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Thermal, photolytic, and oxidative reactions of the homoligand carbonyls of metals in Groups VI – VIII

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Abstract. The mechanisms of thermal, photolytic, and oxidative transformations of metal carbonyls into highly dispersed metallic and oxidic phases are discussed. The bibliography includes 142 references.

I. Introduction

The widespread use of the carbonyls of Group VI – VIII metals in the preparation of metal and oxide powders, films,[1,2] and catalysts for various chemical processes[3] has created a need for a detailed study of the mechanisms of the chemical transformations of the carbonyl complexes of the elements. The most recent reviews[3–5] which include a substantial volume of information on the synthesis and properties of metal carbonyls were published more than 10 years ago. However, during that period many new studies of the reactivity of the carbonyl complexes of Group VI – VIII metals towards thermal, photolytic, and oxidative transformations have been reported. They are discussed in the present review.

II. Thermal decomposition of the carbonyl complexes of metals

Most of the recent work on the thermal decomposition of the metal carbonyls is aimed at the preparation of metallic powders, films, and coatings.[1–3,6,7]

One method of preparing catalysts having a high activity and selectivity relies on the decomposition of metal carbonyls deposited on the surface of a solid support.[6,7] Depending on the properties of the surface and on the nature of the carbonyl we may observe the following processes: physisorption,[6–14] chemisorption with formation of various surface organometallic compounds,[6,10–18] and the decomposition of the starting compounds into polynuclear clusters.[13,19,20]

The interaction of pentacarbonyliron with the surface of silicon and of platinum monocrystals at 110 – 185 K results in the molecular adsorption of $Fe(CO)_5$.[8,9] It has been suggested that the adsorption is accompanied by a change in the molecular geometry of the pentacarbonyliron from a trigonal bipyramid to a square pyramidal form. Above 185 K we observe decarbonylation of the $Fe(CO)_5$, and a thin film of metallic iron is formed on the surface of the monocrystal. A similar process takes place during the photolysis of $Fe(CO)_5$ adsorbed on these supports[8,9] at 170 K, and during the thermal decomposition of pentacarbonyliron on the surface of graphite[6] and of dehydrated NaY zeolite.[14]

Highly dispersed metallic catalysts are prepared by thermal decomposition of the carbonyls $Fe_3(CO)_{12}$, $Ru_3(CO)_{12}$, and $Os_3(CO)_{12}$ supported on a clean carbon surface in a hydrogen or helium atmosphere.[21]

We know that when the surface of zeolites or of metal oxides is dehydroxylated by heat treatment under reduced pressure[7,14] the coordinatively unsaturated ions of the elements (Lewis acids) or the oxygen anions in the crystal lattice (Lewis bases) can act as adsorption centres. Depending on the reactivity of the carbonyl and on the nature of the surface, physisorption or chemisorption can be observed even at room temperature. A further increase in temperature results in the full decarbonylation of the initial compound.[6,7,10–15,22–27]

The decomposition of pentacarbonyliron in the micropores of NaY zeolite at 473 K and above produces the subcarbonyls $[Fe(CO)_{5-x}]_{ads}$, $[Fe(CO)_4]^{2-}$, and $[HFe_3(CO)_{11}]_x^-$.[6,14,23,24] The slowest step in the process is the removal of the last CO ligand from one of these species. The presence of small iron clusters in the pores makes possible the complete conversion of the pentacarbonyliron into metal-containing forms of zeolite.[24] The thermal dissociation of $Fe(CO)_5$ includes the disproportionation of CO to CO_2.

The decomposition of $Mo(CO)_6$ in the cavities of NaY zeolite takes place in two steps.[12,25,26] During the first step (at 373 K) we observe changes in the mass of the sample, corresponding to the loss of two carbonyl groups with formation of $Mo(CO)_4$. However, the IR spectrum of the reaction mixture in the 2000–1700 cm^{-1} region contains several ν_{CO} bands which suggest the presence[26] among the reaction products [in addition to $Mo(CO)_4$] of an unidentified molybdenum compound, possibly $[Mo_2(CO)_8Z_x]^{2-}$ (where Z_x is an adsorption centre). Heating the sample above 473 K results in the irreversible decarbonylation of the starting $MO(CO)_6$ with formation of metallic molybdenum within the zeolite lattice. Introducing H^+ ions into the NaY lowers the decomposition temperature of the molybdenum carbonyl to 333 K and produces more finely divided metal particles.[27] $Cr(CO)_6$ physisorbed on silicalite,[11] $Ru(CO)_{12}$ on V_2O_5, MgO, ZnO, and La_2O_3,[12,18] $Mn_2(CO)_{10}$ on NaY zeolite,[13] and $Mo(CO)_6$

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on dehydroxylated Al_2O_3 [22] all undergo similar types of decomposition.

In the thermal decomposition of metal carbonyls on HY zeolite we observe the formation of hydridocarbonyl surface species, $[HM(CO)_m]^+$, which ultimately dissociate with formation of metallic clusters. [11,15,16,28]

On the surface of metal oxides containing hydroxyl groups the carbonyl complexes undergo nucleophilic attack from the side of the OH groups and are converted into compounds of the $[M_n(CO)_{m-x-y}(OH)_x(OZ)_y]\cdot n[HM_n(CO)_{m-1}]$ type, where Z is a metal ion in the corresponding oxide. [10,12,17,18,22] Further decarbonylation leads to the formation of oxidised forms of the metal with evolution of hydrogen.

Octacarbonylcobalt sublimed on to the surface of various zeolites is converted even at room temperature [13,19,20] into the polynuclear clusters $Co_4(CO)_{12}$ and $Co_6(CO)_{16}$. In this case the final product of the thermal decomposition are metal particles 10–15 Å in diameter.

Thus the nature of the surface of the solid phase plays an important role in determining the purity and the disperseness of the metallic powders prepared by the thermal decomposition of metal carbonyls. The reactivity of carbonyl compounds is unaffected by their physisorption on the clean surfaces of inert supports such as active carbon and monocrystalline silicon or platinum. [8,9,21] Metal oxides and zeolites of the NaY type interact with carbonyl complexes through coordinatively unsaturated ions of their elements or through the oxygen anions of the crystal lattice. [6,7,10–15,22–27] The HY zeolites and the oxides containing hydroxyl groups form surface compounds with the carbonyl complexes. [10–12,15–17,22,28] The detailed mechanism of the thermal decomposition of metal carbonyls on solid surfaces has not yet been investigated.

The synthesis of metallic powders and films by the thermal decomposition of metal carbonyls in the gas phase is widely used in industry. [1–3] A study of its mechanism by the fast IR spectroscopy method showed the presence of coordinatively unsaturated metal carbonyls in the reaction mixtures. [29] Depending on the experimental conditions the decomposition of the carbonyl complexes produces powders, films, or metal whiskers. [1–3,30–32] The solid products contain oxide and carbide impurities. Experiments with labelled atoms showed that the oxygen used to form oxides in the resulting solid phase is provided by the carbonyl ligand. [32]

A study by EPR of the thermal decomposition of pentacarbonyliron [33] established that the process takes place on the surface of the reaction vessel by a chain ion–radical clusterisation mechanism:

$$Fe(CO)_4^{-\cdot} + Fe(CO)_5 \longrightarrow Fe_2(CO)_8^{-\cdot} + CO, \quad (1)$$

$$Fe_2(CO)_8^{-\cdot} + Fe(CO)_5 \longrightarrow Fe_3(CO)_{12}^{-\cdot} + CO. \quad (2)$$

This mechanism describes the formation of anion-radical iron carbonyl clusters on the growing iron surface. When the number of nuclei in the cluster reaches four the carbon monoxide group in the coordination sphere of the anion radical undergoes disproportionation according to the Bell–Boudart scheme [33]

$$[Fe_4]\begin{matrix}CO\\CO\end{matrix}\Big]^{-\cdot} \longrightarrow [Fe_4]\begin{matrix}CO_2\\C\end{matrix}\Big]^{-\cdot} \xrightarrow{-CO_2} [Fe_4]\text{—}C\Big]^{-\cdot} \quad (3)$$

In the presence of an excess of $Fe(CO)_5$ vapour the $[Fe_4]-C^{-\cdot}$ clusters are further converted into clusters with 5 or 6 nuclei. Different ways of generating ion-radical centres on the growing surface by chemisorption, photo-ionisation, and other means have been suggested. [33]

In the thermal decomposition of pentacarbonyliron in the gas phase the formation of new metallic particles is observed mainly during the first stages. Thus, ~80% of all the particles have already been formed when 50% conversion of the $Fe(CO)_5$ is reached. [34]

Carlton and Oxley [35] have shown that the initial rate of decomposition of tetracarbonylnickel vapour at 373 K is proportional to its concentration, and that the resulting carbon monoxide limits the rate of the reaction. They proposed the following scheme for the reaction:

$$Ni(CO)_4 \rightleftharpoons Ni(CO)_3 + CO, \quad (4)$$

$$Ni(CO)_3 \xrightarrow{-CO} Ni(CO)_2 \xrightarrow{-CO} \quad (5)$$

$$\longrightarrow Ni(CO) \xrightarrow{-CO} Ni\,.$$

The activation energy for the thermal decomposition of nickel carbonyl in the gas phase [35] is 91.1 kJ mol^{-1}. The dissociation energy of the first Ni–CO bond in the $Ni(CO)_4$, calculated from quantum chemical [36] and from thermochemical data, [37] is 201.6 and 154.1 kJ mol^{-1} respectively. These values are substantially higher than the activation energy measured [35] for the decomposition of $Ni(CO)_4$: this is probably due to the catalytic effect of the resulting metal particles on the thermal decomposition of tetracarbonylnickel.

The decarbonylation of the tetranuclear clusters $Rh_4(CO)_{12}$, $Rh_2Co_2(CO)_{12}$, $RhCo_3(CO)_{12}$, and $Co_4(CO)_{12}$ has been studied [38] by the programmed decomposition temperature method in a hydrogen stream. The quantity of CO evolved during the complete conversion of $Rh_4(CO)_{12}$ suggests the formation of the $Rh_6(CO)_{16}$ complex, which is relatively stable under the chosen thermal decomposition conditions:

$$3\,Rh_4(CO)_{12} \longrightarrow 2\,Rh_6(CO)_{16} + 4\,CO\,. \quad (6)$$

The decarbonylation of $Co_4(CO)_{12}$ was completed by the formation of a mirror of metallic cobalt on the walls of the reaction vessel, whereas solid deposits of the powdered metal were obtained [38] from $RhCo_3(CO)_{12}$, $Rh_2Co_2(CO)_{12}$, and $Rh_4(CO)_{12}$.

