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COBALT CARBONYL RADICALS AND RADICAL REACTIONS OF COBALT CARBONYLS

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CONTENTS

A. INTRODUCTION

The existence of transition metal carbonyl radicals ** was recognized a long time ago [1]. Up to the last few years, however, research was focused mainly on the isolation of stable paramagnetic molecules [2] and on the use of metal carbonyls as initiators in radical polymerization [3]. Sporadic (prophetic!) hints [4] of the possibility of a more general role for radicals in the chemistry of metal carbonyls were neglected.

A surge of interest can be recognized in the mid-seventies. Probably two factors were responsible for this:

(a) The increasing number of observations which could not be explained by the otherwise excellent 16-18-electron rule made it more and more obvious that a reinterpretation of some experimental facts was necessary; and

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** The term "radical" is traditionally used for species of high kinetic lability. In this work however, to enable a unified treatment, it will also be used generally for stable paramagnetic molecules.

(b) experimental equipment (including observation of fast reactions, ESR, CIDNP, etc.) enabled the investigation of such molecular events and structural features which were practically inaccessible to the majority of chemists earlier.

The beginning of the "new wave" was marked by the almost simultaneous appearance of reviews rich in new ideas and unpublished experimental data [5–11].

This review attempts to summarize some earlier and recent results concerning the role of radicals in the chemistry of cobalt carbonyls.

B. COBALT CARBONYL RADICALS IDENTIFIED

The simplest binary cobalt carbonyl, $Co_2(CO)_8$, was first formulated as being monomeric: $Co(CO)_4$ [12]. The first experimental demonstration of the actual existence of the $\cdot Co(CO)_4$ radical, however, occurred only in 1965. Keller and Wawersik [1c] sublimed $Co_2(CO)_8$ on to a cold (77 K) finger in the magnetic cavity of an ESR spectrometer and obtained the ESR spectrum of the condensed $\cdot Co(CO)_4$ species. Somewhat later, $\cdot Co(CO)_4$ was observed in the mass spectrum of pyrolyzed $Co_2(CO)_8$ [13]. We should note again that the importance of these observations was not fully recognized and thus the next reports appeared only in 1973 and thereafter.

In 1973 Rest et al. [14] succeeded in the matrix isolation of $\cdot Co(CO)_4$ obtained from the pyrolysis of $Co(CO)_3(NO)$. The next year brought the identification of two adducts of $\cdot Co(CO)_4$: Symons et al. [15] isolated $\cdot O_2Co(CO)_4$ in an experiment similar to that of Keller and Wawersik. This dioxygen adduct is trigonal bipyramidal with O_2 in an axial position. The coordination of the O_2 ligand seems to be "bent", i.e. the Co–O–O angle is not 180° as shown by comparison of the $g_{\parallel}$ and $g_{\perp}$ values. Lappert's group [16] isolated "spin-trap" derivatives of a phosphite-substituted mononuclear cobalt radical:

$$\cdot\left[Co(CO)_3P(OEt)_3(ONAr)\right].$$

The so-called metal atom synthesis was used to obtain all $\cdot Co(CO)_n$ ($n = 1, 2, 3, 4$) species for a matrix isolation study [17]. Ozin et al. [17] reported an IR, Raman, UV/VIS and ESR comparative study (employing also isotopic CO enrichment) from which even the geometries of the "carbonylogous" species could be inferred.

$\cdot Co(CO)_4$: Two isomeric forms with distorted C_{3v} (low temp. preference, 6–8 K) and D_{2d} (higher temp. preference, 30–35 K)
$\cdot Co(CO)_3$: planar D_{3h} distorted towards C_{3v}
$\cdot Co(CO)_2$: linear $D_{\infty h}$
$\cdot Co(CO)$: linear $C_{\infty v}$

Possible reasons for the distortions are extensively discussed by supposing "holes" in the coordination sphere and even in the no longer spherical electron distribution around the metal [18]. This aspect may have fundamental importance for the stoichiometric and catalytic reactivity of the $\cdot Co(CO)_n$ radical species.

Based on the IR spectra obtained using a high-pressure infrared cell, Bor et al. [19] reported the presence of $\cdot Co(CO)_4$ radicals in solutions of $Co_2(CO)_8$ in *n*-hexane in the temperature range 120–210°C. This is an important observation because the experimental conditions used by these authors are near (or at least comparable) to those of the technically very important hydroformylation reaction [20,21].

The photochemical generation of $\cdot Co(CO)_n$ ($n = 1, 2, 3, 4$) radicals from $Co_2(CO)_8$ [22a] and $HCo(CO)_4$ [22b] can be demonstrated using matrix isolation techniques.

Recently, the CIDNP observation of caged radical pairs containing $\cdot Co(CO)_4$ was reported [23] by Orchin's group.

