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Oxidation-reduction Reactions of Free Radicals

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The results of experimental studies on the oxidation-reduction reactions of free radicals with organic donors and acceptors and transition metal compounds involving one-electron transfer are surveyed. Attention is concentrated on studies performed in recent years (up to 1976 inclusive) in which the reactions of short-lived radicals have been investigated by pulse radiolysis, stopped flow, ESR, polarographic, and flash photolysis methods. The relation between the structures and reactivities of radicals in such porcesses and the methods for the measurement of their oxidation-reduction potentials are examined. Data on the formation of complexes of radicals with metal compounds are presented.
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I. INTRODUCTION

Various radical reactions proceed in the presence of metal compounds and electron donors and acceptors. Many of them are of biological importance and take place in living organisms. Free radicals, which have a high electron affinity, behave in most cases as vigorous oxidants. However, there are data suggesting that free radicals are in a certain sense amphoteric, i.e. are capable both of capturing an electron to form the carbanion and of transferring the unpaired electron to a sufficiently strong acceptor with formation of the corresponding cation[1]. Radical-ions are strongly involved in oxidation-reduction reactions, behaving as electron donors or acceptors (reactions with organic halides, initiation of polymerisation, exchange reactions, etc.).

There has been an increase of interest in recent years in the oxidation-reduction and complex-formation reactions of radicals in connection with the elucidation of the detailed mechanisms and kinetics of many homogeneous-catalytic processes, particularly liquid-phase oxidation reactions†. Emanuel' and coworkers[2-5] demonstrated the inhibiting or catalytic (depending on the conditions) effect of transition metal compounds on liquid-phase chain oxidation reactions of hydrocarbons.

The interaction of radicals with metal compounds, which are oxidation-reduction or complex-formation processes, has been postulated for a fairly long time. However, only in the last five-ten years numerous experimental data, demonstrating convincingly the occurrence of radical reactions of this class, have been obtained as a consequence of the development of the relevant experimental techniques. This review deals with the results of studies on oxidation-reduction and complex-formation reactions of radicals obtained mainly by the direct recording of the structure of the radicals and of the rates of their destruction. Attention has been concentrated on the reactions of short-lived radicals in the liquid phase.

II. ONE-ELECTRON OXIDATION (REDUCTION) OF RADICALS BY ORGANIC COMPOUNDS

It has been suggested that electron transfer is the elementary step in many organic reactions[1,6]. Numerous experimental data confirming this hypothesis have accumulated in recent years. Examples of the one-electron reduction reactions of organic compounds (R–X) are provided by the reactions with alkali metals, organic anions, or other organic electron donors (R′–Y):

$$R-X + Na \rightarrow R-X^{\cdot-} + Na^{+} ,$$
$$R-X + RO^{-} \rightarrow R-X^{\cdot-} + RO^{\cdot} ,$$
$$RX + R':Y \rightarrow R-X^{\cdot-} + R'-Y^{\cdot+}$$
$$R^{\cdot} + X^{-} \qquad R^{-} + X^{\cdot} \qquad R'^{\cdot} + Y^{+} \quad R'^{+} + Y^{\cdot}$$

In certain cases several electrons can apparently be transferred in a single stage in oxidation-reduction reactions[7]. This hypothesis is based on the general postulate that a many-electron process taking place in one stage requires a smaller expenditure of energy than the overall energy required for the consecutive transfer of several electrons.

One-electron reduction (oxidation) reactions of molecules inevitably lead to the formation of radicals (radical-ions), which may be reduced (oxidised) in the presence of the same donors (acceptors). It has been convincingly demonstrated in many instances that the oxidation of organic compounds leads to the formation of radicals

† The 1st All-Union Symposium on "Oxidation-Reduction Reactions of Free Radicals", organised by the Scientific Councils for Chemical Kinetics and Structure of the USSR Academy of Sciences and the Ukrainian SSR Academy of Science jointly with the Pisarzhevskii Institute of Physical Chemistry of the Ukrainian SSR Academy of Sciences (Chairman of Organising Committee—Corresponding Member of the Ukrainian SSR Academy of Sciences V.D. Pokhodenko) was held in Kiev during October, 1976 [see G.A.Kovtun and I.I.Moiseev, Koord. Khim., 3, 4439 (1977)]).

which are then also oxidised. Thus under certain conditions phenols are oxidised via the reactions‡ [8]

$$PhOH \xrightarrow{-e} PhO^{\cdot} + H^{+} ,$$
$$PhO^{\cdot} \xrightarrow{-e} PhO^{+} .$$
$$PhO^{+} + PhOH \rightarrow \text{products} + H^{+} .$$

The oxidation of BPh_4^- proceeds as follows [9]:

$$BPh_4^- \xrightarrow{-e} BPh_4^{\cdot} \xrightarrow{-e} BPh_4^+ ,$$
$$BPh_4^+ \rightarrow PhPh + BPh_2^+ \xrightarrow{H_2O} Ph_2BOH + H^+ .$$

The problem of the quantitative estimation of the ability of unstable radicals to be oxidised or reduced arises in this connection.

Owing to the development of pulse techniques for the investigation of fast reactions and particularly the wide availability of pulse radiolysis apparatus, it is now possible to measure fairly accurately the rate constants for electron transfer reactions involving radicals. Such reactions are important both for chemical kinetics and the chemistry of free radicals, on the one hand, and for testing the postulates of the electron transfer theory, on the other.

1. The Electron Transfer Theory

During the last three decades, electron transfer reactions (oxidation-reduction reactions) between metal complexes have been investigated vigorously. It has now become usual to divide them into reactions of the inner-sphere and outer-sphere types (see, for example, Refs. 10 and 11). The inner-sphere electron transfer between reactants X and Y can be represented as follows in a general form:

$$X + L + Y \rightleftarrows XL + Y ,$$
$$XL + Y \rightleftarrows XLY ,$$
$$XLY \rightleftarrows {}^{-}XLY^{+} ,$$
$${}^{-}XLY^{+} \rightleftarrows X^{-} + LY^{+} ,$$
$$X^{-} + LY^{+} \rightleftarrows X^{-} + L + Y^{+} ,$$

where L is the third species, constituting a binding ligand (usually an anion).

In inner-sphere electron transfer reactions the transition state is formed in such a way that the L species plays the role of a "bridge" between two metal centres, ensuring a pathway for electron transfer. There is then a possibility of the simultaneous dissociation (or formation) of a bond between the inner orbitals of the metal ion (usually between the *d* orbitals). An alternative electron transfer mechanism does not require the presence of a binding ligand and the formation (dissociation) of new bonds and is referred to as the outer-sphere mechanism§.

In certain cases (see, for example, Thornton and Laurence [13]) one distinguishes reactions in the inner sphere where the rate-limiting stage is either substitution:

$$M^{n+}X_m + L \xrightarrow{\text{slow}} M^{n+}X_{m-1}L \xrightarrow{\text{fast}} M^{(n+1)+}X_{m-1}L^{-}$$

or electron transfer:

$$M^{n+}X_m + L \xrightarrow{\text{fast}} M^{n+}X_{m-1}L \xrightarrow{\text{slow}} M^{(n+1)+}X_{m-1}L^{-} .$$

‡ Here and henceforth Ph=C_6H_5.

§ It has been suggested [12] that the first mechanism be called the "bonded mechanism" and the second the "non-bonded mechanism" in order to avoid confusion in terminology in connection with the inner-sphere and outer-sphere association of species. However, the generally accepted terminology will be used in the present review.

The ideas developed for electron transfer between metal complexes have been applied to electron transfer reactions between metal complexes and organic compounds and between organic molecules.

Criteria have been put forward for the determination of the electron transfer mechanism [12,14]. It is extremely likely that the reaction is of the outer-sphere type if the observed rate is higher than the rate at which ligands are substituted in the species being reduced (oxidised). There are also indirect methods for the determination of the electron transfer mechanism [14]. The necessity to know the electron transfer mechanism is due to the fact that a change in the structure of the metal ion or ligand leads to different types of influence on the rate of electron transfer depending on the reaction mechanism.

From the theoretical standpoint, the mechanism of outer-sphere electron transfer reactions is simpler and the theory of such reactions is developing successfully [15,16] The Marcus theory [17–21] is widely used nowadays for the analysis of experimental data for electron transfer in the outer sphere. According to this theory, the rate constant for the reaction determining the rate of the outer-sphere electron transfer,

$$A^m + B^n \underset{k_{ba}}{\overset{k_{ab}}{\rightleftarrows}} A^{m-1} + B^{n+1} ,$$

is given by the following equation:

$$k_{ab} = Z_{ab} \exp(-\Delta G^*/RT), \quad (1)$$

where Z_{ab} is the frequency factor ($\sim 10^{11}$ litre mole^{-1} s^{-1}) and ΔG^* the free energy of activation. The following relation holds for ΔG^*:

$$\Delta G^* = W + \frac{1}{4}\lambda + \frac{1}{2}\Delta G^0_{ab} + \frac{1}{4\lambda}(\Delta G^0_{ab})^2, \quad (2)$$

where W is the Coulombic term expressing the difference between the amounts of work which must be expended to join and separate reactants A^m and B^n, λ the free energy of the rearrangement of the polarised solvent associated with the change in the nature of the spatial distribution of charges on electron transfer, and ΔG^0 the standard free energy of reaction. In electron transfer reactions between radicals and organic molecules one of the reactants is in most instances uncharged and W may be regarded as zero. Eqn. (2) then simplifies:

$$\Delta G^* = \frac{1}{4}\lambda(1 + \Delta G^0_{ab}/\lambda)^2.$$

For the oxidation (reduction) of radical-ions by the initial molecules, we have

$$\Delta G^0_{ab} = 0 \text{ and } \Delta G^* = \frac{1}{4}\lambda. \quad (3)$$

If the rate of reaction approaches the diffusional rate, the following expression is used for the observed constant k_{ab}:

$$k_{ab} = k_{\text{diff}}\, k_{\text{act}}/(k_{\text{act}} + k_{\text{diff}}), \quad (4)$$

where k_{act} is the reaction rate constant according to Eqn. (1). If it is assumed that the contribution to the parameter λ is due solely to the reorientation of the solvent molecules, one can estimate the reaction radius r_{ab} by means of the equation [17–21]

$$\lambda_0 = \left(\frac{1}{2r_a} + \frac{1}{2r_b} - \frac{1}{r_{ab}}\right)\left(\frac{1}{D_O} - \frac{1}{D_s}\right)(\Delta ze)^2, \quad (5)$$

where Δz is the number of electrons transferred, r_a and r_b are the polarisation radii of the reactants, D_O is the optical dielectric constant of the solvent (the square of the

refractive index), and D_S is the static dielectric constant. It is usually assumed that [22]

$$r_a = r_b = \frac{1}{2} r_{ab}.$$

2. Reactions of Radicals with Nitro-compounds and Other Oxidants

Free radicals are known to react with various electron acceptors—quinones, dyes, nitro-compounds, etc. The study of the reactions of radicals with organic nitro-compounds is of undoubted interest for the elucidation of the mechanism of the radiation-initiated processes in chemical and biological systems. It is suggested that compounds with a sufficiently high electron affinity, particularly aromatic and heterocyclic nitro-compounds, are radiation stabilisers even at low concentrations as a result of secondary reactions involving radicals formed in the biological "targets" [23,26]. The reactions of organic radicals with nitrobenzene, nitromentane, etc. have been investigated by pulse radiolysis and ESR combined with pulse irradiation or the $Ti^{4+}-H_2O_2$ flow system [29-32]. It has been shown that such interactions may involve both addition and electron transfer reactions, the relative contributions of which depend on the nature of the organic radical, the nitro-compound, and the pH of the medium. For example, aliphatic hydroxy-radicals are ionised in an alkaline medium and electron transfer predominates; in neutral solutions, addition to the aromatic ring or the nitro-group is observed together with electron transfer [24].

It has been shown by ESR that α-hydroxy- and α-alkoxy-radicals give up an electron to suitable acceptors [28-30,32]. Alkyl radicals, β-hydroxy-radicals, $OH^{\cdot}$, and $NH_2^{\cdot}$ react with electron acceptors mainly via the addition mechanism [29,33-35].

In the general case radicals participate in oxidation reactions and reactions involving addition to the acceptor. The change in the relative contributions of these reactions as a function of the radical structure can be accounted for by the change in the electron-donating capacity of the radical. It is believed that the electron-donating capacity is characterised by the stability of the carbonium ions obtained from the radicals, which increases in the sequence [30]

$$^{+}CH_2OH < CH_3\overset{+}{C}HOH < (CH_3)_2\overset{+}{C}OH \quad .$$

The tendency towards electron transfer then varies in the sequence [24]

$$(CH_3)_2\dot{C}O^{-} > CH_3\dot{C}HCO^{-} > \dot{C}H_2O^{-} > (CH_3)_2\dot{C}OH > CH_3\dot{C}HOH > \dot{C}H_2OH \quad .$$

The reducing capacity of radicals diminishes in the sequence [25,37]

$$CO_2^{\cdot-} > (CH_3)_2\dot{C}OH > CH_3\dot{C}HOH > \dot{C}H_2OH \quad .$$

Various organic radicals may be oxidised by hydrogen peroxide and other peroxides [53]. For example:

$$\dot{C}O_2H + (CH_3)_3COOR \rightarrow H^{+} + CO_2 + (CH_3)_3C\dot{O} + RO^{-} \quad .$$

[R = H or $C(CH_3)_3$]. It has been suggested that oxygen may oxidise certain organic radicals via one-electron transfer [53]:

$$R^{\cdot} + O_2 \rightarrow R^{+} + O_2^{\cdot-} \quad .$$

The one-electron oxidation of radicals by oxygen competes with the addition reaction—the formation of a peroxy-radical [53]:

$$R^{\cdot} + O_2 \rightarrow RO_2^{\cdot} \quad .$$

The radical-anions of aromatic compounds and certain quinones also react with oxygen via electron transfer [66,87]:

$$R^{\cdot-} + O_2 \rightarrow R + O_2^{\cdot-} \quad .$$

It has been established that the ability of radicals to transfer an electron to O_2 and H_2O_2 varies in the sequence [53]

$$\cdot CO_2H > (CH_3)_2\dot{C}OH > \dot{C}H_2OH > \dot{C}H_2C(CH_3)_2OH, \quad \dot{C}H_2CH(CH_3)OH \quad .$$

$CO_2^{\cdot-}$, a strong reductant, is involved in reductive elimination reactions with various alkyl halides RX: [54]

$$CO_2^{\cdot-} + RX \rightarrow CO_2 + R^{\cdot} + X^{-} \quad .$$

One-electron reactions in which $CO_3^{\cdot-}$ is oxidised by duroquinone, benzoquinone, and 2-methylnaphthoquinone have been discovered [162,167]:

$$CO_3^{\cdot-} + Q \rightarrow \begin{matrix} CO_3 + Q^{\cdot-} \\ \swarrow \quad \searrow \\ CO_2 + 1/2O_2 \end{matrix} \quad .$$

The kinetics of electron transfer reactions between radicals and electron acceptors have been investigated mainly by pulse radiolysis. The course of the reaction can then be followed from the accumulation of the acceptor radicals, which usually absorb light in a spectral region convenient for recording. A study has been made [23] of the oxidation of the radicals obtained from alcohols by aromatic nitro-compounds. The rate constants for the radical oxidation adduct formation reactions increase with increase of the oxidation-reduction potential of the acceptor. This behaviour appears to be fairly general (see end of Section III). However, when the differences between the oxidation-reduction potentials of the acceptors E^0 are fairly small (for example, amounting to several hundredths or tenths of a volt) and the reaction kinetics approach diffusion kinetics, there may be no correlation (see also the end of Section IV, subsection 1). A relation between the rate constants for electron transfer from $O_2^{\cdot-}$, $\dot{C}H_2OH$, and $\dot{C}H_2O$ to quinones with a similar structure, on the one hand, and E^0 for the acceptor, on the other, has not been observed in a number of studies [38-40,47].

