# The Reaction of Iodine with Acylcobalt Tricarbonyl Triphenylphosphine Complexes

BY RICHARD F. HECK

Acylcobalt tricarbonyl triphenylphosphines react with iodine, liberating carbon monoxide by a first-order mechanism independent of the iodine concentration, provided there is more than about a 4-mole excess of iodine. Acetyl-, benzoyl-, and trifluoroacetylcobalt tricarbonyl triphenylphosphines all react with iodine at the same rate, indicating that there is a common intermediate in all three reactions. The common intermediate was shown to be iodocobalt tricarbonyl triphenylphosphine. This reaction provides a new and useful method for preparing this last compound.

Introduction

Many reactions of acylcobalt tetracarbonyl complexes involve a preliminary dissociation step followed by a reaction with a second reagent. The reaction of acylcobalt tetracarbonyls with triphenylphosphine is the most completely studied example of this type of reaction.[1] Reactions of acylcobalt tetracarbonyls with

$$RCOCo(CO)_4 \rightleftharpoons RCOCo(CO)_3 + CO$$

$$RCOCo(CO)_3 + P(C_6H_5)_3 \longrightarrow RCOCo(CO)_3P(C_6H_5)_3$$
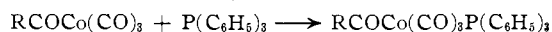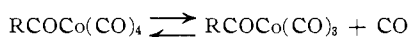
hydrogen,[2] cobalt hydrocarbonyl,[2] dienes,[3] acetylenes,[4] and probably also with olefins[5] are inhibited by carbon monoxide, suggesting that these reactions, too, involve a preliminary dissociation into a lower carbonyl followed by a reaction with another reagent. The reaction of acylcobalt tetracarbonyls with iodine has been used for analysis of these complexes because excess iodine liberates all the coordinated carbon monoxide from the complexes,[6] forming cobalt iodide and an acyl iodide.[2,7] A preliminary dissociation could be involved in this reaction also. This paper describes

$$RCOCo(CO)_4 + I_2 \longrightarrow RCOI + CoI_2 + CO$$
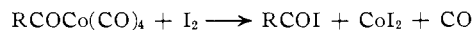
an investigation of the mechanism of the acylcobalt carbonyl–iodine reaction.

Results

The most convenient method for measuring the rate of reaction of iodine with acylcobalt carbonyls was by measuring the rate of gas evolution. The initial experiment showed that acetylcobalt tetracarbonyl reacted at 0° with iodine at a rate too fast to measure with our equipment (half-life less than about 10 sec.). This result proved that the reaction did not involve a preliminary dissociation step because the rate of dissociation was known to be considerably slower under the same conditions[1] (dissociation rate was 1.01×10^{-3} sec.$^{-1}$). Thus a second-order reaction mechanism must be operating. To gain more information about the reaction, the less reactive acylcobalt tricarbonyl triphenylphosphines were investigated. These complexes proved to react with iodine at conveniently measured rates. The data are summarized in Table I. Acetylcobalt tricarbonyl triphenylphosphine reacted with iodine in ether solution at a rate independent of the iodine concentration provided there was at least about 5 moles of iodine per mole of cobalt

complex present initially. With a smaller excess of iodine, the first-order rate constants decreased with time. These results suggested that the cobalt compound rapidly formed a new compound with the iodine and that it was the rate of decomposition of this new compound that was being measured. Measurement of the rates of reaction of benzoyl- and of trifluoroacetylcobalt tricarbonyl triphenylphosphines with iodine showed that these compounds reacted with iodine at about the same rate as the acetyl complex did. Not only do these results provide further evidence against a dissociation mechanism, because the known rates of dissociation of the three complexes are quite different,[1] but they also suggest that all three complexes react with iodine to produce the same intermediate compound. An initial rapid cleavage of the cobalt–carbon bond by the iodine to form an acyl iodide and iodocobalt tricarbonyl triphenylphosphine (I) could explain the data. This type of cleavage has already

$$RCOCo(CO)_3P(C_6H_5)_3 + I_2 \longrightarrow RCOI + ICo(CO)_3P(C_6H_5)_3$$
$$\text{I}$$
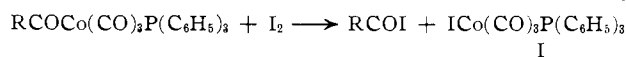
been reported in the acylmanganese pentacarbonyl series[8] and with various other metal–carbon compounds. Compound I is a known compound and was

