and taking into account finding 87% *trans*-dihydroxo product independent of pH between 9.81 and 10.80, the analogous relations for the fraction of *trans* product produced at these respective pH values are

$$\frac{0.995(460 - k_{11,14}) + (460 \times 0.005) - k_{11,16}\left(\frac{0.086}{1.34}\right)}{460} = 0.87 \tag{4}$$

$$\frac{0.950(460 - k_{11,14}) + (460 \times 0.050) - k_{11,16}\left(\frac{0.84}{1.34}\right)}{460} = 0.87 \tag{5}$$

Spectra of *trans*- and *cis*-$\mathrm{Cr(en)_2(OH)Cl^+}$.—Since these complexes have not been reported previously, it is of interest to give the visible absorption spectrum of each at ~25° ($\mu = 0.1$, $\mathrm{LiClO_4}$). These spectra, given in Fig. 2 and 3 (dashed curves), were obtained by mathematical extrapolation based on the experimental rate laws. The molar absorbancy indices are 39 (398 mμ), 28 (458 mμ, min.), and 35 (532 mμ) for the *trans* absorption maxima and minimum and 51 (378 mμ), 30 (455 mμ, min.), and 74 (541 mμ) for the *cis* maxima and minimum. In comparing the *trans*-$\mathrm{Cr(en)_2(OH)Cl^+}$ spectrum with the spectra of *trans*-dichloro[4] and *trans*-dihydroxo[5] cations it is evident that one absorption maximum remains fixed at 396–398 mμ and, as expected from crystal-field theory, the "red" peak is intermediate in wave length (532 mμ) between the dichloro (578 mμ) and dihydroxo (503 mμ) "red" peaks. The 453-mμ absorption band of the dichloro complex is reflected in the chlorohydroxo spectrum as a shallow minimum (458 mμ) and as a deep minimum (444 mμ) in the dihydroxo spectrum. The spectral comparison for the *cis* complexes is less clear-cut, probably because $\mathrm{OH^-}$ and $\mathrm{Cl^-}$ are not far apart in the spectrochemical series and the *cis* complexes have an effectively lower symmetry than the *trans* isomers. The spectra of *cis*-$\mathrm{Cr(en)_2(OH)_2^+}$ and *cis*-$\mathrm{Cr(en)_2Cl_2^+}$ are very similar, with only small shifts of the visible absorption maxima toward shorter wave length in going from the latter to the former. The "blue" peak of *cis*-$\mathrm{Cr(en)_2(OH)Cl^+}$ (378 mμ) lies between the "blue" peaks of the dihydroxo (377 mμ) and dichloro (402 mμ) ions, whereas the "red" peak (541 mμ) lies at a somewhat longer wave length than either dihydroxo (526 mμ) or dichloro (528 mμ) complexes.

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Contribution from the Institute for Atomic Research and Department of Chemistry,
Iowa State University, Ames, Iowa

Exchange and Substitution Reactions of Platinum(II) Complexes. IX.[1a-h] Trichloro-(ethylene)-platinate(II)[2,3]

By Stanley J. Lokken and Don S. Martin, Jr.

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The rates of isotopic exchange between free chloride ion and the chloride ligands *cis* to ethylene in equilibrium solutions of trichloro-(ethylene)-platinate(II) and *trans*-dichloroaquo-(ethylene)-platinum(II) have been determined at 15, 25, and 35°. The rate law was found to be: rate exchange = $k_c[\mathrm{Pt(C_2H_4)Cl_3^-}] + k_c'[trans\text{-}\mathrm{Pt(C_2H_4)Cl_2(H_2O)}] + k_2[\mathrm{Pt(C_2H_4)Cl_3^-}] \times [trans\text{-}\mathrm{Pt(C_2H_4)Cl_2(H_2O)}]$, where at 25°, $k_c = 2.9 \times 10^{-6}$ sec.$^{-1}$, $\Delta H^* = 21$ kcal./mole; $k_c' = 2.8 \times 10^{-5}$ sec.$^{-1}$, $\Delta H^* = 22$ kcal./mole; $k_2 = 8.6 \times 10^{-3}$ sec.$^{-1}$ M^{-1}, $\Delta H^* = 19$ kcal./mole. Acid hydrolysis accounts for the first two terms, but the third term requires that a dimer exist in the transition state.

Introduction

Previous studies in this Laboratory[1a-h] have considered the isotopic exchange of chloride ligands in the complete series of chloro–ammine complexes of platinum(II). For the exchange in these systems acid hydrolysis, in which the reversible replacement of a chloride ligand by $\mathrm{H_2O}$ occurs, provides an important mechanism for the exchanges. Only for $[\mathrm{Pt(NH_3)_3Cl}]^+$ and *trans*-$[\mathrm{Pt(NH_3)_2Cl_2}]$ does an alternative exchange process, first order in both chloride and the complex, compete to a measurable extent. Rate constants for chloride ion independent exchange processes presumably have characterized the second acid hydrolysis rates for several of the complexes. These rates could not be evaluated by other means.

The present work deals with the chloride exchange in solutions of Zeise's salt, $\mathrm{K[Pt(C_2H_4)Cl_3]}$. With the square planar arrangement of ligands, the three chlorides in the anion are not equivalent. An analogous