Many radicals which are important from the biological point of view react with vitamin K_3. [41] The reactions have been investigated by pulse radiolysis. Under the experimental conditions (low doses and low radical concentrations) the rate constants for the reactions of the majority of radicals with vitamin K_3 are $k \geq 2 \times 10^8$ litre $mole^{-1}$ s^{-1}¶. More than 90% of the initial radical concentration is then consumed by reaction with the vitamin. Certain radicals are hardly involved in the electron transfer reaction ($k \ll 1 \times 10^8$ litre $mole^{-1}$ s^{-1}) and participate either in the addition to the vitamin or react with one another. The cause of this may also consist in the formation of several types of radicals with different values of E^{01} under the influence of the electron pulse [41].

It has been established that certain oxidation-reduction reactions of aromatic radicals are reversible [22,66,72,157,166]. The semiquinone radical-anions $Q^{\cdot-}$ are reversibly oxidised by nitroimidazoles S and quinones [72,157]:

$$Q^{\cdot-} + S \rightleftarrows Q + S^{\cdot-} \quad ,$$

$$Q_i^{\cdot-} + Q_j \rightleftarrows Q_i + Q_j^{\cdot-} \quad .$$

Different radicals of pyridine derivatives, including the product of the one-electron reduction of nicotinamide-adenine dinucleotide (NAD$^{\cdot}$) participate in reversible

¶ The constants obtained at room temperature are quoted in this review.

reactions involving electron transfer from flavin-adenine dinucleotide (FAD):[160]

$$NAD^{\cdot} + FAD \rightleftharpoons NAD^{+} + FAD^{\cdot-}$$

The kinetics of numerous electron transfer reactions with participation of free radicals, investigated mainly by pulse radiolysis, have been analysed[22]. It has been established that the experimental data obey the Marcus theory; a satisfastory correlation has been found between $\lg k_{ab}$ and ΔG^{0}_{ab} with $\lambda \simeq 18$ kcal mole^{-1}.[22] Three groups of reactions with participation of radical-anions were examined:

$$O_2^{\cdot-} + Q \rightleftarrows O_2 + Q^{\cdot-}$$

$$RNO_2^{\cdot-} + DQ \rightleftarrows DQ^{\cdot-} + RNO_2$$

$$Q^{\cdot-} + Q^{\cdot-} \rightleftarrows Q + Q^{2-} \text{ (disproportionation of semiquinones),}$$

where Q are 1,4-quinones, $RNO_2^{\cdot-}$ are aromatic radical-anions, and DQ is duroquinone.

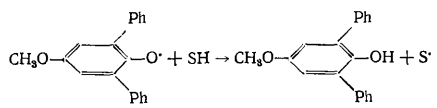
Using Eqn.(5), $r_{ab} \simeq 10$ Å, which is the distance between the centres of the reactants in the transition state for which electron transfer takes place in the given reactions, was obtained.

3. Radical Reduction Reactions

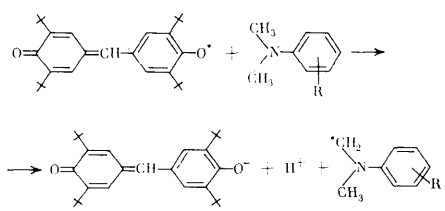
The simplest example of radical reduction reactions is the abstraction of a hydrogen atom from a suitable substrate:

$$R_1^{\cdot} + R_2H \rightarrow R_1H + R_2^{\cdot} \quad . \qquad (6)$$

Reactions of type (6) have been investigated in detail in studies on liquid-phase chain oxidation reactions of hydrocarbons[2]. Reaction (6) with $R_1^{\cdot} = OH^{\cdot}$ constitutes a common method for the generation of various free radicals (see Section VI, Subsection 1)†. Phenoxy-radicals are capable of being reduced to phenols by oxidising solvents containing mobile hydrogen atoms, for example[42]:



It has been shown[43-46] that stable phenoxy-radicals oxidise organic compounds without mobile H atoms via electron transfer:



(7)

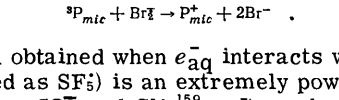
Galvinoxy- and indophenoxy-radicals are reduced to the corresponding phenoxide ions by reaction with OH^{-} and [85,103].

The inorganic radical species $SO_4^{\cdot-}$, $CO_3^{\cdot-}$, $\dot{C}O_3H$, and $Br_2^{\cdot-}$ oxidise disulphides[137], and $Br_2^{\cdot-}$, $CO_3^{\cdot-}$, and $(SCN)_2^{\cdot-}$ oxidise tryptophan[163]. These reactions proceed via one-electron transfer. The quenching of the triplet state of pyrene in micelles by the radical-anion $Br_2^{\cdot-}$ involves the same mechanism[171]:

$$^3P_{mic} + Br_2^{\cdot-} \rightarrow P^{+}_{mic} + 2Br^{-} \quad .$$

The radical obtained when e^{-}_{aq} interacts with SF_6 (tentatively identified as $SF_5^{\cdot}$) is an extremely powerful oxidant, more active than $SO_4^{\cdot-}$ and $Cl^{\cdot}$ [159]. It can be used for the effective generation of other free radicals.

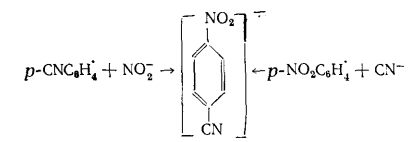
In an acid medium nitroxy-radicals are powerful oxidants. The 2,2,6,6-tetramethylpiperidinyloxy-radical oxidises H_2O_2.[84] The overall reaction equation is



In the presence of various anions, active free radicals participate in competing reactions[48]:

$$R^{\cdot} + A^{-} \begin{cases} \xrightarrow{a} [R-A]^{\cdot-} & (8a) \\ \xrightarrow{b} R^{-} + A^{\cdot} \quad . & (8b) \end{cases}$$

The relative contributions of reactions (8*a*) and (8*b*) depend on many factors—the stability of the radical-anion $[R-A]^{\cdot-}$ and the ease of the oxidation of A^{-} and the reduction of $R^{\cdot}$. The unsubstituted phenyl radical adds to NO_2^{-} or to $(CH_3)_2C{=}NO_2^{-}$, forming the $[R-A]^{\cdot-}$ species, which have been detected by ESR. *p*-Nitrophenol or *p*-cyanophenyl radicals possess powerful electron-accepting properties and, in the presence of a readily oxidisable species A^{-}, reaction (8*b*) takes place. The NO_2^{-} and CN^{-} species, which are more resistant to oxidation, react with these radicals via reaction (8*a*):



Many organic synthetic reactions involve the competing processes (8*a*) and (8*b*) as the intermediate stage[48].

The equilibrium

$$[R-A]^{\cdot-} \rightleftarrows R^{-} + A \qquad (9)$$

may be postulated. Electron transfer then takes place with the preliminary formation of $[R-A]^{\cdot-}$, i.e. via reactions (8*a*) and (9).

4. Oxidation (Reduction) of Radical-anions by the Initial Compounds

The kinetics of electron exchange reactions between organic molecules and the corresponding radical-anions and radical-cations are usually investigated by ESR; the radicals are then generated by various methods, for example by electrochemical reduction (oxidation)[49-51].

The reactions of phenothiazine, 10-methylphenothiazine, phenoxazine, and phenoxanthine radical-cations have been investigated[51]. Much attention has been devoted to the radical-anions derived from compounds such as benzonitrile, phthalonitrile, terephthalonitrile, pyromellitonitrile, 4-cyanopyridine, and a number of others. The ability of the initial neutral molecules to accept an electron is characterised by the rate constant for the reaction

$$R^{\cdot-} + R \xrightarrow{k_{10}} R + R^{\cdot-} \qquad (10)$$

and the ability to give up an electron is characterised by the constant k_{11}:

$$R^{\cdot+} + R \xrightarrow{k_{11}} R + R^{+} \quad . \qquad (11)$$

† In many instances (for example, when R_2H is an aromatic compound) the formation of H_2O and $R_2^{\cdot}$ is preceded by the formation of the adduct HOR_2H.

The above assumption is equivalent to the hypothesis that there is a correlation between the values of $\lg k_{10(11)}$ and certain quantities which may be either calculated or measured. The ability of the molecule to accept an electron is associated with its electron affinity, which in the simplest molecular orbital method is believed to be equal to $-E$, E being the energy of the lowest vacant orbital of the initial molecule. The quantity $\lg k_{10}$ should also be correlated with the electrochemical reduction half-wave potentials $E_{1/2}$. Analogous correlations are to be expected between the values of $\lg k_{11}$, the energies of the highest occupied molecular orbitals (HOMO) of R, and the corresponding oxidation potentials.

Entirely satisfactory correlations have been found between $\lg k_{11}$ and E_{HOMO} and between $\lg k_{11}$ and $E_{1/2}$.[51] Such correlations show that the energy required to remove an electron from the initial molecule may have a decisive influence on k_{11}. An analogous correlation has been obtained for reaction (10) between $\lg k_{10}$ and $E_{1/2}$. Solvation apparently plays an important role for radical-anions and it is not surprising that the values of $\lg k_{10}$ are better correlated with experimental high-wave potentials $E_{1/2}$.[51]

In the electron exchange between a quinone and the corresponding semiquinone, i.e.

$$Q^{\cdot-} + Q \rightleftarrows Q + Q^{\cdot-}$$

no correlation was observed between the rate of electron exchange and the reduction potential of the quinone[157], with no change in geometry in the course of the reaction; the authors[157] believe that the correlations observed[51] between $\lg k_{10}$ and $E_{1/2}$ reflect certain geometrical changes following electron transfer from radical-anions to the initial molecule.

The change in the geometry of the species during the reaction can have a significant influence on the rate constant for electron transfer. For example, the rate constant for the reaction involving cyclo-octatetraene

$$R^{\cdot-} + R^{2-} \rightarrow R^{2-} + R^{\cdot-} \qquad (12)$$

is $k_{12} \simeq 10^9$ litre mole^{-1} s^{-1}, while $k_{10} \simeq 10^5$ litre mole^{-1} s^{-1} or less[52]. The difference is probably caused by the fact that the $R^{\cdot-}$ and R^{2-} species derived from the given molecule are planar while R is non-planar[52].

It is possible to estimate theoretically the rate constant for the electron exchange between the initial molecule and the radical-ion in water. Using Eqns.(1) and (3) and the value $\lambda \simeq 18$ kcal mole^{-1},[22] one obtains $k_{10(11)} \simeq 5 \times 10^7$ litre mole^{-1} s^{-1}. Indeed, $k_{10} = 1 \times 10^7$ litre mole^{-1} s^{-1} has been found for the radical-anion $(CH_3)_2CO^{\cdot-}$.[22] $k = 1 \times 10^8$ litre mole^{-1} s^{-1} for the exchange between the phenoxy-radical and the phenoxide ion[22]. The exchange reaction between the nitromethane radical-anion and nitromethane has a rate constant $k_{10} < 3 \times 10^5$ litre mole^{-1} s^{-1}.[22] Such a low value of k_{10} is probably due to the significant geometrical changes accompanying the radical-anion–molecule transition. The upper limit to the values of k_{11} for the reaction

$$H^+ + H \rightleftarrows H + H^+$$

is 5×10^5 litre mole^{-1} s^{-1}. The low value of k_{11} is associated with the extremely high solvation energy of H^+.[22]

5. The Influence of the Solvent on Electron Transfer Reactions

Reactions (10) and (11) take place between species which are dipoles and between an ion and a dipole. In a solution with a macroscopic dielectric constant D the interaction energy between an ion and a dipole is expressed as follows:

$$E_{13} = ze\mu \cdot \cos(\theta/Dr^2), \qquad (13)$$

where μ is the permanent dipole moment and ze the ionic charge; the orientations of the ion and the dipole are illustrated in Fig. 1; $E_{13} = E_{max}$ when $\theta = 0$. The interaction energy between two dipoles reaches a maximum when they are arranged "head-to-tail" along a straight line:

$$E_{14} = -\frac{2\mu_1\mu_2}{Dr^3} \quad . \qquad (14)$$

The maximum interaction energy between a dipole-anion and a dipole is then given by the expression

$$E_{15} = -\mu_1\left(e + \frac{2\mu_2}{r}\right)\Big/Dr^2 \quad . \qquad (15)$$

For example, $E_{15} = 1.0$ kcal mole^{-1} is obtained for $\mu_1 = \mu_2 = 4D$, $r = 4$ Å, and $D = 35$, and we have $E_{13} = \frac{2}{3}E_{15}$.[51]

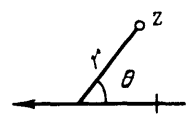


Figure 1. The mutual orientation of the ion and the dipole.

One may assume that the rate constant for electron transfer is given by the equation

$$k = Ae^{-(E_a + E_{15}/RT)}, \qquad (16)$$

where A is independent of the solvent and E_a incorporates all other factors contributing to the activation energy which are independent of the solvent[51]. One can then write $k = Z'e^{-E_{15}/RT}$ $(Z' = Ae^{-Ea})$ or

$$\ln k = \ln Z' + \mu_1(e + 2\mu_2/r)/RTDr^2. \qquad (17)$$

Eqn.(17) predicts a decrease of the rate constant with increase of the dielectric constant of the solvent. Such a tendency has been observed for reactions (10) and (11) in many solvents, with the exception of dioxan[51]. However, one must bear in mind that dioxan has a very low dielectric constant ($D = 2$); the formation of bound ion pairs in such a solvent may play a significant role and may affect the constant.

If the values of $\mu(R)$ and $\mu(R^{\cdot-})$ are known‡, it is possible to obtain from the experimental relations (17) the distance r between the reactants for which electron transfer takes place. Thus $r \simeq 4$ Å has been obtained for the benzonitrile radical-anion[51].

