NMR parameters and chemical shifts, and Dr. J. Hoeschle for assistance in procuring isotopically enriched ^{195}Pt.

Registry No. *cis*-DDP, 15663-27-1; *trans*-DDP, 14913-33-8; *cis*-[Pt(NH_3)$_2$(H_2O)Cl]$^+$, 53861-42-0; *cis*-[Pt(NH_3)$_2$(DMF)Cl]$^+$, 79084-70-1; *trans*-[Pt(NH_3)$_2$(DMF)Cl]$^+$, 128707-47-1; *trans*-[Pt(NH_3)$_2$(H_2O)Cl]$^+$, 44046-05-1; *trans*-[Pt(NH_3)$_2$(dGMP)Cl]$^-$, 128660-88-8; *trans*-[Pt(NH_3)$_2$NdGMP)$_2$]$^{2+}$, 128683-54-5; *cis*-[Pt(NH_3)$_2$(N7-dGMP)Cl]$^-$, 128707-48-2; *cis*-[Pt(NH_3)$_2$(N7-dGMP)(H_2O)], 76243-63-5; *trans*-[Pt(NH_3)$_2$(N7-dGMP)(H_2O)], 76250-59-4; *cis*-[Pt(NH_3)$_2$(N7-dGMP)$_2$]$^{2-}$, 111348-17-5; *cis*-[Pt(NH_3)$_2${d(GpTpG)-N7,N7}], 128660-89-9; *cis*-[Pt(NH_3)$_2${d(ApG)-N7,N7}]$^+$, 128660-90-2; *trans*-[Pt(NH_3)$_2${d(GpcpG)-N7,N7}], 128683-55-6; deoxyguanosine, 961-07-9; glutathione, 70-18-8.

Pressure Effects on Bimolecular Reductive Quenching of the Platinum(II) Dimer $Pt_2(\mu\text{-}\eta^2\text{-}H_2P_2O_5)_4^{4-}$ by Organic Substrates

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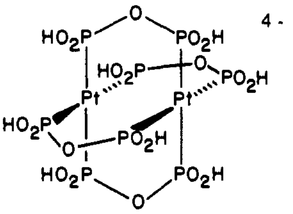
Abstract: Pressure effects are reported for the quenching dynamics of the lowest energy excited state of the d^8–d^8 dimer $Pt_2(\mu\text{-}\eta^2\text{-}H_2P_2O_5)_4^{4-}$ ($^3Pt_2^*$). Volumes of activation (ΔV^*) are reported for the H atom abstraction by $^3Pt_2^*$ from various organic substrates and for O_2 quenching of $^3Pt_2^*$ in methanol solution. The H atom donors studied include a series of benzyl alcohols, allyl alcohol, tributyltin hydride, and benzyl methyl ether. Volumes of activation of -5.4 ± 0.6 cm^3 mol^{-1} and -4.1 ± 0.7 cm^3 mol^{-1} have been measured for quenching by benzyl alcohol and benzyl methyl ether, respectively. These negative ΔV^* values suggest an associative interaction between the excited state dimer and the H atom donor. The mechanistic implications of the pressure effects on the rates for other quenchers are discussed.

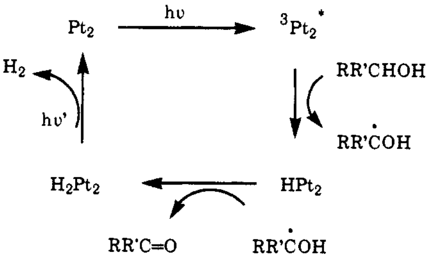
Introduction

The d^8–d^8 dimer of platinum(II) $Pt_2(\mu\text{-}\eta^2\text{-}H_2P_2O_5)_4^{4-}$ (subsequently denoted as $Pt_2(POP)_4^{4-}$ or Pt_2) has drawn considerable attention with regard to its photochemical and photophysical properties in solution.[1] This remarkable metal complex displays weak fluorescence and strong, long-lived phosphorescence in its ambient temperature luminescence spectrum, with a lifetime of about 10 μs and a quantum yield of 0.55 mol/einstein in aqueous solution.[2] Furthermore, the long-lived triplet excited-state $^3Pt_2^*$ has been shown to be active in two-electron processes of interest with respect to the conversion of photochemical radiant energy to chemical potential energy.[3] An example is the photodehydrogenation of alcohols to the homologous ketone for which a sequence of steps such as described in Scheme I might be proposed. The monohydride and dihydride species, Pt_2H and Pt_2H_2, have been demonstrated[4] to form under conditions relevant to the photodehydrogenation; Pt_2H_2 has been shown to undergo H_2 when photolyzed,[4b] but the manner by which Pt_2H_2 forms is uncertain.[4c] Participation in similar photocatalytic cycles leads to quenching of the $^3Pt_2^*$ phosphorescence by a number of different substrates including halogenated hydrocarbons,[5,6] main group hydrides,[5a] and various alcohols.[4a] Although atom abstraction to give an organic free radical plus a Pt(II)–Pt(III) mixed valence dimer is considered to be the probable first step of photoredox paths such as that illustrated by Scheme I, the mechanisms of these chemical quenching pathways are not well characterized.