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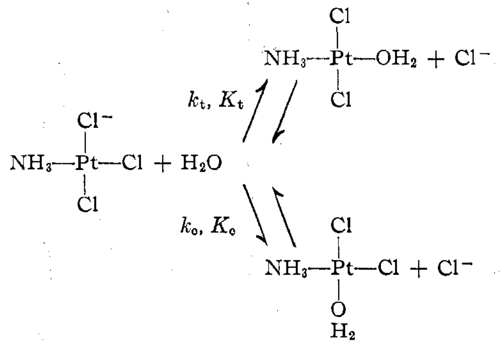
(1) Previous papers in this series: (a) L. F. Grantham, T. S. Elleman, and D. S. Martin, Jr., *J. Am. Chem. Soc.*, **77**, 2965 (1955); (b) T. S. Elleman, J. W. Reishus, and D. S. Martin, Jr., *ibid.*, **80**, 536 (1958); (c) T. S. Elleman, J. W. Reishus, and D. S. Martin, Jr., *ibid.*, **81**, 10 (1959); (d) W. W. Dunning and D. S. Martin, Jr., *ibid.*, **81**, 5566 (1959); (e) C. I. Sanders and D. S. Martin, Jr., *ibid.*, **83**, 807 (1961); (f) J. W. Reishus and D. S. Martin, Jr., *ibid.*, **83**, 2457 (1961); (g) R. J. Adams and D. S. Martin, Jr., "Advances in the Chemistry of the Coordination Compounds," ed. by S. Kirschner, The Macmillan Co., New York, N. Y., 1961, p. 579; (h) F. Aprile and D. S. Martin, Jr., *Inorg. Chem.*, **1**, 551 (1962).

(2) Contribution No. 1183. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

(3) The conclusions of this work were presented as part of the paper, "Ligand Exchange Reactions of Platinum(II) Complexes," symposium on "The Use of Isotopes to Study Inorganic Reaction Mechanisms," Division of Inorganic Chemistry, 143rd National Meeting of the American Chemical Society, Atlantic City, N. J., September, 1962.

situation exists for the ion $[Pt(NH_3)Cl_3]^-$. For this ion, the two reactions represented by eq. 1t and 1c must be considered.

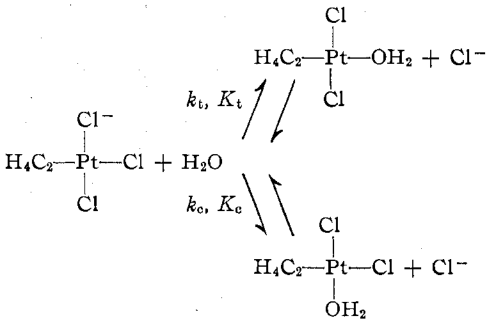


(1t)

(1c)

An equilibrium constant for the acid hydrolysis was determined chemically and found to be 1.4×10^{-2} M at 25°. The systematics for the equilibria of the entire series of chloro–ammine complexes suggest that it is the *trans*-chloride reaction which is so characterized. However, the exchange of all three chloride ligands with free chloride occurs at rates which indicate both types of ligands undergo acid hydrolysis at comparable rates but that $K_c < 0.1K_t$.

The ion, $[Pt(C_2H_4)Cl_3]^-$, is of special interest because of the unusual bonding to the ethylene ligand in which the carbon–carbon axis is at right angles to the plane containing the Pt–Cl bonds.[4] Chatt, *et al.*,[5] and Orgel[6] have indicated that π-bonding with this structure would explain the strong *trans*-directing effect noted by Hel'man[7] for ethylene and other olefins. The two possible acid hydrolysis reactions for $[Pt(C_2H_4)Cl_3]^-$ are written in eq. 2c and 2t. Leden and Chatt[8] reported that equilibrium 2t was established in less than 2 min. so the chloride ligand *trans* to ethylene, unlike ligands in other platinum(II) complexes, was virtually labile. At 25° the equilibrium constant K_t was $3.0 \pm 0.5 \times 10^{-3}$ M. The constancy of K_t implies that either $K_c << K_t$ or that $1/k_c$ was considerably greater than the time of observation. The present investigation was undertaken to establish the rate law for the exchange of the *cis*-chlorides and possibly to evaluate the acid hydrolysis rate constant, k_c.



(2t)

(2c)

Experimental

Materials.—$K[Pt(C_2H_4)Cl_3]$ was synthesized from iridium-free $K_2[PtCl_4]$[1c] by the method of Chatt and Duncanson.[9] The compound was purified by three crystallizations from 3% HCl. After drying for 1 week over $CaSO_4$ desiccant, typical analyses were: Calcd. for $K[Pt(C_2H_4)Cl_3]$: Pt, 52.95; Cl, 28.82; *K*, 10.60. Found: Pt, 53.02; Cl, 29.00; K, 10.90.

Chlorine-36 was obtained from the Isotope Division, U. S. Atomic Energy Commission, Oak Ridge, Tenn., in the form of approximately 2 M HCl.

Distilled water was redistilled from alkaline permanganate before use in the preparation of solutions.

Tetraphenylarsonium chloride reagent was obtained from the Fielding Chemical Company. Tetraphenylarsonium acetate solutions, for use as a precipitating agent, were prepared by passing solutions of the chloride through columns of Dowex 1 anion exchange resin in the acetate form.

Other chemicals utilized were generally of reagent grade and meeting the A.C.S. specifications.

Procedures.—For comparison of results with those for other complexes, it was desired to have the solutions with ionic strength of 0.318 M. The complex rapidly decomposes and the solutions darken in the absence of added acid. However, with a hydrogen ion concentration higher than 0.1 M the solutions appeared unchanged for several months when they were stored in the dark. Therefore, K_2SO_4 and H_2SO_4 were added to the solutions to give an ionic strength of 0.318 and the desired H^+ concentration. The second ionization concentration quotient for H_2SO_4 was needed for calculating the $[H^+]$. Young and Blatz[10] have reviewed the methods for obtaining this quantity. The two most reliable methods for this ionic strength gave values of 0.052 and 0.059; therefore, an average value of 0.055 was used for the temperature range of the experiments, 15–35°.

Ultraviolet spectra for the solutions were obtained by a Cary recording spectrophotometer Model 12.

