Thermal Decomposition of some Platinum Complexes containing Tetrafluoroethylene and Hexafluorobut-2-yne

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The enthalpies and activation energies of dissociation of the ligand, L, from the complexes $PtXCH_3A_2L$ (where X = Cl or Br; A = $AsMe_3$ or $AsMe_2Ph$; and L = tetrafluoroethylene or hexafluorobut-2-yne are reported. A value for the bond energy, $E(Pt-C_4F_6)$ is calculated.

VERY few thermochemical data are available for the strengths of π-bonds between carbon and the platinum metals, although compounds containing such bonds are likely to be formed as intermediates during catalytic processes. Barnes and Pettit [1] have reviewed available information about the stability and structure of olefin and acetylene complexes of platinum, although thermodynamic data refer, in the main, to complexes in solution.

To provide more [2] information about bond strengths in this type of compound we have determined enthalpies of thermal decomposition reactions of the type

$$PtXCH_3A_2L\ (cryst) \longrightarrow trans\text{-}PtXCH_3A_2\ (cryst) + L\ (g)$$

where X = Cl or Br; A = $AsMe_3$ or $AsMe_2Ph$; and L = tetrafluoroethylene, C_2F_4 or hexafluorobut-2-yne, C_4F_6.

In addition, we have used the experimental data to calculate activation energies of the decomposition reactions of the compounds.

EXPERIMENTAL

Compounds.—The complexes were prepared by methods described previously.[3] Analytical data are shown in Table 1.

TABLE 1

Analytical data of complexes $PtXCH_3A_2L$

	Compound			C		H		F	
No.	A	X	L	Calc.	Found	Calc.	Found	Calc.	Found
(1)	$AsMe_3$	Cl	C_2F_4	18·5	18·3	3·6	3·7	13·0	
(2)	$AsMe_3$	Br	C_2F_4	17·2	16·8	3·4	3·8	12·1	11·9
(3)	$AsMe_3$	Cl	C_4F_6	20·4	19·9	3·3	3·8	17·6	
(4)	$AsMe_3$	Br	C_4F_6	19·1	18·7	3·1	3·3	16·5	
(5)	$AsMe_2Ph$	Cl	C_4F_6	32·7	32·7	3·3	3·4	14·8	
(6)	$AsMe_2Ph$	Br	C_4F_6	30·9	30·7	3·1	3·1	13·9	13·2

Calorimetry.—The Perkin-Elmer differential scanning calorimeter (DSC-1) was used to measure the enthalpies of thermal decompositions by a procedure referred to previously.[4]

RESULTS AND DISCUSSION

Enthalpy Data.—Enthalpies of the decomposition reactions are shown in Table 2, in which the symbols T_i, T_p, and T_f refer to the initial, peak (where the rate of ΔH change was greatest), and final temperatures of a dissociation reaction, respectively. In all cases the ΔH values, which refer to the temperature T_p, are the mean of at least five experiments, and the associated uncertainties are mean uncertainty intervals, *i.e.* twice the standard deviations of the mean values. The scan rate in each case was 16°/min and the sensitivity (range) was either 2 or 4 mcal/full scale deflection/s. The observed weight loss (the mean of at least three determinations) and that calculated for complete loss of the ligand, L, are shown.

In the absence of specific-heat data it has not been possible to recalculate the enthalpies of decomposition to a common temperature. However, it is noted that the

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temperatures, T_p, to which the reactions refer vary over a comparatively narrow range of 40°, the mean being 365 K. It is assumed that only small errors, compared with the quoted uncertainties, will be introduced by ignoring these temperature differences. When using the enthalpies of reactions as a measure of the strengths of chemical bonds, it is preferable that such data should refer to gas-phase reactions. Because of the lack of values for the enthalpies of sublimation of these complexes it has not been possible to correct the measured enthalpies so that they refer to the gas phase. We make the assumption that the differences between the enthalpies of sublimation of the solid reactant and product, $PtXCH_3A_2L$ and $PtXCH_3A_2$, are reasonably constant and small for differing halogen, X, and arsine ligand, A. If this assumption is justified, then the measured enthalpies of decomposition will be very similar to those in the gas phase for any particular reaction. Thus, the gas-phase bond-dissociation energies D(Pt–L) are likely to be very similar to the ΔH values of Table 2. It should be emphasised, however, that although the thermochemical data for the condensed phase are precise, the correction to the gas phase depends on an assumption which may not be justified.

