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REACTIONS AND PROPERTIES OF SOME TRIMETHYLENEPLATINUM(IV) COMPLEXES

VII *. KINETICS AND MECHANISM OF DISPLACEMENT OF CYCLOPROPANE BY ALKENES

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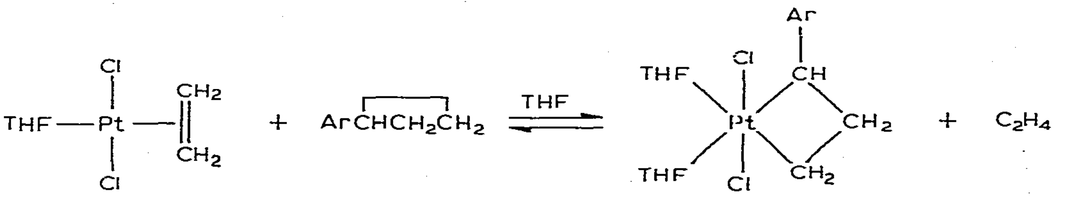
Summary

The kinetics of the reaction of alkenes (e.g. *cis*-pent-2-ene, hex-1-ene, cyclopentene) with $[\overline{PtX_2(CH_2CH_2C}H_2)(THF)_2]$ (X = Cl or Br, THF = tetrahydrofuran) or with $[\overline{PtCl_2(CHPhCH_2C}H_2)(THF)_2]$ in THF solution have been studied. The reactions occur with displacement of cyclopropane or phenylcyclopropane to give $[PtCl_2(olefin)(THF)]$, and follow essentially second order kinetics, first order in both platinum complex and olefin. The mechanism of reaction is discussed.

Introduction

In part V of this series a study of the kinetics of formation of platinacyclobutane complexes in tetrahedrofuran (THF) solution by displacement of ethylene from Zeise's compound by a suitable arylcyclopropane (eq. 1) [2] was reported.



(1)

(I) (II)

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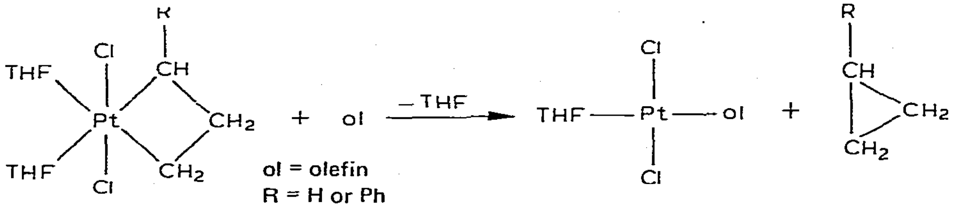
The platinacyclobutane derivatives readily undergo reductive elimination of cyclopropane when treated with soft donor ligands. Thus reaction of $[\overline{PtCl_2(CH_2CH_2CH_2})(C_5H_5N)_2]$, III, with Ph_3P, Ph_3As or Ph_3Sb apparently occurs by initial displacement of pyridine by the added ligand followed by reductive elimination of cyclopropane and formation of $[PtCl_2(YPh_3)_2]$, Y = P, As or Sb [3]. Olefins (e.g. C_2H_4) fail to react with III apparently because they are unable to compete with pyridine as a ligand for platinum(IV) [3], but it is known that olefins will displace cyclopropanes from the tetramers, $[\{\overline{PtCl_2(CH_2CH_2CH_2})\}_4]$ or from their solutions in weakly coordinating solvents [3,4]. This is essentially the reverse of the reaction of eq. 1, and a study of the kinetics of such reactions is now reported.

