Gas-phase kinetics of ground-state platinum with O_2 , NO, N_2O and CH_4

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The gas-phase reactivity of ground-state platinum with O_2 , NO, N_2O and CH_4 is reported. Platinum atoms were produced by the photodissociation of $[Pt(CH_3)_3(C_5H_4CH_3)]$ and detected by laser-induced fluorescence. The reaction rates of platinum with all the reactants are pressure dependent indicating adduct formation; however, the reaction with N_2O has a bimolecular component. The room-temperature limiting low-pressure third-order rate constants in argon buffer are $(2.3 \pm 0.2) \times 10^{-31}$ molecule⁻² cm⁶ s⁻¹, $(4.3 \pm 0.4) \times 10^{-31}$ molecule⁻² cm⁶ s⁻¹, $(3.7 \pm 0.5) \times 10^{-31}$ molecule⁻² cm⁶ s⁻¹ and $(2.1 \pm 0.9) \times 10^{-28}$ molecule⁻² cm⁶ s⁻¹ for O_2 , NO, N_2O and CH_4 , respectively, where the uncertainties are $\pm 2\sigma$. The limiting high-pressure second-order rate constants are $(2.5 \pm 0.5) \times 10^{-12}$ molecule⁻¹ cm³ s⁻¹, $(2.3 \pm 0.8) \times 10^{-11}$ molecule⁻¹ cm³ s⁻¹, $(2.3 \pm 0.3) \times 10^{-12}$ molecule⁻¹ cm³ s⁻¹ for O_2 , NO, N_2O and CH_4 , respectively. The second-order rate constant for the abstraction channel for the reaction with N_2O at 296 K is approximately 1×10^{-13} molecule⁻¹ cm³ s⁻¹.

Gas-phase transition metal (TM) chemistry is an intriguing field of study due to the high multiplicities of the atomic ground states and the large number of low-lying metastable states. The early gas-phase work of TMs focused on the reactions of the cations due to the ability of mass-spectrometric methods to control the kinetic energy and electronic state of the reactant ion selectively and to detect the products sensitively. An understanding of how the low-lying M^+ electronic states govern chemical reactivity is now fairly well established.^{1–5}

The kinetics of the reactions of neutral TM atoms has recently been an active field of study.^{6–48} The cumulative data reported thus far indicate the electronic state is a very important factor in the dynamics of these reactions. For example, for both the termolecular association and abstraction channels with O_2 , TMs with s^1d^{n-1} configurations have been found to be more reactive than their s^2d^{n-2} counterparts.^{26,32,47}

Of the TMs, the 3d and 4d series have garnered the most experimental and theoretical attention^{6-18,21-43} while the 5d series remains relatively unstudied. Quite recently, however, studies involving a few of the 5d TMs have been reported.^{18-20,44-48} The most complete study of the 5d series has involved reactions with hydrocarbons.¹⁸⁻²⁰ In the reactions of TMs with hydrocarbons, the 5d series metals are generally more reactive than the 3d metals. This trend has been explained as arising from the better size match between the 6s and 5d orbitals relative to the 4s and 3d orbitals of the 3d series.¹⁹ This better size match helps drive the chemical reaction due to the increased bond energy of the metal–carbon or metal–hydrogen bonds in the product. For reactions with oxygen-containing molecules, the 5d series again appears to be more reactive than the 3d series, although this trend is based on only a few 5d metals.⁴⁴⁻⁴⁸ More experimental studies are required to substantiate this trend.

In this paper we report a temperature- and pressuredependent kinetic study of the $(6s)^{1}(5d)^{9}$ a ${}^{3}D_{3}$ state of platinum with oxygen, nitric oxide, nitrous oxide and methane. Here we use the more compact Russell–Saunders term symbolism to describe the ground state of platinum rather than the more correct term, $[(d_{3/2})^{4}(d_{5/2})^{5}(s_{1/2})]_{3}$, based on *jj* coupling. Thus, we use the more familiar symbolism even though *L* and S are not rigorously good quantum numbers in platinum due to the large spin-orbit coupling.

The only other kinetic studies involving gas-phase platinum chronicled the reactions of ground-state platinum with small hydrocarbons.^{19,20} We are unaware of any previous kinetic studies involving oxygen-containing oxidants. The reporting of these reactions for platinum will further update the database of TM reactions and allow comparison of platinum's kinetic behavior with other TMs. Unfortunately, theoretical calculations involving the 5d series are extremely difficult owing to the complications arising from electron correlation, relativistic and spin–orbit effects. Moderately successful theoretical studies involving iridium and platinum with methane have been reported.¹⁹ We hope these new kinetic results will inspire further theoretical work in an effort to understand these reactions further.

