

adding the DMF solution to a dilute solution of sodium tetraphenylborate in methanol.

**Bromomercurates.**—A similar procedure—the addition of a solution of the crude phosphonium bromide in methanol to a methanolic solution of mercuric bromide—was used to prepare the bromomercurate derivatives. Purification of the latter was effected by adding their DMF solutions to a solution of mercuric bromide in methanol. Apparently the concentration of the mercuric bromide solutions used in the precipitation and purification steps is critical in determining whether a tribromomercurate or a tetrabromomercurate is formed. As can be seen in Table I, both types of these complex salts resulted in this work. This point was not investigated further.

**Quaternization.**—A methanolic solution of crude diphenylphosphinomethyltriphenylphosphonium bromide and a large excess of methyl bromide were sealed in a pressure bottle and left to stand for eight days at room temperature. The resulting methanolic solution was treated with methanolic sodium tetraphenylborate and mercuric bromide, respectively, to prepare the derivatives listed in Table I. The other crude bromides also were quaternized in this manner.

(3) **Dimethylstibinomethyltriphenylphosphonium Bromide and Its Derivatives.**—A slurry of 1.4 g. (0.006 mole) of dimethylbromostibine<sup>7</sup> in ether was added to a slight excess of triphenylphosphinemethylene in ether. The resulting

(7) We are grateful to Dr. Ludwig Maier of Monsanto Research S.A., Zürich, for a sample of this compound.

heterogeneous reaction mixture was stirred under nitrogen for 40 hr. The solid was filtered, washed well with ether and dried to give a white powder. In air this product turned red and decomposed.

One g. of this product was dissolved in 30 ml. of methanol. The resulting yellow solution was heated at reflux for 2 hr. to give an orange solution. Addition of methanolic sodium tetraphenylborate to this solution precipitated methyltriphenylphosphonium tetraphenylborate in 81% yield, identified by m.p. and mixed m.p.

Three g. of crude dimethylstibinomethyltriphenylphosphonium bromide and 15 ml. of methyl bromide were stirred under nitrogen for 20 hr. in a flask equipped with a low temperature condenser. The resulting white powder was washed well with ether and dried (2.9 g.); m.p. 93°.

*Anal.* Calcd. for  $C_{22}H_{26}Br_2PSb$ : C, 43.83; H, 4.35. Found: C, 44.10; H, 4.35.

A similar derivative,  $[(C_6H_5)_2PCH_2Sb(CH_3)_3]BrI$ , was prepared by the reaction of the crude bromide (2.0 g.) with methyl iodide (18 ml.). The resulting light yellow powder (1.7 g.) sintered before it melted at 107–110°.

*Anal.* Calcd. for  $C_{22}H_{26}BrIPSb$ : C, 40.65; H, 4.03. Found: C, 40.68; H, 4.00.

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[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT DEPARTMENT, ETHYL CORPORATION, BATON ROUGE, LA.]

## Reductive Carbonylation Synthesis of Metal Carbonyls. IV. Synthesis of Group VI-B Metal Carbonyls Using Sodium as the Reducing Agent<sup>1</sup>

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A novel and simple sodium route has been developed for preparing the Group VI-B metal carbonyls in high yields. The method consists essentially of reductively carbonylating the metal chloride with sodium and carbon monoxide in diglyme at -10 to 25°, and then hydrolytic carbonylation at 0°. The metal carbonyl appears to be produced initially as a sodium salt  $Na_2M(CO)_6$ , which subsequently is converted to the metal carbonyl by reaction with mineral acid and carbon monoxide.

Although various metallic reducing agents such as zinc<sup>3</sup> and aluminum<sup>4</sup> have found considerable use for the preparation of molybdenum carbonyl and tungsten carbonyl, metallic reducing agents *per se* have been of little or no value for the preparation of chromium carbonyl.<sup>5</sup> However, respectable yields can be achieved if there are also present appreciable amounts of certain additives, such as iodine when magnesium is employed<sup>6</sup> or aluminum chloride when aluminum is employed.<sup>7</sup> Recently, it was reported<sup>8</sup> that sodium can be used for the preparation of chromium carbonyl in 37% yield from chromic chloride in pyridine. This report prompts us to publish at this time some of

our work on the sodium route to metal carbonyls, particularly the Group VI-B metal carbonyls.<sup>9</sup> Our observations on the course of the reaction in diglyme<sup>10</sup> and conditions for obtaining 80% yields are herein reported.

