High-pressure methods as a tool in organometallic syntheses: facilitation of oxidative addition to platinum(II)

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Abstract: High-pressure (2 GPa) batch reactors now commercially available may offer substantial accelerations of organometallic syntheses, without resort to heating, when the activation process is multicentered or involves the generation and solvation of ions. As an example of the latter class of reactions, the kinetics of the oxidative additions of methyl and ethyl iodides (RI) to dimethyl(2,2'-bipyridine)platinum(II) in acetone have been studied over the pressure range 0–200 MPa. The volumes of activation ΔV_1^{\pm} , if assumed to be constant over this range, are -11.7 ± 0.3 and -9.7 ± 0.7 cm³ mol⁻¹, respectively, implying an acceleration of ca. 3000-fold for a batch synthesis of this sort at 2 GPa. However, a possible slight pressure dependence of ΔV_1^{\pm} may reduce this acceleration to ca. 1 000-fold. The ΔV_1^{\pm} data and the 500-fold retardation on going from R = Me to R = Et are consistent with an S_N2 attack of Pt^{II} on the α -carbon in the alkyl iodides, forming I⁻ and [RMe₂Pt(bpy)]⁺.

Key words: volumes of activation, high pressure, oxidative addition, platinum(II), organometallic syntheses.

Résumé : Lorsque le processus d'activation est multicentrique ou qu'il implique la génération ou la solvatation d'ions, les réacteurs discontinus à haute pression (2 GPa) qui sont maintenant disponibles commercialement peuvent s'avérer utiles pour accélérer de façon convaincante les synthèses d'organométalliques, sans chauffage. À titre d'exemple de réaction impliquant une solvatation d'ions, on a étudié la cinétique des additions oxydantes des iodures de méthyle et d'éthyle (RI) sur le diméthyl(2,2'-bipyridine)platine(II), dans l'acétone, à des pressions allant de 0 à 200 MPa. Si l'on fait l'hypothèse qu'ils sont constants sur l'ensemble de ces pressions, les volumes d'activation, ΔV_1^{+} , de ces deux réactions sont respectivement de -11.7 ± 0.3 et -9.7 ± 0.7 cm³ mol⁻¹ et, pour une synthèse discontinue de cette sorte à 2 GPa, ceci implique une accélération par un facteur de 3000. Toutefois, il est possible qu'une faible dépendance du ΔV_1^{+} sur la pression puisse réduire cette accélération à un facteur d'environ 1000. Les données de ΔV_1^{\pm} et un ralentissement par un facteur de 500 en passant de R = Me à R = Et sont en accord avec un mécanisme d'attaque S_N2 du Pt(II) sur le carbone en α des iodures d'alkyles conduisant à la formation de I⁻ et de [RMe₂Pt(bpy)]⁺.

Mots clés : volumes d'activation, pression élevée, addition oxydante, platine(II), synthèses d'organométalliques.

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The routine use of pressures on the order of 1 GPa (10 kbar) as a synthetic tool has gained acceptance among organic chemists (1–9), but to date has not found significant application in organometallic chemistry. Apart from the obvious advantage of producing enhanced activities of gaseous reactants, pressure P can influence the maximum attainable *yield* of a reaction through the equilibrium constant K if the reaction volume ΔV (the molar volume of the products minus that of the reactants) is nonzero:

$$[1] \quad \Delta V = -RT(\partial \ln K/\partial P)_{\rm T}$$

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¹ Author to whom correspondence may be addressed. Telephone: (403) 220-5358. Fax: (403) 289-9488. E-mail: swaddle@acs.ucalgary.ca Similarly, pressure influences the *rate* constant k of the reaction through the volume of activation ΔV^{\ddagger} (the molar volume of the transition state minus that of the reactants):

 $[2] \quad \Delta V^{\ddagger} = -RT(\partial \ln k/\partial P)_{\rm T}$

It is commonly assumed that ΔV and ΔV^{\ddagger} are independent of pressure, in which case ln K and ln k would be linearly dependent upon P. In principle, one can use the quite precise measurements of ΔV or ΔV^{\ddagger} that can be made at 0.1–200 MPa to predict the outcome of batch syntheses run in autoclaves at 1–2 GPa (pressures now routinely accessible with commercial pressure equipment). In practice, however, $|\Delta V|$ and $|\Delta V^{\ddagger}|$ often become smaller as the pressure is increased beyond 100 MPa. Linear extrapolations of ln K or ln k values from low-pressure measurements will therefore tend to overestimate the pressure effect, but at least they place upper limits on what can be achieved for a given reaction with high-pressure techniques.

