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Reaction of octacarbonyldicobalt with the free radicals galvinoxyl and 2,2-diphenyl-1-picrylhydrazyl. Attempts to scavenge the tetracarbonylcobalt radical

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Dedicated to Professor Andrew Wojcicki in recognition of his pioneering work in metal carbonyl chemistry

Abstract

The addition of galvinoxyl or 2,2-diphenyl-1-picrylhydrazyl to octacarbonyldicobalt in n-octane solution results in the loss of all carbon monoxide ligands and the formation of Co(II)-containing products. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The 17-electron tetracarbonylcobalt radical was first observed during the thermal dissociation of $Co_2(CO)_8$ in the gas phase using high vacuum. It has been isolated on a cold (77 K) finger and its ESR spectrum was recorded [1]. This species was observed also in the mass spectrum of pyrolyzed $Co_2(CO)_8$ [2]. Using the matrix isolation technique, $Co(CO)_4$ [3], and $Co(CO)_n$ (n = 1, 2, 3, 4) [4] were prepared and characterized by their infrared, Raman, UV–Vis and ESR spectra.

Since the thermolysis of the cobalt–cobalt bond in $Co_2(CO)_8$ changes the magnetic susceptibility of the solution owing to the production of $Co(CO)_4$ radicals, the extent of this homolysis was determined by measuring the temperature dependence of the volumetric susceptibility of a gas-phase solution of $Co_2(CO)_8$ in carbon monoxide in the temperature range 120-225 °C. From the temperature dependence of the equilibrium constant $\Delta H = (81.1 \pm 8.5)$ kJ mol⁻¹ and $\Delta S = 123.8 \pm$

17.1 J mol⁻¹ K⁻¹ have been calculated [5]. The bond dissociation energy based on thermochemical calculations has been given as $D_{298}[(CO)_4Co-Co(CO)_4] = 83 \pm 29 \text{ kJ mol}^{-1}$ [6].

The generation of the tetracarbonylcobalt radical by photolysis of $Co_2(CO)_8$ in CO matrices has also been reported [7].

There is ample evidence that the ${}^{\bullet}Co(CO)_4$ radical exists not only in the gas phase or under extreme conditions but also in low concentrations in solutions of $Co_2(CO)_8$ at ambient conditions. Based on high-pressure infrared spectra the presence of ${}^{\bullet}Co(CO)_4$ radicals in solutions of $Co_2(CO)_8$ in *n*-hexane has been confirmed in the temperature range of $120-210 {}^{\circ}C$ [8].

The participation of the 17-electron $^{\circ}Co(CO)_4$ radical in various reactions of cobalt carbonyls has been inferred from the observation that the rates of these reactions were found to be proportional to the square root of $Co_2(CO)_8$ concentration [9–17]. This can be related to the fast equilibrium formation of $^{\circ}Co(CO)_4$ from $Co_2(CO)_8$ which is then involved in the ratedetermining step.

$$\operatorname{Co}_2(\operatorname{CO})_8 \stackrel{K}{\rightleftharpoons} 2^{\bullet} \operatorname{Co}(\operatorname{CO})_4$$

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$$K = \frac{[{}^{\bullet} \text{Co}(\text{CO})_4]^2}{[\text{Co}_2(\text{CO})_8]} \text{ and} \\ [{}^{\bullet} \text{Co}(\text{CO})_4] = K^{0.5} [\text{Co}_2(\text{CO})_8]^{0.5}$$

The tetracarbonylcobalt radical has a high reactivity. It dimerizes spontaneously [1], reacts with O₂ to form $^{\circ}O_2Co(CO)_4$ [18,19] and abstracts a hydrogen atom from transition metal hydrides [5]. According to NMR line-shape analysis, the degenerate hydrogen-atom transfer reaction between HCo(CO)₄ and $^{\circ}Co(CO)_4$ proceeds with activation parameters of $\Delta H^{\ddagger} = 23.5 \pm 2.5$ kJ mol⁻¹ and $\Delta S^{\ddagger} = -68.3 \pm 4.3$ J mol⁻¹ K⁻¹ [5].

