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The Oxidation of $Co_2(CO)_8$, $Mn_2(CO)_{10}$ and $Fe(CO)_5$ by Dibenzoyl Peroxide. Kinetics and Mechanism

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Summary

Dicobalt octacarbonyl in toluene solution can be quantitatively oxidized at room temperature with dibenzoyl peroxide to cobalt(II) benzoate and carbon monoxide. The rate of CO evolution is first order in dicobalt octacarbonyl, first order in dibenzoyl peroxide, and negative first order in CO. Similar behaviour leading to manganese(II) benzoate is observed with dimanganese decacarbonyl. Sixteen electron rather than seventeen electron intermediates are involved in these reactions. In contrast to the dinuclear carbonyls, $Fe(CO)_5$ is oxidized by dibenzoyl peroxide in an autocatalytic reaction.

Introduction

Metal carbonyls can be readily oxidized either chemically(1) or electrochemically(2, 3). Very little is known, however, about these oxidations, especially if peroxo compounds are involved. The oxidation of $Co_2(CO)_8$ and $Fe(CO)_5$ with di-*t*-butyl peroxide results in cobalt(III) and iron(III) alcoholates(4). The oxidation of some first row transition metal carbonyls by peroxydisulfuryl difluoride was reported recently to give fluorosulfates in good yield and purity(5). Nickel(0) complexes are oxidized by dibenzoyl peroxide to nickel(II) benzoate in benzene solution(4). Therefore similar reactions of dibenzoyl peroxide with metal carbonyl may be assumed. To find evidence for a possible radical mechanism in oxidations of transition metal carbonyls by peroxo compounds we studied the reactions of $Co_2(CO)_8$, $Mn_2(CO)_{10}$ and $Fe(CO)_5$ with dibenzoyl peroxide.

Results and Discussions

We found that $Co_2(CO)_8$, $Mn_2(CO)_{10}$ and $Fe(CO)_5$ are readily oxidized at room temperature by dibenzoyl peroxide in toluene solution forming benzoates and carbon monoxide.

Dicobalt octacarbonyl and dibenzoyl peroxide react according to Equation 1.

$$Co_2(CO)_8 + 2\,(PhCO_2)_2 \rightarrow 2\,Co(O_2CPh)_2 + 8\,CO \qquad (1)$$

In a quantitative reaction all carbon monoxide ligands originally bound to cobalt are released and cobalt(II) benzoate can be isolated in excellent yield from the reaction mixtures.

Table 1. Initial rates of CO evolution (r_1) in the reaction of $Co_2(CO)_8$ and $(PhCO_2)_2$ in PhMe solution and the observed rate constants ($k_1 = r_1\,[CO]/[Co_2(CO)_8][(PhCO_2)_2]$) at various initial conditions.

Temp. (°C)	$[Co_2(CO)_8]$ (M)	$[(PhCO_2)_2]$ (M)	$10^2[CO]$ (M)	$10^6 r_1$ ($M.s^{-1}$)	$10^3 k_1$ (s^{-1})
25	0.011	0.149	0.717	1.74	0.76
25	0.071	0.149	0.717	11.14	0.75
25	0.071	0.075	0.717	5.44	0.73
25	0.071	0.037	0.717	2.79	0.75
25	0.071	0.019	0.717	1.41	0.76
25	0.143	0.037	0.717	5.02	0.68
31	0.020	0.041[a)]	0.675	161	13.3[b)]
35	0.011	0.149	0.344	14.0	2.94
35	0.011	0.149	0.657	8.16	3.27
35	0.011	0.149	1.378	3.94	3.31
35	0.011	0.149	2.140	2.48	3.24
35	0.008[c)]	0.032	0.659	0.001	0.0026[d)]
35	0.028	0.062	0.657	7.70	2.92
35	0.028	0.062	0.657	7.74[e)]	2.93
35	0.071	0.037	0.657	11.6	2.90
35	0.112	0.500[f)]	0.717	0.76	
35	0.143	0.018	0.344	19.3	2.58
35	0.143	0.018	0.657	10.0	2.55
35	0.143	0.018	2.156	3.1	2.60
40	0.010	0.041	0.634	4.7	7.3
40	0.020	0.010	0.646	2.1	6.8
40	0.020	0.041	0.638	9.2	7.2
40	0.040	0.041	0.634	19.5	7.5
40	0.040	0.062	0.631	28.1	7.2
40	0.081	0.021	0.634	20.2	7.5
40	0.081	0.062	0.631	55.3	7.0
50	0.040	0.080[f)]	0.602	1.94	

[a)] $PhCO_2–O_2CEt$; [b)] k_1, calcd. from r_1 assuming $k_1' = r_1[CO]/[Co_2(CO)_8][PhC(O)O_2C(O)Et]$; [c)] $Co_4(CO)_{12}$; [d)] k_1'' calc. from r_1 assuming $k_1'' = r_1\,[CO]/[Co_4(CO)_{12}][PhCo_2)_2]$; [e)] measured in the presence of $[PhCH{=}CH_2] = 0.20\,M$; [f)] t-Bu_2O_2.

