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Platinum Complexes with Olefins. IX.[1] Kinetics of Formation for Allyl Complexes[2]

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For reactions of type $PtCl_4^{2-}+ol\rightleftharpoons(ol)PtCl_3^-+Cl^-$ *the kinetics of the forward process have been examined in aqueous chloride media for* ol *equal to* $CH_2{:}CH.CH_2.NH_3^+$, $CH_2{:}CH.CH_2OH$ *and* $CH_2{:}CH.CH_2.SO_3^-$. *The forward rates are strictly first order in each of* $PtCl_4^{2-}$ *and* ol. *This observation and the fact that the rates are independent of chloride ion concentration exclude the possibility that a significant reaction path can involve the* $PtCl_3(H_2O)^-$ *ion. Enthalpies and entropies of activation for the forward and back reactions have been calculated from the temperature dependencies of forward rate constants and formation equilibrium constants. The differences in the measured rates and activation parameters, which are small, support the view that the changes in charge on the ligand result in several effects, some of which work in opposing directions. Stability constants and the enthalpy and entropy of formation for the above reaction where* ol $=$ $CH_2{:}CH.CH_2.SO_3^-$ *have been obtained.*

Introduction

In Parts III-V[4] of this series equilibrium studies are described for reactions of type

$$PtCl_4^{2-}+ol\rightleftharpoons(ol)PtCl_3^-+Cl^- \qquad (1)$$

for *ol* equal to various unsaturated ammonium ions and alcohols. In the present paper we report on the kinetics of formation of the complexes where *ol* is $CH_2{:}CH.CH_2NH_3^+$, $CH_2{:}CH.CH_2OH$ and $CH_2{:}CH.CH_2SO_3^-$. The series of ligands was chosen in order to maximize any effects which might arise through changing the charge on the ligand. Forward rate and equilibrium data for a range of temperatures have been used to calculate enthalpies and entropies of activation for forward and reverse reactions. As for the earlier studies, the solvent was aqueous 1.90 *M* NaCl and 0.100 *M* HCl, except where otherwise noted.

Experimental Section

Materials. The aqueous solvents used were prepared from deionized water and AnalaR reagents.

Solutions containing $PtCl_4^{2-}$ were prepared from Johnson Matthey potassium chloroplatinate(II) which was recrystallized twice from 0.1 *M* hydrochloric acid to minimize traces of platinum(IV). Solutions containing $PtCl_6^{2-}$ were prepared from a sample of potassium chloroplatinate(IV) which was recrystallized from 4 *M* hydrochloric acid.

Allylammonium perchlorate, prepared from allylamine and perchloric acid, was recrystallized from ethanol/ether. For characterization purposes trichloro(allylammonium)platinum(II) was prepared as previously described.[5] Found: C, 10.3; H, 2.4; N, 3.7; Pt, 54.2 $C_3H_8Cl_3NPt$ requires C, 10.0; H, 2.2; N, 3.9; Pt, 54.3).

Allyl alcohol (BDH laboratory reagent) was purified by fractional distillation before use.

Potassium allylsulphonate. Hydrated sodium sulphite (252 g.) and water (350 ml.) were brought to 60° and allyl bromide (125 g.) was added with stirring over about 2 hr. The mixture was held at 60° for an additional 4 hr. and then allowed to cool overnight while stirring was continued. After extraction with ether (discarded) the mixture was filtered, passed through a cation exchange column to convert all the sodium ions to hydrogen ions, and swept with nitrogen for about 12 hr. Bromide was removed quantitatively by filtration after reaction of the analyzed solution with an equivalent amount of moist silver oxide. The solution was then analyzed for sulphate which was then removed quantitatively by filtration following reaction of the solution with an equivalent amount of barium hydroxide. The solution was again passed through a cation exchange column in the hydrogen ion form after which it was neutralized with potassium hydroxide, evaporated to dryness on a rotatory evaporator, dissolved in the minimum volume of cold water, and cooled to 0°. The slow addition of acetone resulted in the formation of white crystalline flakes of the *product* which was washed with acetone and ether, and dried under vacuum at 80°. Analysis for potassium by ion exchange and for unsaturation by bromine consumption gave agreement with calculated values to within 1%.