A flow system with a differential reactor has been used [39–41] to study the kinetics of the gas-phase decomposition of the hexacarbonyls of metals in the chromium subgroup, and the effective activation energies of the processes have been determined: 45.8 and 54.6 kJ mol^{-1} for $Mo(CO)_6$ and $W(CO)_6$ respectively. The low values of the effective activation energy (as compared with the energy required to remove a single CO ligand [42]) suggest a complex process in the thermal decomposition of $M(CO)_6$, probably not involving catalytic stages.

By using pulsed laser photolysis, which suppresses heterogeneous reactions, Lewis et al. [43] studied the homogeneous gas-phase decomposition of mononuclear metal carbonyls (Fe, Cr, Mo, W). Dissociation energies of 171.4, 134.7, 167.2, and 191.5 kJ mol^{-1} for the first metal–ligand bond were obtained for $Fe(CO)_5$, $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ respectively. These values are close to those obtained in thermochemical experiments. [42] It was established [43] that additions of equimolar quantities of carbon monoxide do not affect the rate of the gas-phase decomposition of these metal carbonyls. For the iron, molybdenum, and tungsten carbonyls the rate-determining step of the process is the removal of the first CO ligand. In the thermal decomposition of $Cr(CO)_6$ the fast (equilibrium) elimination of the first CO ligand is followed [43] by the slower (but still at equilibrium) stage of the dissociation of $Cr(CO)_5$ to $Cr(CO)_4$.

Thus the thermal decomposition of the metal carbonyls in the gas phase involves the participation of coordinatively unsaturated species. The process is often retarded by the gaseous product (carbon monoxide), [29,33,35,43] and is catalysed by the resulting metallic phase used for the nucleation and growth of the carbonyl anion radicals. [33] The products of the reaction (metallic powders, whiskers, and films) contain oxide and carbide impurities. [32,33]

Particles of highly dispersed metals, having an average diameter of 63 – 110 Å, have been prepared[44,45,47] by the decomposition of metal carbonyls in liquid media. The thermal dissociation of $Fe(CO)_5$ and $Co_2(CO)_8$ in solutions of surface-active substances has yielded stable colloidal suspensions (ferromagnetic liquids).[45,46]

The decomposition of penta- and nonacarbonyliron in a closed system takes place by the reversible reaction

$$Fe_n(CO)_m \rightleftarrows Fe_n(CO)_{m-1} + CO, \quad (7)$$

and is rate-limited by the evolved carbon monoxide.[47] The coordinatively unsaturated carbonyl $Fe_n(CO)_{m-1}$ which is produced dissociates according to the scheme

$$Fe_n(CO)_{m-1} \rightleftarrows Fe_n(CO)_{m-x-1} + x\,CO; \quad (8)$$

$Fe_n(CO)_m = Fe(CO)_5$ or $Fe_2(CO)_9$.

The thermal decomposition of nonacarbonyliron produces $Fe(CO)_5$, which is relatively stable under the conditions of the experiment.[47] Dodecacarbonyliron decomposes in undecane at 353 – 383 K by the reaction

$$2\,Fe_3(CO)_{12} \longrightarrow 2\,Fe(CO)_5 + Fe_2(CO)_9 + 5\,CO + 2\,Fe. \quad (9)$$

The rate of the thermal decomposition of the iron carbonyls in paraffins is described by a kinetic equation of the first order with respect to the initial concentration of $Fe_n(CO)_m$. The dissociation of dodecacarbonyliron also obeys the first-order kinetic equation with respect to the time-dependent concentration of $Fe_3(CO)_{12}$ up to a 90% extent of reaction.[47]

The thermal stability of the carbonyl complexes of iron increases in the sequence $Fe_3(CO)_{12} < Fe_2(CO)_9 < Fe(CO)_5$. The rate constants for the dissociation of the iron carbonyl complexes in solution have been determined,[47] and in the case of $Fe(CO)_5$ the equilibrium constants and the rate constants of the recombination reaction are also known.

Octacarbonylcobalt is almost quantitatively converted into the dodecacarbonyl after 5 h at 363 K in toluene or in heptane.[48,49] The rate of the process is described by a second-order kinetic equation with respect to $Co_2(CO)_8$. At 363 K the rate constant is 5.27×10^{-6} dm^3 mol^{-1} s^{-1}:

$$\frac{d[Co_4(CO)_{12}]}{dt} = k\frac{[Co_2(CO)_8]^2}{[CO]^n}. \quad (10)$$

The nature of the solvent has a powerful effect on the kinetics of the formation of dodecacarbonylcobalt. Thus, in heptane the parameter n in the expression for the rate of accumulation of $Co_4(CO)_{12}$ [Eqn (10)] is two, but when toluene is used $n = 4$. The following scheme has been proposed[48] to describe the process:

$$Co_2(CO)_8 \rightleftarrows Co_2(CO)_7 + CO, \quad (11)$$

$$Co_2(CO)_7 \rightleftarrows Co_2(CO)_6 + CO, \quad (12)$$

$$2\,Co_2(CO)_6 \longrightarrow Co_4(CO)_{12}, \quad (13)$$

$$Co_2(CO)_8 + Co_2(CO)_6 \longrightarrow Co_4(CO)_{12} + 2\,CO. \quad (14)$$

It is assumed that the main contribution to the formation of dodecacarbonyltetracobalt is provided by reaction (13) in heptane and by reaction (14) in toluene.

The thermal decomposition of tetracarbonylnickel in undecane at 323 – 353 K is slow, and yields the carbon oxides CO and CO_2.[50] After complete decomposition of the $Ni(CO)_4$ the yield of the two gaseous products is 3.2 and 0.4 mol per mole of converted carbonyl for CO and CO_2 respectively. Metallic nickel and nickel carbide can also be detected among the reaction products. Addition of CO to the reaction mixture before the start of the reaction suppresses the thermal decomposition of $Ni(CO)_4$. The rate of the thermal dissociation of tetracarbonylnickel in solutions is described by a first-order kinetic equation. The following scheme has been suggested:[5,50]

$$Ni(CO)_4 \rightleftarrows Ni(CO)_3 + CO, \quad (15)$$

$$Ni(CO)_3 \xrightarrow[-CO]{} Ni(CO)_2 \xrightarrow[-CO]{} NiCO \xrightarrow[-CO]{} Ni, \quad (16)$$

$$Ni(CO)_3 \longrightarrow Ni + (C) + CO + CO_2. \quad (17)$$

The rate constants for the removal of the first CO ligand (k_{15}) and those for the recombination of $Ni(CO)_3$ and CO(k_{-15}) have been determined.[50]

The thermal decomposition of pentacarbonylruthenium in a cyclohexane solution at 298 – 303 K leads to the formation of $Ru_3(CO)_{12}$. The conversion of $Ru(CO)_5$ into $Ru_3(CO)_{12}$ is the result[51] of the primary fission of a Ru – CO bond with formation of $Ru(CO)_4$:

$$Ru(CO)_5 \rightleftarrows Ru(CO)_4 + CO. \quad (18)$$

The tetracarbonylruthenium interacts with the $Ru(CO)_5$, ultimately giving $Ru_3(CO)_{12}$. The activation parameters of the process have been obtained, and the equilibrium constant of reaction (18) has been calculated: 3.0×10^6 mol dm^{-3} at 298 K.

Tunik et al.[52] have studied the kinetics and the mechanism of the conversion of dodecacarbonylrhodium into hexadeca-carbonylrhodium in heptane:

$$3\,Rh_4(CO)_{12} \longrightarrow 2\,Rh_6(CO)_{16} + 4\,CO. \quad (19)$$

The reaction takes place by two independent parallel paths — a dissociative and a nondissociative path — and it goes to completion even at pressures of carbon monoxide in the 360 – 420 bar range.

The dissociative path [process (20) – (23)] includes the reversible elimination of two molecules of carbon monoxide from the $Rh_4(CO)_{12}$, followed by the rate-limiting step, described[52] as the isomerisation of the cluster skeleton to give a cluster nucleus having a new and very different structure. A typical example of this stage is the conversion of the nucleus of the Rh_4 cluster from a tetrahedral configuration into a 'butterfly' configuration.[52] The nondissociative path [processes (24) and (25)] stipulates the activation of the initial cluster by a similar mechanism but without the preliminary dissociation of the CO ligands. The presence of carbon monoxide has no effect on the rate of this process.

$$Rh_4(CO)_{12} \rightleftarrows Rh_4(CO)_{11} + CO \quad (20)$$

$$Rh_4(CO)_{11} \rightleftarrows Rh_4(CO)_{10} + CO \quad (21)$$

$$Rh_4(CO)_{10} \longrightarrow [Rh_4(CO)_{10}]^* \quad (22)$$

$$[Rh_4(CO)_{10}]^* + 2\,Rh_4(CO)_{12} \xrightarrow{fast} 2\,Rh_6(CO)_{16} + 2\,CO \quad (23)$$

$$Rh_4(CO)_{12} \longrightarrow [Rh_4(CO)_{12}]^* \quad (24)$$

$$[Rh_4(CO)_{12}]^* + 2\,Rh_4(CO)_{12} \xrightarrow{fast} 2\,Rh_6(CO)_{16} + 4\,CO \quad (25)$$

Thus in most cases the first step in the decomposition of metal carbonyls in the liquid phase is the equilibrium elimination reaction of a CO ligand. The thermal stability of the carbonyl complexes is strongly influenced by the nature of the metal atom and by the structure of the resulting polynuclear clusters.[37]

III. Mechanisms of the photolytic breakdown of the carbonyls of the elements

The earliest information[1] on the decomposition of the metal carbonyls (in particular, pentacarbonyliron) under the influence of solar radiation appeared at the beginning of the 20th century, but the systematic study of the photolytic breakdown of pentacarbonyliron began in the late 1930s.[53-55]

It was established[53] that the quantum yield of the formation of CO during the decomposition of $Fe(CO)_5$ vapour (at an initial pressure of 5-15 Torr) under the influence of radiation (366, 405, and 465 nm) is 1.16. Additions of various gases (H_2, CO, CO_2, N_2, Ar) in amounts ranging from values close to the concentration of the pentacarbonyliron to a six-fold excess suppressed[35] the decomposition of the $Fe(CO)_5$ by up to ~50% and lowered the quantum yield of the formation of CO to 0.5. In the mechanism proposed to explain these effects the retardation by gaseous additives was ascribed to the deactivation of the excited $[Fe(CO)_5]^*$ molecules:

$$Fe(CO)_5 \xrightarrow{h\nu} [Fe(CO)_5]^*, \quad (26)$$

$$[Fe(CO)_5]^* + Fe(CO)_5 \longrightarrow Fe_2(CO)_9 + CO, \quad (27)$$

$$[Fe(CO)_5]^* + Q \longrightarrow Fe(CO)_5 + Q; \quad (28)$$

$Q = H_2, CO, CO_2, N_2, Ar.$

However, this mechanism was not confirmed by later work.

