1030. *Rates and Mechanism of Substitution Reactions of Five-Co-ordinate Platinum*(II) *Complexes*

By Ralph G. Pearson, Mariel M. Muir, and L. M. Venanzi

The rates of substitution reactions of five-co-ordinate complexes of platinum(II), $[PtX(QAS)]^+$, have been measured in methanol. The reactions are second-order, but the mechanism is complicated by the formation of ion-pairs. The usual order of nucleophile reactivity towards platinum(II) is observed, except that triphenylphosphine is much slower than expected, probably because of steric hindrance. These complexes are much slower to react than the analogous $[PdX(QAS)]^+$ or the square-planar $[PtX(TAS)]^+$.

A GREAT deal of work has been done on the mechanisms of substitution reactions of four- and six-co-ordinated metal complexes.[1] Square-planar metal complexes undergo substitution reactions with kinetics which obey a two-term rate law:

$$\text{rate} = k_1\,[\text{complex}] + k_2\,[\text{complex}][\text{Y}] \qquad (1)$$

where Y is a nucleophile. This has been interpreted as two simultaneous reactions, one with the solvent as the incoming nucleophile and the other with Y as the attacking nucleophile.[2]

The mechanism of substitution in octahedral complexes is quite different. The rate of the reaction does not depend upon the concentration of the incoming nucleophile,[3] except when Y is OH^-. Thus, the evidence indicates that a direct attack by the nucleophile Y on the complex to yield a seven-co-ordinate transition state does not occur. Several mechanisms have been proposed which are variations of a dissociation process.[4]

There has been little work done on the mechanism of substitution in five-co-ordinate complexes, although it is of interest to see whether such reactions would resemble those of four- or of six-co-ordinate compounds. There were no convenient systems available for study until a series of five-co-ordinate complexes of platinum(II) with the tetradentate ligand, tris-(*o*-diphenylarsinophenyl)arsine, $(o\text{-}Ph_2As{\cdot}C_6H_4)_3As$,(QAS) was recently synthesised.[5]

The complexes, [PtX(QAS)]X, where X = Cl, Br, I, or SCN, are 1 : 1 electrolytes and have a trigonal bipyramidal structure.[6] A square-planar complex, $[PtBr(TAS)]ClO_4$, has also been prepared, using the analogous ligand, bis-(*o*-diphenylarsinophenyl)phenylarsine $(o\text{-}Ph_2As{\cdot}C_6H_4)_2AsPh$,(TAS).[5]

A kinetic study of the substitution reactions of these complexes has been carried out to infer a possible mechanism for the reactions of the five-co-ordinate complex. Reactions studied were of the type:

$$[PtX(QAS)]^+ + Y^- \longrightarrow [PtY(QAS)]^+ + X^- \qquad (2)$$

Experimental

Materials.—The complexes $[PtCl(QAS)]ClO_4$, [PtBr(QAS)]Br, $[Pt(SCN)(QAS)]ClO_4$, [PtI(QAS)]I, $[PtI(QAS)]ClO_4$, $[PtBr(TAS)]ClO_4$, and [PdBr(QAS)]Br were samples whose preparations have been previously described.[5,7] $[Pt(N_3)(QAS)][BPh_4]$ was prepared from [PtCl(QAS)]Cl (0·1 g.) and sodium azide (0·1 g.) in methanol (100 ml.). The solution was set aside for 6 hr. at room temperature. $Na[BPh_4]$ (0·1 g.) in 50 ml. methanol was added and

---

[1] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Son Inc., New York, 1958, pp. 91—212.

[2] (*a*) F. Basolo, H. B. Gray, and R. G. Pearson, *J. Amer. Chem. Soc.*, 1960, **82**, 4200; (*b*) H. B. Gray, *J. Amer. Chem. Soc.*, 1962, **84**, 1548.

[3] (*a*) R. G. Pearson and R. D. Lanier, *J. Amer. Chem. Soc.*, 1964, **86**, 765; (*b*) ref. 1, p. 124.

[4] (*a*) T. P. Jones, W. E. Harris, and W. J. Wallace, *Canad. J. Chem.*, 1961, **39**, 2371; (*b*) C. H. Langford *Inorg. Chem.*, 1965, **4**, 265; (*c*) ref. 1, pp. 99—101.

