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Redox Reactions of Atoms and Radicals with Ions in Solution

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The reactions of hydrogen atoms and various radicals ($HO^{\cdot}$, $HO_2^{\cdot}$, $RO_2^{\cdot}$, $RO^{\cdot}$, $R^{\cdot}$, diphenylpicrylhydrazyl) in solution with cations and complexes of metals of variable valency and also with anions are surveyed, and their mechanism is discussed. The rate constants of these reactions are tabulated. A list of 130 references is included.

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1. INTRODUCTION

For a long time research workers studying the changes undergone by free radicals concentrated their attention on reactions with molecules which involve substitution and addition. The reactions of radicals with metal ions—electron-transfer reactions—became a subject for quantitative investigation only in the 1960s. Whereas about 20 papers were published on this topic before 1960, the number of publications which appeared during the 1960s exceeded 100.

The enhanced interest taken by investigators in the reactions of free radicals with ions is due to the active part played by these processes in various chain and free-radical chemical reactions. Redox reactions of hydrogen atoms and hydroxy-radicals with various ions take place in photochemical and radiation-chemical systems[1]. The decomposition of hydrogen peroxide involves the formation of hydroxyl and hydroperoxy-radicals, which react with metal ions[2]. The introduction of ions of metals having variable valency into a system in which radical polymerisation is taking place leads to chain termination as a result of reactions between the metal ions and polymer macroradicals[3]. Reactions between peroxy-radicals and compounds of metals with variable valency play an important part in the catalytic liquid-phase oxidation of hydrocarbons[4]. Reactions between alkyl radicals and salts of heavy metals form the basis of various organic syntheses.

A free radical possesses an unpaired electron, and is able to oxidise a reducing ion by removing an electron from the latter, e.g. $Fe^{2+} + HO\cdot \rightarrow Fe^{3+} + HO^-$, but it is able also to reduce an oxidising ion, by donating its electron to the latter, e.g. $Fe^{3+} + H\cdot \rightarrow Fe^{2+} + H^+$.

The redox reactions of free radicals with ions are often very rapid. For example, the polyacrylamide radical reacts with ferric ions with a rate constant of the order of 10^3 M^{-1} s^{-1}; the hydrogen atom and hydroxyl and hydroperoxy-radicals react in water with ions of metals having variable valency with rate constants of the order of 10^8-10^{10} M^{-1} s^{-1}. The reactions of atoms and radicals with ions of metals having variable valency may have various mechanisms: in one case the radical replaces the solvent molecule in the inner coordination shell of the ion; in another case electron transfer takes place from the ion through the medium to the radical or conversely; and in a third case reaction of the radical with a ligand is followed by rearrangement of the electronic structure of the complex.

The reactions of atoms and radicals with ions and complexes are studied quantitatively by methods developed to measure the rate constants of rapid reactions[5]—flow methods (FM), the flash method (FP), pulse radiolysis (PR), and the inhibiting effect of a reactant on the chain reaction—but the most widely used is the method of competing reactions (MCR), which enables the ratio of the rate constants of two parallel reactions involving the same species (e.g. the hydrogen atom) to be determined from the composition of the products.

2. REACTIONS OF HYDROGEN ATOMS

The hydrogen atom is an active reducing agent, which reacts rapidly with oxidising ions:

$$H^{\cdot} + M^{n+1} \rightarrow H^+ + M^{n+}.$$

Such a reaction occurs either by addition of the hydrogen atom to one of the ligands with rearrangement of the electronic structure of the complex, e.g.

$$FeOH^{2+} + H^{\cdot} \rightarrow FeH_2O^{2+},$$
$$MnO_4^- + H^{\cdot} \rightarrow HMnO_4^- \rightleftharpoons H^+ + MnO_4^-,$$

or as a result of the transfer of an electron from the hydrogen atom to the central atom of the complex.

The rate constant for reaction of hydrogen atoms with ions of metals having variable valency is almost independent of the redox potential of the ion. For the ions Cu^{2+}, $Fe(CN)_6^{3-}$, Fe^{3+}, and Ag^+, for example, the redox potential and $\lg k(H\cdot + \text{ion})$ are respectively 0.15 and 7.77 (Cu^{2+}), 0.36 and 9.60 $[Fe(CN)_6]^{3-}$, 0.77 and 7.34 (Fe^{3+}), and 0.8 and 10 (Ag^+). The hydrogen atom reacts with MnO_4^- and Ag^+ with diffusion-controlled rate constants of the order of 10^{10} M^{-1} s^{-1}.

The hydrogen atom behaves as an oxidant on reaction with reducing ions. For example, hydrogen atoms oxidise I^- to I·, Fe^{2+} to Fe^{3+}, etc. The following mechanism has been suggested[6] for the oxidation of Fe^{2+} ions by hydrogen atoms:

$$H^{\cdot} + Fe^{2+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} FeH^{2+}; \quad FeH^{2+} + H^+ \xrightarrow{k_2} Fe^{3+} + H_2.$$

Approximate values of the rate constants[6] are $k_1 \simeq 10^9$ and $k_{-1}/k_2 \simeq 0.02$. A different mechanism has been proposed[7] for the reaction of hydrogen atoms with I^-, according to which the hydrogen atom adds to a hydrogen ion with the formation of H^+_{2aq}, and this species oxidises the iodide ion:

$$H^\cdot + H^+_{aq} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H^+_{2aq} \quad H^+_{2aq} + I^- \xrightarrow{k_2} H_2 + I^\cdot$$

where $k_1 \simeq 10^2 - 10^3$ M^{-1} s^{-1}.

Table 1 lists rate constants for the redox reactions of hydrogen atoms with various cations and anions. Where the method of competing reactions has been used, the competing compound is indicated. The hydrogen atoms were obtained radiochemically using an aqueous solution or by passing an electric discharge through hydrogen and then bubbling the H_2 + H· through an aqueous solution.

Table 1. Reactions of hydrogen atoms with ions in aqueous solution at room temperature (20–25°C).

