[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUQUESNE UNIVERSITY]

Reducing Action of Sodium Naphthalide in Tetrahydrofuran Solution. I. The Reduction of Cobalt(II) Chloride[1]

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RECEIVED JUNE 13, 1955

The reduction of cobalt(II) chloride by sodium naphthalide in tetrahydrofuran solution has been studied conductometrically and the course of the reduction discussed with the aid of magnetic susceptibility and light absorption data. The reduction probably involves a two-electron change with quantitative formation of metallic cobalt.

While solutions of the alkali metals in liquid ammonia exhibit powerful reducing action, the reduction of inorganic substances by these solutions has been studied extensively.[2] The monovalent anions of many aromatic hydrocarbons are monomeric in tetrahydrofuran solution with one unpaired electron.[3] Their salts serve as convenient reducing agents. Since there is no information concerning the reduction of inorganic substances by these anions, it seemed worth while to compare their reducing properties with the reducing properties of the alkali metal–liquid ammonia system. The reduction of some elements and inorganic compounds by monovalent aromatic hydrocarbon anions in tetrahydrofuran solution will be described in this and subsequent papers.

In this investigation, the reduction of anhydrous cobalt(II) chloride by sodium naphthalide (the sodium salt of the monovalent naphthalene anion) in tetrahydrofuran solution has been studied and the course of the reduction followed conductometrically.

Experimental

Materials.—The purification of naphthalene and tetrahydrofuran has been described previously.[3] "Baker Analyzed" cobalt(II) chloride hexahydrate, dehydrated by prolonged heating under vacuum, was extracted with anhydrous ether and the ether solution evaporated to dryness. The residue, after thorough drying, was analyzed by the usual procedures. *Anal.* Calcd. for $CoCl_2$: Co, 45.38; Cl, 54.60. Found: Co, 45.54; Cl, 54.39.

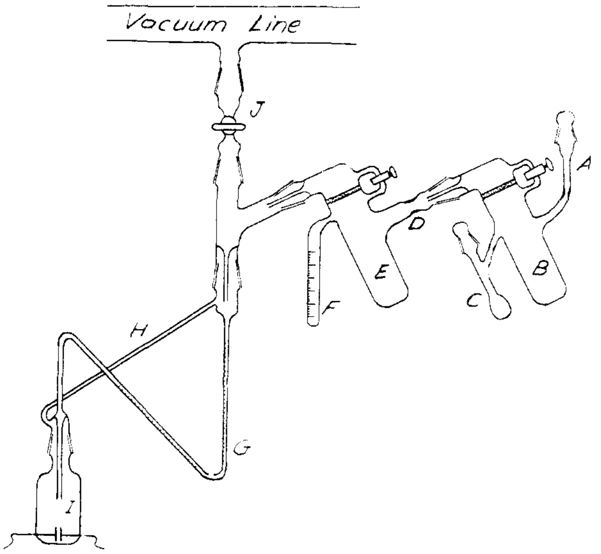

Fig. 1.—Apparatus for conductometric titration.

Apparatus and Procedure for Conductometric Titration.—The apparatus used in the conductometric titration is illustrated in Fig. 1. In order to illustrate the functioning of the apparatus, a typical run is described. About 0.5 g. of naphthalene was placed in side tube C of dumper B and about 1 g. of freshly cut sodium placed in side arm A above the constriction. A weighed amount of anhydrous cobalt(II) chloride, usually of the order of 15 mg., was introduced into the conductance cell I. The apparatus was quickly assembled and attached to the vacuum line. After thorough evacuation, the sodium was melted and allowed to pass through the constriction into dumper B where it was heated again until the sides of the vessel were coated with a thin film of sodium. Naphthalene was sublimed into dumper B and about 20 ml. of predried tetrahydrofuran was distilled in. A measured volume of tetrahydrofuran was distilled into the conductance cell from a 25-ml. graduated pipet. The reaction between sodium and naphthalene took place readily at room temperature and the contents of dumper B was filtered through the fritted glass disc into dumper E after several minutes shaking. Dumper B was sealed off from the apparatus at constriction D. The apparatus, including stopcock J, was detached from the vacuum line and mounted on a ring stand. In carrying out the titration, the dumper E was rotated allowing about 1.5 ml. of the sodium naphthalide solution to filter into the titrating unit, G, which consisted of two 1-ml. graduated pipets sealed together at an angle of approximately 50°. Any desired amount of this solution could be transferred into the conductance cell by simply tilting the ring stand. Usually about 0.05 ml. of the solution was introduced each time. This operation was found to be accurate to 1% when a total of 1 ml. of the solution was delivered. After each successive addition of sodium naphthalide solution, the content of the conductance cell was thoroughly mixed by vigorous shaking until its conductance remained constant. Conductivities were measured at 1000 cycles with an Industrial Instrument Conductivity Bridge, Model RC 16. The titration was carried out at room temperature, which rarely fluctuated more than 2° during the course of the titration.

