Activation Barriers for β-Hydride Elimination: Systematic Study of the Single Mechanistic Step

Henry E. Bryndza

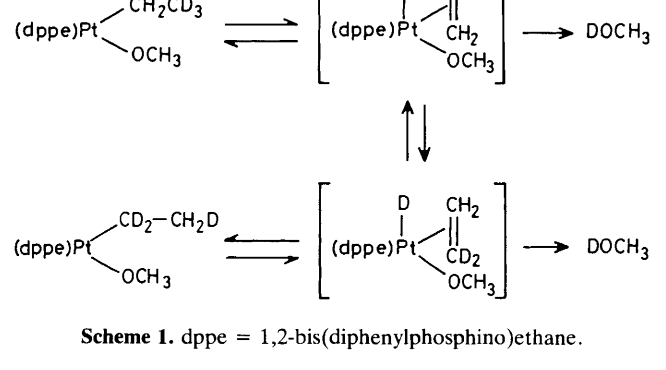
Central Research & Development Department, Experimental Station, E. I. du Pont de Nemours & Company, Wilmington, DE 19898, U.S.A.

The thermolysis of ^{13}C (*) labelled platinum ethyl complexes (cod)Pt($*CH_2CH_3$)$_2$, (cod)Pt($*CH_2CH_3$)Cl, and (cod)Pt($*CH_2CH_3$)I (cod = cyclo-octa-1,5-diene) was studied at 100—110 °C by quantitative ^{13}C n.m.r. spectroscopy, changes in the concentrations of (cod)Pt($*CH_2CH_3$)X and (cod)Pt(CH_2*CH_3)X as a function of time allowing direct quantification of the free energy of activation for β-hydride elimination; barriers for (cod)Pt($*CH_2CH_3$)X were $\Delta G^\ddagger = 28.9 \pm 0.2$ kcal/mol for X = $*CH_2CH_3$, 29.1 ± 0.2 for X = Cl, and 26.9 ± 0.2 for X = I (1 cal = 4.184 J).

The individual mechanistic steps of β-hydride elimination and its microscopic reverse, alkene insertion into an M–H bond, are directly responsible for linear-to-branched product ratios in virtually all homogeneously catalysed hydroformylations, isomerizations, and hydrocyanations.[1] Recently, Spencer and Orpen have identified,[2] crystallographically, the expected β-elimination transition state leaving little doubt about the molecular motions involved. Nonetheless, the factors which govern the rates of these important steps remain unclear. The transient nature of the intermediates involved has made direct observation of these single mechanistic steps impossible[3] although the elegant labelling studies by Whitesides of decomposition of bis(phosphine)platinum(II) dialkyl species[4] leave no doubt that β-elimination and alkene insertion take place by relatively low-energy processes. Recently, Roe[5] and Bercaw[6] have used magnetization transfer techniques to obtain activation barriers to alkene insertion in Rh and Nb alkene hydride systems, respectively. This manuscript details the first measurements of discrete barriers to β-hydride elimination.

Whitesides' studies provide activation data for the three-step dissociation, β-elimination, and reductive elimination sequence thereby providing constraints on the β-elimination single step. Our studies of the decomposition of platinum(II) alkoxides demonstrated[7] the pre-equilibrium nature of β-elimination (prior to reductive elimination) by n.m.r. analysis of deuterium scrambling in a labelled starting material (Scheme 1). Unfortunately, internal kinetic isotope effects in the scrambled ethyl ligands make it difficult to obtain quantitative results in this system.

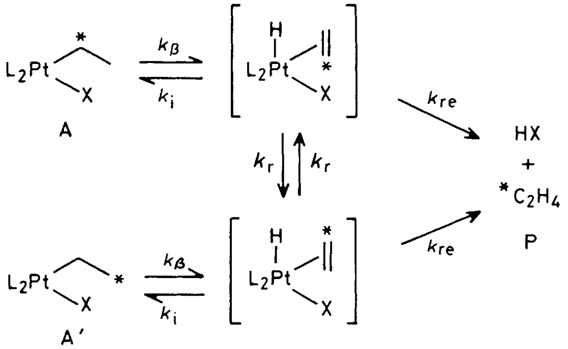
To circumvent the H/D kinetic isotope problem, we resorted to ^{13}C isotopic labelling. Reaction kinetics were measured in xylene by quantitative n.m.r. spectroscopy at 100—110 °C on three ^{13}C labelled ethyl complexes containing the chelating diene ligand cyclo-octa-1,5-diene (cod) (T_1 values are in Table 1).[8]† The systems studied are shown in Scheme 2. Concentrations of (cod)Pt($*CH_2CH_3$)X, (cod)Pt(CH_2*CH_3)X (X = $*CH_2CH_3$, Cl, and I) and their



Scheme 1. dppe = 1,2-bis(diphenylphosphino)ethane.

