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# NUCLEOPHILIC SUBSTITUTIONS IN SQUARE-PLANAR GOLD(III) COMPLEXES

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Several studies have been made on the mechanism of nucleophilic substitutions in square-planar complexes of metals with $d^8$ electronic configuration; up till now, most of the data concern platinum(II) complexes. In fact the reaction rate with several substrates containing Pt is of the order of magnitude suitable to work with usual analytical techniques. There is, at the present time, only a small amount of information about the kinetic behaviour of complexes of other $d^8$ metals, such as $Rh^I$, $Pd^{II}$, $Au^{III}$. Two kinetic studies with complexes of gold(III) have been reported in the last few years. H. Taube[1] has studied the isotopic exchange $AuCl_4^-$–$^*Cl^-$ and Baddley and Basolo[2] report data about nucleophilic displacement of Cl with various reagents in $Au(dien)Cl^{2+}$.

In a systematic study with *trans*-complexes of platinum(II)[3] containing neutral ligands it was not possible to correlate kinetic data with the thermodynamic properties of the ligands present in the complex.

We have studied kinetics of reactions of the type:

$$AuLCl_3 + Y^- \rightarrow AuYCl_3^- + L$$

($L$ = heterocyclic amine, $Y^- = Cl^-, NO_2^-, N_3^-$), in methanol at 25 °C; the object was to see if it is possible to find a relation between the kinetic data and the thermodynamic properties of L. The complexes of this type are neutral and contain only one organic neutral ligand; this means that there are no problems of *cis-trans* isomerisation; the system is very simple indeed.

We expect, with a series of heterocyclic aromatic amines having different basicity, that by increasing the tendency of L to donate the lone pair of electrons to the metal, the substrate will become less electrophilic. We synthesized the complexes with the amines listed in Table I, the basicity covering a range of values of $pK_a$ from 4.95 to 6.75. The values of $pK_a$ are the measure of the basicity with respect to the proton in water; we consider that the change of solvent going from water to methanol will effect the values of $pK_a$ in a proportional way. We are quite confident in using the values of basicity with respect to the proton; in fact

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TABLE I

RATE CONSTANTS, $k_2$ $M \cdot sec^{-1}$, FOR THE REACTIONS: $AuLCl_3 + Y^- \rightarrow AuYCl_3^- + L$ IN METHANOL AT 25 °C.

| $L$ | $pK_a$ | $10^4 \cdot k_1$* | $k_2^{Cl^-}$ | $k_2^{NO_2^-}$ | $k_2^{N_3^-}$ |
|---|---|---|---|---|---|
| Quinoline | 4.95 | 3.0 | 0.245 | 1.47 | 29.1 |
| Isoquinoline | 5.14 | 5.8 | 0.245 | 6.82 | 72 |
| Pyridine | 5.17 | 7.5 | 0.417 | 6.75 | 108 |
| $\beta$-Picoline | 5.68 | 7.0 | 0.195 | 41.4 | 78 |
| $\gamma$-Picoline | 6.02 | 6.1 | 0.096 | 43.0 | 68 |
| 3,5-Lutidine | 6.34 | 7.0 | 0.090 | 34.5 | 51.2 |
| 2,6-Lutidine | 6.75 | 6.2 | 0.039 | 26.1 | 24.7 |
| *trans*-[$Pt(py)_2Cl_2$] | | $10^{-5}$ | $4.5 \cdot 10^{-6}$ | $6.8 \cdot 10^{-6}$ | $1.55 \cdot 10^{-5}$ |

* Values in $sec^{-1}$.

from information obtained using complexes of platinum(II)[3] it appears that complexes with pyridine and piperidine have a very similar kinetic behaviour (nucleophilic discrimination factor, N.D.F. equal to 1 and 0.91 respectively); it is possible to consider[4] that there is no appreciable $\pi$-interaction between empty orbitals of pyridine and full $d$-orbitals of platinum(II).

The complexes with pyridine and quinoline were prepared following the methods reported in the literature[5]. The complexes with other amines were obtained by using similar methods. With piperidine, toluidine and naphthylamine, we observe immediate reduction to metallic gold.

The solubility of all the compounds $LAuCl_3$ in methanol is small; it was possible to follow all the reactions in pseudo-monomolecular conditions (excess of $Y^-$) by spectrophotometric techniques, operating in the ultraviolet region of the spectra. We found that the rates of reactions investigated follow the two terms rate law given by:

$$\text{rate} = k_1[\text{complex}] + k_2[\text{complex}]\,[Y^-]$$

which is usually found in all nucleophilic substitutions in planar complexes[6]. $k_1$ is the rate constant for the solvent path and $k_2$ is for the direct reagent path[3,7].

The first stage of all the reactions always corresponds to the displacement of the organic neutral ligand; this is quite evident in the reactions with $NO_2^-$ and $N_3^-$, in which only the rate of the first step is in fact dependent upon the nature of L; this is also confirmed in the reactions with $N_3^-$ by the fact that, after the first stage, there is an isosbestic point which is independent both in wavelength and extinction coefficient of the substrate used. Speaking in the same terms as with the complexes of platinum(II), it may be possible to say that in these systems the *trans*-effect of chloride is larger than that of one heterocyclic amine; but of course at present time we don't really know if it is possible to speak of *trans*-effect with gold(III) complexes.

In methanol, there is no reduction to gold(I) or metallic gold during the time necessary to follow the substitutions, but a slow, probably photochemical, reduction to metallic gold can be observed in a few days. At the same time the complexes are quite stable in methanol in respect to solvolysis and the solutions obey Beer's law. No difference in reactivity is found by using LiCl or HCl as reagents; this indicates that the reactions go to completion. The addition of a small amount of water to methanol does not appreciably affect the results.

