the gas were used to calculate the entropy changes of the liquid and perfect gas. A Berthelot correction to a perfect gas and the entropy of compression to one atmosphere were combined with the entropy of vaporization to give $\Delta S_{298.19} = 22.4 \pm 0.1$ cal. deg.$^{-1}$ mole^{-1}. The entropy of carbon tetrachloride (gas) is then 73.7 ± 0.3 cal. deg.$^{-1}$ mole^{-1} at 298.19°K.

The entropy values of carbon tetrachloride calculated from Raman spectra and electron diffraction data range from 74.0 to 74.3 cal. deg.$^{-1}$ mole^{-1}. The error in this theoretical value is difficult to estimate, but Kelley[4] has adopted the value 74.2 ± 0.5 which is 0.5 cal. deg.$^{-1}$ mole^{-1} higher than the third law entropy value. This difference is undoubtedly within the limits of error of the two values. There is no reason to suspect any lack of equilibrium in solid carbon tetrachloride which would lead to a low thermal entropy value, nor does the extrapolation below 17°K. seem uncertain. On the other hand, there is a large vibrational contribution to the theoretical entropy which may be uncertain to several tenths of an entropy unit. The third law entropy value, 73.7 ± 0.3 cal. deg.$^{-1}$ mole^{-1} at 298.19°K., is recommended for thermodynamic calculations at the present time.

Summary

The heat capacities of solid and liquid carbon tetrachloride have been measured over their respective ranges from 17 to 300°K. The heat of transition at 225.35°K. is 1095 ± 3 calories per mole. The heat of fusion is 601 ± 2 calories per mole and the melting point is 250.3°K.

The entropy of CCl_4 (liquid) is 51.25 ± 0.15 and of CCl_4 (gas) is 73.7 ± 0.3 cal. deg.$^{-1}$ mole^{-1} at 298.19°K. The third law entropy is in agreement with the value calculated from Raman and electron diffraction data, and is recommended for thermodynamic calculations.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, SYDNEY UNIVERSITY]

The Polarographic Reduction of Rhodium Compounds

BY J. B. WILLIS

In view of the close similarity of the coördination chemistry of trivalent cobalt and trivalent rhodium, it is surprising that the bivalent state of the latter metal is almost unknown. The few compounds of Rh^{II} described in the literature are mostly either of doubtful identity or else only stable over a limited range of conditions at high temperatures (*e. g.*, rhodium monoxide and rhodium dichloride).[1]

Recently, however, Dwyer and Nyholm have systematically investigated the action of reducing agents on Rh^{III} compounds[2] and have prepared stable and well-defined coördination compounds of Rh^{II} with tertiary arsines[3] and with pyridine.[4] Simple inorganic complexes have not, however, been isolated.

It was considered that the polarographic reduction of trivalent rhodium compounds might throw some light on the valence states of rhodium in such cases and possibly enable the reduction potentials to be calculated.

Theory

Although rhodium is more noble than mercury, it is shown in the present work that a number of its complexes are stable toward mercury and yield well-defined polarographic steps. If reduction of Rh^{III} takes place through Rh^{II}, two steps should be obtained, whereas direct reduction of Rh^{III} to rhodium should give one step only. Two general methods were used in the identification of the steps obtained:

(*a*) Application of the Ilkovič equation to evaluate *n*.

$$i_d = 605nD^{1/2}Cm^{2/3}t^{1/6}$$

where i_d is the diffusion current in microamperes, *n* the number of electrons involved in the reduction of one molecule of the reducible substance, *D* the diffusion coefficient of the latter, *C* its concentration in millimoles/liter, *m* the rate of flow of mercury in mg./sec., and *t* drop time in seconds. *D* is conveniently calculated for an ion from λ^0, the equivalent ionic conductance at infinite dilution, by Nernst's equation, which reduces to $D = 2.67 \times 10^{-7}\lambda^0/z$ cm.^{2} sec.$^{-1}$ at 25°[5a] where *z* is the valency of the ion. Conductivity data for rhodium compounds are scarce, but in the case of complex ions the values for the corresponding cobalt or other heavy metal complexes can be used without any serious error since the mobility of such ions depends almost entirely on the relatively large volume of the coördinated groups, and *D* occurs as a square root in the Ilkovič equation.