The absorption spectra of $Fe(CO)_5$ and $Ni(CO)_4$ vapour[55] consist of continuous curves at wavelengths below 410 nm for $Fe(CO)_5$ and 315 nm for $Ni(CO)_4$. This type of spectrum suggests that the potential energy curve of the excited state does not have a minimum, and therefore the excited $[Fe(CO)_5]^*$ and $[Ni(CO)_4]^*$ molecules are unstable and should dissociate. Thus the primary act of the photolysis is the dissociation of the activated $[Fe(CO)_5]^*$ or $[Ni(CO)_4]^*$ molecule to give $Fe(CO)_4$ or $Ni(CO)_3$.

The accumulation of $Fe(CO)_4$ or $Ni(CO)_3$ during the photolysis of $Fe(CO)_5$ or $Ni(CO)_4$ in inert gas matrices at 20 K and in hydrocarbon glasses at 70 K has been confirmed by IR spectroscopy.[56-60] The coordinatively unsaturated metal carbonyl can react reversibly with the matrix to give $[M(CO)_{n-1}]^*Q$ complexes (Q = H_2, Ne, Ar, Xe, CH_4; M = Fe, Ni; n = 5, 4).[57,60]

$$M(CO)_n \xrightarrow{h\nu} [M(CO)_n]^* \underset{-CO}{\rightleftharpoons} \quad (29)$$

$$\rightleftharpoons [M(CO)_{n-1}]^* \xrightarrow[\lambda > 357\ nm]{Q} [M(CO)_{(n-1)}]^*Q$$

By using the pulsed UV photolysis method with fast recording in the IR region it was shown[61,62] that processes like (29) can take place in gas and in liquid phases as well as in a solid matrix.

According to the above arguments the primary reactions taking place during the photolysis of pentacarbonyliron are described by the equations

$$Fe(CO)_5 \xrightarrow{h\nu} [Fe(CO)_5]^*, \quad (30)$$

$$[Fe(CO)_5]^* \longrightarrow Fe(CO)_4 + CO, \quad (31)$$

$$Fe(CO)_4 + Fe(CO)_5 \longrightarrow Fe_2(CO)_9. \ ^\circ C. \quad (32)$$

The photodissociation of pentacarbonyliron has been studied[63-65] in the gas phase with excitation by laser radiation of wavelength 193, 248, and 352 nm in the presence of PCl_3, PF_3, or SF_6, keeping the total pressure in the system below 200 Torr. Additions of PCl_3 and PF_3 or SF_6 were used to identify the carbonyl fragments produced by the reaction. The energy of the laser radiation and the irradiation time were chosen so as to exclude multiple absorption of photons, and the conversion of the $Fe(CO)_5$ was kept below 10%. It was shown that the absorption of one photon by a molecule of pentacarbonyliron in the gas phase leads to the formation of $Fe(CO)_{5-x}$ primary fragments, where x = 1-4, with an overall quantum yield close to unity. The degree of fragmentation of the pentacarbonyliron increases with the energy of the absorbed photon. The mechanism of the photodissociation is described by the scheme

$$[Fe(CO)_5]^* \longrightarrow [Fe(CO)_4]^{**} + CO, \quad (33)$$

$$[Fe(CO)_4]^{**} \longrightarrow [Fe(CO)_3]^{**} + CO, \quad (34)$$

$$[Fe(CO)_3]^{**} \longrightarrow [Fe(CO)_2]^{**} + CO, \quad (35)$$

$$[Fe(CO)_2]^{**} \longrightarrow [Fe(CO)]^{**} + CO. \quad (36)$$

The pentacarbonyliron molecule excited by the absorption of a photon, $[Fe(CO)_5]^*$, loses CO groups successively and forms coordinatively unsaturated intermediates which are in electronically and vibrationally excited $[Fe(CO)_{5-x}]^{**}$ states.[63,64]

In contrast to the photodissociation reaction induced by irradiation with a mercury lamp tetracarbonyliron formed under laser or flash photolysis from pentacarbonyliron retains up to 65% of the absorbed energy in the form of an electronic or a vibrational component, and is therefore very unstable.[64]

According to SCF MO LCAO calculations[66-68] the photochemical excitation of $Fe(CO)_5$ produces a spin-allowed transition to an excited singlet state. Spin-orbit interaction then populates the triplet state, from which the $[Fe(CO)_5]^*$ dissociates with formation of $Fe(CO)_4(T_i)$ and $CO(S_0)$. The calculated enthalpy of the reaction is 178.8 and the experimental value is 246.4 kJ mol^{-1}.[69]

A detailed study of the composition of the products and of the kinetic features of the photolytic decomposition of the iron carbonyls in solutions under the influence of radiation with wavelengths of 253.7 and 366 nm has been reported.[70] In hydrocarbon solutions pentacarbonyliron dissociates photolytically with formation of a mixture of carbon monoxide and of nona- and dodecacarbonyliron. The relative abundance of the polynuclear carbonyls shows that the dodecacarbonyl is produced by the photolytic decomposition of nonacarbonyliron. The photolysis of $Fe_2(CO)_9$ in solution leads to the formation of $Fe_3(CO)_{12}$, CO, and $Fe(CO)_5$. The decomposition of $Fe_3(CO)_{12}$ in octane under the influence of UV radiation is accompanied by the evolution of carbon monoxide, of penta- and of nonacarbonyliron, and also of metallic iron. The quantum yields for the conversion of the initial carbonyl complexes and for the accumulation of their decomposition products suggests that the processes are described by the following equations:

$$2\,Fe(CO)_5 \xrightarrow{h\nu} Fe_2(CO)_9 + CO, \quad (37)$$

$$2\,Fe_2(CO)_9 \xrightarrow{h\nu} Fe(CO)_5 + Fe_3(CO)_{12} + CO, \quad (38)$$

$$2\,Fe_3(CO)_{12} \xrightarrow{h\nu} 2\,Fe_2(CO)_9 + Fe(CO)_5 + Fe + CO. \quad (39)$$

The pentacarbonyliron formed by the decomposition of the nona- and dodecacarbonyls again undergoes photolysis by reaction (37). The nonacarbonyl formed by the photolysis of $Fe_3(CO)_{12}$ contributes to reaction (38). Thus the photolytic transformation of pentacarbonyliron in octane is a complex multistep process including the formation and decomposition stages of polynuclear iron carbonyls.

The synthesis of $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$ takes place also during the photolysis of $Fe(CO)_5$ in inert gas matrices containing pentacarbonyliron in a proportion of 1:1000 relative to the inert matrix.[57,71] The photodissociation of $Fe(CO)_5$ adsorbed on Vycor porous glass or on zeolites produces polynuclear iron compounds.[72,73]

It has been shown [70] that the quantum yield of the formation of CO during the photolysis of the iron carbonyls in solution is unaffected by changes in the wavelength of the light between 253.7 and 366 nm. The rate of decomposition of the iron carbonyls in octane in concentrations below 5×10^{-4} mol dm^{-3} is described by a first-order kinetic equation. The mechanism of the photolysis of the iron carbonyls in solutions is consistent with the following scheme:

$$Fe_n(CO)_m \xrightarrow{h\nu} [Fe_n(CO)_m]^*, \quad (40)$$

$$[Fe_n(CO)_m]^* \longrightarrow Fe_n(CO)_m + h\nu, \quad (41)$$

$$[Fe_n(CO)_m]^* + RH \longrightarrow Fe_n(CO)_m + RH, \quad (42)$$

$$[Fe_n(CO)_m]^* \longrightarrow Fe_n(CO)_{m-1} + CO, \quad (43)$$

$$[Fe_n(CO)_m]^* + Fe_n(CO)_{m-1} \longrightarrow \text{products}; \quad (44)$$

RH is the solvent.

Several workers have reported [66, 69, 74] the formation of the $Fe_n(CO)_{m-1}$ fragment during the irradiation of penta- and nonacarbonyliron in inert gas matrices.

We know that the rates and the quantum yields of photochemical reactions are relatively insensitive to temperature, [75] which usually affects only the dark reactions. The activation energies reported [70] for the evolution of CO in the photolysis of octane solutions of iron carbonyls show that the formation of carbon monoxide by the scheme (40)–(44) during the decomposition of $Fe_n(CO)_m$ is accompanied by a process in which the photochemical act is the bimolecular interaction of an activated with a non-activated molecule of the carbonyl [Eqn (45)]. In this case the scheme of the photodissociation should include the steps (40)–(42), (45) and the deactivation of $[Fe_n(CO)_m]^*$ on other molecules of the carbonyl:

$$[Fe_n(CO)_m]^* + Fe_n(CO)_m \longrightarrow \text{products}, \quad (45)$$

$$[Fe_n(CO)_m]^* + Fe_n(CO)_m \longrightarrow 2\,Fe_n(CO)_m. \quad (46)$$

A kinetic analysis of the mechanism of photolysis of iron carbonyls in solutions shows [70] that the process can follow either of the suggested schemes. In the case of reactions (40)–(44) the quantum yield of the photodissociation of the iron carbonyls (φ_1) is independent of the initial concentration of $Fe_n(CO)_m$ [Eqn (47)]. If the photolysis of the carbonyl complexes takes place according to the scheme (40)–(42), (45), (46) the quantum yield of the reaction (φ_2) becomes a function of the concentration of the carbonyl:

$$\varphi_1 = \frac{2k_{43}}{k_{41}} + k_{42}[RH] + k_{43}, \quad (47)$$

$$\varphi_2 = \frac{2k_{45}[Fe_n(CO)_m]}{k_{41}} + k_{42}[RH] + k_{45}[Fe_n(CO)_m] + k_{46}[Fe_n(CO)_m]. \quad (48)$$

Since the quantum yield of the elimination of CO in the photolytic dissociation of $Fe(CO)_5$ at 293 K is not affected by changes in the initial concentration of the carbonyl we may conclude that under these conditions the photolysis of pentacarbonyliron takes place mainly by the mechanism described by Eqns (40)–(44). At 373 K the dependence of the reciprocal quantum yield on the concentration is described by the expression

$$\varphi_2^{-1} = \frac{k_{45} + k_{46}}{2k_{45}} + \frac{k_{42} + k_{45}[RH]}{2k_{45}[Fe_n(CO)_m]}. \quad (49)$$

A similar dependence is observed in the photolysis of $Fe_2(CO)_9$ in octane at 293 K. Therefore increasing the temperature of the reaction and changing from penta- to nonacarbonyliron increases the contribution of the path described by Eqns (40) to (46) to the photolytic breakdown of the carbonyl complexes of iron.

