

*Anal.* Calcd. for  $C_{13}H_{23}BNO_5Re$ : C, 33.19; H, 4.93; B, 2.30; Re, 39.6. Found: C, 31.65; H, 5.50; B, 2.51; Re, 38.7.

$(C_2H_5)_4N[(H_3B)_2Re(CO)_5]$ .—This compound was prepared by dissolving *ca.* 2.5 g. (5 mmoles) of  $(C_2H_5)_4N[H_3BRe(CO)_5]$  prepared as described in 10 ml. of tetrahydrofuran. The solution was treated with 10 mmoles of diborane for 1 hr. at room temperature. The solution was partially evaporated and ether was added to give yellow-orange crystals of  $(C_2H_5)_4N[(H_3B)_2Re(CO)_5]$ . This complex was distinguished from the monoborane complex by appearance of a doublet in the BH stretching region of the infrared spectrum. The X-ray powder pattern also displayed a slight displacement of one line and minor intensity differences.

*Anal.* Calcd. for  $C_{13}H_{23}B_2NO_5Re$ : B, 4.46; Re, 38.5. Found: B, 5.00; Re, 39.6.

$(C_2H_5)_4N[H_3B-Mn(CO)_4P(C_6H_5)_3]$ .—A solution of 2.2 g. (5.1 mmoles) of triphenylphosphinemanganese tetracarbonyl in 40 ml. of tetrahydrofuran was treated with 12 g. of 1.4% sodium amalgam at room temperature under nitrogen. The red solution soon became yellow-orange and some yellow solid separated.

The suspension was treated with 5.0 ml. of a 1.0 *M* solution of tetraethylammonium chloride in acetonitrile. The solution was partially evaporated, was filtered to remove NaCl, and was evaporated to dryness under reduced pressure. The residue was dissolved in 10 ml. of tetrahydrofuran and was treated with 5 mmoles of diborane. The solution was partially evaporated (to *ca.* 5 ml.) until yellow crystals separated. The crystals were collected by filtration and were dried under reduced pressure.

*Anal.* Calcd. for  $C_{30}H_{38}BMnNO_4P$ : C, 62.8; H, 6.68; B, 1.89. Found: C, 61.80; H, 6.52; B, 1.59.

$(C_2H_5)_4N[Mn(CO)_5]$ .—A mixture of 3.9 g. (10 mmoles) of manganese carbonyl, 70 g. of 1.4% sodium amalgam, and 40 ml. of tetrahydrofuran was stirred at room temperature in a nitrogen atmosphere overnight. The solution was decanted with a hypodermic syringe and was evaporated to 20 ml. under reduced pressure. Tetraethylammonium chloride (20 ml. of 1.0 *M* solution in  $CH_3CN$ ) was added and the NaCl which formed was collected by filtration. The clear, pale green filtrate was evaporated to give a faintly yellow, solid residue. The  $(C_2H_5)_4N[Mn(CO)_5]$  was dried at 25° (0.1  $\mu$ ) for 2 hr. and was sealed in a

glass ampoule. After brief storage, a thin layer of the material on the side of the ampoule toward the light turned green but most of the solid was unaffected.

*Anal.* Calcd. for  $C_{13}H_{23}MnNO_5$ : C, 48.01; H, 6.20; Mn, 16.89; N, 4.31. Found: C, 46.27; H, 6.19; Mn, 13.87; N, 4.21.

$(C_2H_5)_4N[H_3B-Mn(CO)_5]$ .—A solution of 7.0 mmoles of  $(C_2H_5)_4N[Mn(CO)_5]$  in 3 ml. of tetrahydrofuran was allowed to equilibrate with 7 mmoles of diborane and 7 ml. of ether was added. On cooling to -78°, fine yellow crystals separated from the solution. The crystals were collected by filtration and were dried under reduced pressure (25° (0.1  $\mu$ ) for 5 hr.). The sample was stored in glass ampoules at -25° for 5 days until it could be analyzed but some discoloration occurred. Diminution of the B-H stretching absorption in the infrared suggests that loss of diborane occurred.

*Anal.* Calcd. for  $C_{13}H_{23}BMnNO_5$ : C, 46.05; H, 6.84; Mn, 16.20. Found: C, 46.78; H, 6.74; Mn, 14.04.