Experimental

Pseudo-first-order kinetic experiments ([Pt] \ll [oxidant]) were carried out in an apparatus with slowly flowing gas using a laser photolysis/laser-induced fluorescence (LIF) technique. The experimental apparatus and technique have been described in detail elsewhere.⁴⁴ Briefly, the reaction chamber is a stainless-steel reducing four-way cross with attached side arms and a sapphire window for optical viewing. The reaction chamber is enclosed within a convection oven (Blue M, model 206F) for temperature dependence experiments.

Platinum atoms were produced by the 248 nm photodissociation of trimethyl(methylcyclopentadienyl)platinum(IV) [Pt(CH₃)₃(C₅H₄CH₃)] using the output of an excimer laser (Lambda Physics Lextra 200). Platinum atoms were detected *via* LIF using an excimer-pumped dye laser (Lambda Physics Lextra 50/ScanMate 2E) with a KDP doubling crystal tuned to the $[(d_{3/2})^4(d_{5/2})^5(p_{1/2})^1]^{\circ}_3 \leftarrow a^3D_3$ transition at 292.979 nm.⁴⁹ The fluorescence was detected at 90° to the counterpropagated laser beams with a three-lens telescope imaged through an iris. A photomultiplier tube (Hamamatsu R375) was used in collecting the LIF which was subsequently sent to a gated boxcar sampling module (Stanford Research Systems SR250), and the digitized output was stored and analyzed by a computer.

The platinum precursor was entrained in a flow of argon buffer gas. The precursor carrier gas, argon buffer gas, and

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reactant gases flowed through calibrated mass flow meters and flow controllers prior to admission to the reaction chamber. Each sidearm window was purged with a slow flow of buffer gas to prevent deposition of platinum and other photoproducts. Total flows were between 150 and 4000 sccm. Pressures were measured with MKS Baratron manometers, and chamber temperatures were measured with a thermocouple.

The delay time between the photolysis pulse and the dyelaser pulse was varied by a digital delay generator (Stanford Research Systems DG535) controlled by a computer. The trigger source for these experiments was scattered pump laser light incident upon a fast photodiode. LIF decay traces consisted of 200 points, each point averaged for four laser shots.

Materials

Trimethyl(methylcyclopentadienyl)platinum(IV) (Strem, 98%), O2 (MG Industries, 99.8%), N2O (MG Industries, electronic grade, 99.999%), CH₄ (Linde, ultrahigh purity grade, 99.99%) and Ar (Potomac Airgas, 99.998%) were used as received. The NO (Liquid Carbonic, 99%) was passed through a liquid nitrogen/n-pentane trap at ca. -100 °C to condense impurities (primarily NO₂) before entrance into the reaction chamber.

Data analysis and results

The decay rates of the ground state of platinum as a function of reactant pressure were investigated in Ar buffer gas at various temperatures and total pressures. The loss of groundstate platinum is described by the first-order decay constant, k_{1st} :

$$k_{1st} = 1/\tau = k_{o} + k_{obsd} [oxid] \tag{1}$$

where τ is the first-order time constant for the removal of platinum under the given experimental conditions, k_0 is the loss term due to diffusion out of the detection zone and reaction with the precursor and precursor fragments, and k_{obsd} is the second-order rate constant. Typical decay profiles are shown in Fig. 1. A time constant, τ , for each decay profile was determined using a linear least-squares procedure. The second-order rate constant is determined from a plot of $1/\tau$ vs. reactant number density. Typical plots for obtaining second-



Fig. 1 Typical $Pt(a^{3}D_{3})$ decay curves with added oxidant in argon buffer at 296 K: (a) $P_{\text{total}} = 20.0$ Torr, P(NO) = 0.67 Torr, $\tau = 86 \,\mu\text{s}$; (b) $P_{\text{total}} = 20.0$ Torr, $P(\text{O}_2) = 1.18$ Torr; $\tau = 130 \,\mu\text{s}$; (c) $P_{\text{total}} = 10.0$ Torr, P(NO) = 0.78 Torr; $\tau = 197$ µs. The solid lines through the data are least-squares fits. The inset is an ln plot of the data.



Fig. 2 Typical plots for determining k_{obsd} for Pt(a ${}^{3}D_{3}$) + O₂ at 296 K illustrating the dependence of the bimolecular rate constants on total pressure. The solid line for each set of data is a linear regression fit from which k_{obsd} is obtained.

order rate constants are presented in Fig. 2-5; the slope yields the observed rate constant. The relative uncertainty (i.e. the reproducibility) of the second-order rate constants is estimated at $\pm 20\%$ based on repeated measurements of rate constants under identical temperature and total pressure conditions. The absolute uncertainties are conservatively estimated to be $\pm 40\%$ and are based on the sum of the statistical scatter in the data, uncertainty in the flowmeter and flow controller readings (5%) and the total pressure reading (1%), and uncertainties due to incomplete gas mixing.

