ethanol containing one ml. of 20% aqueous sodium hydroxide was refluxed for 2 hours in an atmosphere of nitrogen. The solution was cooled, poured into 100 ml. of water, neutralized with acetic acid, and the aqueous solution was extracted with ether. The residue remaining after evaporation of the ether was taken up in benzene and chromatographed on silica gel. Elution of the column with benzene gave 0.06 g. of phenylnitromethane, identified by infrared spectrum; elution of the column with methylene chloride containing 10% methanol gave benzoic acid, 0.15 g., m.p. and mixed m.p. 120–122°.

Nitration of Mixed Crystals of *threo*- and *erythro*-α-Hydroxy-α'-nitrobibenzyl.—A 1.46-g. sample of the mixed nitroalcohols, m.p. 98–99°, was nitrated with dinitrogen pentoxide as described previously.[11] There was obtained 1.63 g. (94%) of product, m.p. 80–108°, which assayed 67% *threo*-α-nitrato-α'-nitrobibenzyl from its infrared spectrum.

HUNTSVILLE, ALA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI]

On the Mechanism for the Oxo Reaction[1]

BY LAWRENCE KIRCH[2] AND MILTON ORCHIN

RECEIVED OCTOBER 20, 1958

When an excess of 1-hexene is added to a hexane solution of cobalt hydrocarbonyl at room temperature in the presence of one atmosphere of carbon monoxide, approximately one mole of gas is absorbed for every two moles of $HCo(CO)_4$. The rate of gas absorption with various olefinic substrates parallels the relative rates with which the respective olefins undergo hydroformylation. Aldehydes and dicobalt octacarbonyl can be isolated from the reaction mixture. Conjugated diolefins fail to absorb carbon monoxide. On the basis of the observed phenomena, a reaction scheme for the oxo synthesis is proposed.

Very careful studies in a number of laboratories have established that the rate of the oxo reaction is inversely proportional to the partial pressure of carbon monoxide. In accordance with this kinetic requirement, the usual mechanisms suggested for this reaction involve, as a rate-determining step, the displacement by the olefin of a mole of carbon monoxide from the dicobalt octacarbonyl[3–5] added as catalyst, or from the cobalt hydrocarbonyl[6] presumed to be present in the system.

Previous work in this Laboratory[7] showed that under oxo conditions, rapid conversion of dicobalt octacarbonyl to cobalt hydrocarbonyl occurred. In the presence of olefin, no free hydrocarbonyl could be detected but when the hydroformylation was complete and all the olefin consumed, the hydrocarbonyl again appeared uncombined. Because these results clearly showed that olefin–hydrocarbonyl interaction probably by complex formation is the essential catalytic step in the oxo synthesis, attention has been focused on the reaction between olefins and cobalt hydrocarbonyl.

Dilute solutions of cobalt hydrocarbonyl were prepared from hydrocarbon solutions of dicobalt octacarbonyl at 25° under one atmosphere of carbon monoxide by disproportionation[8] with dimethylformamide (DMF) and subsequent acidification of the resulting mixture according to the equations

$$3Co_2(CO)_8 + 12DMF \longrightarrow 2Co(DMF)_6[Co(CO)_4]_2 + 8CO \quad (1)$$

$$Co(DMF)_6[Co(CO)_4]_2 + 2HCl \longrightarrow 2HCo(CO)_4 + CoCl_2 + 6DMF \quad (2)$$

Removal of the acid–DMF phase left a clear yellow solution of cobalt hydrocarbonyl. Addition of excess olefin resulted in *absorption* of one mole of carbon monoxide for each two moles of hydrocarbonyl present. The disappearance of hydrocarbonyl proceeded simultaneously with the absorption of carbon monoxide. Terminal olefins absorbed carbon monoxide faster than internal olefins; the same order of reactivity has been noted[5] in the oxo reaction. If the acid phase is not removed prior to olefin addition, decomposition occurs and carbon monoxide is liberated.