(*b*) By plotting the potential of the dropping mercury electrode $E_{d.e.}$ against $\log i/(i_d - i)$ where *i* is the current at any point on the wave, a straight line is obtained if the reduction is reversible. The slope of this log plot is $0.0591/n$ volts at 25°, *i. e.*, 60 mv. for a one-electron step,

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[1] Wöhler and Müller, *Z. anorg. allgem. Chem.*, **149**, 125 (1925).

[2] Dwyer and Nyholm, *J. Proc. Roy. Soc.*, N. S. W., **75**, 122 (1942).

[3] Dwyer and Nyholm, *ibid.*, **75**, 127 (1942).

[4] Dwyer and Nyholm, *ibid.*, **76**, 275 (1943).

[5] Kolthoff and Lingane, "Polarography," Interscience Publishers, N. Y., 1941; (a) p. 45, (b) pp. 163, 168, (c) p. 64, (d) p. 285.

30 mv. for a two-electron step and 20 mv. for a three-electron step.

Experimental

A manually operated polarograph was used, the potential being applied by a potentiometer and raised by increments of 20 mv. The mean reading of the galvanometer oscillations was taken. These oscillations were greatly reduced by shunting a 2000 microfarad condenser across the galvanometer terminals, thus increasing the natural period from 2.7 to 15 seconds.

The polarographic cell was separated from the external saturated calomel electrode by a sintered glass disk and all measurements were carried out at 25° air being removed by purified nitrogen. The e. m. f. of the calomel electrode was checked at frequent intervals. Throughout the work the mercury reservoir was kept at the same height so that *m* was constant.[5c] The drop time *t* was about three seconds.

Correction for residual current was made by taking a polarogram of the supporting electrolyte alone. Each half-wave potential ($E_{1/2}$) given is the mean of several independent determinations and where quoted to three places of decimals is considered to be correct to within ±5 mv. Unless otherwise stated these potentials are referred to the saturated calomel electrode (S. C. E.).

The solutions used were generally prepared by warming 1 ml. of an analyzed stock solution of rhodium trichloride with excess of the complex-forming substance, which also served as supporting electrolyte, and making the solution up to a known volume.

Results

Cyanide Solutions.—In *M* potassium cyanide one step was obtained, at −1.47 v. The height was proportional to the concentration within the range studied, *viz.*, 0.95×10^{-4} *M* to 3.81×10^{-4} *M*. This step, however, is not very suitable for exact analytical work as owing to the close proximity of the potassium step the height is difficult to measure exactly. The ion present is certainly $[Rh(CN)_6]^{---}$. On extrapolating to infinite dilution the conductivity values of Walden[6] for potassium cobalticyanide and applying the Ilkovič equation it was found that $n = 1.0$ electron, indicating the reduction of $[Rh(CN)_6]^{---}$ to $[Rh(CN)_6]^{----}$. Further reduction does not take place at potentials attainable polarographically; this behavior is similar to that of ferri- and cobalti-cyanides.

The log plot was not a straight line: thus the reduction is irreversible at the dropping mercury electrode and $E_{1/2}$ in *M* cyanide solution is more negative than the reversible oxidation–reduction potential. Now $E_{1/2}$ for cobalticyanide in *M* potassium cyanide[7] is −1.38 v., and the oxidation–reduction potential of the cobalticyanide–cobaltocyanide system[8] is −0.83 v. *vs.* the N. H. E., *i. e.*, −1.08 v. *vs.* the S. C. E.

