CONTRIBUTION FROM MELPAR, INCORPORATED,
RESEARCH DIVISION, CHEMICAL AND
BIOLOGICAL SCIENCES DEPARTMENT,
FALLS CHURCH, VIRGINIA

The Photochemical Reaction of Metal Carbonyls with 1,3-Diketones[1]

BY J. C. GOAN, C. H. HUETHER, AND H. E. PODALL

Received March 13, 1963

The formation of ferric acetylacetonate by heating iron pentacarbonyl with acetylacetone was reported in 1929 by Hieber.[2] The absence of H_2 and CO, expected as products, was attributed to their reaction to form "polychinoartige" substances.[3] The nature of this latter process was not defined. Recently, it was reported that molybdendum(III) acetylacetonate is formed in high yield by heating molybdenum hexacarbonyl with excess acetylacetone at 150–153° for about 7 hr.[4] No mention was made of the fate of the enolic hydrogen and displaced CO. We have found that, in general, reactions of this type are greatly facilitated by ultraviolet irradiation, particularly at moderate temperatures. Moreover, these reactions, when carried out in certain solvents, have been found to produce H_2 and CO in the expected stoichiometric amounts, in contrast with the thermal reactions cited above. Although many photochemical reactions of metal carbonyls are known, these usually involve a simple displacement of carbon monoxide, most often partial, with no change in oxidation state of the metal.[5–8] The reaction we wish to report is novel with respect to the ease and selectivity with which various "active" hydrogen compounds can be caused to interact with metal carbonyls, producing metal chelates.

Experimental[9]

The general procedure employed in this study may be exemplified by the synthesis of chromic hexafluoroacetylacetonate, $Cr(hfa)_3$.

A solution of 2.2 g. (0.01 mole) of chromium carbonyl and 9.4 g. (0.045 mole) of hexafluoroacetylacetone in 50 ml. of CCl_4 was refluxed for 48 hr. in a quartz flask while irradiated by a General Electric 250-watt sun-lamp. The solvent was then removed to yield 5.4 g. (80% yield) of a brown-green solid, m.p. 75–82°. Recrystallization of this material from *n*-hexane gave 3.5 g. of olive-green needles, m.p. 87.5–88° (lit.[10] 84–85°). *Anal.* Calcd. for $C_{15}H_3O_6F_{18}Cr$: C, 26.7; H, 0.45; Cr, 7.7. Found: C, 26.3; H, 0.49; Cr, 7.6[11]; infrared absorption bands at 6.25 (s) (C–O–Cr); 6.44 (w), 6.58 (w), and 7.02 (s) (C=C); 7.40 (w) and 8.0 (vs) (CF_3); 8.27 (s), 8.64 (s), and 8.75 (s) (C–H in-plane bend); 13.47 (m) and 14.83 μ (m) (C–CF_3 stretch).

The gas evolution data for following the rate and extent of reaction were obtained by use of a wet test meter, with provision for gas sampling. All reactions were conducted under dry argon, with a Drierite tube between the reaction system and wet test meter. The gas analysis was carried out *via* gas chromatography employing standard CO–H_2 mixtures. The half-life measurements were generally conducted with 0.010 mole of the metal carbonyl and 0.035 mole of the diketone in 100 ml. of solvent at a fixed distance above the 250-watt sun-lamp. All reactions were conducted under reflux provided by the heat of the lamp.

The results of other preparative experiments include $Fe(hfa)_3$ (from benzene), 80% yield, m.p. 51–52° (lit.[10] 49°); $Cr(AA)_3$ (from benzene), 91% yield, m.p. 216–217° (lit.[12] 216°); $Fe(DBM)_3$[13] (from benzene), 50% yield, m.p. 263–265° (lit.[14] 262–263°); $Mo(AA)_3$ (from isopropyl ether), 95% yield, m.p. 228° (lit.[4] 225–226°); $[WO_2(OH)(AA)]_2$ (from benzene), 84% yield[15]; FeQ_3 (from benzene), 95% yield, dec. 220°.[16]

Results and Discussion

The treatment of certain metal carbonyls with enolizable 1,3-diketones under photochemical conditions has afforded generally high yields of the corresponding metal chelates with evolution of the stoichiometric quantities of H_2 and CO. Thus, for iron pentacarbonyl and acetylacetone in benzene solution the following stoichiometry was obtained.

$$Fe(CO)_5 + 3AAH \xrightarrow[C_6H_6]{h\nu} Fe(AA)_3 + 1.5H_2 + 5CO$$

Ferric acetylacetonate was obtained in 84% yield, m.p. 185–186° (lit.[12] 186°), together with 92% of the theoretical quantity of gas composed of 3.21 moles of CO per mole of H_2 (theory = 3.33).