The infrared spectrum (Nujol mull) showed B-H absorption at 2410 and 2470  $cm^{-1}$  and strong, broad metal carbonyl absorption at 1850  $cm^{-1}$ . However, when the crystals were dissolved in diglyme, no B-H stretching absorption could be detected and the metal carbonyl stretching reverted to a doublet at 1902 and 1876  $cm^{-1}$  as in  $[Mn(CO)_5]^-$ .

**Analytical.**—Considerable difficulty was encountered in obtaining useful carbon analyses on compounds containing both boron and rhenium. Some of the difficulty may have been due to the great hydrolytic sensitivity of the borane complexes. However, the fact that the carbon analyses were always low suggests that some of the carbon may have been converted to an oxidation-resistant carbide during combustion. This supposition is supported by the fact that combustions carried out at high temperatures gave higher carbon values than those carried out at conventional temperatures.

Rhenium analyses were done by X-ray fluorescence measurement on pellets of the complex in an inert solid. Infrared spectra were determined on Perkin-Elmer Models 21 and 237 instruments with NaCl and grating optics, respectively. Proton magnetic resonance measurements were made with a Varian A-60 spectrometer with tetramethylsilane as an internal reference in the specimen.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF KANSAS, LAWRENCE, KANSAS]

## The Formation of Copper(I) Chloride by the Action of Copper(I) Ion on Carbon Tetrachloride in 2-Butanol

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A remarkable reaction between copper(I) perchlorate and carbon tetrachloride in 2-butanol solutions containing small amounts of water has been uncovered and investigated. Copper(I) chloride, two acidic species, one weak and one strong, and an ether of the apparent formula  $CH_3CH_2CHCH_3$  are formed in the reaction.

The production of the acidic species and the ether is reasonably explained in terms of reaction between the bases water and 2-butanol with the trichloromethyl cation,  $(CCl_3)^+$ .

During the course of an investigation of the preparation of copper(I) perchlorate in 2-butanol, an unexpected and novel reaction was encountered. Reduction of hydrated copper(II) perchlorate in 2-butanol solution by means of metallic copper yields colorless solutions of copper(I). Attempts to precipitate the corresponding perchlorate at room temperature by addition of carbon tetrachloride gave a white solid, shown by analysis to be copper(I) chloride. Preliminary experiments soon showed that there were formed no organic products which could arise as a result of a free radical mechanism. The nature of the various products can be accounted for in a reasonable manner in terms of an initial ionic attack of copper(I) on carbon tetrachloride.

### Experimental

**Chemicals.**—Matheson Coleman and Bell Spectroquality carbon tetrachloride and Eastman White Label 2-butanol were used without further purification. Copper(II) perchlorate 6-hydrate (G. F. Smith Chemical Company) was dried under vacuum at 60° for 48 hr. Analysis of the "dried" product for water content by

the Karl Fischer method gave the value 19.55%; theoretical for  $Cu(ClO_4)_2 \cdot 3.5H_2O$ , 19.36%. Commercially available "Chore Girl" pot cleaner was employed as the source of copper metal. Silver nitrate, sodium hydroxide, hydrochloric acid, and perchloric acid solutions were prepared and standardized in the usual manner.

**Apparatus.**—The reaction vessel was a three-necked round-bottomed flask to which was connected a reflux condenser, a nitrogen gas inlet tube, and a thermometer. A gas outlet tube was placed at the top of the condenser and led into a 100-ml. round-bottomed flask containing standardized sodium hydroxide solution.

**General Procedure.**—2-Butanol solutions of copper(I) perchlorate were prepared by the addition of an excess of copper metal to a weighed quantity of  $Cu(ClO_4)_2 \cdot 3.5H_2O$  (*ca.* 0.34 or 0.04 g.) in 50 ml. of the alcohol, followed by refluxing in a nitrogen atmosphere at 80° for 6 hr. The copper(I) perchlorate solution was permitted to cool to room temperature and unreacted copper metal was removed. Deaerated carbon tetrachloride (25 ml./50 ml. of butanol) was then added to the copper(I) solution. After a period of 2-3 min., a white precipitate appeared. The mixture was allowed to stand for varying periods of time and then the white precipitate, which was shown to be copper(I) chloride, was filtered, washed with a 1:1 solution of carbon tetrachloride in 2-butanol, and dried at 110°.