A study of the unimolecular reaction

$$^{\cdot-}NfCH_2 - C_6H_{10} - CH_2Nf \rightleftarrows NfCH_2 - C_6H_{10} - CH_2Nf^{\cdot-}$$

(Nf = α-naphthyl; the $NfCH_2$ substituents are in the 1,4-positions in cyclohexane) established that electron transfer requires the mutual approach of the naphthalene rings to a distance not greater than 7–9 Å.[50] The authors believe

‡ It is sometimes assumed that $\mu(R^{\cdot-}) = \mu(R)$.[51]

that electron transfer does not require a close approach of the reactants, in contrast to the reactions involving the formation of excimers, exciplexes, and charge-transfer complexes.

The electron exchange reaction between benzoquinone (duroquinone) and the corresponding semiquinone (durosemiquinone) involves a radius of 5–6 Å; the molecular radii of the species are smaller approximately by 1.5 Å. Presumably a monomolecular solvation shell remains around the reacting species at the instant of electron transfer [157].

The Marcus theory may be tested by studying the influence of the solvent on $k_{10(11)}$. Since in many instances the values of $k_{10(11)}$ are comparable to those of k_{diff}, it is useful to employ Eqn. (4). It follows from Eqns. (3) and (5) that $\lg k_{10(11)}$ should increase with decrease of the parameter $D_0^{-1} - D_s^{-1}$. However, the experimental values of $\lg k_{\text{obs}}$ and $\lg k_{ab}$ decrease as the above parameter diminishes [51]. In the Marcus theory Z is independent of the solvent. Nevertheless, there is a satisfactory linear correlation between $\lg k_{\text{obs}} - \lg k_{\text{diff}}$ and $D_0^{-1} - D_s^{-1}$; the corresponding plot has a negative slope [51]. Thus in many cases agreement between experiment and the Marcus theory requires the introduction of additional parameters, in particular, one must assume that the frequency factor depends on the solvent.

The influence of the solvent on the kinetics of reaction (10) has been investigated [49] using the radical-anion derived from *N*-(n-butyl)phthalimide as $R^{\cdot-}$. It was observed that k_{10} depends little on the solvent (hexamethylphosphoramide, 1,2-dimethoxyethane, dimethylformamide, acetonitrile, and propionitrile) despite the marked differences between the solvent viscosities and it was found that $k_{10} \simeq 3 \times 10^8$ litre mole^{-1} s^{-1}, which is less than k_{diff} for all the solvents and is close to its value for hexamethylphosphoramide. The activation energies E_{10} are higher by approximately 1 kcal mole^{-1} than the corresponding activation energies for the viscous flow of the solvents. The comparatively high values of E_{10} imply that the ions are surrounded by weakly oriented solvent molecules, which undergo a rearrangement in the transition state. The reaction is slower in 1,2-dimethoxyethane than in the other solvents; E_{10} is greater than the activation energy for the viscous flow of this solvent by 1.6 kcal mole^{-1}, which can be accounted for by the formation of ion pairs in this ether [49]. The above effect can be observed in other solvents when the concentration of the supporting electrolyte is increased [49].

The polarity of the medium has a significant influence on the kinetics of the one-electron reduction of the galvinoxy- and indophenoxy-radicals by substituted amines [reaction (7)]. [43] The rate of reaction increases with increase of the polarity of the medium, so that the dipole moment of the activated complex in the transition state is greater than the sum of the dipole moments of the reactants. The experimental values of k_7 are described satisfactorily by the relation [43]

$$\lg k_7 = \lg k_0 - \frac{A}{T} \cdot \frac{D-1}{2D+1},$$

where A is the constant.

The influence of solvent (water–alcohol) composition on the kinetics of the following reactions has been investigated by pulse radiolysis [55]:

$$CH_3CHO^{\cdot-} + C_6H_5NO_2 \rightarrow CH_3CHO + C_6H_5NO_2^{\cdot-},$$
$$CH_3C_6H_5CO^{\cdot-} + C_6H_5NO_2 \rightarrow CH_3C_6H_5CO + C_6H_5NO_2^{\cdot-},$$
$$CH_3CHO^{\cdot-} + (C_6H_5)_2CO \rightarrow CH_3CHO + (C_6H_5)_2CO^{\cdot-},$$
$$CH_3C_6H_5CO^{\cdot-} + (C_6H_5)_2CO \rightarrow CH_3C_6H_5CO + (C_6H_5)_2CO^{\cdot-}.$$

The rate constants for these reactions in water vary from 8×10^8 to 3×10^9 litre mole^{-1} s^{-1}, which is close to the value of k_{diff}. [56] The solvent was found to have a stronger influence on slow reactions than on fast reactions. There is no regularity in the influence of the solvent on the rate of reactions with the same functional groups and the kinetic parameters of reactions vary in a complex manner with the composition of the binary mixtures [55]. The observed relations cannot be accounted for with the aid of the Marcus theory. In this and other electron transfer theories the activation energy required for the reaction refers solely to the ion–solvent interaction, the solvent being regarded as a continuum [15,17,19]. It appears that a deeper understanding of the influence of the solvent on the rate of electron transfer requires allowance for the microscopic properties of the solvent surrounding the reaction species [55].

III. OXIDATION–REDUCTION POTENTIALS OF FREE RADICALS

The knowledge of the one-electron oxidation-reduction potentials of radicals (E^{01} at pH 7.0 and approximately 25 °C) could serve as a basis for the prediction of the directions and rates of the oxidation-reduction reactions of these species. Waters and Mackinnon [58] noted the important role of the oxidation-reduction potentials in the elucidation of the directions of radical reactions. They suggested that free radicals and the corresponding cations or anions form pairs of reversible oxidation-reduction systems, i.e.

$$R^{\cdot} \rightleftarrows R^+ + e; \quad R^{\cdot} + e \rightleftarrows (R:)^-$$

to which correspond two different oxidation-reduction potentials $E(-e)$ and $E(+e)$. A simple procedure was proposed for the estimation of $E(-e)$. The radicals which are involved in the chain oxidation of the initial compound RH by Fenton's reagent take part in the reaction [58]

$$R^{\cdot} + Fe^{3+} \rightarrow R^+ + Fe^{2+}; \quad R^+ + H_2O \rightarrow ROH + H^+.$$

Consequently $E(-e) < 0.74$ V for these radicals. (The potential of the $Fe^{2+}|Fe^{3+}$ pair is +0.74 V at pH 0. [58])

The ability of the radical to be oxidised has been studied in connection with investigations of the mechanism of the Kolbe electrosynthesis [59,60]. During this process, the oxidation of the carboxylate ion at the anode

$$RCOO^- \rightarrow R^{\cdot} + CO_2 + e^-$$

is followed by further oxidation of $R^{\cdot}$ to the carbonium ion:

$$R^{\cdot} \rightarrow R^+ + e^-, \qquad (18)$$

provided that the ionisation potential I of the radical is less than 8 eV. [59] A linear relation has been observed between I (determined by the electron impact method) and the potential of the electrode at which reaction (18) takes place [59]. (One should also note that there is a linear correlation between the values of I for radicals, determined by the electron impact method, and the energies of the highest occupied molecular orbitals [59].)

In many cases the values of E^{01} can be calculated from known thermodynamic quantities. $E^{01}(CO_2|CO_2^{\cdot-}) = -1.8$ V [170] and $E^{01}(O_2|O_2^{\cdot-}) = -0.16$ V [150] were evaluated in in this way.

The experimental determination of the values of E^{01} for short-lived free radicals involves certain difficulties associated with the necessity to generate radicals and to measure the values of E^{01} rapidly before the radicals are destroyed.

The potentials E^{01} for the reactions of short-lived radicals with electron acceptors and donors have been determined [39,61-64], using mainly dyes and quinonoid compounds as acceptors. The study of the interaction of dyes with radicals is of special interest, since various photochemical and radiation-chemical one-electron reduction reactions of dyes yield substrate radicals capable of reacting with the dye molecules. The proposed method is based on the investigation of the ability of the free radicals $^{\cdot}RH$ to participate in electron transfer reactions with various acceptors A, whose oxidation-reduction potentials are known:

$$^{\cdot}RH + A \rightleftarrows R + A^{\cdot-} + H^{+} \quad . \qquad (19)$$

Depending on the pH of the aqueous solution, the radical species $^{\cdot}RH$ or $A^{\cdot-}$ were found to exist either in the acid or basic form:

$$^{\cdot}RH \rightleftarrows R^{\cdot-} + H^{+} \quad ,$$
$$^{\cdot}AH \rightleftarrows A^{\cdot-} + H^{+} \quad .$$

The studies were performed by pulse radiolysis and kinetic spectrophotometry. The course of reaction (19) was monitored by following the formation of $A^{\cdot-}$ (or the protonated form $^{\cdot}AH$) or the "decolorisation" of the acceptor (usually a dye in such cases).

It was observed that the plot of the efficiency of electron transfer, expressed as a percentage, against E^{0} for the acceptors (donors) is a curve analogous to a titration curve (Fig. 2*a*). The value of E^{0} corresponding to 50% electron transfer was used to calculate E^{01} for the radical [39,52-64]. Thus one-electron potentials were obtained by means of a comparison with the known two-electron potentials, which is not entirely correct. If a correlation is observed between the two-electron potentials and any parameter associated with the one-electron transfer (such as the rate of electron transfer or the energy of the lowest vacant orbital), this implies in essence that in the given instance there is a correlation between the one- and two-electron potentials [164].

Furthermore, in the calculation of E^{01} it was implicitly assumed that equilibrium (19) can be attained and the Nernst equation was used. However, additional experiments showed that there is insufficient time for the attainment of equilibrium (19) during the experimental time interval. For example, the oxidation of the lactic acid radical,

$$CH_3\dot{C}(OH)COO^{-} + A \rightarrow CH_3COCOO^{-} + A^{\cdot-} + H^{+}$$

leads to the formation of pyruvate ions, but the observed rate of formation of the radicals $A^{\cdot-}$ is independent of $[CH_3COCOO^{-}]$. Thus there is insufficient time for the attainment of equilibrium and the reverse reaction is very slow ($k_{-10} \leq 10^{6}$ litre mole^{-1} s^{-1}) compared with the observed value $k_{19} = 3.0 \times 10^{9}$ litre mole^{-1} s^{-1}. [64] An analogous situation was observed also for the other radicals investigated, so that Eqn. (19) is inapplicable. One must therefore consider only the reaction

$$^{\cdot}RH + A \rightarrow R + A^{\cdot-} + H^{+} \quad . \qquad (20)$$

"Titration" curves (Fig. 2*a*) are obtained as a result of competition between radicals (20) and (21) (mechanism I):

$$^{\cdot}RH + {}^{\cdot}RH \rightarrow \text{products} \quad . \qquad (21)$$

and (or) between reactions (20) and (22) (mechanism II)

$$^{\cdot}RH + A \rightarrow {}^{\cdot}RHA \text{ (addition of radical)} \quad . \qquad (22)$$

For the majority of radicals investigated, mechanism I does not apparently play a significant role, since it has been found that under the experimental conditions the efficiency of the formation of $A^{\cdot-}$ (expressed as a percentage) is independent of the ratio $[A]/[^{\cdot}RH]$ in the range of the latter 15–100.

We shall now consider in greater detail mechanism II involving competition between oxidation [reaction (20)] and addition [reaction (22)] reactions. The following expressions can be formulated [23,64]:

$$-\frac{d[^{\cdot}RH]}{dt} = \frac{d[A^{\cdot-}]}{dt} + \frac{d[^{\cdot}RHA]}{dt} = (k_{20} + k_{22})[^{\cdot}RH]\cdot[A] \quad . \qquad (23)$$

Taking into account the relation

$$\frac{d[A^{\cdot-}]}{dt} = k_{20}[^{\cdot}RH]\ [A], \qquad (24)$$

we obtain

$$-\frac{d[^{\cdot}RH]}{dt} = \frac{k_{20} + k_{22}}{k_{20}}\frac{d[A^{\cdot-}]}{dt}. \qquad (25)$$

Integration with respect to time from zero to t gives

$$[^{\cdot}RH] = [^{\cdot}RH]_0 - \frac{k_{20} + k_{22}}{k_{20}}[A^{\cdot-}] \qquad (26)$$

or substituting the resulting expression for $[^{\cdot}RH]$ in Eqn. (24), we obtain the relation

$$\frac{d[A^{\cdot-}]}{dt} = k_{20}[^{\cdot}RH]_0[A] - (k_{20} + k_{22})[A][A^{\cdot-}]. \qquad (27)$$

Provided that reaction (20) has reached completion $\{d[A^{\cdot-}]/dt = 0\}$, it is possible to obtain from Eqn. (27)

$$\frac{[A^{\cdot-}]}{[^{\cdot}RH]_0} = \frac{k_{20}}{k_{20} + k_{22}} = \frac{[R]}{[^{\cdot}RH]_0}. \qquad (28)$$

The quantity $[R]/[^{\cdot}RH]_0$ is called the "percentage electron transfer". Consequently, we finally obtain the following expression for the reaction rate constant [23]:

$$k_{20} = k_{obs} \cdot (\text{percent electron transfer}), \qquad (29)$$

where $k_{obs} = k_{20} + k_{22}$. Fig. 2 presents relations between k_{20} and the oxidation-reduction potentials E^{0} of the acceptors used for the one-electron oxidation of the lactic acid radical and the dependence of the percentage electron transfer on E^{0} at the same instant after the electron pulse. The constants k_{obs} and the percentage electron transfer were also independent of the ratio $[A]/[RH^{\cdot-}]$ in the range 15–100. Examination of Fig. 2 and Eqn. (29) permits the following conclusions:

1. The reaction of the radical with acceptors involving 100% electron transfer (the upper plateau in Fig. 2*a*) is very close to a diffusion-controlled process. In this case $k_{20} = k_{obs}$ and $k_{22} \ll k_{20}$, i.e. reaction (22) is unimportant.
2. For reactions with 0% electron transfer (the lower plateau in Fig. 2*a*), we have $k_{20} \ll 10^{7}$ litre mole^{-1} s^{-1}.

In the intermediate region the efficiency of electron transfer depends on the ratio k_{20}/k_{22}. It is believed [64] that k_{20} depends strongly on E^{0} for the acceptor, while k_{22} varies comparatively little over a narrow range of ΔE^{0} values (here one must apparently assume that the chemical nature of the acceptor also changes little). Consequently, the observed changes in the "titration" curve reflect mainly the changes in k_{20} and in the observed efficiency of the electron transfer reaction (20) as a function of E^{0} for the acceptor.