$$CH_3COMn(CO)_5 + Br_2 \longrightarrow CH_3COBr + BrMn(CO)_5$$
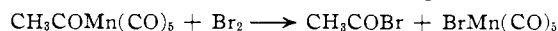
prepared by Hieber by the reaction of iodotrifluoromethane with sodium cobalt tricarbonyl triphenylphosphine.[9] It can be prepared more conveniently and in

$$NaCo(CO)_3P(C_6H_5)_3 + 2ICF_3 \longrightarrow$$
$$ICo(CO)_3P(C_6H_5)_3 + C_2F_6 + NaI$$
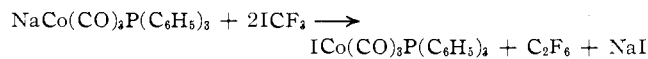
reasonable yields by the reaction of cobalt hydrotricarbonyl triphenylphosphine with iodoform. Similar

$$HCo(CO)_3P(C_6H_5)_3 + CHI_3 \longrightarrow ICo(CO)_3P(C_6H_5)_3 + CH_2I_2$$
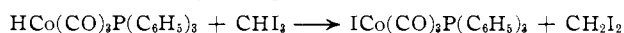
reactions have already been employed to prepare other transition metal halides such as the cyclopentadienylmolybdenum tricarbonyl halides.[10] The rate of reaction of I with iodine was the same as the rates of reaction observed for the acylcobalt tricarbonyl triphenylphosphines with iodine. Conclusive evidence that I was an intermediate in the reaction of iodine with acylcobalt tricarbonyl triphenylphosphines was obtained by using only 1 mole of iodine per mole of cobalt complex and actually isolating the iodo compound from the reaction mixture. Under these conditions, little or no carbon monoxide was evolved. This reaction has been developed into the most convenient method now available for preparing I. Yields of 60% or more are attainable.

(1) R. F. Heck, J. Am. Chem. Soc. 85, 651 (1963).

(2) R. F. Heck and D. S. Breslow, ibid., 83, 4023 (1961).

(3) R. F. Heck, ibid., 85, 3381 (1963).

(4) R. F. Heck, ibid., 86, 2819 (1964).

(5) R. F. Heck, ibid., 85, 3116 (1963).

(6) H. W. Sternberg, I. Wender, and M. Orchin, Anal. Chem., 24, 174 (1952).

(7) R. F. Heck and D. S. Breslow, "Actes du Deuxieme Congres International de Catalyse," Editions Technic, Paris, 1960, p. 671.

(8) T. H. Coffield, J. Kozikowski, and R. D. Closson, J. Org. Chem., 22, 598 (1957).

(9) W. Hieber and E. Lindner, Chem. Ber., 95, 273 (1962).

(10) T. S. Piper and G. Wilkinson, J. Inorg. Nucl. Chem., 3, 104 (1956).

TABLE I

RATES OF REACTION OF ORGANOCOBALT CARBONYL COMPLEXES WITH IODINE AT 0° UNDER 1 ATM. OF CARBON MONOXIDE

Compound	Concn., M	Solvent	Iodine concn., M	$k \times 10^3$ sec.$^{-1}$
$CH_3COCo(CO)_3P(C_6H_5)_3$	0.0053	Ether	0.0476	1.25 ± 0.04
$CH_3COCo(CO)_3P(C_6H_5)_3$	0.0020	Ether	0.0238	1.11 ± 0.02
$CH_3COCo(CO)_3P(C_6H_5)_3$	0.0074	Ether	0.0435	1.12 ± 0.14
$C_6H_5COCo(CO)_3P(C_6H_5)_3$	0.0039	Ether	0.0476	1.43 ± 0.16
$CF_3COCo(CO)_3P(C_6H_5)_3$	0.0013	Ether	0.0476	1.36 ± 0.07
$ICo(CO)_3P(C_6H_5)_3$	0.0020	Ether	0.0444	1.17 ± 0.09
$ICo(CO)_3P(C_6H_5)_3$	0.0046	Ether	0.0217	0.96 ± 0.01
$ICo(CO)_3P(C_6H_5)_3$	0.0070	Ether	0.0385	1.07 ± 0.07
$CH_3COCo(CO)_3P(C_6H_5)_3$	0.0213	Chloroform	0.0667	1.45 to 0.53
$CH_3COCo(CO)_3P(C_6H_5)_3$	0.0073	Chloroform	0.0909	5.85 ± 0.13
$CH_3COCo(CO)_3P(C_6H_5)_3$	0.0084	Chloroform	0.0417	2.71 to 1.45[a]
$ICo(CO)_3P(C_6H_5)_3$	0.0048	Chloroform	0.0455	5.03 to 4.43
$ICo(CO)_3P(C_6H_5)_3$	0.0300	Ether	0.276[b]	31.4 ± 2.4
$ICo(CO)_3P(C_6H_5)_3$	0.0093	Ether	0.106[b]	50.8 ± 7.1
$ICo(CO)_3P(C_6H_5)_3$	0.0100	Ether	0.0736[b]	50.1 ± 4.3
$ICo(CO)_3P(C_6H_5)_3$	0.0105	Ether	0.0426[b]	34 to 37