It was found recently that $Co_2(CO)_8$ in *n*-pentane solution under thermal or photochemical conditions reacts with 2,2,6,6-tetramethylpiperidin-1-oxyl (TMPO) to give a diamagnetic electron-deficient complex $(TMPO)Co(CO)_2$ in good yields. It was assumed that the first step of the complex formation is the reaction of TMPO with \cdot Co(CO)₄, followed by the evolution of two mol of carbon monoxide [20]. Indeed the kinetics of the gas evolution was found to be half order in $Co_2(CO)_8$ concentration which strongly supports the idea that cobaltcarbonyl radicals are scavenged by the organic free radicals [21]. In this paper we describe the results of the reactions of $Co_2(CO)_8$ with two other organic free radicals, namely of galvinoxyl and with 2,2diphenyl-1-picrylhydrazyl. In contrast to the results with TMPO, in both cases we obtained products of simple redox reactions.

2. Experimental

2.1. Chemicals

Octacarbonyldicobalt was prepared from cobalt(II) acetate tetrahydrate, dihydrogen and carbon monoxide in acetic anhydride solution [22]. The crude product of this high-pressure synthesis was doubly recrystallized first from methylene dichloride and then from n-heptane under carbon monoxide. Carbon monoxide was prepared from formic acid and concentrated sulfuric acid and was dried on P₄O₁₀ and deoxygenated on activated BTS catalyst R 3-11 (BASF, Germany). Anhydrous noctane 99%+ (Aldrich, Hungary) was distilled over sodium-wire under carbon monoxide. Galvinoxyl free radical (Aldrich, Hungary) and 2,2-diphenyl-1-picrylhydrazyl (hydrate) free radical (Aldrich, Hungary) were used as received. Stock solutions of Co₂(CO)₈ (0.20 mol dm^{-3}), of galvinoxyl (0.06 mol dm^{-3}), and of 2,2diphenyl-1-picrylhydrazyl (0.0017 mol dm⁻³) in noctane were freshly prepared under carbon monoxide before the kinetic runs.

2.2. Kinetic experiments

Kinetic experiments were performed in a thermostatted glass-reactor fitted with a silicon-disk-capped stopcock, and connected to a gas burette through a reflux condenser (thermostatted to 12.0 °C). The reactions were started by injecting either aliquots of the $Co_2(CO)_8$ stock solution into the solutions of the free radicals in *n*-octane or by injecting aliquots of the freshly prepared stock solutions of the free radicals into the solutions of $Co_2(CO)_8$ in *n*-octane. The initial rate was calculated from the gas burette readings collected in the first $1-5 \min (4-20)$ points). The effect of carbon monoxide concentration on the rate of gas evolution was studied by using different total pressures (0.27-1.0 bar) in the gasometric apparatus and in experiments starting under an argon atmosphere. The rates are reproducible to within 10%.

2.3. Instrumentation

IR spectra were recorded either on a Specord IR-75 or on a Specord M-80 (Carl Zeiss, Jena) spectrometer. Electronic spectra were measured on a Shimadzu UV-160A spectrophotometer. GC analyses of the gas evolved in the reactions were performed on a HP 5890II gas chromatograph equipped with a thermal conductivity detector and a 25 m, 0.53 mm Poraplot Q column. GC MS measurements were recorded on a HP 5890II/5971 GC/MSD at 75 eV. Analyses for C, H, N were performed using a CHNSO Analysator (Carlo Erba). Cobalt analyses were performed using established microanalytical methods.