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The rate of the reaction could be measured by following carbon monoxide evolution. The results, compiled in Table 1, show that the rate of CO evolution is first order in $Co_2(CO)_8$ and first order in dibenzoyl peroxide. From rate measurements at different total pressures of CO a negative first order in carbon monoxide may be deduced.

The presence of styrene did not influence the rate of CO evolution.

The observed kinetic behaviour is in accordance with a fast reversible dissociation of CO from $Co_2(CO)_8$, where the equilibrium is far on the left side, followed by a rate determining reaction between dibenzoyl peroxide and the intermediate $Co_2(CO)_7$.

$$Co_2(CO)_8 \rightleftharpoons Co_2(CO)_7 + CO \qquad (2)$$

$$Co_2(CO)_7 + (PhCO_2)_2 \xrightarrow{\text{slow}} Co_2(CO)_7(PhCO_2)_2 \qquad (3)$$

$$Co_2(CO)_7(PhCO_2)_2 \xrightarrow{\text{fast}} \text{products} \qquad (4)$$

In close similarity to disulfides(6) and to acetylenes(7) the peroxo oxygen atoms may be the site of cobalt attachment replacing, in the slow step, one and then in a consecutive fast step, both of the bridging CO ligands. The electron transfer from cobalt to oxygen should occur rapidly in this latter intermediate.

The mixed peroxide, $PhC(O)O_2C(O)Et$, reacts faster then $(PhCO_2)_2$. This increase of peroxide reactivity may result from an electronic effect, similar to that operating in the Fe^{2+} catalyzed decomposition of substituted diaroyl peroxides(8). Thus the oxidation rate increases as the donor character of R in the acyl peroxides $RC(O)O_2C(O)R$ increases. Nevertheless the steric availability of peroxo oxygen atoms may play an important role too, *e.g.* di-*t*-butyl peroxide reacts very slowly with $Co_2(CO)_8$ under ambient conditions.

It should be noted that $Co_4(CO)_{12}$ is much less reactive towards dibenzoyl peroxide than is $Co_2(CO)_8$.

Dimanganese decacarbonyl reacts with dibenzoyl peroxide leading to manganese(II) benzoate and carbon monoxide according to Equation 5.

$$Mn_2(CO)_{10} + 2\,(PhCO_2)_2 \rightarrow 2\,Mn(O_2CPh)_2 + 10\,CO \qquad (5)$$

The rate of CO evolution is first order in both $Mn_2(CO)_{10}$ and dibenzoyl peroxide and is approximately negative first order in carbon monoxide. Despite the close similarity in kinetic behaviour to $Co_2(CO)_8$, the role of radicals in this reaction cannot be ruled out entirely because the initial rate observed for $Mn_2(CO)_{10}$ is slower in the presence of initially-added styrene (Table 2), which could act as a radical trap.

Table 2. Initial rates of CO evolution (r_5) in the reaction of $Mn_2(CO)_{10}$ and $(PhCO_2)_2$ in PhMe solution and the observed rate constants ($k_5 = r_5[CO]/[Mn_2(CO)_{10}][(PhCO_2)_2]$) at 35 °C.

$[Mn_2(CO)_{10}]$ (M)	$[(PhCO_2)_2]$ (M)	$10^2[CO]$ (M)	$10^6 r_5$ ($M \cdot s^{-1}$)	$10^3 k_5$ (s^{-1})
0.009	0.075	0.697	1.79	1.86
0.018	0.036	0.704	1.67	1.82
0.018	0.075	0.697	3.65	1.89
0.018	0.075	0.695	1.14[a)]	0.59
0.018	0.187	0.697	7.90	1.64
0.041	0.075	0.697	8.24	1.87
0.041	0.075	1.706	3.23	1.81
0.082	0.075	0.697	16.21	1.85

[a)] Measured in the presence of $[PhCH{=}CH_2] = 0.20\,M$.

In the reaction of iron pentacarbonyl with dibenzoyl peroxide carbon monoxide and iron(III) benzoate are formed as final products according to Equation 6.

$$Fe(CO)_5 + 1.5(PhCO_2)_2 \rightarrow Fe(O_2CPh)_3 + 5\,CO \qquad (6)$$

The reaction shows autocatalytic character. Evolution of CO starts slowly but accelerates after an induction period (Figure 1). The observed initial rates are only slightly influenced by the concentrations of both $Fe(CO)_5$ and dibenzoyl peroxide. The induction time and the maximum rate of CO evolution show, however, a significant interdependence. Increasing the $Fe(CO)_5$ concentration leads to a shorter induction time and the observed maximum rate of CO evolution increases. The opposite effect is observed if the concentration

Table 3. Initial rates of CO evolution (r_6) and the induction time (t_{ind}) for developing the maximum rates of CO evolution (r_7) in the reaction of $Fe(CO)_5$ and $(PhCO_2)_2$ in PhMe solution at 25 °C under a CO atmosphere and at various conditions.