Table 1. T_1/s data.

Complex	CH_2	CH_3	T/°C
(cod)Pt(CH_2CH_3)$_2$	5.51	6.82	25
	3.71	4.98	90
	3.15	4.42	110 (extrapolated)
(cod)Pt(CH_2CH_3)Cl	5.80	4.61	25
	5.33	4.37	50
	4.04	3.74	100 (extrapolated)
(cod)Pt(CH_2CH_3)I	2.63	2.64	25
	3.07	2.77	80
	3.23	2.82	100 (extrapolated)



Scheme 2

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† Concentrations were determined by integration of decoupled ^{13}C n.m.r. spectra. T_1 (spin–lattice relaxation) measurements were determined for each complex at several temperatures by standard inversion recovery techniques. These measurements were extrapolated to the 100—110 °C operating temperature where standard pulsed Fourier transform spectra were acquired using 90° pulses followed by pulse recycle delays of 67 s (corresponding to more than 15 T_1 periods for even the slowest relaxing nucleus). Nuclear Overhauser enhancement (n.O.e.) differences for the individual ethyl carbon atoms in a given complex were found to be negligible at a variety of temperatures up to operating conditions so integrals were used directly as obtained from the decoupled spectra. Timing of the kinetics delays was accomplished by the internal pulse-programmer on the Nicolet (GE) NT series 300 MHz WB spectrometer used.

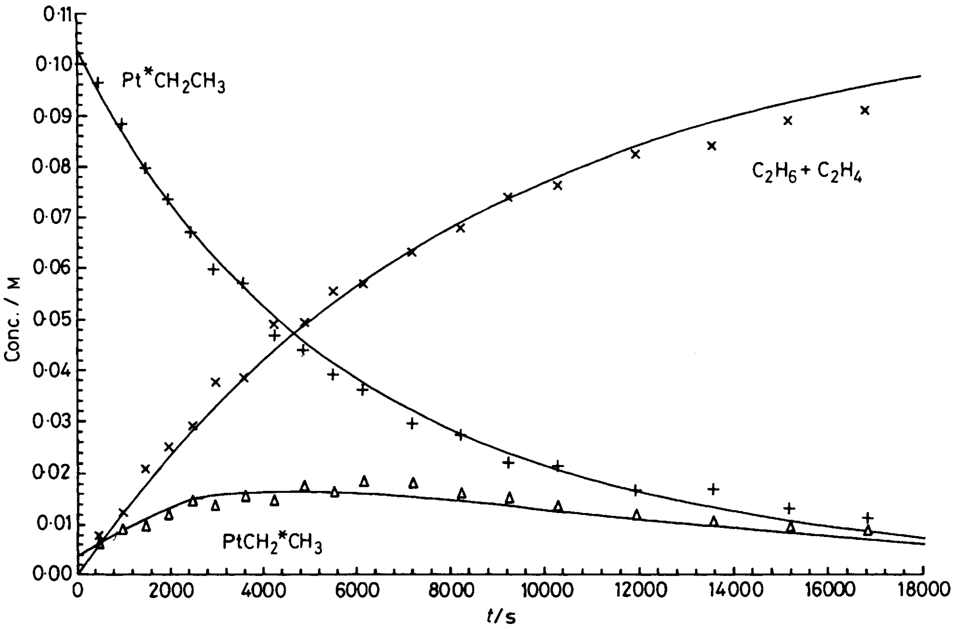

Figure 1. Thermolysis of (cod)Pt(*$CH_2CH_3)_2$ at 110 °C.