Fenske [24] isolated from the reaction of $Co_2(CO)_8$ with bis(diphenylphosphino)maleic anhydride a mononuclear, paramagnetic Co(0) complex which was stable even in air. The X-ray structure determination shows that five electron pairs are donated to the cobalt in this interesting compound. This represents one surplus electron with respect to the krypton configuration, which, according to spectroscopic data, is delocalized over the phosphorus atoms.

A series of dinuclear anionic cobalt carbonyl radicals were generated electrochemically: $[(\mu_2-X_2)Co_2(CO)_6]^{\cdot -}$ (X = acetylene and its derivatives or P_2 and As_2) [25]. The ESR spectra of these species enabled the approximate deduction of the position of the unpaired electron; it occupies a b_2 orbital, largely composed of Co $3d_{z^2}$, with the major axes oriented at 15–20° relative to the Co–Co bond.

The high energy (^{60}Co-γ) irradiation of various cobalt carbonyl complexes (generally at low temperature in 2-Me-THF matrix) enabled the trapping and detection of mono-, di- and tri-nuclear radical anions [26]; e.g., $[Co(CO)_4PbPh_3]^{\cdot -}$ [26a], $[Co(cp)(CO)_2]^{\cdot -}$, $[Co(cp)(CO)]_2^{\cdot -}$, $[Co(cp)(CO)]_3^{-}$ [26b] and $[Co_2(CO)_6(PBu^n_3)_2]^{-}$ [26c].

A considerable amount of work has been published on radicals deduced from the $ECo_3(CO)_9$ heteronuclear cluster unit [27] in which E may be B, RC, RSi, RGe, P, RP, As, S, Se or Te (R = various organic groups, halogens). These tetrahedral molecules demonstrate outstanding stability which may be attributed to electron delocalization in the cluster core [27a]. The bonding force of the "cluster orbitals" is so strong that — as recognized mostly just through the study of the radical species — the molecules can accommodate one or (sometimes) two extra electron(s) in antibonding orbital(s) without "exploding" the cluster.

In the $RCCo_3(CO)_9$ series, two types of radicals were recognized.

The $\cdot CCo(CO)_9$ radical has been proposed [28] on the basis of alkylation and arylation reactions with R_2Hg reagents and is suggested [29] to be involved in the following transformation:

$$HCCo_3(CO)_9 + CH_3COOCH_2CH{=}CH_2 \xrightarrow[\text{reflux}]{\text{AIBN}} CH_3COOCH_2CH_2CH_2CCo_3(CO)_9$$

This reaction is closely analogous to the reaction of chloroform with olefins in the presence of radical initiators (telomerization).

The $RCCo_3(CO)_9$ cluster is able to accommodate an unpaired electron without losing the R group. Such radical anions $[RCCo_3(CO)_9]^{\dot{-}}$ are formed in reduction reactions performed electrochemically or by alkali metals (Na, Cs) [30]. The radicals can be prepared for a variety of R: H, F, Cl, Br, Me, Et, CF_3, CH_2CF_3, $SiMe_3$ and COOH. Some of them can be identified only at lower temperatures (R = H below 223 K; R = Br, $SiMe_3$, COOH below 273 K), but others are found to be quite stable; they can be stored for up to 36 h in ethereal solvents or CH_2Cl_2. Attempts to isolate them in the form of ammonium salts failed, but good-quality ESR, IR and UV spectra can be obtained. The $RCCo_3(CO)_9$ cluster can also take up a second electron, but the $[RCCo_3(CO)_9]^{2-}$ species decompose rapidly.

The surprising paramagnetic $\cdot SCo_3(CO)_9$ cluster was prepared as early as 1961 [2f]. The structure was confirmed by X-ray diffraction [31] and the behaviour of the unpaired electron was studied by matrix ESR studies. The analogous $\cdot SeCo_3(CO)_9$ and $\cdot TeCo_3(CO)_9$ complexes were also studied [32]. This work proves that the unpaired electron is accommodated on an antibonding cluster orbital, as first supposed on the basis of X-ray structural data.

It is, however, surprising that this interesting and easily accessible radical species attracted only very limited attention. We know that reduction with Na/Hg may lead to the unstable $[SCo_3(CO)_9]^-$ species (IR evidence) [27e] (its instability seems to complement the observed instability of the $[RCCo_3(CO)_9]^{2-}$ ions as mentioned above, and some recent observations regarding the stability requirements of the $ECo_3(CO)_9$ (E = P, As) molecules [33]). Reaction of $\cdot SCo_3(CO)_9$ with phosphines leads to decomposition [34]; reaction with elemental sulphur yields diamagnetic $S_2[SCo_3(CO)_7]_2$ [35].

The diamagnetic counterpart of $\cdot SCo_3(CO)_9$ containing one iron atom, $SFeCo_2(CO)_9$ [36], can also be forced to take up an extra electron by electrochemical reduction, yielding $[SFeCo_2(CO)_9]^-$ [37] which was characterized by its ESR spectrum.