If it is assumed that the stabilities of the rhodicyanide and cobalticyanide ions are of the same order, then the above value for $E_{1/2}$ indicates that the potential of the rhodicyanide–rhodocyanide system is still more negative than that of the cobalticyanide–cobaltocyanide one, and can be estimated at about −1.17 v. *vs.* the S. C. E. *i. e.*, −0.92 v. *vs.* the N. H. E., allowing the same overpotential as for the irreversible reduction of cobalticyanide at the dropping mercury electrode. Thus the rhodocyanides should be stronger reducing agents than the cobaltocyanides and should be capable of decomposing water with evolution of hydrogen. Their isolation should prove difficult, if not impossible.

No indications of a complex Rh^{I} cyanide were obtained. Manchot and Schmid[9] by reduction of sodium rhodicyanide obtained an unstable colorless solution which they attributed to the compound $Na_2Rh(CN)_3$ but which Dwyer and Nyholm[2] in the light of their recent work consider to have contained the Rh^{II} complex. In this connection it may be mentioned that polarographic reduction of Co^{III} and Ni^{II} in cyanide media gives no indication of Grube's[10] Co^{I} and Ni^{I} complexes. It is probable that these monovalent compounds are not formed under the conditions prevailing in polarography.

Chloropentammine Rhodic Chloride.—Solutions of the solid substance were made up in different supporting electrolytes, two of which, (a) and (b), contained excess of the complex-forming ions and two, (c) and (d), were "indifferent" electrolytes.

(a) In *M* ammonium chloride a single step was found at −0.928 v. Application of the Ilkovič equation using the conductivity values for chloropentammine cobaltic chloride[11] gave $n = 2.0$ electrons. The log plot was a straight line with a slope of 32.5 mv. in good agreement with the theoretical value, 30 mv., for a reversible two-electron step. In 0.02 *M* ammonium chloride, $E_{1/2}$ was −0.799 v., the Ilkovič equation and the log plot again indicating a two-electron step.

(b) In *M* ammonium chloride-*M* ammonium hydroxide the step again occurred at −0.928 v. The height was proportional to the concentration over the range studied, *viz.*, 0.5×10^{-4} *M* to 2.5×10^{-4} *M*, but application of the Ilkovič equation using the conductivity values for chloropentammine cobaltic chloride[12] gave $n = 1.45$ electrons. On assuming complete aquation of the complex owing to the presence of the hydroxide ion, application of the values for aquopentammine cobaltic chloride[12] gave *n* values of about 1.75. The reason why the Ilkovič equation is not applicable is not evident, but it may be mentioned that heating the solution during its preparation or allowing it to stand for several weeks to attain chloro-aquo equilibrium made no difference to the height of the step. The log plot was again a straight line of slope 32.5 mv.

(c) In *M* potassium nitrate and 0.01% gelatin $E_{1/2}$ was −0.962 v., the Ilkovič equation applied

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[6] Walden, *Z. anorg. allgem. Chem.*, **23**, 373 (1900).

[7] Kolthoff and Lingane (*ibid.*, p. 286) give the value as −1.25 v., but repeated determinations with careful checking of the e. m. f. of the reference electrode gave the value −1.38 v.

[8] Latimer "Oxidation Potentials," Prentice-Hall, New York, N. Y., 1938, p. 201.

[9] Manchot and Schmid, *Ber.*, **63B**, 2782 (1931).

[10] Grube, *Z. Elektrochem.*, **32**, 561 (1926).

[11] Werner and Miolati, *Z. physik. Chem.*, **14**, 511 (1894).

[12] Werner and Miolati, *ibid.*, **21**, 237 (1896).

for the chloro-compound gave $n = 2.0$ electrons and the log plot was a straight line of slope 34 mv.

(d) In 0.5 M potassium sulfate $E_{1/2}$ was again -0.962 v., and the Ilkovič equation indicated $n = 2.0$ electrons. The log plot was a straight line of slope 34 mv.