[a] Second-order rate constants decreased from 2.08 to 1.27×10^{-3} l./mole/sec. [b] t-Butyl hypochlorite concentration.

The reaction of iodine with acylcobalt tricarbonyl triphenylphosphines or I in chloroform solution is apparently second order depending upon both the iodine and cobalt complex concentrations. The kinetics are complicated, however, because much of the reacting iodine is complexed with the reaction products and the actual iodine concentrations were only known at the beginning of the reactions. A crystalline dark red compound has been isolated from the reaction mixtures and found to be a complex between one triphenylphosphine and two iodine molecules.

The mechanism of the first-order reaction of I with iodine in ether solution is not clear from the available data. The two most reasonable mechanisms are: (1) slow dissociation into an iodocobalt dicarbonyl triphenylphosphine and carbon monoxide followed by a rapid reaction with iodine, liberating the remaining carbonyl groups; and (2) rapid formation of a complex between I and iodine followed by a slow decomposition of the complex. An attempt to measure the dissociation rate of I by treating it with more triphenylphosphine at 0° in ether solution led to the rapid formation of cobalt tricarbonyl bis(triphenylphosphine) iodide[11] rather than to carbon monoxide evolution and the formation of iodocobalt dicarbonyl bis(triphenylphos-

$$ICo(CO)_3P(C_6H_5)_3 + P(C_6H_5)_3 \longrightarrow Co(CO)_3[P(C_6H_5)_3]_2{}^+I^-$$

phine). Oxidation of I with t-butyl hypochlorite and with bromine show that dissociation is certainly not necessary for the oxidation to occur because these reagents liberate carbon monoxide more than 20 times faster than iodine does under the same conditions. Although the bromine reaction was too fast to measure at 0°, the t-butyl hypochlorite oxidation could just be measured. This reaction appears to be first order in the iodo complex and zero order in hypochlorite, although it is not certain that the data are reliable for these very fast reactions. The dissociation rate of I is unlikely to be faster than the rate of reaction of this compound with iodine. The hypochlorite oxidation probably does then involve either rapid complex formation between the two reagents followed by a slower decomposition of the complex with liberation of the carbon monoxide or perhaps a direct second-order reaction. The question of whether or not the iodine

(11) A. Sacco, *Gazz. chim. ital.*, **93**, 542 (1963).

reaction involves dissociation or complex formation, however, remains unanswered.

Several attempts were made to use the reactions mentioned above to prepare other cobalt–I halide derivatives but without much success. Cobalt hydrocarbonyl and cobalt hydrotricarbonyl triphenylphosphine both reduce various chloro and bromo compounds such as carbon tetrachloride, carbon tetrabromide, bromoform, and triphenylmethyl chloride and bromide, but it was not possible to isolate or even obtain spectral evidence for the existence of the expected products. (Bromocobalt tricarbonyl triphenylphosphine at least, is known to be stable.[9]) Iodocobalt tetracarbonyl could not be prepared either, even at $-80°$, by the reaction of iodoform with cobalt hydrocarbonyl. The compound seemed to decompose as soon as it was formed. Acetylcobalt tetracarbonyl was treated with 1 mole of iodine and also with 1 mole of bromine at low temperatures, and again, the hoped-for halocobalt tetracarbonyls were not obtained but rather general decomposition seemed to occur. Finally, acetylcobalt tricarbonyl triphenylphosphine was treated at 0° with 1 mole of bromine. Gas was evolved and the infrared spectrum of the reaction mixture showed that the only metal carbonyl compound present was unchanged starting material. If the bromocobalt tricarbonyl triphenylphosphine was formed, it apparently reacted more rapidly with bromine than the bromine did with the starting material.