Results and discussion

The dimer $[Pt_2Cl_4(C_2H_4)_2]$ and tetramer $[\{\overline{PtCl_2(CHPhCH_2CH_2})\}_4]$ have been shown to be monomeric in THF solution with the proposed structures I and II respectively [2]. Thus the reactions with alkenes can be represented by eq. 2



(2)

The olefin platinum(II) complexes could be isolated from the resulting solution, and, when R = H, the gas evolved was over 80% cyclopropane, the rest being propene. A similar reaction occurred in 1,4-dioxane but the platinacyclobutane tetramers were insufficiently soluble for satisfactory investigation of the kinetics. In acetonitrile as solvent the reactions did not occur readily, probably because the nitrile can compete effectively with the added alkene for the coordination sites on platinum.

The kinetics were studied using UV spectrophotometry in the range 250—350 nm using experimental methods described previously [2]. Although unsaturated compounds containing aromatic and carbonyl groups absorb relatively strongly in this region and thus cannot be used as reactants, it is possible to investigate the reaction with a reasonable variety of olefins. The increase in absorption at 290 nm was followed except for $[PtCl_2(C_3H_5Ph)(THF)_2]$ with which the decrease in absorption at 293 or 310 nm was followed.

A considerable excess of the olefin was used and under these conditions the reaction was first order. Some typical plots are shown in Fig. 1. The observed first order rate coefficients (k_{obs}) were reproducible to ±10% and varied linearly with the concentration of olefin. Figures 2 and 3 show a representative selection of data from which it can be seen that with alkenes and pentadiene the lines pass through the origin within experimental error, whereas with cyclic olefins and methyl allyl ether there appears to be a minor component of the reaction which is of fractional order in the unsaturated compound. The slopes of the lines gives the second order rate coefficients (k_2) and Arrhenius plots for the varia-

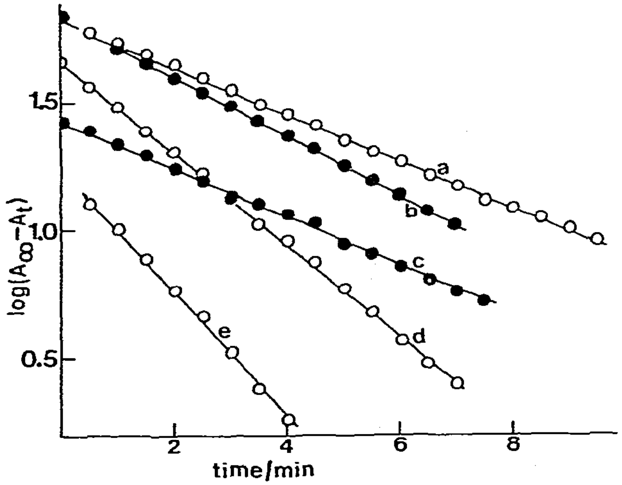


Fig. 1. Typical first order plots for reactions in tetrahydrofuran (S). (a) [$PtCl_2(C_3H_6)S_2$] (5 × 10^{-4} *M*) with *cis*-pent-2-ene (10^{-2} *M*) at 35°C. (b) [$PtCl_2(C_3H_6)S_2$] (5 × 10^{-4} *M*) with cyclopentene (0.142 *M*) at 25°C (abs. ×2). (c) [$PtCl_2(C_3H_5Ph)S_2$] (5 × 10^{-4} *M*) with *cis*-pent-2-ene (7.7 × 10^{-2} *M*) at 20°C. (d) [$PtBr_2(C_3H_6)S_2$] (5 × 10^{-4} *M*) with penta-1,3-diene (2.95 × 10^{-2} *M*) at 27.5°C. (e) [$PtCl_2(C_3H_6)S_2$] (5 × 10^{-4} *M*) with dec-1-ene (9 × 10^{-3} *M*) at 40°C.

tion of k_2 with temperature for some systems are shown in Fig. 4. The temperature range is somewhat small since below 20°C solubility problems make study difficult and above 30—40°C either the reaction is too fast to be followed quantitatively or the platinum(II) olefin product tends to decompose making it impossible to determine A_∞. The kinetic parameters are summarised in Table 1. With methyl and ethyl allyl ethers k_2 is between the values found for penta-1,3-diene and cyclohexene. Allyl chloride and bromide react but it was not possible to obtain A_∞. Vinyl bromide and acrylonitrile do not appear to react.