[5] (*a*) T. E. W. Howell, S. A. J. Pratt, and L. M. Venanzi, *J.*, 1961, 3167; (*b*) J. A. Brewster, C. A. Savage, and L. M. Venanzi, *J.*, 1961, 3699.

[6] G. A. Mair, H. M. Powell, and L. M. Venanzi, *Proc. Chem. Soc.*, 1961, 170.

[7] C. A. Savage and L. M. Venanzi, *J.*, 1962, 1548.

after 1 hr. the yellow *crystals* which formed were filtered and recrystallised, first from acetone then from methanol (Found: C, 60·5; H, 4·04. $C_{78}H_{62}As_4BN_3Pt$ requires C, 59·7; H, 3·93%). All reagents used in kinetic studies were reagent grade. Reagent-grade absolute methanol was used without further purification, since the addition of 1% water caused no change in the rate of reaction.

Determination of Rates.—Spectrophotometric methods were used to follow the reactions. For each reaction the wavelength in the visible region which gave the maximum difference in absorbance between reactant and product complexes was selected. Stock solutions of the complexes in methanol were prepared ($4\cdot0 \times 10^{-4}$M). The spectra of these solutions showed no changes with time, and identical kinetic results were obtained for a given solution for various time intervals after mixing, so fresh solutions of the complex did not need to be prepared for each kinetic run. Methanol solutions of the ligands (Y) were mixed so as to give reaction mixtures with 10—100-fold excess of Y. All solutions were kept at 25° prior to mixing.

Measurements on the TAS complex were made with the stopped-flow method.[8] For the QAS complexes of platinum and $Y = CN^-$, $S{=}C(NH_2)_2$, SCN^-, and I^-, the stopped-flow technique was also used. For $Y = I^-$, PPh_3, and N_3^- the reactions were carried out in 1-cm. quartz cells in the thermostat-controlled cell compartment of a Beckmann DB or Cary 14 spectrophotometer. The reference cell in each case contained a reagent blank. The solution of ligand was added with a syringe. On the DB the chart drive on the attached recorder was started at the moment of mixing and the percentage transmittance was recorded against time, starting about 9 seconds after mixing. For reactions in the Cary 14, about 20 seconds elapsed between mixing and the start of the recording of absorbance *vs.* time.

For $Y = NO_2^-$ a different procedure was followed. The reaction was quite slow and was complicated by a subsequent light-sensitive reaction. Stable infinity readings and reproducible results were obtained by mixing the reactants in a flask which was wrapped in aluminium foil and kept in a water-bath at 25·0° ± 0·1°. At suitable time intervals aliquot portions were transferred to 1-cm. quartz cells in a Beckmann DU spectrophotometer. The transfer of solution and the measurement of its absorbance were carried out rapidly to avoid unnecessary exposure to light.

The analogous palladium complex, [PdBr(QAS)]Br, reacted very rapidly with all reagents. The stopped-flow method could be used to follow the slower reactions, but the limited solubility of the complex in methanol made these measurements quite difficult, since the change in transmittance observed during the reaction was only 2%.

The effect of changing the ionic strength of the solutions on the observed rates was studied on the complex $[PtBr(QAS)]^+$. When the nucleophile was iodide or thiocyanate there was no difference in the rates observed even when an excess (10-fold or greater) of bromide ion was added. It was therefore concluded that ionic-strength effects were not important, and no attempt was made to keep a constant ionic background.

The pseudo-first-order rate constants, k_{obs}, were obtained by plotting $\log 1/(A - A_\infty)$ against t, where A is the absorbance at time t and A_∞ the absorbance at infinite time. The slope of the line is equal to $K_{obs}/2\cdot303$. The reactions gave linear plots for several half-lives.

Several kinetic runs were made in which the concentration of the ligand was equal to or only slightly larger than the concentration of the complex. The usual first-order plot of $\log 1/(A - A_\infty)$ *vs.* t was made but only the initial points were used to give an initial slope and initial k_{obs}.