Measured rate constants for the a ³D₃ state reacting with O₂, NO, N₂O and CH₄ in argon buffer at various pressures are listed in Table 1. The second-order rate constants were also measured at temperatures up to 423 K. Rate constants could not be measured reliably above 423 K owing to the increase in k_0 for platinum at higher temperatures; *i.e.* platinum reacts rapidly with the precursor at temperatures >423K. For the reactions with O₂, NO and CH₄, the rate constants at 423 K and 5 Torr are 3.4×10^{-14} , 6.6×10^{-14} and 5.1×10^{-12} molecule⁻¹ cm³ s⁻¹, respectively. These rate constants are either lower or equal to the room-temperature rate



Fig. 3 Typical plots for determining k_{obsd} for Pt(a ${}^{3}D_{3}$) + NO at 296 K. The solid lines are linear regression fits from which k_{obsd} is obtained.



Fig. 4 Typical plots for determining k_{obsd} for Pt(a³D₃) + N₂O at 296 K. The solid lines are linear regression fits from which k_{obsd} is obtained.

constants at this pressure within experimental error. Thus, the pressure dependence indicates termolecular processes for these reactants while the temperature results indicate either small or no barriers to reaction. For the reaction with N_2O , the



Fig. 5 Typical plots for determining k_{obsd} for Pt(a ${}^{3}D_{3}$) + CH₄ at 296 K. The solid lines are linear regression fits from which k_{obsd} is obtained.

Table 1 Second-order rate constants $(10^{-12}\ molecule^{-1}\ cm^3\ s^{-1})$ for Pt(a $^3D_3)$ with O_2 , NO, N_2O and CH_4 in argon buffer at 296 K

total pressure /Torr	0 ₂	NO	N ₂ O	CH ₄
2.5	_	_	0.13	4.9
5	0.043	0.080	0.18	5.0
10	0.089	0.16	0.23	5.3
20	0.17	0.32	0.36	6.3
30	0.20	_	0.42	_
50	0.32	0.72	0.55	6.2
75	_	—	0.78	_
100	0.54	1.3	0.86	6.2
150	0.77	1.9	1.2	_
200	0.96	2.4	1.3	6.3
250	1.1	3.1	1.4	_
300	1.2	3.7	1.5	6.4

Table 2 Second-order rate constants for $Pt(a^{3}D_{3}) \stackrel{\text{Visw}}{\rightarrow} 0^{\text{rticle}} 2.5^{\text{line}}$ Torr in argon buffer

T/K	$\frac{k_{\rm obsd}}{10^{13} \text{ molecule}^{-1} \text{ cm}^{-3} \text{ s}^{-1}}$		
296	1.3		
373	1.9		
398	2.1		
423	2.8		

second-order rate constants increased slightly with temperature. Rate constants as a function of temperature for this reaction are shown in Table 2.

For the reaction of platinum with methane, the rate constants are only slightly pressure dependent over the pressure range studied here. Furthermore, it appears the fall-off to the high-pressure limit occurs at a relatively low pressure (ca. 20 Torr). It is reasonable to question whether the pressure dependence is real or simply the result of statistical fluctuation in the measurements. The rate constants at 5 and 20 Torr were each measured seven times on six different days. The standard deviations for the measurements for each of these two pressures are both 0.6×10^{-12} . Thus, using the *t*-test, the difference between the rate constants is significant to the 99% confidence level. However, a more convincing argument than a statistical analysis is the result of a flow-tube study for this reaction done by Carroll et al. at very low pressures.¹⁹ The rate constants measured at 1.1 Torr or less are significantly lower than the rate constants measured here. Their use of helium as the buffer gas is not expected to cause such a dramatic difference in the rate constants. Thus, the cumulative evidence supports the conclusion that the reaction is pressure dependent.