TABLE I  
 ANALYTICAL DATA: REACTION OF COPPER(I) PERCHLORATE WITH CARBON TETRACHLORIDE IN 2-BUTANOL<sup>a</sup>

Cu(I), mmoles <sup>b</sup>	Time, min.	CuCl, mmoles	Cl <sup>-</sup> in solution,		CO <sub>2</sub> , mmoles	Total Cl <sup>-</sup> , mmoles corrected <sup>c</sup>	Strong acid, mmoles corrected <sup>c</sup>	Weak acid, mmoles corrected <sup>c</sup>	Total acid, mmoles
			mmoles	mmoles					
2.06	20	1.11	0.47	0.086	1.32	0.19	1.47	1.66	
2.08	20	1.45	.22	.076	1.44	.19	1.51	1.70	
2.06	20	1.56	.17	.080	1.49	.11	1.53	1.64	
2.34	30	1.47	.80						
2.06 <sup>d</sup>	20	1.46	.17	.085	1.37	.0	1.64	1.64	
2.07 <sup>d</sup>	20	1.86	.20	.090	1.79	.0	1.89	1.89	
2.07 <sup>e</sup>	20	1.46	.32	.085	1.52	.15	1.52	1.67	
2.06 <sup>e</sup>	960	1.11	.60	.080	1.47	.11	1.53	1.64	
0.20	2340	0.10	.04						
.28	2730	.29	.09						
.21	2	.07	.28						
.25 <sup>g</sup>	2	.13	.11						
.26 <sup>g</sup>	4	.14	.11						
2.10 <sup>f</sup>				1.054					
2.09 <sup>d,f</sup>				1.299					

<sup>a</sup> Temperature 25°, unless otherwise specified. <sup>b</sup> Calculated on the basis of complete reduction of copper(II) perchlorate. <sup>c</sup> Corrected for the reaction: (H<sub>2</sub>O:CCl<sub>3</sub>)<sup>+</sup> + H<sub>2</sub>O → 4H<sup>+</sup> + 3Cl<sup>-</sup> + CO<sub>2</sub> (see Results and Discussion). <sup>d</sup> Solution made 0.5 M in added water prior to addition of copper metal (see Experimental). <sup>e</sup> Solution made 0.7 M in added water after addition of carbon tetrachloride (see Experimental). <sup>f</sup> Solution subjected to alkaline hydrolysis after reaction with carbon tetrachloride (see Experimental). <sup>g</sup> Experiment carried out at 5°.

*Anal.* Calcd. for CuCl: Cl, 35.82. Found: Cl, 35.84.

The filtrate and the washings were combined, and after the addition of water (100 ml./100 ml. of solution) were analyzed for acidic species and for chloride ion by potentiometric titrations. After titration for acidic species with standard base, the solution was acidified with dilute nitric acid and then titrated with standard silver nitrate.

Carbon dioxide, formed during the course of reaction of the copper(I) perchlorate solution with carbon tetrachloride and during the time the reaction mixture was permitted to stand, was swept from the reaction vessel by nitrogen gas into 25 ml. of 0.1 M sodium hydroxide solution maintained in the 100-ml. round-bottomed flask. A measure of the quantity of carbon dioxide formed was obtained by potentiometric titration of the sodium hydroxide solution with standard acid, after CO<sub>2</sub> absorption.

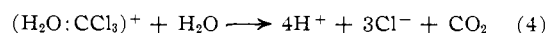
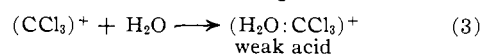
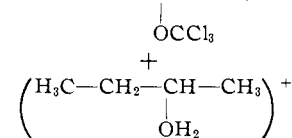
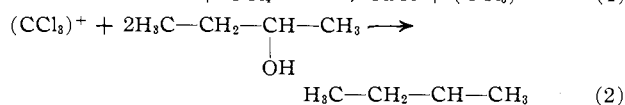
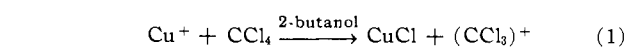
To help establish the nature of the attack of copper(I) perchlorate on carbon tetrachloride by means of organic reaction products formed, several reaction mixtures, which were allowed to stand for *ca.* 20 min. after the addition of carbon tetrachloride, were subjected to gas chromatographic analysis.

**Alkaline Hydrolysis of Reaction Mixture.**—In a number of experiments, a measure was made of the carbon dioxide liberated on alkaline hydrolysis of the copper(I) perchlorate solution-carbon tetrachloride mixture under reflux conditions (*ca.* 80°). The quantities of chemicals used were similar to those described under General Procedure. To the reaction mixture, which was allowed to stand for approximately 20 min. after removal of unreacted copper and addition of carbon tetrachloride, there was added about 25 ml. of 1 M sodium hydroxide solution. The resulting mixture was refluxed for 6–8 hr. under a stream of nitrogen. The solution was then acidified with dilute perchloric acid and again refluxed under nitrogen for 6–8 hr., the carbon dioxide evolved being collected and determined as described above.