In all kinetic runs the value of A_∞ used was the observed value. Spectra of the complexes were taken with a Beckmann DK2 or a Cary 14 spectrophotometer. Reaction products were confirmed by comparing the spectrum of the final reaction mixture with the spectrum of the expected reaction product. This was done for all cases except for products from the reactions of $[PdBr(QAS)]^+$, $[PtBr(TAS)]^+$, and $[PtBr(QAS)]^+$ with triphenylphosphine. In these cases the expected products were not prepared and identified. In the latter reaction the rate was also measured by conductivity changes, in addition to spectroscopy. The final conductance corresponded to a 2 : 1 electrolyte.

Activation energies were obtained for some of the reactions by following the above procedures at temperatures other than 25° and making the standard Arrhenius plot.

Conductance measurements were made, to look for evidence of ion-pairs in solutions of the complexes. A Leeds and Northrup model Jones bridge was used for these measurements.

---

[8] J. W. Moore, Ph.D. Dissertation, Northwestern University, 1964.

RESULTS

When the pseudo-first-order rate constants obtained for the reaction of the QAS complexes of platinum with a large excess of ligand were plotted as in Figure 1, K_{obs} *vs.* [Y], straight lines with non-zero intercepts were obtained. Data from a typical set of reactions are listed in Table 1, and the intercepts and slopes, calculated by a least-square fit, are listed in Table 2. The data do fit a rate law like that observed for square-planar complexes:

TABLE 1

Observed rate constants for some reactions $[\mathrm{PtX(QAS)}]^+ + \mathrm{Y}^- \longrightarrow [\mathrm{PtY(QAS)}]^+ + \mathrm{X}^-$, $T = 25°$

X = Br, Y = SCN				X = Br, Y = N_3	
[Y] × 10^3M	k_{obs} (sec.$^{-1}$)	[Y] × 10^3M	k_{obs} (sec.$^{-1}$)	[Y] × 10^3M	k_{obs} (sec.$^{-1}$)
2·0	$2{\cdot}51 \times 10^{-1}$	4·0	$4{\cdot}4 \times 10^{-1}$	2·0	$1{\cdot}9 \times 10^{-3}$
,,	$2{\cdot}53 \times 10^{-1}$	5·0	$5{\cdot}6 \times 10^{-1}$	4·0	$2{\cdot}8 \times 10^{-3}$
3·0	$3{\cdot}6 \times 10^{-1}$	,,	$5{\cdot}4 \times 10^{-1}$	6·0	$4{\cdot}0 \times 10^{-3}$
,,	$3{\cdot}4 \times 10^{-1}$	8·0	$8{\cdot}5 \times 10^{-1}$	8·0	$4{\cdot}6 \times 10^{-3}$
4·0	$4{\cdot}8 \times 10^{-1}$	,,	$8{\cdot}2 \times 10^{-1}$		

TABLE 2

Data from straight-line plots of k_{obs} *vs.* [Y] (at 25·0°)

Complex	Y	Intercept[a] (sec.$^{-1}$)	Slope[b] (mole^{-1} sec.$^{-1}$)	Complex	Y	Intercept[a] (sec.$^{-1}$)	Slope (mole^{-1} sec.$^{-1}$)
$\mathrm{PtBr(QAS)]^+}$	CN^-	7·3	$1{\cdot}3 \times 10^{4}$	$[\mathrm{PtCl(QAS)}]^+$	I^-	$2{\cdot}5 \times 10^{-1}$	$6{\cdot}3 \times 10^{1}$
	$S{=}C(NH_2)_2$	$1{\cdot}8 \times 10^{-1}$	$1{\cdot}4 \times 10^{3}$		N_3^-	$1{\cdot}4 \times 10^{-3}$	$5{\cdot}6 \times 10^{-1}$
	SCN^-	$6{\cdot}3 \times 10^{-2}$	$9{\cdot}7 \times 10^{1}$		NO_2^-	$1{\cdot}1 \times 10^{-4}$	$3{\cdot}1 \times 10^{-2}$
	I^-	$1{\cdot}0 \times 10^{-1}$	$2{\cdot}9 \times 10^{1}$				
	$P(C_6H_5)_3$	8×10^{-4}	8·9				
	N_3^-	$1{\cdot}0 \times 10^{-3}$	$4{\cdot}6 \times 10^{-1}$				
	NO_2^-	$1{\cdot}8 \times 10^{-5}$	$1{\cdot}4 \times 10^{-2}$				

[a] Interpreted as k_{C}/K, see text.
[b] Interpreted as k_{IP}, see text.