Discussion

$Pt + O_2$

Results for the reaction of platinum with O_2 indicate a termolecular reaction mechanism:

$$Pt + O_2 \xrightarrow{[Ar]} PtO_2; \ \Delta H^\circ = -394 \text{ kJ mol}^{-1} \text{ (ref. 50)} \quad (2)$$

The bimolecular abstraction channel to produce PtO is endothermic by 106 kJ mol⁻¹;^{50,51} thus the thermodynamic barrier prohibits this pathway at the temperatures studied here. The variation with total pressure of the second-order rate constants at room temperature in argon buffer is shown in Fig. 6. The solid lines through the data in Fig. 6 are weighted fits to the simplified Lindemann–Hinshelwood expression⁵²

$$k_{\text{obsd}} = \frac{k_{\text{o}}[\text{Ar}]}{1 + k_{\text{o}}[\text{Ar}]/k_{\infty}}$$
(3)

where k_0 is the limiting low-pressure third-order rate constant, k_{∞} is the limiting high-pressure second-order rate constant, and [Ar] is the buffer gas number density. k_0 and k_{∞} for the reaction of O_2 in argon buffer at 296 K are $(2.3 \pm 0.2) \times 10^{-31}$ molecule⁻² cm⁶ s⁻¹ and $(2.5 \pm 0.5) \times 10^{-12}$ molecule⁻¹ cm³ s⁻¹, respectively. The listed uncertainties are $\pm 2\sigma$. The value of the limiting lowpressure third-order rate constant is relatively large, consistent with other termolecular reactions with O_2 involving s¹dⁿ⁻¹ transition metals. Previous studies of the 3d transition metal association reactions with O_2 indicate that TMs with ground state or low-lying s¹dⁿ⁻¹ configurations are reactive whereas TMs with s²dⁿ⁻² ground-state configurations are unreactive.²⁶ This behavior has been explained in terms of simple molecular orbital concepts. In the approach of the TM to O_2 , the nature of the potential in the region of the onset of orbital



Fig. 6 Pressure dependence of the reaction of $Pt(a {}^{3}D_{3})$ with O_{2} and NO in argon buffer at 296 K. Error bars represent $\pm 20\%$ uncertainty. The solid lines are fits to eqn. (3).

overlap will be determined by the interaction between the sorbital of the TM atom (which has a larger spatial extent than the d-orbitals) and the in-plane π^* -antibonding orbital of O₂. For a TM atom with an s¹ configuration, an electron-pair bond may be formed from the overlap of these orbitals, as in a radical-radical recombination process. In the case of an s² configuration, one of the s-electrons occupies the antibonding molecular orbital between the TM atom and O₂, which destabilizes the complex and leads to a less attractive or a repulsive potential.²⁶

The value of the low-pressure limiting third-order rate constant for platinum is approximately an order of magnitude smaller than another Group 10 atom, nickel.²⁶ k_o for platinum is more similar to the Group 11 copper atom^{21.26} than to nickel. Thus, this reaction is a case where the 3d TM is more reactive than the 5d TM of the same group. The smaller reactivity of platinum relative to nickel is surprising considering the better ability of the 5d orbitals in platinum to be involved in bonding.

Unfortunately, a more thorough quantitative understanding of the dynamics of these reactions awaits accurate theoretical calculations.

Pt + NO

Results of the reaction of $Pt(a^{3}D_{3}) + NO$ indicate a termolecular reaction mechanism.

$$Pt + NO \xrightarrow{[Ar]} PtNO$$
(4)

Production of PtO from the abstraction channel is endothermic by 239 kJ mol^{-1,50,51} The variation with total pressure of the second-order rate constants at room temperature in argon buffer is shown in Fig. 6. The solid lines through the data in Fig. 6 are weighted fits to eqn. (3). k_o and k_∞ for the reaction of NO in argon buffer at 296 K are $(4.3 \pm 0.4) \times 10^{-31}$ molecule⁻² cm⁶ s⁻¹ and $(2.3 \pm 0.8) \times 10^{-11}$ molecule⁻¹ cm³ s⁻¹, respectively.

Termolecular processes are expected for the majority of TM atoms reacting with NO since only the Group 3, 4 and 5 atoms along with tungsten have exothermic abstraction reactions with NO. Thus far, however, extensive pressure-dependent rate constants have been reported only for chromium,²⁵ iron,^{24,43} manganese,⁴³ molybdenum³⁷ and ruthenium.⁴³ The two atoms in the 3d series with s²dⁿ⁻² electron configurations are extremely inefficient processes with NO whereas the TMs with s¹dⁿ⁻¹ configurations have much more efficient reactions. In the s¹ configuration, the singly occupied orbital of the TM might overlap favorably with the unpaired electron on NO, forming a bond. This argument is

the same rationale used to explain the reactivity dependence on electron configuration in the termolecular reactions of 3d TM atoms with O_2 . Even if the d-electrons of the TM atom are involved in the bonding, the reactivity of the s² configuration would still be expected to be lower than that of the s¹ configuration because of its more diffuse nature. The greater efficiency of platinum relative to iron and manganese may be due to the better size match between the 6s- and 5d-orbitals compared to the 4s- and 3d-orbitals of the 3d series. The better size match might help drive the chemical reaction due to the increased incorporation of the d-orbitals in the bonding to yield larger metal–oxygen bond energies in the product. Again, a more thorough quantitative understanding of the dynamics of this reaction awaits accurate theoretical calculations.