Ion	Conditions	lgκ	Method	Ref.
$Cr(NH_3)_5Cl^{2+}$	pH=5	6.255	MCR, $(CH_3)_2CDOH$	8
$CrCl_3(H_2O)^+_4$	pH=5	7.30	MCR, $(CH_3)_2CDOH$	8
Mn^{2+}	pH=6	7.40	MCR, $(CH_3)_2CDOH$	8
Fe^{2+}	pH=0.4 (H_2SO_4)	7.20	MCR, O_2	9
Fe^{2+}	pH=2.1 (H_2SO_4)	7.115	MCR, O_2	9
Fe^{2+}	pH=2.1 (H_2SO_4)	7.13	MCR,	10
Fe^{2+}	0.4 M H_2SO_4	7.30	PR	11
Fe^{3+}	0.4 M HCl	7.90	MCR, O_2	12
Fe^{3+}	pH=0.4	6.08	MCR, O_2	9
Fe^{3+}	pH=1.57	7.34	MCR, O_2	9
Fe^{3+}	pH=2.1	7.98	MCR, O_2	9
Fe^{3+}	0.01 N H_2SO_4	7.98	MCR, D_2	10
Fe^{3+}	0.4 M H_2SO_4	6.20	MCR, Fe^{2+}	13
Fe^{3+}	pH=2 (H_2SO_4)	7.955	PR	14
$FeOH^{2+}$	pH=0.7÷2.7	8.88	MCR, CH_3OH	15
$FeCl^{2+}$	pH=0.1	9.655	MCR, O_2	12
$FeCl^+_2$	pH=0.1	9.955	MCR, O_2	12
$Fe(CN)^{3-}_6$	pH=1÷3	9.60	MCR, $HCOO^-$	16
$Fe(CN)^{3-}_6$	pH=7	9.60	MCR, $(CH_3)_2CHOH$	17
$Fe(CN)^{3-}_6$	pH=7	9.48	MCR, C_2H_5OH	18
$Fe(CN)^{3-}_6$	pH=1.1	9.68	MCR, C_2H_5OH	18
$Fe(CN)^{3-}_6$	acid	9.56	MCR, $(CH_3)_2CHOH$	19
$Co(NH_3)^{3+}_6$	pH=4÷6	6.27	MCR, H·	20
$Co(NH_3)^{3+}_6$	pH=4—6	6.20	MCR, CD_3OH	21
$Co(NH_3)_5H_2O^{3+}$	pH=4—6	5.65	MCR, H	20
$Co(NH_3)_5OH^{2+}$	pH=4—6	7.40	MCR, $(CH_3)_2CDOH$	21
$Co(NH_3)_5OH^{2+}$	pH=4÷6	7.49	MCR, H	20
$Co(NH_3)_5F^{2+}$	pH=4÷6	6.08	MCR, CD_3OH	21
$Co(NH_3)_5F^{2+}$	pH=4÷6	6.04	MCR, H·	20
$Co(NH_3)_5F^{2+}$	0,1 M $HClO_4$	⩽6.30	MCR, C_2H_5OH	22
$Co(NH_3)_5Cl^{2+}$	pH=4÷6	7.86	MCR, H·	20
$Co(NH_3)_5Cl^{2+}$	pH=4—6	8.34	MCR, $(CH_3)_2CDOH$	21
$Co(NH_3)_5Cl^{2+}$	pH=1	9.20	MCR, C_2H_5OH	22
$Co(NH_3)_5Br^{2+}$	pH=4÷6	8.66	MCR, H·	20
$Co(NH_3)_5Br^{2+}$	pH=1	10.15	MCR, C_2H_5OH	22
$Co(NH_3)_5Br^{2+}$	pH=4—6	9.00	MCR, $(CH_3)_2CDOH$	21
$Co(NH_3)_5I^{2+}$	pH=4—6	9.48	MCR, $(CH_3)_2CDOH$	21
$Co(NH_3)_5I^{2+}$	pH=4÷6	9.52	MCR, H·	20
$Co(NH_3)I^{2+}$	pH=1!	10.52	MCR, C_2H_5OH	22
$Co(NH_3)_5CN^{2+}$	pH=4—6	7.57	MCR, $(CH_3)_2CDOH$	21
$Co(NH_3)_5CN^{2+}$	pH=1	7.785	MCR, C_2H_5OH	22
$Co(NH_3)_5CNS^{2+}$	pH=1	9.80	MCR, C_2H_5OH	22
$Co(NH_3)_5N^{2+}_3$	pH=4—6	8.59	MCR, $(CH_3)_2CDOH$	21
$Co(NH_3)_5N^{2+}_3$	pH=1	9.04	MCR, C_2H_5OH	22
$Co(NH_3)_5NO^{2+}_2$	pH=1	8.20	MCR, C_2H_5OH	22
$Co(NH_3)_5(NO_3)_3$	pH=1	8.98	MCR, C_2H_5OH	22
$Co(NH_3)_6PO_4$	pH=1	⩽5.83	MCR, C_2H_5OH	22
$Co(NH_3)_5OCOCH^{2+}_3$	pH=1	⩽6.11	MCR, C_2H_5OH	22
$Co(NH_3)_5OCOCF^{2+}_3$	pH=1	⩽5.43	MCR, C_2H_5OH	22
$Co(NH_3)_5$ fumarate $-H^{2+}$	pH=1	9.785	MCR, C_2H_5OH	22
$Co(CN)^{3-}_6$	pH=1	7.30	MCR, C_2H_5OH	

Table 1 (cont'd.).

Ion	Conditions	lgκ	Method	
$Co(CN)^{3-}_6$	pH=5	8.955	MCR, $(CH_3)_2CDOH$	8
$Co(en)_2Cl^+_2$	pH=5	8.84	MCR, $(CH_3)_2CDOH$	8
$Co(en)_2CO^+_3$	pH=5	<6.30	MCR, $(CH_3)_2CDOH$	8
Ni^{2+}	pH=7	<5.0	MCR, C_2H_5OH	18
Cu^{2+}		7.77	PR	8
Cu^{2+}	pH=7	8.70	MCR, $(CH_3)_2CDOH$	8
Cu^{2+}	pH=1	7.76	MCR, HCO_2H	23
Cu^{2+}	pH=1	8.18	MCR, CH_3COCH_3	24
Cu^{2+}	pH=7	8.78	MCR, $(CH_3)_2CHOH$	17
Cu^{2+}	pH=0.7÷2.7	7.78	MCR, CH_3OH	15
Zn^{2+}	pH=7	<5.0	MCR, C_2H_5OH	18
As^{3+}	pH=2.7	~9.00	MCR, H_2O_2	25
Ag^+	pH=7	10.04	PR	26
Ag^+	pH=7	9.60	MCR, C_2H_5OH	18
Cd^{2+}	pH=7	<5.0	MCR, C_2H_5OH	18
Sn^{2+}	pH=1	10.90	MCR, Fe^{3+}	27
Sn^{4+}	pH=1	6.40	MCR, Fe^{3+}	27
SnF^-_3	pH=5	9.30	MCR, $(CH_3)_2CDOH$	8
SnF^{2-}_6	pH=5	6.955	MCR, $(CH_3)_2CDOH$	8
Hg^{2+}	pH=7	10.40	MCR, $(CH_3)_2CDOH$	18
Tl^{1+}	pH=1,5	8.00	MCR, $(CH_3)_2CDOH$	8
OH^-	pH=11÷13	7.36	MCR, CH_3COCH_3	24
OH^-		7.30	PR	8
OH^-	pH=7.5÷12.5	7.08	MCR, $ClCH_2CO^-_2$	28
OH^-	pH=11.5	~7.30	PR	29
CN^-	pH=7	9.415	MCR, $(CH_3)_2CDOH$	8
CNS^-	pH=7	8.23	MCR, $(CH_3)_2CDOH$	8
HCO^-_3	pH=7	~4.48	MCR, CH_3OH	24
NO^-_2	pH=7	8.78	MCR, CH_3OH	30
NO^-_2	pH=7	8.12	MCR, $(CH_3)_2CHOH$	17
NO^-_2	pH=6	8.78	MCR, $(CH_3)_2CHOH$	8
NO^-_2	pH=7	9.00	MCR, CH_3OH	18
NO^-_2	pH=8	9.38	MCR, C_2H_5OH	22
NO^-_2	pH=6	8.955	MCR, $(CH_3)_2CDOH$	8
NO^-_3	pH=11—13	6.845	MCR, CH_3COO^-	24
NO^-_3	pH=7	7.38	MCR, $(CH_3)_2CHOH$	17
NO^-_3	pH=1.1	7.08	PR	20
NO^-_3	pH=10—13	6.58	PR	20
NO^-_3	pH=7	6.845	MCR, C_2H_5OH	18
NO^-_3	acid	7.36	MCR, $(CH_3)_2CHOH$	19
F^-	pH=8.5	4.175	MCR, CD_3OH	31
CrO^{2-}_4	pH=7	10.00	MCR, C_2H_5OH	18
$Cr_2O^{2-}_7$	pH=7	10.20	MCR, C_2H_5OH	18
MnO^-_4	pH=3	10.45	PR	32
MnO^-_4	pH=3	10.39	PR	33
MnO^-_4		10.27	PR	26
MnO^-_4		10.28	PR	34
BrO^-_3	pH=7	7.30	MCR, $(CH_3)_2CHOH$	8
IO^-_3	pH=7	7.77	MCR, $(CH_3)_2CHOH$	8
I^-_2	pH=3.5÷11	7.255	FP	35

3. OXIDATION OF IONS BY FREE HYDROXYL

The hydroxy-radical is a very active oxidant, rapidly oxidising not only cations of metals of variable valency (Fe^{2+}, Ce^{3+}, Tl^+) but also anions such as HCO^-_3, HSO^-_4, and NO^-_2.