### Results

**Reaction Variable Study.**—It was initially found that little or no carbon monoxide was absorbed upon heating a mixture of chromic chloride and sodium dispersion in various solvents in contact with carbon monoxide. The yield of chromium carbonyl in the best case (75° in diglyme) was only 10–15%. At higher temperatures the yield decreased to 3% or less. In every case it was found that the reaction mixture contained appreciable quantities of black colloidal chromium. At this point the effect of temperature on the yield of chromium carbonyl was investigated carefully. It was found that the yield unexpectedly increased with a decrease in temperature and amounted to about 30% at 0° and a 6:1 mole ratio of sodium to chromic chloride in diglyme. The amount of colloidal chromium also decreased at the lower temperatures.

(1) For paper III, see R. P. M. Werner and H. Podall, *Chem. and Ind.*, in press (1961); paper II, H. Podall, J. H. Dunn and H. Shapiro, *J. Am. Chem. Soc.*, **82**, 1325 (1960).

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(3) K. A. Kocheskov, A. N. Nesmeyanov, *et al.*, *Compt. rend. acad. sci. U.R.S.S.*, **26**, 54 (1940).

(4) D. T. Hurd (to General Electric), U. S. 2,554,194, May 22, 1951.

(5) K. N. Anisimov and A. N. Nesmeyanov, *Compt. rend. acad. sci. U.R.S.S.*, **26**, 58 (1940).

(6) G. Natta, R. Ercoli, F. Calderazzo and A. Rabizzoni, *J. Am. Chem. Soc.*, **79**, 3611 (1957).

(7) E. O. Fischer and W. Hafner (to Badische Anil. and Soda Fabrik.), German Patent 1,007,305, May 2, 1957.

(8) A. N. Nesmeyanov, E. P. Mikheev, K. N. Anisimov and N. P. Filimonova, *Russian J. Inorg. Chem.*, **4**, 889 (1959).

(9) H. E. Podall, U. S. Patents 2,952,521–2–3 (Sept. 1960).

(10) Dimethyl ether of diethylene glycol.

TABLE I  
 TYPICAL RESULTS OF REACTION VARIABLE STUDY

CrX <sub>i</sub> , mole	Na, <sup>a</sup> g. atom	Solvent, ml.	CO, psi. <sup>b</sup>	Mode of contact <sup>c</sup>	Temp., °C.	Time, hr.	M(CO) <sub>i</sub> , % yield <sup>d</sup>
CrCl <sub>3</sub> 0.010	0.100	Diglyme, 35	4000	A	165	13	5
.010	.100	Diglyme, 35	4000	A	125	13	12
.010	.060	Diglyme, 35	3500	A	75	5	12
.010	.060	Diglyme, 35	3500	A	25	16	16
.010	.060	Diglyme, 35	3300	B	0	16	29
.020	.120	Diglyme, 70	2000	C	25	16	30
.020	.120	Diglyme, 70	2000	C	115	6	3
.020	.080	Diglyme, 70	2000	C	25	16	1
.010	.060	THF, <sup>e</sup> 35	3500	B	0	16	23
.020	.120	THF, 70	2000	C	25	16	6
.010	.060	Benzene, 35	3500	A	75	6	0
CrCl <sub>2</sub> .010	.040	Diglyme, 35	3500	B	0	16	16
CrAA, <sup>f</sup> .010	.060	Diglyme, 35	3300	B	25	20	5

<sup>a</sup> 40% dispersion in Nujol. <sup>b</sup> Initial pressure at 25°. <sup>c</sup> A involved contact of the reactants at 25° followed by contact with CO. B involved the use of the metal salt in a sealed ampoule which was then broken in the presence of Na and CO. C involved feeding the Na slowly to the metal halide and CO at the reaction temperature. <sup>d</sup> Yield of chromium carbonyl based on the metal halide charged. In every case the reaction mixture was hydrolyzed at 0° and atmospheric pressure in air to liberate the chromium carbonyl. <sup>e</sup> Tetrahydrofuran. <sup>f</sup> Chromic acetylacetonate—completely soluble in diglyme.