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[1] Part VIII, R. G. Denning, F. R. Hartley and L. M. Venanzi, *J. Chem. Soc.*, (A), 1322 (1967).

[2] Throughout this paper the square brackets normally used to enclose Werner complexes have been omitted to avoid confusion with square brackets used as a symbol for concentration

[3] On leave from Boston University, Boston, Mass., as U.S. National Institutes of Health Special Fellow (1965-66).

[4] (a) R. G. Denning, F. R. Hartley and L. M. Venanzi, *J. Chem. Soc.* (A), 324 (1967); (b) R. G. Denning, F. R. Hartley, and L. M. Venanzi, *J. Chem. Soc.*, (A), 328 (1967); (c) F. R. Hartley and L. M. Venanzi, *J. Chem. Soc.*, (A), 330 (1967).

[5] R. G. Denning and L. M. Venanzi, *J. Chem. Soc.*, 3241 (1963).

(Found: C, 22.6; H, 3.0; S, 20.2. $C_3H_5KO_3S$ requires C, 22.5; H, 3.2; S, 20.0%).

Analyses. Platinum was determined spectrophotometrically by Sandell's method.[6] Carbon, hydrogen, nitrogen and sulphur were determined by Dr. A. Bernhard in the Micro-analytisches Laboratorium im Max Plank Institut, Mülheim (Ruhr), Germany.

Apparatus. Equilibria and rates were examined with use of a Unicam SP. 500 spectrophotometer fitted with a thermostated cell compartment. The temperature of the thermostat bath remained constant to ±0.1° and the temperature of the cell compartment was constant to ±0.2°.

Preparation of Reactant Solutions. Use was made of the following aqueous solvents:

Solvent 1. (2.00 *M* Cl^-, 1.90 *M* Na^+, 0.100 *M* H^+)

Solvent 2. (1.00 *M* Cl^-, 1.00 *M* ClO_4^-, 1.90 *M* Na^+, 0.100 *M* H^+)

Solvent 3. (2.00 *M* Cl^-, 1.80 *M* Na^+, 0.200 *M* H^+)

Solutions of potassium chloroplatinate(II) were prepared from the weighed vacuum dried salt (stored over phosphorus pentoxide). The concentrations of these solutions calculated from the weight of salt agreed to within ±0.5% with concentrations obtained by direct analysis of solutions for platinum.

Allylammonium perchlorate solutions were prepared from the weighed vacuum dried material. The concentration of a water solution of the salt, as determined by passing onto a cation exchange resin in the hydrogen form and titrating the eluted acid, agreed with the value calculated from the weight of the salt.

Allyl alcohol solutions were prepared by dissolving a measured weight of the pure liquid in solvent. Precise concentrations were determined by measurement of bromine consumption.[4c]

Potassium allylsulphonate solutions were prepared by dissolving the weighed vacuum dried material.

Acid Dissociation Constant for Allylsulphonic Acid. A solution of the acid was prepared by adding 0.0200 moles of potassium allylsulphonate to 10 ml. of 2.00 *M* perchloric acid, cooling to ice temperature, and after some minutes filtering off the potassium perchlorate. The resulting solution was analyzed for stoichiometric hydrogen ion by sodium hydroxide titration. A sample of the solution was then added to an equal volume of a 2.00 *M* NaCl solution containing a trace of picric acid. Comparison of the absorbance at 370 mμ for this solution with the absorbancies at this wavelength for a series of solutions consisting of mixtures of NaCl and HCl at total ionic strength 2, each of which contained the same stoichiometric trace concentration of picric acid as the test solution, enabled the equilibrium concentration of hydrogen ion in the allylsulphonic acid solution to be determined. The resulting value for the acid dissociation constant (equal to $[H^+][CH_2{:}CH.CH_2SO_3^-]/[CH_2{:}CH.CH_2SO_3H]$) was 7.8. From this value one estimates that in solvent 1, 98.7% of the allylsulphonate would be in the un-protonated form at 25°.

