found that conditioning of the glass vacuum system with crude $P_2O_3F_4$ obtained from dehydration of $HOPOF_2$ was an effective means of drying the system. Care must also be taken to ensure that POF_2Br is free of any unreacted $HOPOF_2$ or HBr formed in the preparation of POF_2Br because hydrogen bromide reacts readily with $P_2O_3F_4$ to form POF_2Br and $HOPOF_2$. The ^{19}F nmr and infrared spectra and molecular weight of $P_2O_3F_4$ all indicate that the compound can be obtained quite pure by the photolysis of POF_2Br with O_2. The observed ^{19}F nmr spectrum agrees with that reported by Colburn and coworkers for pure $P_2O_3F_4$.[15,16] In agreement with these workers only a two-line spectrum is observed if appreciable $HOPOF_2$ is present.

Acknowledgment.—This work was supported in part by the National Science Foundation (Grants GP-23098 and GP-8892) and by the Petroleum Research Fund of the American Chemical Society (Grant PRF-4563). The authors also thank D. T. Dix and the Dow Chemical Co. for the use of the nmr spectrometer. F. A. H. thanks Goodyear Atomic Corp. for a leave of absence.

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(16) These workers obtained the ^{19}F nmr at 40 Mc in $CFCl_3$ and observed a six-line spectrum. At 56.4 Mc using a neat sample we observed further splitting and the question is under study.

CONTRIBUTION FROM THE INSTITUTE FOR ATOMIC RESEARCH
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Aquation Equilibrium and Isotopic Exchange of Chloride for Chloro(diethylenetriamine)platinum(II) Chloride[1]

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Received December 18, 1970

The concept of the nucleophilicity parameter with its associated nucleophilic discrimination coefficient, since its inception by Belluco, *et al.*,[3] in 1965, has served as an exceedingly useful means for rationalizing trends in the kinetics of ligand substitution reactions for square-planar complexes. In addition, as Basolo, Gray, and Pearson[4] proposed, the rates of chloride or bromide replacements from the $Pt(dien)X^+$ complexes where X is halide and dien is diethylenetriamine are especially informative about trends in entering-group and leaving-group effects. It has been noted that plots of log k_y *vs.* n^0_{Pt} for iodide, bromide, and chloride displacements of the halide in these complexes have given an exceedingly good correlation[5] (see Figure 1) with the exception of the replacement of chloride by chloride. This rate was originally determined by an isotopic exchange procedure in which chloride was separated from the complex by a silver chloride precipitation.[6] Since work in this laboratory has shown that silver chloride precipitates sometimes catalyze the exchange of chloride ligands in platinum(II) complexes, the present study was undertaken to apply an ion-exchange technique for the chloride separation.

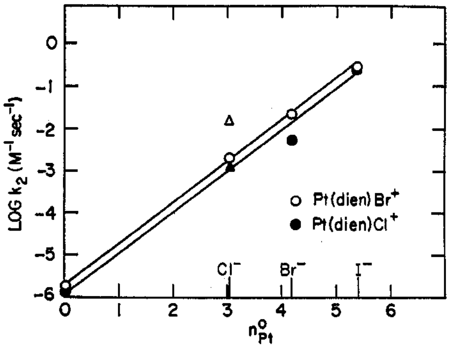

Figure 1.—Dependence of the second-order rate constants (25° and zero ionic strength) for the replacement of Cl^- and Br^- ligands from $Pt(dien)X^+$ upon the nucleophilic reactivity constants of the entering halide nucleophile: △, rate from data of Gray for k_{Cl};[6] ▲, present work.

Experimental Section

The [Pt(dien)Cl]Cl was prepared by the method of Watt.[7] Solutions of LiCl, which served as the source of free chloride and $LiClO_4$ for the control of ionic strength, were prepared from recrystallized reagents. These reagents were required for compatibility with dioxane scintillator solutions used for counting the β rays of ^{36}Cl in a Beckman Liquid Scintillation System, LS 200. In exchange experiments a solution of ^{36}Cl was added to a solution of [Pt(dien)Cl]Cl in LiCl and $LiClO_4$ which had attained equilibrium with respect to the aquation reaction

$$Pt(dien)Cl^+ + H_2O \underset{k_{-s}}{\overset{k_s}{\rightleftharpoons}} Pt(dien)(H_2O)^{2+} + Cl^- \qquad (1)$$

Exchange was quenched by passing aliquots through a 50-cm exchange column, of 14-mm i.d., containing Amberlite IRA 400 resin in the ClO_4^- form.

The aquo ligand in the product of reaction 1 is a measurably strong acid. However, the equilibrium constant is so small that it has not been possible by manual titration techniques to evaluate the concentration of the aquo complex. However, by using an automatic titrator (Radiometer SBR2c/ABU1c/TTA3) such titrations could be completed in 30 sec and the equilibrium constant has been determined directly.

Results and Discussion

The results of the evaluation of concentrations of $Pt(dien)(H_2O)^{2+}$ by titrations are included in Table I.