2.4. Preparation of the cobalt salt of G^-

To a magnetically stirred solution of galvinoxyl (1.72 g, 4.08 mmol) in *n*-octane (70 ml) a solution of $Co_2(CO)_8$ (0.342 g, 1.00 mmol) in *n*-octane (5 ml) was added at 25 °C under a CO atmosphere. In 30 min the gas evolution ceased. A total of 7.88 mmol of CO was collected. The dark bluish-black precipitate was filtered off at 0 °C from the solution, washed with a few milliliters of cold *n*-octane, and dried in vacuum. A black crystalline product (1.78 g, 98.5% yield as Co(G)₂ based on Co₂(CO)₈) with melting point (m.p.) = 205-207 °C was obtained.

Anal. Calc. for $C_{58}H_{82}O_4Co$: C, 77.24: H, 9.15; Co, 6.52. Found: C, 77.0; H, 9.2; Co, 6.36%. The visible spectra in DMSO show a strong absorption at 583 nm ($\varepsilon = 6.6 \times 10^4$ cm² mmol⁻¹).

2.5. Reaction of $Co(G)_2$ with acetic acid

Aqueous acetic acid (0.52 mmol) and *n*-pentane (10 ml) were added to $Co(G)_2$ (0.18 g, 0.20 mmol) at room

temperature (r.t.). After standing overnight, a yellow upper and a pink lower phase were observed. Separation of the phases and removing the solvents in vacuum gave yellow crystals of hydroxygalvinol (HG) (0.154 g, 91.1% yield, m.p. = 153 °C, MS M^+ 422, M-Me 407, M-^tBu 365) and pink crystals (42 mg, 84% yield), respectively.

2.6. Reaction of $Co_2(CO)_8$ with 2,2-diphenyl-1picrylhydrazyl (*P)

A mixture of 2,2-diphenyl-1-picrylhydrazyl hydrate (0.177 g, 0.43 mmol) and $Co_2(CO)_8$ (34.2 mg, 0.1 mmol) in *n*-octane (100 ml was stirred under a carbon monoxide atmosphere at 25 °C. Evolution of 0.728 mmol gas and formation of a brick-red inhomogeneous precipitate was observed after 24 h. The precipitate was removed by filtration and digested with five 50 ml portions of diethyl ether. From the combined ether solution brown-red crystals of 1,1-diphenyl-2-picrylhydrazine (HP) were obtained after cooling at -18 °C for 2 days (0.155 g, 91% yield based on °P. IR in KBr pellets: v(N-H) 3250 and 3280 cm⁻¹). The digested black residue (23 mg) contained > 50% cobalt by analysis.

3. Results

The addition of galvinoxyl free radical (•G) to octacarbonyldicobalt in n-octane or other saturated hydrocarbon solution results in the evolution of carbon monoxide and the formation of a dark purple precipitate. By measuring the amount of carbon monoxide at large (5-20) molar excess of galvinoxyl we found that $Co_2(CO)_8$ releases practically all eight CO ligands during its conversion. Accordingly at the end of the reaction with a total conversion of $Co_2(CO)_8$ the reaction solution and the isolated precipitate show in the infrared spectra no sign of C-O stretching vibrations. The amounts of carbon monoxide released upon gradual addition of galvinoxyl to Co₂(CO)₈ indicated the consumption of four mol of galvinoxyl for the complete conversion of one mol Co₂(CO)₈. By adding less than four mol of galvinoxyl to one mol of octacarbonyldicobalt no v(CO) bands other than those from the unreacted portion of $Co_2(CO)_8$ were observed in the infrared spectra of the reaction solutions. The dark purple precipitate dissolves in dimethyl sulfoxide to give a blue solution. The visible spectra of such solutions show a strong absorption at 583 nm indicating the presence of Co²⁺ ion. Treating the solid isolated from galvinoxyl and $Co_2(CO)_8$ with a 2.6-fold molar excess of aqueous acetic acid at room temperature give a yellow extract with *n*-pentane and a pink-colored aqueous solution. From the yellow extract hydroxygalvinol (HG) as yellow crystals was isolated in 91% yield $(m.p. = 153 \ ^{\circ}C, \text{ lit. } 150-155 \ ^{\circ}C \ [23])$. Its mass spectrum is identical with that described in the literature [23]. Evaporation of water from the aqueous phase gave $Co(CH_3COO)_2 \cdot 4H_2O$ in 95% yield. Reaction 1 and 2 summarize the above results.