$[Fe(CO)_5]$ (M)	$[(PhCO_2)_2]$ (M)	$10^2[CO]$[a)] (M)	$10^6 r_6$ ($M \cdot s^{-1}$)	t_{ind} (min)	$10^6 r_7$ ($M \cdot s^{-1}$)
0.010	0.020	0.36	9.0	6	300
0.010	0.020	0.36	1030[b)]	0	–
0.010	0.020	0.72	8.2	6	240
0.010	0.020	0.72	920[b)]	0	–
0.010	0.020	0.72	470[c)]	0	–
0.010	0.020	0.72	14[d)]	26	900
0.010	0.020	2.16	6.6	6	200
0.010	0.020	2.16	720[b)]	0	–
0.010	0.040	0.72	7.5	8	91
0.010	0.040	0.72	1.2[e)]	22	8.2[e)]
0.010	0.080	0.72	5.6	12	44
0.020	0.020	0.72	11.5	5	820
0.020	0.040	0.72	14.2	6	580
0.040	0.020	0.72	12.5	3	1100

[a)] Calcd. from p_{CO} and the solubility of CO in PhMe(10); [b)] in the presence of initially added $[Fe(O_2CPh)_3] = 0.010\,M$; [c)] in the presence of initially added $[Fe(O_2CPh)_3] = 0.005\,M$; [d)] in the presence of initially added $[Fe(acac)_2] = 0.005\,M$; [e)] in the presence of $[PhCH{=}CH_2] = 0.400\,M$.

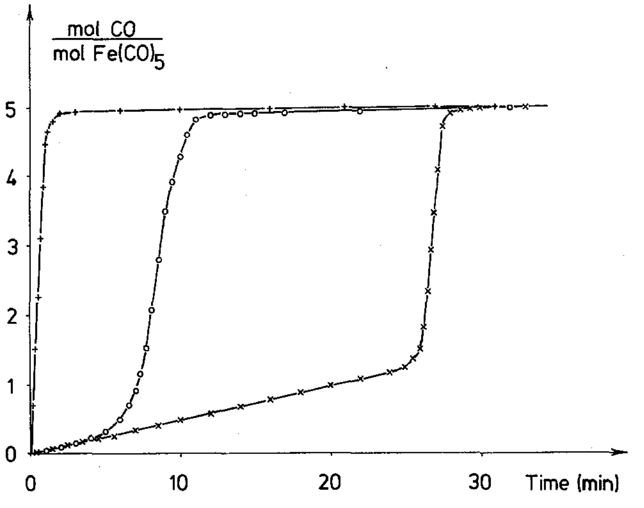

Figure 1. Course of CO evolution in the reaction of $Fe(CO)_5$ with $(PhCO_2)_2$ in PhMe at 25 °C. $[Fe(CO)_5] = 0.010\,M$, $[(PhCO_2)_2] = 0.020\,M$, $[CO] = 0.0072\,M$ (o) without any additives, (+) in the presence of initially added $[Fe(O_2CPh)_3] = 0.010\,M$, (x) in the presence of initially added $[Fe(acac)_2] = 0.005\,M$.

of dibenzoyl peroxide is increased. A rise in the CO concentration results in a slower evolution of CO in both parts of the reaction. Styrene retards both the initial rate and the maximum rate and leads to a longer induction time (Table 3).

Initially-added iron(II) acetylacetonate increases both the induction time and the maximum rate. In the presence of initially-added iron(III) benzoate the evolution of CO starts immediately and the rate is maximum (Figure 1).

The experimental results can be explained by assuming a slow oxidation of $Fe(CO)_5$ leading at first to iron(II) benzoate (Equation 7) and than to iron(III) benzoate (Equation 8) and a rapid oxidation of $Fe(CO)_5^+$ (Equation 10), which latter intermediate may be formed in a reversible electron transfer reaction between $Fe(CO)_5$ and iron(III) benzoate (Equation 9).

$$Fe(CO)_5 + (PhCO_2)_2 \xrightarrow{slow} Fe(O_2CPh)_2 + 5\,CO \qquad (7)$$

$$2\,Fe(O_2CPh)_2 + (PhCO_2)_2 \rightarrow 2\,Fe(O_2CPh)_3 \qquad (8)$$

$$Fe(CO)_5 + Fe(O_2CPh)_3 \rightleftharpoons Fe(CO)_5^+ + Fe(O_2CPh)_2 + PhCO_2^- \qquad (9)$$

$$Fe(CO)_5^+ \xrightarrow[fast]{(PhCO_2)_2} Fe(O_2CPh)_3 \qquad (10)$$

The retarding effect of CO on the rate of CO evolution may correlate with coordinatively unsaturated iron compounds as reactive intermediates in reactions (7) and (10).

