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Mechanisms of Reactions of Binuclear Complexes. I. Cleavage by Olefins of a Halogen-Bridged Complex of Platinum(II)[1]

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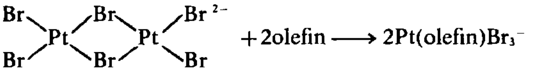
The rates of cleavage reactions of the halogen-bridged, binuclear complex, $[(C_2H_5)_4N]_2[Pt_2Br_6]$, with several olefins were determined in acetone. The rate law was similar to that observed for cleavage of the complex with amines: rate $= (k_1 + k_2[\text{olefin}])[Pt_2Br_6^{2-}]$, but the reactions were slower than the reactions with amines. Unsymmetrical cleavage occurred with the bidentate olefin, 1,5-cyclooctadiene, but all monodentate olefins gave symmetrical cleavage. The rate determining step in the proposed mechanism is cleavage of one bridge by either solvent or nucleophile to give a singly bridged species which is cleaved rapidly to yield products.

Introduction

Halogen-bridged binuclear complexes of platinum(II) are of interest since they can be useful starting materials for otherwise difficult syntheses[2,3] and have been proposed as intermediates in reactions of mononuclear complexes.[4,5] The rates of cleavage of such complexes with monoamines have been studied.[6] The mechanism proposed was similar to mechanisms for substitution reactions of planar complexes. The rate determining step was postulated as the bimolecular attack by either solvent or amine on one platinum, resulting in cleavage of one bridge. Cleavage of the second bridge then occurred rapidly.[6] Reactions of similar complexes with olefins have been reported.[7] Since the reactions are apparently much slower than those with amines, it seemed of interest to study the reactions with a variety of olefins to see if the mechanism is similar for a different type of nucleophile.

The reactions were:



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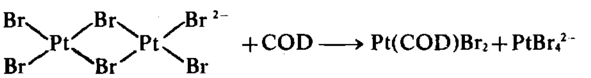

(2)

where olefin = allyl alcohol, 1-hexene, styrene, and cyclohexene, and COD = 1,5-cyclooctadiene. Acetone was used to allow comparison with the reactions of the complex with amines[6] and to facilitate isolation of the products of reaction.

Experimental Section

Materials. Acetone was dried over potassium carbonate for several days and fractionally distilled from Drierite, (bp, 56°). Allyl alcohol was dried over potassium carbonate and distilled, (bp, 97°). Cyclohexene was refluxed over metallic sodium for seven hours and fractionally distilled, (bp, 83°). Styrene was dried over Drierite for several days and vacuum distilled. The middle fraction was collected. 1-Hexene was dried over Drierite and fractionally distilled, (bp, 63°). 1,5-Cyclooctadiene was dried over Drierite and distilled, (bp, 151°).

Complexes. $[(C_2H_5)_4N]_2[Pt_2Br_6]$ was prepared by the method of Harris *et al.*[8] $[(C_2H_5)_4N][Pt(CH_2CHCH_2OH)Br_3]$ was prepared by the addition of an excess of hot allyl alcohol to 0.1 g of $[(C_2H_5)_4N]_2[Pt_2Br_6]$ in 10 ml of acetone. After two days the volume was reduced and yellow needles were obtained. *Anal.* Calcd. for $C_{11}H_{26}NOBr_3Pt$: Pt, 31.3. Found: Pt, 30.8. $[(C_2H_5)_4N][Pt(\text{hexene})Br_3]$ was prepared by the addition of 1.7 ml of 1-hexene to 0.05 g of $[(C_2H_5)_4N]_2[Pt_2Br_6]$, followed by dilution to 50 ml with acetone. When no further change was observed in the spectrum of the mixture, the solution was taken to dryness. The yellow-orange oil was dissolved in 50 ml of ether and cooled in a dry ice-ethanol bath to give a yellow-tan product. *Anal.* Calcd. for $C_{14}H_{32}NBr_3Pt$: Pt, 30.0. Found: Pt, 29.8. $[(C_2H_5)_4N][Pt(\text{styrene})Br_3]$ was prepared by the addition of 1 ml of a 0.177 *M* acetone solution of styrene to an acetone solution containing 0.100 g of $[(C_2H_5)_4N]_2[Pt_2Br_6]$. The mixture was left standing at room temperature for four days. Evaporation of the acetone yielded an orange oil which was treated with acetic acid to yield an orange solid, mp 115° dec. *Anal.* Calcd. for $C_{16}H_{28}NBr_3Pt$: Pt, 29.1. Found: Pt, 28.8. $Pt(COD)Br_2$ was prepared by the addition of 1 ml of a 0.177 *M* acetone solution of 1,5-cyclooctadiene to an acetone solution containing

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[1] Taken from the thesis submitted by E. M. C. to the University of Puerto Rico in partial fulfillment of the requirements for the degree M. Sc.

[2] J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 3858 (1955).

[3] S. E. Livingstone and A. Whitley, *Aust. J. Chem.*, *15*, 175 (1962)..

