

### Discussion

The amount of reaction in combustion calorimetry may be determined either from the mass of the sample or the mass of some combustion product such as  $\text{CO}_2$ , the latter method having been used by Cox, *et al.*,<sup>13</sup> for example. Basing heat of combustion values on the amount of  $\text{CO}_2$  produced has obvious advantages when the sample used may contain unknown amounts of non-isomeric impurity, usually water. However, this investigation has shown that, even with hygroscopic materials such as pyridine, the use of mass of sample as the basis of computation is equally reliable if the sample is pure enough and is handled by techniques that ensure its dryness. Because the amount of reaction can be determined with higher precision, and perhaps better accuracy, from the mass of sample, the method described herein is preferred. With this method, determination of the amount of  $\text{CO}_2$  produced serves as a useful check on the purity and dryness of the samples used.

However, if the amount of  $\text{CO}_2$  produced differs from that corresponding to the mass of sample and there is no reason to suspect incomplete combustion, it is clear that the sample is impure and that more accurate, though less precise, results will be obtained by using the amount of  $\text{CO}_2$  in computing the amount of reaction. This was true in the study of hippuric acid. Although the procedures of previous workers<sup>4,16</sup> were followed carefully in preparing and drying the sample of hippuric acid, some water (about 0.06%) must have remained. The earlier workers did not determine the amount of  $\text{CO}_2$  produced in their experiments, so the almost exact agreement with their results may be fortuitous. The apparent difficulty in preparing pure, dry samples of hippuric acid is an undesirable characteristic for a proposed reference substance. Nevertheless, hippuric acid is satisfactory in other important respects, and the purity problem could be solved if an appropriate organization prepared a suitable large sample for distribution to qualified investigators.

## SPECTROPHOTOMETRIC STUDIES OF *cis*- AND *trans*-DICHLORO-BIS-(ETHYLENEDIAMINE)-COBALT(III) CHLORIDES IN WATER, METHANOL AND IN METHANOL-WATER MIXTURES

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A rate constant of  $1.3 \times 10^{-4} \text{ sec.}^{-1} (\pm 2\%)$  has been obtained by spectrophotometry for the acid hydrolysis of *cis*- $[\text{Co en}_2 \text{Cl}_2]\text{Cl}$  in water at  $25^\circ$ . This value is compared with previously cited values obtained by various methods. The corresponding rate obtained for the *trans* isomer is  $2.7 \times 10^{-5} \text{ sec.}^{-1} (\pm 1.5\%)$ . *cis*- $[\text{Co en}_2 \text{Cl}_2]\text{Cl}$  is completely converted into the thermodynamically more stable *trans* isomer in methanol, following a first-order rate law throughout (rate constant =  $2.2 \times 10^{-5} \text{ sec.}^{-1} (\pm 2\%)$ ) at  $25^\circ$ . The hydrolysis rates of the *cis* isomer in methanol-water mixtures are also reported.

### Introduction

A number of values for the acid hydrolysis rate constants of *cis*- and *trans*- $[\text{Co en}_2 \text{Cl}_2]\text{Cl}$  at  $25^\circ$  have been reported. These (listed below) show considerable variations which are partly attributed to a number of misconceptions. The present work aims to clarify the situation.

### Experimental

A Hilger Uvispek spectrophotometer was fitted with a water-jacketed cell holder which could be kept at  $25 \pm 0.1^\circ$ . Some of the measurements were made with the aid of a photomultiplier-recorder unit. *trans*-Dichloro-bis-(ethylenediamine)-cobalt(III) chloride was prepared by a published method.<sup>1</sup> A small amount of tris-(ethylenediamine)-cobalt(III) chloride was present and this, being less soluble, was removed by filtering a saturated aqueous solution, then precipitating the pure *trans*-dichloro compound with ethanol and recrystallising it from methanol in which it was shown to be stable over a considerable period of time. Some of this *trans*-compound was converted into the *cis*-isomer by evaporating an aqueous solution to dryness on a water-bath. Any unchanged *trans*-compound was removed by adding a little water during filtration under suction when it dissolved preferentially. The sample was dried over phosphoric oxide. The *cis*-aquo-chloro compound was prepared as described by Werner.<sup>2</sup>

Methanol was purified by the method of Maryott.<sup>3</sup> Stopped quartz cells were tried for the kinetic studies but they were not completely successful owing to some evaporation losses. Such errors were, however, eliminated by keeping the reaction solution in a stoppered flask in the thermostat and pipetting portions into the cells (emptied by suction jet) at timed intervals for each reading. The cells were not handled once they had been placed in the cell holder.