The second order kinetics are probably due to a pre-equilibrium step, involv-

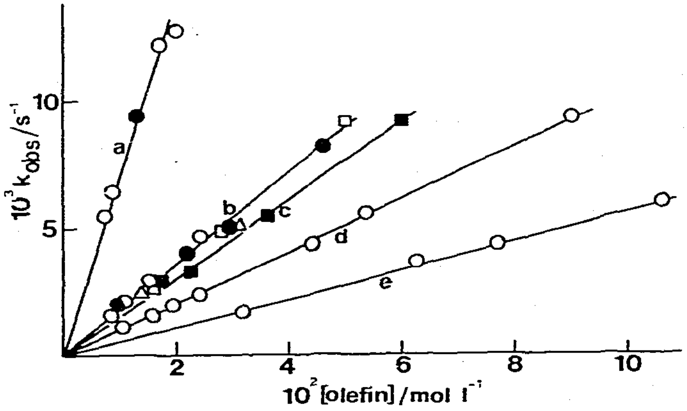
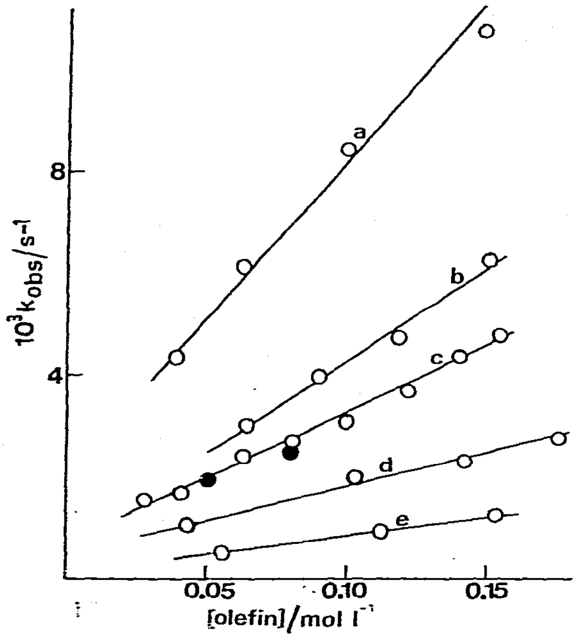


Fig. 2. Dependence of the first order rate coefficients (k_{obs}) for reactions in tetrahydrofuran (S) on the concentration of olefin. (a) [$PtCl_2(C_3H_6)S_2$] with dec-1-ene at 35°C; (●) *cis*-pent-2-ene. (b) [$PtCl_2$-($C_3H_6)S_2$] with: (○) dec-1-ene, (●) *cis*-pent-2-ene, (□) 4-methylpent-1-ene, (△) hex-1-ene. Temp., 20°C. (c) [$PtBr_2(C_3H_6)S_2$] with *cis*-pent-2-ene at 20°C. (d) [$PtCl_2(C_3H_6)S_2$] with penta-1,3-diene at 25°C. (e) [$PtCl_2(C_3H_5Ph)S_2$] with *cis*-pent-2-ene at 20°C.