$$\operatorname{Co}_2(\operatorname{CO})_8 + 4^{\bullet}G \to 8\operatorname{CO} + 2\operatorname{Co}(G)_2 \tag{1}$$



In order to obtain information about the mechanism of reaction 1, the effects of $\text{Co}_2(\text{CO})_8$, •G, and CO concentrations on the initial rate of carbon monoxide evolution (r_{CO}) were studied at 15 °C using *n*-octane as the solvent. The results compiled in Table 1 indicate that the rate of gas evolution is practically first order in $\text{Co}_2(\text{CO})_8$ concentration and first order in galvinoxyl concentration. The concentration of carbon monoxide does not influence the rate in the studied range.

The addition of 2,2-diphenyl-1-picrylhydrazyl (•P) to octacarbonyldicobalt in n-octane solution also results in evolution of carbon monoxide but with the formation of a brick-red inhomogeneous precipitate. The amount of gas evolution corresponds to the release of all eight carbon monoxide ligands from octacarbonyldicobalt when at least four moles of 2,2-diphenyl-1-picrylhydrazyl are present as a reactant. After the complete conversion of octacarbonyldicobalt no C-O stretching absorptions can be seen either in the infrared spectra of the reaction solution or that of the isolated precipitate. The solid product of the reaction dissolves partially in diethyl ether or in methylene dichloride. The remaining insoluble solid residue is black or brown and contains various amounts of cobalt depending on the extent of extraction. The red-brown extract however, contains no cobalt and gives red crystals in high yield upon cooling. The infrared spectra of the crystalline product in KBr pellets show characteristic v(N-H) bands at 3250 and 3280 cm^{-1} . Single crystal X-ray structure determination [24] confirmed that this product is 1,1-diphenyl-2picrylhydrazine (HP).

Reaction 3 summarizes the above results.

٠P

 $Co_{2}(CO)_{8} + 4^{\bullet}P \cdot H_{2}O \rightarrow 8CO + 2Co(OH)_{2} + 4HP \quad (3)$ $\xrightarrow{Ph}_{Ph} N - \dot{N} \rightarrow NO_{2} \qquad \xrightarrow{Ph}_{N-NH} NO_{2} \rightarrow NO_{2}$

ΗP

The effect of $\text{Co}_2(\text{CO})_8$, •P, and CO concentrations on the initial rate of carbon monoxide evolution (r_{CO}) at Table 1

Initial rate of carbon monoxide evolution ($r_{CO} = 8 \times r$, where r is the gross reaction rate) and the observed rate constant ($k_{obs} = r_{CO}/[Co_2(CO)_8][^{\bullet}G]$) in the reaction of octacarbonyldicobalt with the free radical galvinoxyl ($^{\bullet}G$) at 15 °C in *n*-octane solution at various concentrations

Experiment	$10^2 \times [Co_2(CO)_8] \text{ (mol dm}^{-3})$	$10^2 \times [{}^{\bullet}G] \pmod{dm^{-3}}$	$10^2 \times [CO]^a \text{ (mol dm}^{-3})$	$10^5 \times r_{\rm CO} \ ({\rm mol} \ {\rm dm}^{-3} \ {\rm s}^{-1})$	$k_{\rm obs} ({\rm dm^3 \ mol^{-1} \ s^{-1}})$
TR135	0.033	2.00	0.981	0.63	0.96
TR452	0.056	1.10	0.997	0.66	0.97
TR133	0.13	2.02	0.981	2.63	1.00
TR451	0.23	1.00	0.995	2.56	1.11
TR131	0.73	2.04	0.979	13.87	0.93
TR99	1.46	0.10	0.976	1.40	0.96
TR125	1.46	0.12	0.986	1.78	1.04
TR124	1.46	0.20	0.986	2.61	0.91
TR454	0.23	0.18	0.989	0.49	1.13
TR456	0.23	1.00	0.536	2.07	0.92
TR457	0.23	1.00	0.260	2.17	1.03
TR460	0.23	1.00	0 ^b	2.71	1.14

^a Calculated from the P_{CO} and the solubility of CO in *n*-octane cf. [21].