Determination of Equilibrium Constants for Complex Formation (K_1). For allylsulphonate ion equilibrium constants and the enthalpy and entropy of reaction were obtained in solvent 1, with use of methods described elsewhere.[4] As before, reaction (2) was taken into account.

$$PtCl_4^{2-} + H_2O \rightleftarrows PtCl_3(H_2O)^- + Cl^- \qquad (2)$$

The values of K_1 obtained, with standard deviations in parentheses, are: 35.0°, 2884 (±40); 45.0°, 2123 (±35); 55.6°, 1539 (±20). A plot of log K *versus* 1/T(°K) gives $\Delta H = -6.1\ (\pm 0.2)$ kcal mole^{-1} and $\Delta S = -4.1\ (\pm 0.7)$ e.u. These data for allylsulphonate together with corresponding values for allylammonium ion and allyl alcohol are tabulated below.

Determination of Rates. The rates of formation of the olefin complexes were observed also at 295 mμ with the platinum(II) concentration held close to 10^{-3} *M*. Solutions of potassium chloroplatinate(II) were generally prepared the day before each series of kinetic runs and were held in the thermostat to allow prior establishment of the aquation equilibrium (reaction (2)).[4a] Reacting solutions were kept in the thermostat bath and the reaction was followed by periodic removal of aliquots which were then rapidly examined in the spectrophotometer.

The concentration of complex at any time *t* could be calculated from

$$[(ol)PtCl_3^-] = [Pt]_T[(A_t - A_o)/A_c - A_o)] \qquad (3)$$

where $[Pt]_T$ is the stoichiometric platinum(II) concentration, A_t is the measured absorbance at the given time, A_o is the absorbance at zero time (obtained with use of a blank containing no olefin and by extrapolation of A_t values for the first few minutes back to zero time), and A_c is the absorbance which the solution would have *if* the reaction were to go to *completion* (with the conversion of all the platinum to $(ol)PtCl_3^-$). As first estimates for A_c one could use the measured values of A_t after equilibrium had been established (A_{oo}) in the cases where the olefin was in largest excess to the platinum. The actual value of A_c was obtained by correcting such measured A_{oo} values for the small amount of platinum not present as the olefin complex with use of the appropriate value of K_1. The maximum fraction of platinum which could be in the form of $PtCl_3(H_2O)^-$ was always very small (for solvent 1 at 25°, <0.7%)[4a] and the aquo complex was thus neglected in calculating the concentrations of $(ol)PtCl_3^-$ during progress of the reaction. The major contribution to the A_o values was from $PtCl_4^{2-}$, but contributions also arose from the trace concentrations of $PtCl_3(H_2O)^-$ and even smaller traces of $PtCl_6^{2-}$. No measurable differences in rates were observed, however, in cases where: (1) the potassium chloroplatinate(II) solutions were prepared immediately prior to kinetic runs to preclude prior establishement of the aquation equilibrium; (2) different preparations of potassium chloroplatinate(II) were used; and (3) aliquots of potassium chloroplatinate(IV) in excess to amounts which could be present in potassium chloroplatinate(II) were deliberately added to the system. Experiment (3) shows that

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(6) E. B. Sandell, "Colorimetric Determination of Trace Metals", Interscience, New York, 3rd edn., p. 726 (1959).

platinum(IV): (1) does not catalyze the reaction and (2) does not build up during the reaction. Under typical reaction conditions A_o values were in the range 0.018-0.022, while A_∞ values for the highest olefin concentrations were in the range 0.7-0.8.

The rates of formation of the olefin complexes were found to be strictly second order, being first order in each of the two reactants. No evidence was found for a ligand independent path, even though the reactions were studied over wide ranges of olefin concentrations (for allylammonium ion a 70-fold range in olefin concentration was used; for both allyl alcohol and allylsulphonate an 8-fold range was examined).

The rates of the back reaction are first order in one of the two products (complex) with no apparent dependence on the other (since chloride is at constant concentration).

When the free olefin concentration at zero time is significantly greater than the $PtCl_4^{2-}$ concentration, and especially for short reaction times, the reverse reaction need not be considered and the integrated rate expression for the forward reaction takes the simple form

$$\frac{1}{B_o-A_o}\log_{10}\frac{A_o(B_o-x)}{B_o(A_o-x)} = \frac{k_2}{2.303}t \qquad (4)$$

where k_2 is the second order forward rate constant, $A_o=[PtCl_4^{2-}]_o$ and $B_o=[ol]_o$ with the subscript indicating zero time, and $x=[(ol)PtCl_3^-]$. Individual values of k_2 were obtained for each kinetic run from the least squares straight line for the second order rate plot. The values obtained are listed below, where the numbers in parentheses refer to the standard deviations. The pairs of values refer to $ol\times10^3$ (M) and $k_2\times10^3$ (M^{-1} sec^{-1}) respectively:

Allylammonium Ion in Solvent 1.