Thus the method proposed [62,63] does not yield the true oxidation-reduction potentials of free radicals. The potentials corresponding to 50% electron transfer on the "titration" curves must be regarded as "kinetic" potentials E_k^{01} based on two-electron oxidation-reduction potentials of the acceptor (donor) [64]. The values of E_k^{01} are fairly close to those of E^{01}. [61-64] The differences between the numerical values are due to the fact that corrections based on the Nern equation are not used in the determination of E_k^{01}. $E^{01} < E_k^{01}$ for the oxidation of free radicals and $E^{01} > E_k^{01}$ for their reduction. The E_k^{01} scale is of definite practical value for the prediction of the rates of radical reactions. It has been found for a large class of radicals that the values of E_k^0 explain correctly the course of one-electron reactions between these radicals and the electron donors and acceptors [39,62,64,65].

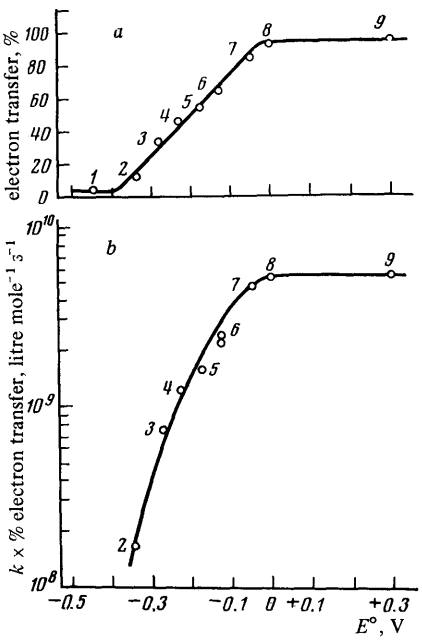


Figure 2. The one-electron oxidation of the $CH_3\dot{C}(OH)CO_2^-$ radical by different acceptors A in aqueous solution [64]: *a*) dependence of the percentage electron transfer on E^0 of the acceptor; *b*) variation of the observed rate constant for the destruction of the radical multiplied by the percentage electron transfer. The same acceptors are designated by identical numerals; the data were obtained after the elapse of the same time interval from the pulse.

The oxidation-reduction potentials of radicals make it possible to account for the relation between the ratio of the rate constants for the oxidation and addition reactions, on the one hand, and the radical structure, on the other (see Section II). Measurements of E^{01} and E_k^{01} [39,62-64] have shown that the basic forms of all the radicals investigated are stronger reductants than the acid forms. For example, $E_k^{01}[CH_3\dot{C}(OH)COOH] > E_k^{01}[CH_3\dot{C}(OH)COO^-] > E_k^{01}[CH_3\dot{C}(O^-)COO^-]$, the corresponding values being +0.16, −0.20, and −0.34 V respectively.

Electron transfer reactions may require considerable activation energies. Despite the favourable relation between the thermodynamic potentials E^{01} of the radical (provided that it is known accurately) and the acceptor (donor), the reaction cannot proceed in this case at a rate sufficient to be able to compete with other radical destruction pathways, for example, reaction (21). The kinetic potentials characterise the ability of the radical to reduce the acceptor (or to oxidise the donor) in kinetic competition with other reactions [64].

For simple aliphatic radicals and the radicals of pyrimidine basis which have been investigated [62-64], reaction (20) is not reversible [64], but the radical-anions derived from quinones and aromatic and heterocyclic nitro-compounds as well as $O_2^{\cdot-}$ participate in reversible reactions with quinones Q (see the end of Section II, subsection 2):

$$X^{\cdot-} + Q \rightleftarrows X + Q^{\cdot-} \quad . \qquad (30)$$

The true one-electron potentials at pH 7.0 have been determined for these radical-anions by pulse radiolysis [36,164-166]. These quantities have been designated by E_7^1.

Equilibrium (30) is established fairly rapidly; the destruction of radicals via the $X^{\cdot-} + X^{\cdot-}$ and $Q^{\cdot-} + Q^{\cdot-}$ reactions is much slower [36,164-166]. It has been shown that the observed spectral changes are caused solely by electron transfer. The observed first-order reaction rate constant (relaxation to the equilibrium value) is given by the relation

$$k_{obs} = k_{30}[Q] + k_{-30}[X].$$

In order to measure the one-electron potential $E_7^1(X|X^{\cdot-})$, the values of $K_{30} = \{[Q^{\cdot-}][X]/[X^{\cdot-}][Q]\}$ were obtained, Q being the reference quinone whose one-electron potential is known§. In order to calculate K_{30}, the concentrations of all the reactants under equilibrium conditions were determined, whereupon $E_7^1(X|X^{\cdot-}) = E_7^1(Q|Q^{\cdot-}) - 0.059 \lg K_{30}$. [164]

$E_7^1(O_2|O_2^{\cdot-}) = -0.155$ V was obtained by this method [164], in agreement with the calculated value [150] (see above). The values $E_7^2(O_2^{\cdot-}|O_2^{2-}) = 0.865$ V, $E_7^2(DQ^{\cdot-}|DQ^{2-}) = 0.355$ V, $E_7^1(MQ|MQ^{\cdot-}) = -0.203$ V, and $E_7^1(BQ|BQ^{\cdot-}) = 0.1$ V were also obtained (MQ = 2-methyl-1,4-naphthoquinone and BQ = 1,4-benzoquinone) together with the one-electron potentials of many other quinones and nitro-compounds [36, 164-166].

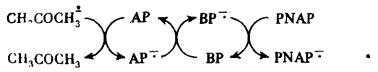
It is believed that mainly the nitro-group is involved in electron transfer from the nitro-compound RNO_2 and from the radical-anions of nitro-compounds [165]. It is therefore reasonable to seek a relation between the spin density at the nitro-group and the one-electron potentials of the radicals. The correlation $E^{01}(RNO_2|RNO_2^{\cdot-}) = 0.315 - 0.054 a^N_{NO_2}$ (volts) has been found [165]. Thus the lower the spin density at the nitro-group, the smaller the absolute value of the negative one-electron potential. Consequently, the one-electron oxidation-reduction potentials of the radical-anions of nitro-compounds can be obtained from ESR spectra, provided that certain precautions are observed [36].

The radical-anions $RNO_2^{\cdot-}$, for which $E_7^1(RNO_2|RNO_2^{\cdot-}) < E_7^1(DQ|DQ^{\cdot-})$, react effectively with DQ, whereupon the constants k_{30} vary in the range $3 \times 10^8 - 1 \times 10^8$ litre mole^{-1} s^{-1}. [36] On average, k_{30} increases as E_7^1 decreases [36].

§ The value $E_7^1(DQ|DQ^{\cdot-}) = -0.235$ V was obtained for the first time for duroquinone (DQ) in a study by Meisel and Czapski [164].

Strictly speaking, one should not expect a clear-cut correlation between the rate of electron transfer and the difference between the one-electron potentials ΔE_7^1 or the two-electron potential E^0 of the acceptor (donor). The rate of electron transfer is influenced by various factors, but in the majority of cases there is a tendency towards its increase with increasing ΔE^1 or E^0 for the acceptor within certain limits. Indeed, $\Delta E \simeq -\Delta G^\circ$ and $\Delta G^* \simeq \Delta G^0$ [see Eqns. (1) and (2)].

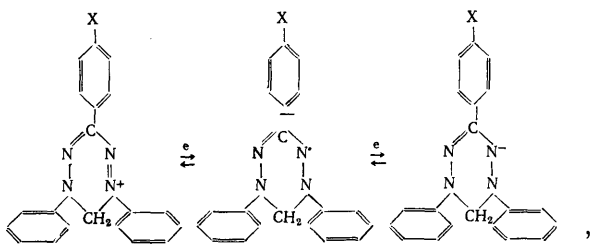
Electron transfer takes place in the acceptor molecule which has a higher (more positive) potential. Many of the so called "cascade" electron transfer processes can be accounted for on the basis of the differences between the oxidation-reduction potentials of donors and acceptors. An interesting example of the cascade electron transfer "initiated" by the electron pulse is the system containing isopropyl alcohol, acetone, acetophenone (AP), benzophenone (BP), and *p*-nitroacetophenone (PNAP):[24]



Under the experimental conditions, [AP] > [BP] > [PNAP]. It has been shown by kinetic absorption spectroscopy that the process does indeed proceed in the above sequence[24].

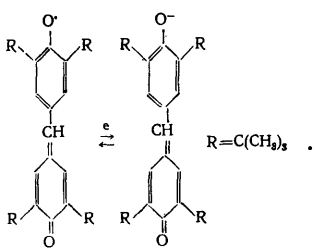
IV. THE POLAROGRAPHY OF FREE RADICALS

Certain stable radicals, for example *C*-phenyl-substituted triphenylverdazyls, are capable of undergoing reversible oxidation or reduction at a dropping mercury electrode[67], which results in one oxidation wave and one reduction wave:



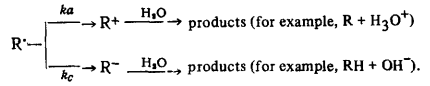
where X = H, Cl, NO_2, CH_3, or OCH_3.

The polarographic reduction of the galvinoxy-radical is also reversible with $E_{1/2} = 0.07$ V:[68]



The polarographic detection of short-lived radicals obtained as a result of an electron pulse has been used in a number of studies[70,71,154]. Such experiments yield oscillograms reflecting the time-dependence of the current. The variation of the concentration of radicals in the bulk of the solution can be investigated in the usual way—by kinetic spectrophotometry. The cathodic and anodic currents give rise to positive and negative signals respectively. The polarograms thus obtained consist of irreversible waves and cannot therefore be used to determine the oxidation-reduction potentials, but they yield valuable information about the behaviour of radicals at the mercury electrode and can be used to identify new radicals formed in the experiments on pulse radiolysis.

In contrast to stable molecules, which can give rise either to an anodic or a cathodic wave (mercury electrode in water, potentials between +0.2 and −1.9 V relative to the calomel electrode), short-lived free radicals usually give rise to both waves in the above potential range. Experiments have shown that the radicals are usually oxidised and reduced at comparable rates in a definite potential range[70]. The oxidation and reduction of radicals may be regarded as competing processes in accordance with the following scheme:



The majority of the waves obtained are completely irreversible, since the oxidation or reduction products of many radicals (such as carbonium ions or carbanions) rapidly react with water before the reverse reaction can take place at the electrode.

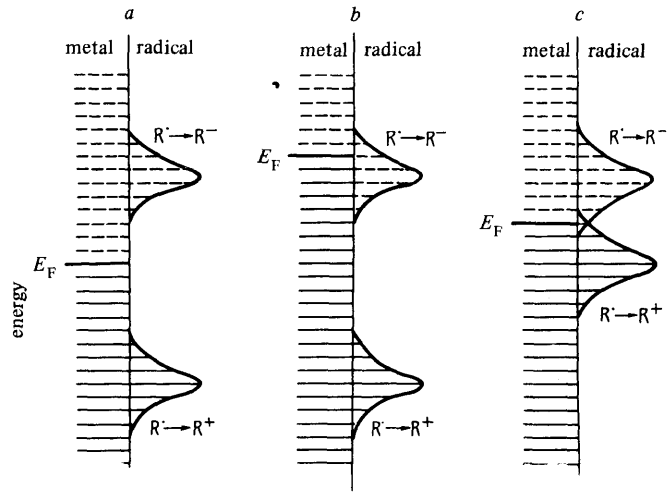


Figure 3. Schematic illustration of the distribution of the occupied and vacant levels of a metallic electrode and a radical. The vacant levels of the electrode (radical) are shown as dashed lines and the occupied levels are shown as continuous lines; E_F is the Fermi level separating the occupied and vacant levels.

The oxidation and reduction of radicals at the electrode can be considered in terms of the scheme illustrated in Fig. 3.[70] Electron transfer can take place only between levels with identical electrode energies in the following system: $R^\cdot \rightarrow R^-$ (reduction) or $R^\cdot \rightarrow R^+$ (oxidation). Thus, according to this scheme, there is neither oxidation nor reduction of R· in case *a*. With increase of the electrode potential, the energy of the occupied levels increases. Fig. 3*b* illustrates the situation where the reduction of R· should occur. (The situation where R· is oxidised may be represented analogously—for this to occur, the value of E_{ph} must be fairly low.) In the case represented in Fig. 3*c* both oxidation and reduction can take place at comparable rates.

A polarographic study of $CO_3^{\cdot-}$ confirmed the ability of this radical-anion to participate in both oxidation and reduction reactions; it has been established that $E^1(CO_3^{\cdot-}|CO_3^{2-}) > E^1(CO_3|CO_3^{\cdot-})$.[158] The study of the polarograms of radicals has made possible definite conclusions about their structures[70].

V. THE R· + R· → PRODUCTS REACTION: RECOMBINATION, DISPROPORTIONATION, OR ELECTRON TRANSFER?

It was shown above (Sections II–IV) that free radicals are capable of being both reduced and oxidised in reactions with stable species. Presumably, when two radicals differing in their oxidation-reduction potentials react, electron transfer will again occur. This hypothesis was put forward by Hayon and coworkers[62] on the basis of a study of the oxidation-reduction potentials of short-lived radicals. Indeed, if the radical $\cdot R_2H$ in the reaction

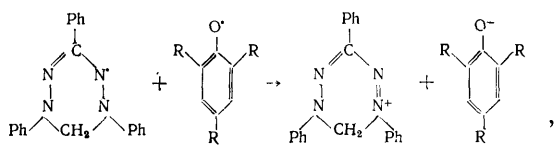
$$\cdot R_1H + \cdot R_2H \rightarrow R_1 + R_2H_2$$

has a more positive potential, then, according to the ideas developed above (Section III), one may expect electron transfer from $\cdot R_1H$ to $\cdot R_2H$.[62] The final reaction products will be the same as in the generally accepted mechanism of radical disproportionation (via H atom transfer).

Pokhodenko and coworkers[73–75] observed one-electron transfer in reactions between many stable free radicals:

$$R_1^{\cdot} + R_2^{\cdot-} \rightarrow R_1^{+} + R_2^{-} \quad , \qquad (31)$$

where, for example, $R_1^{\cdot}$ = triphenylverdazyl and $R_2^{\cdot}$ = 2,4,6-tri-t-butylphenoxyl, galvinoxyl, indophenoxyl, etc. The radical of Wurster's blue oxidises certain triphenylverdazyl radicals and is itself oxidised to the corresponding doubly-charged cation by nitroxy-, phenoxy-, and a number of other stable radicals[75]. The reaction products were identified on the basis of their absorption spectra and the reaction kinetics were followed from the time variation of the intensity of the ESR signal of one of the radicals. It was shown that the reaction



$R=C(CH_3)_3$, (32)

in chlorobenzene is described by the second-order kinetic equation: $k_{32} = 8 \times 10^8 \exp(-16\,300 \pm 500)/RT)$ litre mole^{-1} s^{-1}.[73]

Evidently a significant charge separation takes place in the transition states of reactions (31) and (32), so that k_{32} increases with increasing polarity of the medium[73]. The generation of an e.m.f. in electron transfer reactions between two stable free radicals has also been observed[74].