By contacting the chromic chloride suspension in diglyme with the sodium dispersion for varying periods of time prior to carbonylation, it was found that increased contact times gave generally lower yields and increased amounts of chromium metal. This difficulty was alleviated by combining the reactants below 0° and preferably at -20°.

Highest yields of chromium carbonyl were obtained at about a 6:1 mole ratio of sodium to chromic chloride. At a 4:1 mole ratio the yield was appreciably lower, while at a 10:1 ratio there was no improvement over the yield obtained at 6:1, and there was increased reduction to chromium metal.

The order of effectiveness of different solvents on the yield of chromium carbonyl was

diglyme > tetrahydrofuran > Et<sub>2</sub>O > > benzene

Typical results of the reaction variable study for chromium carbonyl are summarized in Table I.

**Reaction in the Absence of Carbon Monoxide.**—Chromous chloride and chromic chloride each were found to be essentially insoluble in diglyme at 0–100°. Catalytic quantities of sodium dispersion or chromous chloride added to chromic chloride had no effect upon the latter's solubility. The same was true for chromous chloride. On the other hand, contact of chromic chloride with sodium dispersion at a 6:1 mole ratio of sodium to chromic chloride in diglyme resulted in essentially complete dissolution of the chromic chloride at 25° in about 2 hr., with the formation of a violet colored solution and gray solids. In 4 hr. the solution became colorless again and black colloidal chromium was evident. The colloidal form of chromium produced in this reaction was found to be reactive with water, liberating about one mole of hydrogen per g.-atom of chromium with the formation of the blue chromous aquo complex ion. Chromous chloride appeared to react somewhat faster with sodium in diglyme at 25° than did chromic chloride, to produce colloidal chromium directly without the formation of a violet colored solution. It was noted that the

reduction reactions involving chromous chloride or chromic chloride were considerably slower in diethyl ether than in diglyme at 25° and still slower in benzene.

**Work-up of the Reaction Mixtures.**—The reaction mixtures from the carbonylation runs were worked up by hydrolysis with dilute aqueous hydrochloric or sulfuric acid at 0–25°, and then extraction with carbon tetrachloride. The extract then was analyzed for its chromium carbonyl content by infrared analysis. Prior to hydrolysis the reaction mixtures generally consisted of some unreacted chromic chloride, black solids and a yellow, air-sensitive solution. Infrared examination of the yellow solution indicated in every case the absence of chromium hexacarbonyl. However, infrared absorption bands suggestive of a different type of a chromium carbonyl moiety were present. It was then found that the infrared spectrum of a diglyme solution of Na<sub>2</sub>Cr(CO)<sub>5</sub> prepared from chromium carbonyl and sodium amalgam in diglyme was very similar to that of the yellow filtrate of the reaction mixture.

Hydrolysis of 0.010 mole of Na<sub>2</sub>Cr(CO)<sub>5</sub> in diglyme with dilute aqueous hydrochloric acid at -20 to 0° was found to produce only 0.006 mole of chromium carbonyl together with 0.007 mole of carbon monoxide and 0.003 mole of hydrogen. It appeared therefore that the maximum yield of chromium carbonyl obtainable by the sodium route employing hydrolysis at atmospheric pressure was only about 60%, with the 30% yields obtained corresponding on this basis to 50% of theoretical.

It was felt that the hydrolytic oxidation-reduction of Na<sub>2</sub>Cr(CO)<sub>5</sub> could be minimized by conducting the hydrolysis under carbon monoxide pressure. Accordingly, 0.010 mole of Na<sub>2</sub>Cr(CO)<sub>5</sub> in diglyme was quenched slowly at 0° with dilute aqueous hydrochloric acid under 2000 psi. of carbon monoxide. It was found that 0.0093 mole of chromium carbonyl resulted. It appeared therefore that the undesirable oxidation-reduction could be essentially eliminated by conducting the hydrolysis under carbon monoxide pressure.

**Optimum Conditions.**—A detailed investigation of the sodium route to the Group VI-B metal carbonyls employed low temperatures for combining the reactants (*e.g.*,  $-20^{\circ}$ ) and for conducting the carbonylation reaction ( $-10$  to  $25^{\circ}$ ). The metal carbonyl was liberated from its sodium salt by hydrolyzing the reaction mixture slowly with dilute aqueous sulfuric acid in the presence of 500–1000 psi. of carbon monoxide at  $0^{\circ}$ . It appears necessary to employ dry reagents and very dry, oxygen-free diglyme to achieve consistently high yields.