$Pt + N_2O$

The pressure dependence of the rate constants for the reaction of platinum with N_2O indicate the termolecular channel is important. However, a fit of the rate constants to eqn. (3) gave unsatisfactory results (see below). Furthermore, the rate constants (Table 2) increase with temperature; thus, a bimolecular abstraction channel is also indicated. The abstraction channel:

Pt + N₂O → PtO + N₂;

$$\Delta H^\circ = -225 \text{ kJ mol}^{-1} \text{ (ref. 50 and 51)} (5)$$

is exothermic so there are no thermodynamic barriers for this reaction. However, the pressure dependence of the rate constants indicates the termolecular component is also operative. The variation with total pressure of the second-order rate constants at room temperature in argon buffer gas is shown in Fig. 7. The dashed line in Fig. 7 is the fit to eqn. (3). A better fit to the data is obtained by fitting the rate constants to the equation:

$$k_{\text{obsd}} = \frac{k_{\text{o}}[\text{Ar}]}{1 + k_{\text{o}}[\text{Ar}]/k_{\infty}} + k_{\text{abs}}$$
(6)

where k_{abs} is the rate constant for the bimolecular abstraction channel. The solid line through the data in Fig. 7 is a weighted fit to eqn. (6). k_o , k_∞ and k_{abs} for the reaction of N₂O in argon buffer at 296 K are $(3.7 \pm 0.5) \times 10^{-31}$ molecule⁻² cm⁶ s⁻¹, $(2.3 \pm 0.3) \times 10^{-12}$ molecule⁻¹ cm³ s⁻¹ and $(1.1 \pm 0.2) \times 10^{-13}$ molecule⁻¹ cm³ s⁻¹, respectively. In fitting the rate constants to eqn. (6), the assumption is made that the abstraction channel is independent of the termolecular



Fig. 7 Pressure dependence of the reaction of $Pt(a^{3}D_{3})$ with N₂O in argon buffer at 296 K. Error bars represent $\pm 20\%$ uncertainty. The solid line is a fit to eqn. (6). The dotted line is the fit determined from eqn. (3).

channel. This may not, however, be the case. There is the possibility that the mechanism for this reaction resembles the mechanism proposed for the reaction of $Al + CO_2$; *i.e.* an energized intermediate is formed which can decompose along three different paths.^{53,54} If the mechanism for the reaction of platinum with N₂O involves an energized intermediate complex (PtON₂*):

$$Pt + N_2O \xrightarrow[k_1]{k_1} PtON_2^* \xrightarrow[k_2]{k_2} PtON_2$$
(7)
$$PtON_2 + PtON_2$$
(7)

then the experimentally observed rate constant is:53

$$k_{\rm obsd} = k_1 \left(\frac{k_2 + k_3 [\text{Ar}]}{k_{-1} + k_2 + k_3 [\text{Ar}]} \right)$$
(8)

According to this mechanism the Pt and N₂O react to form an energized complex, $PtON_2^*$, with rate constant k_1 . This complex can then be stabilized by collisions $(k_3[Ar])$ or can either react to produce PtO product (k_2) or decompose back to reactants (k_{-1}) . Thus, the physical interpretation of eqn. (8) is that the experimentally observed rate constant is equal to the rate of energized complex formation multiplied by the fraction of energized complexes which do not decompose back to reactants. The only rate constant which can be determined absolutely from the data is k_1 ; only relative values of the other constants can be determined. A least-squares fit of the rate constants to eqn. (8) yields $(2.3 \pm 0.3) \times 10^{-12}$ molecule⁻¹ cm³ s⁻¹ for k_1 . The ratios k_2/k_3 and k_{-1}/k_3 are 2.1 \pm 2.1 and 51 ± 20 molecule cm⁻³, respectively. k_2/k_3 is obviously not determined very well from our data. These parameters yield essentially the same goodness of fit to the data as the parameters reported previously for the fit to eqn. (6). In the limit of zero buffer gas pressure, eqn. (6) reduces to:

$$k_{\rm obsd} = k_1 \left(\frac{k_2}{k_{-1} + k_2} \right) \tag{9}$$

which corresponds to the rate of the abstraction reaction in the absence of buffer gas. Substitution of the fitted parameters from eqn. (8) to eqn. (9) yields a value of 9.0×10^{-14} molecule⁻¹ cm³ s⁻¹ for the rate constant of the abstraction channel in the absence of buffer gas. Further experiments in which the pressure dependence of the yield of PtO product is determined would help to resolve the correct mechanism.