The rate constant for oxidation of the Fe^{2+} ion by hydroxyl is 3×10^8 M^{-1} s^{-1}, which exceeds the rate of substitution of the water molecules in the inner coordination sphere of the $Fe(H_2O)^{2+}_6$ ion by factors of 10^2-10^3. Hence the oxidation of Fe^{2+}_{aq} does not involve entry of the hydroxyl into its inner coordination sphere. Two alternative mechanisms can be suggested for this process—electron transfer from Fe^{2+}_{aq} to HO· through the solvent or

abstraction by hydroxyl of a hydrogen atom from a water molecule in the inner coordination sphere of Fe^{2+}_{aq}:

$$HO^{\cdot} + Fe(H_2O)_6^{2+} \rightarrow H_2O + Fe(H_2O)_5OH^{2+}.$$

The $Fe(CN)_6^{4-}$ ion is oxidised by hydroxyl with a diffusion rate constant of $\sim 10^{10}$ M^{-1} s^{-1}; oxidation probably occurs by transfer of an electron from the complex ion to hydroxyl. The Cu^{2+} ion is oxidised by hydroxyl to tervalent copper.

The rate constant of the reaction between hydroxyl and the chloride ion depends on pH:

pH	0	1	2	3
lg$k$	9.60	8.60	7.60	7.20
$k/[H^+]$	$4\cdot10^9$	$4\cdot10^9$	$4\cdot10^9$	$1.6\cdot10^{10}$.

A possible explanation is that oxidation of Cl^- is accomplished by the reaction

$$HO^{\cdot} + HCl \rightarrow H_2O + Cl^{\cdot}.$$

Table 2. Reactions of hydroxyl radical with ions in aqueous solution at room temperature.

Ion	Conditions	lgκ	Method	Ref.
Cr^{3+}	acid	8.49	MCR, H_2	36
Mn^{2+}	pH=7	>8.15	PR	37
Fe^{2+}	pH=1	8.48	MCR, H_2	38
Fe^{2+}	pH=1	8.505	MCR, H_2	39
Fe^{2+}	pH=1.6	8.505	MCR, H_2	9
Fe^{2+}	pH=2.1	8.40	MCR, H_2	9
Fe^{2+}	pH=2	8.415	PR	40
Fe^{2+}	pH=0.4	8.43	PR	41
Fe^{2+}		8.54	MCR	42
$Fe(CN)_6^{4-}$	pH=2.5÷10.5	9.32	MCR, HCO_2^-	43
$Fe(CN)_6^{4-}$	pH=7	10.23	PR	44
$Fe(CN)_6^{4-}$	pH=10.7	9.915	MCR, C_2H_5OH	45
$Fe(CN)_6^{4-}$	pH=9	9.875	MCR, $NOC_6H_4N(CH_3)_2$	46
$Fe(CN)_6^{4-}$	pH=3—10	10.03	PR	47
Cu^{2+}	pH=7	8.545	PR	48
Sn^{2+}	pH=1	9.30	MCR, Fe^{2+}	27
Tl^{1+}	pH=7	9.88	PR	49
Tl^{1+}	pH=1	9.95	MCR, Ce^{3+}	50
Ce^{3+}		8.34	MCR	51
Ce^{3+}		8.54	MCR, H_2	8
Ce^{3+}	pH=1	8.34	MCR, HCO_2H	50
OH^-		8.555	FP	52
NO_2^-	pH=7	9.60	MCR	8
NO_2^-	pH=7	9.40	MCR, H_2O_2	53
NO_2^-	pH=7	9.555	MCR, CO_3^{2-}	54
NO_2^-	pH=7	9.40	PR	55
NO_2^-	pH=7	9.38	MCR, NO	56
NO_2^-	pH=9	9.69	MCR, $NOC_6H_4N(CH_3)_2$	46
NO_3^-	pH=9	<5.7	MCR	8
N_3^-	pH=9	9.81	MCR, $NOC_6H_4N(CH_3)_2$	46
CN^-	pH=9	9.43	MCR, $NOC_6H_4N(CH_3)_2$	46
PO_3^{3-}	pH=10.7	9.28	MCR, CO_3^{2-}	54
$H_2PO_2^-$	pH=10.7	8.97	MCR, CO_3^{2-}	54
$H_2PO_2^-$	pH=7	<7.0	MCR, I^-	57
SO_3^{2-}	pH=7	9.08	MCR, CO_3^{2-}	55
HSO_3^-	pH=7	9.32	MCR, CO_3^{2-}	55
H_2SO_4	pH=1	5.60	MCR	58
HSO_4^-	pH=1	7.52	MCR, HCO_2H	27
HSO_4^-		5.30	MCR, H_2	59
HSO_4^-		5.70	MCR, H_2	36
HSO_4^-		7.30	FP	59
CNS^-	pH=7	9.82	PR	54
CNS^-	pH=7	9.115	PR	55
CNS^-	pH=13.5	9.00	PR	60
CNS^-	pH=2	9.76	MCR, thymine	61
Cl^-	pH=0	9.60	MCR, thymine	62

Table 2 (cont'd.).

Ion	Conditions	lgκ	Method	Ref.
Cl^-	pH=1	8.60	MCR, thymine	62
Cl^-	pH=2	7.60	MCR, thymine	62
Cl^-	pH=4	6.60	MCR, thymine	62
Cl^-	pH=3	7.20	MCR	63
Cl^-	pH=9	5.85	MCR, $NOC_6H_4N(CH_3)_2$	46
Cl^-	pH=0	9.60	MCR, OH	64
Cl^-	pH=0	9.60	PR	65
Cl^-	pH=3	7.30	PR	65
AsO_2^-	pH=10.7	9.66	MCR, CO_3^{2-}	54
AsO_2^-	pH=9	9.66	MCR, $NOC_6H_4N(CH_3)_2$	46
SeO_3^{2-}	pH=7	9.43	PR	54
Br^-	pH=0	10.20	MCR, OH	64
Br^-	pH=0—2	10.555	MCR, H_2	66
Br^-	pH=7	8.115	MCR, C_2H_5OH	67
Br^-	pH=2	9.70	PR	68
Br^-	pH=3	9.34	MCR	63
Br^-	pH=7	9.00	PR	68
Br^-	pH=5—9	9.08	PR	69
Br^-	pH=7	9.20	MCR, NO	70
Br^-	pH=7	9.13	MCR, H_2O_2	71
Br^-	pH=7	8.115	PR	55
Br^-	pH=10.5	8.89	MCR, $C_6H_5CO_2^-$	45
Br^-	pH=1.3	9.765	MCR, C_2H_5OH	72
Br^-	pH=9	8.83	MCR, $OC_6H_4(CH_3)_2$	73
I^-	pH=7	9.20	FP	52
I^-	pH=7	9.845	PR	32
I^-	pH=3	9.52	MCR	63
I^-	pH=7	10.01	PR	44
I^-	pH=10.5	9.96	MCR, $C_6H_5CO_2^-$	45
I^-	pH=9	9.935	MCR, $NOC_6H_4N(CH_3)_2$	46
CO_3^{2-}	pH=7	7.90	PR	55
CO_3^{2-}	pH=10.7	8.30	MCR, CNS^-	54
CO_3^{2-}	pH=11.6	8.62	PR	74
CO_3^{2-}	pH=13	7.64		8
CO_3^{2-}	H_2O, pH=11	8.48	PR	44
CO_3^{2-}	H_2O, pH=10.5	8.48	MCR, $C_6H_5CO_2^-$	45
HCO_3^-	H_2O, pH=7	7.00	PR	75
$C_2O_4^{2-}$	H_2O, pH=9	7.70	MCR, $NOC_6H_4N(CH_3)_2$	46
$C_2O_4^{2-}$	H_2O	6.78	MCR, C_2H_5OH	72
$C_2O_4H^-$	H_2O	7.545	MCR, C_2H_5OH	72
$C_2O_4H_2$	H_2O	7.0	MCR, C_2H_5OH	72

A somewhat analogous reaction takes place in the oxidation of bromide ions, since here, too, k increases with the hydrogen-ion concentration:

pH	0	2	3	7
lg$k$	10.20	9.70	9.34	9.00 .