Typical results are summarized in Table II.

TABLE II  
SYNTHESIS OF METAL CARBONYLS BY THE SODIUM ROUTE

MCl, mole	Na, <sup>a</sup> g. atoms	Di- glyme, ml.	CO, psi.	Time at $-20^{\circ}$ , hr.	Time at $0-25^{\circ}$ , hr.	H <sub>2</sub> - SO <sub>4</sub> , <sup>b</sup> quench time, hr.	M- (CO) <sub>6</sub> , % yield <sup>c</sup>	
CrCl <sub>3</sub>	0.20	1.20	470 <sup>d</sup>	700	3	16	2	52
	.20	1.20	470 <sup>e</sup>	800	4	16	2	80
MoCl <sub>5</sub>	.20	1.20	500 <sup>d</sup>	900	4	16	3	65 <sup>f</sup>
WCl <sub>6</sub>	.10	1.40	470 <sup>d</sup>	900	4	16	3	75 <sup>g</sup>

<sup>a</sup> 40% dispersion in Nujol. <sup>b</sup> Employed excess oxygen-free aqueous sulfuric acid. <sup>c</sup> Isolated yield of pure metal carbonyl based on charged metal chloride. <sup>d</sup> Dried over lithium aluminum hydride. <sup>e</sup> Dried by sodium-benzophenone procedure. <sup>f</sup> Unreacted molybdenum halide was present before distillation. <sup>g</sup> Free tungsten metal or lower chloride of tungsten was present before distillation.

### Discussion

The principal differences responsible for the superior yields of chromium carbonyl obtained in this study over those reported by Nesmeyanov and co-workers<sup>3</sup> appear to be (1) the use of lower temperatures for contacting the reactants and conducting the reaction proper, (2) hydrolysis of the reaction mixture under carbon monoxide pressure, (3) higher mole ratios of sodium to chromic chloride and (4) use of diglyme instead of pyridine as the reaction solvent. Each of these factors appears to have a marked influence upon the course and extent of the desired reaction.

The results of this study indicate that highest yields of chromium carbonyl are obtained when the reactivity of the sodium toward chromic chloride is sufficiently moderated to permit carbonylation to occur at a rate comparable to that of reduction. The importance of synchronizing the reduction and carbonylation reactions is clearly indicated by the results of experiments employing different modes of mixing the reactants.<sup>11</sup>

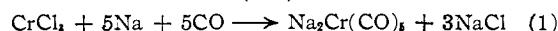
It is felt that the reaction does not proceed *via* metallic chromium, because of the failure of various forms of chromium, including that obtained from the reaction of chromic chloride with sodium in diglyme, to undergo carbonylation. However, the possibility that the reaction proceeds *via* atomic chromium cannot be absolutely ruled out. On the other hand, we have found that the metals in the higher oxidation states, such as chromic *vs.* chromous chloride, provide higher yields of the metal carbonyl.

(11) Nesmeyanov and co-workers<sup>3</sup> employed a sealed ampoule procedure (wherein the sodium was contained in a sealed ampoule which was broken in an autoclave containing a pyridine solution of chromic chloride under 1500 p.s.i. of carbon monoxide at  $22^{\circ}$ ) in an effort to achieve simultaneous contact of the reactants.

It would appear therefore that the carbonylation sets in at least at the oxidation state of  $+1$  or higher. In accord with this hypothesis, it has been observed that molybdenum pentachloride and tungsten hexachloride undergo carbonylation more readily than does chromic chloride in the sodium route as well as in other reductive carbonylation routes.<sup>1</sup> These results may derive from the fact that the metals in higher oxidation state have a longer way to go to be completely reduced, and consequently there is a greater opportunity for one of the lower oxidation states to undergo carbonylation.