### Results and Discussion

(i). *cis*- $[\text{Co en}_2 \text{Cl}_2]\text{Cl}$ .—The several values which have been published for the hydrolysis rate constant of *cis*- $[\text{Co en}_2 \text{Cl}_2]\text{Cl}$  in water are

$1.22 \times 10^{-4} \text{ sec.}^{-1}$  (Mathieu,<sup>4</sup> conductance)

$2.5 \times 10^{-4} \text{ sec.}^{-1}$  (Pearson, Boston and Basolo,<sup>5</sup> spectrophotometry)

$1.76 \times 10^{-4} \text{ sec.}^{-1}$  (Selbin and Bailar,<sup>6</sup> chloride-concentration cell)

Mathieu<sup>4</sup> reported that the rate of loss of optical activity of *l-cis*- $[\text{Co en}_2 \text{Cl}_2]\text{Cl}$  is one-tenth as fast as its rate of acid hydrolysis and attributed this to the formation of either the *trans*-aquo-chloro product

(3) A. A. Maryott, *J. Am. Chem. Soc.*, **63**, 3079 (1941).

(4) J. P. Mathieu, *Bull. soc. chim.*, **3**, 2121 (1936).

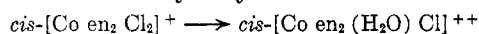
(5) R. G. Pearson, C. R. Boston and F. Basolo, *J. Phys. Chem.*, **59**, 304 (1955).

(6) J. Selbin and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **79**, 4285 (1957).

(1) "Inorganic Syntheses," Vol. II, McGraw-Hill Book Co., Inc., New York, N. Y., 1946, p. 222.

(2) A. Werner, *Lieb. Ann.*, **386**, 17 (1911).

or its racemic *cis*-isomer. This means that the maximum rate of formation of the *trans*-aquochloro compound is only one-tenth of the rate of acid hydrolysis. Pearson, Meeker and Basolo<sup>7</sup> showed that the loss of optical activity was in fact due to the formation of the *trans*-aquochloro compound and, using the rates determined by Mathieu,<sup>4</sup> calculated that the maximum concentration of this *trans*-aquochloro isomer is 20%. The value<sup>5</sup> of  $2.5 \times 10^{-4} \text{ sec.}^{-1}$  for the acid hydrolysis of *cis*-[Co en<sub>2</sub> Cl<sub>2</sub>]Cl depended on an  $\epsilon_{\infty}$  value obtained by "levelling off"  $\epsilon$ , the molecular extinction coefficient to a minimum, but this minimum value would be influenced by the 20% formation of *trans*-[Co en<sub>2</sub> (H<sub>2</sub>O) Cl]<sup>++</sup> so would not therefore give a true indication of the acid hydrolysis



The effect which the 20% *trans*-aquochloro compound has on  $\epsilon_{\infty}$  was determined in the present work where an aqueous solution of *cis*-[Co en<sub>2</sub> (H<sub>2</sub>O) Cl]<sup>++</sup> was made up and its absorptions extrapolated to zero time, the average value of  $\epsilon$  being 55 at 540 m $\mu$  whereas the acid hydrolysis of *cis*-[Co en<sub>2</sub> Cl<sub>2</sub>]<sup>+</sup> experimentally gave an average value of  $\epsilon = 45$ . In addition, the value of  $\epsilon_0$  obtained by these workers<sup>5,8</sup> for *cis*-[Co en<sub>2</sub> Cl<sub>2</sub>]<sup>+</sup> is 75.8 at 530 m $\mu$ . Their absorption curve and the present work showed 530 m $\mu$  to be an absorption maximum so that their value is very low compared with 98 (Mathieu<sup>4</sup>), 92 (Uspensky and Tschibisoff<sup>9</sup>) and 93 (Brown and Ingold<sup>10</sup>, in methanol), all these values are for 540 m $\mu$ .