After the titration, a known volume of sodium naphthalide solution in dumper E was transferred into sampling tube F (a 5-ml. graduated pipet) which was then removed from the apparatus. This solution was hydrolyzed and titrated with standard hydrochloric acid using a Beckman Model G *p*H meter. The concentration of sodium naphthalide solution was calculated from the amount of sodium hydroxide liberated on hydrolysis.

Measurements of Absorption Spectrum and Magnetic Susceptibility.—The absorption spectra and magnetic susceptibilities of several reaction mixtures in the course of the titration were measured. A Pyrex absorption cell, 1 cm. thick, for light absorption measurements, and a Pyrex tube, 11 mm. diameter and 20 cm. long, for magnetic susceptibility measurements, were attached to the neck of the conductance cell through a fritted glass disc of fine porosity. After the titration proceeded to the desired stage, the resulting mixture was filtered into the absorption cell and the sample tube for susceptibility measurements. Both were sealed off while under vacuum.

The magnetic susceptibility was measured by the Gouy method; the experimental set-up and calibration of sample tube have already been described.[3] The absorption spectrum was measured using a Beckman Model DU spectrophotometer.

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(1) Taken in part from the M.S. thesis of J. V. Friel, Duquesne University, 1955.

(2) G. W. Watt, *Chem. Revs.*, **46**, 289 (1950).

(3) T. L. Chu and S. C. Yu, THIS JOURNAL, **76**, 3367 (1954).

Results and Discussion

The conductometric titration of cobalt(II) chloride with sodium naphthalide in tetrahydrofuran solution was carried out several times; the results were generally reproducible. A typical run is presented in Fig. 2 in which the conductivity of the reaction mixture is plotted against the volume of sodium naphthalide solution added. The volume change during the course of the titration was corrected in the usual manner. The tetrahydrofuran solution of sodium naphthalide is intense green while that of cobalt(II) chloride is light blue. When a small amount of the sodium naphthalide solution was added to the cobalt(II) chloride solution, the latter turned to dark green immediately and its conductivity increased. The color of this solution was considerably more intense than what would be expected from merely a mixing of these two solutions. As more sodium naphthalide solution was introduced, the conductivity of the solution increased linearly and reached a maximum at which the mole ratio of $NaC_{10}H_8/CoCl_2$ was approximately 0.62. The solution appeared cloudy on approaching this composition. Further addition of sodium naphthalide solution decreased the conductance, and at a mole ratio, $NaC_{10}H_8/CoCl_2$, of approximately 2.0, a well defined minimum occurred. It is worth while to mention that the reduction of cobalt(II) chloride with sodium–potassium alloy in tetrahydrofuran solution was followed qualitatively. Similar to the reduction by sodium naphthalide, the reaction mixture first turned an intense green with simultaneous increase in conductivity. As the reaction proceeded further, the conductivity decreased rapidly and metallic cobalt separated as a black precipitate.