Another paramagnetic $ECo_3(CO)_9$ type complex was reported in 1975: $RPCo_3(CO)_9$ (R = *t*-Bu, Ph, NEt_2) [38]. These compounds also contain one unpaired electron, accommodated most probably on a cluster orbital. The structure assignment is based on IR spectroscopic data and the X-ray diffraction structure determination [39] of one representative (R = *t*-Bu), as well as on magnetic susceptibility measurements. Chemical reactions have not been reported.

The existence of a paramagnetic tricobalt species showing catalytic properties was suggested by Pregaglia et al. [40]. This compound is, however, not yet fully characterized.

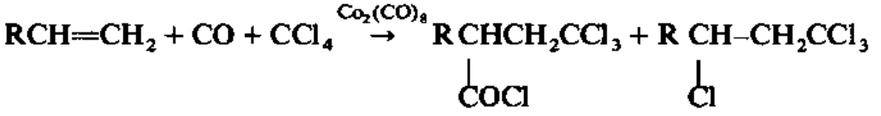
There are also some examples of paramagnetic cobalt carbonyls in the high nuclearity [41] series. Interestingly, both known examples are anionic "carbido" clusters (i.e. structures which contain interstitial carbon atom(s)): $[Co_6C(CO)_{14}]^-$ [42,43] and $[Co_{13}C_2(CO)_{24}]^{4-}$ [42,44]. X-ray diffraction [42–44] and ESR [45] studies showed that the extra electron seems to be localized on certain parts of the molecule (instead of being delocalized as is supposed for the tetrahedral structures), and causes deformations in the transition metal skeleton of the structure. These deformations most probably contribute to the widening of the intermetallic cavity for accommodation of the carbon atom. In other words the expanding influence of the interstitial main group atom enhances the uptake of the extra (unpaired) electron.

C. COBALT CARBONYL RADICALS IN MECHANISTIC (KINETIC) STUDIES

Some reactions of cobalt carbonyls show features which are characteristic of radical species as intermediates.

Higher nuclearity cobalt carbonyls (e.g. $Co_4(CO)_{12}$ [46] and $RCCo_3(CO)_9$, R = H, *i*-Pr, Ph, F, Cl, Br, C_2F_5 [47]) were found to have comparable or even higher initiator activity in the presence of tetrahalomethanes than the usual radical initiators (AIBN, etc.) in the polymerization of vinyl-type monomers (methylmethacrylate, AN, 4-vinylpyridine, etc.). It was observed [46] that $Co_4(CO)_{12}$ initiates four polymerization chains, which was explained by proposing the formation of one $\cdot CCl_3$ radical and one Co–Cl bond per Co atom. It is probable that the formation of the radical is preceded by the formation of an odd-electron cobalt species.

Dinuclear cobalt carbonyls were found to catalyze a co-telomerization-like reaction of olefins and CO in the presence of CCl_4 [48]:

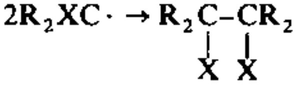


$$\mathrm{RCH{=}CH_2 + CO + CCl_4 \xrightarrow{Co_2(CO)_8} R\underset{\textstyle COCl}{CH}CH_2CCl_3 + R\underset{\textstyle Cl}{CH}{-}CH_2CCl_3} \qquad (1)$$

Dihalomethane derivatives and activated organic monohalocompounds undergo coupling reactions under the influence of cobalt carbonyls [49,50]. Reactions (2)–(5) were suggested [49] as the most probable route:

$$R_2CX_2 + [Co(CO)_4]^- \rightarrow [R_2XC \cdots X \cdots Co(CO)_4]^-$$

$$\rightarrow R_2XC\cdot + [XCo(CO)_4]^- \qquad (2)$$



$$2R_2XC\cdot \rightarrow R_2\underset{X}{C}-\underset{X}{C}R_2 \qquad (3)$$

$$[XCo(CO)_4]^- \rightarrow X^- + \cdot Co(CO)_4 \qquad (4)$$

$$2\cdot Co(CO)_4 \rightarrow Co_2(CO)_8 \qquad (5)$$

Similar reaction steps can be proposed in the formation of $RCCo_3(CO)_9$ complexes from RCX_3 trihalides and $[Co(CO)_4]^-$ or $Co_2(CO)_8$ [27a,49,51]. The formation of $[Co(CO)_4]^-$ from $Co_2(CO)_8$ under the influence of halide ions [52] may be of importance in this respect.

An ESR study of the reaction of alkyl halides with carbonylmetallate anions indicated a one-electron (radical pair) reaction route competing with the S_N2 path [53]. A similar result was achieved by recent work [54] on the carbonylation of aryl halides with the NaH/*t*-PentOH/Na$[Co(CO)_4]$/CO system, where an $S_{NR}1$ mechanism was proposed.