Apart from the reactions with $Cl^-$ when $AuCl_4^-$ is formed, we were unable to isolate the reaction products. With $N_3^-$ and $NO_2^-$ the products are unstable and in attempting to isolate the product from a stoichiometric reaction with $NaN_3$, we obtained a very small amount of a very explosive solid.

In reactions both with $N_3^-$ and $NO_2^-$, the succeeding steps are slower than the subsitution of L. This does not mean that a possible *trans*-effect is absent. In fact reaction between a negative substrate and a negative entering group is unlikely to give a transition state with two negative charges.

The results are summarized in Table I. In the same table there are some results with one platinum(II) complex, for purposes of comparison.

The reactivity of gold(III) complexes is higher than that of platinum(II) complexes; this agrees with the results of Taube[1], Baddley and Basolo[2] and may indicate, as suggested[2], the great importance of the bond-making in the transition state. This fact is probably related to the different effective nuclear charge, acting on the orbitals which are used to form the penta-coordinated transition structure.

To correlate the results obtained with the various complexes we used the ratio $k_2/k_1$ between the constant for the reaction with the nucleophilic agent $Y^-$ and that for the reaction with the solvent. This ratio is, in fact, a discrimination factor for every complex between various nucleophilic agents; in this way it is possible to neglect some factors concerning the leaving group, as for instance the change in solvation of L in the formation of the transition state; we consider that some factors concerning the leaving group are—in first approximation—independent from the nature of the entering group. Any way, the same considerations may be made using the values of $k_Y$ (with less precision); it is another indication of the great importance of the bond-making in all these processes.

Considering the reactions with chloride ion, it is possible to observe that, plotting as in Fig. 1, $\log (k_2^{Cl}/k_1)$ *versus* $pK_a$, a straight line is obtained. The ratio decreases (as does the reactivity itself) as the $pK_a$ increases; in other words it decreases with increasing ability of L to donate negative charge to the metal in a $\sigma$ fashion.

The substrate with more negative charge near the metal will be less electrophilic and will be involved with more difficulty in a nucleophilic attack; in other words, it is more difficult to form the transition state with the negative incoming group; at the same time we must point out that the reactivity towards the solvent (neutral nucleophilic agent) does not change very much with the nature of L (see values of $k_1$ in Table I).

It is impossible to expect such a simple relationship in the reactions with

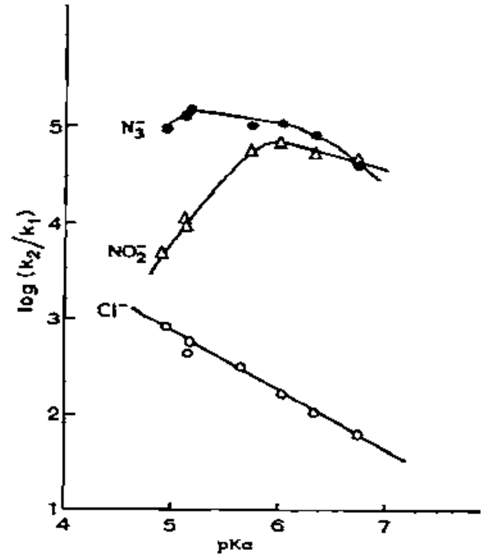

Fig. 1. Plot of log $(k_2/k_1)$ *versus* $pK_a$.

$NO_2^-$; this entering group is well known to have a particular behaviour; when acting as a nucleophile, some electrophilic ability is also developed, the energy of an empty antibonding M.O. being lowered making it able to accept charge in a $\pi$-fashion from the filled *d*-orbitals of the metal. This behaviour was found in platinum(II) complexes[7,8] ("biphilicity of $NO_2$") as well as in some octahedral complexes of ruthenium[10] ("amphilicity"). The same is true for $N_3^-$ but is not so important, because the empty antibonding orbital is not in a position for good overlap with the *d*-orbitals of the metal[9]. In fact, in kinetics with platinum(II) complexes the behaviour of $N_3^-$ is that of a nucleophilic reagent; it may be that in gold(III) complexes the great importance of the bond-making is to be related with the observation of the small "biphilicity" of azido ion.

It is possible to explain the results of the reactions with azido and nitrito ions, as they appear in Fig. 1, by considering that increasing $pK_a$ first of all stabilizes the transition state by $\pi$-interaction with a better delocalization of the negative charge. On the other hand, the bond between the metal and the leaving group becomes stronger and the electrophilicity of the substrate decreases; this should lead to a decrease in reactivity which we do indeed observe in the reactions when the reagent has no electrophilic properties, *e.g.* with chloride. With the amines having lower values of $pK_a$ the first effect predominates but a point is reached where the second effect becomes predominant.

Al the same time it should be pointed out that $NO_2^-$ and $N_3^-$ are generally more similar to one another in these reactions than in those with platinum(II) complexes, where $NO_2^-$ is more like $Cl^-$ (data reported in Table I and ref. 3); in the reactions with $Au^{III}$ complexes basicity could be more important in determining the order of reactivity, because of the different nuclear charge; in fact, basicity becomes an increasingly important factor in determining nucleophilic reactivities as the positive charge on the substrate increases[11].

Finally one different type of observation should be made; in all cases the behaviour of the complex with 2,6-lutidine is well related with that of the other complexes; this means that the methyl groups in α-positions do not have an appreciable different interaction with the rest of the substrate in the ground state and in the transition state. In other words there is no retardation due to steric effects and all the kinetic data can be discussed without taking into consideration, steric hindrance.

The results lead to the conclusion that, using a series of ligands with different basicity unable to interact in a π-fashion with the metal, it is possible to observe a simple relationship in reactions with such simple nucleophilic agents as the chloride ion; the sequence of basicity in respect to the proton is maintained in respect to gold(III).

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