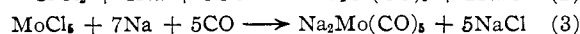
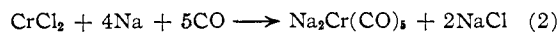
The temporary formation of a violet colored solution on contacting chromic chloride with sodium in diglyme parallels that obtained from chromic chloride and a catalytic quantity of zinc dust in tetrahydrofuran (THF). In the latter case a violet colored complex, CrCl<sub>3</sub>·3THF, was isolated.<sup>12</sup> Accordingly, it would appear that a similar complex is formed in diglyme, such as (diglyme)CrCl<sub>3</sub>, with the diglyme functioning as a tridentate ligand. The exact role of the sodium here is not clear. One possibility is that the crystalline lattice of chromic chloride must be sufficiently disrupted, in this case by partial reaction with sodium, for the residual chromic chloride moiety to be reactive. The reductive carbonylation reaction in diglyme is therefore considered to proceed via a diglyme complex, with the diglyme stabilizing a lower oxidation state of chromium, probably the  $+1$  state, for carbonylation.

From the infrared results and other experiments on the hydrolysis of the reaction mixture in the absence and in the presence of carbon monoxide, it appears fairly certain that the product from the reaction of chromic chloride with sodium and carbon monoxide is the sodium salt of chromium carbonyl, Na<sub>2</sub>Cr(CO)<sub>6</sub>.<sup>13</sup> The optimum 100% excess of sodium (6:1 mole ratio instead of a 3:1 mole ratio of sodium to chromic chloride) over that required for reduction of chromic chloride to a formal oxidation state of zero in chromium hexacarbonyl therefore can be explained in terms of the formation of Na<sub>2</sub>Cr(CO)<sub>6</sub>. Chromium hexacar-



bonyl was found to react only very slowly with sodium dispersion in diglyme at  $25^{\circ}$ . Higher temperatures were generally required to effect significant reaction. It appears therefore that the sodium salt of chromium carbonyl arises from a chromium carbonyl moiety other than chromium hexacarbonyl.

Similar reactions may be expected for chromous chloride, molybdenum pentachloride and tungsten hexachloride, with the proportions



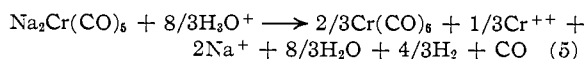
At appreciably higher mole ratios of sodium to the metal halide than indicated by these reaction

(12) W. Herwig and H. H. Zeiss, *J. Org. Chem.*, **23**, 1404 (1958).

(13) This compound first was reported by von H. Behrens and R. Weber, *Z. anorg. u. allgem. Chem.*, **291**, 122 (1957), from the reaction of chromium carbonyl with sodium in liquid ammonia.

ratios, reduction to the free metal becomes significant.

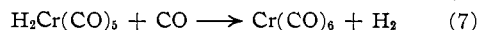
Hydrolysis of  $\text{Na}_2\text{Cr}(\text{CO})_6$  in the absence of carbon monoxide appears to proceed



The reaction is believed to occur via the formation of the metastable hydrochromium carbonyl,  $\text{H}_2\text{Cr}(\text{CO})_6$ .

Hydrolysis of the sodium salt of chromium carbonyl in the presence of 500–1000 psi. of carbon monoxide essentially eliminated the oxidative decomposition reaction, presumably because carbon monoxide reacts rapidly with the hydrochromium carbonyl intermediate to produce chromium hexacarbonyl. The carbonylation of a sodium salt of  $\text{Na}_2\text{Cr}(\text{CO})_6 + 2\text{H}_3\text{O}^+ \longrightarrow \text{H}_2\text{Cr}(\text{CO})_6 + 2\text{Na}^+ + 2\text{H}_2\text{O}$

(6)



a metal carbonyl under hydrolytic conditions might be conveniently described as a hydrolytic carbonylation reaction.

In conclusion, the sodium–diglyme reductive carbonylation reaction coupled with hydrolytic carbonylation of the intermediate sodium salt of the metal carbonyl provides a convenient high yield route to the Group VI-B metal carbonyls.

#### Experimental<sup>14</sup>

**Materials.**—The metal chlorides used were the same as previously described.<sup>1</sup> The sodium dispersion was about 40% in Nujol (Plough, Inc.) and was prepared from 168 g. of sodium, 252 g. of Nujol and 1.5 ml. of Triton X-100. Use of Primol D (Esso) in place of the Nujol gave similar results in the metal carbonyl synthesis.