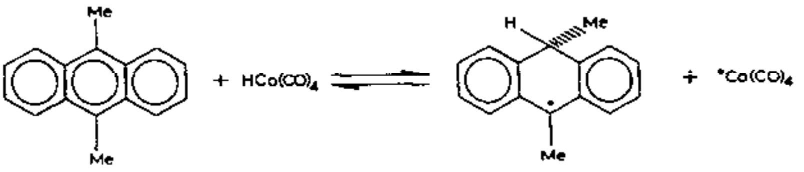
The interesting insertion reaction of $SnCl_2$ into a Co–Co bond (reaction 6) was explained by the formation of

$$[Co(CO)_3PBu_3]_2 + SnCl_2 \rightarrow [Co(CO)_3PBu_3]_2SnCl_2 \qquad (6)$$

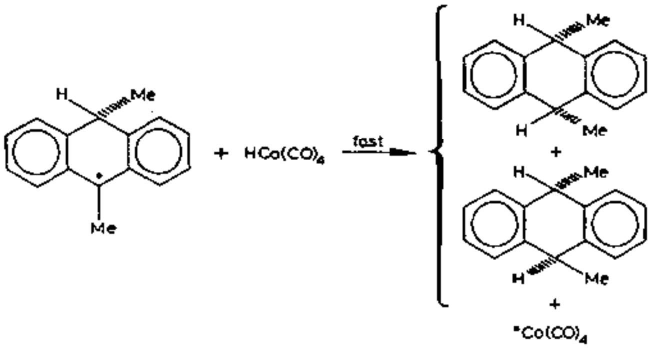
a geminate radical pair generated by the homolytic dissociation of the starting complex [55].

Cobalt tetracarbonyl hydride plays a key role in the technically very important hydroformylation reaction. This reaction was discovered about four decades ago and successfully used in industrial aldehyde and alcohol synthesis, but some details of its mechanism are still not clear. It is well known that $HCo(CO)_4$ is a strong acid in polar solvents, but in the last few years some observations were published which suggest that homolytic fission of the Co–H bond may also be important in determining the chemistry of this molecule.

An example of this is the stereochemistry of the products obtained from the hydrogenation of 9,10-dimethylanthracene with $HCo(CO)_4$ [56] (reactions 7–9).



(7)



(8)

$$2 \cdot Co(CO)_4 \overset{fast}{\rightarrow} Co_2(CO)_8 \tag{9}$$

Carbon monoxide is catalytically hydrogenated to methanol in the presence of $HCo(CO)_4$ at 200°C and 30 MPa synthesis gas ($H_2 : CO = 1 : 1$) pressure in benzene or dioxane solvent [57]. Based on thermodynamic considerations this reaction has been proposed to proceed as shown in eqns. (9)–(11):

$$CO + HCo(CO)_4 \overset{slow}{\rightarrow} H\dot{C}O + \cdot Co(CO)_4 \tag{10}$$

$$H\dot{C}O + HCo(CO)_4 \overset{fast}{\rightarrow} H_2CO + \cdot Co(CO)_4 \tag{11}$$

$$2 \cdot Co(CO)_4 \overset{fast}{\rightarrow} Co_2(CO)_8 \tag{9}$$

Kinetic measurements were performed on the stoichiometric hydrogenation of olefinic double bonds conjugated to aromatic ring(s) [58]. For 1,1-diphenylethylene and $HCo(CO)_4$, a reaction first order in $Ph_2C{=}CH_2$ and $HCo(CO)_4$, and an inverse isotope effect were observed. It could be proposed that the organic and metalorganic products are formed in fast reactions (9 and 13) from the radical pair generated in the rate determining step (12).

$$Ph_2C{=}CH_2 + HCo(CO)_4 \overset{slow}{\rightleftharpoons} [Ph_2\dot{C}CH_3, \cdot Co(CO)_4] \rightarrow$$

$$\rightarrow Ph_2\dot{C}CH_3 + \cdot Co(CO)_4 \tag{12}$$

$$Ph_2\dot{C}CH_3 + HCo(CO)_4 \overset{fast}{\rightarrow} Ph_2CHCH_3 + \cdot Co(CO)_4 \tag{13}$$

$$2 \cdot Co(CO)_4 \overset{fast}{\rightarrow} Co_2(CO)_8 \tag{9}$$

This interpretation is based on an explanation of the behaviour of $HMn(CO)_5$ under comparable conditions [59,60].

The mechanisms shown in the reactions (7)–(9), (10), (11), (9) and (12), (13), (9) have in common homolytic fission of the Co–H bond and recombination of the $\cdot Co(CO)_4$ radicals.