[4] J. E. Teggins, D. R Gano, M. A. Tucker, and D. S. Martin, Jr., *Inorg. Chem.*, *6*, 69 (1967).

[5] J. E. Teggins and D. S. Martin, Jr., *Inorg. Chem.*, *6*, 1003 (1967).

[6] R. G. Pearson and M. M. Muir, *J. Am. Chem. Soc.*, *88*, 2163 (1966).

[7] J. Chatt, N. P. Johnson, and B. L. Shaw, *J. Chem. Soc.*, 1662 (1964).

[8] C. M. Harris, S. E. Livingstone, and N. C. Stephenson, *J. Chem. Soc.*, 3697 (1958).

0.100 g of $[(C_2H_5)_4N]_2[Pt_2Br_6]$. The mixture was left standing for four days. At the end of this period the solution was taken to dryness. Shiny yellow crystals were formed. *Anal.* Calcd. for $C_8H_{12}Br_2Pt$: Pt, 42.1. Found: Pt, 42.0. Analyses for platinum were done by ignition of the samples.

Rates of Reaction. Reactions were carried out in acetone with a large excess of olefin to give pseudo first-order conditions. The concentration of the complex was 1.0×10^{-3} *M* in most cases. Standard spectrophotometric techniques were used to follow the reactions. To the complex in a 1 cm quartz cell in the thermostated cell compartment of a Hitachi-Perkin Elmer 139 spectrophotometer was added the thermostated solution of the olefin and the transmittance was recorded as a function of time on a Heath EU20-M recorder. A syringe was used for mixing so that recording could begin within ten seconds of mixing. Pseudo first-order rate constants were obtained from plots of $\log(1/(A_t-A_\infty))$ against time, where A_t is the absorbance at time *t* and A_∞ is the absorbance after ten or more half-lives. These plots were linear for several half-lives and final absorbance values were stable well beyond ten half-lives. Arrhenius activation energies were determined by measuring the rates at several temperatures. Products were confirmed by comparing the spectrum of the final reaction mixture with the spectrum of the expected product. In some cases the products could be isolated from the reaction mixture.

Results and Discussion

The dependence of the pseudo first-order rate constants, k_{obs}, on the concentration of the olefin was found by plotting k_{obs} against the concentration of the olefin, as shown in Figure 1. Straight lines with small, non-zero intercepts were obtained. The rate law can be written:

$$\text{rate} = k_{obs}[Pt_2Br_6^{2-}] = (k_1+k_2[Y])[Pt_2Br_6^{2-}] \qquad (3)$$

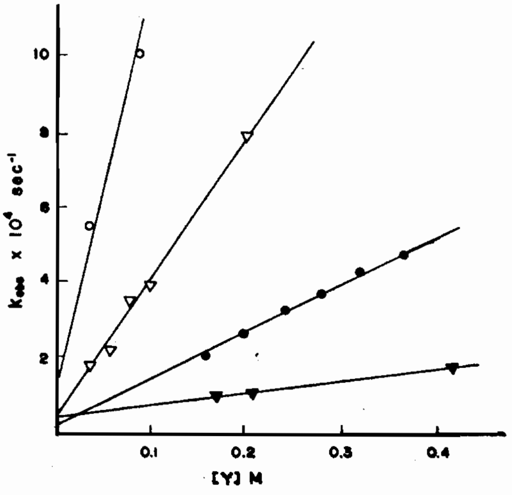

Figure 1. Dependence of k_{obs} on the concentration of olefin for reactions of $Pt_2Br_6^{2-}$ in acetone ○, allyl alcohol; ▽, 1,5-cyclooctadiene (COD); ●, 1-hexene; ▼, styrene.

where k_2, the slope, is interpreted as the rate constant for initial cleavage by an olefin and k_1, the intercept, as the rate constant for initial cleavage by the solvent. Values of k_2 are given in Table I. Only the order of magnitude of k_1 could be determined. The values were between 10^{-5} and 10^{-4}, which means they fall within the limits of error of the values of k_1 which were previously reported for reactions with amines.[6] This supports the idea of k_1 as the rate constant for the solvent path.

Table I. Second order Rate Constants for Reactions of $Pt_2Br_6^{2-}$ in Acetone with Olefins

Temp., °C	Olefin	10^2k_2, M^{-1} sec^{-1}
24.4	styrene	0.0410 [a]
	1-hexene	0.138
	COD	0.270
	cyclohexene	slow [b]
25.0	allyl alcohol	1.18
13.9	1-hexene	0.0765
	COD	0.241
15.0	allyl alcohol	0.933
33.4	1-hexene	0.164
	COD	0.390
35.0	allyl alcohol	1.86

[a] Standard deviations in k_2 were about 5% of the value of k_2, obtained from least squares analyses of the data. [b] Reactions with cyclohexene did not go to completion.

