800	387	14 000	3.9	166
	465	8 000	—	—	—	166
	496	9 500	—	—	—	166
9,10-Anthraquinone-2,6-disulphonic acid	395	—	390	—	3.2	158[c]
	525	—	—	—	—	158[c]
	520	8 000	—	—	2.3	153
Riboflavin	560[f]	170	560	5 130	8.3	105
Flavin mononucleotide	—	—	560	3 050	—	106
9,10-Phenthrenequinone-3-sulphonate	—	—	485; 525	—	7.5	169
Chloranil[g]	—	—	420	7 300	—	89
	—	—	435	7 700	—	89
	—	—	448	6 000	—	89

The compositions of the aqueous solutions were as follows: *a*) 1 M isopropyl alcohol and 1 M acetone; *b*) 1–2 M t-butyl alcohol; *c*) 5 M isopropyl alcohol and 2 M acetone; *d*) 3 M isopropyl alcohol; *e*) solution in cyclohexane; *f*) not absorption maximum; *g*) solution in dioxan. In the remaining cases the solvent was water.

Certain neutral semiquinone radicals are capable of combining with an H^+ ion and of being converted into an acid form:

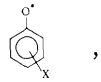
$$QH \overset{H^+}{\rightleftarrows} QH_2^+.$$

Thus, Land and Porter [148] and Land and Swallow [105] showed that the pK values for this type of equilibrium involving the durosemiquinone and flavosemiquinone radicals are respectively −1.1 and 2.3.

VII. KINETICS OF THE DESTRUCTION OF RADICALS

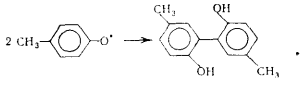
1. Phenoxy-radicals

Dimerisation is one of the most important reactions in the chemistry of phenoxy-radicals. It constitutes the basis of the oxidative coupling of phenols and leads to the formation of C−C, C−O, and O−O bonds [25]. Dimerisation involving the C−C and C−O bonds proceeds exclusively in the *ortho*- and *para*-positions with respect to the phenoxy-oxygen [26]. For example, *p*-cresol oxidised under different conditions by potassium hexacyanoferrate(III) in an alkaline solution gives rise to different final products: the *o*-dimer (2,2′-dihydroxy-5,5′-dimethylbiphenyl), the trimer, pummerer's ketone, and polymers [26]. The formation of more complex products can be account for by further interaction of the dimers with phenoxy-radicals or by the isomerisation of the dimers. The kinetics of the destruction of the *p*-methylphenoxy-radical, obtained in the pulse photolysis of *p*-cresol, have been investigated in detail [50]. It was found that the reaction obeys second-order kinetics, i.e. the radicals disappear by dimerisation. The experimental values of k/ϵ remain constant within the limits of the error over a wide range of concentrations of the initial *p*-cresol [50]. The rate constants and the values of k/ϵ are listed in Table 3, which includes data for phenoxy-radicals of the type



where X are various substituents.

The main product of the dimerisation of the *p*-methylphenoxy-radical in aqueous solution saturated with nitrogen is the *o*-dimer:



The dimerisation of two unsubstituted phenoxy-radicals results in the formation of a much greater number of products (about ten). [26] In the dimerisation of two α-naphthoxy-radicals almost all the possible products of *ortho*- and *para*-coupling are obtained and there are none containing the C−O bond; β-naphthoxy-radicals are destroyed with formation of binaphthols containing mainly the $C_{(1)}-C_{(1)}$ bond and to a much smaller extent the $O-C_{(1)}$ bond [174].

The absolute values of the rate constants for the destruction of phenoxy-radicals naturally depend markedly on the extinction coefficient adopted and are on average smaller than the k_{diff} calculated from the Debye formula [45,51,72,137]. The unduly high values of the constants frequently obtained by the Debye formula [175] can be partly accounted for by the lack of rigour in the assumptions made in its derivation.

A relation has been established [72] between the structure and the rate constant for the recombination of phenoxy-radicals.

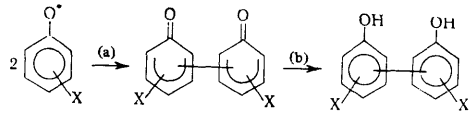
In another study [137] the rotating sector method was employed in combination with irradiation of the α-diketone in an ESR cavity in the presence of phenol. This method makes it possible to determine the rate constants for the dimerisation of phenoxy-radicals. In benzene the rate constants vary from 1.7×10^7 litre mole^{-1} s^{-1} for the *p*-methylphenoxy-radical to 4.5×10^9 litre mole^{-1} s^{-1} for the 2-naphthoxy-radical at 30°C (Table 3). As a rule, the rate constants in benzene are an order of magnitude higher than in chlorobenzene, but are smaller than k_{diff}.