The solvents were of the highest purity commercially available and were dried shortly before use. Diglyme and tetrahydrofuran were dried by the sodium-benzophenone procedure<sup>15</sup> with the following modifications. To the solvent was added small quantities of the 40% sodium dispersion at room temperature in a dry nitrogen box until gas evolution ceased. Successive quantities of benzophenone and sodium dispersion then were added until a blue to violet color persisted for several hours. The diglyme was distilled at 35 mm., while the tetrahydrofuran was distilled at atmospheric pressure under nitrogen, reserving in each case the central boiling fraction for use. Benzene was dried over calcium hydride. The ether solvents were stored in the dry nitrogen box.

**Analysis.**—The infrared method of analysis was the same as that previously described.<sup>1</sup>

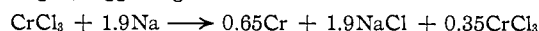
**Reaction of Chromic Chloride with Sodium.**—To a 100-ml. three-necked round-bottomed flask was added 1.59 g. (0.010 mole) of chromic chloride, 35 ml. of diglyme and 4.0 ml. (0.060 g. atom) of the sodium dispersion. The mixture then was stirred magnetically under nitrogen at 25°. Within about 2 hours a violet colored solution was formed with only gray solids evident. In 4 hr. black solids were present and the violet color was gone. After 20 hr. no further change was evident, and the mixture was hydrolyzed at 0° with 5 ml. of isopropyl alcohol and 10 ml. of water. The evolved hydrogen amounted to 0.022 mole. Addition of 10 ml. of concentrated hydrochloric acid resulted in the evolution of an additional 0.004 mole of hydrogen. The total gas evolved is in accord with the reaction given, wherein 0.025 mole of hydrogen should have been evolved upon hydrolysis.



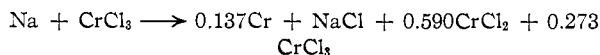
(14) All melting points uncorrected, in a sealed capillary.

(15) Procedure of Dr. G. V. D. Tiers, described in M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Non-Metallic Substances," Prentice-Hall, Inc., New York, N. Y., 1954, p. 25.

Reaction of 0.020 mole of chromic chloride with 0.038 g. atom of sodium in diglyme at 25° for 20 hr. resulted in black solids with some unreacted chromic chloride evident. Hydrolysis by the above procedure produced 0.014 mole of hydrogen, suggesting the reaction ratios



Reaction of 0.020 mole of chromic chloride with 0.020 g. atom of sodium under similar conditions resulted in black solids with no chromic chloride evident this time. Hydrolysis yielded only 0.0027 mole of hydrogen, consistent with the proportions



**Preparation of  $\text{Na}_2\text{Cr}(\text{CO})_6$  in Diglyme.**—To 5.5 ml. of triply-distilled dry mercury was added slowly 0.69 g. (0.030 g. atom) of sodium, cut up into small pieces, under nitrogen at 25° with magnetic stirring. To the approximately 1% sodium amalgam thus prepared was added 100 ml. of diglyme and 2.20 g. (0.010 mole) of chromium hexacarbonyl. The mixture was then heated with stirring to 105° under a cold water condenser. Within about 3 hr. 0.010 mole of carbon monoxide was evolved and the reaction ceased. After cooling under nitrogen, the yellow-green solution of  $\text{Na}_2\text{Cr}(\text{CO})_6$  was decanted from the mercury and excess sodium in the dry nitrogen box.

The sodium salt of chromium carbonyl was also prepared quantitatively in tetrahydrofuran by refluxing a mixture of 0.010 mole of chromium carbonyl and 0.030 g. atom of sodium as a 1% amalgam in tetrahydrofuran for about 5 hr.

**Hydrolysis of  $\text{Na}_2\text{Cr}(\text{CO})_6$  under Carbon Monoxide Pressure.**—To a 250-ml. Magne-Dash autoclave in a dry nitrogen box was added 100 ml. of a diglyme solution containing 0.010 mole of  $\text{Na}_2\text{Cr}(\text{CO})_6$  prepared from 0.010 mole of chromium carbonyl. To a 100-ml. Magne-Dash autoclave, employed as a reservoir, was added 25 ml. of a 1.6 M aqueous solution of sulfuric acid, and the autoclave was pressurized with nitrogen to 3500 psi. The reactor autoclave containing the  $\text{Na}_2\text{Cr}(\text{CO})_6$  was then pressurized with carbon monoxide to 3000 psi. with stirring and cooled to 7–8° in an ice-bath. The sulfuric acid solution now was transferred in increments to the reactor autoclave, *via* a transfer line containing a pressure regulating valve, over a period of about 4.5 hr. To the reaction mixture obtained from the reactor autoclave was then added 100 ml. of water and the mixture was extracted with four 65-ml. portions of carbon tetrachloride. Infrared analysis of the carbon tetrachloride extract indicated a yield of 0.0093 mole (93% theory) of chromium carbonyl.