For the exchange experiments, the desired quantities of $K[Pt(C_2H_4)Cl_3]$, KCl, and Na_2SO_4 were weighed into a flask which was wrapped with black, opaque tape to exclude light. The correct amount of H_2O and standard H_2SO_4 was added, and the solution was allowed to age for several days in a thermostat to attain equilibrium for the acid hydrolysis of the *cis*-chlorides. To start the exchange, the tracer HCl was added from a micropipet. The volume and the chloride concentration were not changed appreciably by this addition. At intervals, aliquots were withdrawn from the solution. A fourfold excess of tetraphenylarsonium acetate was added to the solution and the $[As(C_6H_5)_4][Pt(C_2H_4)Cl_3]$ precipitated immediately. Because of the rapidly established equilibrium (2t) the *trans*-$[Pt(C_2H_4)(H_2O)Cl_2]$ in the solution reacts with Cl^- and precipitates also as $[Pt(C_2H_4)Cl_3]^-$. Precipitates were filtered quickly onto weighed filter papers and washed twice with H_2O. They were air-dried for 1 day and the specific activity, S (counts/min. mole of Cl), was determined by the methods which have been described previously.[1a,c] At least four samples always were taken after the exchange was >99% complete to provide values for S_∞.

Results

Evidence for the *cis*-Acid Hydrolysis.—Changes in the ultraviolet spectrum, shown in Fig. 1, provide evidence for the acid hydrolysis of the *cis*-chlorides. Spectrum 1 is for a freshly prepared solution of Zeise's salt. However, equilibrium already was established for the acid hydrolysis of the *trans*-chloride and the predominant species is *trans*-$[Pt(C_2H_4)Cl_2(H_2O)]$. It can be seen that small but definite changes occurred in this spectrum as it aged in the dark to yield eventually spectrum 2. The half-times of these changes were noted to

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[4] J. A. Wunderlich and D. P. Mellor, *Acta Cryst.*, **7**, 130 (1954).

[5] J. Chatt, L. A. Duncanson, and L. A. Venanzi, *J. Chem. Soc.*, 4456 (1955).

[6] L. E. Orgel, *J. Inorg. Nucl. Chem.*, **2**, 137 (1956).

[7] A. D. Hel'man, *Compt. rend. acad. sci. USSR*, **16**, 351 (1937).

[8] I. Leden and J. Chatt, *J. Chem. Soc.*, 2936 (1955).

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[10] T. F. Young and L. A. Blatz, *Chem. Rev.*, **44**, 93 (1949).

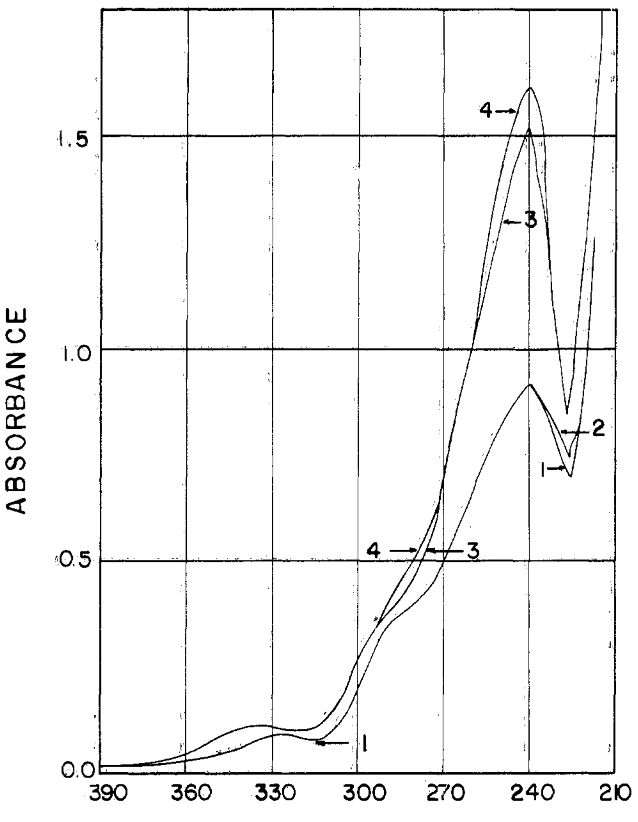
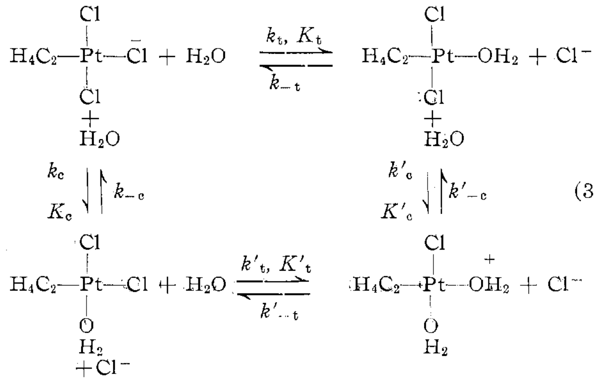


Fig. 1.—Spectral changes in 5.00×10^{-4} *M* solution of K[Pt(C_2H_4)Cl_3] at 25° in 1.00-cm. cells; H_2SO_4 and K_2SO_4 added to give $[H^+] = 0.142$ *M*, $\mu = 0.318$ *M*: (1) 5 min. after dissolving the salt; (2) 4 hr. to 4 weeks after dissolving; (3) 2 min. after adding KCl to solution to give 0.134 *M* KCl; (4) 4 hr. to 2 weeks after adding KCl.

be of the order of 1 hr. and no further changes were observed over a 2-week interval. At that time, a high concentration of KCl was added to the solution and spectrum 3 was recorded promptly. This addition produced a pronounced change in the spectrum as *trans*-[Pt(C_2H_4)(H_2O)Cl_2] was largely converted to [Pt(C_2H_4)Cl_3]$^-$. Again small changes in the spectrum occurred slowly which could be attributed to the replacement of *cis*-H_2O by chloride to give finally spectrum 4, which was indistinguishable from the spectrum of a fresh solution of Zeise's salt dissolved with excess chloride.