Table 3. The rate constants for the destruction of phenoxy-radicals by second-order reactions.

X	Medium, temperature, °C	k/ϵ, cm s^{-1}	k, litre mole^{-1} s^{-1}	References
H	Water, 17-23	$3.5 \cdot 10^5$	$5.4 \cdot 10^8$	45
»	Water, 25	—	$5.6 \cdot 10^9$	50
»	Benzene, 29-31	—	$6.3 \cdot 10^8$	137
»	Chlorobenzene, 29-31	—	$5.5 \cdot 10^7$	137
»	Water, 12	$1.2 \cdot 10^5$	$2.8 \cdot 10^8$	72
2-CH_3[a]	Water, 12	$4.7 \cdot 10^4$	$1.6 \cdot 10^8$	72
3-CH_3	Water, 12	$2.5 \cdot 10^4$	$7.5 \cdot 10^7$	72
4-CH_3	Water, 25	$4.3 \cdot 10^5$	$6.5 \pm 0.3 \cdot 10^9$	50
»	Water, 25	$5.9 \pm 0.3 \cdot 10^5$	$1.9 \pm 0.3 \cdot 10^9$	51
»	Benzene, 29-31	—	$1.5 \cdot 10^9$	137
»	Water, 12	$4.4 \cdot 10^4$	$1.1 \cdot 10^8$	72
Tyrosine radical	Water, 25	$4.5 \pm 0.2 \cdot 10^5$	$1.2 \pm 2 \cdot 10^9$	51
»	Water, 12	$1.2 \cdot 10^5$	$2.7 \cdot 10^8$	147
4-CH_3O	Benzene, 29-31	—	$1.7 \cdot 10^7$	137
»	Chlorobenzene, 29-31	—	$1.4 \cdot 10^6$	137
2,6-Di-t-butyl-4-methyl	CCl_4, 17-23	$8.2 \cdot 10^4$	$1.5 \cdot 10^8$	45
2,6-Di-t-butyl-4-ethyl	CCl_4, 17-23	$7.4 \cdot 10^3$	$1.3 \cdot 10^7$	45
2,4-di-t-butyl	Liquid paraffin, 17-23	$1.1 \cdot 10^4$	$2.0 \cdot 10^7$	45
3-NO_2	Water, 12	$2.6 \cdot 10^4$	$1.3 \cdot 10^7$	72
2,4-Dibromo	Water, 12	$2.7 \cdot 10^4$	$1.0 \cdot 10^8$	72
4-I	Water, 20	$1.9 \cdot 10^5$	$5.5 \cdot 10^8$	146
2-OH	Water, 20	$8.0 \cdot 10^5$	$3.9 \cdot 10^8$	172
3,6-Di-t-butyl-2-hydroxy	Toluene, 27	—	$5.4 \cdot 10^6$	173

[a] E_a = 3.1 kcal mole^{-1} in toluene [11].

The activation energies for the dimerisation reactions of 14 phenoxy-radicals in benzene and chlorobenzene have been measured [176]. Comparison of these results with those obtained by the thermochemical analysis of the intermediates formed in the dimerisation reactions showed that the radicals investigated can be divided into two classes. Those for which the heat of formation of the initial intermediate (the keto-dimer) exceeds 20 kcal mole^{-1} have absolute dimerisation rate constants and activation energies which agree with the diffusion theory. For certain other radicals, for example, 4-phenyl- and 4-methoxy-phenoxy-radicals, the heat of formation of the intermediate keto-dimer is much less than 20 kcal mole^{-1} and the rate constants and activation energies differ significantly from the values predicted by the theory [176]. The final products of the destruction of PhO·, formed via the isomeric intermediate diketo-compound, are obtained as a result of the dimerisation of PhO· and subsequent enolisation with formation of the final products [137,138].



(3)

In organic solvents (benzene, chlorobenzene) stage *b* may be rate-limiting and the addition of acid sharply accelerates the process. The same mechanism of the recombination of PhO· is applicable also to an aqueous medium.

Despite the fact that the rate of process *b* should be high in an aqueous medium [176], it was found [147] that k_3 increases with decrease of pH from 8 to 1. Thus $k_3 = 1.6 \times 10^8$ litre mole^{-1} s^{-1} at pH 8 and 1.9×10^8 litre mole^{-1} s^{-1} at pH 1 for *o*-methylphenoxy-radicals. A similar conclusion can be reached by considering other experimental data [50,51].

The introduction of alkali metal salts into aqueous solutions of *o*-cresol reduces the dielectric constant of the solution and hence the rate constant for the recombination of the polar species—phenoxy-radicals [177].

