The Micro and Rapid Determination of Cobalt Carbonyl Anion in Organic Solvents by Titration with Methylene Blue

By Ryoji IWANAGA

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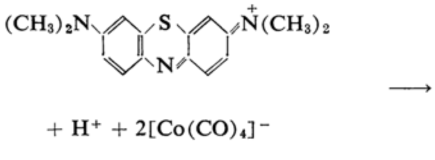
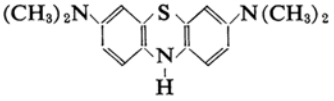
In the course of an investigation of catalysts for oxo reactions, the rate of which seems to be dependent to a large extent on the rate of regeneration of cobalt hydrocarbonyl during the reaction, it was desired to measure rapidly a small amount of cobalt hydrocarbonyl or of cobalt carbonyl anion in various organic solvents. For a quantitative determination of cobalt carbonyl anion, the gasometric method of Sternberg et al.[1] and the gravimetric method of Hieber et al.[2] have been proposed. Neither of these methods, however, is suitable for a determination of the micrograms of the anion in Lewis-base solutions such as methanol and acetone, owing to the difficulty of a quantitative precipitation of the complex salt of the anion in Lewis-base solutions.

Reppe[3] mentioned briefly that " the acidimetric value of cobalt hydrocarbonyl with sodium hydroxide shows practical agreement with the reduction value titrated with methylene blue in the acid pH range ", but quantitative results were not presented. The present author has, therefore, investigated on the conditions for titrimetric determination of the micrograms of the cobalt carbonyl anion in various organic solvents, especially in Lewis bases such as alcohols, ketones or aldehydes with methylene blue.

The cobalt carbonyl anion in the aqueous solution was primarily oxidized to dicobalt octacarbonyl by weak oxidizing reagents such as air, methyl orange, methyl red, ferric chloride or cupric sulfate[4]. Methylene blue also may oxidize the anion, and then a leuco-compound may be produced as follows:



$+ H^+ + 2[Co(CO)_4]^-$



$+ Co_2(CO)_8$ (1)

In the preliminary test it was observed that the above reaction did not take place quantitatively in a strong acid or in an alkaline medium.

The author has first investigated the effect of the pH of the titration medium on the stoichiometry of the titration of the anion with methylene blue. The end point of this titration was easily detected at the point where the blue color of the methylene blue added to the solution does not disappear for several minutes. By the titration of the anion in aqueous solutions of various pH, it was found that the stoichiometric reaction given by Eq. 1 can be held only at the pH range from 1.9 to 5.2 of titration solutions; at a higher pH range than 5.2 the molar ratio of the added methylene blue to the anion decreases below 1 : 2 with the increasing pH, and at a lower pH range than 1.9 it increases over 1 : 2 with the decreasing pH. From these results it was found that the quantitative titration of the anion with methylene blue according to Eq. 1 can be performed only in the pH range from 1.9 to 5.2.

Examining further a titration in a nonaqueous medium by using glacial acetic acid as a solvent for methylene blue titrant and for the titration medium, it was found that the titration could also be performed in good agreement with the reaction given by Eq. 1.

When a titration of the anion in Lewis bases such as methanol and acetone is carried out, methylene blue may be consumed excessively in more than the above ratio, in which case the end point becomes indistinguishable. This may be due to the occurrence of " the base reaction "[5], i. e., the reaction between dicobalt octacarbonyl formed from the anion according to Eq. 1 and a Lewis base, during the titration.

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[1] H. W. Sternberg, I. Wender and M. Orchin, *Anal. Chem.*, **24**, 174 (1952).

[2] W. Hieber and H. Frankel, *Ber.*, **86**, 710 (1953).

[3] W. Reppe, " Neue Entwicklung auf dem Gebiet der Chemie des Acetylens und Kohlenoxyds ", Springer-Verlag (1949), p. 120; W. Reppe, *Ann.*, **582**, 122 (1953).

[4] W. Hieber and W. Hübel, *Z. Elektrochem.*, **57**, 331 (1953).

[5] W. Hieber et al., *Ber.*, **86**, 700 (1953); **87**, 25, 789 (1954); **91**, 1146, 1156 (1958). Alcohols, ketones, cyclic ethers, nitriles and isonitriles, as well as amines, react with dicobalt octacarbonyl and produce cobalt carbonyl anion as follows:

$$3Co_2(CO)_8 + 2x\ \text{Base} \rightarrow 2[Co(\text{Base})_x][Co(CO)_4]_2 + 8CO$$

The author has thus then investigated the conditions needed to decrease " the base reaction " with methanol, because methanol is one of the Lewis bases which reacts rapidly with dicobalt octacarbonyl, and has found that the influence of "the base reaction" on the analysis of the anion could be decreased effectively by diminishing the rate of the base reaction, by diluting the sample solution with a 1 : 1 mixture of glacial acetic acid and toluene, and by lowering the treating temperature as low as possible, about 0°C being satisfactory (see Fig. 4). On the basis of the above results, the author proposes a rapid and simplified method for determining a small amount of the anion in organic solvents, especially in Lewis bases. The author examined the proposed method for the titration of samples of a known concentration of the anion in the presence of water, methanol, acetone, dicobalt octacarbonyl and acetoaldehyde, and could determine the anion in all within a percentage of error of only about one percent.