Therefore a complete treatment must consider the cycle of reactions



(3)

Presumably, the equilibrium characterized by K'_t also would be established rapidly since it is the replacement of the ligand *trans* to ethylene. The slow changes in the spectra can be attributed to the formation of *cis*-[Pt(C_2H_4)(H_2O)Cl_2] and *cis*-[Pt(C_2H_4)$(H_2O)_2$Cl]$^+$. The observed half-time of 1 hr. for these changes, together with information from exchange rates, provides a rough estimate of the amounts of these species formed at equilibrium, which estimate will be discussed later.

Treatment of Data.—For the preliminary treatment the extent of the *cis*-acid hydrolysis was considered negligible, *i.e.*, $K_c << K_t$ and $K'_c << K_t$. Leden and Chatt's value of $3.0 \pm 0.5 \times 10^{-3}$ *M* for the equilibrium quotient K_t at 25° and $\mu = 0.1$, possesses considerable experimental uncertainty. However, it appeared that no significant improvement on their evaluation could be effected. Therefore, their value was used for the conditions of the present work which were at $\mu = 0.318$ *M* and temperatures of 15 to 35°. Since the charges are symmetric in reaction 2t, no large ionic strength effect is expected; and, generally, ΔH^0 for the acid hydrolysis of platinum(II) complexes have not been large, *i.e.*, never more than *ca.* 5 kcal./mole. With these assumptions the following equations apply

$$[trans\text{-Pt}(C_2H_4)Cl_2(H_2O)] = a - [\text{Pt}(C_2H_4)Cl_3] \quad (4)$$

$$K_t = [trans\text{-Pt}(C_2H_4)Cl_2(H_2O)] \times \{b + [trans\text{-Pt}(C_2H_4)Cl_2(H_2O)]\}/[\text{Pt}(C_2H_4)Cl_3] \quad (5)$$

where *a* is concentration of K[Pt(C_2H_4)Cl_3] dissolved (*M*) and *b* is concentration of KCl dissolved (*M*). These equations yield the explicit expression for the concentration of *trans*-[Pt(C_2H_4)Cl_2(H_2O)]

$$[trans\text{-Pt}(C_2H_4)Cl_2(H_2O)] = \{-(K_t + b) + \sqrt{(K_t + b)^2 + 4K_ta}\}/2 \quad (6)$$

In the system for which eq. 4–6 apply, there are only two classes of chlorine atoms which are not in a rapidly established isotopic equilibrium. One class, designated as the *cis*-chloride, comprises the chloride ligands *cis* to (C_2H_4) in both [Pt(C_2H_4)Cl_3]$^-$ and *trans*-[Pt(C_2H_4)Cl_2(H_2O)]. The two complexes with *cis*-chloride are in labile equilibrium and are not chemically separable. The other class contains the free chloride ion and the chloride *trans* to (C_2H_4) in the complex. The rates of exchange, R_{ex}, of chloride between these two classes are evaluated from the experiments with Cl^{36}. For the equilibrium solutions in an exchange experiment under the assumed conditions 4–6

[*cis*-chloride] = 2*a* (moles/l.)
[(free and *trans*)-chloride] = *a* + *b* (moles/l.)
concentration of Cl^{36} = *I* (counts/min. l.)
concentration of Cl^{36} in *cis*-chloride = *u* (counts/min. l.)
specific activity of *cis*-chloride = S_u = $u/2a$ (counts/min. mole of Cl)
specific activity of (free + *trans*)-chloride S_s = $(I - u)/(a + b)$ (counts/min. mole of Cl)
specific activity at $t = \infty$ $S_\infty = I/(3a + b)$ (counts/min. mole of Cl)

The rate of appearance of activity in the *cis*-chloride is given by

$$du/dt = R_{ex}(S_s - S_u) \quad (7)$$

With the initial condition for the exchange experiment that $S_u = 0$, $S_s = I/(b + a)$ at time $t = 0$, the solution of eq. 7 yields

$$u = \frac{2aI}{(b + 3a)} [1 - \exp(-R_{ex})(b + 3a)t/2a(b + a)] \quad (8)$$

The precipitate formed by the tetraphenylarsonium ion contains both the *cis*-chloride and the *trans*-chloride. The specific activity of this precipitate, S_p, which is the quantity actually determined in the experiments is given by

$$S_p = (u + aS_s)/3a \text{ (counts/min. mole of Cl)} \quad (9)$$

With appropriate substitutions in eq. 9, S_p can be given as a function of t and the equation follows

$$(S_\infty - S_p)/S_\infty = \frac{2b}{3(b + a)} [\exp(-R_{ex})(b + 3a)t/2a(b + a) \quad (10)$$

$(S_\infty - S_p)/S_\infty$ corresponds to the quantity $(1 - F)$, where F = fraction of exchange, that is usually plotted for a simple isotope exchange process. Equation 10 predicts that a semilogarithmic plot of this function for an experiment will be a straight line with an intercept of $2b/3(b + a)$ and a slope of $-R_{ex}(b + 3a)/2a(b + a)$. The exchange curves therefore have the appearance of an initial immediate exchange which results from the presence of the *trans*-chloride in the precipitate. A plot of the results of several exchange experiments is given in Fig. 2. It can be seen that the data fell very satisfactorily along straight lines. This feature and the good agreement of the measured intercepts of the lines with the calculated values serve to attest to the effectiveness of the separation procedure. Table I includes the results of the exchange experiments at $\mu = 0.318$ *M* and $[H^+] = 0.142$ *M*. The rates of exchange have been calculated by the equation

$$R_{ex} = (\ln 2)2a(b + a)/(b + 3a)t_{1/2} \quad (11)$$

where $t_{1/2}$ was the half-time taken from the semilogarithmic exchange curve plots. The kinetics experiments covered a fivefold range in concentration of the complex. The concentration of KCl extended over a 100-fold range.