The influence of atmospheric oxygen on the kinetics of the destruction of the majority of short-lived phenoxy-radicals is insignificant [72].

Disproportionation is the reaction whereby certain 4-alkyl-2,6-di-t-butylphenoxy-radicals are destroyed [13]. For example, 2,6-di-t-butyl-4-isopropylphenoxy-radicals are destroyed via second-order reactions with formation of the initial phenol and a quinone methide [48]. The deviation from second-order kinetics in the radical anihilation reaction and its occurrence in accordance with first-order kinetics, observed for 2,6-di-t-butyl-4-methylphenoxy-radicals and certain others, has been explained [45,178,179] by the isomerisation of the phenoxy-radical to the hydroxybenzyl radical with migration of the hydrogen atom of the *p*-methyl group to the phenoxy-oxygen atom. However, a more convincing explanation of the change from second-order to first-order kinetics in the radical annihilation reaction involves the formation of the intermediate 2,6-di-t-butyl-4-(2,6-di-t-butyl-4-methylphenoxy)-4-methylcyclohexa-2,6-dienone [183].

The experimental observation that there is no interconversion of the unsubstituted phenoxy- and *p*-hydroxyphenyl radicals [73] is consistent with the high activation energy for this process (more than 100 kcal mole^{-1}), calculated by the MINDO/2 method [146]. The kinetics of the reactions involving the destruction of phenoxy-radicals with comparatively complex structures have also been examined in other studies [13,180-182].

The rate of annihilation of the 2,6-di-t-butyl-4-methylphenoxy-radicals in acetonitrile in the presence of tetrabutylammonium hydroxide (TBAH) is described by a first-order kinetic equation [184]. With increase of TBAH concentration, the rate of consumption of the phenoxy-radical falls. The authors believe that TBAH forms a donor–acceptor complex with the phenoxy-radical, which may reduce the rate of consumption of the latter as a result of its stabilisation.

2. Semiquinone Radicals

The disappearance of semiquinone radicals is described by second-order kinetics. The annihilation of neutral semiquinone radicals proceeds via a disproportionation reaction:

$$QH^{\cdot} + QH^{\cdot} \rightarrow Q + QH_2, \qquad (4)$$

while the destruction of radical-anions probably involves an electron transfer reaction:

$$Q^{\cdot -} + Q^{\cdot -} \xrightarrow{+2H^+} Q + QH_2. \qquad (5)$$

The rate constants for the annihilation of neutral semiquinone radicals at room temperature in non-viscous solvents are usually about 10^9 litre mole^{-1} s^{-1} (Table 4). The diffusion constant calculated from the Debye formula is of the same order of magnitude, but, as for phenoxy-radicals, is in most cases numerically larger.

The rate constants for the destruction of radical-anions are an order of magnitude smaller than those for the destruction of the corresponding neutral radicals (Table 4). The simplest possible explanation of this finding is that, when the interaction of radical-anions is largely determined by diffusion, then the rate constant for the diffusion-controlled reaction of the charged species can be calculated from the Debye formula, which takes into account the Coulombic repulsion (or attraction):

$$k_{diff.} = \frac{8RT}{3000\,\eta} \cdot \frac{\delta}{e^{\delta} - 1},$$

where η is the viscosity of the solvent and δ a quantity which depends on the product of the charges of the reacting species. The quantity $\delta/(e^{\delta} - 1) < 1$ for species having charges of the same sign. For example, this term is 0.1 when the charges on the species are -1 and the distance of closest approach is 2 Å. [188]

Table 4. The rate constants for the destruction of semiquinone radicals via second-order reactions at about 20°C.