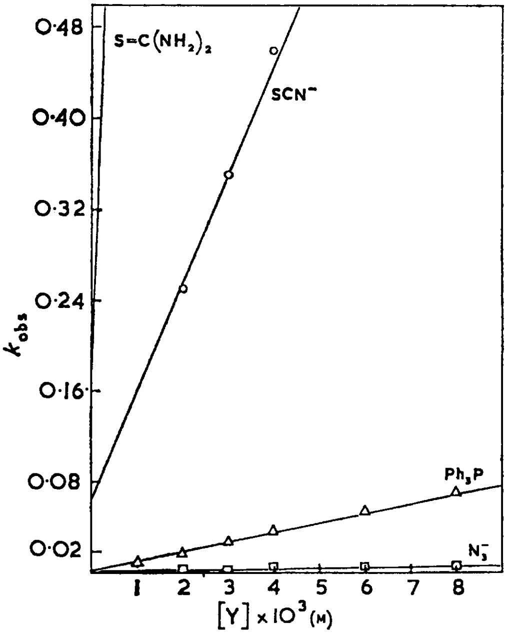

FIGURE 1. Plot of k_{obs} *vs.* [Y] for several nucleophiles, Y, with the complex $[\mathrm{PtBr(QAS)}]^+$

$$k_{\mathrm{obs}} = k_1 + k_2[\mathrm{Y}] \qquad (3)$$

The interpretation cannot be the same, however. The value of k_1, the intercept, would have to be the same for all ligands Y in methanol if the mechanism was like that discussed above for square-planar complexes, since in such a mechanism, k_1 is the rate obtained from the reaction of complex with solvent. The data in Table 2 clearly show large differences in the intercepts.

Previous work on square-planar complexes has shown other cases in which the value of k_1 varied. One explanation of a low value of k_1 is that there is competition between the leaving group and the entering nucleophile for the intermediate formed by the reaction of the complex with the solvent. This has been discussed by several workers,[2b, 9] who show that reactions at very low values of $[\mathrm{Y}]^-$can be used to find the true value of the rate constant. In these cases, the variation in the value of k_1 is small. The explanation will not account for variations of the magnitude observed in the intercepts listed in Table 2.

Thus, the behaviour of the plots of k_{obs} *vs.* [Y] was examined at low values of [Y], in order to check the values of the intercepts. If the graphs are linear, as drawn in Figure 1, then the initial rates should fall on the extrapolated portion of the line. If these initial rates are plotted with the other data (Figure 2) it is evident that the graph is linear only at the larger values of [Y], and has marked curvature at low values of [Y]. The rate at zero [Y] is apparently zero.

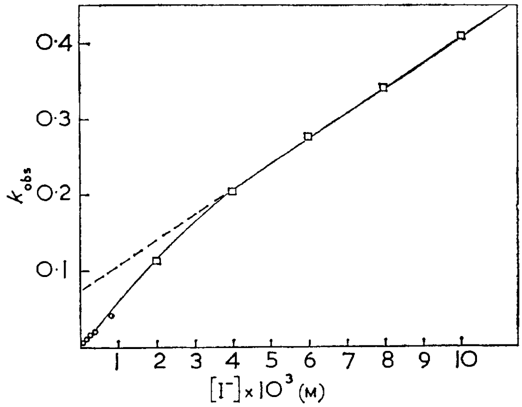

FIGURE 2. Plot of k_{obs} *vs.* $[\mathrm{I}^-]$ for the reaction of $[\mathrm{PtBr(QAS)}]^+$ with I^-:
○ initial values, for less than 10-fold excess of I^-;
☐ values for pseudo-first-order conditions