The only other termolecular reaction involving a TM with N_2O thus far reported is the a ${}^4F_{9/2}$ state of iridium. Iridium's reaction efficiency, however, is over two orders of magnitude smaller than the termolecular parameters reported here for platinum.⁴⁸ Recent experiments in our laboratory indicate the reaction of nickel with N_2O is also pressure dependent with rate constants similar in magnitude to those reported here for platinum.

Abstraction reactions of all TM atoms with N₂O are exothermic owing to the formation of the stable N₂ and metal oxide molecules. Despite this exothermicity, metal-atom reactions with N₂O have been observed to have significant energy barriers. These barriers have been attributed to the requirement of a non-adiabatic transition along the reaction pathway.⁵⁵ In order to conserve electron spin, the ¹Σ⁺ ground state of N₂O correlates adiabatically to O(¹D₂) + N₂(¹Σ⁺), 15868 cm⁻¹ above the O(³P₂) + N₂(¹Σ⁺) asymptote.⁵⁶ Thus, the lowest-energy reaction pathway requires a transition from reactant surfaces of O(¹D₂) character to surfaces of O(³P) character in order to access the low-energy product states.

Recently, Fontijn and co-workers have advanced a resonance interaction model^{57–60} to predict barriers to reaction and rate constants for metal atoms reacting with N_2O . In this model, the activation barriers are calculated by taking into account the ionization potential and sp promotion energy of

the metal, the electron affinity of N₂O, and the bond energy of the metal oxide product. The resonance interaction model predicts a room-temperature rate constant of 2×10^{-19} molecule⁻¹ cm³ s⁻¹ for platinum,⁵⁷ a value over five orders of magnitude smaller than the smallest experimentally measured rate constant here.

$Pt + CH_4$

The two most plausible reaction pathways for the reaction of platinum with methane are the termolecular insertion channel to produce $H-Pt-CH_3$ and the bimolecular H_2 elimination reaction to produce $Pt-CH_2$. Our experimental results combined with the previously reported flow tube results¹⁹ indicate this reaction follows a termolecular reaction mechanism:

Pt + CH₄
$$\xrightarrow{[Ar]}$$
 H-Pt-CH₃;
 $\Delta E = -134 \text{ kJ mol}^{-1}$ (ref. 19) (10)

The variation with total pressure of the second-order rate constants at room temperature in argon buffer is shown in Fig. 8. The solid lines through the data in Fig. 8 are weighted fits to eqn. (3). The open squares in Fig. 8 are rate constants from ref. 19 and were not included in the fit to eqn. (3). k_o and k_∞ determined from the rate constants reported here for the reaction of CH₄ in argon buffer at 296 K are $(2.1 \pm 0.9) \times 10^{-28}$ molecule⁻² cm⁶ s⁻¹ and $(6.3 \pm 0.3) \times 10^{-12}$ molecule⁻¹ cm³ s⁻¹, respectively.

Of the four reactions reported here, extensive calculations have only been reported for the reaction of platinum with methane. These calculations make a clear prediction that the product of this reaction is the collisionally stabilized, long-lived H-Pt-CH₃ insertion complex rather than H₂ elimination. A condensation of the primary findings reported by Carroll *et al.* follows.¹⁹

The calculations by Carroll *et al.* indicate the electronic structure of platinum is an important factor in the dynamics of this reaction. The calculations investigated both the lowest triplet and singlet potential-energy surfaces along paths leading from $Pt + CH_4$ to the C-Pt-H bond insertion intermediate and finally on to elimination of H_2 . The s¹d⁹ ground state has the proper configuration to form two covalent bonds in the H-Pt-CH₃ insertion complex. This contributes to the large binding energy (134 kJ mol⁻) of the insertion complex relative to the ground-state asymptotes. Equally important, however, is the presence at relatively low energy of the d¹⁰ ¹⁵S₀ state which diminishes long-range repulsion and correlates in spin to the deep H-Pt-CH₃ insertion complex. When combined, these two features allow ground-state Pt to access the

Fig. 8 Pressure dependence of the reaction of $Pt(a^{3}D_{3})$ with CH_{4} in argon buffer at 296 K. Error bars represent $\pm 20\%$ uncertainty. The solid line is a fit to eqn. (3). Open squares are data points from ref. 19.

deep insertion well. The considerable strength of the covalent Pt-H and $Pt-CH_3$ bonds causes the triplet-singlet crossing to occur at a low energy. The intersection between triplet and singlet surfaces is calculated to be only 5 kJ mol⁻¹ above ground-state reactants, which enables the triplet ground-state reactants to access the singlet insertion well by collisions at thermal energies.