Initial quinone	Rate constants for annihilation reaction, mole^{-1} s^{-1}		solvent	References
	$QH^{\cdot}$	$Q^{\cdot -}$		
p-Benzoquinone[c]	$1.1 \cdot 10^9$	$1.7 \cdot 10^8$	Water	154
	$1.2 \cdot 10^9$	$5.5 \cdot 10^7$	Water[a]	163
	$1.5 \cdot 10^9$	—	Isopropyl alcohol	87
	$5.4 \cdot 10^9$	—	Dioxan	87
	$2.7 \cdot 10^8$	—	Ethanol	187
Duroquinone[d]	$1.8 \cdot 10^9$	$1.2 \cdot 10^8$	Water–propanol	185
	$7.2 \cdot 10^8$	$2.9 \cdot 10^7$	Water[a]	163
	$8.0 \cdot 10^8$	$4.6 \cdot 10^6$	Ethanol–water	89
	$7.3 \cdot 10^8$	—	Isopropyl alcohol	87
	$2.9 \cdot 10^9$	—	Dioxan	87
Chloranil	—	$4.06 \cdot 10^6$	Ethanol	88
	—	$1.16 \cdot 10^7$	Methanol	88
	$1.7 \cdot 10^8$	—	Isopropyl alcohol	87
	$8.2 \cdot 10^8$	—	Dioxan	87
1,4-Naphthoquinone	$1.3 \cdot 10^9$	$1.0 \cdot 10^8$	Water[a]	163
	$2.3 \cdot 10^8$	—	Isopropyl alcohol	87
	$9 \cdot 10^8$	—	Dioxan	87
	$2.6 \cdot 10^8$	—	Ethanol	187
Vitamin K_3	$3.4 \cdot 10^9$	$5.5 \cdot 10^8$	Water	165
	$1.3 \cdot 10^9$	$1.6 \cdot 10^8$	Water[a]	163
Anthraquinone	—	$4.9 \cdot 10^7$	Isopropyl alcohol	87
	$1.2 \cdot 10^9$	—	Dioxan	87
Anthraquinone-1-sulphonate	$1.6 \cdot 10^9$	—	Water[a]	74
Riboflavin	$1.14 \cdot 10^9$	$7.0 \cdot 10^8$	Water	105
	$3.5 \pm 0.5 \cdot 10^9$[b]	—	Water	186
	—	$(1.0 \pm 0.5) \cdot 10^8$	DMF	186
Flavin mononucleotide	$3.5 \cdot 10^8$	$1.0 \cdot 10^8$	Water	106
Lumiflavin	$(0.75-1.0) \cdot 10^9$	—	Water	113

[a] The solutions contained 1–3 M isopropyl alcohol. [b] The ionic strength was $I \simeq 0$; a decrease of the rate constant for the radical annihilation reaction has been observed [186] with increase of ionic strength. [c] For the annihilation of the neutral radical, $E_{act} = 3.7 \pm 0.3$ and 3.9 ± 0.4 kcal mole^{-1} in isopropyl alcohol and dioxan respectively [187]. [d] For the annihilation of the neutral radical, $E_{act} = 3.3 \pm 0.3$ and 3.8 ± 0.4 kcal mole^{-1} in isopropyl alcohol and dioxan respectively [87].

The kinetics of the destruction of semiquinone radicals have been studied by pulse radiolysis [115,125-129,132], flash photolysis [79,80,82,83,88,106,111,113,147,149,153] (including detection by ESR), and by ESR in combination with the rotating sector method [87,187]; some of the results are presented in Table 4.

The data in Tables 3 and 4 show that in many cases the rate constants for the annihilation of phenoxy- and semiquinone radicals differ markedly under similar conditions (data of different workers). The causes of such differences remain obscure; possibly the main errors may be attributed to an inaccurate determination of the concentration of the radicals (extinction coefficients).

It has been found[87] that the rate constants for the destruction of a number of neutral semiquinone radicals in dioxan are approximately four times greater than is isopropyl alcohol (Table 4), owing to the difference between the viscosities of these solvents. This may be an indication that the radical-annihilation reaction is diffusion-controlled[87]. Other workers[187] also believe that the rate of destruction of many neutral semiquinone radicals in organic solvents is diffusion-controlled and that rotational diffusion of the radicals in the cage is a factor which influences the rate of reaction.

The annihilation of the anthrasemiquinone radical-anion $AQ^{\cdot-}$ in isopropyl alcohol follows second-order kinetics[87]. The authors proposed the following mechanism for the destruction of $AQ^{\cdot-}$, which is apparently general for semiquinone radical-anions in organic non-alkaline media:

$$AQ^{\cdot-} + H^+ \rightleftarrows AQH^{\cdot}, \quad (6)$$

$$2\,AQH^{\cdot} \rightarrow AQ + AQH_2. \quad (7)$$

Thus the differential equation for the rate of destruction of $AQ^{\cdot-}$ is that for second-order reactions:

$$-\frac{d[AQ^{\cdot-}]}{dt} = \frac{k_7[H^+]}{k_6}[AQ^{\cdot-}]^2$$

and $k_{obs} = k_6[H^+]/k_7$.

