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Radiation Synthesis of Organometallic Compounds. Radiolysis of Benzene Solutions of $Co_2(CO)_8$*

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Abstract

The radiation-induced synthesis of $\mu_2(\eta^2$-cyclohexyne)hexacarbonyl dicobalt (Co–Co) and μ_3(2-cyclopenten-1 methylidine)-cyclo-tris(tricarbonyl cobalt)(3Co–Co) from benzene and $Co_2(CO)_8$ is reported. The metal carbonyl species act as traps for some of the radiation-induced excited species.

Introduction

Radiation-induced reactions of solutions of metal carbonyls have received little attention [1, 2]. Under radiation, metal carbonyls easily lose a CO molecule leading to very reactive intermediates [1] and, if reactive species are present, stable organometallic compounds may be formed. When the CO recombination reaction is very fast, as for tetracarbonyl nickel, the carbonyl metal compound behaves as a very efficient 'energy sink' protecting the system from radiation damage [2–4].

Following a previous report on the gas phase reactivity of $Fe(CO)_5$ and $Ni(CO)_4$ with organic radicals and ions obtained by radiolysis [5], here we describe some of the complexes obtained by radiolysis of a benzene solution of $Co_2(CO)_8$. Radiation effects on solutions of $Co_2(CO)_8$ have been reported only in relation to catalytic and autocatalytic processes [6, 7].

Experimental

$Co_2(CO)_8$ (Merck) was used without further purification. Benzene (C. Erba R.P.) was dryed over Dri-Na (Backer), distilled and stored over 4 Å molecular sieves. $Co_4(CO)_{12}$ was prepared by refluxing a $Co_2(CO)_8$ solution in light petrol (boiling point (b.p.) 40–70 °C) for 2.5 h at 323 K under nitrogen and crystallized from n-pentane. CO and H_2 (SIAD: Società Italiana Acetilene e Derivati) were used without further purification. 2.0×10^{-2} molar solutions of $Co_2(CO)_8$ or 7.1×10^{-3} molar solutions of $Co_4(CO)_{12}$ in benzene were prepared under inert atmosphere and sealed under vacuum in pyrex ampoules. In some runs CO or H_2 were added to the samples at partial pressure of 21 KPa for the former and of 81 KPa for the latter.

The samples were irradiated in a 220 Gammacell (Nuclear Canada Ltd) up to a dose of 8×10^5 Gy with a dose rate of 9×10^3 Gy h^{-1}. The dose was tested by Frick dosimetry. During the irradiation the temperature of the samples was raised to about 313 K.

After irradiation the solutions were evaporated under reduced pressure. The soluble components of the residue were separated by preparative TLC on 20×40 cm plates coated with Kiesegel PF_{254} glipshatlig (Merck) using light petrol as eluent. Lobar Lichroprep RP-8, Size A, column (Merck) was also used to separate $Co_2(CO)_6C_2H_2$ from Complex I, using ethanol as eluent.

IR, NMR and mass spectra were recorded on Perkin-Elmer 580 B (using NaCl cell), Jeol JNK 270 FT and Kratos MS 80, respectively.

Results

The solvent distilled at reduced pressure and appeared yellow in many instances.

The TLC plates of the $Co_2(CO)_8$ runs showed seven colored bands, plus one which was detectable only under UV light. The colored bands belong to Co-containing compounds, whereas the UV band corresponds to organic materials, mainly diphenyl and phenylcyclohexene. When CO was added to the samples before radiolysis the yield of the Co-containing compounds was reduced by about 30%.

After repeated separations, four Co-containing compounds have been identified. Two of them, $Co_2(CO)_6C_2H_2$ (~0.1% *vs.* Co) and $Co_4(CO)_{12}$ (0.3% yield on Co basis), are well known and have been reported in the literature [8, 9]. The other two com-

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pounds, **I** (~0.1% yield *vs.* Co) and **II** (~0.3% yield *vs.* Co), have never been reported.

Compound **I** is a yellow–orange oil which shows, in the CO stretching region of the IR spectrum, absorption maxima at 2092(m), 2053(s) and 2028(s) cm^{-1} (CCl_4 solution). Its electron impact mass spectrum displays the molecular ion at m/z 366, followed by the loss of six carbonyl groups, and therefore the molecular formula $Co_2(CO)_6C_6H_8$ can be suggested. It is very unstable at about 300 K under inert atmopshere and also decomposes slowly at 250 K under N_2.