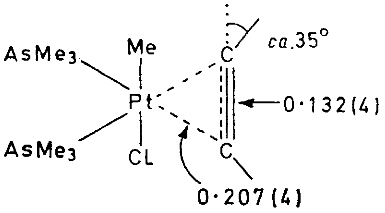
TABLE 2

No.	Compound A	 X	 L	T_i/K	T_p/K	T_f/K	ΔH/kJ mol^{-1}	Wt. loss % Obs.	 Calc.
(1)	$AsMe_3$	Cl	C_2F_4	355	380	390	51·6 ± 0·6	17·0 ± 0·1	17·07
(2)	$AsMe_3$	Br	C_2F_4	365	385	405	48·2 ± 1·0	15·8 ± 0·1	15·87
(3)	$AsMe_3$	Cl	C_4F_6	350	385	400	68·6 ± 1·6	25·2 ± 0·1	25·01
(4)	$AsMe_3$	Br	C_4F_6	345	385, 405 *	410	61·0 ± 1·6	23·5 ± 0·1	23·41
(5)	$AsMe_2Ph$	Cl	C_4F_6	310	345, 370 †	380	73·4 ± 1·4	21·3 ± 0·3	20·99
(6)	$AsMe_2Ph$	Br	C_4F_6	320	355	370	80·3 ± 0·8	20·0 ± 0·4	19·85

* Two peaks observed, the second was very small. † Two quite distinct, though not completely separated peaks observed. The value of ΔH corresponding to the first peak is *ca.* 35 kJ mol^{-1}.

In the dissociation process the C_2F_4 or C_4F_6 molecule will undergo extensive reorganisation and a more realistic value for the strength of the metal–carbon bond in the complex molecule would be obtained by taking into account the energy of this reorganisation process.

Bonding of the unsaturated molecule to the metal atom has been considered [5–8] to result from simultaneous charge transfer from the filled ligand orbitals to unfilled metal orbitals and from essentially non-bonding metal orbitals to antibonding ligand orbitals. For the acetylene compounds $PtXCH_3A_2,C_4F_6$, the extent of this electron transfer is indicated by (i) the change in stretching frequency, $\Delta\nu_{C\equiv C}$, of the carbon–carbon triple-bond [3] (values lie in the range 430—462 cm^{-1}) and (ii) the lengthening of this bond. Preliminary *X*-ray data [9] indicate a carbon–carbon bond length, 0·132 nm, which is longer than in hexafluorobut-2-yne, 0·122 ± 0·09 nm,[10] and close to the double bond in ethylene, 0·1339(2) nm.[11] These data also lead to the conclusion that only one of the two π-bonds of the C_4F_6 molecule is involved in bonding it to the Pt atom.



From the carbon–carbon bond lengths, it seems likely that in the complex, the strength of this bond will be very similar to that of the double bond [12] in ethylene, E(C=C) = 600 kJ mol^{-1}. On dissociation, the bond strength will increase, probably by *ca.* 200 kJ mol^{-1}, to a value close to that of the triple bond [12] in acetylene, E(C≡C) = 800 kJ mol^{-1}. Consequently, the bond energy of the platinum–carbon bond in the complex is greater than the observed enthalpy of dissociation by at least this amount, and we calculate a value for $E(Pt{-}C_4F_6)$ of 270 ± 20 kJ mol^{-1}. Since no *X*-ray data are available for the analogous C_2F_4 compound, we are not able to obtain a value for $E(Pt{-}C_2H_4)$.

Returning to a consideration of the measured dissociation enthalpies, ΔH, it is noteworthy that, for the compounds (1) to (4), where A = $AsMe_3$, the ΔH value is only *ca.* 15 kJ mol^{-1} greater for the acetylenic ligand, C_4F_6, than for the olefin C_2H_4. The conclusion, that only one of the two π-bonds of the C_4H_6 molecule is involved in bonding it to the Pt atom, is in keeping with the observed carbon–carbon distance in the bonded molecule, 0·129 nm. In the compound $Co_2(CO)_6$-$(C_6H_5C{\equiv}CC_6H_5)$, where both of the acetylenic π-bonds are used in bonding to the cobalt, the carbon–carbon distance is much longer, at 0·146 nm.[13] Moreover, the Pt–C distance of 0·207(4) nm is very similar to that, 0·203(3) nm, found [14] in $Pt(PPh_3)_2(Cl_2C{=}CCl_2)$.

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Kinetic Treatment.—Differential-scanning calorimetry provides an opportunity for measuring not only the overall enthalpy change, ΔH, of a decomposition reaction, but also the rate of this reaction. This can lead, in principle, to information about the kinetic parameters and associated mechanisms of the process. We adopt the following expression, which may be derived from the more comprehensive equations of Šesták and Berggren,[15] relating the rate of reaction, $d\alpha/dt$, where α is the degree of conversion, to the temperature, T, and activation energy, E.

$$-\log \frac{d\alpha}{dt} + n \log (1 - \alpha) = -\frac{E}{2{\cdot}303R} \cdot \frac{1}{T} - \log C$$

The particular value of n has generally been selected so as to give a best linear plot of $[-\log (d\alpha/dt) + n \log (1 - \alpha)]$ against $1/T$. Thus, Beech and Kauffman[16] have used values of n varying between 0·2 and 1·5, depending on the particular part of reaction investigated, in the α range 0·01 to 0·90, whilst Rogers and Smith[17] have used a value of $n = 1{\cdot}3$ for the thermal decomposition of RDX (hexahydro-1,3,5-trinitro-*s*-triazine), in the α range 0·07—0·80.