decomposition products‡ were measured as a function of time. The kinetic parameters of Scheme 2 reduce to a system of three differential equations and four unknown rate constants, assuming ^{13}C isotope effects are negligible. The system requires $-dA/dt$, dA'/dt, and dP/dt to be functions of k_β, k_i/k_r, and k_{re}/k_r. If one assumes that alkene rotation is fast, as indicated by the work of Hoffmann and Thorn,§ the data can be fitted numerically as shown in Figure 1. The data are remarkably sensitive to k_β and lead to a single acceptable value of k_β and ratios of k_i/k_r and k_{re}/k_r. For (cod)Pt(*$CH_2CH_3)_2$, the barrier to β-elimination is 28.9 ± 0.2 kcal/mol (1 cal = 4.184 J) at 110 °C; for (cod)-Pt(*CH_2CH_3)Cl, a barrier of 29.1 ± 0.2 kcal/mol was observed at 100 °C and for the comparable iodide a lower barrier of 26.9 ± 0.2 kcal/mol was measured at 100 °C.

The acceptable fit of the kinetic model in Scheme 2 to the experimental data suggests it is appropriate for this system. There is no loss of ^{13}C or ^{195}Pt coupling to either the protons or carbon atoms of the cod ligand in the starting materials, demonstrating that we are not dealing with a rapid pre-equilibrium dissociation of ligand. Addition of cod does not affect the observed rates of reaction in accord with this conclusion. These observations are consistent with Whitesides' conclusion that chelating ligands need not dissociate from (chel)PtEtX complexes for decomposition to take place. We cannot rule out dissociation of one alkene ligand concomitant with β-elimination though this seems unlikely; for (cod)PtEtX complexes, the X = Et system has the strongest *trans*-labilizing σ-ligand yet it undergoes β-elimination slower than (cod)PtEtI which has the weakest *trans*-labilizing ligand of the three studied.[9] This observation was also made for the (dppe)PtEtX system where X = Et and OMe.[7] The good fit of data to the kinetic model also suggests that platinum metal does not play a role in these reactions. While (cod)$PtEt_2$ decomposes to generate ethane, ethylene, cod, and platinum metal, no indication of autocatalysis was detected and addition of mercury to the system to scavenge free platinum metal did not affect the rate of decomposition.[10]¶

The trend in activation barriers in the three complexes studied is not clear with so little data yet available; the activation barriers are perhaps consistent with the ease of deformation of the square-planar platinum centre as Hoffmann and Thorn predict,§ but additional systematic study of such complexes with a variety of ligands will be necessary before predictive understanding can develop. We are measuring β-elimination barriers for (dppe)Pt(*CH_2CH_3)X {X = Cl, Br, I, alkyl, aryl, amido, alkoxo, M′ [such as (η^5-C_5H_5)Mo(CO)$_3$], and OM′ [such as OHf($C_5Me_5)_2$H]} in order to establish such an understanding.

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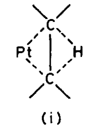
‡ The concentration of ^{13}C containing products (either ethane and ethylene in the case of the diethyl complex or ethylene in the case of the other complexes) was determined by summing the concentrations of platinum ethyl signals and subtracting this total from the initial platinum ethyl signals. Nicolet (GE) KINET software was used for this purpose.

§ A large number of geometries for $P_2Pt(H)(C_2H_4)X$ complexes were evaluated and, in each case, alignment of the C–C double bond with the Pt–H single bond proved to be an energy maximum rotamer. Thus, rotation away from this β-elimination geometry was found to be a process with no intrinsic activation barrier. See, for example, D. L. Thorn and R. Hoffmann, *J. Am. Chem. Soc.*, 1978, **101**, 2079; D. L. Thorn, *Diss. Abstr. Int. B.*, 1978, **39(1)**, 230; T. A. Albright, R. Hoffmann, S. C. Thibeault, and D. L. Thorn, *J. Am. Chem. Soc.*, 1979, **101**, 3801.

¶ Our data cannot rule out a ^{13}C exchange mechanism involving concerted interchange of one β-hydrogen with concomitant migration of a platinum(II) centre *via* an intermediate such as (i). We



(i)

acknowledge Professor R. G. Bergman for bringing this possibility to our attention. We have seen no evidence for Pt–X (X = I or Cl) bond heterolysis in the xylene or decene solvents used. However, we have not studied these thermolyses in solvents likely to stabilize free ions. We can conclude that $\Delta G^{\ddagger}_{B}$ does not correlate with the expected tendencies of X^- to dissociate from Pt^+ in our non-polar solvents.

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