After a number of orienting trials, the following procedure was used in one particular experiment. The clear yellow solution of hydrocarbonyl in hexane was prepared as above. The infrared absorption spectrum of a small aliquot of the solution was determined. The solution spectrum of the hydrocarbonyl was essentially identical with its reported vapor spectrum and showed the absence of dicobalt octacarbonyl. To the balance of the solution, there was added excess 1-hexene. After one mole of carbon monoxide per two moles of hydrocarbonyl had been absorbed, absorption ceased (10 min.). The reaction flask was cooled to Dry-Ice temperature whereupon bright orange crystals of dicobalt octacarbonyl (melting point, infrared spectrum) separated in about 80% yield. The infrared spectrum of the filtrate showed: the absence of appreciable dicobalt octacarbonyl; sharp bands in the 4.8–4.9 μ region which were not identical with either octacarbonyl or hydrocarbonyl; the presence of 1-hexene; the presence of internal olefins; the presence of aldehydes. Gas chromatographic analysis indicated that about 35% of the unreacted olefin was 2-hexene and/or 3-hexene. Treatment of the reaction mixture with 2,4-dinitrophenylhydrazine gave a mixture of hydrazones whose analysis was consistent with heptaldehyde 2,4-dinitrophenylhydrazine.

It is clear from the above evidence that the room temperature hydroformylation of 1-hexene must be

---

[1] For a preliminary communication on this subject see L. Kirch and M. Orchin, THIS JOURNAL, **80**, 4428 (1958).

[2] Taken in part from this author's dissertation submitted to the graduate faculty of the University of Cincinnati in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[3] A. R. Martin, *Chemistry & Industry*, 1536 (1954).

[4] G. Natta, R. Ercoli, S. Castellano and P. H. Barbieri, THIS JOURNAL, **76**, 4049 (1954).

[5] I. Wender, S. Metlin, S. Ergun, H. W. Sternberg and H. Greenfield, *ibid.*, **78**, 5401 (1956).

[6] G. Natta, R. Ercoli and S. Castellano, *Chimia et ind.*, **37**, 6 (1955).

[7] M. Orchin, L. Kirch and I. Goldfarb, THIS JOURNAL, **78**, 5450 (1956).

[8] I. Wender, H. Sternberg and M. Orchin, *ibid.*, **74**, 1216 (1952).

written as

$$2HCo(CO)_4 + CO + \text{olefin} \longrightarrow Co_2(CO)_8 + \text{aldehyde} \quad (3)$$

It is reasonable to assume that such a reaction would be unlikely to occur by a simultaneous collision of the four molecules involved.

A possible mechanism which rationalizes the results, involves the formation and subsequent decomposition of a complex formed from cobalt hydrocarbonyl–olefin–carbon monoxide. Such a complex may be postulated to form in a first and rate-determining stage

$$2HCo(CO)_4 + RCH{=}CH_2 + CO \longrightarrow [HCo(CO)_4]_2\cdot RCH{=}CH_2CO \quad (4)$$

In a second stage, the complex may rapidly decompose to the observed products

$$\text{complex} \longrightarrow Co_2(CO)_8 + RCH_2CH_2CHO$$

An alternate possibility is that a complex is formed stepwise from the reaction between olefin, carbon monoxide, and one mole of $HCo(CO)_4$, reaction (5), and such a complex is subsequently split in a rapid step by a second mole of $HCo(CO)_4$

$$HCo(CO)_4 + CO + RCH{=}CH_2 \longrightarrow \text{complex} \quad (5)$$

$$\text{Complex} + HCo(CO)_4 \longrightarrow \text{products}$$

All attempts to isolate or characterize a complex corresponding to reactions 4 or 5 were unsuccessful, but such complexes, if they existed, would be expected to be quite labile.

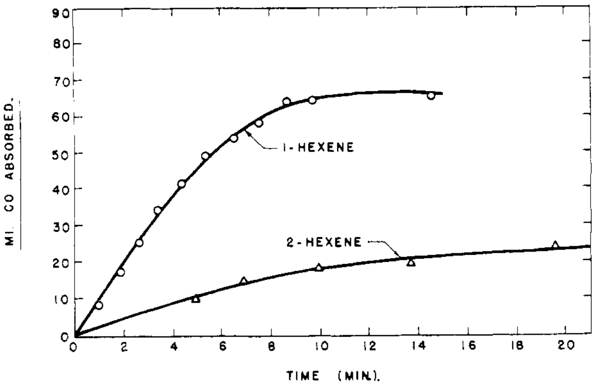

Fig. 1.—Rate of carbon monoxide absorption by cobalt hydrocarbonyl.