The photolysis of $Co_2(CO)_8$ and $Co_4(CO)_{12}$ is nonane under the influence of UV light produces a colour change in the solution, accompanied by the evolution of carbon monoxide. [76] An analysis of the spectra of the reaction mixtures obtained during the irradiation of $Co_2(CO)_8$ showed that octacarbonylcobalt is converted into $Co_4(CO)_{12}$ by the photolysis.

The initial rate of accumulation of CO in the photodissociation of the cobalt carbonyls is directly proportional to the number of quanta absorbed, and an increase in the wavelength of the light from 253.7 to 366 nm has almost no effect on the quantum yield of the formation of carbon monoxide. The quantum yield for the decomposition of octacarbonylcobalt (2.9×10^{-3}) and for the formation of the reaction products $Co_4(CO)_{12}$ (1.5×10^{-3}) and CO (6.0×10^{-3}) suggest that the photolysis of $Co_2(CO)_8$ is described by the equation

$$2Co_2(CO)_8 \xrightarrow{h\nu} Co_4(CO)_{12} + 4\,CO. \quad (50)$$

The kinetic order of the decomposition of $Co_2(CO)_8$ in nonane under the influence of UV radiation is close to unity; increasing the temperature from 293 to 313 K has no effect on the quantum yields of the photodissociation of the cobalt carbonyls.

The changes in the spectra recorded during the photolysis of $Co_4(CO)_{12}$ show that under the influence of radiation dodecacarbonylcobalt is converted into $Co_6(CO)_{16}$: [76]

$$2\,Co_4(CO)_{12} \xrightarrow{h\nu} Co_6(CO)_{16} + 8\,CO + 2\,Co. \quad (51)$$

The order of the reaction leading to the photolytic dissociation of $Co_4(CO)_{12}$ in nonane is close to unity.

The scheme of the photolytic dissociation of octacarbonylcobalt in solution is analogous to the photolysis mechanism of the iron carbonyls [Eqns (40)–(44)]. [76] A kinetic analysis of this scheme and the experimental dependence of the reciprocal quantum yield for the photolysis of $Co_2(CO)_8$ on its reciprocal concentration, described by Eqn (49), show that the elimination of a CO ligand from the excited carbonyl molecule plays only a minor role in this process. On the other hand, in the thermal dissociation of $Co_2(CO)_8$ in solutions it is the rate-determining step. [48] An electronically excited state relatively stable towards decarbonylation is probably created as a result of the absorption of a light quantum by octacarbonylcobalt. This effect can be attributed to the presence of a large number of bonds in $Co_2(CO)_8$, which allow the energy of the absorbed quantum to be redistributed. [76] As a result most of the activated carbonyl molecules are deactivated by processes such as (41), (42), and (46), leading to low values of the quantum yields in the photolysis of $Co_2(CO)_8$. A graphical analysis of the dependence of the reciprocal quantum yield on the reciprocal concentration of $Co_2(CO)_8$ suggests that the ratio of the rate constants of the bimolecular deactivation of the excited $Co_2(CO)_8$ molecule [Eqn (46)] and of the direct photochemical reaction [Eqn (45)] can be as high as 30. [76]

Early studies of the photolysis of tetracarbonylnickel in a CCl_4 solution [55] and in the gas phase [77] had established that this process results in the formation of four moles of CO. As in the case of pentacarbonyliron the primary act of the photolysis is the absorption of a light quantum and the conversion of the molecule into the excited $[Ni(CO)_4]^*$ state, from which it decomposes with the elimination of one CO group. The resulting $Ni(CO)_3$ is unstable and decomposes to the metal and carbon monoxide. Additions of CO suppress the decomposition of

$Ni(CO)_4$ in both the gas phase [77] and the liquid phase.[50] The observed[77] lifetime of the activated $[Ni(CO)_4]^*$ molecule was 7×10^{-9} s. The quantum yield of the photolytic decomposition of the tetracarbonyl in solution irradiated with 313 nm light was 1.8; the order of the photolysis reaction was close to unity.[50] According to a number of reports[50,55,77] the photolysis of nickel carbonyl takes place by an induced mechanism which includes reversible stages:

$$Ni(CO)_4 \xrightarrow{h\nu} [Ni(CO)_4]^*, \quad (52)$$

$$[Ni(CO)_4]^* \rightleftharpoons Ni(CO)_3 + CO, \quad (53)$$

$$[Ni(CO)_4]^* + M \longrightarrow Ni(CO)_4 + M, \quad (54)$$

$$Ni(CO)_3 \xrightarrow{-CO} Ni(CO)_2 \xrightarrow{-CO} \longrightarrow NiCO \xrightarrow{-CO} Ni, \quad (55)$$

$$Ni(CO)_4 + Ni(CO)_2 \longrightarrow 2\,Ni(CO)_3; \quad (56)$$

M = RH, CO.

The effective rate constant of the photolysis of tetracarbonylnickel in undecane was found to be[50] 1.47×10^{-5} s^{-1}.

Studies by IR spectroscopy of the photolysis of $Ru(CO)_5$ and $V(CO)_6$ in the gas phase revealed coordinatively unsaturated fragments, highly reactive towards the starting carbonyls with which they form binuclear complexes.[78,79] The mechanism of the process has not been studied in detail.

The photolysis of the carbonyls of the chromium subgroup in the gas phase, initiated by laser radiation with wavelengths of 351, 308, and 248 nm, takes place by the successive elimination of the CO ligands from the excited carbonyl molecule.[80–85] The number of particles into which the original carbonyl molecule becomes fragmented depends on the energy of the absorbed photon. Photolysis with light of 351 and 308 nm produces only $M(CO)_5$ molecules, whereas light of 248 nm wavelength generates mainly $M(CO)_4$.[80,83] $M(CO)_5$ and $M(CO)_4$ are both very reactive, and they readily attack the initial $M(CO)_6$ molecule or the CO in the gas phase.

The irradiation of metal hexacarbonyls isolated in a matrix (N_2, Ar, CH_4, petroleum jelly) at 12–293 K with UV or visible light leads to the reversible elimination of one carbonyl group with formation of a relatively unstable pentacarbonyl of the metal, which interacts with the material of the matrix:[85–87]

$$M(CO)_6 \xrightarrow{h\nu} [M(CO)_6]^* \xrightarrow{-CO} \longrightarrow [M(CO)_5]^* \xrightarrow{Q} [M(CO)_5]^*Q; \quad (57)$$

M = Cr, Mo, W; Q = N_2, Ar, CH_4, petroleum jelly.

Complexes with organic and with inorganic ligands are formed also during the photolysis of the carbonyls of the chromium subgroup in the gas phase in the presence of various gaseous additives[81,88] or in solutions.[89–92] The coordinatively unsaturated carbonyl $M(CO)_5$ is generated as two structures: square pyramidal (C_{4v}) and trigonal bipyramid (D_{3h}), with a lifetime not greater than 20 μs.[89–91] During this time the carbonyl forms complexes with the solvent or with the additive, the rate of interaction of the triplet (D_{3h}) form being 2.3 times greater than that of the reaction of $M(CO)_5$ in the square pyramidal (singlet) form.[91] In the solvated $[M(CO)_5]^*Q$ complexes (where Q is an alcohol or an alkane) coordination takes place at the alkyl group.[90]

Thus the primary stage in the photolysis of the hexacarbonyls of chromium, molybdenum, and tungsten, and of tetracarbonylnickel (in condensed and in gaseous media) is the reversible elimination of one CO ligand and the formation of a coordinatively unsaturated metal carbonyl. The photolytic decomposition of the iron and cobalt carbonyls includes, in addition to the unimolecular decomposition of $[M_n(CO)_m]^*$, the interaction of this species with a non-excited carbonyl molecule. The contribution from the bimolecular reaction increases with increasing temperature, and also on changing from $Fe(CO)_5$ to $Fe_2(CO)_9$, and it becomes predominant in the case of $Co_2(CO)_8$. The photolysis of polynuclear metal carbonyls has been studied most fully[93–99] for the decacarbonyls of manganese and of rhenium, and for their mixed derivatives.

The primary stages in the decomposition of the $M_2(CO)_{10}$ complexes (M = Mn, Re) have been studied[93–98] by pulsed laser photolysis in the gas phase, in an argon matrix, and in solutions in hydrocarbons. It has been established that the electronic excitation of the decacarbonyls of these metals induces two types of primary reaction: (1) the breaking of the metal–metal bond, with formation of $M(CO)_5$ species, and (2) the elimination of one CO group, with formation of an $M_2(CO)_9$ species containing a bridging carbonyl group:

$$M_2(CO)_{10} \overset{h\nu}{\rightleftharpoons} 2\,M(CO)_5, \quad (58)$$

$$M_2(CO)_{10} \overset{h\nu}{\rightleftharpoons} (CO)_4M(\mu\text{-}CO)M(CO)_4. \quad (59)$$

The relative yield of $M_2(CO)_9$ increases with the quantum energy of the chosen radiation. Thus, for $Mn_2(CO)_{10}$ in cyclohexane the ratio of the quantum yields of reactions (58) and (59) was found to be 0.21, 0.37, and 0.74 at wavelengths of 266, 337, and 355 nm respectively. For decacarbonylrhenium the ratio of the quantum yields for the photolytic decomposition by these two channels is 0.13 at 355 nm.[94,95] Particles of $M(CO)_5$ and $M_2(CO)_9$ are removed in the reverse reactions (58) and (59), with rate constants of 8.8×10^8 and 3.6×10^9 dm^3 mol^{-1} s^{-1} for $Mn(CO)_5$ and $Re(CO)_5$ respectively, and 1.2×10^5 and 4.4×10^4 dm^3 mol^{-1} s^{-1} for $Mn_2(CO)_9$ and $Re_2(CO)_9$ respectively.[94,95] The free-radical nature of the carbonyls $Re(CO)_5$ and $Re_2(CO)_9$ formed in the photolysis of $Re_2(CO)_{10}$ in CH_2Cl_2 has been demonstrated by the ESR method using spin traps.[99]

Information on the photochemical reactions of the binuclear carbonyls of metals of the iron subgroup [except $Co_2(CO)_8$] is scarce and fragmentary. Thus, it has been shown by the matrix isolation method[74,100] that the primary photochemical reaction of the iron and osmium nonacarbonyls is the dissociation of the excited molecule with formation of the $M_2(CO)_8$ fragment:

$$M_2(CO)_9 \xrightarrow{h\nu} [M_2(CO)_9]^* \longrightarrow M_2(CO)_8 + CO; \quad (60)$$

M = Fe, Os.