Any proposed mechanism for the reaction must account for both the linear and curved portions of the graph of k_{obs} *vs.* [Y]. If two second-order reactions were occurring, one between the complex and the ligand, and the other between an ion-pair of the complex and the ligand, a curve of the observed type would be obtained. To test for the presence of ion-pairs, the conductivities of solutions in methanol of $[\mathrm{PtI(QAS)}]\mathrm{ClO_4}$ with and without added amounts of potassium iodide were measured. If no ion-pairing occurs, the sum of the specific conductances of a solution of the complex and a solution of the iodide should be nearly equal to the specific conductance of a solution containing both the complex and the iodide, in the same concentrations used for the separate solutions. The data for various concentrations of complex and iodide are listed in Table 3. The sizeable deviations from additivity suggest appreciable ion-association. The spectral changes, which have been observed when the anion of a QAS complex is varied, support the idea that ion-pairs are formed in solution.[5b] A mechanism which fits the experimental facts is:

$$\mathrm{RX^+ + Y^-} \xrightleftharpoons{K} \mathrm{(RX^+, Y^-)} \tag{4}$$

$$\mathrm{RX^+ + Y^-} \xrightarrow{k_{\mathrm{O}}} \mathrm{RY^+ + X^-} \tag{5}$$

$$\mathrm{(RX^+, Y^-) + Y^-} \xrightarrow{k_{\mathrm{IP}}} \mathrm{(RY^+, Y^-) + X^-} \tag{6}$$

The rate law for this mechanism is:

$$\text{rate} = \frac{k_{\mathrm{O}}[\mathrm{Y}] + k_{\mathrm{IP}}[\mathrm{Y}]^2K}{1 + K[\mathrm{Y}]}(a - x) \tag{7}$$

$$k_{\mathrm{obs}} = \frac{k_{\mathrm{O}}[\mathrm{Y}] + k_{\mathrm{IP}}K[\mathrm{Y}]^2}{1 + K[\mathrm{Y}]} \tag{8}$$

---

[9] U. Belluco, L. Cattalini, and A. Turco, *J. Amer. Chem. Soc.*, 1964, **86**, 226.

TABLE 3

Conductivity data and equilibrium constants estimated from conductivity data

Solutes	M $\times 10^4$	Resistance, R $\times 10^{-4}$ (ohms)	Specific conductance $L \times 10^5$ (ohm^{-1} cm.$^{-1}$)	Λ_M (cm.^{2} mole^{-1} ohm^{-1})	K (mole^{-1})
$[PtI(QAS)]ClO_4$	1·33	2·80	1·54	116	
KI	1·33	2·82	1·53	115	
$[PtI(QAS)]ClO_4$	1·33	1·77	2·70	(101)[a]	$2·4 \times 10^3$
+KI	1·33				
$(1·54 + 1·53) - 2·70 = 0·37 = \Delta L.$ $\Delta\Lambda = 14$[b]					
$[PtI(QAS)]ClO_4$	1·00	3·50	1·15	115	
KI	2·00	2·08	2·25	112	
$[PtI(QAS)]ClO_4$	1·00	1·54	3·18	(105)[a]	$2·4 \times 10^3$
+KI	2·00				
$(1·15 + 2·25) - 3·18 = 0·22 = \Delta L.$ $\Delta\Lambda = 9$					
$[PtI(QAS)]ClO_4$	6·18	6·60	0·67	109	
KI	6·18	6·23	0·72	117	
$[PtI(QAS)]ClO_4$	6·18	3·88	1·26	(102)[a]	$3·8 \times 10^3$
+KI	6·18				
$(0·67 + 0·72) - 1·26 = 0·13 = \Delta L.$ $\Delta\Lambda = 11$[b]					

[a] These values are obtained using the sum of the concentrations of the complex and KI in the expression for Λ_M. [b] $\Delta\Lambda$ = the difference between the average of the molar conductances of the complex and KI, and the value calculated for the mixture as in (*a*).

where RX^+ = complex, (RX^+, Y^-) = ion-pair, a = original concentration of the complex, and x = concentration which has reacted.

Any possible solvent reaction path is ignored in this mechanism. The rate for a solvent path must be small, since it cannot exceed the smallest observed rate constant. In other words, the solvent rate constant cannot be much greater than the smallest intercept listed in Table 2. Also it was observed that the complexes are stable in methanol alone for a very long time. If piperidine is added to a solution of $[PtBr(QAS)]^+$ it does undergo a reaction which is much slower than the slowest reaction recorded in Table 2.

