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The Formation of π-Olefinic Platinum(II) Complexes Catalyzed by Free Olefins[1]

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The rate of chloride displacement in the reaction $PtCl_4^{2-}$ + olefin $\rightarrow$ Pt(olefin)Cl_3^- + Cl^- (where olefin is allyl alcohol, allylsulfonate anion, or *trans*-crotylammonium cation) is increased by the presence of allyltriethylarsonium cation (L_π). The rate of ethylene absorption is also increased. The kinetic data relative to these reactions in water (1.9 *M* NaCl and 0.1 *M* HCl at three different temperatures) are reported. The kinetics obey the two-term rate law $k_{obsd} = k'[L_\pi] + k''\cdot$[olefin]. The results are discussed in terms of the *trans*-labilizing power of the catalyst olefin. The k' term is related to a bimolecular attack of L_π on $PtCl_4^{2-}$, followed by the fast entry of the incoming olefin *trans* to L_π leading to the formation of a labile intermediate which then loses L_π to give the thermodynamically stable product, Pt(olefin)Cl_3^-. The same product can be obtained by direct attack of the olefin on $PtCl_4^{2-}$.

Introduction

It is already known that olefins coordinated to transition metals can undergo fast exchange reactions with free olefins. In the case of Zeise's salt the rate of ethylene exchange has been found to be so fast, even at −80°, that the kinetics cannot even be followed by nmr techniques.[3] On the contrary, the rate of coordination of an olefin to platinum(II) in homogeneous conditions is usually low. For instance, allyl alcohol at 25° displaces chloride from $PtCl_4^{2-}$ to form $Pt(CH_2{=}CHCH_2OH)Cl_3^-$ with a second-order rate constant $k_2 = 10^{-3}\ M^{-1}\ sec^{-1}$.[4] Quantitative data are not available for ethylene, but a solution of $PtCl_4^{2-}$ absorbs ethylene at 25° (1.5 atm) to give Pt(ethylene)Cl_3^- within 10 days.[5]

The mechanisms of formation of π-olefinic complexes are of remarkable interest because of the relationship with the problems of homogeneous catalysis. Various studies have been made in the last few years with the aim to accelerate the rate of formation of a bond between an olefin and a transition metal ion.[3] In the case of $PtCl_4^{2-}$ the presence of $SnCl_3^-$ ion has been found to increase the rate of ethylene absorption in acidic aqueous solution by several orders of magnitude.[6] We have kinetically investigated this $SnCl_3^-$ catalytic effect and the catalytically active species was found to be a compound containing Pt–Sn bonds—probably the isomer *cis*-$Pt(SnCl_3)_2Cl_2^{2-}$—the accelerating effect being interpreted in terms of the high *trans*-labilizing power of the coordinated $SnCl_3^-$.[7]

During some investigations on the rate of formation of π-olefinic platinum(II) complexes starting from $PtCl_4^{2-}$ and using different olefins, there was observed a dependence of the reaction rate on the nature of the entering olefin. Thus, the (allyl)$As(C_2H_5)_3^+$ cation displaces chloride from tetrachloroplatinate(II) anion with a rate greater than that of the other olefins examined, namely, allyl alcohol, allylsulfonate, and *trans*-crotylammonium.[4,8] This observation, together with the previous one concerning the fast exchange of olefins in π-olefinic platinum(II) complexes, prompted us to study the possible catalysis in the formation of these complexes in the presence of a catalytic amount of a very reactive olefin, such as (allyl)$As(C_2H_5)_3^+$.

Experimental Section

Olefins.—Potassium allylsulfonate,[4] *trans*-crotylammonium chloride,[9] and As,As,As-triethylallylarsonium perchlorate[10] have been prepared according to the methods reported in the literature. Allyl alcohol was a commercial, reagent product distilled over KOH before use.

K_2PtCl_4 was a pure commercial product which was recrystallized from 3 *M* HCl in order to eliminate possible traces of platinum(IV).

Kinetics.—The kinetic measurements have been carried out spectrophotometrically by taking the spectrum of the reacting mixture at time intervals with a Beckman DK2A or an Optica CF4R recording spectrophotometer. The values of the pseudo-first-order rate constants, k_{obsd} (sec^{-1}), have been obtained from the linear plots of log ($A_\infty - A_t$) *vs.* time, where A_t and A_∞ are the optical densities of the reaction mixture at 295 mμ at time t and after 10 half-lives of the reaction. At this wavelength the difference between the absorption of starting complex and that of the final product was largest. The reactions have been carried out in a 1-cm silica cell, thermostated at the desired temperature of 25, 35, and 45°. The reaction medium was water 1.9 *M* in NaCl and 0.1 *M* in HCl.