Oxidation of the iodide ion by hydroxyl is independent of pH:

$$I^- + HO^{\cdot} \rightarrow I^{\cdot} + HO^-.$$

Table 2 gives rate constants for the oxidation of ions by hydroxyl radicals, which were obtained photochemically and radiation-chemically. In most cases the method of competing reactions was used to measure the rate constants.

Measured rate constants quoted in different papers usually show good agreement. The mean logarithms of the rate constants are

$$\lg k(Fe^{2+} + HO^{\cdot}) = 8.47 \pm 0.04,\ \lg k(Fe(CN)_6^{4-} + HO^{\cdot}) = 9.85 \pm 0.28,$$

$$\lg k(Ce^{3+} + HO^{\cdot}) = 8.40 \pm 0.09,\ \lg k(I^- + HO^{\cdot}) = 9.75 \pm 0.25,\ \lg k(CO_3^{2-} + HO^{\cdot}) = 8.30 \pm 0.$$

The rate constant of the reaction ·OH + Ion is independent of the free energy of reaction:

Ion	Br^-	Ce^{3+}	Mn^{2+}	I^-	Fe^{2+}	$Fe(CN)_6^{4-}$
ΔG, kcal mole^{-1}	−3	−8	−10	−18	−26	−36
lg$k$	9.0	8.4	8.1	9.5	8.5	9.9 .

4. REACTIONS OF ALKYL AND ARYL RADICALS WITH SALTS OF METALS HAVING VARIABLE VALENCY

Reaction of the Type $R\cdot + MX_n \rightarrow RX + MX_{n-1}$

The Sandmeyer reaction—decomposition of ArN_2X under the influence of CuX—involves the intermediate formation of an aryl radical. This is evident if only from the formation of the aryl iodide by the reaction[76]

$$Ar\cdot + I_2 \rightarrow ArI + I\cdot$$

when the arenediazonium chloride is decomposed by copper(I) chloride in the presence of molecular iodine. Kochi proposed the following mechanism for this reaction[76]

$$ArN_2^+ + CuCl_2^- \rightleftharpoons ArN_2CuCl_2\,,$$
$$ArN_2CuCl_2 \rightarrow Ar\cdot + CuCl_2 + N_2\,,$$
$$Ar\cdot + CuCl_2 \rightarrow ArCl + CuCl\,.$$

The last stage involves oxidation of the aryl radical by copper(II) chloride occurring as a radical substitution.

A similar primary step occurs in the Meyerwein reaction, whose mechanism can be represented[76,77]

$$ArN_2^+ + CuCl_2^- \rightleftharpoons ArN_2CuCl_2 \rightarrow Ar\cdot + N_2 + CuCl_2\,,$$
$$Ar\cdot + CH_2{=}CHY \rightarrow ArCH_2\dot{C}HY \quad (I)\,,$$
$$ArCH_2\dot{C}HY + CuCl_2 \rightarrow ArCH_2CHYCl + CuCl\,.$$

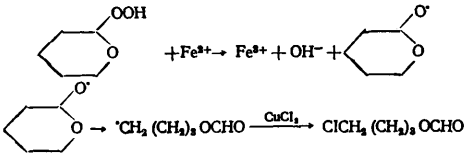
The final product $ArCH_2CHYCl$ is formed by oxidation of the radical(I) by copper(II) chloride. Addition of the aryl radical to the alkene is accompanied by the parallel reaction[77]

$$Ar\cdot + CuCl_2 \rightarrow ArCl + CuCl\,.$$

Occurrence of the reaction $R\cdot + CuCl_2 \rightarrow RCl + CuCl$ is indicated by the appearance of compounds containing chlorine when hydroperoxides are decomposed in aqueous solution by Fe^{2+} ions in the presence of copper(II) chloride. For example, methyl chloride is formed in the decomposition of t-butyl hydroperoxide as a result of the reactions[78]

$$(CH_3)_3COOH + Fe^{2+} \rightarrow (CH_3)_3CO\cdot + OH^- + Fe^{3+}\,,$$
$$(CH_3)_3CO\cdot \rightarrow CH_3COCH_3 + \dot{C}H_3\,,$$
$$\dot{C}H_3 + CuCl_2 \rightarrow CH_3Cl + CuCl\,.$$

The decomposition of tetrahydropyran hydroperoxide is accompanied by the formation of $ClCH_2[CH_2]_3OCHO$ by the mechanism[78]



Similarly, the decomposition of tetrahydrofuran hydroperoxide yields $ClCH_2[CH_2]_2OCHO$ [79].

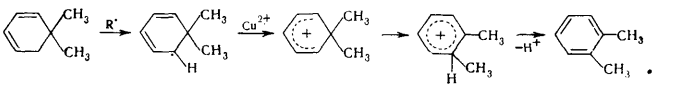
Reaction of the Type $R\cdot + M^{(n+1)+} \rightarrow R^+ + M^{n+}$

Alkyl radicals are oxidised by copper ions with formation of an alkene and an alcohol[80-82]. The carbonium ion is most probably the precursor or both products, and oxidation of the alkyl radical results from electron transfer from the radical to the copper(II) ion:

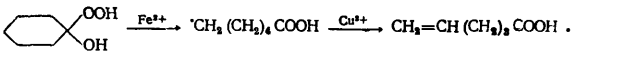
$$R\cdot + Cu^{2+} \rightarrow R^+ + Cu^{1+}\,,$$
$$R^+ \rightarrow Alkene + H^+\,,$$
$$R^+ + H_2O \rightarrow ROH + H^+\,.$$

In the oxidation of various radicals by copper ions the yield of alcohol is greater the more stable is the carbonium ion formed[80]: the ratio [Alcohol]/[Alkene] has the values 0.81, 3.4 and 9.1 for C_2H_5, s-C_4H_9, and t-C_4H_9 respectively, while the allyl radical is oxidised solely to the alcohol. This is consistent with the hypothesis of a carbonium ion as kinetically independent species formed in the oxidation of an alkyl radical.