Determination of the Exchange Rate Law.—If exchange occurred only by the acid hydrolysis reactions indicated in eq. 3 then the rate expression is predicted to be

$$R_{ex} = k_c[Pt(C_2H_4)Cl_3^-] + k_c'[\textit{trans}\text{-}Pt(C_2H_4)Cl_2(H_2O)] \quad (12)$$

which becomes

$$R_{ex} = k_c a - (k_c' - k_c)[\textit{trans}\text{-}Pt(C_2H_4)Cl_2(H_2O)] \quad (13)$$

Then, a plot of R_{ex} *vs.* $[\textit{trans}\text{-}Pt(C_2H_4)Cl_2(H_2O)]$ for a single value of a would be a straight line with the intercept $k_c a$ and the slope $(k_c' - k_c)$. However, the possibility of the chloride dependent terms must be considered also. A more general expression including these terms is

$$R_{ex} = k_c[Pt(C_2H_4)Cl_3] + k_c'[\textit{trans}\text{-}Pt(C_2H_4)Cl_2(H_2O)] + k_{Cl}[Pt(C_2H_4)Cl_3][Cl^-] + k_{Cl}'[\textit{trans}\text{-}Pt(C_2H_4)Cl_2(H_2O)][Cl^-] \quad (14)$$

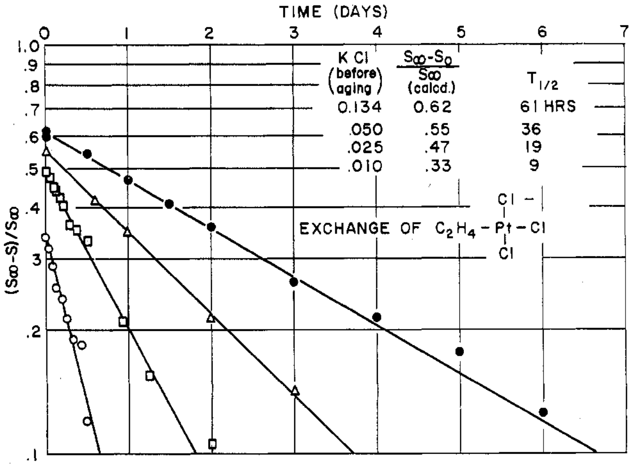


Fig. 2.—Isotopic exchange experiments for the *cis*-chloride: initial concentration of $[Pt(C_2H_4)Cl_3^-]$ before aging = 0.0100 *M*; $[H^+] = 0.142$ *M*; $\mu = 0.318$ *M* at 25°.

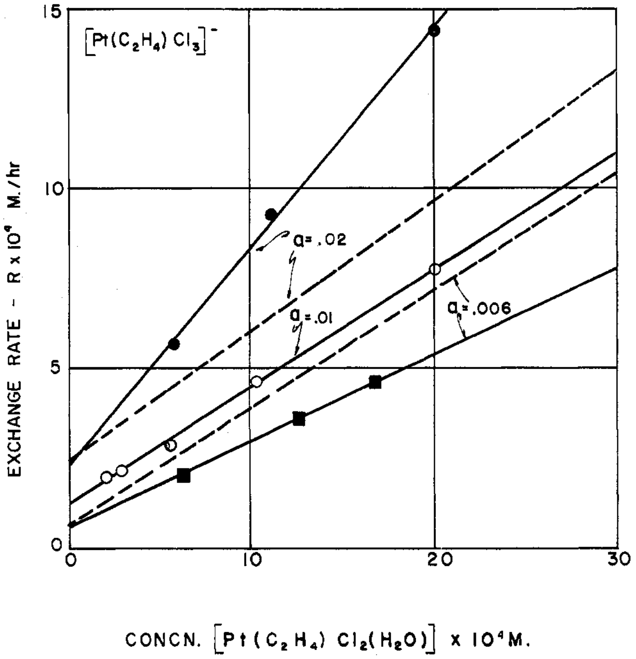


Fig. 3.—Plot of the exchange rate *vs.* the concentration of *trans*-$[Pt(C_2H_4)Cl_2(H_2O)]$ for 25°: $[H^+] = 0.142$ *M*; $\mu = 0.318$ *M*.

Since $[\textit{trans}\text{-}Pt(C_2H_4)Cl_2(H_2O)][Cl^-] = K_t[Pt(C_2H_4)Cl_3]$, the last term in eq. 14 is of the same form as the first and the two mechanisms cannot be distinguished kinetically.

In Fig. 3, the exchange rate was plotted against the concentration of *trans*-$[Pt(C_2H_4)Cl_2(H_2O)]$. For $a = 0.01$ *M* the points fell along a straight line with a positive slope. Since the chloride concentration becomes larger as $[\textit{trans}\text{-}Pt(C_2H_4)Cl_2(H_2O)]$ decreases, it is apparent that the third term of eq. 14, corresponding to a chloride-dependent exchange of $[Pt(C_2H_4)Cl_3]^-$, is negligible. However, eq. 13 is not satisfactory. The dashed lines in Fig. 3 show the calculated lines which are expected for $a = 0.006$ and 0.02 *M* on the basis of the experiments at $a = 0.01$ *M*. It can be seen that the experimental points do not agree with these dashed lines. Next the quantity $R_{ex}/[Pt(C_2H_4)Cl_3]$ was plotted *vs.*