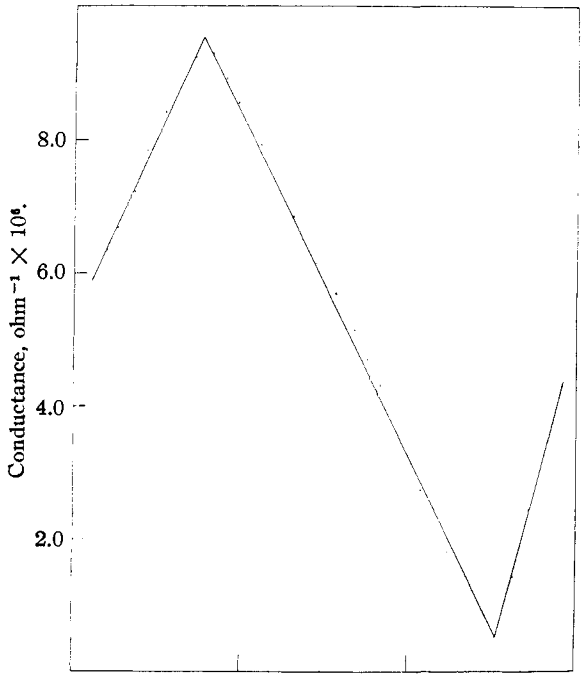

Fig. 2.—Conductometric titration of 0.114 mmole of $CoCl_2$ in 23.5 ml. of tetrahydrofuran with 0.1774 *M* sodium naphthalide at room temp.

In the initial stage of the titration, the reaction mixture appeared extremely clear. It exhibited a very high, positive magnetic susceptibility indicating the presence of ferromagnetic species. The ferromagnetism must be due to metallic cobalt in the colloidal state, since true solutions, in which the electron spins are randomly distributed, do not exhibit this phenomenon. The reduction of cobalt (II) chloride by sodium naphthalide is most probably the two-electron change

$$CoCl_2 + 2NaC_{10}H_8 = 2NaCl + 2C_{10}H_8 + Co$$

The absorption spectrum of the solution with composition corresponding to the maximum conductance, together with those of tetrahydrofuran solutions of cobalt(II) chloride and a cobalt(II) chloride–lithium chloride mixture, are plotted in Fig. 3. It can be seen that the absorption bands of cobalt(II) chloride are shifted and the relative intensities of the bands altered by the addition of lithium chloride, owing to the formation of cobalt(II) chloride complexes. The solution with composition corresponding to the maximum conductance exhibited absorption bands similar to a solution of the cobalt(II) chloride–lithium chloride mixture, except in the relative intensities of the absorption bands. This difference may be attributed to interference by the colloidal cobalt. It is reasonable to conclude that cobalt(II) chloride complexes were formed during the initial stage of the reduction of cobalt(II) chloride with sodium naphthalide. Sodium chloride is insoluble in tetrahydrofuran; however, the sodium chloride formed during the reduction process complexes with unreacted cobalt(II) chloride and hence increases the conductivity of the

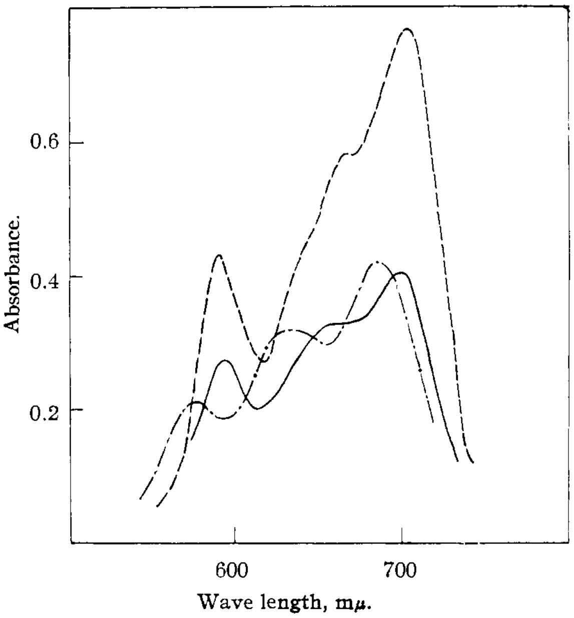

Fig. 3.—Absorption spectra in tetrahydrofuran solution: dash and dotted line, 0.0024 *M* $CoCl_2$; dashed line, 0.0024 *M* $CoCl_2$–0.0024 *M* LiCl; solid line, reaction mixture of $CoCl_2$ and $NaC_{10}H_8$ with maximum conductivity; light path = 1.0 cm.

reaction mixture. The equation may be written as

$$x\text{CoCl}_2 + (2x - 4)\text{NaC}_{10}\text{H}_8 = (x - 2)\text{Co} + (2x - 4)\text{C}_{10}\text{H}_8 + 2\text{Na}_{x-2}\text{CoCl}_x$$

Since the conductance maximum in the titration curve corresponds to the maximum concentration of $\text{Na}_{x-2}\text{CoCl}_x$; the complex formed has the formula NaCoCl_3. On further addition of sodium napthalide, NaCoCl_3 is reduced to colloidal cobalt according to the equation

$$\text{NaCoCl}_3 + 2\text{NaC}_{10}\text{H}_8 = 3\text{NaCl} + 2\text{C}_{10}\text{H}_8 + 2\text{Co}$$

Sodium chloride, because of its insolubility, makes no contribution to the conductance and consequently the conductivity of the reaction mixture decreases to a minimum at a $\text{NaC}_{10}\text{H}_8/\text{CoCl}_2$ mole ratio of 2.0 where the reduction is complete. The conductance then increases rapidly beyond the end point due to the presence of sodium naphthalide.