Experimental and Results

Titration of Cobalt Hydrocarbonyl and Cobalt Carbonyl Anion

Reagents.—A test solution of a known concentration of cobalt hydrocarbonyl was prepared as follows: about 1 g. of dicobalt octacarbonyl was dissolved in 5 ml. of pyridine; after the solution turned clear pink, 1 : 1 aqueous sulfuric acid was dropped into the solution at about −5°C, and the cobalt hydrocarbonyl gas evolved was introduced, together with oxygen-free nitrogen, into an oxygen-free water or methanol through a U-tube filled with phosphorus pentaoxide and a trap cooled at −20°C. The concentration of cobalt hydrocarbonyl in the solution was determined by total cobalt analysis, and this value showed quite a good agreement with a value obtained from the titration with sodium hydroxide6). The test solution of cobalt carbonyl anion was also prepared by introducing the cobalt hydrocarbonyl gas evolved as described above into an oxygen-free aqueous or methanol solution of sodium hydroxide, until the solution was neutralized with phenolphthalein as an indicator; the concentration of this was also determined from the total cobalt content.

Standard methylene blue titrant of 1 meq./l. was prepared by dissolving 374 mg. of the special grade crystals of $C_{16}H_{18}N_3SCl \cdot 3 H_2O$ (Junsei Pure Chemicals Co., Ltd.) into 500 ml. of oxygen-free glacial acetic acid and then filling the container with oxygen-free toluene to 1 l.

All of the above-mentioned oxygen-free solvents were prepared by being refluxed for 1 hr., cooled to room temperature and reserved under a slightly more positive pressure of nitrogen than the atmosphere.

Apparatus.—Figure 1 illustrates a titration apparatus. Titration is carried out in a 100 ml. Erlenmeyer flask with two holes on each side, one of which holes is for inserting a thermometer and another for introducing the samples and the solvent. To the stopper of the flask, a 25 ml. buret and two glass tubes are attached, one of which is an inlet for nitrogen and another an outlet, the outer end of which is closed by a mercury valve.

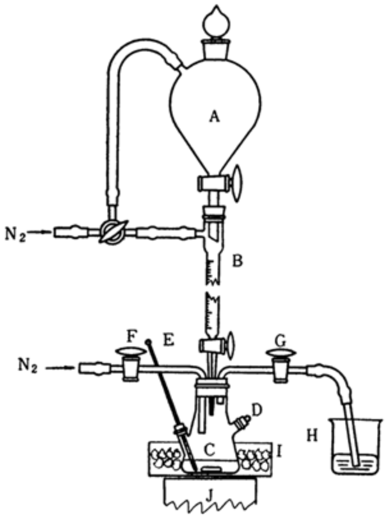

Fig. 1. Apparatus for titration of cobalt carbonyl anion.

A Titrant holder
B Buret
C Titration flask
D Inlet of sample
E Thermometer
F Inlet tube of N_2
G Outlet tube of gas
H Mercury valve
I Ice-water bath
J Magnetic stirrer

Procedures.—Because cobalt carbonyl anion in solutions is very sensitive and easily oxidized with air, a sample to be analyzed, as well as the titration solvents and the methylene blue titrant, must be strictly protected from the air. After all the system has been flushed with nitrogen, the standard methylene blue titrant is introduced into a holder A under a counter-current flow of nitrogen and poured into a buret B. Twenty milliliters of a mixture of glacial acetic acid and toluene are then introduced into the titration flask, which is placed in an ice-water bath, through a side hole D under a counter-current flow of nitrogen; this is cooled to about 0°C by stirring. After the solvent has been cooled, a suitable aliquot of the solution to be analyzed is pipetted into the solvent through D and titrated immediately with the methylene blue titrant while being stirred. While the blue color of methlene blue dropped disappears immediately, the solution titrated becomes light brown due to the formation of dicobalt octacarbonyl, and as soon as its color changes to light green, the titration is

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6) This titration was made according to the procedure reported by W. Hieber and W. Hübel, *Z. Elektrochem.*, 57, 235 (1953).