The calculations further exclude H_2 elimination as the reaction pathway. The calculations indicate a large potential barrier separates $H-Pt-CH_3$ from H_2 elimination products which are substantially (30 kJ mol⁻¹) endoergic from the ground-state asymptote. The possibility that the platinum reaction proceeds all the way to H_2 elimination becomes highly unlikely when the barrier to α -elimination is considered. The calculations find this barrier to lie an additional 99 kJ mol⁻¹ higher than the final products. This barrier is attributed to the bonding in the transition state which is of the four-center type. Since the Pt atom cannot form more than two bonds using the s¹d⁹ state, the H_2PtCH_2 complex is formed with two covalent bonds to the carbene and a molecularly bound hydrogen molecule. The formation of a dihydride product would require a very large promotion energy to the excited s¹d⁸p¹ atomic state and is therefore unfavorable.

Our results indicate the saturated termolecular limit for the reaction of platinum with methane is reached at a relatively low pressure (*ca.* 20 Torr). This implies a slow unimolecular decay rate of the collision complex; *i.e.* the complex lifetime is very long. Arguments for the plausibility of a long lifetime for this complex have been advanced previously by Carroll *et al.*¹⁹ The necessity for singlet complexes to regain access to the triplet asymptotic surface before dissociating presumedly increases the lifetime of this complex compared to the case of a reaction which occurs on a single potential surface.

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References

- 1 K. Eller and H. Schwarz, Chem. Rev., 1991, 91, 1121.
- 2 J. C. Weisshaar, Acc. Chem. Res., 1993, 26, 213.
- 3 J. L. Elkind and P. B. Armentrout, J. Phys. Chem., 1987, 91, 2037.
- 4 P. B. Armentrout, in *Gas Phase Inorganic Chemistry*, ed. D. H. Russell, Plenum Press, New York, 1989.
- 5 P. B. Armentrout, Annu. Rev. Phys. Chem., 1990, 41, 313.
- 6 D. Ritter and J. C. Weisshaar, J. Am. Chem. Soc., 1990, 112, 6425.
- 7 D. Ritter, J. J. Carroll and J. C. Weisshaar, J. Phys. Chem., 1992, 96, 10636.
- 8 M. R. A. Blomberg, P. E. M. Siegbahn, U. Nagashima and J. Wennerberg, J. Am. Chem. Soc., 1991, 113, 424.
- 9 J. J. Carroll and J. C. Weisshaar, J. Am. Chem. Soc., 1993, 115, 800.
- 10 J. J. Carroll, K. L. Haug and J. C. Weisshaar, J. Am. Chem. Soc., 1993, 115, 6962.
- J. J. Carroll, K. L. Haug, J. C. Weisshaar, M. R. A. Blomberg, P. E. M. Siegbahn and M. Svensson, J. Phys. Chem., 1995, 99, 13955.
- 12 Y. Wen, A. Yethiraj and J. C. Weisshaar, J. Chem. Phys., 1997, 106, 5509.
- 13 M. A. Blitz, S. A. Mitchell and P. A. Hackett, J. Phys. Chem., 1991, 95, 8719.
- 14 C. E. Brown, S. A. Mitchell and P. A. Hackett, *Chem. Phys. Lett.*, 1992, **191**, 175.
- 15 L. Lian, S. A. Mitchell and D. M. Rayner, J. Phys. Chem., 1994, 98, 11637.
- 16 K. Senba, R. Matsui and K. Honma, J. Phys. Chem., 1995, 99, 13992.
- 17 M. L. Campbell, J. Am. Chem. Soc., 1997, 119, 5984.
- 18 J. M. Parnis, R. D. Lafleur and D. M. Rayner, J. Phys. Chem., 1995, 99, 673.