Acetylcobalt dicarbonyl bis(trimethylolpropane phosphite)[12] does react with 1 mole of iodine to give iodocobalt dicarbonyl bis(trimethylolpropane phosphite) in good yield. The complex is pale yellow and much more stable than I. The related yellow-brown iodocobalt dicarbonyl bis(triphenylphosphine), prepared by Sacco,[11] has quite similar properties.

$$CH_3COCo(CO)_2(TMPP)_2 + I_2 \longrightarrow ICo(CO)_2(TMPP)_2 + CH_3COI$$

Experimental

Acylcobalt Tricarbonyl Triphenylphosphines.—The preparation of these compounds has been described previously.[13]

Kinetic Measurements.—The apparatus employed has already been described.[14] Solutions of the cobalt compound at the re-

(12) R. F. Heck, *J. Am. Chem. Soc.*, **85**, 1220 (1963).
(13) R. F. Heck and D. S. Breslow, *ibid.*, **84**, 2499 (1962).
(14) R. F. Heck and D. S. Breslow, *ibid.*, **83**, 1100 (1961).

action temperature were injected into stirred iodine solutions under 1 atm. of carbon monoxide at the reaction temperature. After allowing about a minute for equilibrium to be reached, the rate of gas evolution was measured. Rate constants were calculated on the basis of the experimental infinity values. About six to twelve separate readings were taken in each run during three to five half-lives. The t-butyl hypochlorite reactions were carried out by injecting pure t-butyl hypochlorite into a stirred solution of the cobalt complex at the reaction temperature under 1 atm. of carbon monoxide and measuring the rate of gas evolution.

Iodocobalt Tricarbonyl Triphenylphosphine from Cobalt Hydrocarbonyl.—In the same apparatus used for the rate measurements above, was placed 23.5 ml. of 0.25 M cobalt hydrocarbonyl in pentane solution[15] at 0° under 1 atm. of carbon monoxide. Then, 5.9 ml. of 1.0 M triphenylphosphine in ether solution was added. About 120 ml. of gas was evolved in 2 min. and the reaction stopped. Some of the product, cobalt hydrotricarbonyl triphenylphosphine, separated from the solution as tan crystals. To this solution and solid was added 25 ml. of 0.25 M iodoform in methylene chloride. The solution immediately turned a dark red and about 5 ml. of gas was evolved. After 15 minutes at 0°, the solvent was removed *in vacuo* and the solid was taken up in methylene chloride, all operations being carried out under nitrogen. The black extracts were centrifuged and the clear black solution was concentrated at room temperature under vacuum to about 3 ml., and 10 ml. of pentane was added. Black crystals of the product soon separated. After cooling in Dry Ice, the product was separated by centrifuging and then was recrystallized again from methylene chloride–pentane with cooling in Dry Ice. There was obtained 1.60 g. of brown-black needles, m.p. 141–144° dec. The infrared spectrum in methylene chloride solution had a sharp, strong carbonyl band at 1995 cm.$^{-1}$ and a much weaker band at 1920 cm.$^{-1}$.

Iodocobalt Tricarbonyl Triphenylphosphine from Acetylcobalt Tricarbonyl Triphenylphosphine.—In a cappable heavy-walled

(15) H. W. Sternberg, I. Wender, R. A. Friedel, and M. Orchin, *J. Am. Chem. Soc.*, **75**, 2717 (1953).