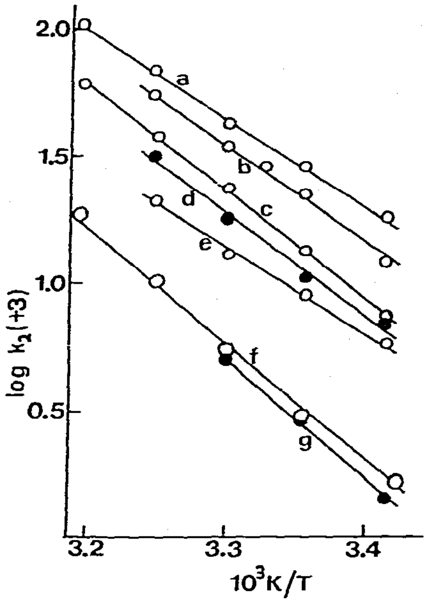


Fig. 3. Dependence of the first order rate coefficients (k_{obs}) for reactions in tetrahydrofuran (S) with the concentration of unsaturated compound. (a), (d), (e) [$PtCl_2(C_3H_6)S_2$] with cyclopentene: (a) 40, (d) 25; (e) 20°C. (b) [$PtCl_2(C_3H_5Ph)S_2$] with cyclopentene at 19.3°C (ord. × 0.1, abs. × 2). (c) [$PtCl_2(C_3H_6)S_2$] with methyl allyl ether (o) and ethyl allyl ether (●) at 25°C.

Fig. 4. Variation of the second order rate coefficients (k_2) with temperature. (a) [$PtCl_2(C_3H_3H_6)(THF)_2$] and dec-1-ene. (b) [$PtBr_2(C_3H_6)(THF)_2$] and penta-1,3-diene. (c) [$PtCl_2(C_3H_6)(THF)_2$] and cyclopentene. (d) [$PtCl_2(C_3H_6)(THF)_2$] and penta-1,3-diene. (e) [$PtCl_2(C_3H_5Ph)(THF)_2$] and *cis*-pent-2-ene. (f) [$PtCl_2$-($C_3H_5Ph)(THF)_2$] and cyclopentene. (g) [$PtCl_2(C_3H_6)(THF)_2$] and cyclohexene. (a), (b), (d) and (e): ord. +1.

TABLE 1

RATE PARAMETERS FOR REACTIONS IN TETRAHYDROFURAN

Platinum compound	Olefin	$10^3 k_2$ [a]	E [b]	A [c]	$\Delta S^{\neq}$ [d]
		(l mol^{-1} s^{-1})	(kJ mol^{-1})	(l mol^{-1} s^{-1})	(J K^{-1} mol^{-1})
$PtCl_2 \cdot C_3H_6$	*cis*-Pent-2-ene Hex-1-ene 3-Methylpent-1-ene Dec-1-ene	176	68	2.3×10^{11}	−27
	Penta-1,3-diene	69	77	3.6×10^{12}	−4
	Cyclopentene	7.4	80	1.3×10^{12}	−13
	Cyclohexene	1.4	89	1.0×10^{13}	4
$PtCl_2 \cdot C_3H_5Ph$	*cis*-Pent-2-ene	57.6	65	2.3×10^{10}	−46
	Cyclopentene	1.7	88	8.7×10^{12}	3
$PtBr_2 \cdot C_3H_6$	*cis*-Pent-2-ene	153			
	Penta-1,3-diene	119	73	1.2×10^{12}	−14

[a] Second order rate coefficient at 20.0°C. Estimated error, ±5%. For methyl allyl ether, $k_2 = 25.5 \times 10^{-3}$ l mol^{-1} s^{-1} at 25°C. [b] Overall activation energy. Estimated error, ±3 kJ mol^{-1}. [c] Overall pre-exponential factor. [d] Overall entropy of activation. Estimated error, ±6 J K^{-1} mol^{-1}..