The rate of carbon monoxide displacement is dependent upon the nature of the 1,3-diketone and the solvent, in addition to the presence of ultraviolet light. Ultraviolet irradiation of a benzene solution of iron pentacarbonyl and hexafluoroacetylacetone at 80° produced within 2 hr. 50% of the gas expected for the for-

---

[1] Photochemical Oxidative Decarbonylation Reactions of Metal Carbonyls. I.

[2] W. Hieber, *Sitzungsber. Heidelberg Akad. Wiss.*, **3**, 3 (1929); *Chem. Zentr.*, **I**, 2029 (1929). The reaction is reported to occur to only 40% completion unless a large excess of acetylacetone or base is added.

[3] W. Hieber and G. Bader, *Z. anorg. allgem. Chem.*, **190**, 193 (1930).

[4] M. L. Larson and F. W. Moore, *Inorg. Chem.*, **1**, 856 (1962).

[5] W. Strohmeier, K. Gerlach, and D. V. Hobe, *Chem. Ber.*, **94**, 164 (1961).

[6] W. Strohmeier and K. Gerlach, *Z. Naturforsch.*, **15b**, 622 (1960).

[7] J. Chatt, P. L. Pauson, and L. M. Venanzi, "Organometallic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1960, p. 482. Complete displacement of CO from nickel carbonyl by its thermal reaction with various ligands is, however, well known.

[8] I. W. Stolz, G. R. Dobson, and R. K. Sheline, *J. Am. Chem. Soc.*, **84**, 3589 (1962); *Inorg. Chem.*, **2**, 323 (1963).

[9] All melting points are uncorrected. Elemental analysis and infrared spectra were obtained for each compound reported here and were in satisfactory agreement with the required values.

[10] M. L. Morris, R. W. Moshier, and R. E. Sievers, *Inorg. Chem.*, **2**, 411 (1963).

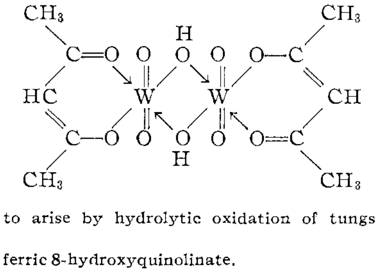
[11] Attempted decomposition of the compound in boiling sulfuric acid led only to volatilization of the compound. Alkaline hydrolysis permitted its decomposition for chromium analysis.

[12] N. V. Sidgwick, "The Chemical Elements and their Compounds," Vol. II, Oxford University Press, London, 1950, pp. 1362, 1020.

[13] $Fe(DMB)_3$ = ferric chelate of dibenzoylmethane.

[14] L. Wolf, E. Butter, and H. Weinelt, *Z. anorg. allgem. Chem.*, **306**, 87 (1960).

[15] The compound has been assigned the following tentative structure based solely on elemental and infrared analysis.



It is believed to arise by hydrolytic oxidation of tungsten(III) acetylacetonate.

[16] FeQ_3 = ferric 8-hydroxyquinolinate.

mation of ferric hexafluoroacetylacetonate. In the absence of ultraviolet light no reaction was evident even after 40 hr. at 80°. Moreover, continuous irradiation of the solution was found necessary since cessation of the reaction occurred when the irradiation was interrupted. At higher temperatures, on the other hand, such as in refluxing toluene or the dimethyl ether of diethylene glycol, the thermal reaction becomes more important, as would be expected, and the effect of ultraviolet light less pronounced.

In contrast to the clean reactions of iron and chromium carbonyls, the carbonyls of molybdenum and tungsten gave labile products with 1,3-diketones. Molybdenum carbonyl and acetylacetone produced the air-sensitive Mo(III) acetylacetonate,[4] while only an oxyacetylacetonate was isolated from the reaction of tungsten hexacarbonyl and acetylacetone.[15]

It was found that the reactivity of the active hydrogen compound paralleled its acidity; with the following order of decreasing reactivity prevailing for the photochemical reaction of iron pentacarbonyl in benzene.

	hfaH >	$(C_6H_5CO)_2CH_2$ >	AAH >	8-hydroxyquinoline
$t_{1/2}$, hr.	2	6	7	13

The reactivity of the metal carbonyls with acetylacetone in benzene or isopropyl ether under ultraviolet irradiation decreased qualitatively as follows.

$$Fe(CO)_5 > W(CO)_6 > Mo(CO)_6 >> Cr(CO)_6$$

The effect of different solvents on the photochemical reaction of iron pentacarbonyl with acetylacetone in the refluxing solvent was

	CCl_4 >	C_6H_6 >	isopropyl ether >	THF
$t_{1/2}$, hr.	3	7	8	48

The results obtained in carbon tetrachloride require some comment. Although chromic acetylacetonate was obtained in good yield from this solvent, the reactions of the other metal carbonyls employed in this study were complicated by side reaction with the carbon tetrachloride to produce hydrogen chloride and the metal chlorides.