Results and Discussion

The examined reactions are of the type

$$PtCl_4^{2-} + \text{olefin} \xrightarrow{L_\pi} Pt(\text{olefin})Cl_3^- + Cl^- \qquad (1)$$

(olefin is allyl alcohol, allylsulfonate anion, *trans*-crotylammonium cation; L_π = (allyl)$As(C_2H_5)_3^+$). A catalytic effect of (allyl)$As(C_2H_5)_3^+$ has been also observed in the absorption of ethylene 25° (1.5 atm)

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Table I

Values of k_{obsd} (sec^{-1}) for Reaction 1 in Water, Where [NaCl] = 1.9 *M*, [HCl] = 0.1 *M*, and [$PtCl_4^{2-}$] = 10^{-3} *M*

Expt no.	10^3[entering olefin], *M*	10^3 [catalyzing (allyl)As-($C_2H_5)_3^+$, L_π], *M*	Temp, °C	Pseudo-first-order rate constant, 10^6k_{obsd}, sec^{-1}
	Olefin, *trans*-$CH_2CH=CHCH_2NH_3^+$			
1	9.0	1	25	2.65
2	15.0	1	25	3.85
3	25.0	1	25	5.00
4	9.0	2	25	3.60
5	15.0	2	25	4.75
6	25.0	2	25	5.90
7	9.0	3	25	5.00
8	15.0	3	25	6.00
9	25.0	3	25	7.90
10	9.0	2	35	6.90
11	15.0	2	35	9.20
12	25.0	2	35	12.50
13	9.0	2	45	14.8
14	15.0	2	45	22.0
15	25.0	2	45	30.1
	Olefin, $CH_2=CHCH_2OH$			
16	4.5	2	25	7.0
17	9.0	2	25	12.2
18	15.0	2	25	16.6
19	19.6	2	25	20.7
20	25.5	2	25	26.2
21	30.0	2	25	31.4
22	4.5	2	35	23.1
23	9.0	2	35	37.4
24	15.0	2	35	59.0
25	19.6	2	35	68.0
26	25.5	2	35	96.2
27	30.0	2	35	122.0
28	4.5	2	45	27.4
29	9.0	2	45	52.5
30	15.0	2	45	79.8
31	25.5	2	45	132.0
	Olefin, $CH_2=CHCH_2SO_3^-$			
32	4.5	2	25	8.5
33	9.0	2	25	14.5
34	15.0	2	25	20.8
35	19.6	2	25	26.5
36	25.5	2	25	33.0
37	30.0	2	25	38.5
38	4.5	2	35	17.0
39	9.0	2	35	34.0
40	15.0	2	35	48.3
41	19.6	2	35	62.5
42	25.5	2	35	79.8
43	30	2	35	96.4
44	9.0	2	45	44.5
45	15.0	2	45	69.2
46	19.6	2	45	89.3
47	25.5	2	45	115.0

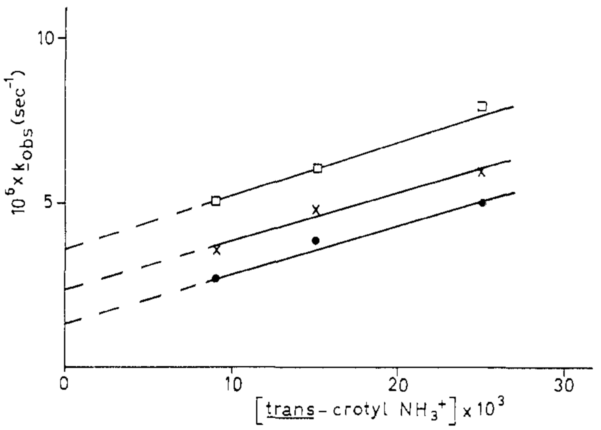


Figure 1.—Plot of k_{obsd} (sec^{-1}) for reaction 1 against the concentration of the *trans*-crotylamine at [L_π] = constant and 25°: ●, [L_π] = 10^{-3} *M;* ×, [L_π] = 2 × 10^{-3} *M;* □, [L_π] = 3 × 10^{-3} *M*. [$PtCl_4^{2-}$] = 10^{-3} *M*.