Semiquinone radicals differ appreciably in their ability to react with oxygen, which has been the subject of a number of investigations[149,153,157,158,164,189,199]. Thus the radical-anions derived from anthraquinone-2,6-disulphonic acid ($AQ^{\cdot-}$) and the anthraquinone-2-sulphonic acid interact effectively with oxygen:

$$AQ^{\cdot-} + O_2 \rightarrow AQ + O_2^{\cdot-}$$

($k = 5 \times 10^8$ litre mole^{-1} s^{-1}, 95% of water, 5% of isopropyl alcohol–acetone mixture, 20°C [164]), while the radical-anions derived from *p*-benzoquinone ($BQ^{\cdot-}$) do not interact[149,164]. The reverse process—the transfer of an electron from the superoxide ion to the quinone—has been studied for *p*-benzoquinone and a number of other quinones (trimethylbenzoquinone, vitamin K_3, etc.)[157,189,190]:

$$BQ + O_2^{\cdot-} \rightarrow BQ^{\cdot-} + O_2$$

($k = 9.6 \times 10^8$ litre mole^{-1} s^{-1}, aqueous solution containing 1 M t-butyl alcohol, 20°C [157]). Duroquinone (DQ) is involved in the reversible reaction

$$O_2^{\cdot-} + DQ \rightleftarrows O_2 + DQ^{\cdot-} \quad (8)$$

[$K_{C_8} = (2.3 \pm 0.2) \times 10^{-2}$, 95% of water, 5% of isopropyl alcohol–acetone mixture, 20°C].[164] The semiquinone radicals formed in the photochemical reduction of quinones do not react with the solvent radicals (radical-cations)[88]. However, the semiquinone radicals obtained as a result of the photochemical oxidation of inorganic anions by excited quinone molecules or in the photochemical reduction of quinones by excited pigment molecules interact effectively with the radical-anions and radical-cations formed[141,152,153]. For example, the radical-anion derived from anthraquinone-2,6-disulphonic acid ($AQ^{\cdot-}$) is destroyed via the reactions

$$AQ^{\cdot-} + CO_3^{\cdot-} \rightarrow AQ + CO_3^{2-}, \quad (9)$$

$$AQ^{\cdot-} + Chl^{\ddagger} \rightarrow AQ + Chl, \quad (10)$$

where $k_9 = 1.4 \times 10^9$ litre mole^{-1} s^{-1} in aqueous solution and $k_{10} = 2.3 \times 10^9$ litre mole^{-1} s^{-1} in methanol at room temperature, $Chl^{\ddagger}$ being the chlorophyll radical-cation[152].

VIII. INTERACTION WITH METAL COMPOUNDS

The study of the mechanisms of the inhibiting and catalytic effects of metal compounds in liquid-phase oxidation reactions is closely associated with the study of the joint action of these compounds with a series of important inhibitors (phenols, hydroquinone, catechol, and others). The corresponding phenoxy- and semiquinone radicals formed in the system can interact with the metal compounds. In many chemical and biochemical systems, where phenoxy- and semiquinone radicals are formed, transition metal ions and compounds are present and therefore the study of the interaction of these radicals with metal compounds is of considerable interest. Radical reactions of this type have been comparatively little investigated, although they are of fundamental importance both for the chemistry of free radicals and for the elucidation of the mechanisms of many processes in homogeneous catalysis.

It has been shwon[147] that the interaction of phenoxy- and semiquinone radicals with transition metal compounds proceeds via one of the following pathways.

$$R^{\cdot} + M^{n+}Li_m \begin{cases} \rightarrow R^{\pm} + M^{(n\mp1)+}Li_m & \text{electron transfer,} \quad (11) \\ \rightarrow {}^{\cdot}RMLi_{m-1} + Li & \text{ligand substitution,} \quad (12) \\ \rightarrow R^{\cdot} \ldots M^{n+}Li_m & \text{formation of charge-transfer complex.} \quad (13) \end{cases}$$

If reactions (11)–(13) are not dominant, then reactions (3)–(5) as a rule occur simultaneously in the system.

A change in the absorption spectrum and in the kinetics of the destruction of *o*-methylphenoxy-radicals has been observed[177] in an acid aqueous solution containing CuCl, owing to the formation of a charge-transfer complex. Spectroscopic-kinetic evidence for the existence of complexes of *o*-methylphenoxy-radicals with Cu^{2+}, Mn^{2+}, and Fe^{2+} ions was obtained similarly. The bond in the complexes is fairly weak and their formation in a polar medium is a reversible process, since their dissociation is facilitated by solvation of the ion and radical formed. The stabilisation of phenoxy-radicals due to the formation of their complexes can be observed in media of low polarity[11].