The fast reaction of $HCo(CO)_4$ and organic radicals was successfully modelled [61] by the reaction of cobalt tetracarbonyl hydride with triphenylmethyl radical:

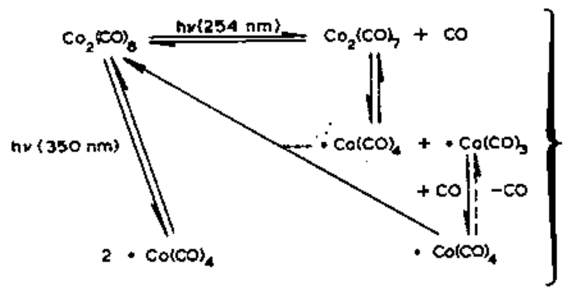
$$Ph_3C\cdot + HCo(CO)_4 \rightarrow Ph_3CH + \dot{C}o(CO)_4 \tag{14}$$

$$2\cdot Co(CO)_4 \rightarrow Co_2(CO)_8 \tag{9}$$

The intermediacy of the radical pair in eqn. (12) was proved by the CIDNP-effect of the methyl protons of the product, 1,1-diphenylethane [23]. Similar behaviour has also been observed in the reaction of some other styrene derivatives with $HCo(CO)_4$ [62]. These experiments, however, were performed in a halogenated solvent (CH_2Cl_2), which might favour the formation of radicals (cf. for example ref. 46).

The kinetic investigation of the reaction of styrene with $HCo(CO)_4$ [63] showed that not only the formation of the ethylbenzene (analog of 1,1-diphenylethane in the former study [58]) can be interpreted in terms of the formation of a radical pair, but that of the carbonylation product as well [63]. This observation has important implications in the elucidation of the mechanism of hydroformylation of certain olefins.

The mechanism of the photo- or thermo-lysis of $Co_2(CO)_8$ involves a series of radical reactions as shown by the results of a matrix isolation study [22a] (reaction 15).



(15)

In solution the thermal decomposition of $Co_2(CO)_8$ leads to the formation of $Co_4(CO)_{12}$. The mechanism of this reaction is still the subject of conflicting opinions [22a,64,65].

The substitution of $Co_2(CO)_8$ with soft Lewis bases as tertiary phosphines, arsines, stibines, phosphites, etc. also apparently proceeds through radical intermediates. This reaction cannot be regarded as being well understood although a recent study by Brown et al. [66,67] made a significant contribution. The reaction is proposed to start by the formation of an

"S_N2"-type adduct of $Co_2(CO)_8$ and the Lewis base (L), followed by a Co–Co bond homolysis (17), which starts radical chain reactions consisting of an electron transfer (18), a fast dissociation (19) and a subsequent substitution (20) step.

$$Co_2(CO)_8 + L \rightleftharpoons Co_2(CO)_8(L) \tag{16}$$

$$Co_2(CO)_8(L) \rightarrow \cdot Co(CO)_3(L) + \cdot Co(CO)_4 + CO \tag{17}$$

$$\cdot Co(CO)_3(L) + Co_2(CO)_8 \rightarrow [Co(CO)_3L]^+ + [Co_2(CO)_8]^{\dot{-}} \tag{18}$$

$$[Co_2(CO)_8]^{\dot{-}} \rightarrow [Co(CO)_4]^- + \cdot Co(CO)_4 \tag{19}$$

$$\cdot Co(CO)_4 + L \rightarrow \cdot Co(CO)_3L + CO \tag{20}$$

The substitution products, $Co_2(CO)_6L_2$ (L = PBu^n_3, $P(OPh)_3$), showed an analogous photochemistry [68]. The Co–Co bond in these complexes was cleaved homolytically upon irradiation, giving rise to the $\cdot Co(CO)_3(L)$ species. These were detected by reactions with Mn and Fe carbonyls as well as by their proposed role as activators of H in H_2 or $HSiEt_3$. It should be noted, however, that the ability of phosphine-substituted cobalt carbonyl radicals to activate H in H_2, $HSi(OEt)_3$ or $CH_3C_6H_{11}$, as well as CO, has seriously been doubted in a recent paper by Mirbach et al. [69].

The substitution of $Cl_3SnCo(CO)_4$ with soft Lewis bases (L = PBu^n_3, PPh_3, $AsPh_3$) was investigated and interpreted as shown in eqns. (21) and (22) representing the starting steps of the chain process [70] (cf. reactions 16 and 17).

$$Cl_3SnCo(CO)_4 + L \rightleftharpoons Cl_3(L)SnCo(CO)_4 \tag{21}$$

$$Cl_3(L)SnCo(CO)_4 \xrightarrow{\Delta \text{ or } h\nu} Cl_3\dot{Sn}L + \cdot Co(CO)_4 \tag{22}$$

It has been observed recently that the presence of $Co_2(CO)_8$ influences the rate of certain reactions where the stoichiometry would not require such a dependence.