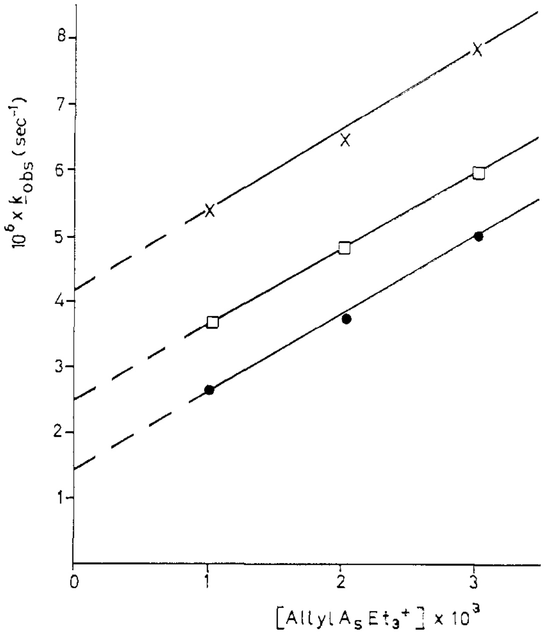


Figure 2.—Plot of k_{obsd} (sec^{-1}) for the reaction $PtCl_4^{2-}$ + *trans*-crotylNH_3^+ (+L_π) → Pt(*trans*-crotylNH_3^+)Cl_3^- + Cl^- against the L_π concentration at [*trans*-crotylNH_3^+] = constant and at 25°: ●, [*trans*-crotylNH_3^+] = 9 × 10^{-3} *M;* □, [*trans*-crotylNH_3^+] = 15 × 10^{-3} *M;* ×, [*trans*-crotylNH_3^+] = 25 × 10^{-3} *M*. [$PtCl_4^{2-}$] = 10^{-3} *M*.

by $PtCl_4^{2-}$ to form Zeise's salt. In this case the absorption occurs in about 1 day instead of 10 days. The reactions have been carried out in water 1.9 *M* in NaCl and 0.1 *M* in HCl, at different temperatures. The rate constants obtained under pseudo-first-order conditions, k_{obsd} (sec^{-1}), which depend on the concentrations of the entering olefin ((5–30) × 10^{-3} *M*) and of the catalyst L_π ((1–3) × 10^{-3} *M*), are reported in Table I. The concentration of the starting substrate in any kinetic run was kept constant and equal to 10^{-3} *M*. In all cases the reactions went to completion.

By plotting the k_{obsd} values against the concentration of the entering olefin at [L_π] = constant, straight lines are obtained with nonzero intercepts (Figure 1). The values of the intercept increase with the increasing concentration of L_π. At constant concentration of the entering olefin, linear plots are obtained with nonzero intercepts for k_{obsd} *vs.* the concentration of L_π (Figure 2).

In Figure 3 are reported the k_{obsd} (sec^{-1}) for reaction 1 against the concentration of the various entering olefins at constant L_π concentration (2 × 10^{-3} *M*). The same nonzero intercepts obtained correspond exactly to the reactivity of L_π olefin, as independently found.

TABLE II

VALUES OF k' (M^{-1} SEC^{-1}) AND k'' (M^{-1} SEC^{-1}) FOR REACTION 1

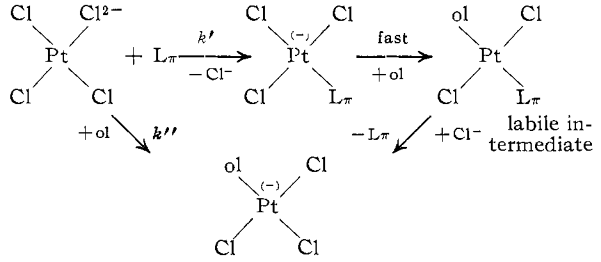
Entering olefin	$10^3k'$, M^{-1} sec^{-1}	$10^3k''$, M^{-1} sec^{-1}	Temp, °C
trans-$CH_2CH{=}CHCH_2NH_3^+$	1.05 (0.950)[a]	0.150 (0.170)[a]	25
	2.05 (2.051)[a]	0.320 (0.335)[a]	35
	4.70 (4.45)[a]	0.850 (0.721)[a]	45
$CH_2{=}CHCH_2OH$	1.00	0.970 (1.031)[b]	25
	2.00	3.620 (2.43)[b]	35
	4.50	4.85 (5.26)[b]	45
$CH_2{=}CHCH_2SO_3^-$	1.00	1.15 (0.870)[b]	25
	2.00	3.00 (1.88)[b]	35
		4.05 (4.08)[b]	45

[a] Values in parantheses are unpublished data obtained by G. Dolcetti and L. M. Venanzi for the reaction $PtCl_4^{2-}$ + olefin ⇌ Pt(olefin)Cl_3^- + Cl^- under the same experimental conditions. [b] Data from ref 4.