The radical-anions of sulphoanthraquinones ($AQ^{\cdot-}$) react with the 4-hydroxy-2,2,6,6-tetramethylpyridino-1-oxy-radical (RNO·) via electron transfer[57]:

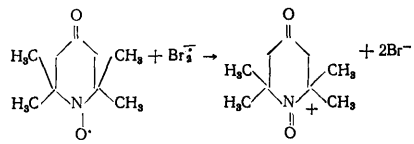
$$AQ^{\cdot-} + RNO^{\cdot} \rightarrow AQ + RNO^{\cdot-} \quad .$$

Reaction (32) has a high activation energy and is comparatively slow at room temperature. It is of interest to elucidate the possibility of the occurrence of electron transfer steps in rapid reactions of short-lived radicals with stable radicals or with one another. The stable nitroxy-radical 2,2,6,6-tetramethyl-4-oxopiperidino-1-oxyl (TAN) (AP·) reacts with a wide variety of organic and inorganic radicals[76,155]. The rate constants for these reactions are close to the diffusional values. It is not clear whether these reactions involve addition or electron transfer or whether both pathways are involved in competition[76,155]:

$$R^{\cdot} + AP^{\cdot} \rightarrow R - AP \quad , \qquad (33)$$

$$R^{\cdot} + AP^{\cdot} \rightarrow R^{+} + AP^{-} \; (R^{-} + AP^{+}) \quad . \qquad (34)$$

However, it can be regarded as proved that the fast reaction



(35)

involves electron transfer with $k_{35} = 1.6 \times 10^9$ litre mole^{-1} s^{-1}.[76] Indirect evidence has been obtained[73] that the reaction between the active acetyl radical and the triphenylverdazyl radical also involves electron transfer:

$$\rangle N^{\cdot} + CH_3COO^{\cdot} \rightarrow \rangle N^{+} + CH_3COO^{-} \quad .$$

The fast reaction of the radical-anion of anthraquinone-2,6-disulphonic acid ($A^{\cdot-}$) with the $NO_3^{\cdot}$ radical proceeds via the same mechanism[77]:

$$A^{\cdot-} + NO_3^{\cdot} \rightarrow A + NO_3^{-} \quad , \qquad (36)$$

$$k_{36} = 1.0 \cdot 10^8 \text{litre mole}^{-1}\,\text{s}^{-1}.$$

There is at present no convincing evidence showing that the reactions of uncharged short-lived radicals with one another involve electron transfer. However, hypotheses of this kind have been put forward in a number of studies[62,69,70,148,154]. Radicals capable of being both reduced and oxidised with equal case should have overlapping levels[70] (Fig. 3*c*, Section IV). It can be assumed that such radicals may be destroyed as a result of the formation of ion pairs on collision in solution[70]:

$$R^{\cdot} + R^{\cdot} \rightarrow R^{+} + R^{-} \quad .$$

This process should probably be regarded as involved in competition with the usual radical destruction reactions—recombination and disproportionation via the transfer of a hydrogen atom. For example, the destruction of hydroxycyclohexadienyl radicals can be represented as follows[154]:

$$\begin{array}{l} \cdot C_6H_6OH + \cdot C_6H_6OH \rightarrow C_6H_6OH^{+} + C_6H_6OH^{-} \\ \qquad\qquad\qquad\qquad\qquad\qquad \downarrow \qquad\qquad \downarrow \\ \qquad\qquad\qquad\qquad\qquad\qquad C_6H_5OH + H^{+} + C_6H_6 + OH^{-} \quad . \end{array} \qquad (37)$$

The detection among the products of reactions between two R· species of compounds whose formation via recombination or disproportions cannot be postulated [for example, C_6H_6 in reaction (37)] would constitute evidence in support of one-electron transfer. The solvent may influence the rate of reaction between two R· species in the manner predicted by the electron transfer theory; such data must be regarded as indirect evidence for electron transfer.

It is well known that alkyl radicals recombine with formation of a new chemical bond between carbon atoms having an unpaired electron:

$$RCH_2CH_2^{\cdot} + R'CH_2CH_2^{\cdot} \rightarrow R\,(CH_2)_4R' \qquad (38)$$

(in the special case where R = R′). The rates of the majority of these reactions are limited by diffusion and their activation energies are close to zero[78]. If one of

the radicals has an H atom in the β-position relative to the radical centre, there is a possibility of a competing disproportionation reaction [78]:

$$RCH_2CH_2^{\cdot} + R'CH_2CH_2^{\cdot} \rightarrow RCH_2CH_2 + R'CH{=}CH_2 \quad . \qquad (39)$$

Reaction (39) is also diffusion-controlled [78]. The recombination (disproportionation) of such radicals via electron transfer is apparently impossible. In contrast to reactions (38) and (39), the electron transfer reaction

$$RCH_2CH_2^{\cdot} + R'CH_2CH_2^{\cdot} \rightarrow RCH_2CH_2^{+} + R'CH_2CH_2^{-} \begin{cases} \rightarrow \\ \rightarrow R(CH_2)_4R' \\ \rightarrow RCH_2CH_3 + R'CH{=}CH_2 \end{cases} \qquad (40)$$

requires an activation energy ΔG^{*} [Eqn.(1)] and in addition the formation of a carbonium ion and a carbanion is a highly endothermic process.

On the other hand, many long-lived or stable radicals with different E^{1} values cannot participate in recombination (disproportionation) reactions and are converted into diamagnetic products via electron transfer [reaction (31)]. One can probably postulate that there exists an "intermediate" class of radicals for which ΔG^{*} [Eqn.(1)] is comparable to $\Delta G^{\neq}$ for recombination (disproportionation) reactions and the radical destruction reaction is in fact reaction (40) involved in competition with reactions (38) and (39).

The reaction

$$R^{\cdot} + R^{\cdot} \rightarrow \text{products} \qquad (41)$$

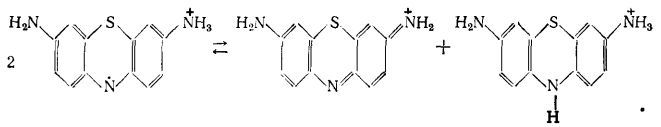
is one of the fundamental processes in the chemistry of short-lived radicals. If it is indeed found that certain radical destruction reactions proceed via electron transfer (the rate-limiting stage), then the kinetics and mechanisms of these reactions in different solvents have to be described in terms of the concepts developed for electron transfer reactions (Section II).

Reaction (41) involves electron transfer if the R$^{\cdot}$ species are radical-ions. Examples of these reactions are the disproportionation of the radical-anions of quinones (Q) or aromatic molecules (Ar):

$$Q^{\cdot-} + Q^{\cdot-} \rightleftarrows Q^{2-} + Q \ ,$$

$$Ar^{\cdot-}, M^{+} + Ar^{\cdot-}, M^{+} \rightleftarrows Ar^{2-}, 2M^{+} + Ar \ .$$

Radical-cations also disproportionate in solutions, for example [79]:



Rapid electron transfer reactions between radical-cations and radical-anions,

$$R_1^{\cdot-} + R_2^{\cdot+} \rightarrow R_1^{\cdot} + R_2 + h\nu \ ,$$

are frequently accompanied by chemiluminescence.

It is noteworthy that rotational diffusion, leading to the mutual orientation of the reactants in the solvent cage required for the occurrence of their reaction, should apparently play a smaller role in bimolecular reactions involving the destruction of radical-ions than in the reactions where uncharged radicals are destroyed [78,79]. This can be understood if account is taken of the fact that the electron transfer takes place over fairly long distances (see Section II, subsection 5).

VI. REACTIONS OF RADICALS WITH METAL COMPOUNDS

Different classes of organic compounds can undergo chemical transformations via a free-radical mechanism in the presence of transition metal compounds. Examples of such processes are the decomposition of peroxides, the halogenation of aliphatic compounds, the amination of aromatic compounds, certain cyclisation reactions, and other processes catalysed by transition metal compounds. Many photochemical reactions of complex compounds lead to the formation of free radicals, which are then involved in dark reactions with metal compounds. In a general form, one can postulate that the interaction of a radical with a metal compound proceeds via one (or several simultaneously) of the following pathways [80,168]:

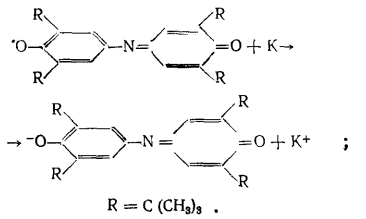
$$R^{\cdot} + M^{n+}L_m \begin{cases} \rightarrow RH + L'M^{n+}L_{m-1} & \text{(abstraction of hydrogen),} \\ \rightarrow RL + M^{n-1}L_{m-1} & \text{(ligand transfer),} \\ \rightarrow R^{\pm} + M^{(n\mp1)+}L_m\,(M^{n+}L^{\mp}L_{m-1}) & \text{(electron transfer),} \\ \rightarrow {}^{\cdot}RM^{n+}L_{m-1} + L & \text{(ligand substitution),} \\ \rightarrow R^{\cdot}\ldots M^{n+}L_m & \text{(formation of charge-transfer complexes).} \end{cases}$$

Examples of these reactions and the rules that they obey are discussed below.

The influence of transition metal compounds on many organic reactions with radical mechanisms is discussed in a number of reviews [11,81,101,168] and a monograph [82]. Since the publication of the review [83] devoted to the kinetics of the reactions of radicals with metal compounds, many new data have become available.

1. Oxidation-reduction Reactions of Radicals with Metals and Their Compounds

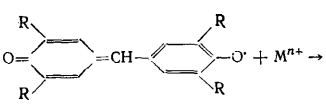
Alkali metals, which are powerful reductants, are capable of reducing various organic species, including free radicals. The indophenoxy- and galvinoxy-radicals react with metallic potassium and are converted into the corresponding phenoxide anions [85,103]:

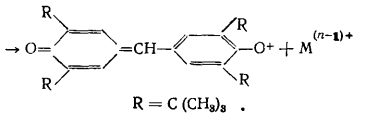


Aromatic radical-anions are reduced to the corresponding dianions [87]:

$$Ar^{\cdot-}, K^{+} + K \rightarrow Ar^{2-}, 2K^{+} \ .$$

Apart from electron-accepting properties, stable phenoxy-radicals can exhibit the properties of electron donors. 2,4,6-Tri-t-butylphenoxy-, galvinoxy, and indophenoxy-radicals undergo one-electron oxidation in the presence of Lewis acids $MHal_n$ (M = Sb^{V}, Nb^{V}, Ti^{IV}, Sn^{IV}, or Al^{III}; Hal = Cl or Br), as well as $VOCl_3$ and $AgClO_4$ in various solvents. For example:





$R = C(CH_3)_3$. (42)

The occurrence of reactions of this kind has been demonstrated convincingly by ESR, NMR, spectrophotometric, and polarographic methods [88,89]. The stability of the diamagnetic salts obtained in reactions (42) depends on the structure of the radicals being oxidised, the nature of the oxidant, and the medium. The rate of reaction (42) is described by a second-order kinetic equation: $k_{42} \simeq 10-10^3$ litre mole^{-1} s^{-1} for different $NHal_n$. The study of the interaction of 2,2,6,6-tetramethyl-4-oxopiperidino-1-oxy-radical and DPPH with Group III metal halides showed that the nitroxy-radicals form a complex with $MHal_3$ while DPPH is oxidised to the corresponding cation [89-91]. The results permit the conclusion that the electron-donating properties of the radicals in many respects determine the kinetic parameters of the reaction of stable radicals with $MHal_3$. When the galvinoxy-radical is converted into DPPH, the activation energy of the type (42) reaction increases, owing to the weaker electron-donating properties of DPPH ($E_{1/2} > 0.5$ V) compared with the galvinoxy-radical ($E_{1/2} = 0.38$ V). The nitroxy-radical has a higher oxidation potential ($E_{1/2} \simeq 0.9$ V) and the reaction stops in this instance at the stage involving the formation of the complex [89-91].

A classical example of the manifestation of the electron-donating capacity of free radicals is the reduction of heavy metal salts by the triphenylmethyl radical [92]:

$$Ph_3C^{\cdot} + AgClO_4 \rightarrow Ph_3C^+ClO_4^- + Ag \ .$$

The oxidation of organic compounds via a radical process in the presence of metal ions has been investigated in the course of eight decades with the aid of Fenton's reagent; this involves the following fundamental processes [93]:

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + OH^{\cdot} \ , \quad (43)$$

$$HO^{\cdot} + Fe^{2+} \rightarrow Fe^{3+} + OH^- \ , \quad (44)$$

$$HO^{\cdot} + RH \rightarrow H_2O + R^{\cdot} \ . \quad (45)$$

The radicals formed participate in the destruction reaction

$$R^{\cdot} + R^{\cdot} \rightarrow \text{products}, \quad (46)$$

and can regenerate Fe^{2+} or be reduced, oxidising Fe^{2+} at the same time:

$$R^{\cdot} + Fe^{3+} \rightarrow Fe^{2+} + \text{products} \quad (47)$$

$$R^{\cdot} + Fe^{2+} \xrightarrow{+H^+} Fe^{3+} + RH \ . \quad (48)$$

Apart from Fenton's reagent, other $H_2O_2 + M^{n+}$ systems are used to generate radicals (see subsection 3 of this section).

In later investigations organic radicals were generated in different systems by pulse radiolysis or by a flow technique, the radicals being identified on the basis of their ESR spectra [95]. Here the active reactant is OH$^{\cdot}$, obtained in the radiolysis of water (pulse radiolysis [66]) or on decomposition of H_2O_2 (using a flow technique).

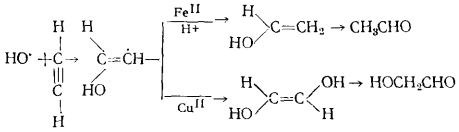
The data accumulated make it possible to classify radicals in terms of their capacity to participate in oxidation-reduction reactions. The radicals forming comparatively stable carbonium ions oxidise iron(III) effectively and quantitatively [reaction (47)]. They include radicals containing an OH or OR group, amide nitrogen, and tertiary alkyl substituents in the α-position. Primary and secondary alkyl radicals are inert in relation to iron-(III), while allyl and benzyl radicals occupy an intermediate position. All these species effectively oxidise copper(II). [93]

Conjugated carbonyl radicals and related radicals giving rise to comparatively stable anions are inert with respect to oxidation by copper(II) or iron(III). They are readily reduced by iron(II) [reaction (48)], for example [96]:



Furthermore, iron(II) reduces the radicals derived from carboxylic acids with a free valence in the α-position, for example $R(R')\dot{C}CO_2H$, $\dot{C}H_2CO_2H$, and $\dot{C}H(CO_2H)_2$. [97]

Radicals derived from alcohols and carboxylic acids show the opposite tendencies in their capacity to oxidise or reduce iron ions. It has been shown [97] that the ability of hydroxyacid radicals $\dot{R}(OH)CO_2H$ to participate in oxidation-reduction reactions with iron ions is determined by the OH group and not the CO_2H group. Vinyl radicals, obtained as a result of attack by hydroxy-radicals on acetylene, are unique in the sense that they are capable of being both oxidised by copper (II) [but not by iron(III)] and of being reduced by iron(II). [93] Thus acetylene is converted by Fenton's reagent into acetaldehyde in the absence of copper(II) and into hydroxyacetaldehyde in the presence of copper(II):



The oxidation of iron(II) proceeds selectively and the efficiency of the oxidation varies in parallel with the stabilities of the carbonium ions obtained [93].