Perhaps the most convincing evidence of formation of a carbonium ion is the formation of *o*-xylene from 5,5-dimethylcyclohexadiene in the presence of a peroxide (source of radicals) and copper ions[83]. This fact is explained by the following mechanism[83], involving formation of a carbonium ion:



The oxidation of alkyl radicals by copper ions is used for the preparation of certain unsaturated compounds: e.g. [82]



The thermal and photochemical decarboxylation of aliphatic (butyric, isobutyric) acids under the influence of cobalt(III) and cerium(IV) ions is accompanied by oxidation of alkyl radicals by these ions[84,85]. Evidence of this is provided by the formation of 2-methylpropene and an ester as a result of decarboxylation of pivalic acid (where $R\cdot = (CH_3)_3C\cdot$):

$$(RCOO)_3Co \rightarrow (RCOO)_2Co + RCO_2^\cdot\,,$$
$$RCO_2^\cdot \rightarrow R\cdot + CO_2\,,$$
$$R\cdot + Co^{III} \rightleftarrows R'Co^{III}\,,$$
$$R'Co^{III} \rightarrow R^+ + Co^{II}\,,$$
$$(CH_3)_3C^+ \rightarrow (CH_3)_2C{=}CH_2 + H^+\,,$$
$$(CH_3)_3C^+ + RCOOH \rightarrow RCOOC(CH_3)_3 + H^+\,.$$

In the decarboxylation of n-butyric acid the radical $R\cdot$ is converted mainly into RH, since the reaction $R\cdot + RCOOH \rightarrow RH + R'\cdot$ occurs more rapidly than the reaction $R\cdot + Co^{III}$ or $R\cdot + Ce^{IV}$. In the presence of copper ions, however, $n\text{-}C_3H_7\cdot$ is oxidised with the formation of propene and an ester[84,85]. Hence copper(II) ions react with alkyl radicals much more rapidly than do cobalt(III) and cerium(IV) ions, although the latter are stronger oxidants than are copper ions.

The oxidation of n-pentanol by cerium nitrate[86] gives an 11–15% yield of 2-methyloxolan. Formation of this compound can be explained by the mechanism

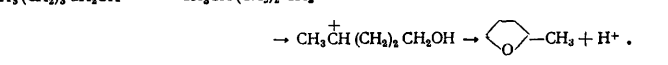


Table 3 lists rate constants for the oxidation of various alkyl radicals by copper complexes. The rate constants were measured by the method of competing reactions.

Reaction of the Type $R\cdot + M^{n+} \rightarrow R^- + M^{(n+1)+}$

Reducing ions (Ti^{3+}, V^{2+}, Cr^{2+}) are able to convert the methyl radical to the carbanion. This is proved by the

formation of DCH_3 from methyl radicals in the presence of metal ions in heavy water[82]:

$$CH_3^{\cdot} + M^{n+} \rightarrow CH_3^- + M^{(n+1)+},$$
$$CH_3^- + D_2O \rightarrow CH_3D + DO^-.$$

The experimental $[CH_4]/[CH_3D]$ ratio (methane is formed by the reaction $CH_3\cdot$ + RH) is lower the stronger the reductant: it has the values 2100, 32, 11, and 4.6 for Fe^{2+}, Ti^{3+}, V^{2+}, and Cr^{2+} respectively.

Table 3. Rate constants of R· + CuL_4^{2+} reactions measured by MCR method in 1 : 1.5 CH_3CN-CH_3COOH at 25.5°C.[87]

Ion	Radical	lg*k*
$Cu(NCCH_3)_4^{2+}$	$CH_3CH_2CH_2CH_2^{\cdot}$	6.49
$Cu(C_{10}H_8N_2)^{2+}$	$CH_3CH_2CH_2CH_2^{\cdot}$	7.23
$Cu(NCCH_3)_4^{2+}$	$(CH_3)_3CCH_2^{\cdot}$	5.65
$Cu(C_{10}H_8N_2)^{2+}$	$(CH_3)_3CCH_2^{\cdot}$	4.40
$Cu(NCCH_3)_4^{2+}$	$C_6H_5CH_2CH_2^{\cdot}$	6.20
$Cu(C_{10}H_8N_2)^{2+}$	$C_6H_5CH_2CH_2^{\cdot}$	7.145
$Cu(NCCH_3)_4^{2+}$	p-$CH_3OC_6H_4CH_2CH_2^{\cdot}$	4.32
$Cu(C_{10}O_2N_2)^{2+}$	p-$CH_3OC_6H_4CH_2CH_2^{\cdot}$	6.48
$Cu(NCCH_3)_4^{2+}$	$(CH_3)_2CH^{\cdot}$	6.70

Complexes of the Type $(R\cdot M)^{n+}$

Kochi and Rust studied the decomposition of t-butyl hydroperoxide in aqueous solution, and found that the yield of ethane increased in the presence of ions of metals with variable valency[88]: the ratio $[C_2H_6]/[CH_4]$ = 0.33 in the absence of ions, and increases to 0.95, 0.95, and 4.9 in the presence of Mn^{2+}, Co^{2+}, and Ni^{2+} respectively. The yield of ethane in the presence of Fe^{2+} decreases with increasing concentration of F^- ions, which form a complex with Fe^{2+}. A similar phenomenon is observed if ethyl radicals are generated in the solution[88]: the ratio $[C_4H_{10}]/[C_2H_6]$ has the values 0.27 in the absence of metal ions, 1.05 in the presence of Co^{2+}, and 1.17 in the presence of Ni^{2+}. This result was explained by complex formation:

$$R^{\cdot} + M^{n+} \rightleftharpoons (R^{\cdot}M)^{n+},$$
$$R^{\cdot} + (R\cdot M)^{n+} \rightarrow R{-}R + M^{n+},$$
$$2(R\cdot M)^{n+} \rightarrow R{-}R + 2M^{n+}.$$

The alkyl radical is less active in the complex; this lowers the yield of methane in the case of methyl radicals, and of ethane in the case of ethyl radicals.

A similar conclusion was reached by Brackman and his coworkers in a study of the products of the radiolysis of methanol[89]. In the absence of metal ions the oxidising radicals formed by radiolysis combine rapidly to give ethylene glycol: $2\cdot CH_2OH \rightarrow HOCH_2CH_2OH$. In the presence of metal ions formaldehyde is produced, its appearance being explained by complex formation:

$$\cdot CH_2OH + M^{n+} \overset{K}{\rightleftharpoons} (\dot{M}CH_2OH)^{n+},$$
$$(\dot{M}CH_2OH)^{n+} + \cdot CH_2OH \overset{k}{\rightarrow} CH_2O + CH_3OH + M^{n+}.$$

The products *kK* of these constants calculated from the experimental results at 30°C have the values:

Ion:	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
kK:	0.043	0.124	4.87	3.13	15.6	0.215

5. REACTIONS OF MACRORADICALS WITH IONS OF METALS HAVING VARIABLE VALENCY

The introduction of ions of variable valency into a system in which radical polymerisation is occurring results in retardation of the chain polymerisation owing to the termination of chains by interaction between macroradicals and metal ions. Termination takes place both on oxidising ions (Fe^{3+}, Cu^{2+}, $CeOH^{3+}$) and on reducing ions (Cr^{2+}, V^{2+}, Ti^{3+}). The mechanism of chain polymerisation in the presence of inhibitor ions can be

Table 4. Rate constants for reactions of macroradicals with metal ions.