These results fit the two-term rate law[11]

$$k_{obsd} = k'[L_\pi] + k''[\text{olefin}] \qquad (2)$$

The presence of a significant concentration of chloride ion in the reaction mixture is intended to minimize the aquation of $PtCl_4^{2-}$. The presence of HCl prevents the possibility that the entering olefin acts as a bidentate ligand, since under these experimental conditions the basic tooth of the molecule is protonated. The values of the second-order rate constants, k'' (M^{-1} sec^{-1}), are in excellent agreement with those obtained for some of these reactions carried out in the absence of the catalyst (Table II). In the two-term rate law (eq 1), the term k'' refers to the direct bimolecular attack of the incoming olefin on $PtCl_4^{2-}$ and the k' term may therefore be attributed to a bimolecular substitution of a Cl^- by L_π followed by a fast coordination of the olefin leading to the formation of a labile intermediate which then rapidly gives the product Pt(olefin)Cl_3^-



where L_π is (allyl)As$(C_2H_5)_3^+$, and k' and k'' are comparable.

The proposed reaction scheme is formally analogous to that operating in the substitutions at square-planar four-coordinate platinum(II) complexes, where the ligand displacement occurs simultaneously by a direct attack of the entering group and *via* solvolysis and subsequent fast substitution of the weakly coordinated solvent molecule. The parallelism is, however, only formal. In the present case, in fact, the catalyzed path involves the slow attack of L_π (as in the solvolytic path), but this is followed by the fast substitution of the ligand *trans* to it. The labile intermediate so formed would then release L_π to form the thermodynamically stable product. The suggested formation of the intermediate *trans*-Pt(olefin)$(L_\pi)Cl_2$ is supported by the existence of the thermically unstable complex *trans*-Pt$(C_2H_4)_2Cl_2$ which can be obtained on treating Zeise's salt with ethylene at −80°.[12]

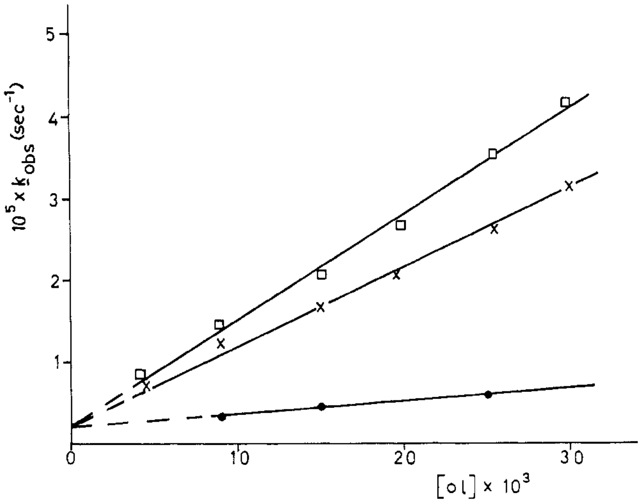


Figure 3.—Plot of the k_{obsd} (sec^{-1}) for reaction 1 at 25° against the concentration of the entering olefins with $[L_\pi] = 2 \times 10^{2-}$ M, constant: ●, [*trans*-crotylNH_3^+]; ×, allyl alcohol; □, allylsulfonate.

It seems to us that also the exchange between coordinated olefins and free olefins investigated by Cramer[3] should occur through a bimolecular attack leading to the formation of an unstable intermediate, *trans*-Pt(olefin)$_2Cl_2$.

The accelerating effect in the formation of the π-olefinic platinum(II) complexes in the presence of (allyl)As$(C_2H_5)_3^+$ or $SnCl_3^-$ (L_π) can be interpreted in a unique way, according to the following considerations. Both these catalysts—(allyl)As$(C_2H_5)_3^+$ and $SnCl_3$—are good π-bonding ligands having high *trans*-labilizing effect and therefore they facilitate the entry of the incoming olefin in the *trans* position. A labile reaction intermediate is formed with two *trans*-incompatible π ligands competing for the same out-of-plane nonbonding d orbital of the metal.

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(11) The solvent-controlled path (k_1, sec^{-1}) usually found in the square-planar substitution is not present here. See F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions," John Wiley and Sons, New York, N. Y., 1967, and ref 4 and 8.

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