The iron(III)–EDTA system oxidises different radicals obtained on radiolysis of alcohols, aldehydes, ketones, and dicarboxylic acids [98]. The principal factor influencing the ability of the radical to be oxidised is its structure. Radicals with an unpaired electron in the α-position relative to the functional group as well as radicals without functional groups which would prevent the attainment of the necessary mutual orientation of iron(III) and the reaction centre of the radical are oxidised by iron(III). The oxidation can be very rapid; for example, $k_{47} > 4 \times 10^8$ litre mole^{-1} s^{-1} has been estimated for $\dot{C}H_2OH$. [93] In contrast to this, the ligand exchange reactions of iron(III) have rate constants $k < 10^4$ litre mole^{-1} s^{-1}. These two findings thus agree with an outer-sphere electron transfer mechanism involving the formation of a product of the carbonium ion type:

$$R^{\cdot} + Fe^{III} \rightleftarrows R^+ + Fe^{II} \ . \quad (49)$$

Primary and secondary alkyl radicals are not oxidised, probably because in this case equilibrium (49) is displaced to the left [96,99].

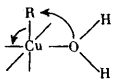
The reduction of many organic radicals by iron(II) is also a very rapid process with $k \geqslant 10^7$ litre mole^{-1} s^{-1} [100] and proceeds more effectively the greater the stability of the resulting carbanion, which also indicates an outer-sphere electron transfer mechanism [93]:

$$Fe^{II} + R^{\cdot} \rightleftarrows Fe^{III} + R^- \ .$$

Iron(II) is oxidised by disulphide radical-cations [137]:

$$Fe^{II} + RSSR^+ \rightarrow Fe^{III} + RSSR \ .$$

As stated above, reaction (47) is reversible for primary and secondary alkyl radicals. One can therefore postulate that copper(II), the weakest oxidising agent, cannot oxidise these radicals via an outer-sphere mechanism. It has been shown [93,101] that the radicals are oxidised with formation of an intermediate organocopper compound, which decomposes into hydroxylated products and copper(I):



Oxidation with the aid of copper(II) is usually slower than oxidation by iron(III).[93] The oxidation rate constants for alkyl radicals are $k \simeq 10^6-10^8$ litre mole^{-1} s^{-1},[102] and ligand substitution in the coordination sphere of copper then proceeds fairly rapidly (the bimolecular rate constants are $k \simeq 10^9-10^{10}$ litre mole^{-1} s^{-1}). Consequently the rate-limiting stage in these inner-sphere reactions is electron transfer (see Section II, subsection 1).

It is noteworthy that copper(II) is in general highly reactive in relation to free radicals [11,53,66,94,101,102,104]. Copper(I) compounds can be readily oxidised to copper(II) in their turn. These properties apparently constitute the explanation of the wide-scale employment of copper compounds as catalysts in reactions involving free radicals. Cu^{2+} ions effectively oxidise certain aromatic radicals—chloranil radical-anions ($CQ^{\cdot-}$), anthraquinone-2,6-disulphonic acid radical-anions ($AQ^{\cdot-}$), and 2-hydroxy-1-naphthoxy-radicals [Nf(OH)O$^{\cdot}$]:

$$CQ^{\cdot-} + Cu^{2+} \rightarrow CQ + Cu^{+};\ k = 1.0\cdot10^9 \text{ litre mole}^{-1}\text{ s}^{-1}$$

(in a 9 : 1 mixture of propanol and water by volume) [80],

$$AQ^{\cdot-} + Cu^{2+} \rightarrow AQ + Cu^{+};\ k = 1.0\cdot10^6 \text{ litre mole}^{-1}\text{ s}^{-1}$$

(in water) [140],

$$Nf(OH)O^{\cdot} + Cu^{2+} \rightarrow \text{products};\ k = (3.2 \pm 0.6)\cdot10^6 \text{ litre mole}^{-1}\text{ s}^{-1}$$

(in water) [141].

The oxidation of alkyl radicals by many transition metal compounds in solution leads to the formation of olefins and alkyl derivatives [102]. The following mechanisms may be postulated for these reactions:

$$\rangle CH-\dot{C}\langle \rightarrow \rangle C=C\langle + H^+ + e \quad \text{(oxidative elimination);}$$

$$\rangle CH-\dot{C}\langle + N \rightarrow \rangle CH-\overset{|}{\underset{|}{C}}-\overset{+}{N} + e \quad \text{(oxidative substitution).}$$

Here N is a nucleophile (HOAc, HOR, CH_3CN, ArH, etc.);

$$M^{n+}(OAc^-)_n + e \rightarrow M^{(n-1)+}(OAc^-)_n \quad \text{(reduction of metal compound).}$$

The rates of oxidation of n-butyl, isopropyl, and neopentyl radicals by a copper(II) carboxylate have been determined in acetonitrile–acetic acid mixtures [102]. The neopentyl radical is oxidised much more slowly than the other alkyl radicals. An alkylcopper compound is also postulated as an intermediate [102]:

$$(CH_3)_3C\dot{C}H_2 + Cu^{II} \rightleftarrows [(CH_3)_3CCH_2Cu],$$
$$[(CH_3)_3CCH_2Cu] \rightarrow Cu^{I} + (CH_3)_3CCH_2^+ .$$

Whereas iron(II) ions are capable of reducing only radicals forming comparatively stable anions, titanium(III) ions reduce a wide variety of radicals—alkyl and hydroxyalkyl radicals, radicals derived from carboxylic acids, etc.[97] The reaction

$$Ti^{III} + \dot{C}H(COOH)_2 \rightarrow \text{products } (Ti^{IV}) \qquad (50)$$

was investigated by ESR combined with radiolysis *in situ*: $k_{50} = 8 \times 10^6$ litre mole^{-1} s^{-1}.[97] The authors [97] believe that the mechanism of this reaction is similar to that adopted for the reduction of hydrogen atoms by iron(II), which includes the formation of a metal hydride intermediate:

$$Fe^{II} + H^{\cdot} \rightarrow Fe^{II}-H^{\cdot},$$
$$Fe^{II}-H^{\cdot} + H^+ \rightarrow Fe^{III} + H_2 .$$

This mechanism can be adopted for the reduction of radicals with an unpaired electron at the carbon atom:

$$R^{\cdot} + M^{n+} \rightarrow M^{n+}-R,$$
$$M^{n+}-R + H^+ \rightarrow M^{(n+1)+} + RH .$$

These are apparently inner-sphere reactions [97,105].

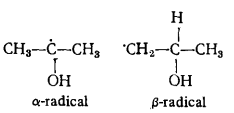
Titanium(III) ions oxidise formic acid radicals [106]:

$$^{\cdot}CO_2H + Ti^{III} \rightarrow Ti^{II} + CO_2 + H^+ \qquad (51)$$

with $k_{51} \simeq 5 \times 10^6$ litre mole^{-1} s^{-1}. One may claim (see Section III) that the rate constant for the interaction of the radical-anion with titanium(III) is still greater. Comparison of the rate of substitution by ligands in the coordination sphere of titanium(III) with the rate of reaction (51) suggests that the reaction with titanium(III) proceeds via an outer-sphere mechanism [106].

Europium(III) ions also oxidise $^{\cdot}CO_2H$ and $CO_2^{\cdot-}$; the rate constant is $k > 7 \times 10^6$ litre mole^{-1} s^{-1}. The reaction does not proceed with ytterbium(III), chromium(III), and scandium(III). It follows from a comparison of the standard oxidation-reduction potentials that chromium(III) is most readily reducible. However, the outer-sphere conversion of chromium(III) into chromium(II) requires a large reorganisation energy in view of the presence of tetragonal distortions in the high-spin chromium(II) complex. The inner-sphere reaction is ruled out in view of the inertness of chromium(III) in relation to substitution [106].

The ability of radicals to participate in oxidation-reduction reactions with metal compounds depends significantly on the structure of the radicals. For example, the α-radical of isopropyl alcohol is oxidised by titanium(IV), iron(III), and chromium(III) more effectively than the β-radical [107]:



because the carbonium ion corresponding to the α-radical is more stable (see Section II, subsection 2).

The inorganic radical-anions $Cl_2^{\cdot-}$ and $Br_2^{\cdot-}$ oxidise Fe^{2+}, Co^{2+}, and Mn^{2+} ions [13,108,109]. The reactions were investigated by flash photolysis. The reaction

$$Cl_2^{\cdot-} + Fe^{2+} \rightarrow Fe^{3+} + 2Cl^- \qquad (52)$$

proceeds via an outer-sphere mechanism with $k_{52} = (1.0 \pm 0.2) \times 10^7$ litre mole^{-1} s^{-1}. The inner-sphere reaction

$$Cl_2^{\cdot-} + Fe^{2+} \rightarrow FeCl^{2+} + Cl^- \qquad (53)$$

has a smaller rate constant: $k_{53} = (4.0 \pm 0.6) \times 10^6$ litre mole^{-1} s^{-1} [13].

The oxidation of $Cl_2^{\cdot-}$ and $Br_2^{\cdot-}$ by Mn^{2+} ions takes place with formation of an intermediate complex, which then decomposes into products [109]. The rate-limiting stage in this inner-sphere reaction is electron transfer. The oxidation of Fe^{2+} by the $Br_2^{\cdot-}$ radical-anion and of Co^{2+} by $Cl_2^{\cdot-}$ also proceeds via an inner-sphere mechanism, the rate-limiting stage being the substitution reaction [13,108]. The second-order rate constants have been obtained for all the inner-sphere reactions: $k = 10^6$ litre mole^{-1} s^{-1} [13, 108,109].

The $N_3^{\cdot 2-}$ radical-anion oxidises Fe^{2+} via an inner-sphere mechanism

$$N_3^{\cdot} + Fe^{2+} \rightarrow Fe^{III} + N_3^-$$

with $k > 1.7 \times 10^9$ litre mole^{-1} s^{-1}.[156]

The reduction of OH$^{\cdot}$ by Fe^{2+} ions has been investigated by pulse radiolysis[110] and it has been established that the reaction proceeds as an outer-sphere electron transfer:

$$OH^{\cdot} + Fe^{2+}(H_2O)_6 \rightarrow Fe^{3+}(H_2O)_6,\ OH^- \xrightarrow{H^+} Fe^{3+}(H_2O)_6 + H_2O \qquad (54)$$

with $k_{54} = (2.3 \pm 0.2) \times 10^8$ litre mole^{-1} s^{-1}.[110] The corresponding reaction of OD$^{\cdot}$ radicals in D_2O is characterised by the rate constant $k_{54} = (9.4 \pm 0.8) \times 10^7$ litre mole^{-1} s^{-1}. The difference between the rates of these reactions is due to the difference between the free energies of hydration of the ions in the solvents[110]. Many other oxidation-reduction reactions of the OH$^{\cdot}$ radical have been examined[83,169].

The reaction between pentammine(ligand)cobalt(III) complexes and the *p*-nitrobenzoate radical-anion has been investigated by pulse radiolysis:

$$[Co^{III}(NH_3)_5X] + {}^-O_2N\text{–}C_6H_4\text{–}CO_2^- \rightarrow Co^{2+}_{aq} + 5NH_3 + X + NO_2\text{–}C_6H_4\text{–}CO_2^- \qquad (55)$$

where X = NH_3, $PhCO_2^-$, p-$O_2NC_6H_4CO_2^-$, Br^-, pyridine, or m-$H_2NCOC_5H_4N$. The reaction proceeds via an outer-sphere mechanism in all cases with $k_{55} \simeq 10^6$–10^7 litre mole^{-1} s^{-1}. The reactants initially form an outer-sphere ion pair (they approach one another to a distance equal to the reaction radius) and then electron transfer takes place:

$$[Co^{III}(NH_3)_5X] + {}^-O_2CC_6H_4NO_2^{\cdot 2-}\text{-}n \rightleftarrows [Co^{III}(NH_3)_5X,\ {}^-O_2CC_6H_4NO_2^{\cdot 2-}\text{-}n] \xrightarrow{k_{56}} Co^{2+}_{aq} + 5NH_3 + p\text{-}O_2NC_6H_4CO_2^- + X \qquad (56)$$

The intramolecular electron transfer reaction

$$[Co^{III}(NH_3)_5(O_2CC_6H_4NO_2\text{-}n)]^+ \rightarrow Co^{2+}_{aq} + 5NH_3 + p\text{-}O_2NC_6H_4CO_2^- \qquad (57)$$

was found to have $k_{57} = 2.6 \times 10^3$ s^{-1} with $k_{57} < k_{56}$, i.e. the intramolecular transfer is slower. The most probable explanation of this is that the carboxylate ion exhibits a comparatively low "electron permeability"[111].

The rate constants for reactions with participation of *m*- and *o*-nitrobenzoate radical-anions, analogous to reaction (57), are 1.5×10^2 and 4.0×10^5 s^{-1} respectively[112,166]. The increase of the rate of reaction by several orders of magnitude for the ortho-isomer is probably due to the overlapping of the orbitals of the nitro- and carboxy-groups, which generates an effective pathway for electron transfer. The study of the distribution of spin density in the radical helps to interpret the kinetic data[166].

The strong reductant $CO_2^{\cdot -}$ is oxidised by various cobalt(III) complexes[111]:

$$CO_2^{\cdot -} + Co^{III}(NH_3)_5X^{2+} \rightarrow CO_2 + \text{reduced complex.} \qquad (58)$$

The reaction has been investigated by pulse radiolysis combined with the method of competition kinetics: $k_{58} = 10^7$–10^9 litre mole^{-1} s^{-1}. The complexes investigated can be divided into two groups: (1) highly reactive complexes whose reactions involve direct attack on the ligand and electron transfer to an available orbital localised at the ligand; (2) complexes exhibiting a moderate reactivity in which ligand orbitals of lower energies are saturated and the available antibonding orbitals have high energies. As in the study of Land and Swallow[113] (see below), no direct correlation was observed between k_{58} and the overall charge of one of the reactants (in the present instance the complex). k_{58} is more influenced by the properties of the complex as a whole than by the properties of any one free ligand X. Nor was a correlation observed between the rate constants for electron transfer from the $CO_2^{\cdot -}$ and $^{\cdot}CH_2OH$ radical species to the $Co^{III}(NH_3)_5X^{2+}$ complexes [reaction (58)] and E^0 for the complex. This can be explained by the comparatively low values of E^0 for such complexes (see Section II, subsection 2), which corresponds to a small difference between their free energies. One can then expect that other factors affect the rate constant for the electron transfer reaction[38].