T=25.0°: 5.00, 1.85 (±0.22); 10.0, 1.81 (±0.13);
15.0, 1.88 (±0.02); 20.0, 1.84 (±0.05);
25.0, 1.87 (±0.02); 30.0, 1.86 (±0.02);
35.0, 1.87 (±0.02).
Mean value of $k_2=1.86\ (\pm0.02)\times10^{-3}\ M^{-1}$ sec^{-1}.

T=35.0°: 5.00, 4.15 (±0.12); 10.0, 4.22 (±0.09);
15.0, 4.27 (±0.04).
Mean value of $k_2=4.21\times10^{-3}\ M^{-1}$ sec^{-1}.

T=45.0°: 5.00, 9.28 (±0.04); 10.0, 9.11 (±0.08);
15.0, 9.08 (±0.01).
Mean value of $k_2=9.16\times10^{-3}\ M^{-1}$ sec^{-1}.

Allylammonium Ion in Solvent 2

T=25.0°: 10.0, 1.93 (±0.04); 20.0, 1.90 (±0.02);
40.0, 1.86 (±0.02).
Mean value of $k_2=1.90\times10^{-3}\ M^{-1}$ sec^{-1}.

Allylammonium Ion in Solvent 3.

T=25.0°: 10.0, 1.84 (±0.02); 20.0, 1.83 (±0.08);
40.0, 1.84 (±0.02).
Mean value of $k_2=1.83\times10^{-3}\ M^{-1}$ sec^{-1}.

Allyl Alcohol in Solvent 1.

T=25.0°: 4.90, 1.018 (±0.100); 9.80, 1.028 (±0.013);
14.7, 1.032 (±0.022); 19.6 (1.019 (±0.019);
24.5, 1.041 (±0.008); 29.4, 1.031 (±0.012);
34.3, 1.031 (±0.005); 39.2, 1.034 (±0.008).
Mean of last 7 values of
$k_2=1.031\ (\pm0.016)\times10^{-3}\ M^{-1}$ sec^{-1}.

T=35.0°: 9.78, 2.44 (±0.03); 19.56, 2.44 (±0.02);
29.3, 2.41 (±0.01).
Mean value of $k_2=2.43\times10^{-3}\ M^{-1}$ sec^{-1}.

T=45.0°: 9.74, 5.28 (±0.04); 19.48, 5.26 (±0.03);
29.2, 5.24 (±0.01).
Mean value of $k_2=5.26\times10^{-3}\ M^{-1}$ sec^{-1}.

Allylsulphonate Ion in Solvent 1.

T=25.6°: 5.00, 0.889; 10.0, 0.877 (±0.025);
20.0, 0.873 (±0.010); 30.0, 0.875 (±0.007);
40.0, 0.875 (±0.010).
Mean value of $k_2=0.876\pm0.014\times10^{-3}\ M^{-1}$ sec^{-1}.

T=35.2°: 9.96, 1.88 (±0.05); 19.92, 1.87 (±0.03);
29.9, 1.90 (±0.02).
Mean value of $k_2=1.88\times10^{-3}\ M^{-1}$ sec^{-1}.

T=45.0°: 9.92, 4.07 (±0.09); 19.84, 4.09 (±0.02);
29.8, 4.08 (±0.01).
Mean value of $k_2=4.08\times10^{-3}\ M^{-1}$ sec^{-1}.

The mean values of k_2 in solvent 1 were used to obtain activation parameters from least squares plots of log k_2 *versus* 1/T (°K). The slopes of these plots, which were linear within the experimental limits of error in the k_2 values, allowed calculation of the activation energies and hence, by standard procedures,[7] the entropies of activation for the forward reaction. These values together with the enthalpies and entropies of reaction were used to obtain the enthalpies and entropies of activation for the reverse reaction.