Since the room temperature reaction of olefin with hydrocarbonyl requires absorption of carbon monoxide, one would expect that the hydrocarbonyl would remain unchanged in the presence of olefin if carbon monoxide were excluded from the system. Attempts to verify this expectation were not conclusive. In the absence of an atmosphere of carbon monoxide, some hydrocarbonyl decomposes and furnishes "*in situ*" carbon monoxide. However, it was noted that the disappearance of hydrocarbonyl was definitely slower in the absence of an atmosphere of carbon monoxide.

It is known that conjugated diolefins and α,β-unsaturated carbonyl compounds add hydrogen under oxo conditions.[9] In the present study, addition of isoprene to a solution of hydrocarbonyl resulted in a slight gas evolution rather than the usual gas absorption and although results were secured with a very small quantity of material, 2-methyl-2-butene was identified among the reaction products by vapor chromatography.

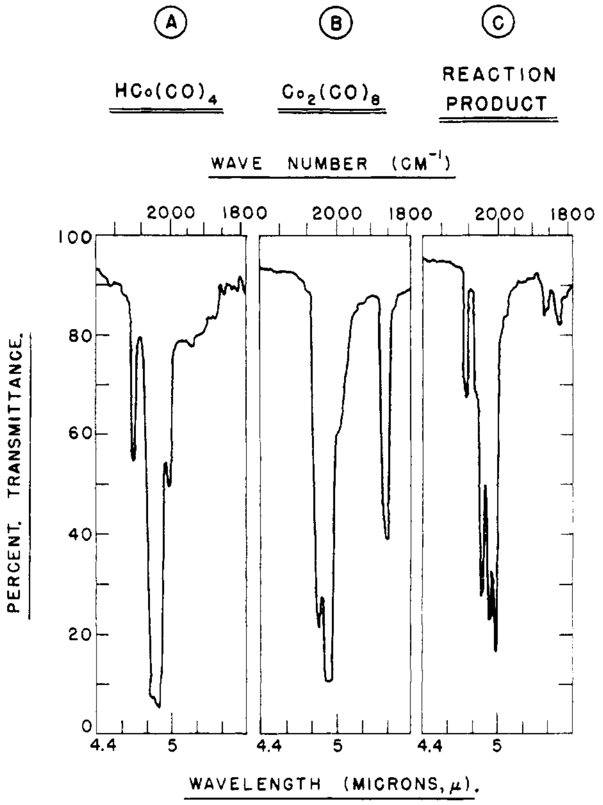

Fig. 2.—Infrared spectra of carbonyl solutions in the 4.5–5.5 μ region (hexane, reference solvent): (A) cobalt hydrocarbonyl in hexane; (B) dicobalt octacarbonyl in hexane; (C) reaction products from hydrocarbonyl and 1-hexene after removal of dicobalt octacarbonyl.

Finally it should be noted that the discovery of dicobalt octacarbonyl as a product of room temperature hydroformylation makes it theoretically possible to operate a continuous room temperature oxo process *via* reactions 1, 2 and 3 until extinction of the cobalt carbonyl as cobalt(II) ion.

Experimental

Determination of Relative Rate of Olefin Reaction with Cobalt Hydrocarbonyl.—A solution of 1.03 g. (3.0 mmoles) of $Co_2(CO)_8$ in 10 ml. of hexane was injected into a 125-ml. round-flask attached to a 500-ml. gas buret and 2.5 ml. of DMF was injected into the carbonyl solution. Gas evolution started at once. The disproportionation was complete within one hour. A clear two-phase system resulted. The upper hexane system was colorless and the lower layer was red. Then 4 ml. of concentrated HCl was injected into the system and the mixture stirred for 15 minutes. The acid layer (dark blue) was withdrawn with a syringe through a serum stoppered side arm and 10 ml. of wash water was injected into the system and withdrawn after 5 minutes of stirring. The resulting acid-free solution of cobalt hydrocarbonyl in hexane was clear yellow; 10 ml. (80 mmole) of 1-hexane was injected into the system. The solution gradually became darker as carbon monoxide was absorbed. After 10 minutes all the hydrocarbonyl had reacted and 2.03 mmoles of carbon monoxide had been absorbed. An identical experiment was conducted in decalin as a solvent and similar results obtained although carbon monoxide absorp-