The ions of metals in unusual valence states inhibit or catalyse various chemical reactions. Reactions of Ni^+ ions with radicals have been investigated[114]. The Ni^+ ions and organic radicals were generated by an electron pulse, the intermediates being detected on the basis of the absorption spectra and conductimetrically. It was found that Ni^+ is capable of reducing various radicals extremely effectively and of forming intermediate complexes:

$$Ni^+ + {}^{\cdot}CH_2C(CH_3)_2OH \rightarrow Ni^{2+} + CH_2 = C(CH_3)_2 + OH^-,$$
$$Ni^+ + CO_2^{\cdot -} \rightarrow NiCO_2,$$
$$Ni^+ + {}^{\cdot}CH_2OH \rightarrow NiCH_2OH^+,$$
$$Ni^+ + \dot{C}(CH_3)_2OH \rightarrow NiC(CH_3)_2OH^+.$$

The complexes interact with water:

$$NiCH_2OH^+ + H_2O \rightarrow Ni^{2+} + CH_3OH + OH^-$$

or with another Ni^+ ion, forming metallic nickel

$$Ni^+ + NiC(CH_3)_2OH^+ \rightarrow Ni^{2+} + Ni + (CH_3)_2\dot{C}OH.$$

Pb^{2+} ions oxidise via a one-electron transfer mechanism hydroxyalkyl radicals and the $CO_2^{\cdot -}$ radical-anion[161]:

$$Pb^{2+} + CO_2^{\cdot -} \rightarrow Pb^+ + CO_2,$$
$$Pb^{2+} + (CH_3)_2\dot{C}OH \rightarrow Pb^+ + (CH_3)_2CO + H^+.$$

Pb^+ ions may be reduced to metallic lead in reactions with hydroxyalkyl radicals[161]:

$$Pb^+ + (CH_3)_2\dot{C}OH \rightarrow Pb\dot{C}(CH_3)_2OH^+ \rightarrow Pb + H^+ + (CH_3)_2CO.$$

The reaction proceeds via the formation of an intermediate radical-ion complex.

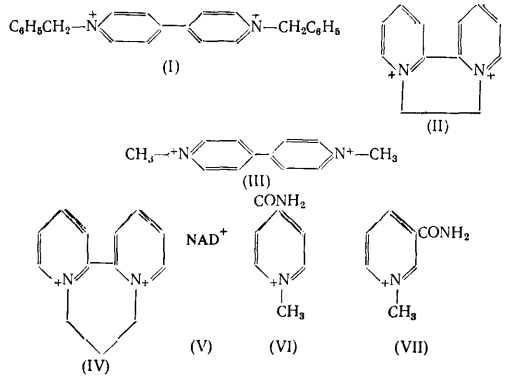
Pb^+ ions are oxidised by the radicals obtained on radiolysis of solutions in t-butyl alcohol and cyclopentane[161]:

$$Pb^+ + {}^{\cdot}CH_2(CH_3)_2COH \rightarrow Pb^{2+} + OH^- + CH_2 = C(CH_3)_2,$$
$$Pb^+ + C_5H_9^{\cdot} \xleftarrow{H_2O} Pb^{2+} + C_5H_{10} + OH^-.$$

Cytochrome *c* effectively oxidises various radicals:

$$Fe^{III}\ cyt\ c + R^{n+} \rightarrow R^{(n+1)+} + Fe^{II}\ cyt\ c. \qquad (59)$$

$k_{59} = 2.4 \times 10^8$ litre mole^{-1} s^{-1} for lactic acid radicals[115], $k_{59} = 5 \times 10^8$ litre mole^{-1} s^{-1} for $CO_2^{\cdot -}$ radical-anions[116], and $k_{59} = 1.8 \times 10^8$ litre mole^{-1} s^{-1} for radicals derived from ethanol[115]. The oxidation of pyridine radicals by cytochrome *c* has been studied by pulse radiolysis[113]. The radicals were obtained by the one-electron reduction of the following bypyridylium and pyridylium compounds:



The resulting rate constants can be divided into two groups. It was found that $k_{59} = (1.8 \pm 0.4) \times 10^8$ litre mole^{-1} s^{-1} for the radical species derived from the bipyridylium salts (I)–(IV) and $k_{59} = (8 \pm 1) \times 10^8$ litre mole^{-1} s^{-1} for the radical species obtained from compounds (V)–(VII).[113] The difference between the values of k_{59} for these groups of radical species may be accounted for by the presence of the positive charge in the radical species from compounds (I)–(IV), which should retard the reaction with the positively charged cytochrome *c*, but this effect is weakened owing to the high ionic strength of the solution. The main reason for the difference may be that the oxidation-reduction potentials of compounds (I) to (IV) are in the range between −0.3 and −0.55 V,[117] while those of compounds (V)–(VII) are in the range between −0.9 and −1.1 V.[113] The reaction apparently proceeds via attack on the part of the porphyrin ring remote from Fe(III), which is confirmed by the high values of k_{59} and resembles the reaction with an organic acceptor rather than with a simple metal complex[41,113].

2. Complexes of Radicals with Transition Metal Compounds

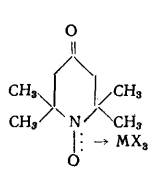
The oxidation-reduction reactions between radicals and metal compounds involving inner- or outer-sphere mechanisms terminate with the decomposition of the intermediate complex or the collision complex into the final products. However, in both cases complexes of the charge-transfer type, association complexes, or coordination compounds with radical ligands may be formed when no oxidation-reduction reactions are observed. Apart from the chemical affinity between the radical and the metal compound, paramagnetic interactions may play an important role in the formation of such complexes, because many metal ions have unfilled or partly filled orbitals, Complexes of radicals and metal compounds (ions) are of great interest, because complex formation alters greatly the reactivity of the radicals. In many cases this entails a relative stabilisation of the radical.

Depending on the degree of charge transfer, the structures of the complexes can be conventionally described by the following formulae:

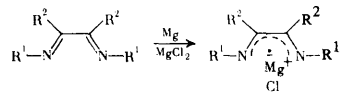
$$R^{\cdot}\,M^{n+};\quad R^{+}M^{(n-1)+};\quad R^{-}M^{(n+1)+}.$$

The metal in complexes of this kind is frequently in an unusual valence stage. The radical ligand has an unpaired electron which is highly delocalised. Under these conditions, the splitting of the ESR spectral lines of the radical, caused by the interaction of the unpaired electron with the paramagnetic metal nucleus, is observed in many instances[66,101]. Despite this, the radical retains its nature in many complexes, which has been confirmed by ESR studies[101].

Stable aliphatic nitroxy-radicals form in solution complexes with aluminium(III) and gallium(III) halides[90,91]. The existence of complexes of the 2,2,6,6-tetramethyl-4-oxopiperidino-1-oxy-radical with the above compound has been demonstrated by ESR. The most probable structure of the complexes is shown below:

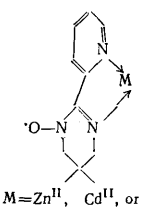


Here the vacant orbital of the Lewis acid interacts with the 3-π-electron fragment N...O, which leads to a slight distortion of the planar configuration of the complex at the nitrogen atom and to an increase of a_N compared with the initial nitroxy-radical[91]. Stable radicals capable of forming complexes with ions having filled electron shells (d^0 or d^{10}) may be obtained by the one-electron reduction of molecules containing the fragments shown below:



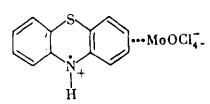
These may be $\alpha\alpha'$-bipyridyl, *o*-phenanthroline, etc. The ESR spectra of a number of such complexes of glyoxal-bis-*N*-t-butylimine (R_1 = t-butyl and R_2 = H) have been recorded[118]. The ESR data have shown that the unpaired electron is delocalised over the entire complex MLCl, including the halogens.

Paramagnetic ligands capable of delocalising the unpaired electron over diamagnetic metal atoms are extremely rare. Complexes of this kind are of interest for the investigation of metal–ligand bonds as well as spin labels linked to the metal ion in proteins. When such labels are employed, spin density is transferred from the radical ligand via the metal to the remaining part of the ligand environment. The stable pyridyliminonitroxy-radical forms complexes with various diamagnetic metal ions[119]:

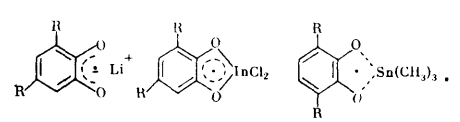


M=Zn^{II}, Cd^{II}, or Hg^{II}.

In certain cases complexes of radicals with metal compounds may be isolated in a crystalline state[120]. The tetrachloro-oxomolybdate of the phenothiazinium radical-cation, isolated in the solid state, gives rise to an ESR spectrum with a single broad signal (g = 1.98), while the ESR spectrum of the complex in solution consists of two superimposed singlets with different g-factors[120]:



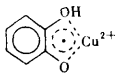
The ions of Groups I–III metals form complex with *o*-quinone radical-anions[121–125]. ESR data have shown that the majority of the complexes remain π-radicals and the degree of transfer of spin density to the metal ion is low[124]. The nature of the oxygen–metal bond has a marked influence on the distribution of the unpaired electron density in the *o*-semiquinone and on the hyperfine interaction with the paramagnetic nucleus of the central atom. Complexes with alkali metal ions, for example, complex (VIII), can be regarded as contact ion pairs:



(VIII) (IX) (X)

R = $C(CH_3)_3$

Complexes formed with thallium(I) or indium(III) ions [for example, compound (IX)] are apparently chelates[123]. Significantly higher constants for the hyperfine interaction with metal nuclei compared with contact ion pairs have been obtained from the ESR spectra of the chelates[123]. The ESR spectrum of the tin-containing radical (X), which can be usefully regarded as an organoelemental radical rather than a complex, has been measured[128]. Thus the ESR data for radical complexes make it possible to investigate the nature of the oxygen–metal bond. The complexes of neutral semiquinone radicals having a chelate unit have been recorded by flash photolysis[86]:



The complexes of short-lived radicals with transition metal compounds are destroyed via second-order reactions, like the radicals themselves, but the rate constants are significantly lower than those for the destruction of free radicals. Complexes of the *p*-benzoquinone radical-anion ($Q^{\cdot-}$) with Cu^{n+} ions have been detected[104]. The rate constants for the reactions

$$Q^{\cdot-} + Q^{\cdot-} \xrightarrow{2H^+} Q + QH_2 \qquad (60)$$

$$Q^{\cdot-}Cu^{+} + Q^{\cdot-}Cu^{+} \rightarrow \text{products.} \qquad (61)$$

are $k_{60} = 1.2 \times 10^8$ litre mole^{-1} s^{-1} and $k_{61} = 1.6 \times 10^7$ litre mole^{-1} s^{-1} (in water).

The complex $Pb\dot{C}(CH_3)_2OH^+$, formed by the Pb^+ ion with the α-radicals derived from isopropyl alcohol, has a much longer life in solution than the initial radical[161]. However, the ion pairs involving radical-anions are destroyed faster than the initial radicals. The rate constants for the reactions

$$T^{\cdot-} + T^{\cdot-} \rightleftarrows T^{2-} + T \ , \qquad (62)$$

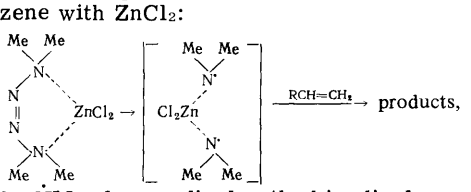
$$T^{\cdot-}, Na^+ + T^{\cdot-}, Na^+ \rightleftarrows T^{2-}, 2Na^+ + T \qquad (63)$$

of the tetraphenylethylene (T) radical-anions in tetrahydrofuran (THF) have been estimated: $k_{62} < 10^3$ and $k_{63} < 8 \times 10^6$ litre mole^{-1} s^{-1}.[129] In this case the Coulombic repulsion of the similarly charged species [reaction (62)] has a decisive influence on the kinetics[129]. The rate constant $k_{64} = 1 \times 10^7$ litre mole^{-1} s^{-1} has been obtained for the reaction between the ion pair and the radical:

$$T^{\cdot-}, Na^+ + T^{\cdot-} \rightleftarrows T^{2-}, Na^+ + T \ . \qquad (64)$$

Reaction (63) is slower than reaction (64), since two Na^+ ions are desolvated simultaneously in the transition state of reaction (63).[129]

As stated above, the reactivity of the radicals changes markedly on formation of complexes. Evidence has been obtained[130] for the existence of a biradical complex formed on thermal decomposition of the complex of tetramethyl-2-tetrazene with $ZnCl_2$:



In contrast to the $\dot{N}Me_2$ free radicals, the biradical reacts very selectively with olefins, forming aminoalcohols. The coordinated radicals with O- and N-centres are apparently inactive in chain transfer steps in oxidation and polymerisation reactions, which is important in connection with the problem of the inhibiting activity of phenols, aromatic amines, and related compounds[131,132].

The ability of transition metal ions to catalyse the recombination of methyl radicals is explained by the formation of an intermediate species—the complex of the alkyl radical with the metal ion, which is stable in relation to the abstraction of a hydrogen atom and participates only in the reaction with the analogous complex[133]:

$$CH_3^{\cdot} + M^{n+} \rightleftarrows {}^{\cdot}CH_3M^{n+} \ ,$$

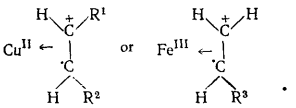
$$2\dot{C}H_3M^{n+} \rightarrow C_2H_6 + 2M^{n+} \ .$$

Studies by pulse radiolysis have shown that $OH^{\cdot}$ forms a complex with benzoatopentamminecobalt(III),[134] adding to the ligand—the benzoate anion:

$$(NH_3)_5\,Co^{III}\,(O_2CC_6H_5OH)$$

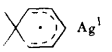
The complex is destroyed via a second-order reaction: $k = 9.3 \times 10^7$ litre mole^{-1} s^{-1}, which is significantly less than the rate constants for the reactions of $OH^{\cdot}$ radicals and their adducts with benzoic acid and benzoate ion (1.2×10^8 and 4.4×10^8 litre mole^{-1} s^{-1} respectively)[134].

When s-butyl-lithium was oxidised with the aid of di-isopropyl salicylate or copper(II) or iron(III) acetylacetonate, ESR spectra were recorded[126]. The absence of splitting by the copper nucleus and the low constants for the hyperfine splitting by protons enabled the authors to attribute the following structure to the complexes:



The unpaired electron is localised in an orbital of the carbon atom[126].

Hyperfine splitting by the silver nucleus has been observed in the ESR spectra of many silver(I)–olefin radical complexes ($g = 2.0017$) formed when polycrystalline silver complexes of olefins are subjected to γ-irradiation[127]. Analogous complexes with a radical ligand have been obtained on irradiating compounds of silver perchlorates with cyclohexa-1,3-diene or cyclohexa-1,4-diene. The constants for hyperfine splitting by the protons in the complex



are virtually the same as in the spectrum of the free cyclohexadienyl radical, which indicates a weak interaction between the hydrocarbon radical and the nucleus of the metal ion[127].