Compound **II** is a purple solid showing IR absorptions, in the CO stretching region, at 2101(m), 2050(vs), 2035(s) and 2015(m) cm^{-1} (CCl_4 solution). The electron impact mass spectrum exhibits the molecular ion at m/z 508 followed by the loss of nine carbonyl groups; therefore the molecular formula $Co_3(CO)_9C_6H_7$ is suggested. Its ^1H NMR spectrum shows four resonances at 5.9 ppm (2m, H_b), 4.9 (2m, H_c), 2.5 (4bm, $H_{d,e}$) and 1.8 (1m, H_a) (see Fig. 1). The ^{13}C NMR spectrum consists of six signals at: 200.3 ppm (CO), 137.2 ppm (d_1 $^1J_{CH}$ = 160 Hz), 132.2 ppm (d_1 $^1J_{CH}$ = 160 Hz), 72.7 ppm (d_1 $^1J_{CH}$ = 133 Hz), 37.8 ppm (t_1 ^1J = 133 Hz) and 32.2 ppm (t_1 ^1J = 130 Hz). This indicates the existence of two different sp^2 CH, one sp^3 CH and two CH_2, respectively. The apical ^{13}C resonance is expected at very low field [10] but the limited amount of sample available did not allow us to detect it.

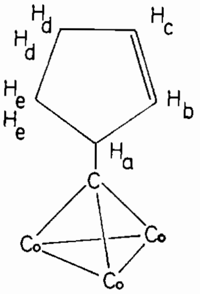

Fig. 1. μ_3(2-cyclopenten-1-methylidine)-cyclo-tris(tricarbonyl cobalt)(3Co–Co).

Compound **II** is quite stable; in n-octane solution under 70 KPa of H_2 it did not decompose after 2 h at 373 K. Compounds **I** and **II** are the most abundant and, as already reported, **II** is obtained in slightly higher yield than **I**. If benzene solutions of $Co_2(CO)_8$ were radiolyzed under H_2 a tenfold increase of the yields of **I** and **II** was observed.

When benzene solutions of $Co_4(CO)_{12}$ were radiolyzed, six Co-containing bands plus one of organic material, mainly diphenyl and phenilcyclohexene, were observed on TLC plates. No $Co_2(CO)_6C_6H_8$ and $Co_2(CO)_6C_2H_2$ were obtained whereas $Co_3(CO)_9C_6H_7$ was recovered in higher yield. In no instances was the compound $Co_4(CO)_9C_6H_6$ observed [11].

1,3- and 1,4-cyclohexadienes were refluxed at 328 K for four hours under nitrogen with solutions of $Co_2(CO)_8$ in light petroleum. None of the compounds observed in radiolysis experiments were obtained.

The dose effect on a benzene solution of $Co_2(CO)_8$ was studied under H_2 atmosphere: decreasing the dose from 8×10^5 to 5×10^4 Gy, the yields of **I** and **II** decreased by a factor of ~60 and ~20, respectively, while a large amount of $Co_2(CO)_8$ was recovered unreacted.

Discussion

Thermal and photochemical decomposition paths of $Co_2(CO)_8$ are reported in the literature [12, 13]. The radical Co–carbonyl species are known to be very reactive in many type of reactions [14]. The few reported effects on γ radiation on $Co_2(CO)_8$ are in good agreement with the reported reaction pattern [6, 7] which leads to $Co_4(CO)_{12}$, insoluble polymeric material, metal powder and CO as final products.

Radiolysis of benzene has been carefully studied [15]. In the liquid phase the main products are H_2, C_2H_2, cyclohexadienes and polymeric materials, mainly phenilcyclohexene and diphenyl. The mechanisms for the formation of each product have been proposed [16]. Photochemical isomerization of the aromatic ring has also been reported [17] and radiation isomerization of hexafluorobenzene to Dewar benzene has been demonstrated [18].