Ion	Conditions	Temp., [°C]	lg*k*	lg*A*	*E*	Ref.
Radical CH_2-$CHCINH_2$						
Ti^{3+}	D_2O, 0.0,8H_2SO_4	25	2.91	—	—	90
Ti^{3+}	H_2O, 0.8 H_2SO_4	25	2.76	12.0	11.1	90
Ti^{3+}	H_2O, 1*M* $HClO_4$	25	1.28	12.0	14.6	91
VO_2^+	H_2O, 0.08 *N* H_2SO_4	25	3.04	—	—	90
V^{3+}	H_2O, 0.08 *N* H_2SO_4	25	5.04	—	—	90
Cr^{3+}	H_2O, 0.08 *N* H_2SO_4	25	5.45	—	—	90
Fe^{2+}	H_2O, pH=1	25	3.30	—	—	92
Fe^{3+}	H_2O, 1M $HClO_4$	25	3.45	5.16	2.35	91
Fe^{3+}	D_2O, 1M $HClO_4$	25	3.41	5.20	2.44	91
$FeOH^{2+}$	H_2O —	25	4.04	—	—	92
$FeOH^{2+}$	H_2O —	25	4.325	—	—	90
$FeCl^{2+}$	H_2O —	25	4.91	—	—	90
$FeCl_2^+$	H_2O —	25	4.23	—	—	90
$FeCl_3$	H_2O —	25	6.00	—	—	90
$FeBr^{2+}$	H_2O —	25	6.22	—	—	90
FeN_3^{2+}	H_2O —	25	6.19	—	—	90
$FeCNS^{2+}$	H_2O —	25	7.13	—	—	90
$Fe(bipy)_3^{3+}$	H_2O	25	4.91	—	—	90
Fe (*o*-phen)$_3^{3+}$	H_2O	25	5.49	—	—	90
Fe (5-CH_3-*o*-phen)$_3^{3+}$	H_2O	25	5.415	—	—	90
Fe (5-C_6H_5-*o*-phen)$_3^{3+}$	H_2O	25	5.71	—	—	90
Fe (5-Cl-*o*-phen)$_3^{3+}$	H_2O	25	5.36	—	—	90
$Fe(CN)_6^{3-}$		25	5.93	—	—	90
Cu^{2+}	H_2O. I *M* $HClO_4$	25	3.07	7.04	5.4	91
Cu^{2+}	D_2O. I *M* $HClO_4$	25	3.145	7.00	5.3	91
Mo^{3+}	D_2O. I *M* $HClO_4$	25	3.845	—	—	90
$CeOH^{2+}$	H_2O. I *M* $HClO_4$	25	3.51	5.30	2.45	91
Eu^{2+}	H_2O, 0.8 H_2SO_4	25	4.925	—	—	90
Hg^{2+}	H_2O, 0.1 *M* $HClO_4$	25	0.02	4.62	6.2	91
Ti^{3+}	H_2O, 0.1 *M* $HClO_4$	25	1.53	1.32	2.5	91
Fe^3	H_2O	25	1.725	7.4	7.7	93
$FeOH^{2+}$	H_2O	25	3.24	11.3	11	93
(Fe — $NH_2COC(CH_3)$ = CH_2)$^{2+}$	H_2O	25	3.785	7.7	5.5	93
Radical ~CH_2-C·HCN						
$Fe(CN)_6^{3-}$	H_2O	25	6.83	—	—	94
$FeCl_3$	CHON $(CH_3)_2$	25	3.81	—	—	95
$FeCl_3$	CHON $(CH_3)_2$	25	3.91	—	—	96
radical ~ CH_3 — Ċ (CH_3) CN						
$FeCl_3$	CHON $(CH_3)_2$	25	2.79	—	—	95
radical ~ CH_3 CHC_6H_5						
$FeCl_3$	CHON $(CH_3)_2$	25	4.73	—	—	95
radical ~ CH_2Ċ (CH_3) $COOCH_3$						
$CuCl_2$	CHON $(CH_3)_2$	60	5.89	—	—	97

represented by the simple scheme (where M is the monomer [and Me the metal])

$$\text{Initiator} \rightarrow r^{\cdot} \xrightarrow{M} M^{\cdot},$$
$$M^{\cdot} + M \xrightarrow{k_p} M^{\cdot},$$
$$M^{\cdot} + M^{(n+1)+} \xrightarrow{k_x} M^{+} + M^{n+},$$
$$M^{+} + H_2O \rightarrow MOH + H^{+},$$
$$M^{+} \rightarrow \text{Alkene} + H^{+}.$$

The rate of polymerisation in this system is $w = k_p[M^{\cdot}][M] = k_p[M]w_i/k_x[Me^{(n+1)+}]$ (where w_i is the rate of initiation). Measurement of the rate of polymerisation at different ionic concentrations gives the ratio of the constants k_p/k_x, and values of k_x are calculated for known values of k_p (this method has been used for the k_x in Table 4).

If values of $\lg k$(Radical + Fe^{III}) are compared for H· (Table 1) and ~$CH_2CHCONH_2$ (Table 4), where Fe^{III} reacts in the forms Fe^{3+}, $FeOH^{2+}$, $FeCl^{2+}$, a linear relation is observed:

$$\lg k(\sim CH_2CHCONH_2) = -3.2 + 0.835 \lg k(H).$$

6. REACTIONS OF PEROXY-RADICALS WITH COMPOUNDS OF METALS HAVING VARIABLE VALENCY

Salts of metals with variable valency are widely used as catalysts for the liquid-phase oxidation of hydrocarbons. The primary reason for their accelerating action on oxidation is that they break down hydroperoxides to form free radicals, and thus ensure that a chain oxidation shall be rapid. In some cases, however, salts of metals having variable valency behave as inhibitors: they retard oxidation. This is due to the termination of chains as a consequence of reactions between peroxy-radicals and the lower-valency form of the catalyst[98]: e.g.

$$RO_2^{\cdot} + St_2Co \rightarrow St_2CoOH + R'{=}O,$$
$$RO_2^{\cdot} + St_2Mn \rightarrow St_2MnOH + R'{=}O.$$

The inhibiting effect of cobalt and manganese stearates on the oxidation of cyclohexane[93], α-pinene[99], synthin[100], n-octane[101], and n-decane[102] is observed only if the catalyst is added in sufficiently high concentration (when $k[St_2Co][RO_2^{\cdot}] > k_6[RO_2^{\cdot}]^2$) in the lower valency state (Co^{III} and Mn^{III} do not retard oxidation) and if it is added at the start of oxidation (when hydroperoxide is absent, and the catalyst does not take part in the initiation of chains). During the oxidation the retarding effect of the catalyst usually disappears, firstly because a hydroperoxide has appeared and the catalyst is involved in chain initiation, and secondly as a reaction of the type $RO_2^{\cdot}$ + Co^{II} → Mol. products + Co^{III} ceases to cause chain termination, for Co^{III} immediately reacts with an oxidation product of the hydrocarbon (alcohol, ketone, or aldehyde) to form a free radical. Thus during an oxidising process the reactions between peroxy-radicals and the catalyst are converted from chain-terminating steps into chain-propagating steps involving the catalyst. This explains also the influence of the catalyst on the composition of the oxidation products of the hydrocarbons cyclohexane[103], n-decane[102], and alkanes[104]. This aspect has been discussed in detail in a review[105] and in a monograph[4].

Critical phenomena characteristic of the inhibited oxidation of hydrocarbons[106] are observed also in catalysed oxidations. A detailed study of this phenomenon has been made by Gol'dberg and Obukhova on the oxidation of n-decane in the presence of a potassium–manganese catalyst[107-109]. When a mixture of potassium and manganese stearates is added to n-decane undergoing oxidation, more prolonged inhibition is observed than in the case of manganese stearate alone. The induction period is directly proportional to $[KSt.MnSt_2]^3$. This is explained by formation of the strongly inhibiting complex $3KSt.3MnSt_2$ [107]. Complex formation is proved by electron spin resonance. A critical phenomenon is observed on the introduction of the potassium–manganese catalyst into oxidised n-decane containing a hydroperoxide[108]. When the hydroperoxide content of the decane was less than 2.3 mole % (at 140°C), addition of the catalyst was found to halt the process; but when the hydroperoxide content exceeded this value, the reaction was rapidly accelerated. The occurrence of a critical hydroperoxide concentration in this system is due to the fact that the catalyst initiates chains by reacting with the hydroperoxide at a rate $k_i[St_2Mn][ROOH]$ and terminates chains[108] by the reaction of peroxy-radicals with the complex $3KSt.3MnSt_2$.