The coordinatively unsaturated iron carbonyl $Fe_2(CO)_8$ can exist in two forms: bridged and nonbridged.[74] Octacarbonylosmium does not contain bridging carbonyl ligands, probably because the Os–Os bond is much longer than the Fe–Fe bond and therefore hinders the bridging coordination of the carbonyl ligand.[100] Lengthy photolysis of nonacarbonylosmium isolated in an argon matrix results in cleavage of the metal–metal bond, with accumulation of the mononuclear carbonyl $Os(CO)_5$ among the final products.[100] Homolytic cleavage of the iron–iron bond has not been observed.[74]

Very little has been published on the photochemistry of clusters containing three or more metal atoms.[70,76,101–106] It has been shown[101–105] that after the absorption of a photon the $M_3(CO)_{12}$ carbonyl clusters of the iron subgroup can undergo two types of change. When the energy of the absorbed quanta is high we observe elimination of one of the carbonyl ligands from the initial complex, with formation of an intermediate which can add on another ligand or a solvent molecule. At low photon energies the excited $[M_3(CO)_{12}]^*$ molecule

undergoes isomerisation into a nonradical cluster, different from the initial structure, which then suffers fragmentation:

$$M_3(CO)_{12} \xrightarrow[\lambda > 420\ nm]{h\nu} [M_3(CO)_{12}]^* \longrightarrow \quad (61)$$

$$\longrightarrow [M_3(CO)_{12}] \xrightarrow{L} M(CO)_4L + M_2(CO)_8L;$$

L = CO, C_2H_4.

$$M_3(CO)_{12} \xrightarrow[\lambda > 420\ nm]{h\nu} [M_3(CO)_{12}]^* \xrightarrow{-CO} \quad (62)$$

$$\longrightarrow [M_3(CO)_{11}] \xrightarrow{Q} [M_3(CO)_{11}]^*Q;$$

Q is the solvent [PPh_3, $P(OM_3)_3$, etc.]

Cleavage of one of the metal–metal bonds and changes in the cluster skeleton were observed also in the photochemical initiation ($\lambda > 340$ nm) of the reaction of dodecacarbonylcobalt with alkynes.[106]

After irradiation with visible or UV light, metal carbonyl molecules are converted into an unstable electronically excited state. The next stage is the elimination of one CO ligand by a unimolecular or bimolecular reaction. The resulting coordinatively unsaturated fragment can recombine with CO or with the initial carbonyl molecule, or it can form a complex with a solvent molecule or with another ligand. Binuclear and polynuclear carbonyl compounds also undergo fragmentation with cleavage of the metal–metal bond: in polymetal carbonyls this stage is followed by isomerisation of the cluster skeleton.

IV. Oxidation of the metal carbonyls by oxygen, ozone, and peroxides

1. Oxidation of the metal carbonyls by oxygen

The earliest information on the oxidation reactions of metal carbonyls was published with the first reports of the synthesis of these compounds. The reaction of carbonyl complexes with oxygen is used at present to prepare various oxide materials, including ferromagnetics.[1-3]

The mechanism first put forward[35,53,107-110] to explain the decomposition of pentacarbonyliron in the presence of oxygen postulated the conversion of the primary photolysis product of the $Fe(CO)_5$ [the nonacarbonyl $Fe_2(CO)_9$] into iron oxide:

$$Fe(CO)_5 \xrightarrow{h\nu} [Fe(CO)_5]^* \longrightarrow Fe(CO)_4 + CO, \quad (63)$$

$$Fe(CO)_4 + Fe(CO)_5 \longrightarrow 2\,Fe_2(CO)_9, \quad (64)$$

$$Fe_2(CO)_9 + \left(3+\frac{x}{2}\right)O_2 \longrightarrow Fe_2O_3 + (9-x)CO + x\,CO_2. \quad (65)$$

A detailed study[76,111] of the photochemical interaction of $Fe_n(CO)_m$ (n = 1, 2, 3; m = 5, 9, 12) with oxygen in hydrocarbon solvents failed to confirm this scheme. The photooxidation of these iron carbonyls in solutions is accompanied by the evolution of the carbon oxides CO and CO_2 and by the formation of a highly dispersed, X-ray amorphous form of Fe_2O_3 containing iron compounds characterised by the Fe–CO bond.[76,111] Accumulation of gaseous products takes place at the same time as the disappearance of the initial iron carbonyl from the reaction mixture. The relative yields of CO and CO_2 remain constant up to a 70%–80% conversion of the initial carbonyl. The quantum yields of the formation of products and of the disappearance of the $Fe_n(CO)_m$, calculated from the initial rates of the appropriate reactions, have been reported.[76,111] The interaction of $Fe_n(CO)_m$ with oxygen, initiated by UV radiation, is described by the equations

$$2\,Fe(CO)_5 + \tfrac{5}{2}O_2 \xrightarrow{h\nu} Fe_2O_3 + 8\,CO + 2\,CO_2, \quad (66)$$

$$Fe_2(CO)_9 + 2\,O_2 \xrightarrow{h\nu} Fe_2O_3 + 8\,CO + CO_2, \quad (67)$$

$$2\,Fe_3(CO)_{12} + \tfrac{11}{2}O_2 \xrightarrow{h\nu} 3\,Fe_2O_3 + 22\,CO + 2\,CO_2. \quad (68)$$

The initial rate of the photo-oxidation of these iron carbonyls is directly proportional to the number of quanta absorbed, and is independent of temperature between 278 and 313 K. The photo-initiated oxidation of $Fe_n(CO)_m$ by molecular oxygen in nonane is kinetically of first-order with respect to the initial iron carbonyl. In the case of pentacarbonyliron the order of the reaction with respect to oxygen is zero. For the nona- and dodecacarbonyls the rate of the photooxidation decreases with increasing oxygen pressure.

A spectrophotometric analysis of the reaction mixtures carried out during the oxidation showed the absence of photolysis products of the initial iron carbonyls. This suggests that the initial rates of the photochemical interaction of $Fe_n(CO)_m$ with O_2 are approximately an order of magnitude greater than the initial rate of the photolysis.[76,111] Since the concentrations of the carbonyl solutions did not exceed 10^{-4} mol dm^{-3}, and since the quantum yields of the oxidation of $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$ are much lower than unity, the presence of chain reactions in the oxidation process seems unlikely. In keeping with these results the following mechanism has been proposed[76] for the photochemical oxidation of $Fe(CO)_5$ by oxygen through the formation of oxo and peroxo complexes of iron:

$$Fe(CO)_5 \xrightarrow{h\nu} [Fe(CO)_5]^*, \quad (69)$$

$$[Fe(CO)_5]^* \longrightarrow Fe(CO)_5 + h\nu, \quad (70)$$

$$[Fe(CO)_5]^* \longrightarrow Fe(CO)_4 + CO, \quad (71)$$

$$[Fe(CO)_5]^* + M \longrightarrow Fe(CO)_5 + M, \quad (72)$$

where M = $Fe(CO)_5$, O_2, RH.

$$[Fe(CO)_5]^* + O_2 \longrightarrow (CO)_3Fe\begin{matrix}O\\|\\O\end{matrix} + 2\,CO, \quad (73)$$

$$[Fe(CO)_5]^* + O_2 \longrightarrow (CO)_3Fe{=}O + CO + CO_2, \quad (74)$$

$$Fe(CO)_4 + O_2 \longrightarrow (CO)_3Fe\begin{matrix}O\\|\\O\end{matrix} + CO, \quad (75)$$

$$Fe(CO)_4 + O_2 \longrightarrow (CO)_3Fe{=}O + CO_2, \quad (76)$$

$$(CO)_3Fe\begin{matrix}O\\|\\O\end{matrix} + (CO)_3Fe{=}O \longrightarrow Fe_2O_3 + 6\,CO. \quad (77)$$

A kinetic analysis produced a satisfactory correspondence between the proposed scheme and the experimental data. The formation of oxo and peroxo complexes of iron has been observed during the oxidation of the $Fe(CO)_5^-$ anions by oxygen in the gas phase and in the interaction of iron atoms with O_2 in argon matrices at 15 K.[113]

The experimentally observed negative kinetic order with respect to oxygen in the photooxidation of nona- and dodecacarbonyliron suggests that the mechanism of the process includes the reversible formation of a complex between an excited carbonyl molecule and oxygen, and the dissociation of this complex as a result of bimolecular reactions with O_2 and with the solvent.[111]

$$Fe_n(CO)_m \xrightarrow{h\nu} [Fe_n(CO)_m]^* \quad (78)$$

$$[Fe_n(CO)_m]^* \xrightarrow[\text{non-radiative deactivation}]{\text{radiative and}} Fe_n(CO)_m \quad (79)$$

$$[Fe_n(CO)_m]^* + O_2 \rightleftarrows [Fe_n(CO)_m^*O_2]^* \quad (80)$$

$$[Fe_n(CO)_m^*O_2]^* \longrightarrow \text{products} \quad (81)$$

$$[Fe_n(CO)_m^* O_2]^* + RH \longrightarrow Fe_n(CO)_m + O_2 + RH \quad (82)$$

$$[Fe_n(CO)_m^*O_2]^* + O_2 \longrightarrow Fe_n(CO)_m + 2\,O_2 \quad (83)$$

This mechanism provided a basis for the mathematical modelling of the kinetics of the oxidation of nona- and dodecacarbonyliron by oxygen.[111] The solution of the direct kinetic problem gave the time dependences of the concentrations of $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$ during the photooxidation. Comparing the calculated concentrations with experimental values gave a satisfactory agreement.[111] The effect of the initial concentrations of the reactants on the rate of the photooxidation of the carbonyls was also satisfactorily consistent with experiment.

We have studied the possibility of complex formation between pentacarbonyliron and oxygen by measuring the specific heat and the IR spectra of a mixture of reactants at 150–273 K.[114] It was found that the structure of the absorption bands of the Fe–CO bending vibrations in the pure pentacarbonyliron and in its mixtures with oxygen is strongly affected by replacing the gas phase by a solid phase (or vice versa). No difference was detected between the spectra of the pure pentacarbonyliron and those of $Fe(CO)_5$ with additions of O_2. The temperature dependence of the specific heat of the carbonyl complex deviates from a monotonic curve at 153–175 K, both with and without oxygen additions. However, the $C_p = f(T)$ curves of mixtures of these reactants and those of pure $Fe(CO)_5$ are almost identical.