The products observed upon radiolysis of benzene solutions of $Co_2(CO)_8$ or $Co_4(CO)_{12}$ appear to be due to the interaction of the radiolysis intermediates of Co-carbonyls and the radiolytic species of benzene. Acetylene is one of the major products of the radiolysis of benzene [15] and it is also known to react in mild conditions with $Co_2(CO)_8$ to give $Co_2(CO)_6C_2H_2$ [19]. The appearance of such a compound in the radiolyzed solution could then be attributed to the reaction of $Co_2(CO)_8$ or $Co_2(CO)_6$ with acetylene, although the Co–carbonyl species do not behave as scavengers for acetylene. In fact, the C_2H_2 yield is reduced but not suppressed [20].

The increase of the yields of both compounds **I** and **II**, when the solution was radiolyzed under dihydrogen, indicates that a reactive intermediate from the reaction of a H radical with benzene (*i.e.*, a cyclohexadienyl species) is a precursor for both complexes.

Cyclohexadienyl radicals have been observed during radiolysis of benzene [21], and cyclohexadienes have been obtained as final products. The ratio of 1,3- to 1,4-cyclohexadienes has been reported to be about 1:2.7 independent of the dose and the nature of the radiation [22].

Complex **I**, which is less abundant than **II** (about 1:3 ratio), appears to be formed by the reaction of an excited precursor of 1,3-cyclohexadiene [23] which isomerizes to cyclohexyne on reaction with the $Co_2(CO)_8$ or $Co_2(CO)_6$ species and is stabilized to a compound which has been tentatively identified as $\mu_2(\eta^2$-cyclohexyne)hexacarbonyl dicobalt (Co–Co). The low stability of such a compound, which has prevented further structural investigations, seems to be due to the high strain of the cyclohexyne ring [24]. Two compounds with the same formula as complex **I** have been reported in the literature the latter not isolated in a pure form: (a) $\mu_2(\eta^2$-1-hexan-5-yne)hexacarbonyldicobalt (Co–Co) [25a] and (b) $Co_2(CO)_6C_6H_8$ from the thermal reaction of $Co_2(CO)_6$ and 1,3-cyclohexadiene [25b]. A more stable Co-complex, showing the coordination to two metal atoms of a six-membered carbocyclic ring containing a triple bond, has also been reported as $Co_2(CO)_6C_6F_6$ [26]. Its higher stability is apparently due to the fluorine and to the presence of both a double and a triple bond in the carbon ring.

Compound **II**, which is obtained in higher yield than complex **I**, appears to be formed by an excited cyclohexadienyl species (probably the excited radical precursor of 1,4-cyclohexadiene) which on reaction with the carbonyl isomerizes to 2-cyclopenten-1-methylidine. The isomerization of excited six-membered rings to five-membered rings has been observed for benzene, which isomerizes to fulvene and benzvalene, in both gas and liquid phases [16–18]; for cyclohexene [27] and cyclohexane [28, 29] in gas phase. The excited tri-radical 2-cyclopenten-1-methylidine acts as a tri-electron donor to $Co_3(CO)_9$ which acts as energy sink leading to the very stable complex **II**: μ_3-(2-cyclopenten-1-methylidine)cyclo-tris(tricarbonyl cobalt) (3Co–Co).

Possible radiation-induced transformation of complex **I** into complex **II** can be excluded by the finding that as the radiation dose increases 16 times the yield of **I** increases by a factor of 60, whereas the yield of **II** increases only 20 times.

The larger increase of the yield of **I** with the dose and the finding of large amounts of unreacted $Co_2(CO)_8$ at low radiation doses indicate that the organic precursor of complex **I** reacts mainly with the radiation-unaffected carbonyl, whereas complex **II** derivates from an already formed polymeric carbonyl species, e.g. $Co_4(CO)_{12}$.

It has been found that when solutions of $Co_4(CO)_{12}$ are radiolyzed, the yield of **II** is sharply increased and that the presence of CO reduces the yields of all the complexes. These findings indicate that the clustering of the carbonyl is an important step in the reaction and that the formation of complex **II** could be attributed to the following reaction:

$$Co_4(CO)_{12} + C_6H_7 \longrightarrow Co_3(CO)_9C_6H_7 + Co(CO)_3$$

Conclusion

Ionizing radiations induce many excited species in the absorbing media; unfortunately, some of them could not be isolated because of collisional deactivation or further reactions which modify their structures. The finding that some unusual species can be trapped as part of metal carbonyl complexes is a further example of the particular reactivity of metal carbonyls and provides a new tool for the study of radical (and possibly ionic) high energy reactive intermediates.

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