The conductometric titration of cobalt(II) iodide with sodium naphthalide in tetrahydrofuran solution yielded a similar curve as in the case of cobalt(II) chloride. However, the end-point is not distinct because sodium iodide is slightly soluble in tetrahydrofuran and makes an appreciable contribution to the conductivity of the reaction mixture.

At the end-point of the titration of cobalt(II) chloride with sodium naphthalide, it was noted that the content of the cell was dark brown and that no precipitate settled on long standing. The dark brown solution was ferromagnetic and showed no characteristic absorption bands in the visible region, indicating the colloidal nature of the reaction product. The stability of colloidal cobalt in tetrahydrofuran is probably due to the presence of naphthalene which is adsorbed by the colloidal particles and lowers the interfacial tension thus preventing coagulation. Colloidal cobalt is relatively unstable on prolonged exposure in air. It coagulates and is rapidly oxidized as is shown by the disappearance of its ferromagnetism. The reactivity of colloidal cobalt may be further illustrated by its reaction with copper(II) chloride in tetrahydrofuran, the latter being reduced immediately to the insoluble copper(I) chloride.

As a conclusion, the process of reduction of metal salts by means of sodium naphthalide in tetrahydrofuran solution consists essentially of the addition of one or more electrons from the naphthalide ion to the metal ion. The sodium ions present and naphthalene formed during the reduction take no part in the reaction and the reduction proceeds quantitatively to completion. In the liquid ammonia system, the reduction of metal ions by alkali metals is frequently incomplete because the metal produced may catalyze the reaction between the alkali metal and the solvent and react with the amide formed.

Acknowledgment.—This research was supported in part by the Frederick Gardner Cottrell grants from the Research Corporation whose financial assistance is gratefully acknowledged.

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Anion-exchange Studies. II. The Effect of Cross-linkage on the Elution of Several Transition Elements

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RECEIVED JANUARY 22, 1955

A number of samples of the strongly basic anion-exchange resin Dowex-1 have been studied with reference to their capacity, water content and elution behavior. Column experiments on the elution of Mn(II), Co(II), Cu(II) and Zn(II) with HCl show that in each case retention of the anion complex is dependent on the cross-linkage of the exchanger. While 15 cm. columns of 12% DVB Dowex-1 will effectively separate Mn^{52}–Na^{22} mixtures, 2 and 4% DVB resins will not effect this separation even in 12 *N* HCl. A convenient instrumental arrangement for determining elution behavior of ion-exchange resins is described.

In contrast to the early literature on anion-exchange resins in which scant attention had been paid to the relationship between cross-linkage of the exchanger and other properties such as diffusion, water content, capacity and the elution behavior of different ions, several papers[2] in the recent literature have examined these relationships in detail for the strongly basic anion exchanger, Dowex-2.

Walton[3] has pointed out there is a modest correlation between the ion-exchange equilibrium constant and the ionic radius of the exchanging ion—up to a point, the larger the unsolvated ion, the better it is held by an exchanger.

Kunin and Myers,[4] using both strong-base and weak-base ion exchangers concluded that an increase in the degree of cross-linking is accompanied by a decrease in exchange capacity for both resin series. Using penicillin G, they further note that at high degrees of cross-linking, practically no adsorption of the large penicillin anion can be detected.

The present study is an investigation of the behavior of Mn(II) in hydrochloric acid solutions on several samples of Dowex-1 of varying degrees of cross linkage, and the effect of cross-linkage of the exchanger on the elution behavior of Co(II), Cu(II) and Zn(II).

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(3) H. F. Walton, *J. Chem. Ed.*, **23**, 454 (1946).

(4) R. Kunin and R. J. Myers, *Disc. Faraday Soc.*, **7**, 114 (1949).