In this article, we consider only the kinetic aspect — specifically, the potential of high pressures to accelerate syntheses that would otherwise be too slow, without resort to heating that might bring about thermal decomposition. Theoretical expectations for such accelerations, based on typical negative ΔV^{\ddagger} values (assumed to be independent of P), are given in

Fable 1.	Rate	constar	its k _P	at high	pressu	res rela	ative to	
tmosphe	ric pr	essure :	for so	me typ	ical vol	umes o	of activation	ation."

<i>P</i> /MPa		$/k_0^{b}$ at 25°C for Δ	
	-10	-20	$-30 \text{ cm}^3/\text{mol}^{-1}$
0	1	1	I
100	1.50	2.24	3.35
200	2.24	5.02	11.25
400	5.02	25.2	126.6
1000	56.5	3.19×10^{3}	1.80×10^{5}
2000	3.19×10^{3}	1.02×10^{7}	3.24×10^{10}

"Assumed independent of pressure.

^bAcceleration factors, or retardation factors for the corresponding positive values of ΔV^{+} .

Table 1. For positive ΔV^{\ddagger} values, these would be retardation factors; pressure-induced retardation could be useful synthetically in suppressing unwanted side reactions if these have a positive ΔV^{\ddagger} while that of the reaction of interest is negative or near zero.

An armchair experimentalist might identify at least three types of organometallic reaction as being likely candidates for high-pressure synthetic procedures.

- 1. Slow reactions that involve the formation of several bonds between initially separate molecules (cf. Diels– Alder reactions in conventional organic chemistry). These can be expected to have strongly negative ΔV^{\dagger} values, and so to be accelerated by hydrostatic pressure. Ryabov (10) points out that organometallic reactions requiring such multicentered activation tend to have high ΔH^{\ddagger} and strongly negative ΔS^{\ddagger} , and hence are often too slow for conventional synthetic operations. In general, however, trends in ΔV^{\ddagger} values tend to parallel those in ΔS^{\ddagger} , so we may anticipate very favorable pressure-induced accelerations for this class of reactions.
- 2. Syntheses with unwanted homolytic side reactions. Homolytic bond fission is generally associated with positive ΔV^{\ddagger} . Indeed, this has been demonstrated for some organometallic cases, viz., Cr—C homolysis pathways in the decompositions of aqueous (H₂O)₅CrCH(CH₃)₂²⁺, (H₂O)₅CrC(CH₃)₂OH²⁺, and (H₂O)₅CrCH₂C₅H₄NH³⁺, for which $\Delta V^{\ddagger} = +26$ (low-pressure limit), +15, and +19 cm³ mol⁻¹, respectively. In these reactions, the homolytic pathway is progressively "squeezed out" and the heterolytic alternative, where significant, emerges as the pressure is increased (11, 12).
- 3. Slow reactions involving a substantial increase in solvation. Any development of electric charge en route to the transition state demands an increase in solvation and hence a negative contribution to the volume of the system. This may overwhelm any positive contributions from bond breaking, so that the overall ΔV^{\pm} can be strongly negative even for a dissociatively activated process (13). Organometallic *oxidative addition* reactions can be of this type; for example, the slow addition of methyl iodide to β -diketonatobis(triphenylphosphite)rhodium(I) complexes evidently involves a rate-determining step that produces iodide and methylrhodium(III) ions, and ΔV^{\pm} values of -9,

-18, -19, and -23 cm³ mol⁻¹ were found for the trifluorobenzoylacetone complex in 1,2-dichloroethane, dichloromethane, acetone, and chloroform, respectively (14).