Results and Discussion

The kinetic and thermodynamic values for reaction (1) in solvent 1 are given with probable limits of error in Table I.

The forward rates for reactions of type 1 are clearly first order in each of the two reactants, as shown by the linearity of the second order rate plots and the constancy of second order rate constants over wide ranges of olefin concentrations (see tabulated rate constants). That there is a strict first order dependence on olefin concentration may be demonstrated alternatively by plotting pseudo first order rate constants against initial olefin concentrations. Plots of this type exhibit excellent linearity with no indication of finite intercepts at zero olefin concentration for any of the three olefins examined. The rate law for the forward reactions thus takes the simple form:

$$\text{rate}=d[(ol)PtCl_3^-]/dt=k_2[PtCl_4^{2-}][ol] \qquad (5)$$

The form of the rate law most obviously suggests a mechanistic path involving direct reaction of $PtCl_4^{2-}$ with the olefin.

The possible existence of a contributing path involving aquation of $PtCl_4^{2-}$ to $PtCl_3(H_2O)^-$ (reaction (2)) followed by reaction of the aquo-complex with olefin (reaction (6)) nevertheless warrants careful examination, especially because of the commonly observed

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(7) *E.g.*, see J. F. Bunnett, in "Technique of Organic Chemistry", Eds. S. L. Friess, E. S. Lewis and A. Weissberger, Vol. VIII, Part 1, Interscience, New York, p. 199 (1961).

Table I. Kinetic and Thermodynamic Data for Reaction 1 in Solvent 1 at 25.0°. (k_2 and k_r refer to forward and reverse rate constants respectively; subscripts "f" and "r" on activation parameters refer to forward and reverse reaction, respectively).

	$CH_2{:}CH.CH_2NH_3^+$	$CH_2{:}CH.CH_2OH$	$CH_2{:}CH.CH_2SO_3^-$
K_1	$3.47\ (\pm 0.05) \times 10^3$ [a]	$1.63\ (\pm 0.06) \times 10^4$ [b]	$4.04\ (\pm 0.06) \times 10^3$
ΔH (kcal)	$-7.1\ (\pm 0.2)$ [a]	$-8.1\ (\pm 0.5)$ [b]	$-6.1\ (\pm 0.2)$
ΔS (e.u.)	$-7.6\ (\pm 0.7)$ [a]	$-7.8\ (\pm 1.5)$ [b]	$-4.1\ (\pm 0.7)$
$-T\Delta S$ (kcal)	$+2.3\ (\pm 0.2)$ [a]	$+2.3\ (\pm 0.5)$ [b]	$+1.2\ (\pm 0.2)$
k_2 (M^{-1} sec^{-1})	$1.86\ (\pm 0.02) \times 10^{-3}$	$1.03\ (\pm 0.02) \times 10^{-3}$	$8.32\ (\pm 0.14) \times 10^{-4}$
ΔH_f^* (kcal)	$+14.5\ (\pm 0.1)$	$+14.8\ (\pm 0.1)$	$+14.4\ (\pm 0.2)$
ΔS_f^* (e.u.)	$-22.5\ (\pm 0.4)$	$-22.6\ (\pm 0.4)$	$-24.3\ (\pm 0.7)$
$-T\Delta S_f^*$ (kcal)	$+6.7\ (\pm 0.1)$	$+6.8\ (\pm 0.1)$	$+7.3\ (\pm 0.2)$
k_r (M^{-1} sec^{-1})	$5.36\ (\pm 0.10) \times 10^{-7}$	$6.32\ (\pm 0.30) \times 10^{-8}$	$2.06\ (\pm 0.05) \times 10^{-7}$
ΔH_r^* (kcal)	$+21.6\ (\pm 0.3)$	$+22.9\ (\pm 0.6)$	$+20.5\ (\pm 0.4)$
ΔS_r^* (e.u.)	$-15\ (\pm 1)$	$-15\ (\pm 2)$	$-20\ (\pm 1.5)$
$-T\Delta S_r^*$ (kcal)	$+4.4\ (\pm 0.3)$	$+4.5\ (\pm 0.6)$	$+6.1\ (\pm 0.4)$

two-term law for substitution at platinum(II),[8,9] and more particularly because the $PtCl_4^{2-}$–$*Cl^-$ exchange appears to proceed entirely by means of reversible aquation even in solutions of moderately high chloride ion concentrations.[10] For our system the path under consideration is:

$$PtCl_4^{2-} + H_2O \underset{k''}{\overset{k'}{\rightleftarrows}} PtCl_3(H_2O)^- + Cl^- \qquad (2)$$