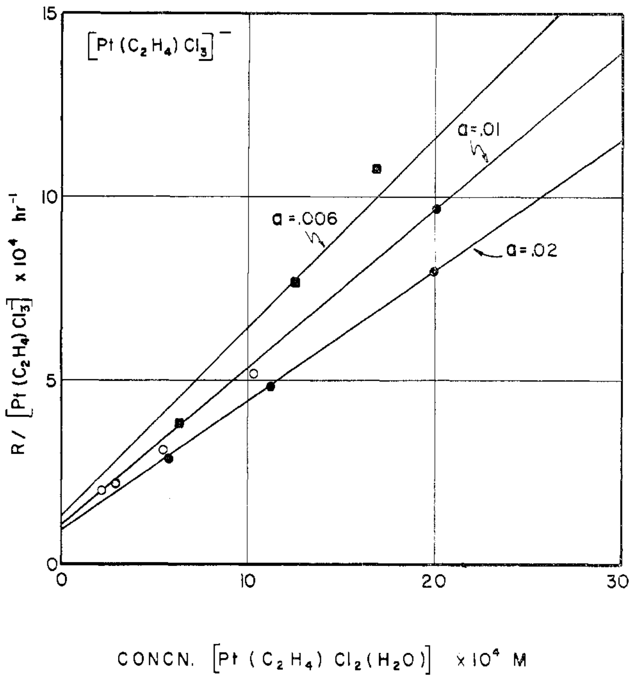


Fig. 4.—Plot of the function $R_{ex}/[Pt(C_2H_4)Cl_3^-]$ *vs.* concentration of *trans*-$[Pt(C_2H_4)Cl_2(H_2O)]$ for 25°: $[H^+] = 0.142\ M$; $\mu = 0.318\ M$.

[*trans*-$Pt(C_2H_4)Cl_2(H_2O)$] in Fig. 4. For each series at constant a the points fell along a steeply sloping curve; and furthermore, there appeared to be a real decrease in the slope of the curves as a increased. Therefore, the simplest function which would adequately describe the rate was of the form

$$R_{ex} = k_c[Pt(C_2H_4)Cl_3] + k_2[trans\text{-}Pt(C_2H_4)Cl_2(H_2O)] \times [Pt(C_2H_4)Cl_3] + k_c'[trans\text{-}Pt(C_2H_4)Cl_2(H_2O)] \quad (15)$$

The set of rate constants was chosen for each temperature which gave the minimum value for the average value of $\Sigma|R_{ex}(\text{obsd.}) - R_{ex}(\text{calcd.})|/R_{ex}(\text{obsd.})$. This quantity amounted to about 5% for each of the series of experiments at various temperatures. Equation 15 gave a better fit to the experimental data than any other simple function of the concentration variables with three or fewer constants. The final set of constants, together with the indicated enthalpy and entropy of activation, is given in Table II. The uncertainty in k_c was placed at ±5%, in line with the agreement between calculated and observed exchange rates and the consideration that this term in the rate expression becomes dominant in the high chloride solutions. The higher uncertainties for k_2 reflect an uncertainty in the equilibrium constant, K_t, determined by Leden and Chatt.[8] This component is at least partially canceled in the uncertainty of ΔH^*. The constant K_c' was given least accurately since the corresponding processes were always a minor component of the exchange.

Table I

Conditions and Results for Isotopic Exchange Reactions[a]

$[Pt(C_2H_4)Cl_3^-]$ (before aging) a, mM	Cl^- (before aging) b, mM	*trans*-$[Pt(C_2H_4)Cl_2(H_2O)]$ (at equilibrium), mM	Half-time of exchange, hr.	Exchange rate obsd., mM/hr.	Exchange rate calcd.,[b] mM/hr.
		At 15°			
10.0	10.0	2.00	27.9	0.248	0.237
10.0	50.0	0.560	110.4	.0942	.0962
10.0	25.0	1.03	60.0	.147	.147
10.0	134.	0.219	206.4	.0589	.0566
30.0	30.0	2.53	24.0	.865	.855
6.0	10.0	1.26	44.5	.105	.107
20.0	50.0	1.11	63.0	.280	.298
		At 25°			
10.0	134.	0.219	61.2	.198	.191
10.0	100.	.290	54.7	.214	.218
10.0	50.0	.560	36.0	.289	.320
10.0	10.0	2.00	8.95	.774	.780
10.0	25.0	1.03	19.0	.464	.484
6.0	10.0	1.26	13.0	.366	.361
20.0	25.0	2.00	10.2	.144	.151
6.0	25.0	0.629	29.0	.206	.224
10.0	10.0	2.00	8.90	.779	.780
20.0	100.	0.579	36.4	.571	.610
20.0	50.0	1.11	19.0	.928	.959
6.0	6.0	1.68	8.95	.465	.440
30.0	30.0	2.53	7.40	.281	.270
30.0	30.0	2.53	7.30	.284	.270
30.0	75.0	1.14	17.9	.148	.143
		At 35°			
10.0	10.0	2.0	2.70	.256	.243
10.0	134.	0.219	19.2	.634	.613
10.0	50.0	.560	10.2	.102	.101
10.0	25.0	1.03	5.70	.155	.152
10.0	10.0	2.00	2.70	.256	.243
6.0	25.0	0.629	9.00	.665	.709
20.0	100.	.579	11.5	.181	.191
30.0	75.0	1.17	6.00	.441	.453

[a] Solutions in the dark, H_2SO_4 and K_2SO_4 added to give $[H^+] = 0.142\ M$ and $\mu = 0.318\ M$. [b] Calculated by eq. 15 with the constants from Table II.

Table II

Rate Constants and the Indicated Enthalpy and Entropy of Activation for the Exchange Rate Law, Eq. 15

Temp., °C.	$k_c \times 10^5$, sec.$^{-1}$	$k_c' \times 10^5$, sec.$^{-1}$	$k_2 \times 10^3$, sec.$^{-1}$ M^{-1}
15	0.083 ± 0.004	0.69 ± 0.10	2.8 ± 0.28
25	0.29 ± 0.014	2.8 ± 0.42	8.6 ± 0.86
35	0.97 ± 0.048	9.2 ± 1.4	25.8 ± 2.6
ΔH^* (kcal./mole)	21 ± 0.6	22 ± 1.6	19 ± 1.0
ΔS^* (e.u.)	−13 ± 2	−5 ± 5	−2 ± 3