TABLE I

AQUATION EQUILIBRIUM FOR $Pt(dien)Cl^+$

Temp, °C	Ionic strength, M	[$Pt(dien)Cl^+$], mM	10^4K_s, M
25.0	0.100	0.5–5.0	1.96 ± 0.03
25.0	0.318	0.5–5.0	2.52 ± 0.03
35	0.100	0.5–2.5	2.09 ± 0.01
35	0.318	0.5–2.5	2.43 ± 0.04

The values at μ = 0.100 M have been used in treating the exchange data. The values at the two ionic strengths are consistent with anticipated behavior of the ionic activity coefficients.[8] The K_s at 0.318 M is somewhat lower than the value of 3.7×10^{-4} M esti-

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(1) Work performed in the Ames Laboratory of the U. S. Atomic Energy Commission. Contribution No. 2848.

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(3) U. Belluco, L. Cattaline, F. Basolo, R. G. Pearson, and A. Turco, *J. Amer. Chem. Soc.*, **87**, 241 (1965).

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(6) H. B. Gray, *J. Amer. Chem. Soc.*, **84**, 1548 (1962).

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mated by Bahn and Martin,[9] who used a relatively imprecise tracer technique. A value of K_s can also be determined from the experimental values of k_s and k_{-s} reported by Gray and Olcott.[10] However, their studies were with very dilute solutions and the comparison must include the ionic strength effects. Such consideration predicts a value of 1.68×10^{-4} M at 0.100 M ionic strength, a rather satisfactory agreement.

For the exchange experiments the rate of exchange was evaluated from the half-time of exchange by means of the McKay equation.[11]

With a chloride concentration of 12 mM, the complex concentration was varied from 0.500 to 12.00 mM. With 5.0 mM complex, the chloride concentration ranged from 12.0 to 100 mM. In applying the McKay equation, account was taken of the extent of aquation according to eq 1. For each experiment a pseudo-first-order rate constant, k_{obsd} = (exchange rate)/[Pt(dien)-Cl^+], was evaluated. The observed exchange rate was represented by the normal equation which applies to many ligand substitution reactions of platinum(II)

$$k_{\text{obsd}} = k_s + k_{\text{Cl}}[\text{Cl}^-] \qquad (2)$$

Plots of k_{obsd} *vs.* $[\text{Cl}^-]$ are presented in Figure 2 for 25 and 35°.

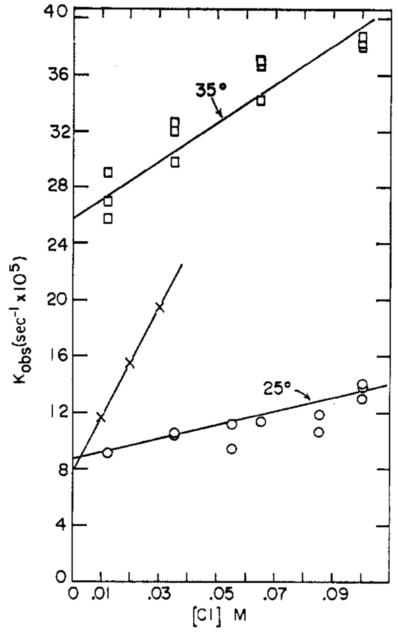

Figure 2.—Plots of k_{obsd} *vs.* $[\text{Cl}^-]$ with Pt(dien)Cl^+, ionic strength 0.10M. × represents points reported by Gray[6] for 25°.

The rate constants, indicated by a least-squares treatment of the data in Figure 2, and the kinetic parameters are included in Table II. Values for k_s, its $\Delta H^{\ddagger}$, and negative $\Delta S^{\ddagger}$ are substantially consistent with values indicated in a number of ligand substitution reactions.[5] It can be seen that k_{Cl} is not given precisely because the direct, second-order exchange process never contributes more than about 30% of the reaction.

TABLE II

RATE CONSTANTS AND KINETIC PARAMETERS FROM ISOTOPIC EXCHANGE STUDIES FOR Pt(dien)Cl^+ (μ = 0.100 M)

Temp, °C	$10^6 k_s$, sec^{-1}	$10^5 k_{\text{Cl}}$, sec^{-1} M^{-1}
25	87 ± 3	42 ± 5
30	258 ± 5	137 ± 11
$\Delta H^{\ddagger}$, kcal/mol	19 ± 1	21 ± 4
$\Delta S^{\ddagger}$, cal/mol deg	13 ± 3	−4 ± 13

The rate constant k_s is expected to be nearly independent of ionic strength. However, the process, described by k_2 should have a strong dependence upon ion strength since the transition state is formed upon the approach of two ions to one another. This dependence will be expressed by

$$k = k^0\Gamma(\mu) \qquad (3)$$

where k^0 is the value of the rate constant at zero ionic strength. Chan[12] has reported that for the second-order displacement reaction of Cl^- or Br^- from Pt-(dien)X^+ by I^- the ionic strength effect is described by the expression

$$\Gamma(\mu) = -1.05\mu^{1/2} \qquad (4)$$

The k_{obsd} values from Gray's experiments were resolved into k_s and k_{Cl} terms. The k_{Cl} term was corrected for ionic strength and then recombined with a k_s to give the k_{obsd} from a μ of 0.1 M. These values of k_{obsd} have also been included in Figure 2. The observed rate constants in the present work are seen to fall well below this curve.

The value of k_{Cl} for 25° from the present study was converted to zero ionic strength by eq 3 and 4. These are plotted in Figure 1 for the indicated nucleophilicity of Cl^-. It can be seen that this value falls closely on the line for replacements of chloride ligands by other nucleophiles. The plot also indicates that there is little difference between chloride and bromide as leaving groups from the platinum(II) complexes for this series of nucleophiles.

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