---

(9) H. Adkins and G. Krsek, THIS JOURNAL, **71**, 3051 (1949).

tion was slower. Figure 1 shows the volume of gas absorbed, plotted against time for 1-hexene and 2-hexene.[10]

Identification of Reaction Products.—A solution of hydrocarbonyl in hexane was prepared as above except that 4.9 mmoles of $Co_2(CO)_8$ was used. The spectrum of the hydrocarbonyl in the 4.4 to 5.6 μ region is shown in Fig. 2A. To this solution there was then added 20 ml. of 1-hexene. Gas absorption commenced immediately and was complete when 1.03 mmoles of carbon monoxide per 2 mmoles of hydrocarbonyl (6 min.) was absorbed. The solution was cooled to Dry-Ice temperature and the precipitated dicobalt octacarbonyl filtered and air-dried (0.9 g., 81% of theory). Recrystallization gave material of m.p. 51–52°. The infrared spectrum in hexane (Fig. 2b) was identical with authentic dicobalt octacarbonyl. After removal of the dicobalt octacarbonyl, the infrared absorption spectrum of the filtrate was determined. The 4.4–5.6 μ portion of this spectrum is shown in Fig. 2C. It will be noted that in the region shown, the broad band which appears in the 4.9 μ region in both hydrocarbonyl and octacarbonyl has been resolved into several sharp bands. The significance of this change is under study. The spectrum of the reaction mixture also showed bands at 5.8 (heptaldehyde), 5.5 and 6.1 (1-hexene), 10.1 (1-hexene), 10.38 (2-hexene), 10.98 (1-hexene), 14.4 μ (2-hexene). The absence of appreciable absorption at 5.4 and 14.2 μ indicated that neither much octacarbonyl nor hydrocarbonyl was present. Chemical tests (nickel *o*-phenanthroline) also indicated the absence of these carbonyls. An aliquot of the reaction mixture was analyzed by gas chromatography using a silicone column. Comparison with a known mixture of hexane, 1-hexene and 2-hexene showed that the reaction mixture contained approximately 65% 1-hexene, 20–25% 2-hexene and the balance (10–15%) probably 3-hexene. The balance of the reaction mixture was treated with an alcoholic solution of 2,4-dinitrophenylhydrazine to which a few drops of sulfuric acid had been added. After refluxing for several hours, followed by cooling, the precipitated crystals were separated. These melted over a wide range with complete melting below 100°. Recrystallization did not improve the melting point. It was assumed that the crystals were a mixture of hydrazones from various C-7 aldehydes. *Anal.* Calcd. for $C_{13}H_{18}N_4O_4$: C, 53.05; H, 6.17. Found[11]: C, 52.51; H, 6.01. The formation of octacarbonyl according to the reaction scheme proposed here should coincide with the disappearance of a complex and the appearance of product aldehyde. Qualitative data on the rate of aldehyde formation could not be secured owing to experimental difficulties with the small quantities involved.

Equivalence of Hydrocarbonyl Disappearance and Carbon Monoxide Absorption.—The reaction of hydrocarbonyl with 1-hexene was carried out as described above but at 0°. At this temperature gas absorption took several hours. After 1.2 mmoles of carbon monoxide had been absorbed, the mixture was analyzed for remaining hydrocarbonyl by nickel *o*-phenanthroline precipitation[12] and 1.5 mmoles of $HCo(CO)_4$ was found (theory, 1.6 mmoles based on amount of carbon monoxide absorbed).