The above results show that the process occurring at the electrode involves two electrons per molecule of chloropentammine rhodic chloride. This would appear to correspond to the formation of uncharged $[Rh(NH_3)_5Cl]$ from the $[Rh(NH_3)_5Cl]^{++}$ ions. The further decomposition of the substance formed is not recorded by the polarograph. The reduction is quite reversible in solutions containing ammonium and chloride ions and even in "indifferent" solutions. It is important to note that chloropentammine cobaltic chloride gave a similar polarogram with a two-electron step at -1.26 v., while hexammine cobaltic chloride[5d] gives *two* steps corresponding to stepwise reduction through the $[Co(NH_3)_6]^{++}$ ion to cobalt. Closer investigation of the polarographic reduction of such ions is now in progress.

Thiocyanate Solutions.—A 3.80×10^{-4} M solution of rhodium trichloride in 0.89 M potassium thiocyanate was used. A step was obtained at -0.394 v., just after the end of the anodic thiocyanate step. On the assumption that the ion present was $[Rh(CNS)_6]^{---}$ by analogy with the chromium and platinum compounds formed in this way, application of the Ilkovič equation using the conductivity data of Rosenheim[13] for potassium chromithiocyanate gave n = two electrons. This would appear to indicate reduction to a Rh^{I} complex. The formation of such a compound is, however, unlikely as no complexes of Rh^{I} are known. It seems more probable that the step observed here is the second stage of the reduction, the first stage, $Rh^{III} \rightarrow Rh^{II}$, taking place at more positive potentials where the polarographic step would be masked by the thiocyanate wave. In this case the step observed would correspond to reduction of the Rh^{II} complex to metallic rhodium. The log plot of the step was a straight line with a slope of 44 mv., which makes it improbable that the reduction is completely reversible.

Pyridine Solutions.—3.80×10^{-4} M solutions of rhodium trichloride in M pyridine–M potassium chloride and in M pyridine–M potassium bromide were used. The pyridine had been freshly distilled just before use and was quite colorless. A step was observed at -0.414 v., in both solutions, which seems to indicate the presence of the same ion, *viz.*, $[Rh\ py_6]^{+++}$ in each case. It is true that no Rh^{III} complexes have been isolated containing more than four pyridine molecules coördinated to the rhodium ion,[14] but Dwyer and Nyholm[4] by reduction of pyridine-containing solutions of rhodium trichloride have isolated hexa-pyridine rhodous salts which, except in the presence of pyridine, readily lose one or two molecules of pyridine. This indicates the presence of the $[Rh\ py_6]^{+++}$ ion in the solutions used here. There are no conductivity data available for such complexes, but using the values for the hexammine cobaltic ion,[11] n was calculated as 0.9 electron. The diffusion coefficient of the hexa-pyridine rhodic ion would be less than that of the hexammine ion, thereby increasing n somewhat. The step thus appears to be due to reduction of Rh^{III} to Rh^{II}. The log plot was not a straight line.

A pyridine–potassium chloride medium would probably be most suitable for the analytical determination of rhodium as the step is very well-defined.

Other Solutions.—Solutions of rhodium trichloride in M potassium chloride were rapidly decomposed by mercury, thus indicating that the $[RhCl_6]^{---}$ ion is not very stable.

Solutions which gave no step before the decomposition potential of the electrolyte were

3.80×10^{-4} M rhodium trichloride in M sodium nitrite
3.80×10^{-4} M rhodium trichloride in M di-potassium oxalate
7.77×10^{-4} M rhodium trichloride in M di-potassium tartrate
3.86×10^{-4} M rhodium trichloride in M ethylenediamine–M potassium chloride

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Summary

1. A number of rhodium complexes are stable toward mercury and give well-defined polarographic steps.

2. Analytical determination of rhodium by the polarograph is possible.

3. Polarographic reduction of a number of trivalent rhodium complexes, both cationic and anionic, was found to take place through the rhodous stage. In no case was direct reduction of Rh^{III} to metallic rhodium observed.

4. Some rhodium complexes do not give polarographic steps.

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[13] Rosenheim, *Z. anorg. allgem. Chem.*, **27**, 293 (1901).

[14] Delépine, *Bull. soc. chim.*, [4] **45**, 225 (1929).