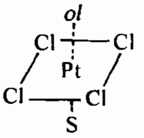
$$PtCl_3(H_2O)^- + ol \overset{k'''}{\rightleftarrows} (ol)PtCl_3^- + H_2O \qquad (6)$$

The observed simple second order rate law precludes the possibility that a significant reaction path can involve rate determining formation of $PtCl_3(H_2O)^-$ followed by its rapid reaction with olefin, or that the aquo ion can be maintained at steady state concentrations with comparable rates for its reaction with Cl^- and olefin. Maintenance of the aquo ion at equilibrium concentrations, however, would lead to the overall rate law

$$\text{rate} = \left\{ k_2' + \frac{k'k'''}{k''[Cl^-]} \right\} [PtCl_4^{2-}][ol] \qquad (7)$$

where the term in the braces would now represent the observed k_2. The maintenance of $PtCl_3(H_2O)^-$ at equilibrium or close to equilibrium concentrations would be unlikely, however, especially during the kinetic studies at higher olefin concentrations, because equilibration of $PtCl_4^{2-}$ with respect to the aquo ion is not particularly rapid.[10]

The kinetic experiments with allylammonium ion in solvent 2 were conducted with the object of obtaining a more clear cut conclusion on the possible role of the aquo ion. Solvent 1 and 2 have the same ionic strength but the latter has only one-half of the chloride ion concentration (one-half of the chloride in solvent 1 having been replaced by perchlorate). Although such a partial replacement of chloride by perchlorate results in a general change in the ionic atmosphere, such a change alone would be expected to have very little influence on the substitution rate.[11] The reduction in chloride ion concentration could nevertheless possibly have affected the reaction rate in two more specific ways. Firstly, the change from solvent 1 to solvent 2 would double the equilibrium concentrations of $PtCl_3(H_2O)^-$ (from 0.7% to 1.4% of the $PtCl_4^{2-}$)[4a] and should thus double any contribution to the overall rate arising from an aquo ion dependent path. Secondly, at the lower chloride concentration the concentration of species of type



($S = H_2O$ or ions of the electrolyte)

might be greater, since Cl^- would presumably be accommodated in axial positions more readily than ClO_4^-. Here too, the change from solvent 1 to solvent 2 might have been expected to result in an increase in rate. In practice, the change in solvent was observed to have no experimentally significant effect on the observed second order rate constant (for solvent 1 at 25.0°, $k_2 = 1.86\ (\pm 0.02) \times 10^{-3}\ M^{-1}$ sec^{-1}; for solvent 2 at 25.0°, $k_2 = 1.90\ (\pm 0.03) \times 10^{-3}\ M^{-1}$ sec^{-1}). The results indicate that a reaction path involving $PtCl_3(H_2O)^-$ can be of no importance in the $PtCl_4^{2-}$-allylammonium ion reaction, and it is reasonable to assume that a similar situation will prevail for the other olefins studied. The results also suggest that, for the solvents examined, the axial positions in $PtCl_4^{2-}$ will not be accommodated by a preponderance of chloride ions.

It can therefore be concluded that the substitution proceeds via a single mechanistic path involving direct reaction between $PtCl_4^{2-}$ and olefin. The most reasonable interpretation is that there is a rapidly established pre-equilibrium in which the incoming ligand becomes co-ordinated in an axial position, followed by rate determining displacement of a equatorial group (Cl^- for the forward reaction; olefin for the reverse reaction).[8] The interpretation that this rate determining process involves the formation of a five-coordinate trigonal bipyramidal intermediate is consistent with our observations.

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[8] (a) H. B. Gray, *J. Amer. Chem. Soc.*, *84*, 1548 (1962); (b) H. B. Gray and R. J. Olcott, *Inorg. Chem.*, *1*, 481 (1962); (c) F. Basolo and R. G. Pearson, *Progr. Inorg. Chem.*, *4*, 381 (1962); (d) U. Belluco, L. Cattalini, F. Basolo, R. G. Pearson, and A. Turco, *Inorg. Chem.*, *4*, 925 (1965).