The first observation of this kind was published in 1974 reporting [71] that the thermal decomposition of $HCo(CO)_4$ (eqn. (23)) proceeds more rapidly in the presence of $Co_2(CO)_8$.

$$2\ HCo(CO)_4 \rightarrow H_2 + Co_2(CO)_8 \tag{23}$$

More detailed quantitative studies [61,72] have demonstrated that the kinetic order of $Co_2(CO)_8$ is 0.5, which suggests $\cdot Co(CO)_4$ radicals as intermediates. The kinetic observations were interpreted in terms of a mechanism shown by eqns. (9) and (24)–(28).

$$Co_2(CO)_8 \rightleftharpoons 2 \cdot Co(CO)_4 \tag{9}$$

$$\cdot Co(CO)_4 \rightleftharpoons \cdot Co(CO)_3 + CO \tag{24}$$

$$\cdot Co(CO)_3 + HCo(CO)_4 \rightleftharpoons \cdot HCo_2(CO)_7 \tag{25}$$

$$\cdot HCo_2(CO)_7 + HCo(CO)_4 \rightarrow H_2Co_2(CO)_7 + \cdot Co(CO)_4 \tag{26}$$

$$H_2Co_2(CO)_7 \rightarrow H_2 + Co_2(CO)_7 \tag{27}$$

$$Co_2(CO)_7 + CO \rightleftharpoons Co_2(CO)_8 \tag{28}$$

Among these steps special attention should be paid to the facile CO loss from $\cdot Co(CO)_4$ (eqn. (24)) which not only fits the kinetic results but is supported by a large body of observations with other metal carbonyls [73]. This ability of radical species may play an important role in their catalytic chemistry since in this manner vacant coordination sites for substrate coordination become easily available.

The importance of the interaction of $Co_2(CO)_8$ with $HCo(CO)_4$ is well demonstrated by the belief that $HCo(CO)_4$ is a slightly yellow substance very readily decomposing to $Co_2(CO)_8$. It turned out recently, however, that $HCo(CO)_4$ which is absolutely free of $Co_2(CO)_8$ is a colourless liquid displaying considerable stability [74]. It could be shown by spectrophotometric methods that samples of cobalt tetracarbonyl hydride prepared by the usual methods always contain some $Co_2(CO)_8$, which then catalyses the thermal decomposition of $HCo(CO)_4$ [72]. Curiously enough, this important fact remained hidden for decades.

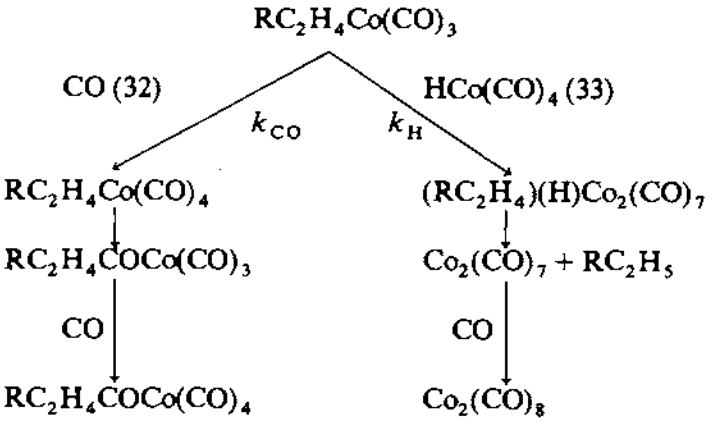
Similar to the decomposition of $HCo(CO)_4$, kinetic 0.5 order has been observed for $Co_2(CO)_8$ in the hydrogenation [75] and carbonylation [76,77] of certain olefins (1-heptene, cyclohexene, ethylacrylate), suggesting $\cdot Co(CO)_4$ as intermediate. The role of the cobalt tetracarbonyl radical could be promotion of the formation of the olefin-substituted derivative of $HCo(CO)_4$ as sketched in reactions (28)–(33).

$$Co_2(CO)_8 \overset{K_1}{\rightleftharpoons} 2 \cdot Co(CO)_4 \tag{28}$$

$$\cdot Co(CO)_4 + RCH{=}CH_2 \overset{K_2}{\rightleftharpoons} \cdot Co(CO)_3(RCH{=}CH_2) \tag{29}$$

$$\begin{aligned} \cdot Co(CO)_3(RCH{=}CH_2) + HCo(CO)_4 \underset{\text{slow}}{\overset{k_a}{\rightarrow}} {} & HCo(CO)_3(RCH{=}CH_2) \\ & + \cdot Co(CO)_4 \end{aligned} \tag{30}$$

$$HCo(CO)_3(RCH{=}CH_2) \overset{K_3}{\rightleftharpoons} RC_2H_4Co(CO)_3 \tag{31}$$



Most of the above results parallel the hydroformylation reaction, the most important homogeneous molecular catalytic reaction. None of the results outlined above are mentioned, however, even in the most excellent and thorough reviews treating this reaction [20,21].

D. PRODUCT DISTRIBUTION STUDIES

In the preceding sections we have treated the results of spectroscopic and kinetic investigations which, as mentioned earlier, constitute the majority of work dealing with radical species in reactions of cobalt carbonyls.