^b Experiment started under argon atmosphere.

Table 2 Initial rate of carbon monoxide evolution ($r_{CO} = 8 \times r$, where r is the gross reaction rate) and the observed rate constant (k_{obs}) = $r_{CO}/[CO_2(CO)_8]^{0.5}[^{\circ}P]$ in the reaction of octacarbonyldicobalt with the free radical 2,2-diphenyl-1-picrylhydrazyl ($^{\circ}P$) at 15 $^{\circ}C$ in *n*-octane solution at various concentrations

Experiment	$10^2 \times [Co_2(CO)_8]$ (mol dm ⁻³)	$10^2 \times [^{\bullet} P]$ (mol dm ⁻³)	$10^2 \times [CO]^a$ (mol dm ⁻³)	$10^5 \times r_{\rm CO}$ (mol dm ⁻³ s ⁻¹)	$k_{\rm obs}$ ((dm ³ mol ⁻¹) ^{0.5} s ⁻¹)
TR213	0.087	0.15	0.985	0.49	0.110
TR208	0.17	0.16	0.985	0.67	0.100
TR209	0.43	0.12	0.985	0.88	0.112
TR198	0.50	0.024	0.985	1.99	0.117
TR199	0.50	0.050	0.985	4.07	0.115
TR200	0.50	0.094	0.985	7.12	0.107
TR205	0.50	0.13	0.985	10.1	0.106
TR469	0.67	0.14	0 ^b	1.05	0.092
TR468	0.68	0.14	0 ^b	1.24	0.108
TR210	0.69	0.15	0.985	1.23	0.099
TR211	1.04	0.15	0.985	1.38	0.091

^a Calculated from the P_{CO} and the solubility of CO in *n*-octane cf. [21]. ^b Experiment started under argon atmosphere.

15 °C using *n*-octane as the solvent can be seen in Table 2. The results compiled in Table 2 show that the rate of gas evolution is practically first order in 2,2-diphenyl-1-picrylhydrazyl concentration, half order with respect to the $Co_2(CO)_8$ concentration, and independent of the concentration of carbon monoxide in the concentration range studied.

4. Discussion

The first order dependence of the reaction of $Co_2(CO)_8$ with galvinoxyl with respect to both the $Co_2(CO)_8$ and the galvinoxyl concentrations and the zero order dependence with respect to carbon monoxide suggests a rate-determining associative step which is followed by fast electron-transfer steps from cobalt to

the galvinoxyl moiety leading finally to cobalt(II) and the galvinol anion (G^{-}).

The kinetics of the reaction of $Co_2(CO)_8$ with 2,2diphenyl-1-picrylhydrazyl hydrate also show a zero order dependence with respect to the carbon monoxide concentration and a first order dependence with respect to the 2,2-diphenyl-1-picrylhydrazyl hydrate concentration, but the observed kinetic order of $Co_2(CO)_8$ is 0.5. In this case $Co(CO)_4$ formed in a fast preequilibrium from $Co_2(CO)_8$ might participate in the rate-determing one-electron transfer reaction with 2,2-diphenyl-1-picrylhydrazyl. The transfer of the second electron from the cobalt(I) intermediate to another molecule of 2,2diphenyl-1-picrylhydrazyl might happen in a fast consecutive step leading to cobalt(II). The isolated organic product of the reaction is 1,1-diphenyl-picrylhydrazine, which is probably formed by a fast protonation of the intermediate anion.

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