TABLE I. TITRATIONS OF $HCo(CO)_4$ AND $Na[Co(CO)_4]$ IN TOLUENE-ACETIC ACID SOLVENT WITH 1 meq./l. METHYLENE BLUE TITRANT

Sample	ml.	Compound added	$[Co(CO)_4]^-$ obtained from total amount of Co	(μ.eq.) found	Std. dev. %
$HCo(CO)_4$ in water	1	—	7.29	7.26	−0.4
$Na[Co(CO)_4]$ in water	1	—	20.75	20.58	−0.8
$HCo(CO)_4$ in methanol	1	—	21.40	21.40	0
$HCo(CO)_4$ in methanol	2	Methanol 10 ml.	42.80	42.80	0
$Na[Co(CO)_4]$ in methanol	1	—	26.70	26.60	−0.4
$HCo(CO)_4$ in methanol	1	Acetone 10 ml.	21.40	21.40	0
$HCo(CO)_4$ in methanol	1	$Co_2(CO)_8$ 1 mg. Toluene 10 ml.	21.40	21.55	+0.7
$HCo(CO)_4$ in methanol	1	Acetaldehyde 1 ml.	21.40	21.40	0
Oxo product*1	3		34.56*2	36.78	+6.4

*1 This product was obtained as follows: a solution containing 2 eq./l. of methylacrylate and 9.11 meq./l. of $Co_2(CO)_8$ in toluene was treated with 1 : 1 CO and H_2 under 200 kg./cm^2 at 120°C.

*2 The amount of $[Co(CO)_4]^-$ was measured by *o*-phenanthroline method.

stopped. Weights of the anion in the sample are calculated as follows:

$$\text{mg. of } [Co(CO)_4]^- = \text{ml. of methylene blue titrant added} \times 0.342$$

Results.—In order to examine the present method, aliquots of a solution of a known concentration of $HCo(CO)_4$ or $Na[Co(CO)_4]$ were pipetted and titrated, alone or in the presence of a large amount of methanol, acetone or dicobalt octacarbonyl. In addition, a titration in the presence of acetoaldehyde was tested. The results of these analyses, listed in Table I, are shown to be in good agreement with the values obtained from the total cobalt contents within a deviation of 1%. The larger deviation on the practical oxo reaction product (in Table I) was presumably due to the inaccuracy of the value obtained from the precipitate of Co-*o*-phenanthroline complex salt with the anion.

Effect of Hydrogen Ion

A pH determination was made by means of a glass electrode which was inserted into a 200 ml. titration flask. After all the system had been flushed with nitrogen, 50 ml. of oxygen-free distilled water were first introduced into the flask, and to this solution was added sulfuric acid, acetic acid or sodium hydroxide under a counter-current flow of nitrogen to give various pH values. Then, 1 ml. aqueous solution of $Na[Co(CO)_4]$ was added and titrated with 1 meq./l. aqueous methylene blue titrant at 20°C. At the end point of titration, the pH of the solution was measured. Figure 2 shows the curve of the molar ratio of methylene blue reacting with the anion at various pH values at the end point.

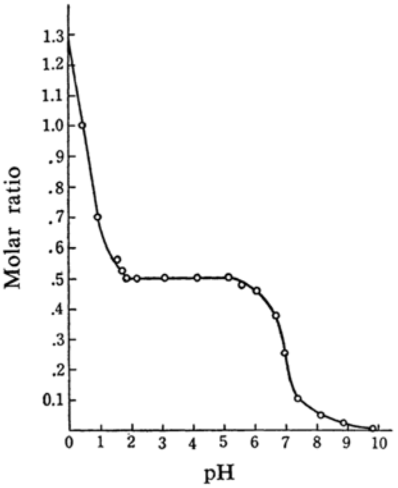

Fig. 2. Variations of molar ratio of methylene blue reacted with $[Co(CO)_4]^-$ at the end point of a titration as a function of pH.

Rates of Base Reaction of Dicobalt Octacarbonyl with Methanol in Various Solvents

Dicobalt octacarbonyl was recrystallized from oxygen-free toluene before use. Reactions of dicobalt octacarbonyl with methanol were carried out in a 100 ml. Erlenmeyer flask, as is shown in Fig. 1, at 20 and 0°C. After the flask had been thoroughly flushed with oxygen-free nitrogen, 25 ml. of oxygen-free methanol and 25 ml. of the oxygen-free solvent to be tested were introduced into the flask and kept at the temperature to be tested. Then a solid of about 0.5 g. of dicobalt octacarbonyl was vigorously stirred in at the controlled temperature. After various periods of reaction time, 1 ml. of the solution was pipetted out, and the amount of the anion formed in it was determined by the titration described above. Figure 3 shows the rates of formation of the anion in various solvents at 20 and 0°C. In Fig. 3, $[\mathrm{Co}]_0$ gives the concentration of the total cobalt in the solution, and $[[\mathrm{Co(CO)_4}]^-]_t$ is of the anion formed after the reaction had proceeded for t minutes.