Reaction of Isoprene with Cobalt Hydrocarbonyl.—To a solution of 4 mmoles of $HCo(CO)_4$ in 16 ml. of decalin at 25° there was injected 3 ml. (30 mmole) of isoprene (99.8% isoprene by vapor fractometer analysis[13]); 50 ml. of gas was evolved in 0.5 hour. The solution was cooled to $-78°$ in a Dry Ice-bath and the low-boiling olefin distilled at a pressure of 2 mm. as the olefin warmed up to room temperature. Vapor fractometer[13] analysis revealed 1% 2-methyl-2-butene in the isoprene which corresponds to an approximately 16% yield of product.

Acknowledgment.—The authors wish to thank the Houdry Process Corporation for a generous fellowship which made this work possible, and Drs. G. Alex Mills and Sol Weller for stimulating discussions. The authors also wish to thank Bernard Krabacher for valuable technical assistance.

---

[10] Several dozen experiments on carbon monoxide absorption by 1-hexene in hexane containing cobalt hydrocarbonyl indicated that the carbon monoxide absorption was slightly greater on the average than the ratio $2HCo(CO)_4{:}1CO$, possibly due to slight decomposition of complexes.

[11] Geller Laboratories, Bardonia, N. Y.

[12] H. Sternberg, I. Wender and M. Orchin, *Anal. Chem.*, **24**, 174 (1954).

[13] Analysis by the Analytical Division, The Houdry Process Corp.

CINCINNATI 21, OHIO

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

The Action of Elementary Fluorine upon Organic Compounds. XXII. The Fluorination of Some Amides, Nitriles and of Methyl Thiocyanate[1]

BY JOHN A. ATTAWAY,[2a] RICHARD H. GROTH[2b] AND LUCIUS A. BIGELOW

RECEIVED NOVEMBER 29, 1958

The substituted amides $HCON(CH_3)_2$ and $HCONHCH_3$ were cleaved when fluorinated under vigorous conditions. The former yielded pure $(CF_3)_2NF$ (38%), $(CF_3)_3N$ and $(CF_3)_2N{-}N(CF_3)_2$; while the latter gave $CF_2{=}NF$, CF_3NF_2 and $(CF_3)_2NF$. Unsubstituted acetamide under mild conditions was cleaved even before the replacement of hydrogen atoms, giving CH_3COF (52%) and elementary nitrogen. The perfluoronitriles CF_3CN and CF_3CF_2CN when fluorinated under very mild conditions yielded the new perfluoroazo compounds $CF_3CF_2N{=}NCF_2CF_3$ and $CF_3CF_2CF_2N{=}NCF_2CF_2CF_3$, while CF_3CF_2CN under vigorous conditions gave pure $CF_3CF_2CF_2NF_2$ not previously fully reported. Finally, methyl thiocyanate, CH_3SCN, under mild conditions gave the new SF_5CN, and under vigorous conditions the new $SF_5CF_2NF_2$, along with much SF_6 and other products. Possible mechanisms for these reactions have been presented.

This paper describes the results of the direct fluorination of three not entirely unrelated classes of organic compounds containing either nitrogen or both nitrogen and sulfur as so-called additional elements. In an earlier report from this Laboratory[3] it was stated that in the direct fluorination of N-dimethylformamide under relatively mild conditions the primary attack of the fluorine which led to fluorinolysis was directly upon the nitrogen atom at least for the most part, since $(CF_3)_2NF$ was produced in good yield while none of the dimer $(CF_3)_2N{-}N(CF_3)_2$ could be isolated from the product. This fluorination has now been repeated under more vigorous conditions and, for example, at the molar

---

[1] This material was presented at the September, 1956, Meeting of the American Chemical Society in Atlantic City, N. J., and has been abstracted in part from the Doctorate Thesis presented by John A. Attaway to Duke University in January, 1957.

[2] (a) Research Assistant, Office of Ordnance Research, Summer, 1954; Office of Naval Research, 1954–1955, Fall, 1956; Allied Chemical and Dye Corporation Fellow, 1955–1956. Grateful acknowledgment is also made to the Duke University Research Council for a grant. (b) Post-doctorate Research Associate, Office of Naval Research, 1956.

[3] F. P. Avonda, J. A. Gervasi and L. A. Bigelow, THIS JOURNAL, **78**, 2798 (1956).