It therefore would seem that pressure acceleration could be used to advantage to force to useful degrees of completion those oxidative addition reactions that are thermodynamically feasible but normally too slow for practical purposes. To evaluate the likely usefulness of this approach in platinum chemistry and to gain mechanistic insights, we have used highpressure stopped-flow spectrophotometry to study the addition of methyl and ethyl iodides (RI) to dimethyl(2,2'-bipyridine)platinum(II):

[3] $RI + Me_2Pt(bpy) \xrightarrow{k_1} [RMe_2Pt(bpy)]^+ + I^ \xrightarrow{k_2} RMe_2Pt(bpy)I$

Reactions of this type are of special interest in that they afford routes to organometallic polymers (15, 16), and in any event they provide informative models of the process of oxidative addition at d^8 square-planar centers, which is of industrial importance (e.g., in the Monsanto process for acetic acid). Thus, for reaction [3] with R = Me in acetonitrile solvent, Crespo and Puddephatt (17) were able, using ¹H NMR at -40° C, to detect the actual Pt^{IV} intermediate $[Me_3Pt(bpy)]^+$ and demonstrate that it contained a molecule of coordinated solvent; as the solution warmed to 0°C, iodide ion replaced the coordinated CH₃CN, trans to the added methyl group. Detection of major concentrations of the intermediate implied that the rate constant k_1 was greater than k_2 at these temperatures in CH₃CN, but for O-donor solvents such as acetone and methanol (which have less affinity for Pt than does CH₃CN), this was possible only at -80° C. Over the range -7.5 to 20° C in acetone, addition of MeI to Me₂Pt(bpy) proceeded to form Me₃Pt(bpy)I with monophasic second-order kinetics, corresponding to a rate-controlling initial step characterized by k_1 with $\Delta H_1^{+} = 24.9 \text{ kJ mol}^{-1}$ and $\Delta S_1^{+} = -129 \text{ J K}^{-1} \text{ mol}^{-1} (18).^2$ These kinetic data are consistent with the addition of the solvent molecule to Pt synchronously with the attack of Pt^{II} on the methyl iodide (an S_N2 mechanism, as opposed to radical or radical-chain alternatives (17, 18)) together with the augmented solvation associated with the development of ions in this initial step.

This strongly negative ΔS_1^{\dagger} for RI = MeI for reaction [3] in acetone led us to anticipate a correspondingly strongly negative ΔV_1^{\dagger} , and hence good prospects for synthetically useful pressure-induced accelerations of other, slower, oxidative additions at Pt^{II} centers (e.g., reaction [3] with methyl acetate in place of MeI). The S_N2 mechanism implies slower substitution with more sterically hindered nucleophiles, and we therefore studied reaction [3] with both EtI and MeI to ascertain whether ΔV_1^{\dagger} is significantly affected by steric factors.

After this work was completed, we learned of the high-pressure kinetic study by Dücker–Benfer, van Eldik and Canty (19) of the *palladium* analogue of reaction [3] (R = MeI, solvent = acetone), which differs in that both the oxidative addition ($\Delta V^{\pm} = -11.9 \pm 0.6 \text{ cm}^3 \text{ mol}^{-1}$) and subsequent reductive

² The activation energy cited in ref. 18 is in fact the enthalpy of activation.

Fig. 1. Pressure dependence of k_1 for addition of MeI to Pt(bpy)Me₂ in acetone at 25°C. Circles: [MeI] = 4.02 mmol L⁻¹. Down triangles: [MeI] = 3.01 mmol L⁻¹. Up triangles: [MeI] = 2.01 mmol L⁻¹. Each data point is the mean of three k_1 values. Broken line: linear regression (eq. [4]). Solid curve: quadratic regression (eq. [5]).



elimination of ethane $(\Delta V^{\ddagger} = -17 \pm 1 \text{ cm}^3 \text{ mol}^{-1})$ could be observed — reductive elimination in the Pt^{IV} complex is negligible because of its high activation energy, even though addition of MeI to the Pt^{II} complex is faster than to the Pd^{II} (18). Comparison of our results with ΔV^{\ddagger} for the latter pathway is instructive.