When $K[Y]$ is much greater than unity, equation (8) becomes:

$$k_{obs} = (k_C/K) + k_{IP}[Y] \qquad (9)$$

which is the equation of the straight line obtained at larger concentrations of Y. The slope is k_{IP}; the rate constant for the reaction of the ion-pair with Y, and the intercept is k_C/K, which is not a constant.

Separation of k_C and K would require fitting equation 8 using data at small [Y]. However, the values obtained in this region are of limited accuracy since they are obtained only from initial slopes and since the " initial " value of [Y] is not equal to the amount of [Y] put in solution, due to formation of ion-pairs. For these reasons, k_C and K cannot readily be separated.

Estimates of k_C and K can be made, however. It seems reasonable to assume that most of the variation in the intercepts is in k_C, with K remaining more or less constant for various ligands, since the range of values of k_{IP} is the same as the range of k_C/K. Two estimates of the order of magnitude of K can be made. The value of [Y] for which $K[Y]$ is no longer $\gg 1$ can be found by observing the point at which deviation from linearity occurs on the k_{obs} *vs.* [Y] curve. This gives $K \approx 10^4$ M^{-1} for Y = I^- and SCN^-. Conductivity data can also be used to estimate K, using the expression:

$$K = [RX^+, Y^-]/[RX^+][Y^-] \qquad (10)$$

$$[\text{ionic species}] = [RX] + [Y] = L \times 1000/\Lambda_{av.} \qquad (11)$$

$$[\text{ion pairs}] = [RX]_{initial} + [Y]_{initial} - [\text{ions}] \qquad (12)$$

where L = specific conductance of the solution and $\Lambda_{av.}$ = the average of the molar conductances of the complex and the anion, Y. Results of several calculations of K using the above procedure are given in Table 3. From this data, $K \gtrsim 3 \times 10^3$. The two estimates of K are fairly close. Using $K = 10^4$, the values of k_C are found to be of the same order as k_{IP}.

The reactions of [PtBr(TAS)]ClO$_4$ with I$^-$, SCN$^-$, CN$^-$, and S=C(NH$_2$)$_2$ were too fast to follow with the stopped-flow technique. The reaction with N$_3^-$ was within the limit of this technique, however. Assuming the mechanism observed for other square-planar complexes holds, the values of k_1 and k_2 were found to be 3·0 sec.$^{-1}$ and $3{\cdot}2 \times 10^3$ M^{-1}, respectively. A comparison with the data on the reaction of N$_3^-$ with [PtBr(QAS)]$^+$ shows that the square-planar complex reacts faster than the trigonal bipyramidal complex by about 10^4. The TAS complex is also much more reactive than other square-planar platinum(II) complexes which have been studied. This is presumably due to the very high *trans*-effect of arsenic compared to the much lower *trans*-effects of the groups usually present in the *trans*-position.

The [PdBr(QAS)]$^+$ complex reacted with N$_3^-$ at about the same rate as the TAS complex of platinum, but the experimental difficulties discussed earlier prevented an exact determination of the kinetic behaviour of the palladium complex. The order of magnitude of the rate is certain, however. For reaction with 2×10^{-3}M-azide ion, k_{obs} for [PdBr(QAS)]$^+$ is of the order of 10, and for [PtBr(QAS)]$^+$ k_{obs} is of the order of 10^{-3}, so that the palladium complex is 10^4 faster than the platinum complex.

The Arrhenius activation energies for three reactions were determined. The values listed in Table 4 refer to the reactions of the ion-pair, k_{IP}. Since both K and k_C will vary with temperature, the activation energy for the reaction of the free complex cannot be determined. The values of $\Delta S^‡$ are also recorded.

TABLE 4

Activation energies and entropies of activation for k_{IP}

Reactants	E_a (kcal./mole)	$\Delta S^‡$ (e.u.)
[PtCl(QAS)]$^+$ + I$^-$	12·1	−12·2
[PtBr(QAS)]$^+$ + I$^-$	11·2	−16·6
[PtBr(QAS)]$^+$ + N$_3^-$	12·5	−20·8

DISCUSSION

The kinetic data for reactions of QAS complexes of platinum clearly indicate a six-co-ordinate transition state, but examination of a model of the QAS complex shows that there is very little room for the attack on platinum by any reagent. Two of the more probable structures which can be drawn for the transition state are shown in Figure 3.