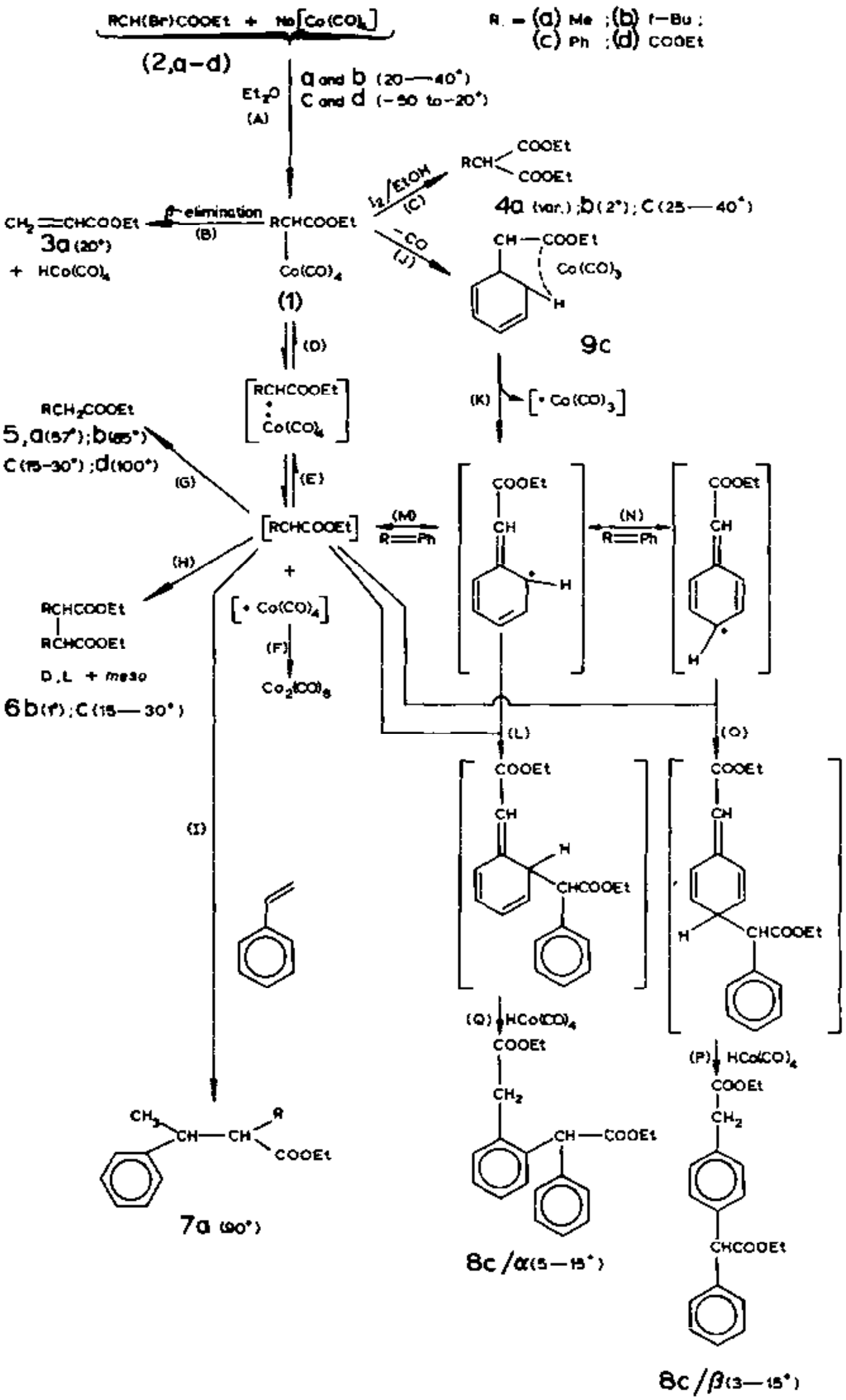
In the following part of this paper we describe some of our own (partly unpublished) results obtained with mono- [50] and tri-nuclear [78] cobalt carbonyls which are based mainly on product distribution studies.

In an attempt to find a suitable source of mononuclear cobalt carbonyl radical(s) we turned our attention to the thermal decomposition of alkylcobalt carbonyls. Based on experience with stable non-fluorinated alkylcobalt tetracarbonyls [79–81] we chose the $RCo(CO)_4$ series (**1**) of compounds with R = CH(X)COOEt (X = (**a**) Me; (**b**) *t*-Bu; (**c**) Ph; (**d**) COOEt) as models. These could be obtained from the reaction of the corresponding bromo compounds (**2**) and $Na[Co(CO)_4]$ [82].

The observed reactions are shown and rationalized in Scheme 1. The following points should be emphasized:

(a) none of the compounds (**1a**–**d**) inserted CO to form the corresponding acylcobalt carbonyl at atmospheric pressure under CO; and

(b) most of the organic products **5**–**8** can be derived from radical-type decomposition of **1**. The thermal stability of compounds **1c**–**d** decreases in the order Me > Ph > tBu ≫ COOEt.