The formation of a complex by the benzyl radical and chromium(II) has been reported[135]:

$$PhCH_2^{\cdot} + Cr^{II} \rightleftarrows PhCH_2Cr^{II} \ .$$

Complexes of related aromatic radicals—semiquinone and phenoxy-radicals—have been discussed in a review[66].

Many complexes of radicals and transition metal ions (compounds) have structures resembling very closely those of ion pairs formed by aromatic radical-anions and alkali metal ions. The difference consists in the absence of electrostatic attraction which holds together ion pairs[101].

The study of the interaction of peroxy-radicals $RO_2^{\cdot}$ with transition metal compounds is of interest in connection with the investigation of homogeneous-catalytic liquid-phase oxidation of hydrocarbons. The existence of complexes formed by peroxy-radicals $RO_2^{\cdot}$ with vanadyl, cobalt, and manganese acetylacetonates and naphthenates has been suggested[136–138]. The studies were performed by the ESR method, solutions of the hydroperoxide ROOH and $M^{n+}L_m$ being mixed. The authors believe that the formation of the complex stabilises $RO_2^{\cdot}$. However, it is

not stated[136-138] whether ROOH has been completely consumed at the time when the ESR spectra of the stabilised $RO_2^{\cdot}$ were observed. If ROOH were present in solution, then fairly high $RO_2^{\cdot}$ concentrations might have been observed for a long time simply owing to the decomposition of the hydroperoxide[139], which throws doubt on the conclusions reached by the authors[136-138].

3. Interactions of the Hydroperoxy-radicals with Metal Ions

Under certain conditions, hydroperoxy-radicals capable of interacting with metal ions are formed in systems of the type of Fenton's reagent. In the presence of an excess of H_2O_2, $HO_2^{\cdot}$ radicals are formed by the reaction[142]

$$Ce^{4+} + H_2O_2 \rightarrow Ce^{3+} + H^+ + HO_2^{\cdot} \qquad (65)$$

or via the reactions[142-144]

$$M^{n+} + H_2O_2 \rightarrow M^{(n+1)+} + OH^- + OH^{\cdot}\ , \qquad (66)$$

$$OH^{\cdot} + H_2O_2 \rightarrow H_2O + HO_2^{\cdot}\ , \qquad (67)$$

$M^{n+} = Ti^{3+}$, Fe^{2+}, V^{4+}, or Cr^{2+}.

The interaction of the hydroperoxy-radical with metal ions was studied on stopped flow apparatus with two mixing chambers: the $HO_2^{\cdot}$ radical was formed in the first chamber via reaction (65) and, when the latter had reached completion, the solution was mixed with the solution of the metal ions in the second chamber. The changes in the system were followed on the basis of the ESR spectra.

The method of flash photolysis with detection of intermediates by ESR is convenient for kinetic measurements. $HO_2^{\cdot}$ radicals are then generated via reaction (67) and

$$H_2O_2 + h\nu \rightarrow 2OH^{\cdot}$$

in a cell located in the cavity of the ESR spectrometer. It is also possible to investigate the reactions of $HO_2^{\cdot}$ radicals by the method of steady-state radiolysis in combination with a flow system and ESR.

The existence of complexes of $HO_2^{\cdot}$ with a number of transition metal ions, such as Ti^{4+}, Zr^{4+}, Ce^{3+}, V^{5+}, Th^{4+}, U^{6+}, Mo^{6+}, etc. has been established[142,145-151]:

$$M + HO_2^{\cdot} \rightleftarrows M{-}HO_2^{\cdot}\ . \qquad (68)$$

The complexes may be formed not only via reaction (68) but in many instances also as a result of the interaction of the $HO_2^{\cdot}$ or $OH^{\cdot}$ radicals with the $M-H_2O_2$ complex[142]:

$$M{-}H_2O_2 + HO_2^{\cdot} \rightarrow M{-}HO_2^{\cdot} + H_2O_2\ ,$$

$$M{-}H_2O_2 + OH^{\cdot} \rightarrow M{-}HO_2^{\cdot} + H_2O\ .$$

In the presence of ions of two metals, M and M′, ESR spectra due to two species have been recorded: $M-HO_2^{\cdot}$ and $M'-HO_2^{\cdot}$. The occurrence of the reversible reaction[142]

$$M{-}HO_2^{\cdot} + M' \rightleftarrows M'{-}HO_2^{\cdot} + M \qquad (69)$$

was demonstrated. This may be a bimolecular reaction [Eqn.(69)] or it may proceed via the association of the complex $M-HO_2^{\cdot}$ [the reverse process in reaction (68)] followed by the formation of the complex with the M′ ion. Reaction (69) involving many pairs of ions has been observed: $U^{6+}-Th^{4+}$, $Th^{4+}-Zr^{4+}$, $Zr^{4+}-U^{6+}$, $Th^{4+}-Ti^{4+}$, $U^{6+}-Ti^{4+}$, $V^{5+}-Ti^{4+}$.[142] Kinetic studies have shown that the exchange reaction between Cu^{2+} and Th^{4+} ions is more likely to proceed via the direct transfer of $HO_2^{\cdot}$ than via a dissociation-association mechanism[145]:

$$Cu^{2+} + [Th{-}HO_2]^{4+} \rightleftarrows [Cu{-}HO_2^{\cdot}]^{3+} + Th^{4+}\ , \qquad (70)$$

where $K_{70} = 3 \times 10^2$.

Apart from the $M-HO_2^{\cdot}$ complexes, more involved $M-HO_2-M'$ complexes may exist[145]. The $HO_2^{\cdot}$ radical disproportionates in solution:

$$HO_2^{\cdot} + HO_2^{\cdot} \rightarrow H_2O_2 + O_2 \qquad (71)$$

with $k_{71} = 6.7 \times 10^5$ litre mole^{-1} s^{-1}.[152] Under the experimental conditions, the lifetime of the $HO_2^{\cdot}-M$ complexes is significantly longer than that of $HO_2^{\cdot}$. This is one of the reasons why the ESR spectra of many such complexes have been recorded. The Zr^{4+}, Th^{4+}, and U^{6+} complexes are destroyed via first-order reactions for higher values of [M]. The lifetime of such complexes varies from several tenths of a second to several seconds[142]. The lifetime of the $Nb^{5+}-HO_2^{\cdot}$ and $La^{3+}-HO_2^{\cdot}$ complexes is significantly shorter, which gives rise to certain difficulties in their detection[146].

Apart from their involvement in complex-formation reactions, the $HO_2^{\cdot}$ and $O_2^{\cdot-}$ radical species participate in oxidation-reduction reactions. Thus Cu^{2+} oxidises the $HO_2^{\cdot}$ radical[152]:

$$Cu^{2+} + HO_2^{\cdot} \rightarrow Cu^+ + H^+ + O_2 \qquad (72)$$

with $k_{72} \simeq 1 \times 10^8$ litre mole^{-1} s^{-1}. Reaction (72) also proceeds via the formation of a complex[145]:

$$Cu^{2+} + HO_2^{\cdot} \rightleftarrows [Cu{-}HO_2^{\cdot}]^{2+}\ , \qquad (73)$$

$$[Cu{-}HO_2^{\cdot}]^{2+} \rightarrow Cu^+ + H^+ + O_2 \qquad (74)$$

[$K_{73} = (5.1 \pm 1.0) \times 10^7$ litre mole^{-1}, and $k_{74} = 30 \pm 5$ s^{-1}] and reaction (74) determines the rate of oxidation for higher values of $[Cu^{2+}]$.

The oxidation of $O_2^{\cdot-}$ by Cu^{2+} ions also proceeds with formation of an intermediate complex[149,151,152]:

$$Cu^{2+} + O_2^{\cdot-} \rightarrow [CuO_2]^+ \rightarrow Cu^+ + O_2 \qquad (75)$$

with $k_{75} = (1.7 \pm 0.3) \times 10^9$ litre mole^{-1} s^{-1}¶[150,151].

It has been found that the complex of $O_2^{\cdot-}$ and Cu^{2+} exists and that its lifetime is shorter than that of the complex with $HO_2^{\cdot}$.[145,152] This is quite reasonable, since $O_2^{\cdot-}$ is a stronger reducing agent than $HO_2^{\cdot}$: $E^0_c(O_2|O_2^{\cdot-}) < E^0_c|HO_2^{\cdot})$ [39] (see Section III). Cu^+ ions reduce $HO_2^{\cdot}$ and $O_2^{\cdot-}$:[152]

$$Cu^+ + O_2^{\cdot-} \xrightarrow{2H_2O} Cu^{2+} + H_2O_2 + 2OH^-\ , \qquad (76)$$

$$Cu^+ + HO_2^{\cdot} \xrightarrow{H^+} Cu^{2+} + H_2O_2 \qquad (77)$$

with $k_{76} > 10^9$ litre mole^{-1} s^{-1} and $k_{77} \simeq 10^{10}$ litre mole^{-1} s^{-1}.

In contrast to Cu^{2+} ions, Fe^{3+} ions oxidise $O_2^{\cdot-}$ via an outer-sphere mechanism:

$$Fe(H_2O)_6^{3+} + O_2^{\cdot-} \rightarrow Fe(H_2O)_6^{3+},\ O_2^{\cdot-} \rightarrow Fe^{2+} + O_2 \qquad (78)$$

with $k_{78} = (8 \pm 2) \times 10^8$ litre mole^{-1} s^{-1}.[49,150]

Titanium(IV) and vanadium(V) ions form fairly stable complexes with $O_2^{\cdot-}$.[149] Analysis of the results of ESR studies of these complexes and the interpretation of the structures of the complexes with the aid of the molecular orbital method have shown that the molecular oxygen in the coordination spheres of these metal ions should have a singlet ground state[149]. This conclusion makes it possible to explain the relative stability of the radical complexes with respect to electron transfer within the inner-sphere. The highest molecular orbitals of $O_2^{\cdot-}$ are designated by π^* (HOMO) and $\bar{\pi}^*$. The energetically most favourable direct electron transfer $\pi^* \rightarrow t_{2g}$ with formation of singlet oxygen in the coordination sphere is forbidden by symmetry considerations. Electron transfer

¶ According to Rabani et al.[152], $k_{75} = 8 \times 10^9$ litre mole^{-1} s^{-1}.

from the $\bar{\pi}$ orbital to the t_{2g} orbital requires a large activation energy, since it leads to the formation of oxygen in the excited triplet state [149].

The high rate of electron transfer within the inner sphere in the $Cu^{2+}O_2^-$ complex is apparently caused by the σ-coordination of oxygen [149].

The kinetics and mechanism of the formation and destruction of radical complexes in the titanium(IV)–H_2O_2–cerium(IV) system have been investigated in detail [147] by ESR. The accumulation of the radical $Ti^{IV}O_2^-$ complex in this system proceeds via the reactions

$$Ti^{IV}(O_2^{2-}) + Ce^{IV} \underset{k_b}{\overset{k_a}{\rightleftarrows}} Ti^{IV}(O_2^{2-})\,Ce^{IV} \xrightarrow{k_{79}} Ti^{IV}(O_2^-) + Ce^{III}, \quad (79)$$

$k_a = 5 \cdot 10^4$ litre mole s^{-1}, $k_b = 130\ s^{-1}$, $k_{79} = 75\ s^{-1}$.

The $Ti^{IV}O_2^-$ complex is destroyed via the reactions:

$$Ti^{IV}O_2^- + Ce^{IV} \rightleftarrows Ti^{IV}(O_2^-)\,Ce^{IV} \xrightarrow{k_{80}} Ti^{IV} + Ce^{III} + O_2, \quad (80)$$

$$Ti^{IV}O_2^- + H^+ \rightleftarrows HO_2^{\cdot} + Ti^{IV}, \quad (81)$$

$$Ti^{IV}O_2^- + Ti^{IV}O_2^- \rightarrow \text{products}, \quad (82)$$

$$Ti^{IV}O_2^- + HO_2^{\cdot} \rightarrow \text{products} \quad (83)$$

$k_{80} = 7\ s^{-1}$, $k_{81} = 2$ litre $mole^{-1}\ s^{-1}$, $k_{82} \leqslant 500$ litre $mole^{-1}\ s^{-1}$, $k_{83} \geqslant 2{,}8 \cdot 10^5$ litre $mole^{-1}\ s^{-1}$, $k_{-81} \geqslant 2{,}8 \cdot 10^9$ litre $mole^{-1}\ s^{-1}$.

The reversible formation of copper(II) complexes of O_2^- has also been observed in an organic medium [153]. In the oxidation of methanol in an alkaline medium and of cumene, it was observed that the catalytic effect of the copper complexes of *o*-phenanthroline (*o*-P) is due to the formation of the complex $Cu^I(o\text{-P})_2$ in the system, which coordinates oxygen, forming a copper(II) complex:

$$Cu^I(o\text{-P})_2 + O_2 \rightleftarrows Cu^{II}(o\text{-P})_2O_2^-$$

---o0o---

Thus many reactions involving free radicals proceed via one-electron transfer. Fairly extensive experimental data on the oxidation-reduction reactions of radicals have now accumulated, which makes it possible to establish certain structural-kinetic rules. Kinetic data are very important for the theory of electron transfer and for its further development.

The vast majority of free radicals are short-lived in liquid solutions, which necessitated the use of flow or pulse techniques in order to obtain reliable information about reactions involving them. The use of the pulse radiolysis method proved to be extremely promising for the measurement or estimation of one-electron potentials of free radicals. The knowledge of such potentials permits in the majority of instances a correct prediction of the direction and rate of the oxidation-reduction reaction.

The study of one-electron transfer reactions involving cytochromes, oxygen, quinones, flavins, and pyridine bases is of interest for the elucidation of the detailed mechanism of electron transport in biological systems.

Transition metal compounds are widely used as catalysts in radical reactions. The reactions of macroradicals with transition metal complexes play an important role in radical polymerisation and in the stabilisation of polymers. Different metal complexes or salts can have a significant influence on the kinetics and mechanisms of radical oxidation and reduction reactions of organic compounds.

The study of the influence of the magnetic field on the kinetics of oxidation-reduction reactions of radicals with transition metal compounds having different electronic configurations may promote a further development of the theory of magnetic effects in radical reactions.

The study of coordination compounds with radical ligands constitutes a new field in the chemistry of complex compounds. On formation of the complex with a transition metal compound, the reactivity of the radical changes; in most cases short-lived radicals become more stable on forming a complex.

The oxidation-reduction reactions of free radicals can have a wide variety of practical applications. The electron transfer reactions between certain stable free radicals generate an e.m.f. The one-oxidation of CO_3^- constitutes the basis of the reduction of oxygen by the action of visible light on the duroquinone–carbonate ion system and thus provides a valuable means of utilising solar energy.

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