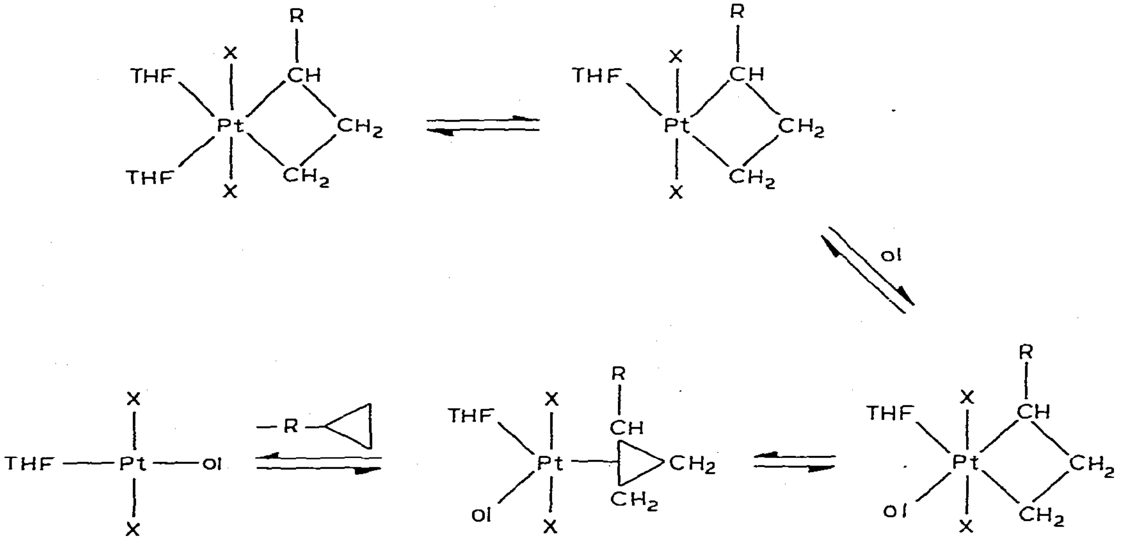
ing the removal of a THF molecule, followed by reaction between the five coordinate platinum intermediate and the unsaturated compound (ol) to give the products, as shown in eqs. a and b [2].

$$[PtX_2(C_3H_5R)(THF)_2] \overset{K_a}{\rightleftharpoons} [PtX_2(C_3H_5R)(THF)] + THF \qquad (a)$$

$$[PtX_2(C_3H_5R)THF] + ol \overset{k_b}{\rightleftharpoons} [PtX_2(ol)(THF)] + C_3H_5R \qquad (b)$$

Provided the equilibrium constant (K_a) is small, the second order rate coefficient $k_2 = k_b K_a/[THF]$. For this mechanism the experimental kinetic parameters are given by: $E = E_b + \Delta H_a^{\ominus}$ and $\Delta S^{\neq} = \Delta S_b^{\neq} + \Delta S_a^{\ominus}$ where $\Delta H_a^{\ominus}$ and $\Delta S_a^{\ominus}$ are the standard enthalpy and entropy changes for reaction a. It can be seen that any variation in k_2 for the reaction of one of the platinum compounds with different olefins is due to variation in k_b, i.e., in E_b or $\Delta S_b^{\neq}$ or both. Since the reaction of eq. b may involve coordination of the olefin followed by reductive elimination of cyclopropane [2], it will be clear that the observed kinetic parameters cannot be associated with any one elementary reaction. The proposed detailed mechanism is shown in Scheme 1, and is clearly closely related to the mechanism of the reverse reaction [2].

Scheme 1



From the data in Table 1 it can be ssen that the reactivity of platinacyclobutanes towards *cis*-pent-2-ene follows the order $[PtCl_2(CH_2CH_2CH_2)(THF)_2] \sim [PtBr_2(CH_2CH_2CH_2)(THF)_2] > [PtCl_2(CHPhCH_2CH_2)(THF)_2]$. There is very little difference in the rates of reaction of various terminal alkenes or of *cis*-pent-2-ene with $[PtCl_2(CH_2CH_2CH_2)(THF)_2]$, but cyclic alkenes and penta-1,3-diene react considerably more slowly and the lower rate is due to an increase in the activation energy rather than a less favorable entropy of activation. Cyclopentene and cyclohexene appear to coordinate more weakly to silver(I) than do 1-hexene and similar alkenes, as evidenced by smaller contact shifts due to the olefinic carbon atoms in the ^{13}C NMR spectra of the free and coordinated alkenes [5], and a similar effect could explain the present kinetic data if the cycloalkenes are relatively weak ligands for platinum also.