RCH(Br)COOEt + Na[Co(CO)4]
(2,a–d)
R = (a) Me ; (b) t-Bu ; (c) Ph ; (d) COOEt
Et2O (A)
a and b (20—40°)
c and d (−50 to −20°)
RCHCOOEt
Co(CO)4
(1)
β-elimination (B)
CH2=CHCOOEt
3a (20°)
+ HCo(CO)4
½ I2/EtOH (C)
RCH(COOEt)2
4a (var.); b (2°); c (25—40°)
−CO (J)
CH—COOEt
Co(CO)3
H
9c
(D)
[RCHCOOEt · Co(CO)4]
(E)
(K)
[· Co(CO)3]
RCH2COOEt
5, a (57°); b (85°); c (15–30°); d (100°)
(G)
[RCHCOOEt]
+
[· Co(CO)4]
(F)
Co2(CO)8
(H)
RCHCOOEt
RCHCOOEt
D,L + meso
6b (1°); c (15—30°)
(M) R=Ph
COOEt
CH
H
(N) R=Ph
(I)
(L)
(O)
CHCOOEt
(Q) HCo(CO)4
(P) HCo(CO)4
CH2
CH—COOEt
CH3
CH—CH
R
COOEt
7a (90°)
8c/α (5—15°)
CHCOOEt
8c/β (3—15°)

Scheme 1

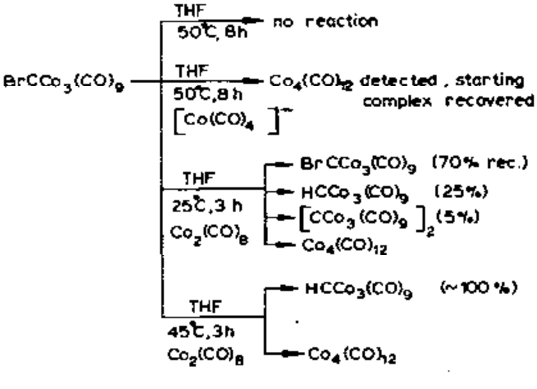
An explanation which is very similar to equilibrium (D) was advanced recently [83] for the formation of hydrogenated and coupling products in the reaction of benzyl halides with $Co_2(CO)_8$ under phase transfer conditions.

The other part of our work reported here concerns the preparative detection of the $\cdot CCo_3(CO)_9$ radical. One of the very first papers describing the preparation of $YCCo_3(CO)_9$ complexes from YCX_3 ($X = Cl, Br$) compounds [84] reported the formation of $HCCo_3(CO)_9$ in the reaction of CX_4 compounds with $[Co(CO)_4]^-$ in ethereal solvents. We were able to reproduce these reactions under rigorously anhydrous conditions. In a subsequent systematic study we found that the H derivative and the dimeric (coupling) product of reaction (34) could be detected only if excess $Co_2(CO)_8$ was present, and their quantity increased with increasing Co/CX_4 ratio. These facts suggest a radical-type transformation of the intermediate $XCCo_3(CO)_9$ cluster instead of a nucleophilic dehalogenation of the "last" C–X bond.

$$[Co(CO)_4]^- + CX_4 \xrightarrow[45°C,5\,h]{THF} \begin{array}{l} \rightarrow XCCo_3(CO)_9 \\ \rightarrow HCCo_3(CO)_9 \\ \rightarrow [CCo_3(CO)_9]_2 \end{array} \tag{34}$$

Further evidence for radical reactions could be found by a reinvestigation of the reaction of CBr_4 with $Co_2(CO)_8$ in benzene. We confirmed (as reported by Ercoli et al. [51]) the formation of $BrCCo_3(CO)_9$ in good yield, but observed also the formation of the phenyl derivative $C_6H_5CCo_3(CO)_9$ (~ 1–5% with respect to the main product). This latter complex may be formed by reaction of the $\cdot CCo_3(CO)_9$ radical with solvent.

The last observation directed our attention to the chemistry of $BrCCo_3(CO)_9$. Here again $Co_2(CO)_8$ is important. The results are summarized in reaction (35).



(35)

These reactions can plausibly be interpreted in terms of the formation of $\cdot CCo_3(CO)_9$ radicals.

E. CONCLUDING REMARKS

After a brief and sometimes subjective review of the most important results concerning the role of radicals in reactions of cobalt carbonyls we can deduce some generalizations.

(i) Solid experimental evidence supports the existence of mono- and tri-nuclear cobalt carbonyl radicals.

(ii) Indirect evidence renders it very probable that such radicals take part in the elementary steps of well known reactions of cobalt carbonyls much more frequently than believed earlier.

(iii) Unjustified generalizations should be avoided. Very recently some papers appeared proving that reactions which were believed to be of radical character are in fact proceeding through other elementary steps [85–87]. Special attention should be called to the pioneering work of Fachinetti et al. [88–90] who presented, in the last 3 years, a series of preparative observations which may allow an unexpected paired-electron explanation of certain observations interpreted by one-electron elementary steps. These reservations are also true for the interpretation of the product distribution results described in the final part of this paper.

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