**Reaction Variable Study.**—This study employed a 100-ml. Magne-Dash autoclave for the batch and sealed ampoule runs and a 250-ml. Magne-Dash autoclave for the runs where the sodium was fed under pressure. The exact contact procedures employed have been described previously.<sup>1</sup> Some of the results are summarized in Table I. It should be noted that in all these runs the reaction mixtures were hydrolyzed at atmospheric pressure and the chromium carbonyl yields were determined by infrared analysis of the carbon tetrachloride extract.

**Preparation of Chromium Carbonyl.**—To a 1-liter Parr autoclave equipped with a turbine-type stirrer was added 470 ml. of diglyme and 80 ml. (1.20 g.-atom) of the 40% sodium dispersion in Nujol in the dry nitrogen box. The autoclave was cooled in a Dry Ice bath to –20°, and 31.7 g. (0.20 mole) of anhydrous powdered chromic chloride was added under nitrogen. The autoclave then was sealed, placed in an ice-salt bath and pressurized with carbon monoxide to 800 psi. at –20 to –10° with stirring. After about 1.5 hr., 120 psi. of carbon monoxide was absorbed, and the reaction temperature was permitted to rise to –5°. After about 30 minutes at this temperature, during which time the carbon monoxide uptake was very slow, the ice was removed and the temperature was permitted to rise to room temperature (about 30°). Stirring was continued for 16 hr. at this temperature under full cylinder pressure of carbon monoxide (about 800 psi.).

A solution of 22.2 ml. (0.40 mole) of concentrated sulfuric acid and 228 ml. of oxygen-free water was placed into a 200-ml. high-pressure container equipped with a high-pressure sight glass. The solution was then added continuously under 1000 psi. of nitrogen to the reaction mixture at –5° to 0° in the presence of 800 psi. of carbon monoxide.

oxide over a period of 2 hr. The reaction was exothermic and the temperature was permitted to rise to room temperature toward the end of the addition.

The contents of the autoclave then were transferred with water to a 2-liter three-necked round-bottomed flask. One hundred milliliters of water and 100 ml. of concentrated hydrochloric acid were added, and the chromium carbonyl was co-distilled with water at atmospheric pressure with stirring. The yield of chromium carbonyl recovered was 35.2 g. (80%), m.p. 152–155°.

Essentially the same procedure was employed for the preparation of molybdenum carbonyl and tungsten carbonyl

except for the quantities of the reactants, which are shown in Table II.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENTS, STATE UNIVERSITY OF NEW YORK, LONG ISLAND CENTER, OYSTER BAY, AND BROOKHAVEN NATIONAL LABORATORY, UPTON, NEW YORK]

## The Kinetics of the Oxidation of Iron(II) Ions and of Coordination Complexes<sup>1a</sup>

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The kinetics of the oxidation of iron(II) ions by  $\text{Ag}(\text{phen})_2^{+2}$ ,  $\text{Ag}(\text{dipy})_2^{+2}$ ,  $\text{Ru}(\text{dipy})_3^{+3}$ ,  $\text{Os}(\text{dipy})_3^{+3}$  and  $\text{IrCl}_6^{-2}$  have been investigated in perchloric and sulfuric acid solutions. The rates of oxidation of the iron(II) ions were found to increase with the standard free energy changes of the reactions. The oxidation of iron(II) ions by  $\text{IrCl}_6^{-2}$  is more rapid than the oxidation by  $\text{Fe}(\text{phen})_3^{+3}$  although the standard free energy changes of the two reactions are identical. The increased rate of the former reaction was found to be due to a less negative entropy of activation. The reactions between positively-charged complexes as well as those between oppositely-charged complexes proceed with rate constants which are larger than  $10^8 \text{ l. mole}^{-1} \text{ sec.}^{-1}$ . On the other hand the oxidations of ferrocyanide ions by  $\text{IrCl}_6^{-2}$ ,  $\text{MnO}_4^-$  and  $\text{OsCl}_6^{-2}$  are considerably slower and increase with the standard free energy changes of the reactions. The oxidation-reduction reactions between the complex ions are discussed in terms of the Marcus theory of these reactions, and the free energies required to reorganize the inner coordination shells of the various complexes are estimated.