Pulse photoexcitation of *o*-cresol in benzene, toluene, and hexane leads to the formation of the *o*-methylphenoxy-radical ($\lambda max = 405$ nm in all solvents)[11]. The introduction of cobalt acetylacetonate as an additive into the solutions alters the absorption spectra of the intermediates by causing the appearance of a new absorption band in the range 440–450 nm. Such changes in the absorption spectra of the *o*-methylphenoxy-radical are due to the formation of a complex by the fast reaction

$$PhO^{\cdot} + Co(acac)_2 \rightarrow PhO^{\cdot} \ldots Co(acac)_2. \quad (14)$$

The destruction of phenoxy-radicals and their complexes with $Co(acac)_2$ follows second-order kinetics:

$$2PhO^{\cdot} \ldots Co(acac)_2 \rightarrow \text{products.} \quad (15)$$

It was observed that $k_{15} < k_{14}$. The activation energies for the annihilation reactions of the phenoxy-radicals and their complexes in benzene were found to be 3.1 and 6.5 kcal mole^{-1} respectively. The decrease in the rate constant for the destruction of the complexes and the increase in the activation energy compared with the destruction of

the phenoxy-radicals themselves shows that $Co(acac)_2$ behaves kinetically as a spatially bulky substituent in the phenoxy-radical[11]. Changes in the absorption spectrum and in the kinetics of the destruction of the *p*-methylphenoxy-radical, indicating the formation of a new species (complex), were observed in the flash photolysis of *p*-cresol in toluene in the presence of $Fe(acac)_2$.[147]

Aromatic compounds are known to be capable of forming complexes with transition metal ions and coordination compounds. This applies particularly to aromatic free radicals. The difference is that, in the formation of a complex by an unstable (in the thermodynamic sense) radical and the metal compound, the free valence is not as a rule annihilated and complexes of this type are also unstable. The unpaired electron is then delocalised over the electron shell of the metal, which may increase the relative stability of the complex.

The existence of a complex of the stable 2,4,6-tri-t-butylphenoxy-radical and $Co(acac)_2$ has been observed by ESR.[191] An interaction was discovered between the unpaired electron and the cobalt nucleus; in addition to a triplet corresponding to the phenoxy-radical, an octet due to the presence of the complex was found.

It has been concluded[11] that $Co(acac)_2$ must nave the properties of an inhibitor of liquid-phase chain oxidation reactions of hydrocarbons. Indeed, the study of the liquid-phase oxidation of cumene and the presence of $Co(acac)_2$ showed that the latter behaves as a powerful inhibitor. The oxidation of cumene in the presence of *o*-cresol and $Co(acac)_2$ is a complex process in which the intermediate complex of the *o*-methylphenoxy-radical with a chelate plays a definite role and influences the induction period[192].

The absorption spectrum of the *p*-benzoquinone radical-anion ($Q^{\cdot-}$) has been recorded in a water–propanol solvent during the flash photolysis of hydroquinone (QH_2).[193] The disappearance of the $Q^{\cdot-}$ absorption bands and the appearance of bands due to other intermediates formed via the reactions

$$Q^{\cdot-} + Cu^{+} \rightleftarrows X_1^{\cdot} \qquad (16)$$

$$Q^{\cdot-} + Cu^{2+} \rightleftarrows X_2^{+} \qquad (17)$$

was observed in the photolysis of QH_2 in the presence of Cu^{+} and Cu^{2+}. The complexes were shown to have the 1 : 1 compositions. The equilibrium constants for reactions (16) and (17) were calculated with the aid of the relation

$$\frac{1}{[X_{1,2}^{\cdot}]} = \frac{1}{K_i[Q^{\cdot-}]_0 \cdot [Cu^{n+}]} + \frac{1}{[Q^{\cdot-}]_0}.$$

The two reactions are between ions bearing charges of different sign and therefore, other conditions being equal, K_{17} should be larger than K_{16}, which is consistent with the experimental values obtained: $K_{16} = 7.0 \times 10^3$ litre mole^{-1} and $K_{17} = 1.0 \times 10^4$ litre mole^{-1} at 20°C. The importance of the Coulombic interaction in the formation of these complexes is noteworthy. When QH_2 was introduced into an acid solution (at pH 1.0; the radical $QH^{\cdot}$ is then formed), of the salts CuCl and $CuSO_4$, the formation of complexes with $QH^{\cdot}$ was not observed; the absorption spectra of the intermediates were the same as those of $QH^{\cdot}$ and the effect on the kinetics of the annihilation of $QH^{\cdot}$ was insignificant. Calculations by the MINDO/2 method of the charges on the oxygen atoms in the water molecule, the neutral *p*-benzosemiquinone radical, and the corresponding radical-anion showed that the highest charge is that of the oxygen atom in the radical-anion, which displaces a water molecule from the coordination sphere of the copper ion, and the smallest charge is in the neutral benzosemiquinone radical, which did not form any complexes. Thus the complex-formation reaction is apparently a nucleophilic substitution process[147].