Discussion

The value of k_c, given in Table II, represents an upper limit for the acid hydrolysis rate constant. It is extraordinarily small and at 25° is about one tenth as large as any of the acid hydrolysis rate constants for the chloro–ammine series of complexes, all of which fall within a fourfold range. The ethylene group, which strongly labilizes the *trans*-group, exerts a moderate delabilizing effect on the *cis*-chloride. The effect appears to be due to the higher activation energy since the entropy of activation of −13 e.u. is very similar to that of $[Pt(NH_3)Cl_3^-]$. The absence of a chloride-dependent exchange with the negative complex is not surprising. Although the constant k_c' is given least precisely, it appears to have a value at 25° in line with those of the chloro–ammine series. If given correctly, the activation energy seems to be unusually high and the entropy of activation

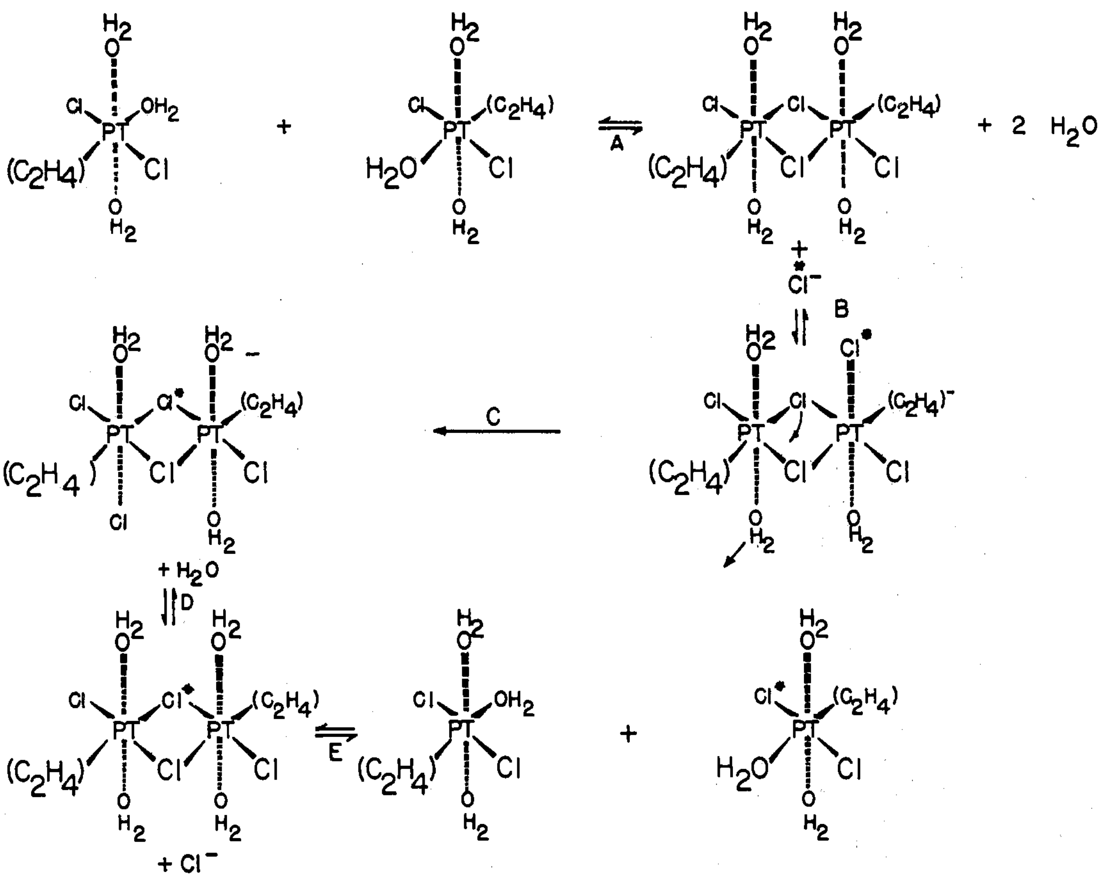


Fig. 5.—Proposed mechanism to account for the second order term in the kinetics expression for the exchange process.

correspondingly low for this second acid hydrolysis step.

The unexpected second order term in eq. 15, characterized by k_2, was actually dominating in the majority of the experiments. It appears that the transition state must contain a dimer. A plausible mechanism is illustrated in Fig. 5. The complex in H_2O is considered to have a distorted octahedral configuration with H_2O ligands at the axial positions which are in labile equilibrium with the solvent. Step A is the rapidly established equilibrium between two molecules of *trans*-$[Pt(C_2H_4)Cl_2(H_2O)]$ and *sym*-*trans*-di-μ-chlorodichlorobis-(ethylene)-diplatinum(II). This species is the well characterized dimer which is normally crystallized from ethanol solutions. However, in aqueous systems the dimer is rapidly converted to monomer and the equilibrium constant for the reaction of step A must be very small. An axial H_2O of the dimer then is reversibly replaced by a tracer chloride which in turn replaces a *cis*-chloride of the double chloride bridge in step C. This mechanism will contribute an exchange rate term, $k[trans\text{-}Pt(C_2H_4)Cl_2(H_2O)]^2[Cl^-]$, which is exactly equivalent to the second term of eq. 15. Thus the ethylene, in addition to providing rapid substitution of the *trans*-ligand also permits the rapid formation of the dimers with bridge groups *trans* to ethylene. The dimers formed can then participate in the exchange by this process which is not observed for the chloro–ammine–aquo complexes of platinum(II).

The exchange kinetics gave at least maximum values for the acid hydrolysis constants for the *cis*-chlorides, *i.e.*, k_c and k_c'. It was then possible to obtain some idea of the possible extent of this process in the equilibrium solutions. For the system in (3), the rate expression (16) below is expected to apply.