### Introduction

Recent investigations<sup>2,3</sup> of the kinetics of the oxidation of iron(II) ions by substituted 1,10-phenanthroline complexes of iron(III) ions have shown the existence of a linear relationship between the free energies of activation and the standard free energy changes of the reactions. It was found that the rate constants determined for the oxidation of iron(II) ions by the 4,4'-dimethyl-2,2'-dipyridine, 2,2'-dipyridine and 2,2',2''-tripyridine complexes of iron(III) did not satisfy the linear relationship found for the phenanthroline complexes. We have extended these studies to other reactions between oxidizing and reducing agents, which differ in their sizes, structures and charges.

Sheppard and Wahl<sup>4</sup> have reported that the permanganate-manganate isotopic exchange reaction is catalyzed by ferricyanide ions. They suggested that this catalysis could be explained in terms of the permanganate-ferrocyanide oxidation-reduction reaction and calculated a second order rate constant of approximately  $10^4 \text{ l. mole}^{-1} \text{ sec.}^{-1}$  for this reaction. Such a rate can be measured with a flow apparatus.

### Experimental

**Chemicals.**—Solutions of ferrous perchlorate and the substituted phenanthroline and dipyridine complexes of iron(III) were prepared as previously described.<sup>2,3</sup> Tris-(2,2'-dipyridine)-osmium(II) perchlorate was prepared from osmium tetroxide according to the procedures described by Dwyer and Hogarth<sup>5</sup> and by Burstall, Dwyer and Gyrfas.<sup>6</sup>

Bis-(1,10-phenanthroline)-silver(II) nitrate and bis-(2,2'-dipyridine)-silver(II) nitrate were prepared by dissolving silver(II) oxide in 6*F* nitric acid which had been cooled to about  $-10^\circ$ . Excess base (1,10-phenanthroline and 2,2'-dipyridine, respectively) was added, and the color of the solutions changed from deep brown to deep red. More nitric acid was added and the solutions cooled in a salt-water-ice bath, whereupon the nitrate salts of the respective silver(II) complex ions crystallized. The crystals were filtered off, rapidly washed with cold water and dried in air. The preparation of the stock solutions for the kinetic runs was accompanied by appreciable reduction to the silver(I) state. A sample of ammonium hexachloroiridium(IV), prepared from hexachloroiridic acid and ammonium chloride, was kindly donated by Dr. Garman Harbottle of Brookhaven National Laboratory. The following compounds were used without further purification: tris-(2,2'-dipyridine)-ruthenium(II) chloride (G. Frederick Smith Chemical Co.), potassium permanganate (Baker Analyzed Reagent), potassium hexacyanoiron(II) (Baker Analyzed Reagent), ammonium hexachlorosmium(IV) (Johnson, Mathey and Co.), perchloric acid (Baker Analyzed Reagent) and sulfuric acid (Baker and Adamson). Tris-(2,2'-dipyridine)-osmium(III) and tris-(2,2'-dipyridine)-ruthenium(III) were prepared from the corresponding osmium(II) and ruthenium(II) complexes by oxidation with lead dioxide and sulfuric acid.

Triply-distilled water was used in preparing the solutions for the kinetic measurements.

**Procedure.**—The reactions were followed using the rapid-mixing and flow apparatus which has been previously described.<sup>2,3</sup> The "continuous flow" rather than the "stopped flow" procedure was used to follow the faster reactions. Temperature was maintained by circulating water from a constant temperature bath through the jacket which housed the mixing chamber and flow tube and was constant to  $\pm 0.1^\circ$ . Activation energies were calculated from determinations of the rate constants at 15, 25 and 35°.

### Results

The reactions were found to be first order with respect to each of the reactants by independent variations of the concentration of each reactant

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