**Isolation of Organic Reaction Product.**—In a number of runs, the reaction mixture, after removal of copper(I) chloride, was extracted at least ten times with water to remove dissolved copper salts and 2-butanol. The organic phase was then vacuum distilled at 30° (1 mm.). The distillation left a very small (*ca.* 2 drops) residue of yellow oil. The infrared spectrum of this oil in Nujol was obtained on a Perkin-Elmer Model 421 spectrophotometer.

## Results and Discussion

The analytical data obtained from a number of typical reactions between copper(I) perchlorate and carbon tetrachloride in 2-butanol under a variety of conditions are summarized in Table I. Attention should be called to the following features of these reactions: (a) the formation of copper(I) chloride as a precipitate; (b) the existence of some chloride ion in solution; (c) the evolution of carbon dioxide; and (d) the formation in solution of both weakly and strongly acidic species under the appropriate conditions. These features can be reasonably accounted for in terms of the following reactions



Justification for these reactions follows.

A number of factors rule out the possibility that the initial attack by copper(I) of carbon tetrachloride in 2-butanol occurs with free radical formation. In the first place, when reaction occurs at 25°, no products such as chloroform and 2-butanone, expected on the basis of the formation of the ·CCl<sub>3</sub> radical,<sup>1</sup> are formed. Moreover, a radical reaction would yield the Cu<sup>2+</sup> ion as an intermediate, along with chloride ion, and this combination would be expected to chlorinate 2-butanone,<sup>2</sup> if the latter product were formed. No chlorinated ketone was observed.

The formation of both weak and strong acids is demonstrated by the dotted titration curve in Fig. 1. Their production can be explained by reactions 2 and 3. The trichloromethyl cation, (CCl<sub>3</sub>)<sup>+</sup>, formed as a result of ionic attack on carbon tetrachloride by copper(I) ion, functions as a strong Lewis acid and adds to the two bases, water and 2-butanol, present in the reaction mixture. Water, being much more basic than the alcohol, forms the weaker acid. Although there is relatively little water present, supplied primarily by hydrated copper(II) perchlorate, its more basic nature results in the weaker acid being the predominant acidic species (Table I). Consistent with this viewpoint is the fact that the presence of additional water *prior* to the addition of carbon tetrachloride to the reaction medium (Table I) essentially eliminates the formation of strong acid. However, if the water is added *after*

(1) G. A. Razuvaev, B. N. Moryganov, and A. S. Volkova, *Zh. Obshch. Khim.*, **25**, 463 (1955).

(2) J. K. Kochi, *J. Am. Chem. Soc.*, **77**, 5274 (1955).

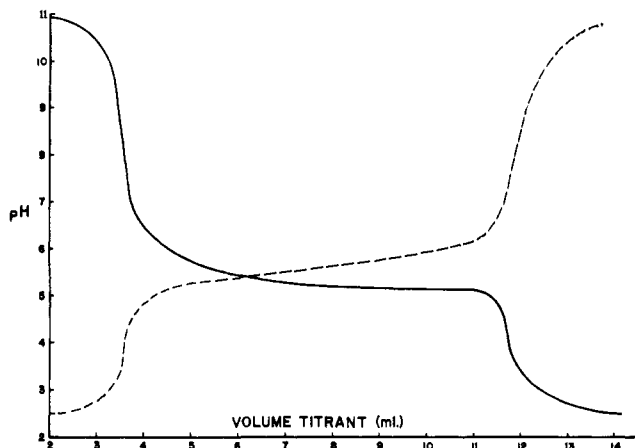


Fig. 1.—Titration curves: broken line, curve for titration of acidic species; solid line, curve for reverse titration.

the carbon tetrachloride, there is virtually no change in the relative amounts of weak acid and strong acid produced.

It is noteworthy that the titration of the acidic species with standard base (broken curve, Fig. 1) can be reproduced *exactly* in the reverse direction on titration of the conjugate bases with standard acid (solid curve). This characteristic demonstrates the stability of both acid species and their conjugate bases. Another indication of the stability of the weakly acidic species is the small amount of carbon dioxide liberated when the reaction is carried out under ordinary conditions, even when large amounts of water are present. It is difficult to explain the production of carbon dioxide by any reaction other than (4).