Pyrex tube was placed 0.43 g. (1 mmole) of acetylcobalt tricarbonyl triphenylphosphine.[12] The tube was capped with a butyl rubber-lined metal cap with two holes in it for "hypodermic" injections and flushed with nitrogen through a 20-gauge needle. Methylene chloride (3 ml.) was injected and then this solution was added to 0.25 g. of iodine contained at a similar tube under nitrogen (evacuated at Dry Ice temperature to keep the iodine from evaporating) precooled in a Dry Ice–acetone bath. The mixture was shaken and allowed to warm up slightly until the solid iodine had all dissolved (about 10 min.) and then warmed to 0° and concentrated to about 1 ml. under vacuum. The addition of about 2 ml. of pentane caused a black oil to separate. This was quickly removed by centrifuging and the addition of about 5 ml. more of pentane to the solution caused black crystals of the product to crystallize out. After cooling to −80° these crystals were separated by centrifuging and then dried *in vacuo* at room temperature. There was obtained 0.332 g. of product (62%), m.p. 142 up to 189° depending upon the sample and the rate of heating. The infrared spectrum was identical with that obtained from the cobalt hydrocarbonyl reaction product above.

Anal. Calcd. for $C_{21}H_{15}O_3PICo$: C, 47.39; H, 2.84; I, 23.85. Found: C, 47.53; H, 3.29; I, 23.97.

Iodocobalt Dicarbonyl Bis(trimethylolpropane phosphite).—A solution of 0.48 g. of acetylcobalt dicarbonyl bis(trimethylolpropane phosphite)[12] in 10 ml. of methylene chloride at 0° under a nitrogen atmosphere was treated with 20 ml. of 0.05 M iodine in methylene chloride solution. In 30 min. almost 16 ml. of gas had been evolved and the reaction stopped. The solution was evaporated to about 3 ml. *in vacuo* at room temperature, and the product was precipitated by adding 10 ml. of ether. A green oil separated initially and on standing it crystallized. The complex was recrystallized twice more from tetrahydrofuran–ether. There was obtained 0.35 g. of pale yellow crystals, m.p. 261–263° dec. The infrared spectrum in chloroform solution had a strong band at 2020 cm.$^{-1}$ and a weaker one at 2045 cm.$^{-1}$.

Anal. Calcd. for $C_{14}H_{22}O_8IP_2Co$: C, 29.70; H, 3.92. Found: C, 29.17; H, 4.57.

Phosphonitrilic Compounds. III.[1] Molecular Inclusion Compounds of Tris(o-phenylenedioxy)phosphonitrile Trimer

By H. R. Allcock and L. A. Siegel

Tris(o-phenylenedioxy)phosphonitrile trimer forms crystalline inclusion compounds when recrystallized from organic solvents. Similar adducts are formed by an unusual spontaneous inclusion process, accompanied by a change in crystal structure, which occurs when the solid is brought into contact with the liquid or vapor of many organic compounds. For these adducts, the ratio of host to guest compound depends on the molecular dimensions of the included species. In specific cases, one included compound can be displaced from the adduct by another, and selective absorption from mixed liquids also takes place. X-Ray single crystal and powder diffraction data suggest that at 25° the pure phosphonitrilic compound exists as a monoclinic or triclinic structure with an eight-molecule unit cell. In the adduct form, the material exists as a hexagonal structure which contains two molecules of phosphonitrilic compound and generally not more than one included molecule. The mode of crystal packing is discussed, and the results are interpreted in terms of clathrate or channel-compound formation.

Results and Discussion

The Evidence for Adduct Formation.—The preparation and identification of tris(o-phenylenedioxy)phosphonitrile trimer (I) was described in a recent paper.[1]

I
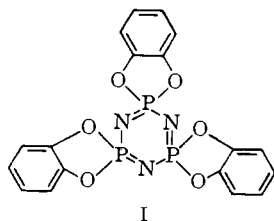
This compound, when purified by sublimation, was a white, crystalline solid, m.p. 244–245°. It was only sparingly soluble in most organic liquids. The ability

(1) Part II: H. R. Allcock, *J. Am. Chem. Soc.*, **86**, 2591 (1964).

of I to form stable inclusion compounds was indicated by the following unusual behavior. When sublimed samples of I were brought into contact with organic liquids or vapors, a rapid swelling and disintegration of the crystallites occurred, and the solids, after careful drying, were found to have undergone a weight increase. X-Ray powder patterns of these treated samples were distinctly different from that of the starting material, which indicated that a structural transformation had taken place. Microanalysis, infrared spectroscopy, and mass spectrometry also demonstrated that molecules of the organic compound were present in the solid products. Similar results were obtained for samples of I which had been recrystallized from organic solvents. For these recrystallized products, the unit-cell molecular weight, calculated from single-crystal X-ray data and density