For the present studies, various concentrations of the *cis*-salt were made up into aqueous and 0.1 M nitric acid solutions at  $25 \pm 0.1^\circ$ . Optical densities were then extrapolated to zero time and Beer's law was found to hold within experimental error giving  $\epsilon_0 = 94$  at 540 m $\mu$ . Changes in the optical absorptions of a 0.00465 M solution of the *cis*-salt in 0.10 M nitric acid were followed continuously for 7 hours and then periodically over 7 days. The results were treated by the method of Guggenheim<sup>11</sup> plotting  $\log (\epsilon_t - \epsilon_{\infty})$  against time ( $t$ ), where  $\epsilon_t' = \epsilon_{t+s}$  and  $s$  is a suitable constant interval of time.  $k/2.303$  was obtained from the slope (least mean square) of the graph giving a rate constant  $k$  of  $1.4_0 \times 10^{-4} \text{ sec.}^{-1}$ . Since  $\epsilon_0$  and  $\epsilon_{\infty}$  need not be known, this method of calculation is useful in cases such as this where subsequent reactions made the determination of  $\epsilon_{\infty}$  uncertain. Substituting  $\epsilon_0 = 94$  and  $\epsilon_{\infty} = 55$  into

$$k = \frac{2.303}{t} \log \frac{(\epsilon_0 - \epsilon_{\infty})}{(\epsilon_t - \epsilon_{\infty})} \quad (1)$$

gave the rate constant of  $1.3_9 \times 10^{-4} \text{ sec.}^{-1}$  ( $\pm 2\%$ ) for the first 75 minutes of the hydrolysis. After 75 minutes, the rate was found to decrease appreciably due to the effect of the formation of the *trans*-aquochloro compound on the above extinction coefficient figures.

(ii). *trans*-[Co en<sub>2</sub> Cl<sub>2</sub>]Cl.—Previous values for the acid hydrolysis of this compound are

$1.6 \times 10^{-5} \text{ sec.}^{-1}$  (Werner and Herty,<sup>12</sup> conductance and f.p. depressions)

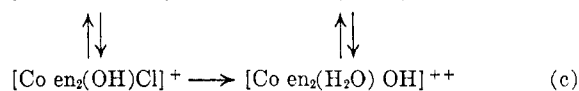
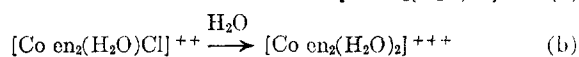
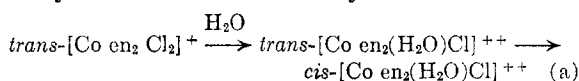
$3.2 \times 10^{-5} \text{ sec.}^{-1}$  (Pearson, Boston and Basolo,<sup>13</sup> spectrophotometry)

$2.75 \times 10^{-5} \text{ sec.}^{-1}$  (Mathieu,<sup>4</sup> conductance)

$1.8 \times 10^{-5} \text{ sec.}^{-1}$  (Haworth, Neuzil and Kittsley,<sup>14</sup> spectrophotometry)

The most recent work is that of Haworth, Neuzil and Kittsley.<sup>14</sup> A value of  $k = 1.8 \times 10^{-5} \text{ sec.}^{-1}$  at  $25^\circ$  was obtained by extrapolating their values quoted at 26, 35.3, 40 and  $50^\circ$  from the least mean squares slope of  $\log k$  against  $1/T^\circ\text{K}$ . The reason why this figure is so different from the other spectrophotometric values is that these workers assumed the reaction to be *trans*  $\rightarrow$  *cis* isomerism rather than hydrolysis, so they used extinction coefficients which are not relevant. The differences between the values quoted by Mathieu<sup>4</sup> and Pearson, Boston and Basolo<sup>13</sup> are greater at other temperatures, e.g. at  $35^\circ$  they are  $9.6 \times 10^{-5} \text{ sec.}^{-1}$  and  $1.6 \times 10^{-4} \text{ sec.}^{-1}$ ; these figures lead to a large uncertainty in activation energies.