If our interpretation of the reaction between copper(I) and carbon tetrachloride is correct, there should be a 1:1 molar correspondence between the total quantity of chloride ion and total acidic species formed, provided a correction is made for the amounts of these species produced in reaction 4. Examination of the data of Table I reveals, however, that the amount of acidic species exceeds by about 15% the quantity of chloride ion. Most of this small discrepancy is readily explained by the fact that a little copper(I) invariably is oxidized to the dipositive condition presumably by air oxidation on introduction of carbon tetrachloride to the system, and is titrated in hydrated form as a weak acid during the determination of the acidic species. Part of the discrepancy is attributed to the fact that the "Chore Girl" was not pure copper, but contained a small percentage of zinc, which would contribute weakly acidic zinc ions to the reaction mixture. A better estimation of the quantity of weak acid produced than presented in Table I can therefore be obtained by subtracting the number of millimoles of strong acid from the total number of millimoles of chloride. It is significant that when this is done the molar amount of carbon dioxide evolved upon alkaline hydrolysis under reflux approaches the amount of weak acid in solution. For example, in solutions containing about 2 mmoles of copper(I), the number of millimoles of weak acid produced averaged about 1.3 in solutions containing no added water and 1.6 in solutions 0.5 *M* in added water, and when similar solutions were subjected to alkaline hydrolysis under reflux, 1.05 and 1.3 mmoles of carbon

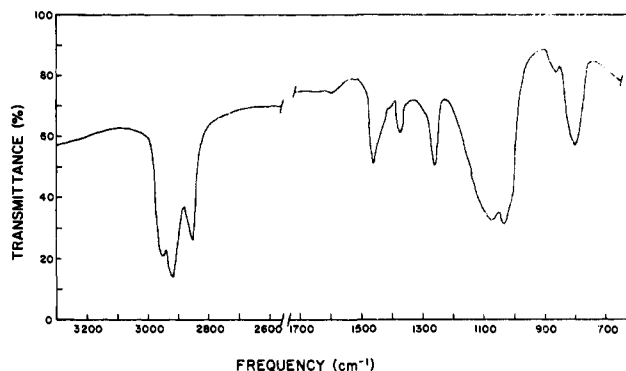


Fig. 2.—The infrared spectrum of yellow oil.

dioxide, respectively, were produced. On the basis of eq. 4, a 1:1 molar correspondence between total carbon dioxide liberated and weak acid originally present would be expected.

In addition to a 1:1 molar correspondence between the total quantity of chloride ion and the total acidic species formed, there should be a similar correspondence between copper(I) and total chloride ion. We have established the fact that the copper(II) originally present as the perchlorate is quantitatively reduced to the monopositive state by the free metal prior to the addition of carbon tetrachloride. It can be seen, however, from the data of Table I that the quantity of total chloride ion in the runs involving about 2 mmoles of copper(I) is usually about 25% lower than that of the copper(I). At least part of this discrepancy undoubtedly can be accounted for by the fact that after the addition of carbon tetrachloride there is always some copper(II) present in the reaction mixture (see above). In addition, the fact that our calculation of available copper(I) was based on the assumption that the "Chore Girl" was pure copper also contributes to the discrepancy.

If eq. 2 is correct, there should be produced, besides strong acid, the chlorinated ether species depicted. Since only a small quantity of strong acid is formed (Table I), only small amounts of the ether would be expected. Work-up of the reaction mixtures as described under Isolation of Organic Reaction Product gave amounts of a yellow oil, too small for elemental analysis. However, the infrared spectrum of this material (Fig. 2) shows absorption bands in the 1040  $\text{cm}^{-1}$  region and a band in the 800  $\text{cm}^{-1}$  region. The bands in the 1040  $\text{cm}^{-1}$  region are characteristic of the C-O-C group<sup>3,4</sup> and that at 800  $\text{cm}^{-1}$  is characteristic of the  $\text{CCl}_3$  group.<sup>5</sup> Thus the absorption data provide strong indication that the chlorinated ether is indeed formed. At the very least, these data show the presence of an ether and the  $\text{CCl}_3$  group in the yellow oil.

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(3) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, Chapter 7.

(4) Sadler Standard Spectra, No. 8031, 9682, and 16348, Sadler Research Laboratory, Philadelphia, Pa.

(5) See ref. 4, spectrum No. 2224.