- 19 J. C. Carroll, J. C. Weisshaar, P. E. M. Siegbahn, A. M. Wittborhline and M. R. A. Blomberg, J. Phys. Chem., 1995, 99, 14388.
- 20 J. J. Carroll and J. C. Weisshaar, J. Phys. Chem., 1996, 100, 12355.
- 21 C. Vinckier, J. Corthouts and S. DeJaegere, J. Chem. Soc., Faraday Trans. 2, 1988, 84, 1951.
- 22 D. Ritter and J. C. Weisshaar, J. Phys. Chem., 1989, 93, 1576.
- 23 D. Ritter and J. C. Weisshaar, J. Phys. Chem., 1990, 94, 4907.
- 24 S. A. Mitchell and P. A. Hackett, J. Chem. Phys., 1990, 93, 7822.
- 25 J. M. Parnis, S. A. Mitchell and P. A. Hackett, J. Phys. Chem., 1990, 94, 8152.
- 26 C. E. Brown, S. A. Mitchell and P. A. Hackett, J. Phys. Chem., 1991, 95, 1062.
- 27 A. S. Narayan, P. M. Futerko and A. Fontijn, J. Phys. Chem., 1992, 96, 1290.
- R. E. McClean and L. Pasternack, J. Phys. Chem., 1992, 96, 9828.
 M. L. Campbell and R. E. McClean, J. Phys. Chem., 1993, 97,
- 7942.
- 30 D. E. Clemmer, K. Honma and I. Koyano, J. Phys. Chem., 1993, 97, 11480.
- 31 M. Helmer and J. M. C. Plane, J. Chem. Soc., Faraday Trans., 1994, 90, 31.
- 32 M. Helmer and J. M. C. Plane, J. Chem. Soc., Faraday Trans., 1994, 90, 395.
- 33 A. Fontijn, A. S. Blue, A. S. Narayan and P. N. Bajaj, Combust. Sci. Technol., 1994, 101, 59.
- 34 M. L. Campbell, R. E. McClean and J. S. S. Harter, Chem. Phys. Lett., 1995, 235, 497.
- 35 M. L. Campbell and J. R. Metzger, Chem. Phys. Lett., 1996, 253, 158.
- 36 M. L. Campbell, J. Chem. Phys., 1996, 104, 7515.
- 37 R. E. McClean, M. L. Campbell and R. H. Goodwin, J. Phys. Chem., 1996, 100, 7502.
- 38 M. L. Campbell, J. Chem. Soc., Faraday Trans., 1996, 92, 4377.
- 39 R. Matsui, K. Senba and K. Honma, Chem. Phys. Lett., 1996, 250, 560.
- 40 R. E. McClean, M. L. Campbell and E. J. Kölsch, J. Phys. Chem. A, 1997, 101, 3348.
- 41 M. L. Campbell, K. L. Hooper and E. J. Kölsch, Chem. Phys. Lett., 1997, 274, 7.
- 42 R. Matsui, K. Senba and K. Honma, J. Phys. Chem. A, 1997, 101, 179.
- 43 R. E. McClean, M. L. Campbell, M. D. Vorce, in preparation.
- 44 M. L. Campbell and R. E. McClean, J. Chem. Soc., Faraday Trans., 1995, 91, 3787.
- 45 J. S. S. Harter, M. L. Campbell and R. E. McClean, Int. J. Chem. Kinet., 1997, 29, 367.
- 46 M. L. Campbell, J. Phys. Chem., 1996, 100, 19430.
- 47 M. L. Campbell and K. L. Hooper, J. Chem. Soc., Faraday Trans., 1997, 93, 2139.
- 48 M. L. Campbell, J. Phys. Chem. A, 1997, 101, 9377.
- 49 W. F. Meggers, C. H. Corliss and B. F. Scribner, Tables of Spectral-Line Intensities, Part I, Arranged by Elements, NBS Mono., 145, U.S. Government Printing Office, Washington, DC, 1975.
- 50 D. D. Wagman, W. H. Evans, V. B. Parker, R. H. Schumm, I. Halow, S. M. Bailey, K. L. Churney and R. L. Nuttall, The NBS tables of chemical thermodynamic properties, *J. Phys. Chem. Ref. Data*, 1982, **11**, suppl. 2.
- 51 J. B. Pedley and E. M. Marshall, J. Phys. Chem. Ref. Data, 1983, 12, 967.
- 52 P. J. Robinson and K. A. Holbrook, Unimolecular Reactions, Wiley-Interscience, New York, 1972.
- 53 J. M. Parnis, S. A. Mitchell and P. A. Hackett, *Chem. Phys. Lett.*, 1988, **151**, 485.
- 54 N. L. Garland, C. H. Douglass and H. H. Nelson, J. Phys. Chem., 1992, 96, 8390.
- 55 C. D. Jonah, R. N. Zare and C. J. Ottinger, J. Chem. Phys., 1972, 56, 263.
- 56 C. E. Moore, NBS Circular 467, U.S. Department of Commerce, Washington DC, 1971, vol. I.
- 57 P. M. Futerko and A. Fontijn, J. Chem. Phys., 1991, 95, 8065.
- 58 P. M. Futerko and A. Fontijn, J. Chem. Phys., 1992, 97, 3861.
- 59 P. M. Futerko and A. Fontijn, J. Chem. Phys., 1993, 98, 7004.
- 60 D. P. Belyung, P. M. Futerko and A. Fontijn, J. Chem. Phys., 1995, 102, 155.