Experimental

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Preparation of dimethyl(2,2'-bipyridine)platinum(II)

In our hands, $Pt(bpy)Me_2$ was best prepared via $Pt(COD)Cl_2$ (COD = 1,5-cyclooctadiene), by variations of the methods of Clark and Manzer (20) and Puddephatt et al. (16, 21). $Pt(COD)Cl_2$ was made in 88% yield by heating K₂PtCl₄ (1.7 mmol) in aqueous 1-propanol with COD (1.46 mL) at 60°C for 1.5 h. Addition of NaI to a suspension of $Pt(COD)Cl_2$ in acetone gave $Pt(COD)I_2$ quantitatively. Treatment of this solid with methyllithium in diethyl ether under N₂ at 0°C for 2 h, followed by hydrolysis with ice-cold saturated aqueous NH₄Cl, ether extraction, and evaporation of the ether layer gave $Pt(COD)Me_2$. Reaction of this solid with bpy in acetonitrile gave a 75% yield of moisture-sensitive $Pt(bpy)Me_2$, which was recrystallized from acetone to give red needles, the authenticity of which was confirmed by CHN analyses and NMR spectroscopy (22).

High-pressure kinetics

Freshly prepared solutions of Pt(bpy)Me₂ and a 20-fold excess of MeI (or 5000-fold excess of EtI) in redistilled anhydrous acetone were loaded into an HPSF-56 high-pressure stoppedflow spectrophotometer (Hi-Tech Scientific Ltd., Salisbury, U.K.) thermostated at 25.0 \pm 0.1°C. Pressures were measured with an Autoclave Engineers digital gauge, calibrated (\pm 0.2 MPa) against a Pressurements T3800/4 deadweight gauge. After each pressurization, the system was allowed to re-equilibrate thermally for 30–45 min before firing reagent mixing shots. At least three shots were fired for each pressure and set of concentrations, and the progress of the reaction after mixing was monitored spectrophotometrically through the decay of the absorbance maximum of Pt(bpy)Me₂ at 475 nm (molar absorbance $\varepsilon = 1828 \pm 6 \text{ L} \text{ mol}^{-1} \text{ cm}^{-1}$). The absorbance data were collected and analyzed in terms of a pseudo-first-order rate equation on a dedicated Apple IIe computer. The reaction with EtI at atmospheric pressure was actually slow enough to follow by conventional spectrophotometry with lower [EtI], but the high-pressure experiments required the stopped-flow approach because of the long thermal equilibration times.

Results

It was confirmed by NMR spectroscopy that the products of the reactions of Pt(bpy)Me₂ with MeI and EtI in acetone were indeed Me₃Pt(bpy)I and Me₂EtPt(bpy)I, respectively. The stopped-flow data gave excellent fits to the pseudo-first-order rate equation — better than $\pm 0.1\%$ in the calculated rate constant \hat{k}_{obsd} — and values of k_{obsd} were accurately proportional to [MeI] or [EtI] (supplementary material, Table S1³). There was no evidence for the formation of a long-lived intermediate $[Me_3Pt(bpy)(Me_2CO)]^+$ in the reaction with MeI; furthermore, the reaction of 0.19 mmol L^{-1} Pt(bpy)Me₂ with 4.0 mmol L^{-1} EtI, which was slow enough to follow in a conventional spectrophotometer, showed a strictly maintained isosbestic region at 378-385 nm. Therefore, since the spectra obtained immediately after mixing corresponded to Pt(bpy)Me2 and the final spectra to RMe₂Pt(bpy)I, $k_{obsd}/[RI]$ values represent k_1 for reaction [3].

Figures 1 and 2 show the pressure dependences of $\ln k_1$ for reaction [3] in acetone with R = Me and Et, respectively. Linear least-squares regression (eq. [4]) represents the data adequately for both MeI and EtI addition, giving $k_1^{0} = 53 \pm 1 \text{ L} \text{mol}^{-1} \text{ s}^{-1}$ with $\Delta V_1^{\pm} = -11.7 \pm 0.3 \text{ cm}^3 \text{ mol}^{-1}$ for the combined data for MeI, and $k_1^{0} = 0.104 \pm 0.004 \text{ L} \text{ mol}^{-1} \text{ s}^{-1}$ with $\Delta V_1^{\pm} = -9.7 \pm 0.7 \text{ cm}^3 \text{ mol}^{-1}$ for EtI, at 25.0°C. The zero (\approx atmospheric) pressure rate constant k_1^{0} for MeI agrees satisfactorily with 49 L mol⁻¹ s⁻¹ extrapolated from the data of Puddephatt et al. (18).