Efforts to produce mixed carbonyl acetylacetonates, such as $Fe(CO)_2(AA)_2$, by photochemical reaction of the metal carbonyl with the required amount of the 1,3-diketone have thus far given only the simple chelate. However, studies with bistriphenylphosphine iron tricarbonyl have shown that the triphenylphosphine ligand is considerably less labile than the CO ligand to displacement by diketones. Photochemical reaction of bistriphenylphosphine iron tricarbonyl with two moles of hexafluoroacetylacetone in 1:1 benzene–methylene chloride solution resulted in a yellow solid, m.p. 183–185° (from the filtrate), which possessed triphenylphosphine but no CO ligand.[17] Contact of bistriphenylphosphine iron tricarbonyl with acetylacetone, on the other hand, under similar conditions resulted in little or no reaction.

In conclusion, it appears from this and other work currently in progress in our laboratory that this reaction should be of broad synthetic value.

Acknowledgment.—The author wishes to thank Miss T. L. Iapalucci and Mr. E. Berg for experimental assistance and Dr. H. DeSchmertzing and Mr. L. Shubin for analytical assistance.

---

[17] Elemental and infrared analyses suggest the product to be primarily $(C_6H_5)_3PFeCl_3$.

CONTRIBUTION FROM THE PARMA RESEARCH LABORATORY,
UNION CARBIDE CORPORATION, PARMA 30, OHIO

Magnetic and Electric Properties of Monosulfides and Mononitrides of Thorium and Uranium

BY R. DIDCHENKO AND F. P. GORTSEMA

Received April 6, 1963

In connection with studies of the electric and magnetic properties of rare earth monosulfides and nitrides,[1] it was established using the Gouy method that EuS, contrary to the earlier measurements of Klemm,[2] is ferromagnetic with a Curie point at 18°K., in excellent agreement with the recent findings of McGuire, *et al.*[3] Extension of the studies of the monosulfides and nitrides of uranium and thorium, which, like their rare earth counterparts, crystallize in a NaCl lattice, revealed that US is also ferromagnetic with a Curie point at 180°K. and a molar susceptibility of 6280×10^{-6} e.m.u. at 298°K. ($\mu^{B} = 2.46$), in disagreement with previous values,[4,5] while ThS and ThN are diamagnetic. The metallic components of these materials are thus present in the +4 state.

The magnetic behavior in the U–N system is more complicated, as may be seen from Fig. 1. Samples of the indicated composition were obtained by thermal decomposition of UN_2, which, in contrast to previous claims,[6] can be prepared easily by passing ammonia gas over UH_3 while raising the temperature to 1000°. This has been confirmed by analysis and X-ray data, which showed the presence of a face-centered cubic lattice with $a_0 = 5.300 \pm 0.005$ Å., in excellent agreement with the value of Rundle[6] for UN_2 prepared by a high pressure method. The magnetic susceptibility measurements on this phase were rather irreproducible but showed definitely that the Curie–Weiss law was not obeyed. Phases of the compositions $UN_{1.33}$ and $UN_{1.22}$ were obtained reproducibly by heating UN_2 in a tantalum crucible in argon for 4 hr. to 1250 and 1900°, respec-

---

[1] R. Didchenko and F. P. Gortsema, *J. Phys. Chem. Solids*, to be published.

[2] W. Klemm and H. Senff, *Z. anorg. allgem. Chem.*, **241**, 259 (1939).

[3] T. R. McGuire, B. E. Argyle, M. W. Shafer, and J. S. Smart, *Appl. Phys. Letters*, **1**, 17 (1962).

[4] E. D. Eastman, L. Brewer, L. A. Bromley, P. W. Gilles, and N. L. Lofgren, *J. Am. Chem. Soc.*, **72**, 4019 (1950).

[5] M. Picon and J. Flahaut, *Bull. soc. chim. France*, 772 (1958).

[6] R. E. Rundle, *et al.*, "The Uranium Nitrogen System, Chemistry of Uranium," Collected Papers, Report TID 5290, U. S. Atomic Energy Commission, 1958, p. 53.