Various concentrations of this isomer were found to obey Beer's law and the average  $\epsilon_0$  extrapolated to zero time was 8.5. The mechanism of acid hydrolysis has been described by Mathieu<sup>4</sup> as



The rate of acid hydrolysis of the second chlorine from the aquo complex as in (b) is very slow whereas the hydroxo complex (c) aquates fairly rapidly. The effect of carrying out this hydrolysis in acid solution is to suppress reactions (b) and (c) without affecting reaction (a). The first hydrolysis was carried out with 0.00963 M *trans*-[Co en<sub>2</sub> Cl<sub>2</sub>]Cl in 0.0105 M nitric acid. Applying the Guggenheim<sup>11</sup> method of calculation gave a rate constant of  $2.7 \times 10^{-5} \text{ sec.}^{-1}$  consistent with  $\epsilon_{\infty} = 51.0$ .  $\epsilon_{\text{max}}$  experimentally was found to be 51.6 after 3 days decreasing to a final  $\epsilon_{\infty}$  of 49.6 after one week so that  $\epsilon_{\infty}$  obtained by "levelling off" again does not agree with that obtained above. A larger difference in the "levelling off" and extrapolated values are obtained for this *trans*-isomer since Mathieu<sup>4</sup> claims 100% conversion of the *trans*-aquochloro into the *cis*-aquochloro compound. Substituting  $\epsilon_0 = 8.5$  and  $\epsilon_{\infty} = 51.0$  in equation 1 showed the rate to be  $2.7_0 \times 10^{-5} \text{ sec.}^{-1}$  ( $\pm 1.5\%$ ) for 180 minutes increasing slightly to  $3.05 \times 10^{-5} \text{ sec.}^{-1}$  after 7 hours. Similar treatment of the absorption values obtained with a 0.00956 M aqueous solution in the absence of acid gave a rate constant of  $2.8_7 \times 10^{-5} \text{ sec.}^{-1}$  for one hour when the aquation of the hydroxo com-

(7) R. G. Pearson, R. E. Meeker and F. Basolo, *ibid.*, **78**, 2673 (1956).

(8) F. Basolo, *J. Am. Chem. Soc.*, **72**, 4394 (1950).

(9) A. Uspensky and K. Tschibisoff, *Z. anorg. allgem. Chem.*, **164**, 326 (1927).

(10) D. D. Brown and C. K. Ingold, *J. Chem. Soc.*, 2686 (1953).

(11) E. A. Guggenheim, *Phil. Mag.*, **2**, 538 (1926).

(12) A. Werner and A. Herty, *Z. physik. Chem.*, **38**, 331 (1901).

(13) R. G. Pearson, C. R. Boston and F. Basolo, *J. Am. Chem. Soc.*, **75**, 3089 (1953).

(14) D. T. Haworth, E. F. Neuzil and S. L. Kittsley, *ibid.*, **77**, 6198 (1955).

pound (c) became apparent, the rate constant increased rapidly.

(iii). **Mixed Solvents.**—Brown and Nyholm<sup>15</sup> have studied the rate of isomerization of *cis*-[Co en<sub>2</sub> Cl<sub>2</sub>]Cl in methanol where there are no complications due to the formation of stable methanol complexes nor due to solubilities. At equilibrium, the *cis*-isomer is almost quantitatively transformed into the *trans*-form. Basolo and Pearson<sup>16</sup> explain the racemization in methanol as being due to the formation of unstable *trans*-[Co en<sub>2</sub>(CH<sub>3</sub>OH)Cl]<sup>++</sup>. Absorptions consistent with Beer's law again were obtained in methanol, the average  $\epsilon_0$  extrapolated to zero time being 93.9 which decreased to 11.3 after 3 days in agreement with the extinction coefficient of *trans*-[Co en<sub>2</sub> Cl<sub>2</sub>]<sup>+</sup> at this wave length in methanol. The absorptions were taken every 30 minutes for 10 hours and were analyzed by both Guggenheim's method<sup>11</sup> and by substitution into equation 1, both methods giving a first-order rate of  $2.2_0 \times 10^{-5}$  sec.<sup>-1</sup> ( $\pm 2\%$ ). Brown and Nyholm did not obtain data at 25° but

their values at higher temperatures extrapolate to  $2.1 \times 10^{-5}$  sec.<sup>-1</sup> at this temperature. Basolo<sup>8</sup> has stated that *cis*-[Co en<sub>2</sub> Cl<sub>2</sub>]Cl remains virtually unchanged for several weeks in methanol-water (99%). This solvent was used in the present study but was found to give the same rate of isomerization as in pure methanol. Pearson, Boston and Basolo<sup>13</sup> have also studied the aquation of *trans*-[Co en<sub>2</sub> Cl<sub>2</sub>]Cl in 50% methanol-water and obtained a rate of  $1.3 \times 10^{-5}$  sec.<sup>-1</sup> in water. Corresponding isomerization/aquation rates obtained for *cis*-[Co en<sub>2</sub> Cl<sub>2</sub>]Cl in methanol-water in the present work are shown here