[9] C. H. Langford and H. B. Gray, "Ligand Substitution Processes", Benjamin, New York, p. 22 (1965).

[10] L. F. Grantham, T. S. Elleman, and D. S. Martin, *J. Amer. Chem. Soc.*, *77*, 2965 (1955).

[11] See Ref. 9, p. 39.

It has been noted that aquo ions of platinum(II) are often highly reactive,[10,12] and it is of interest to speculate on possible reasons for the absence of the ligand independent path in our system. Preparative experiments show that the general chemical stability of olefins decreases as the overall positive charge of the complex increases. This is probably due to a contraction of the *d*-orbitals of the platinum atom and, consequently, a decrease in overlap with the olefin π^*-orbitals. A similar *d*-orbital contraction would occur when $PtCl_4^{2-}$ forms $PtCl_3(H_2O)^-$ and, therefore, the interaction between olefin and substrate would be lower in the case of the latter substrate leading to a large difference between reaction rates of the two substrates with olefins.

Because of the considerable precision with which the k_2 values could be measured, the enthalpy and entropy terms could also be obtained with a reasonable degree of precision. These values apply also, of course, to the presumed single reaction path.

Any attempt to interpret the measured quantities in Table I necessitates careful consideration of the various factors which could influence the values.

In considering differences between reactants and products, or between reactants and transition states, experimental ΔH and ΔS values will in general be a measure both of differences in internal bonding effects as well as differences in solute-solvent interactions. Among the various interactions, consideration should be given in the present case to the relative σ-donor and π-acceptor capacities of the olefins, differences in charge types for reactants, possible interactions between the solubilizing allyl substituents and other parts of the complexes, and the importance of differences in solute-solvent interactions.

In view of the complexities implied by the above considerations it is perhaps not surprising that the change from allylammonium ion (I) to allylalcohol (II) to allylsulphonate ion (III) does not appear to give rise to any particularly regular behavior.

The most stable of the three complexes is that formed by allyl alcohol. In attempting to explain this observation and particularly the relative ΔH and ΔS values for the three reactions, the following points should be considered: (a) the σ-donor capacities of the olefins should increase in the order I to III while the π-acceptor capacities should decrease from I to III, as judged from the Hammet σ_{meta} values for the $-NH_3^+$, $-OH$ and $-SO_3^-$ substituents;[13] (b) molecular models indicate the possibility of attractive interactions between a *cis*-chloride and the $-NH_3^+$ and $-OH$ groups of I and II; (c) because of the different charge types, decreases in solute-solvent interaction might be expected to accompany the reaction of I (which forms a zwitter ion), but such effects would be likely to become less marked, or even reversed, as one proceeds to the reactions of II and III. Several of the above factors will work in opposing directions in their effect on the relative stabilities and values of ΔH and ΔS.

In considering the rates of both forward and reverse processes there are again no obvious correlations of rate constants or activation parameters with charge type. This is not unexpected, particularly since charge type has been shown to be of little importance in some other platinum(II) substitutions,[14] and any such effects in the present case would be minimized by the necessarily high ionic strength. As with the thermodynamic properties, though, the changes in olefin are likely to have significant influences on such effects as σ- and π-bonding, solvation, etc. As the differences for the forward reactions are small, the differences in measured rates and activation parameters for the reverse reactions are more marked and are a moderate reflection of the measured differences in the thermodynamic values. Thus, the complex of allyl alcohol (II), which is thermodynamically the most stable of the three, is also kinetically the least reactive. While it is possible to rationalize the relative thermodynamic and kinetic parameters for the three reactions in terms of a plausible balance between π-acceptor capacities of the olefins, specific interactions between the solvating groups of the olefins and other parts of the complex, and solvation effects, it would be premature to attempt to spell out these suggestions in detail. Additional experimental information should first be sought.

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(12) See Ref. 9, p. 42.

(13) (a) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions", Wiley and Sons, New York, N. Y., p. 173 (1963); (b) H. H. Jaffé, *Chem. Revs.*, *53*, 222 (1953).

(14) D. S. Martin, *et al.*, see Ref. 9, p. 42.