The kinetics of the destruction of radical species in the systems investigated were second-order[193]:

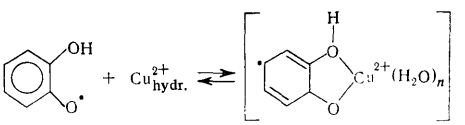
$$X_1^{\cdot} + X_1^{\cdot} \rightarrow \text{products.} \qquad (18)$$

$$X_2^{+\cdot} + X_2^{+\cdot} \rightarrow \text{products.} \qquad (19)$$

In a water–propanol medium at 20°C, $k_{18} = 1.6 \times 10^7$ and $k_{19} = 3.8 \times 10^6$ litre mole^{-1} s^{-1} at an ionic strength $I = 0$.

The above values of k_{18} and k_{19} show that the interaction of the semiquinone radical with copper ions lead to the formation of more stable radical species. The increased stability of the complexes compared with the initial radical can be caused by the partial delocalisation of the unpaired electron over the electron shell of copper and possibly by the appearance of steric hindrance in the recombination of the complexes. *o*-Benzosemiquinone and flavosemiquinone radicals can give rise to radical complexes, behaving as bidentate ligands. *o*-Benzosemiquinone radical-anions and their derivatives form complexes with many Group I–III metal ions and certain others[194–197]. These complexes, which have been investigated by ESR, consist of contact or solvent-separated ion pairs[197] or inner-sphere complexes[172,194].

The absorption spectrum of the neutral *o*-benzosemiquinone radical, obtained in a water–propanol solution in the flash photolysis of catechol has been recorded[172]. The *o*-benzosemiquinone radical forms an inner-sphere complex with the Cu^{2+} ion, where apparently $n \leq 4$:



The spectroscopic-kinetic characteristics of this complex, the complex formation constants and the rate constant for its formation and decomposition, have also been obtained. It has been established that the complex has the 1 : 1 composition. The rate constant for the destruction of the complex is two orders of magnitude larger than the rate constant for the disproportionation of *o*-benzosemiquinone radicals ($I = 0$). Thus the formation of the complex stabilises the radical as a result of the screening of the reaction centre by the oxygen atom and the delocalisation of the unpaired electron over the electron shell of the Cu^{2+} ion[172].

The study of the interaction of various flavin radical compounds with metal ions is important in the investigation of the nature of the active centres in metal-containing flavoproteins.

The complexes of flavosemiquinone radical-anions and Zn^{2+} and Cd^{2+} ions have been investigated[127,170,198,199] by electronic spectroscopy and ESR. The equilibrium

$$Fl + FlH_2 \rightleftarrows 2FeH^{\cdot}$$

shifts to the right in the presence of these metal ions:

$$Fl + FlH_2 + 2M^{2+} \rightleftarrows 2[FlM]^{+} + 2H^{+}.$$

The spin concentration then increases by a factor of 15, reaching approximately 34% of the total concentration of the flavin. It was shown that certain neutral flavosemiquinone radicals, with electron-donating substituents in the isoalloxazine ring, are capable of forming complexes with these ions[127].

The absorption spectrum of the $Fl^{\cdot-}$ radical-anion was recorded in the photoexcitation of riboflavin in dimethylformamide in the presence of a base[186]. The destruction of $Fl^{\cdot-}$ follows second-order kinetics:

$$Fl^{\cdot-} + Fl^{\cdot-} \rightarrow \text{products.} \quad (20)$$

In the presence of the salts $CdCl_2$ and $ZnSO_4$ the kinetics of the destruction of the intermediate compounds consist of two components (fast and slow). Reactions (20) and (21) correspond to the fast component:

$$Fl^{\cdot-} + M^{2+} \rightarrow \dot{F}l\,M^{+}, \quad (21)$$

and the annihilation of the complexes formed corresponds to the slow component:

$$\dot{F}lM + \dot{F}lM^{+} \rightarrow \text{products.} \quad (22)$$

$k_{22} = 2.5 \times 10^6$ and 1.0×10^6 litre mole^{-1} s^{-1} for the cadmium and zinc complexes respectively[186]. The flavosemiquinone radical-anion behaves as a bidentate ligand capable of forming complexes with metal ions having *d* electrons. On formation of the complex, the unpaired electron is delocalised over the electron shell of the metal, which stabilises the radical. The formation of a complex by the radical and the metal ion leads to a change in the redox potential. In relation to biological oxidation-reduction processes involving organometallic flavoenzymes, this implies that the system can embrace a wide range of potentials, undergoing not only $Fl \leftrightarrows FlH_2$ but also $Fl \leftrightarrows MFl^{\ddagger}$ and $MFl^{\ddagger} \leftrightarrows FlH_2$ transitions[127,186].