In a study of the decomposition of manganous hydrate formate $Mn(HCOO)_2,2H_2O$, Thomas and Clarke[18] have shown that over the more restricted α range 0·19—0·46, the value $n = 0$ is most appropriate. Their method is convenient to apply as it requires measurement only of A, the total area of the thermogram peak, and dH/dt, the rate of enthalpy change with time, which is simply the pen deflection or peak height at a given time. The term $d\alpha/dt$ in the equation is replaced by $dH/dt \times 1/A$. A value of E_A is then obtained for the α range over which the plot of $\log (dH/dt)$ against $1/T$ is linear. This part of the reaction is identified as the interfacial reaction.

We have applied this method in an interpretation of the thermograms of the six platinum compounds. The thermograms for compounds (1)—(4) and (6) were similar in having a single major peak, although for compound (4) a minor peak appeared towards the end of the decomposition. For compound (5), however, the thermogram consisted of two, roughly equal peaks (corresponding to $\alpha = 0$ to 0·5 and 0·5 to 1·0), indicating that the decomposition occurred in two distinct stages. The calculated values of E_A and C are shown in Table 3. The E_A and $\log C$ values are the mean values from at least five determinations, and the associated uncertainties are the standard deviations of the means.

The salient features that emerge from the values of activation energies are the following. (i) For compounds (4) and (6), the E_A values are very similar, with the value for compound (4; $A = AsMe_3$) being slightly greater than for compound (6; $A = AsMe_2Ph$). (ii) For compounds (3) and (4) the E_A values are also very similar, although for $X = Br$ the E_A value is a little greater than for $X = Cl$. (iii) For compounds (1) and (2) where $L = C_2F_4$, the E_A values are much greater than for compounds (3), (4), and (6), where $L = C_4F_6$. (iv) Whereas for compounds (3) and (4) ($L = C_4F_6$) halogen change has little effect on E_A, for compounds (1) and (2) ($L = C_2F_4$) the change of halogen from Cl to Br has a marked effect on the E_A value. (v) Compound (5) has a different decomposition path from the others and cannot be included in the comparisons. (vi) In all cases, the activation energy is much greater than the enthalpy of decomposition, by a factor of 2 or 3 for C_4F_6 compounds, and a factor of 6 or 7 for the C_2F_4 compounds. For compound (3) the activation energy, 163 kJ mol^{-1}, is virtually the mean of the observed enthalpy of decomposition, 69 kJ mol^{-1}, and the calculated bond energy, 270 kJ mol^{-1}, where $X = Br$.

TABLE 3

Values for the activation energy E_A and the constant C

No.	Compound A	 X	 L	E_A kJ mol^{-1}	$\log C$	α Range
(1)	$AsMe_3$	Cl	C_2F_4	360 ± 4	50·2	0·06—0·24
(2)	$AsMe_3$	Br	C_2F_4	281 ± 5	38·4	0·06—0·51
(3)	$AsMe_3$	Cl	C_4F_6	163 ± 2	22·4	0·01—0·21
(4)	$AsMe_3$	Br	C_4F_6	174 ± 3	23·9	0·03—0·32
(5)	$AsMe_2Ph$	Cl	C_4F_6	(i) 114 ± 2	17·2	(i) 0·05—0·30
				(ii) 93 ± 2	13·3	(ii) 0·50—0·74
(6)	$AsMe_2Ph$	Br	C_4F_6	161 ± 5	23·9	0·07—0·49

Some of these points are considered in more detail. (i) To the extent that the stability of the complex is dependent on the *trans*-influence of L, one would expect the compound with $L = AsMe_2Ph$ to have a lower activation energy than with $L = AsMe_3$. The electron-withdrawing phenyl group will increase the d_π–d_π back co-ordination, Pt → As, which will, in turn, tend to decrease the $d \rightarrow \pi^*$ component of the platinum–acetylene bond, making dissociation of the C_4F_6 easier. In the overall dissociation process, this effect is masked by other changes in bond strength, in that the enthalpy of dissociation is greater for $L = AsMe_2Ph$, 80·3 ± 0·8, than for $L = AsMe_3$, 61·0 ± 1·4 kJ mol^{-1}.

(ii) For the compounds (3) and (4) $PtXCH_3(AsMe_3)_2C_4F_6$, the greater electron-withdrawing power of Cl leads to a lower activation energy ($E_A = 163 \pm 2$) than is found for $X = Br$ ($E_A = 174 \pm 3$ kK mol^{-1}). Again, this is the reverse of the trend in ΔH values for the dissociation.

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