Methanol	Rate $\times 10^4$ (sec. <sup>-1</sup> )	Time for which this rate was constant
0	1.4 ( $\pm 2\%$ )	1.25 hours
20%	1.2	2 hours
40%	0.86	3 hours
60%	0.64	4 hours
80%	0.39	6 hours
100%	0.22 ( $\pm 2\%$ )	To completion

(15) D. D. Brown and R. S. Nyholm, *J. Chem. Soc.*, 2696 (1953).

(16) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 266.

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## THE KINETICS OF POLYMER ADSORPTION ONTO SOLID SURFACES

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The kinetics of adsorption of polyvinyl acetate from dilute benzene solution ( $10^{-4}$  to  $10^{-6}$  g./ml.) onto the surface of chrome-plate was studied by a radioactive tracer method using C<sup>14</sup>-labelled polymer. The initial rate of adsorption was found to be rapid. This early stage of the adsorption from very dilute solutions can be represented by a kinetic equation of the Langmuir type. It is concluded that the initial adsorption of polyvinyl acetate from very dilute solutions is two-dimensional rather than three-dimensional, with little or no interaction between adsorbed molecules up to fairly high surface coverages. The adsorption from more concentrated solutions, however, seems to be predominantly three-dimensional.

### Introduction

Recently the equilibrium sorption of polymer molecules from solution onto solid surfaces has been studied by many authors.<sup>1,2</sup> Few data on the rate of adsorption, however, are available in the literature, owing partly to the experimental difficulties encountered in the measurement of the rate of this fast process. We wish to report some preliminary results on the kinetics of adsorption of C<sup>14</sup>-labelled PVAC from dilute benzene solution ( $10^{-4}$  to  $10^{-6}$  g./ml.) onto the surface of chrome-plate.

### Experimental

The adsorbent surfaces used were squares of chrome-plate about one centimeter on a side. Surfaces were cleaned preparatory to the adsorption by a procedure similar to that used by Gottlieb.<sup>3</sup> After a gentle flaming to remove any organic surface contamination, each plate was cooled in air for 20 seconds and immediately immersed in the solution of the radioactive adsorbate. Plates were immersed for various periods of time. On removal from the solution, each plate was immediately given a quick dip in solvent in

order to remove clinging excess solution. The plate was then drained, dried and counted. The adsorption of polymer in base moles/cm.<sup>2</sup> then was calculated from the measured radioactivity on the plate and the apparent area of the plate. Plates cooled in air and plates cooled in benzene<sup>3</sup> before adsorption gave essentially the same results. Radioactive polyvinyl acetate having a specific activity of 1.1 mc./g. was obtained from Tracerlab, Inc. The radioactive polymer had been prepared by irradiation-polymerization of vinyl acetate labelled with C<sup>14</sup> at the two-vinyl position. Molecular weight has been estimated as 140,000 from intrinsic viscosity measurements. The chrome-plate used was commercial ferrotype plate. Samples were obtained from Apollo Metal Works, Chicago, Illinois. C.p. benzene was purified by distillation from sodium.

### Results

Typical experimental results are plotted in Figs. 1 and 2. Values were reproduced readily when plate-to-plate variations were taken into consideration. It is noteworthy that curve C (solution concentration equals  $2.30 \times 10^{-5}$  mole/l.) appears to reach a plateau at about  $1 \times 10^{-9}$  mole/cm.<sup>2</sup> adsorbed within a few minutes and remains near that value for a rather prolonged period. It is seen that the curve ultimately attains a maximum ordinate value of about  $1.6 \times 10^{-9}$  mole/cm.<sup>2</sup> at several hundred hours duration. This final value we shall call the "maximum adsorption" as

(1) J. Koral, R. Ullman and F. R. Eirich, *J. Phys. Chem.*, **62**, 541 (1958).

(2) E. R. Gilliland and E. B. Gutoff, *J. Appl. Polymer Sci.*, **3**, 26 (1960).

(3) M. Gottlieb, *J. Phys. Chem.*, **64**, 427 (1960).