The observed changes in the IR spectra of $Fe(CO)_5$ and in the temperature dependence of its specific heat at 150–190 K suggest the occurrence of specific processes in the substance during heating. The enthalpy of the process observed in this work was 16.22 ± 0.02 kJ mol^{-1}. These effects could be due to changes in the symmetry of the molecular structure of the pentacarbonyliron (for example, a transition from a configuration with D_{3h} symmetry to one with C_{4v} symmetry). Calculations[114] suggest that the ground state of $Fe(CO)_5$ is a singlet with a configuration of D_{3h} symmetry. An assessment of the possibility of finding pentacarbonyliron in a tetragonal bipyramid form (C_{4v} symmetry) gave a difference in energy $E(C_{4v}) - E(D_{3h}) = 22.5$ kJ mol^{-1}. The calculated value is substantially greater than the experimental enthalpy of the process. The discrepancy arises partly from the seriously overestimated energy of the transition of the $Fe(CO)_5$ molecule from a D_{3h} to a C_{4v} state, due to the chosen method of calculation, and partly from the possibility of a more radical change in the structure of the $Fe(CO)_5$ molecule while only a slight deformation is observed owing to the distortion of the Fe–C–O angles.

Thus the IR spectroscopic and calorimetric studies of the interaction of pentacarbonyliron with oxygen at 150–273 K have failed to establish unambiguously the formation of donor–acceptor complexes between the reactants. However, the possible existence of these complexes has been suggested by the quantum chemical method. Calculations of the potential energy curve for the interaction between pentacarbonyliron and oxygen[114] show that the $Fe(CO)_5 + O_2$ system can be stabilised by the formation of the $Fe(CO)_5O_2^*$ complex, whose energy of dissociation into separate molecules is 20–30 kJ mol^{-1}. This result indicates only a tendency towards complex formation betwen $Fe(CO)_5$ and O_2. The calculated dissociation energy of $Fe(CO)_5O_2^*$ is extremely high.

We know[5] that the crystalline cobalt carbonyls $Co_2(CO)_8$ and $Co_4(CO)_{12}$ are converted into the blue carbonates when stored in air. The oxidation of $Co_2(CO)_8$ by oxygen in toluene was shown[115] to be autocatalytic, leading to the formation of $CoCO_3$, CO, and CO_2:

$$5\,Co_2(CO)_8 + 13\,O_2 \longrightarrow 10\,CoCO_3 + 24\,CO + 6\,CO_2. \quad (84)$$

It was suggested[115] that the interaction of octacarbonylcobalt with oxygen is a chain reaction in which the active species are the $Co_2(CO)_7$ particles formed by the thermal dissociation of $Co_2(CO)_8$. A study of the interaction of $Co_2(CO)_8$ with oxygen in nonane[116] failed to confirm this hypothesis.

The oxidation of the octa- and the dodecacarbonyl of cobalt in solution was found to be accompanied by the formation of carbon oxides and by the deposition of a solid phase containing $CoCO_3$, Co_2O_3 and CoO. The composition of the solid phase depends on the nature of the carbonyl and on the ratio of the initial concentrations of the reactants.[116] The kinetic order of the reaction of octacarbonylcobalt with oxygen in nonane with respect to the initial concentration of the carbonyl is close to unity. Changes in the oxygen pressure over the solution from 300 to 500 Torr do not affect the rate of oxidation. The activation energy of this process is 56.9 ± 2.0 kJ mol^{-1} (in the range of 283–313 K). Additions of CO at the start of the reaction lower the rate of oxidation.

Irradiation of a solution of $Co_2(CO)_8$ with UV light having a wavelength of 366 nm accelerates the oxidation of the cobalt carbonyl. The quantum yield of this process is much higher than unity ($\varphi = 5$), which suggests a chain mechanism for the reaction. Since the formation of $Co_2(CO)_7$ by the photolysis of $Co_2(CO)_8$ in solution has a low probability[76] it has been suggested that the $^{\cdot}Co(CO)_4$ radicals behave as active intermediates in the oxidation of octacarbonylcobalt by oxygen.[116] The energy of the metal–metal bond has been reported by various workers to be in the range between 48 and 125 kJ mol^{-1}, which is much lower than the energy needed to break the Co–CO bond (134.9 kJ mol^{-1}).[37] The $^{\cdot}Co(CO)_4$ radicals were detected by EPR during the sublimation of $Co_2(CO)_8$ on to a surface cooled to 77 K. Carrying out this process in the presence of oxygen produces[117] $(CO)_4CoOO^{\cdot}$ peroxide radicals. The creation of active intermediates during the oxidation of $Co_2(CO)_8$ by oxygen in a polystyrene matrix is also indicated by the partial decomposition of the polymer.[118]

As reported,[116] peroxide radicals are formed during the oxidation of $Co_2(CO)_8$ in solutions. However, the application of various physicochemical methods of detecting free-radical species during the interaction of octacarbonylcobalt with oxygen in nonane (EPR, spectrophotometric analysis of the aqueous phase after hydrolysis of the reaction mixture in the presence of H_2O_2, effect of ionol additions on the rate of the process) produced ambiguous results. Nevertheless the accurately determined quantum yields of these reactions confirm that a chain mechanism is involved:[116]

$$Co_2(CO)_8 + h\nu\,(\Delta) \longrightarrow [Co_2(CO)_8]^*, \quad (85)$$

$$[Co_2(CO)_8]^* \longrightarrow 2\,^{\cdot}Co(CO)_4, \quad (86)$$

$$^{\cdot}Co(CO)_4 + O_2 \longrightarrow {}^{\cdot}OOCo(CO)_4, \quad (87)$$

$$^{\cdot}OOCo(CO)_4 \rightleftarrows [OOCo(CO)_{4-x}] + x\,CO, \quad (88)$$

$$[OOCo(CO)_{4-x}] + Co_2(CO)_8 \longrightarrow$$
$$\longrightarrow (CO)_{4-x}CoOOCo(CO)_4 + {}^{\cdot}Co(CO)_4, \quad (89)$$

$$[OOCo(CO)_{4-x}] \longrightarrow CoO + CO_2 + (3-x)CO, \quad (90)$$

$$(CO)_{4-x}CoOOCo(CO)_4 \xrightarrow{} 2\,CoO + (8-x)CO \quad (91)$$
$$\xrightarrow{O_2} 2\,CoCO_3 + (6-x)CO \quad (92)$$
$$\xrightarrow{O_2} Co_2O_3 + CO_2 + (7-x)CO. \quad (93)$$

In addition to reactions (85)–(93) the deactivation of the excited $[Co_2(CO)_8]^*$ also takes place (on the solvent molecules, and on the reactants) during the photooxidation of $Co_2(CO)_8$.

The dependence of the composition and yield of the oxidation products of octacarbonyldicobalt on the initial concentrations of $Co_2(CO)_8$ and O_2 is due to reactions (89) – (93). Thus, increasing the oxygen pressure increases the amount of Co_2O_3 and CO_2 in the product, whereas an increase in the concentration of the carbonyl increases the amount of carbonate in the deposit, owing to the increased contribution of reaction (92).[116]

The interaction of dodecacarbonylcobalt with oxygen in nonane is slower (by a factor of 10) than the oxidation of $Co_2(CO)_8$, but it is accelerated by the action of UV radiation. The order of the reaction with respect to the initial concentration of the carbonyl is close to unity. Increasing the oxygen pressure over the solution has no effect on the rate of the process. The activation energy of the oxidation of $Co_4(CO)_{12}$ in solution is 74.6 ± 3.0 kJ mol^{-1} (at temperatures between 278 and 313 K). Additions of carbon monoxide to the gas phase at the start of the reaction do not affect the reaction rate. The quantum yield of the oxidation of $Co_4(CO)_{12}$ by oxygen, initiated by UV light having a wavelength of 366 nm, is 0.3. These results led to the conclusion[116] that the reaction of dodecacarbonylcobalt with oxygen does not involve a chain mechanism.

The oxidation of tetracarbonylnickel by oxygen has a period of induction and critical pressure limits, depending on the pressure and on the diameter of the vessel.[35] These observations suggest that the $Ni(CO)_4$ is oxidised by oxygen in the gas phase by a chain mechanism with chain breaking on the walls of the vessel.[35] The initial stage of the process is the elimination of one CO ligand from the excited carbonyl molecule, and the final products of the reaction are the carbon oxides CO and CO_2 and nickel oxide containing unchanged carbonyl.[107]

The oxidation of tetracarbonylnickel by oxygen in solutions is relatively slow.[50] Thus, at 293 K only 10% of the initial carbonyl is oxidised in 5 h. Irradiation of the reaction mixture with 313 nm light increases the rate of interaction of the $Ni(CO)_4$ with oxygen. The quantum yield of the oxidation of the nickel carbonyl is 1.12. Each mole of converted $Ni(CO)_4$ produces 2.92 mol of CO and 0.96 mol of $NiCO_3$. The kinetic order of the reaction with respect to the carbonyl compound is 1.2. A change in the pressure of oxygen over the solution from 300 to 500 Torr has no effect on the initial rate of the process. Adding the solid products of the oxidation of carbonylnickel to the reaction mixture has no effect on the rate of the interaction with oxygen. However, adding carbon monoxide before the start of the reaction lowers the rate of oxidation of the carbonyl complex. The experimental results are consistent with the following mechanism for the oxidation:[50]

$$[Ni(CO)_4]^* \rightleftarrows Ni(CO)_3 + CO, \quad (94)$$

$$Ni(CO)_3 \xrightarrow{-CO} Ni(CO)_2 \xrightarrow{-CO} \longrightarrow Ni(CO) \xrightarrow{-CO} Ni, \quad (95)$$

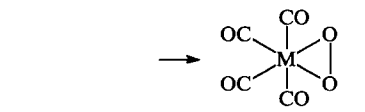
$$Ni(CO)_3 \longrightarrow Ni + (C) + CO + CO_2, \quad (96)$$

$$Ni(CO)_3 + O_2 \longrightarrow NiCO_3 + 2\,CO. \quad (97)$$

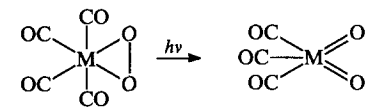
The interaction of the nonexcited $Ni(CO)_4$ molecule with O_2 can be ignored because the rate of the dark process is much lower than the rate of the photooxidation. A kinetic analysis of Eqns (94) – (97) showed that these reactions are consistent with experimental data. The effective rate constant for the oxidation of $Ni(CO)_4$ by oxygen at 293 K was 1.41×10^{-4} s^{-1}, which exceeds by an order of magnitude the rate of its photolytic decomposition.[50]

The oxidation of the carbonyls of the chromium subgroup in inert gas matrices has been studied by Almond et al.,[119–122] who showed that the primary stage of the process was the decomposition of an activated molecule of the carbonyl with formation of the pentacarbonyl of the metal and carbon monoxide. Further photolysis of the matrix leads to mixed carbonyl complexes which ultimately give the metal oxides MO_3 (or MO_2), CO, and CO_2.