For simplicity, let

$$z = [cis\text{-}Pt(C_2H_4)Cl(H_2O)_2]$$
$$y = [cis\text{-}Pt(C_2H_4)Cl_2(H_2O)]$$
$$x = [trans\text{-}Pt(C_2H_4)Cl_2(H_2O)]$$

Then

$$[Pt(C_2H_4)Cl_3^-] = a - x - y - z$$
$$[Cl^-] = b + x + y + 2z$$
$$d(y + z)/dt = -\left\{\frac{k_{-c}[Cl^-]^2 + k'_{-c}K'_t\,[Cl^-]}{[Cl^-] + K_t} + k_c\right\} \times (y + z) + k_c(a - x) + k'_c(x) \quad (16)$$

With high chloride and a rapidly established equilibrium for the *trans*-hydrolysis, the last two terms as well as the coefficient of $(y + z)$ are substantially constants and the equation is approximately linear, first order with constant coefficients. The coefficient of $(y + z)$ becomes $\ln(2)/t_{1/2}$ which, as noted earlier, was estimated as 1 hr. from changes in the spectra. One obtains then the quantity

$$(y + z)_\infty = [k_c(a - x) + k_c'x]t_{1/2}/0.693 \qquad (17)$$

From the values of $(y + z)$ calculated by the use of eq. 17, upper limits of K_c and K_c' were estimated to be 4.5 × 10^{-4} and 1.4 × 10^{-4} M, respectively. These values are sufficiently smaller than K_t that the necessary simplifying assumptions were satisfactory for the treatment of the isotopic exchange.

Additional observations for this system are to be noted. Since the equilibrium constant was not known precisely, the treatment of the exchange data was rerepeated with values of K_t taken as 2×10^{-3} and 4×10^{-3} *M*. In neither case did the calculation indicate any different type of rate law, but the rate constants k_2 and k'_c were changed accordingly. In other experiments a change in hydrogen ion concentration over the range of 0.01 to 0.243 gave no change in the observed half-time. When some of the solutions were exposed to light, a precipitate had formed within an 8-day aging period, whereas the solutions were stable for at least several weeks in the dark. The sensitivity to light was apparently influenced by the presence of sulfate since solutions of $K[Pt(C_2H_4)Cl_3]$ in dilute HCl have been stored for months in the light with no evidence of decomposition. One exchange solution, aged in the dark but exposed to light upon the addition of Cl^{36}, appeared to have an initial rate 25% higher than the same solution in the dark. However, the solution in the light decomposed before the completion of the exchange.

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The Visible and Ultraviolet Spectra of Some Molybdenum Complexes[1]

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The visible and ultraviolet spectra have been examined for several complexes of the type $MoOCl_3 \cdot 2L$ (L = oxygen donor), and for $MoCl_5 \cdot (C_6H_5)_3AsO$ and $NH_4MoOCl_4 \cdot CH_3CN$. In all cases the ligand field bands observed at approximately 14,000 and 23,000 cm.$^{-1}$ are believed to be due to a strong tetragonal field created by the oxygen atom. The spectrum of Mo(V) in a field of six Cl^- ligands was obtained by examining KCl pellets of KCl–$MoCl_5$ melts. A single asymmetric band was observed in the visible region at 24,100 cm.$^{-1}$ and assigned to the transition $^2T_2 \rightarrow {}^2E$ in $MoCl_6^-$. The compound $[(CH_3)_4N]_2MoCl_6$ was prepared and characterized by conductance, magnetic moment, and visible and infrared spectra. Two bands which probably are due to ligand field transitions were observed in the visible spectrum at approximately 22,000 and 25,800 cm.$^{-1}$.

Introduction

Some attention has been accorded the electronic spectra of d^1-type oxycations. Ballhausen and Gray[2] published a complete study of oxovanadium(IV), and the spectra of several of its complexes have been reported from this Laboratory.[3] Gray and Hare[4] have reported the electronic structures and spectra of the CrO^{3+} and MoO^{3+} ions. The preparation of several MoO^{3+} compounds has been reported earlier by us,[5] and a report of their visible spectra seemed a suitable extension of the work. In addition we set out to prepare a salt of the $MoCl_6^-$ ion in order to examine the spectrum of a d^1 ion in an undistorted octahedral field.

The spectra of the MoO^{3+} compounds were all very much like that of $MoOCl_5^{2-}$, as reported by Gray and Hare,[4] and earlier by Jørgensen.[6] In each case, the octahedrally coördinated species was observed to be subjected to strong tetragonal distortion due to the molybdenyl oxygen. Distortions to still lower symmetry than C_{4v} by non-equivalent ligands other than the oxygen atom seemed unimportant.

Various attempts to prepare the $MoCl_6^-$ ion led to the preparation of the compounds $[(CH_3)_4N]_2MoCl_6$ and $NH_4MoOCl_4 \cdot CH_3CN$, whose spectra subsequently were studied. Finally, $MoCl_5$ was fused in the presence of excess dry powdered KCl, and the resulting mixture pressed into a translucent KCl pellet. The spectrum of this material indicates that the molybdenum exists as the $MoCl_6^-$ ion in the melt.

Experimental

Reagents.—Reagent grade chemicals were used without further purification except in the cases noted. Molybdenum pentachloride was obtained from Climax Molybdenum Company.

Analyses.—Carbon, hydrogen, and nitrogen analyses were performed by Micro-Tech Laboratories, Skokie, Ill. Molybdenum and chlorine were determined in the manner described previously.[5]

Measurement of Magnetic Susceptibility.—Magnetic susceptibilities were determined by the Gouy method as described previously.[5]

The μ_{eff} values for Mo in the KCl–$MoCl_5$ melts presented a special problem. After a sample of the powdered melt was subjected to the usual susceptibility measurements, the contents of the tube were analyzed for Mo. The calculations of the μ_{eff} value assumed that all the Mo existed as $KMoCl_6$ and that KCl made up the residue of the sample weight.

Conductance Measurements.—Conductivities were measured in nitrobenzene solution at 25° in the manner described elsewhere.[7] The concentrations were approximately 10^{-3} *M*.

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[1] Presented at the Eastern Regional Meeting of the American Chemical Society, Gatlinburg, Tennessee, Nov., 1962.

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