In the course of the catalytic oxidation of n-decane the process ceases after some time. A linear relation is observed between the catalyst and hydrocarbon concentrations at this point[109]: in other words, there is a critical ratio between the concentration of the K–Mn catalyst and that of the hydrocarbon in the catalysed oxidation of n-decane.

Hence reactions of peroxy-radicals with compounds of metals having variable valency play a very important part in the mechanism of catalysed liquid-phase oxidation.

In a hydrocarbon medium peroxy-radicals react rapidly with a salt of a metal with variable valency. The rate constant for the reaction of manganese stearate with the peroxy-radical $(CH_3)_2(CN)COO\cdot$ in chlorobenzene measured by a chemiluminescent method is[110]

$$k = 2.8 \cdot 10^8 \exp(-4800/RT)\ M^{-1}\,s^{-1}.$$

The rate constant for the reaction between cobalt(II) acetylacetonate and peroxy-radicals of styrene $C_6H_5CH(OO\cdot)CH_2\sim$ in chlorobenzene is[111]

$$k = 2.9 \cdot 10^9 \exp(-7800/RT)\ M^{-1}\,s^{-1}.$$

The peroxy-radical most probably adds to the cation of the salt of the metal with variable valency, and is then converted into stable molecular products. It has been established[112] that a ketone is formed by reaction of a secondary peroxy-radical with manganese stearate, so that we can write the mechanism

$$RO_2^{\cdot} + MnSt_2 \rightarrow ROO{-}MnSt_2 \rightarrow HOMnSt_2 + R'{=}O.$$

A different type of reaction takes place between the peroxy-radical and the metal complex if the latter contains a ligand having a labile O–H or N–H bond. In this case the peroxy-radical reacts with the ligand as with an ordinary inhibitor. When copper stearate and phenyl-2-naphthylamine are added together to n-decane undergoing oxidation, they cause prolonged inhibition of the reaction[113]; the amine inhibitor is consumed rapidly, but oxidation is inhibited for many hours after it has been exhausted. The explanation offered is that the amine forms with the copper stearate a complex which has a strongly inhibiting action by reacting rapidly with the peroxy-radicals:

$$R_1R_2NH + CuSt_2 \rightleftharpoons StH + StCu\dot{N}R_1R_2,$$
$$RO_2^{\cdot} + St_2Cu\dot{N}R_1R_2 \rightarrow \text{Mol.products}.$$

Study of the inhibiting action of hydroxyquinoline complexes of metals on the oxidation of ethylbenzene[114] has provided kinetic evidence of the reaction of a peroxy-radical with a ligand in the complex. It was established by a chemiluminescent method that, with excess of hydroxyquinoline in the system, chains were terminated by reaction between peroxy-radicals and the metal–hydroxyquinoline complex, whereas the duration of the inhibition was determined by the concentration of hydroxyquinoline OxH in the solution. This corresponds to the following mechanism of inhibition:

$$M^{z+} + OxH \rightleftharpoons MOxH^{z+},$$
$$RO_2^{\cdot} + MOxH^{z+} \rightarrow ROOH + MOx^{z+}.$$

It is interesting that free hydroxyquinoline has a very weak inhibiting effect on oxidation, whereas its complexes react rapidly with peroxy-radicals.

It has been established[115] that the oxidation of cumene is inhibited by the complex of cobalt with dimethylglyoxime DM of composition $Co(DM)_2pyCl$. In this case, too, the peroxy-radical probably reacts with an O–H bond of dimethylglyoxime in the complex.

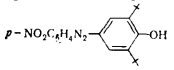
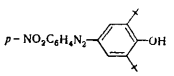
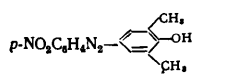
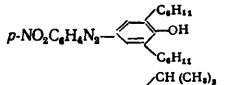
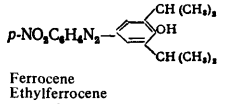
In contrast to the peroxy-radicals from hydrocarbons, the hydroperoxy-radical $HO_2\cdot$ is able to react either as oxidant or as reductant with ions of variable valency[116]:

$$HO_2^{\cdot} + Fe^{2+} \rightarrow HO_2^{-} + Fe^{3+},$$
$$HO_2^{\cdot} + Fe^{3+} \rightarrow O_2 + H^+ + Fe^{2+}.$$

The hydroxyperoxy-radical formed in the oxidation of an alcohol possesses similar dual reactivity[117]. As a consequence, copper ions are ideal negative catalysts for the chain oxidation of alcohols, which they inhibit for an infinite time[117]. The usual inhibitors are consumed during oxidation, and inhibition ceases when the inhibitor is exhausted. Negative catalysis by copper ions in an alcohol undergoing oxidation is due to the reactions

$$>C(OH)OO^{\cdot} + Cu^{2+} \rightarrow >C{=}O + O_2 + H^+ + Cu^{1+},$$
$$>C(OH)OO^{\cdot} + Cu^{1+} \rightarrow >C(OH)OO^{-} + Cu^{2+},$$
$$>C(OH)OO^{\cdot} + H^+ \rightleftharpoons >C(OH)OOH \rightleftharpoons >C{=}O + H_2O_2.$$

Table 5. Rate constants for reactions of peroxy-radicals with ions and complexes of metals.

Ion	Conditions	Temp., [°C]	lg k	Ref.
	Radical $HO_2\cdot$			
Fe^{2+}	H_2O, 0.5 *M* H_2SO_4	23	5.86	120
Fe^{2+}	H_2O, pH = 2.05	25	5.52	121
Cu^{2+}	H_2O, pH = 2.3	23	7.18	122
Cu^{2+}	H_2O	25	8.04	118
Cu^{1+}	H_2O	25	9.63	118
MnO_4^-	H_2O, pH = 3	23	6.90	33
Br_2^-	H_2O	23	9.175	123
Br_2^-	H_2O	23	9.58	123
Br_2^-	H_2O	23	9.20	124
Br_3^-	H_2O	23	8.00	124
CNS^-	H_2O, pH = 1	23	9.20	60
	Radical $C_6H_5CH(CH_3)OO\cdot$			
Mn EDTA^{2-}	$CH_3COOH + C_6H_5CH_2CH_3$	60	6.00	114
Co EDTA^{2-}	$CH_3COOH + C_6H_5CH_2CH_3$	60	5.58	114
Co $(Oxin)_2$	$CH_3COOH + C_6H_5CH_2CH_3$	60	7.955	114
Cu $(Oxin)_2$	$CH_3COOH + C_6H_5CH_2CH_3$	60	5.90	114
Mn $(Oxin)_2$	$CH_3COOH + C_6H_5CH_2CH_3$	60	5.62	114
Ni $(Oxin)_2$	$CH_3COOH + C_6H_5CH_2CH_3$	60	5.35	114
Mn^{2+} complexes of azo-compounds				
	$CH_3COOH + C_6H_5CH_2CH_3$	60	5.575	114
	$CH_3COOH + C_6H_5CH_2CH_3$	60	6.52	114
	$CH_3COOH + C_6H_5CH_2CH_3$	60	7.29	114
	$CH_3COOH + C_6H_5CH_2CH_3$	60	7.48	114
	$CH_3COOH + C_6H_5CH_2CH_3$	60	5.96	114
Ferrocene	$CH_3COOH + C_6H_5CH_2CH_3$	60	5.38	119
Ethylferrocene	$CH_3COOH + C_6H_5CH_2CH_3$	60	5.255	119
Phenylferrocene	$CH_3COOH + C_6H_5CH_2CH_3$	60	4.92	119
Acetylferrocene	$CH_3COOH + C_6H_5CH_2CH_3$	60	4.52	119
Cyanoferrocene	$CH_3COOH + C_6H_5CH_2CH_3$	60	3.60	119
Ferrocenecarboxylic acid	$CH_3COOH + C_6H_5CH_2CH_3$	60	4.08	119
	Радикал $(CH_3)_2(CN)COO\cdot$			
Mn $[OOC(CH_2)_{16}CH]_2$	C_6H_5Cl	70	5.38	110
Co $(acac)_2$	C_6H_5Cl	74	4.36	111
	Radical ~ $CH_2CH(C_6H_5)OO\cdot$			
Co $(acac)_2$*	C_6H_5Cl	55–85	4.69 (80°)	111
	Радикал 			
Cu^{2+}	cyclo-$C_6H_{11}OH$ + 10% H_2O	75	6.505	117