[4] $\ln k_1 = \ln k_1^0 - (\Delta V_1^*/RT)P$

For MeI addition, however, a possible slight nonlinearity of the ln k_1 vs. P plot is discernible for the combined data. For simplicity, the data may be fitted to the quadratic expression

[5]
$$\ln k_1 = \ln k_1^0 - (\Delta V_1^{0^{\ddagger}}/RT)P + (\Delta \beta^{\ddagger}/2RT)P^2$$

giving $k_1^{0} = 51 \pm 1 \text{ L mol}^{-1} \text{ s}^{-1}$ (in still better agreement with Puddephatt et al. (18)), the limiting zero-pressure volume of activation $\Delta V_1^{0\pm} = -14.4 \pm 0.7 \text{ cm}^3 \text{ mol}^{-1}$, and the compress-

³ Table S1, showing pressure dependences of rate constants for the reactions of MeI and EtI with Pt(bpy)Me₂ in acetone at 25°C (1 page) has been deposited as supplementary material and can be purchased from: The Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, Canada K1A 0S2.

Fig. 2. Pressure dependence of k_1 for addition of EtI to Pt(bpy)Me₂ in acetone at 25°C. Each data point is the mean of three k_1 values. Solid line: linear regression (eq. [4]).



ibility coefficient of activation $\Delta\beta^{\ddagger} = -(\partial\Delta V_1^{\ddagger}/\partial P)_T = -0.027 \pm 0.007 \text{ cm}^3 \text{ mol}^{-1} \text{ MPa}^{-1}$ (all uncertainty limits are standard deviations σ). Thus, for reaction [3] with RI = MeI, the curvature of the ln k_1 vs. *P* plot is significant, though barely so, at the 95% confidence level ($\approx 2\sigma$). If eq. [5] is adopted, then the ΔV_1^{\ddagger} values from the linear regressions represent the mean or mid-range (100 MPa) value of this parameter. For RI = EtI, use of eq. [5] rather than eq. [4] is clearly unwarranted (Fig. 2).

Discussion

The ΔV_1^{\dagger} values from the linear fits are not very different for R = Me and Et, and imply that, if a 2 GPa press for batch samples is available, the greatest pressure accelerations of reactions of the type [3] that might be anticipated would be about 3000fold at ambient temperature (cf. Table 1). This is probably an overestimate, since the data for MeI suggest that $\Delta\beta^{\dagger}$ is nonzero, but $|\Delta\beta^{\dagger}|$ itself can be expected to decrease with pressure - there is no general agreement on equations for extrapolation of the pressure dependences of rate or equilibrium constants far beyond the data base (23), and certainly eq. [5], the simplest nonlinear regression equation, is acceptable only for interpolation of data at best. Taking these results together with those for the Pd analogue of reaction [3] (19) and oxidative addition at Rh¹ centres (14), we conclude that a synthetic organometallic chemist may expect pressure accelerations of oxidative addition reactions of some three orders of magnitude if a 2 GPa press is used.

The large (500-fold) retardation in reaction [3] in acetone on going from MeI to EtI, together with the similar moderately strongly negative values of ΔV_1^* for the two reactants, supports Puddephatt's view of the mechanism as an S_N2 process (17, 18). Nucleophilic attack of Pt^{II} on the α -carbon of RI along the axis perpendicular to the plane of the square-planar complex would clearly be very susceptible to steric hindrance from substituent groups on that carbon atom. Volume decreases due to R—Pt bond formation, plus solvation of the incipient ions together with any coordination of solvent in the sixth site of the Pt^{1V} intermediate, will overwhelm the positive contribution to ΔV_1^{+} from C—I bond breaking. The striking similarity of our ΔV_1^{+} value for reaction [3] with RI = MeI to that reported by van Eldik's group (19) for the ca. 10-fold slower but otherwise analogous Pd^{II} reaction ($\Delta V_1^{+} = -11.9 \pm 0.6 \text{ cm}^3 \text{ mol}^{-1}$) supports this interpretation.

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