It is interesting to compare the rate coefficients and kinetic parameters for reactions in either direction. The rate coefficients for the reaction of the terminal alkenes, as well as *cis*-pent-2-ene, with $[\overline{\mathrm{PtCl_2(CH_2CH_2CH_2}})\mathrm{(THF)_2}]$ at 20°C are the same and the activation parameters are identical within experimental error (Table 1). If it is assumed that this is also the case for the reaction of alkenes (including ethylene) with $[\overline{\mathrm{PtCl_2(CHPhCH_2CH_2}})\mathrm{(THF)_2}]$, as seems reasonable, then a direct comparison of phenylcyclopropane for ethylene displacement and the reverse reaction can be made. The data are given below [2].

Reaction	$k_2^{25^\circ C}$ (l mol^{-1} s^{-1})	E(kJ mol^{-1})	$\Delta S^{\neq}$ (J K^{-1} mol^{-1})
$PtCl_2(C_3H_5Ph)$ + *cis*-pent-2-ene	8.94×10^{-2}	65	−46
$PtCl_2(C_2H_4) + C_3H_5Ph$	1.66×10^{-2}	65.5	−59

The ratio of rate coefficients is ca. 5.4 and (assuming unit activity of THF) this should approximate the equilibrium constant K at 25°C for the reaction of eq. 3.

$$[\mathrm{PtCl_2(C_3H_5Ph)(THF)_2}] + \text{alkene} \overset{K}{\rightleftharpoons} [\mathrm{PtCl_2(alkene)(THF)}] + \mathrm{PhC_3H_5} + \mathrm{THF} \quad (3)$$

It has so far not been possible to measure the equilibrium constant directly and so to check this prediction. The activation energies are approximately equal for reaction in either direction, implying that the standard enthalpy change $\Delta H^{\ominus}$, is approximately zero (K varying only slightly with temperature). However, the standard entropy change, $\Delta S^{\ominus}$, is approximately +13 J K^{-1} mol^{-1}, the entropy of activation being more favourable for displacement of the cyclopropane by olefin than for the reverse [2]. This, in turn, may be due to the dissociative step involving dissociation of THF in eq. a, rather than in a rate-determining step. The ability of cyclopropanes to compete with olefins for coordination to platinum is remarkably high, and is a further result of the unsaturated character induced by ring strain.

Finally, we note that no products of the kind expected in alkene metathesis reactions were formed. Thus no ethylene or styrene were detected in reactions of complexes containing $\overline{\mathrm{PtCH_2CH_2CH_2}}$ or $\overline{\mathrm{PtCHPhCH_2CH_2}}$ groups with alkenes. Such products would be expected if facile isomerisation of platinacyclobutanes to carbene (alkene) platinum complexes occurred [6].

Experimental

The platinum(IV) compounds, $[\mathrm{PtCl_2(C_3H_6)}]_4$, $[\mathrm{PtBr_2(C_3H_6)}]_4$ and $[\mathrm{PtCl_2(C_3H_5Ph)}]_4$ were prepared by literature methods [7,8]. Tetrahydrofuran was distilled under nitrogen from calcium hydride. The unsaturated compounds were fractionally distilled in vacuo before use. The purity of the middle fraction was checked by gas-liquid chromatography and the absence of peroxides was verified by shaking a sample with iron(II) thiocyanate solution. Standard solutions of the reactants were prepared just before use in the kinetic studies [2].

The gas evolved from the reactions of $[\mathrm{PtX_2(C_3H_6)(THF)_2}]$ (X = Cl, Br) was analysed by GLC using a 9 ft. 12% Squalene on Chromosorb P column at 30°C. At the end of the reactions the solvent and excess olefin were removed by evaporation in vacuo and the solids left characterised by mass spectroscopy and NMR.

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