* The following abbreviations have been adopted:

EDTA = $(-OOC)_2NCH_2CH_2N(COO^-)_2$; Oxin =

acac = $CH_3C(O^-)=CH-C(=O)CH_3$

Table 5 lists rate constants for the reactions of peroxy-radicals with ions and complexes of metals of variable valency. The $HO_2\cdot$ + Ion rate constants were measured by the pulse radiolysis method, except in the case of the reaction $Cu^+ + HO_2\cdot$, whose rate constant was measured by a flow method[118]. The rate constants for the reactions of peroxy-radicals with metal complexes were determined by chemiluminescence methods[114,119], except in the cases of the $RO_2\cdot$ + $Co(acac)_2$ reaction, where the rate of consumption of Co^{II} was determined[107], and the $RO_2\cdot$ + Cu^{2+} reaction, where the rate constant was calculated from the dependence oxidation of the rate on the concentration of copper ions[117].

7. OXIDATION OF FERROUS IONS BY DIPHENYLPICRYLHYDRAZYL

Several studies have been made of the oxidation of Fe^{2+} ions by diphenylpicrylhydrazyl[121–123]. In aqueous alcohol the rate constant of this bimolecular reaction is 2.7×10^{11} exp $(-13\,500/RT)$ and 1.2×10^{8} exp $(-8100/RT)$ M^{-1} s^{-1} for alcohol contents of 50%[125] and 80%[126] respectively.

It is assumed that a hydrogen atom is abstracted by the radical from a ligand (alcohol molecule)[125]:

$$R^{\cdot} + Fe(ROH)_n^{z+} \rightarrow RH + [Fe(ROH)_{n-1}RO]^{z+}.$$

8. REACTIONS OF OTHER RADICALS WITH IONS

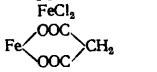
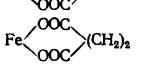
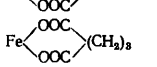
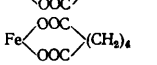
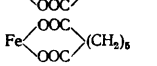
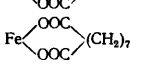
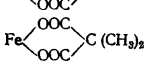
Alkoxy-radicals are oxidants and react with reducing ions. When t-butyl hydroperoxide decomposes in the presence of reducing cations in solution, t-butyl alcohol is formed[128]. This indicates that the reaction

$$(CH_3)_3CO^{\cdot} + M^{n+} \rightarrow (CH_3)_3CO^{-} + M^{(n+1)+}$$

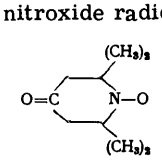
occurs in parallel with the breakdown of $(CH_3)_3CO\cdot$ into acetone and a methyl radical. Values of the [Alcohol]/-[Acetone] ratio are given below for various reducing ions[128]:

Ion	Ti^{3+}	Fe^{2+}	Cr^{3+}	V^{3+}	$Fe(CN)_6^{4-}$	S_4O_6
[Alcohol]/[Acetone]	0.59	1.0	4.26	1.0	9.0	19

Table 6. Oxidation of iron ions by diphenylpicrylhydrazyl.

Ion	Conditions	Temp., °C	lg$k$	Ref.
Fe^{2+}	$H_2O:C_2H_5OH = 1:1$	20	1.36	125
Fe^{2+}	$H_2O:C_2H_5OH = 1:4$	20	2.03	126
Fe^{2+}	CH_3OH	22.5	2.825	127
$FeCl_2$	CH_3OH	22.5	5.565	127
Fe^{2+}	C_2H_5OH	22.5	1.46	127
$FeCl_2$	C_2H_5OH	22.5	2.875	127
Fe^{2+}	n-C_3H_7OH	22.5	1.505	127
$FeCl_2$	n-C_3H_7OH	22.5	3.85	127
Fe^{2+}	$(CH_3)_2CHOH$	22.5	2.00	127
$FeCl_2$	$(CH_3)_2CHOH$	22.5	3.70	127
Fe^{2+}	n-C_4H_9OH	22.5	1.505	127
$FeCl_2$	n-C_4H_9OH	22.5	3.59	127
Fe^{2+}	n-$C_5H_{11}OH$	22.5	1.20	127
$FeCl_2$	n-$C_5H_{11}OH$	22.5	3.54	127
Fe^{2+}	n-$C_7H_{15}OH$	22.5	1.84	127
$FeCl_2$	n-$C_7H_{15}OH$	22.5	3.475	127
	n-C_4H_9OH 0.05 M $NaClO_4$	20	3.33	127
	n-C_4H_9OH 0.05 M $NaClO_4$	20	2.195	127
	n-C_4H_9OH 0.05 M $NaClO_4$	20	2.04	127
	n-C_4H_9OH 0.05 M $NaClO_4$	20	1.895	127
	n-C_4H_9OH 0.05 M $NaClO_4$	20	1.875	127
	n-C_4H_9OH 0.05 M $NaClO_4$	20	1.855	127
	n-C_4H_9OH 0.05 M $NaClO_4$	20	2.095	127

The reaction of the nitroxide radical



with iron ions has been studied[129]. In the presence of 0.1M HCl and 0.4M NaCl in water the rate constant is

$$k = 8.1 \cdot 10^{10} \exp(-7000/RT)\ M^{-1}\ s^{-1}\ .$$

The active radical $\cdot NO_3$ is a strong oxidant, and oxidises Ce^{3+} to Ce^{4+}. At 23 °C the rate constant of this reaction is $1.70 \times 10^6\ M^{-1}\ s^{-1}$, with $E = 1$ kcal mole^{-1}.[130]

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Great success has been achieved by chemical kinetics during recent years in the quantitative investigation of rapid ion–radical reactions involving such species as H·, HO·, $HO_2\cdot$, and macroradicals. With few exceptions, however, the detailed mechanism of such reactions still remains obscure. An atom (a radical) may react with an ion after an intermediate stage involving substitution of a ligand in the inner coordination sphere, it may react with one of the ligands of the complex (by detaching an atom or adding to the ligand), or finally electron transfer may occur through the solvent. As is evident from the present Review, a conclusion can be reached in some cases, but in many cases the detailed mechanism of interaction between radicals and ions is obscure. A more profound understanding of the mechanism of these reactions will require elucidation of the effect of the solvent and of the ionic strength on ion–radical reactions. It is also important to know the activation energy of these reactions (in most cases the rate constants have been measured at a single temperature).

A very promising field of investigation is the formation of complexes between metal ions and free radicals. As yet such complex formation can be judged only from the changed composition of the products from radicals in the presence of ions. Such complexes are obviously short-lived labile structures. Some of them, of course, possess unusual reactivity for free radicals. Investigation of the reactions of such complexes, e.g. by a flow method, is of undoubted scientific interest.

Hardly any quantitative study has yet been made of the reactions of many radicals with ions of metals of variable valency. Such radicals include, for example, alkyl, phenyl, alkoxyl, carboxyl, and hydroxyalkyl radicals. The lack of quantitative data on the rate of these reactions does not permit assessment of their role or value in various transformations of organic compounds in the presence of ions.

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