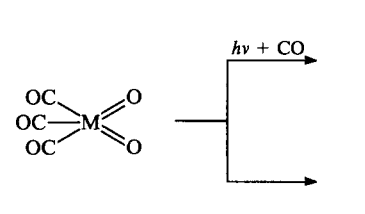
$$M(CO)_6 \xrightarrow[CH_4,\ Ar,\ 12\ K]{h\nu + O_2} M(CO)_5 + CO \xrightarrow{h\nu + O_2}$$



$$+ CO \quad (98)$$



$$+ CO \quad (99)$$



(100)

(101)



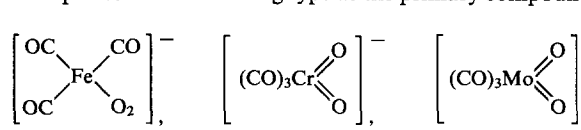
$$\longrightarrow (\eta\text{-}O_2)M(CO)_3O_2 \xrightarrow{h\nu} \quad (102)$$

$$\longrightarrow MO_3 + CO_2 + 2\,CO$$

The structure of the intermediate carbonyl–oxygen complexes was determined by IR spectroscopy, using the ^{18}O oxygen isotope.[120] It was shown by the isotope substitution method[122] that the MO_3 molecules (M = Mo, W) are formed from the peroxide $(\eta^2\text{-}O_2)M(CO)_3O_2$, which decomposes under the influence of the UV radiation to give MO_3 and oxygen atoms in the excited ^1D state. A sample of chromium dioxide having ferromagnetic properties and metallic conduction was obtained[121] by the photolysis of carbonylchromium in an argon matrix with O_2 additions.

It has been reported[123,124] that the arenetricarbonyls of metals (chromium, molybdenum, and tungsten) react with oxygen by previous coordination of the reactants.

The interaction with oxygen, in the gas phase and at room temperature, of the transition metal carbonyls $M(CO)_n^-$ (where M = Cr, Mo, W, Mn for $n = 5$; M = Fe, Co for $n = 4$), prepared by the electron impact method, leads to the formation of complexes of the following type as the primary compounds:



which are then converted into the metal oxides.[112,125]

Radicals of the peroxides $Re(CO)_5O_2^{\bullet}$ and $Mn(CO)_5O_2^{\bullet}$ were detected by EPR by using spin traps during the photolysis of $Re_2(CO)_{10}$ and $Mn_2(CO)_{10}$ in CH_2Cl_2 solutions in the presence of oxygen.[99,126] The active $Re(CO)_5O_2^{\bullet}$ species detach a hydrogen atom from a solvent molecule and form a hydroperoxide which dissociates further to give the radicals $Re(CO)_5^{\bullet}$ and $HOO^{\bullet}$.

Thus the oxidation of the carbonyl complexes of elements of Groups VI – VIII by oxygen in gaseous or liquid media is accompanied by the formation of the oxides and of the carbonate of the metal, and of carbon oxides. The composition and the yield of the reaction products are strongly dependent on the nature of the carbonyl complex and on the condition used for the oxidation. The process is accelerated under the influence of irradiation, and it can be hindered by additions of CO. The mechanism of the reaction includes the formation of intermediate carbonyl complexes of the metal in both radical and nonradical forms.

2. Oxidation of metal carbonyls by ozone

Data on the interaction of metal carbonyls with ozone are few. A study of the oxidation of pentacarbonyliron vapour by ozone–helium mixtures at room temperature and low pressure has been reported.[127] The product of the reaction was a highly dispersed diamagnetic aerosol of Fe_2O_3, formed according to the scheme

$$Fe(CO)_5 + O_3 \longrightarrow Fe(CO)_4 + CO_2 + O_2, \quad (103)$$

$$Fe(CO)_4 + O_3 \longrightarrow FeO + 4\,CO + O_2, \quad (104)$$

$$FeO + O_3 \longrightarrow Fe_2O_3 + O_2. \quad (105)$$

The oxidation of $Fe(CO)_5$ and $Ni(CO)_4$ vapours by ozone is accompanied by chemiluminescence in the 500–600 nm region,[128] due to the emission of light quanta by the excited FeO and NiO molecules formed in the exothermic reaction of the metal carbonyl with ozone. The oxidation of tetracarbonylnickel by ozone has been used in the purification of industrial effluents.[129]

Studies of the composition of the products and of the kinetics in the reaction of iron, cobalt, and nickel carbonyls with ozone in organic solvents have been reported.[50,130,131] The carbonyls of the iron subgroup were oxidised by an ozone–oxygen mixture by bubbling the gases through the liquid at 223–293 K. The final products of the reaction were the oxide and carbonate of the metal and the oxides of carbon; their composition and yield depended on the nature of the carbonyl complex.[50,130,131] The transformation of the metal carbonyl is accompanied by oxidation of the solvent. The rate of oxidation of pentacarbonyliron, octa- and dodecacarbonylcobalt, and tetracarbonylnickel in the liquid phase is determined by the rate of diffusion of ozone from the gas phase into the solution. The interaction of dodecacarbonyliron with ozone in nonane is activation-controlled, with an activation energy of 24.2 ± 5.3 kJ mol^{-1} at 255–293 K. The number of moles of ozone used to oxidise one mole of the carbonyl complex varies between 1 and 14, depending on the nature of the metal in $M_n(CO)_m$. In some cases (dodecacarbonyliron, tetracarbonylnickel) this number is smaller than the value calculated from the yield of oxygen-containing products. This is due to the contribution of oxygen to the oxidation of the metal carbonyl.[50,131]

The kinetic features of the interaction of metal carbonyls with O_3 in the liquid phase[132] and the increase in the reaction rate produced by increasing the polarity of the medium show that the rate-limiting step of the process is the attack of the metal–ligand bond by the ozone molecule.

Unlike the oxidation of metal carbonyls by oxygen, the interaction of $M_n(CO)_m$ with ozone is relatively fast and produces a large yield of CO_2 and of carbonate anions. The detailed mechanism of this process has not yet been established.

3. Oxidation of the metal carbonyls by peroxides

Pentacarbonyliron reacts violently with hydroperoxides to give iron(III) oxide and carbon monoxide.[133] Di(*tert*-butyl) peroxide oxidises the iron and cobalt carbonyls to $Fe(OBu^t)_3$ and $Co(OBu^t)_3$ (Schott and Wilke[134]). The kinetics and the mechanism of the interaction of $Co_2(CO)_8$, $Mn_2(CO)_{10}$, and $Fe(CO)_5$ with dibenzoyl peroxide in toluene at 293–333 K have been studied by volumetric and IR spectral methods.[135] The reaction is of the first order with respect to the cobalt and manganese carbonyls and to the peroxide. The interaction of $Fe(CO)_5$ with benzoyl peroxide is autocatalytic. Additions of styrene and of carbon monoxide suppress the oxidation of the manganese and iron carbonyls. The process is described by the reactions

$$Co_2(CO)_8 + 2\,PhC(O)OOC(O)Ph \longrightarrow 2\,Co(OOCPh)_2 + 8\,CO, \quad (106)$$

$$Mn_2(CO)_{10} + 2\,PhC(O)OOC(O)Ph \longrightarrow 2\,Co(OOCPh)_2 + 8CO, \quad (107)$$

$$Fe(CO)_5 + 1.5\,PhC(O)OOC(O)Ph \longrightarrow Fe(OOCPh)_3 + 5\,CO. \quad (108)$$

The formation of free-radical species during the oxidation of metal carbonyls by benzoyl peroxide has been suggested.[135] The rate-limiting step of the interaction of $Fe(CO)_5$ with PhC(O)OOC(O)Ph is the conversion of the carbonyl complex into iron(II) compounds, followed by their fast oxidation to $Fe(OOCPh)_3$.

Complexes of zero-valent nickel are oxidised by dibenzoyl peroxide and by di(*tert*-butyl) peroxide, giving nickel benzoate and *tert*-butoxide.[134] Studies[136] of the interaction of chromium, molybdenum, tungsten, and iron carbonyls with organosilicon peroxides suggest that the primary stage in the reaction of $Fe(CO)_5$ with $Me_2Si(OOBu^t)_2$ is the coordination of two molecules of the peroxide to the carbonyl ligands of the pentacarbonyliron. The interaction of $Mo(CO)_6$ with cyclohexyl and 1-methylcyclohexyl peroxides in heptane also leads to the formation of out-of-sphere complexes with an enthalpy of formation of 6.3 kJ mol^{-1}.[137]

Hexacarbonylmolybdenum is oxidised by *tert*-butyl and cumyl hydroperoxides in alkanes at temperatures above 373 K.[138] The use of an aromatic hydrocarbon as the solvent increases the rate of the oxidative degradation of the $Mo(CO)_6$ by hydroperoxides because of the conversion of the initial metal complex into an arenemolybdenumtricarbonyl complex. The latter species is readily oxidised to molybdenum oxides and peroxides. The hydroperoxides are catalytically decomposed on these products, and the resulting intermediates interact with the $Mo(CO)_6$.[138]

The EPR method with spin traps has been used[139] to study the free-radical dissociation of Bu^tOOBu^t in the presence of various metal carbonyls in hydrocarbon solutions. The formation of adducts of $Bu^t\dot{O}$ radicals with the spin traps was demonstrated, and a scheme which included an initial electron transfer from the carbonyl to the peroxide was proposed.