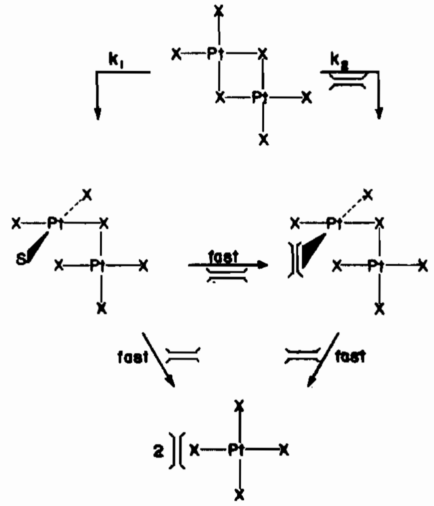

Figure 2. Mechanism proposed for cleavage of $Pt_2Br_6^{2-}$ by Olefins S, solvent; $\succ\!=\!\prec$, olefin.

Thus, both the rate law and the magnitudes of the rate constants indicate that cleavage proceeds by the mechanism shown in Figure 2. The spectral changes during the reaction suggest that k_1 and k_2 correspond to cleavage of the first bridge by solvent or olefin, respectively. Cleavage of the second bridge and replacement of the solvent by nucleophile occur in rapid subsequent steps. The second-order rate constants for olefins were smaller than those for amines,[6] which is in general agreement with rate studies in square planar complexes.[9] The differences in the second-order rate constants for the monoolefins are readily understood in terms of steric effects. Reactions with cyclohexene did not go to completion, and the approach to equilibrium was slow.

The bidentate olefin, 1,5-cyclooctadiene (COD), gave rates of the same magnitude as the other olefins. Pseudo first-order plots were linear for several half-lives, and there was no evidence in the kinetics for further reactions. The final spectrum of the reaction mixture in acetone corresponds to the formation of the chelated product, $Pt(COD)Br_2$. A preparative scale reaction, however, showed clearly that two products were formed, $Pt(COD)Br_2$ and $PtBr_4^{2-}$, which precipitated from acetone solution as the tetraethylammonium salt. Several kinetic runs were repeated and careful examination revealed precipitate on the bottom of the cell. The solution remained clear. When reactions of the complex with COD were carried out in N,N-dimethylformamide, the $PtBr_4^{2-}$ which formed remained in solution and eventually reacted with excess COD to give $Pt(COD)Br_2$. The kinetics showed marked deviation from linearity in pseudo first-order plots, which indicated that the subsequent reaction of the $PtBr_4^{2-}$ was not sufficiently rapid to be a fast subsequent step like the fast steps indicated in Figure 2. This is the expected result if the species reacting is really $PtBr_4^{2-}$ and not a solvated species, $Pt(solvent)Br_3^-$, since such solvated species react rapidly in the case of monodentate olefins or amines.[6]

In other words, the second halogen bridge is not cleaved before the step in which the second olefin in the cyclooctadiene forms the chelate. Presumably, it is the chelation step itself which cleaves the second bridge. If the second cleavage occurred more rapidly than chelation, then, by analogy to the reactions of monoolefins, there should be rapid formation of two molecules of $Pt(COD)Br_2$, not one. Since $PtBr_4^{2-}$ was formed and reacted slowly, not rapidly, the singly bridged intermediate shown in Figure 2 must have a life-time sufficiently long to allow chelation of the diolefin to occur.

Activation parameters for the bimolecular reactions between olefins and the bridged complex are given in Table II. Values for reaction of the same complex with pyridine[10] and ethylenediamine[11] are included for comparison. The enthalpy of activation, ΔH^*, and entropy of activation, ΔS^*, were derived from the Arrhenius activation energies, E_a, for k_2.[12] The deviations in k_1 were too large to permit determination of the activation energies. The values for the amines in Table II are similar to values reported for reactions in other d^8 complexes.[13] For the olefins, the values for ΔS^* are more negative, which can indicate both rigidity in the transition state and the importance of bond-making. The values are probably reasonable in view of the restrictions on the geometry for bonding between metal ions and olefins. The smaller ΔH^* values for olefins also seem reasonable. The large *trans* effect of an olefin is normally explained by its ability to stabilize, through π-bonding, the five-coordinated transition state. This same effect should give a lower ΔH^*.

Table II. Activation Parameters for Cleavage of $Pt_2Br_6^{2-}$ in Acetone

Reagent	ΔH*, kcal/mole [a]	ΔS*, eu
allyl alcohol	5.5	—49
COD	3.6	—58
1-hexene	6.3	—51
pyridine [b]	10	—33
ethylenediamine [c]	7.2	—36

[a] Deviations in ΔH* are less than 1 kcal/mole. [b] Values taken from reference 10. [c] Values taken from reference 11.

Thus all the experimental evidence suggests a mechanism for reaction of halogen-bridged complexes of Pt^{II} with olefins like that for reaction with amines in which the rate determining step is cleavage of the first bridge. The singly bridged species lasts long enough for unsymmetrical cleavage to occur with the chelating diolefin, COD. The initial cleavage follows the same rate law as that observed for reactions of square planar complexes, as expected from the geometry of the complex.

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