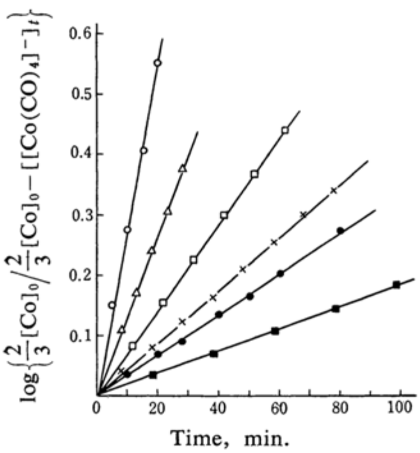

Fig. 3. Effect of solvent and temperature on the rate of base reaction.

- ○ Methanol 50 ml. at 20°C
- ● Methanol 50 ml. at 0°C
- △ Methanol 25 ml. and toluene 25 ml. at 20°C
- × Methanol 25 ml. and glacial acetic acid 25 ml. at 20°C
- □ Methanol 25 ml. and 1 : 1 glacial acetic acid and toluene 25 ml. at 20°C
- ■ Methanol 25 ml. and 1 : 1 glacial acetic acid and toluene 25 ml. at 0°C

Discussion

This titration is based upon the reduction of one-valenced methylene blue cation into a no-valenced leuco-compound with cobalt carbonyl anion in an acid pH range. However, Fig. 2 shows that the stoichiometry of the reaction of titration as given by Eq. 1 does not always exist in the whole pH range. It may be due to other types of reactions of methylene blue in addition to the above reaction, the possibility of the former being postulated from the different redox-potentials of methylene blue at various pH's(7). Therefore, it is convenient to use a mixture of acetic acid and toluene as the solvent, because the pH of the solution to be titrated does not have to be adjusted to 1.9～5.2. Furthermore, this solvent has the advantages over aqueous acetic acid or glacial acetic acid not only of its miscibility with the anion dissolved in organic solvents, but also of its lower freezing point.

It was found from Fig. 3 that the base reaction of dicobalt octacarbonyl with methanol is of the first order with respect to a concentration of dicobalt octacarbonyl, that the rate of the reaction is most effectively decreased by lowering the reaction temperature, and that in the base reaction at 0°C by using a 1 : 1 mixture of glacial acetic acid and toluene as solvent, the amount of the anion formed by the base reaction in a minute can be decreased by less than 0.1 mol. % of the cobalt of dicobalt octacarbonyl.

If a base reaction thoroughly proceeds during the titration, the amount of methylene blue which may be consumed may be triple that corresponding to the initial amount of cobalt carbonyl anion. The author could really observe such a result when a methanol solution of $\mathrm{Na[Co(CO)_4]}$ was titrated for a long time at an atmospheric temperature. Therefore, for determining the anion in Lewis-base solutions, it is important to cool the sample and titrate it as rapidly as possible.

If substances easily oxidized with methylene blue are presented in the sample to be analyzed, it is impossible to determine the anion in the sample by this method. However, from the fact as is shown in Table I that no significant interference of aldehydes was observed under the conditions in this method, it seems to be possible to determine the anion in an oxo reaction product. Furthermore, this method may be especially suitable for the determination of the anion in solutions during oxo, base or other reactions, as it requires only a small amount of the anion (less than 1 mg. as a sample) and takes only about 0.5 to 1 min. for one titration.

Summary

An accurate and rapid method is described for the direct titration of cobalt carbonyl anion in organic solvents. This method is based upon the oxidation reaction of the anion with methylene blue in acid media. The stoichiometry of the reaction of 2 mol. of the anion with 1 mol. of methylene blue is found only at the pH range from 1.9 to 5.2 or in the acetic acid medium. By using a 1 : 1 acetic acid-toluene mixture as solvent, and by carrying out the titration at about 0°C, the anion in Lewis bases such as methanol and acetone is titrated successively without any interference by the base reaction. This method is very suitable for the

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7) L. Michaelis and S. Granick, *J. Am. Chem. Soc.*, **63**, 1636 (1941); H. W. Meyer and W. D. Treadwell, *Helv., Chim. Acta*, **35**, 1444 (1952).

determination of the cobalt carbonyl anion in solutions in the course of various reactions.

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Central Research Laboratory
Ajinomoto Co., Inc.
Suzuki-cho, Kawasaki