The writers have studied[140,141] the oxidation of the carbonyl complexes of the elements of the iron subgroup by *tert*-butyl and cumyl hydroperoxides and by *tert*-butyl peroxide in paraffin solutions, and by hydrogen peroxide in water. The reaction is very fast at room temperature, and is accompanied by the formation of solid deposits, carbon oxides, and transformation products of the peroxide fragments. The solid phase precipitated from the reaction mixture is an oxide or carbonate of the metal, or a mixture of the two compounds, containing adsorbed molecules of the solvent or of water. In the case of pentacarbonyliron the precipitate contains (in addition to iron oxide) iron compounds in which the metal atom is attached to CO groups.[141]

Complete conversion of $M_n(CO)_m$ (where M = Fe, CO) is achieved with an excess of hydroperoxide (6-fold and 30-fold for the iron and the cobalt carbonyl respectively). The excess of hydroperoxide in comparison with the stoichiometric amount is attributed to the catalytic decomposition of the peroxidic compound into products containing metal atoms in different states of oxidation. The interaction of $M_n(CO)_m$ with the organic hydroperoxides is accompanied by the oxidation of the paraffin used as solvent to a mixture of secondary alcohols in a yield of up to 10% relative to the ROOH consumed.[141]

The reactivity of the metal carbonyls towards organic hydroperoxides decreases as the nucleus of the cluster is increased in the sequence $Fe(CO)_5 > Fe_2(CO)_9 > Fe_3(CO)_{12}$ and $Co_2(CO)_8 > Co_4(CO)_{12}$. The reaction of $M_n(CO)_m$ with hydroperoxides is accompanied by oxidation of the central atom and of the ligands. Inner sphere changes in the ligands probably take place, as suggested by the presence of an oxalate ester among the reaction products.[141]

EPR studies of the oxidation of metal carbonyls by peroxidic compounds have shown that the spectra of a reaction mixture of pentacarbonyliron or its monotriphenylphosphine derivative with organic hydroperoxides in hexane or toluene at 203–293 K include signals from paramagnetic species, in particular from $Fe(CO)_5^{+\cdot}$ or $Fe(CO)_4PPh_3^{+\cdot}$. A signal from the $RO_2^{\cdot}$ radical has also been detected in the EPR spectrum of the products of the interaction of *tert*-butyl or cumyl hydroperoxide with the carbonyl derivatives of iron. This radical is generated by the catalytic decomposition of alkyl hydroperoxides. By using the 2- methyl-2-nitrosopropane spin trap in these measurements the writers established the presence of adducts with RO$^{\cdot}$ radicals.[141]

The oxidation of the carbonyls of metals in the iron subgroup by peroxidic compounds can be described by taking pentacarbonyliron as an example:

$$Fe(CO)_5 + ROOH \longrightarrow \{HO^-, Fe(CO)_5^{+\cdot}, RO^{\cdot}\} \longrightarrow \quad (109)$$

$$\longrightarrow RO^{\cdot} + [HO^-, Fe(CO)_5^{+\cdot}],$$

$$[HO^-, Fe(CO)_5^{+\cdot}] \longrightarrow [(CO)_4Fe{-}OH]^{\cdot} + CO, \quad (110)$$

$$[(CO)_4Fe{-}OH]^{\cdot} + ROOH \longrightarrow [(CO)_4Fe{-}OOR]^{\cdot} + H_2O, \quad (111)$$

$$[(CO)_4Fe{-}OOR]^{\cdot} \longrightarrow 4\,CO + FeO + RO^{\cdot}, \quad (112)$$

$$[(CO)_4Fe{-}OOR]^{\cdot} \longrightarrow CO_2 + [(CO)_3Fe{-}OR]^{\cdot}, \quad (113)$$

$$[(CO)_4Fe{-}OOR]^{\cdot} \longrightarrow [(CO)_3Fe{-}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{C}}{-}OR]^{\cdot}, \quad (114)$$

$$[(CO)_3Fe{-}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{C}}{-}OR]^{\cdot} + OR^{\cdot} \longrightarrow (CO)_2Fe\begin{matrix}\overset{\overset{O}{\|}}{C}(O)OR \\ \underset{\underset{O}{\|}}{C}(O)OR\end{matrix} \longrightarrow$$

$$\longrightarrow \begin{matrix}C(O)OR \\ C(O)OR\end{matrix} + FeO + 2\,CO, \quad (115)$$

$$[(CO)_nFe{-}OH\ (\text{or } OR)]^{\cdot} + {}^{\cdot}OR \longrightarrow$$

$$\longrightarrow n\,CO + FeO + ROH\ (\text{or } ROR), \quad (116)$$

$$2\,[(CO)_nFe{-}OH\ (\text{or } OR)]^{\cdot} \longrightarrow$$

$$\longrightarrow H_2O\ (\text{or } ROH) + CO + [(CO)_3FeOFe(CO)_3]; \quad (117)$$

$n = 3, 4.$

$$2\,[(CO)_4Fe{-}OOR]^{\cdot} \longrightarrow (CO)_2Fe\begin{matrix}\overset{\overset{O}{\|}}{C}(O)OR \\ \underset{\underset{O}{\|}}{C}(O)OR\end{matrix}\!\!\begin{matrix}\\ \\ OFe(CO)_4\end{matrix} \longrightarrow$$

$$\longrightarrow \begin{matrix}C(O)OR \\ C(O)OR\end{matrix} + 4\,CO + [(CO)_2FeOFe], \quad (118)$$

$$Fe^{n+} + ROOH \longrightarrow RO^{\cdot} + Fe^{(n+1)+} + HO^-, \quad (119)$$

$$Fe^{(n+1)+} + ROOH \longrightarrow RO_2^{\cdot} + Fe^{n+} + H^+; \quad (120)$$

Fe^{n+} denotes any oxidised form of the carbonyl complex.

$$RO^{\cdot}(\text{or } RO_2^{\cdot}, [Fe]^{\cdot}) + SH \longrightarrow$$

$$\longrightarrow ROH\ (\text{or } ROOH, [Fe]H) + S^{\cdot}. \quad (121)$$

SH is the solvent.

The primary step in this process is the transfer of an electron from the carbonyl to the peroxide with formation of an ion–radical pair. This reaction may be preceded by complex formation between the reactants, as was shown for the hexacarbonyls of the Group VI metals.[136, 137] The subsequent transformation of the ion–radical pair and the interaction of the resulting species with a molecule of the peroxide cause the accumulation of oxygenated iron compounds, carbon oxides, and oxalate esters. The appearance of oxidised forms of iron in the system is responsible for the catalytic decomposition of the hydroperoxide.

The interaction of metal carbonyls with peroxidic compounds is a complicated process with a radical-chain mechanism. Its primary stage is the transfer of an electron from the carbonyl to the peroxide with formation of cation-radical carbonyls of the metals.

V. Conclusions

The thermal, photolytic, and oxidative degradation processes of the carbonyl complexes of metals are widely used in the preparation of highly dispersed powders and of films. The great diversity of the known metal carbonyls makes it impossible to describe their thermal, photolytic, and oxidative transformations in terms of a single mechanism.

However, in most cases of the thermal and the photodecomposition of metal carbonyls the primary stage consists in the elimination of one CO ligand from a thermally or photochemically activated $[M_n(CO)_m]^*$ molecule with formation of a coordinatively unsaturated fragment. During thermal decomposition this stage is at equilibrium, and the rate of the process is suppressed by additions of carbon monoxide for many typical compounds in this class. In contrast to the thermal processes, in the photolysis of the metal carbonyls the contribution of the recombination of the coordinatively unsaturated fragment with the carbon monoxide is insignificant, since for the majority of metal carbonyls this interaction is formally spin forbidden. The coordinatively unsaturated fragment dissociates by further elimination of CO radicals, or alternatively it can react with the initial molecule (producing a binuclear carbonyl) or form a solvato complex.

Instead of the removal of one CO ligand from the excited carbonyl complex of the metal the primary photochemical act leading to the observed products may consist in the bimolecular interaction of an activated $[M_n(CO)_m]^*$ molecule with a nonactivated molecule. In binuclear and polynuclear metal carbonyls another possibility is fragmentation with breaking of a metal–metal bond, preceded in some cases by the isomerisation of the skeleton of the complex.

The stability of the iron carbonyls towards thermal decomposition decreases in the order $Fe(CO)_5 > Fe_2(CO)_9 > Fe_3(CO)_{12}$. In the photolytic decomposition the same compounds are arranged in the opposite stability sequence. Evidently the photochemical excitation of the dodeca- and nonacarbonyliron to the triplet state (from which the initial compound can dissociate) requires a greater expenditure of energy than the activation of $Fe(CO)_5$. This difference is due to the presence (in the former compounds) of many bonds over which the energy of the absorbed photon has to be redistributed.

The thermal and the photolytic decomposition of the carbonyl complexes are complicated by catalytic reactions on the resulting metallic surface, which adsorbs pentacarbonyliron and assists the nucleation of anion radicals. The latter interact with the initial molecule of the carbonyl complex and are converted into polynuclear anion radicals which ultimately decompose and contaminate the metal with carbide and oxide impurities. In some cases CO molecules are incorporated into the metallic phase.

The interaction of metal carbonyls with oxygen, ozone, and peroxides is accompanied by the formation of oxides and carbonates of the metals and by the oxidation of CO to CO_2. The reaction of $M_n(CO)_m$ with O_2 is initiated by UV radiation. The rate of the photo-oxidation of the carbonyls of Group VIII metals is approximately an order of magnitude greater than the rate of their photochemical decomposition. This is probably because the reaction between the coordinatively unsaturated carbonyl $M_n(CO)_{m-1}$ (or the metal carbonyl radical) and oxygen is spin-allowed and fast.[142] The reverse recombination of $M_n(CO)_{m-1}$ and CO is forbidden. The photolysis of the carbonyls of Group VI metals takes place through the reversible elimination of one carbonyl group.

The competition between CO and O_2 for the reaction with $M(CO)_5$ is apparently responsible for the lower reactivity of the chromium, molybdenum, and tungsten carbonyls towards the oxidation by oxygen. The mechanism of the oxidation of the carbonyl complexes is strongly dependent on the nature of the resulting intermediate species, varying from a radical mechanism (peroxidic metal carbonyl radicals of cobalt, manganese, etc.) to a molecular mechanism (carbonyl–oxygen complexes of iron, chromium, molybdenum, tungsten, etc.).

The reaction of the carbonyls of Group VIII metals with peroxidic compounds is a free-radical chain process in which the primary stage is electron transfer from the metal carbonyl to the peroxide, with formation of cation radicals of the metal carbonyls. It may be assumed that a stage of complex formation between the reactants occurs before the electron transfer. In conclusion we should note that in spite of some useful advances in identifying the products of the oxidative reactions of the carbonyls of elements in Groups VI–VIII, their kinetic features, and the influence of the medium and of other factors, the detailed mechanisms of these processes have not yet been established.

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