For a more detailed understanding of these reactions further kinetic work and spectroscopic evidence are necessary.

Experimental

Materials

PhMe was dried over Na wire and was distilled under a CO atmosphere. $Co_2(CO)_8$ was doubly recrystallized, first from CH_2Cl_2 and then from *n*-heptane under CO. Stock solutions in PhMe, prepared under CO (0.2 M), were used in the kinetic experiments. $Mn_2(CO)_{10}$ (Strem) was recrystallized from PhMe and saturated solutions in PhMe (0.14 M at 25 °C) were used in the experiments. $(PhCO_2)_2$ was recrystallized from CH_2Cl_2 by preparing a saturated solution at room temperature and chilling it to −79 °C, and 0.27 M stock solutions in PhMe were prepared for the kinetic experiments. $Co_4(CO)_{12}$ was prepared from $Co_2(CO)_8$ in boiling PhMe. $PhCH{=}CH_2$ was freshly distilled under CO. $Fe(CO)_5$ (Fluka), iron(II) acetyl acetonate (Fluka) and *t*-Bu_2O_2 (Fluka) were used without purification. Benzoyl propionyl peroxide was prepared by the published procedure(9).

Kinetics

Kinetic runs were performed under CO in a gasometric apparatus fitted with a Hg-filled gas burette. A 5 L buffer flask was connected to the levelling vessel of the gas burette and kept at the pressure of the reaction vessel. All parts of the apparatus were thermostatted (± 0.05 °C). The actual total pressure was determined in mmHg by using an open mercury manometer measuring the pressure difference between the atmosphere and the reaction vessel. The reactions were started by injecting aliquots of $(PhCO_2)_2$ stock solutions to known amounts of transition metal carbonyls in PhMe. The change of gas volume was plotted as a function of time and the initial rates were determined for less than 5% conversion. The i.r. spectra of the reaction mixtures at different percentage conversions between 1600 and 2200 cm^{-1} showed only the C–O stretching bands of the starting compounds and the final products. The reverse order of additions did not change the observed initial rates.

Preparations

Cobalt(II) benzoate

To $(PhCO_2)_2$ (2.43 g, 10 mmol) in PhMe (35 cm^3) was added $Co_2(CO)_8$ (1.71 g, 5 mmol) in PhMe (25 cm^3) with stirring at room temperature. Gas evolution started immediately and ceased completely after 2 h of stirring at 60 °C. Gas (982 cm^3/14.5 °C, 741 mmHg) saturated with PhMe was evolved corresponding to CO (39.7 mmol). The violet precipitate was filtered, washed with PhMe (10 cm^3) and dried *in vacuo*. Cobalt(II) benzoate (2.95 g, 9.8 mmol, 98% yield) results as a pale violet powder. (Found: Co, 19.4. $C_{14}H_{10}CoO_4$ calcd.: Co, 19.6%).

Manganese(II) benzoate

From collected reaction mixtures of the kinetic measurements containing $Mn_2(CO)_{10}$ (1.78 mmol) and $(PhCO_2)_2$ (5.94 mmol), a dark brown precipitate was formed on storage at room temperature. After 10 days, 250 mg brown powder (Found: Mn, 18.2. $MnC_{14}H_{10}O_4$, calcd.: Mn, 18.5%) of manganese(II) benzoate (0.84 mmol, 23% yield) was isolated. The composition of the mangenese complex in the mother liquor was not investigated.

Iron(III) benzoate

To $Fe(CO)_5$ (1.30 g, 6.62 mmol) in PhMe (40 cm^3) was added $(PhCO_2)_2$ (2.43 g, 10 mmol) in PhMe (30 cm^3) dropwise in 20 min with stirring at room temperature. Gas evolution started immediately and ceased completely after 1 h. Gas (827 cm^3/14 °C, 742 mmHg) saturated with PhMe was evolved corresponding to CO (33.5 mmol). After 1 h of additional stirring at 50 °C, the red brown precipitate was filtered and washed with PhMe (2 cm^3) and dried *in vacuo*.

Iron(III) benzoate (1.77 g, 4.12 mmol, 62% yield) results as a brick coloured powder. (Found: Fe, 13.3, C, 60.2, H, 3.6. $C_{21}H_{15}FeO_6$ calcd.: Fe, 13.3, C, 59.55, H, 3.8%). The reverse order of addition of the starting compounds lead to a greenish-brown product with higher iron content.

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