The complexes formed by paramagnetic ligands with diamagnetic metal ions are very rare. They are of interest for the investigation of the nature of the metal–ligand bond and also for the formation of spin labels bound to the metal in enzymes. The use of such labels is extremely promising in the study of the properties of enzymes, since it must involve the transfer of spin via the metal to the remaining parts of the ligand environment.

The absorption spectrum of the flavosemiquinone radical $FlH^{\cdot}$ has been recorded in the flash photolysis of riboflavin in water. The introduction of metal salts (including those of cadmium and zinc) into an aqueous flavin solution did not result in the formation of complexes. Some decrease of k_{20}, caused by the increase of the ionic strength, was then observed. Thus the *p*-benzosemiquinone radical can serve as a model for the elucidation of complex-formation processes involving more complicated semiquinone radicals: the $Fl^{\cdot-}$ radical-anion can form complexes with metal ions, in contrast to the neutral radical $FlH^{\cdot}$.[147]

Apart from the complex-formation reactions with transition metal ions, oxidation-reduction reactions have been observed for semiquinone radicals.

The influence of Cu^{+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, Mn^{2+}, Ho^{3+}, Cd^{2+}, Co^{2+}, Mg^{2+}, Hg^{2+}, Zn^{2+}, Ni^{2+}, and K^{+} ions on the kinetics of the annihilation of the radical-anions obtained from 2-methyleneanthraquinone has been studied[149]. In certain cases the metal ions greatly reduced the lifetime of the radicals, although in others they had little or no influence on the kinetics of the destruction of the radical-anion. On average, paramagnetic ions had a greater effect than diamagnetic ions. The sharp decrease of the lifetime of the radical, observed when Cu^{2+} and Fe^{3+} ions are added, is due to the oxidation of the semiquinone by the metal ion:

$$M^{n+} + SQ^{\cdot-} \rightarrow M^{(n-1)+} + SQ.$$

p-Benzoquinone radicals are involved in oxidation-reduction reactions with iron ions. The reactions

$$Q^{\cdot-} + Fe^{2+} \xrightarrow{+2H^{+}} QH_2 + Fe^{3+}, \quad (23)$$

$$QH^{\cdot} + Fe^{2+} \xrightarrow{+H^{+}} QH_2 + Fe^{3+}, \quad (24)$$

$$QH^{\cdot} + Fe^{3+} \xrightarrow{-H^{+}} Q + Fe^{2+} \quad (25)$$

in aqueous propanol have been investigated by flash photolysis[185]. The rate constants $k_{23} = 4.3 \times 10^5$, $k_{24} = 1.5 \times 10^5$, and $k_{25} = 7.0 \times 10^5$ litre mole^{-1} s^{-1} were obtained at 20°C. It is suggested that the oxidation-reduction reactions between transition metal ions and organic radicals proceed via the formation of a complex of the radical with the metal ion, which decomposes with formation of the reduction products of the radical and oxidation of the ion[200]. Possibly reactions (23) and (24) proceed via the same mechanism and the observed rate constants refer to the rate-limiting stage of this two-stage process[185].

IX. SOME QUANTUM-CHEMICAL CALCULATIONS ON PHENOXY- AND SEMIQUINONE RADICALS

Phenoxy- and semiquinone radicals have been the subject of a number of theoretical investigations[20,201–205]. Attention was concentrated on the calculation of the distribution of spin densities. Calculations on phenoxy-radicals by the Hückel molecular orbital method lead to a poor agreement with experiment[201]. In calculations of spin densities, Porter and coworkers[202] took into account the contributions of five excited doublet states, which led to a qualitative agreement with ESR data.

Calculations of spin density in a number of phenoxy-radicals by the molecular orbital method in terms of the Hückel and McLachlan approximations and by the valence bond method led to results in agreement with experiment[203]. The distribution of spin density in benzosemiquinone radical-anions has been calculated[204] by the LCAO-SCF-MO method in terms of the McLachlan approximation with variation of the molecular orbital parameters; the results of the calculation are in good agreement with experiment.

INDO calculations have been made on the simplest phenoxy-radical[20]. The geometry of the phenoxy-radical, the π-electronic charges on its O and C atoms, the hyperfine coupling constants, and certain other parameters were evaluated. It was found that, compared with the isoelectronic benzyl and anilino-radicals, the benzene ring is least distorted in the phenoxy-radical. A similar conclusion may be reached by considering the contributions of various valence bond schemes to the radical structure. An *ab initio* calculation has been made[205] for the unsubstituted phenoxy-radical. The electronic, nuclear, and total energies of the radical, the eigenvalues of a series of operators for various wave functions, and the hyperfine coupling constants were obtained; these data are in qualitative agreement with experimental results. In general *ab initio* calculations on such systems give a less satisfactory agreement with experimental data than calculations by semiempirical methods.

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