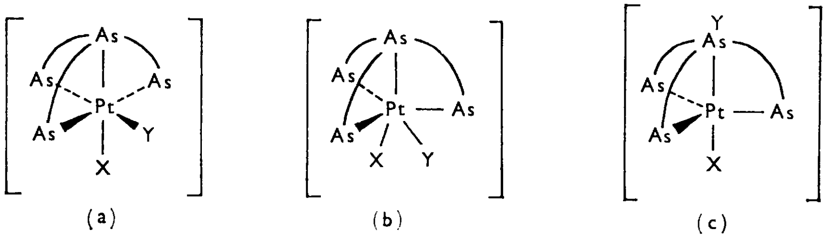

FIGURE 3. (a and b) Possible structure for the transition state in reactions of [PtX(QAS)]$^+$; (c) representation of the ion-pair formed by [PtX(QAS)]$^+$

Structure (*a*) shows a transition state with quasi-octahedral structure. Although this arrangement would cause distortion of the organic ligand in order to accommodate the attacking reagent, it is not unlikely. Stable octahedral complexes of the type [M$^{(n+)}$X$_2$(QAS)]$^{(n-2)+}$ have been isolated[10] and an X-ray-crystallographic study of [RuBr$_2$(QAS)] shows that the bond angles of the co-ordination octahedron range between 82° and 98°.[11] In this connection it is interesting to note that the structures of the complexes [PtX(QAS)]$^+$ are unlikely to be those of a *regular* trigonal bipyramid. This can be deduced from the visible and ultraviolet spectra of the complexes[12] and from the

[10] J. G. Hartley, L. M. Venanzi, and D. C. Goodall, *J.*, 1963, 3930, and previous references quoted therein.

[11] R. H. B. Mais, H. M. Powell, and L. M. Venanzi, *Chem. and Ind.*, 1963, 1204.

[12] G. Dyer and L. M. Venanzi, *J.*, 1965, 2771.

X-ray-crystallographic study of $[PtI(QAS)][BPh_4]$ which shows that in the equatorial plane the As–Pt–As bond angles are, 122°, 119°, and 103° and the As–Pt bond lengths opposite to these angles are 2·49, 2·43, and 2·45 Å, respectively.[6,12,13] The other transition state seems to be structure (*b*), in which the configuration of the QAS remains essentially unchanged, while the Pt–X bond is stretched and moves away from the vertical axis as the Pt–Y bond forms. The region around the ligand X is the least sterically hindered in the molecule. Examination of molecular models does not show which of the two models is the more likely.

Formation of associated species or ion-pairs has been postulated. For steric reasons it seems likely that something like structure (*c*) occurs. If the anion were in the region near X, rather than near the axial As atom as drawn, the attack by an unco-ordinated Y ion would be less probable than an attack by the Y co-ordinated in the outer sphere, which would not yield the term in $[Y]^2$ in the kinetic expression (8). Ion-pair formation between univalent ions in methanol is not unknown.[14] In the present case it is likely that Van der Waals' forces are more important than electrostatic forces. Both the complex and the various nucleophiles are quite polarisable, or "soft." Non-ionic thiourea and triphenylphosphine behave in the same way as the anionic ligands and only Van der Waals' forces can be invoked in these two cases.

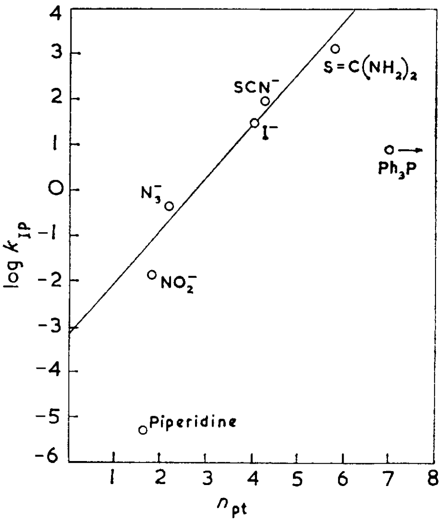

FIGURE 4. Plot of log k_{IP} for $[PtBr(QAS)]^+$ *vs.* n_{Pt}

The orders of reactivity of the ligands and of the complexes shows the importance of steric factors in the QAS complexes. The orders are:

$$CN^- > S{=}C(NH_2)_2 > SCN^- \sim I^- \sim Ph_3P > N_3^- > NO_2^- \gg C_5H_{11}N,$$

$$[PdBr(QAS)]^+ \sim [PtBr(TAS)]^+ \gg [PtBr(QAS)]^+ \gg [PtBr(dien)]^+.$$

The nucleophiles are in the order which has been observed[15] for planar(II) complexes with the exception of triphenylphosphine, which reacts much more slowly than expected with the QAS complex.

A more quantitative comparison is shown in Figure 4 in which log k_{IP} for $[PtBr(QAS)]^+$ is plotted against the n_{Pt} values of Belluco *et al.*[15] The n_{Pt} are relative rate constants for the substitution reactions of various Y ligands with *trans*-$[PtCl_2(py)_2]$. The solvent

---

[13] G. M. Mair and H. M. Powell, private communication.

[14] (*a*) R. G. Pearson, F. Basolo, and P. M. Henry, *J. Amer. Chem. Soc.*, 1957, **79**, 5379, 5382; (*b*) B. Bosnich, C. K. Ingold, and M. L. Tobe, *J.*, 1965, 4074.

[15] U. Belluco, L. Cattalini, F. Basolo, R. G. Pearson, and A. Turco, *J. Amer. Chem. Soc.*, 1965, **87**, 241.

methanol has $n_{\text{Pt}} = 0$ on this scale. A rough value for k_{IP} of piperidine is included in Figure 4. This comes from a single run at 0·3M-piperidine. The value of n_{Pt} to which it is compared is actually for NH_3. The figure shows evidence for abnormally slow reactions with the nucleophiles Ph_3P, NO_2^-, and piperidine. Also, the solvent rate constant is predicted to be about 10^{-3} sec.$^{-1}$, whereas our estimate is that the solvent rate constant is less than 10^{-5} sec.$^{-1}$. In all these cases it is likely that steric crowding in the transition state is responsible for the reduced reactivity. The slope of Figure 4 is 1·0, which is an intermediate value for the discrimination factor *S*.[15]

The difference in rate between $[PdBr(QAS)]^+$ and $[PtBr(QAS)]^+$ is of the same order as has been observed for planar complexes of the same two metal ions.[16] The difference in rate between the TAS and QAS complexes is large, 10^4, and probably arises because of the greater steric crowding in the QAS complex. In fact, the five-co-ordinated system can be regarded as being intermediate in its steric properties, and kinetic behaviour, between planar complexes, which are quite open to attack, and octahedral complexes which are closed to nucleophilic attack. However, the QAS complexes are less hindered than the "pseudo-octahedral" complex of Baddley and Basolo, $[PdBr(Et_4dien)]^+$, which behaves like a typical octahedral complex kinetically.[17]

The activation energies and entropies listed in Table 4 are quite similar to a number of others found for planar platinum(II) and gold(III) complexes.[18]

The authors thank Dr. G. Dyer for the preparation of, and spectral measurements on, several complexes, Dr. R. J. Mawby for a supply of QAS and helpful discussions, and Professor F. Basolo for several valuable suggestions. Mrs. M. M. Muir carried out the work during the tenure of a National Science Foundation Predoctoral Fellowship, 1962—1965. Computer time was furnished by the Northwestern University Computing Centre. This research was supported in part by the U.S. Atomic Energy Commission.

(R. G. P. and M. M. M.) DEPARTMENT OF CHEMISTRY,
NORTHWESTERN UNIVERSITY, EVANSTON, ILLINOIS.
(L. M. V.) INORGANIC CHEMISTRY LABORATORY,
UNIVERSITY OF OXFORD.

[*Received, March* 15*th*, 1965.]

---

[16] F. Basolo, J. Chatt, H. B. Gray, R. G. Pearson, and B. L. Shaw, *J.*, 1961, 2207.

[17] W. H. Baddley and F. Basolo, *J. Amer. Chem. Soc.*, 1964, **86**, 2075.

[18] W. H. Baddley, Ph.D. Dissertation, Northwestern University, 1964.