$Pt_2(POP)_4^{4-}$ =



Scheme I



$Pt_2 = Pt_2(\mu\text{-}\eta^2H_2P_2O_5)_4^{4-}$

A technique that has provided valuable mechanistic insight into the intimate mechanisms of both thermal and photochemical reactions is the investigation of pressure effects on reaction dynamics.[7,8] Although there have been several studies on the effect of pressure on the unimolecular deactivation pathways of metal complex excited states,[9] little work has been reported for pressure

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effects on bimolecular deactivation pathways.[10] Described here is an investigation of the quenching of the luminescence from Pt_2^* by various organic substrates that may act as hydrogen atom donors.

Experimental Section

Materials. The salts $K_4[Pt_2(POP)_4]$ and $(TBA)_4[Pt_2(POP)_4]$ (TBA = *tetra-n*-butylammonium (POP = μ-η^2-$H_2P_2O_5^{2-}$)) were prepared according to published procedures.[11] Acetonitrile and methanol (both Burdick & Jackson high-purity grade) were used without further purification. Allyl alcohol (Aldrich), 4-methyl-1-penten-3-ol (Pfaltz & Bauer), benzyl alcohol (Aldrich Gold Label), benzhydrol (Pfaltz & Bauer), 1-phenyl-1-propanol (Aldrich), 1-phenyl-1-ethanol (Aldrich), and 1-phenyl-1-deuterio-1-ethanol (gift from Erica Harvey of the California Institute of Technology) were distilled before use. Tributyltin hydride (Aldrich) was used as received and was stored under nitrogen in a refrigerator. Benzyl methyl ether (Eastman Kodak) was used as received after scrutinizing the infrared spectrum for benzyl alcohol impurity.

Sample Preparation for High-Pressure Luminescence Experiments. Except where noted, all solutions were deaerated by bubbling with high-purity dinitrogen. Methanol and acetonitrile solutions of the platinum dimer salts were prepared in the concentration range 20–50 μM. Deaerated liquid quenching agents were added quantitatively via microsyringe. For the solid quencher benzhydrol, a 0.5 M deaerated solution in methanol was prepared and then 1.00 mL of this was added to 4.00 mL of $Pt_2(POP)_4^{4-}$ solution. Some of the resulting solution was loaded into a quartz capsule (25 mm in length, 8 mm in diameter) that was subsequently capped with a Teflon piston fitted with two O-rings. (The capsule/piston combination was designed to transmit the applied hydrostatic pressure without exchanging solution with the surrounding medium.) The quartz capsule was then placed into a modified Nova-Swiss four-window, 400-MPa (4 kbar) high-pressure spectroscopic cell.[9a] This high-pressure cell was then filled with deaerated solvent (CH_3OH or CH_3CN), which served as the pressure transmitting fluid, and sealed.

Apparatus. The high-pressure cell loaded as described was attached to an Enerpac hand pump and gauge, which were used to generate and measure the applied pressure. The apparatus used for lifetime measurements employed a Quanta Ray DCR-1A Nd:YAG pulse laser with harmonic generator operating at 355 nm (third harmonic) as the excitation source; the laser power was typically 6 mJ/pulse. The emission was monitored at right angles at 515 nm with an RCA 8852 or EMI 9816A photomultiplier tube through a Spex double monochromator. The signal from the PMT was processed by a Tektronix 8912AD transient digitizer and a Zenith personal computer.

A Spex Fluorolog 2 spectrofluorometer interfaced to a Datamate computer station was used to determine Stern–Volmer quenching constants at ambient pressure by determining the effects of added quenchers on emission intensity quenching.

Experimental Procedures for Lifetime Measurements. Experiments were carried out either at 25 °C with a thermostated water circulator or at room temperature (20 ± 1 °C). Three to six luminescence lifetime measurements (each consisting of the signal average of 4 to 64 emission decay traces) were made at each pressure. Approximately 10 min was allowed for equilibration subsequent to changing pressure in the cell. For at least one elevated pressure, e.g., 100 MPa, the excited-state lifetime was measured twice at different times during the experiment to check for any hysteresis or reaction affecting the emission lifetime.

Results

A. Quenching Constants at Ambient Pressure. There were some discrepancies between values of k_q reported earlier and those measured here in the high-pressure cell at ambient pressure. For this reason values of k_q for several quenchers were determined from both lifetime and excited-state emission intensity measurements at ambient pressure in a 1.0-cm fluorimetry cell prior to the study of pressure effects.

Allyl Alcohol. A deaerated methanol solution of $(TBA)_4[Pt_2(POP)_4]$ displayed a triplet excited-state lifetime of 9.3 ± 0.1 μs. Sequential additions of deaerated allyl alcohol via microsyringe caused both the phosphorescence intensity and the phosphorescence lifetime to decrease. Lifetimes and emission intensities were measured after each addition of allyl alcohol, and exponential emission decay traces were observed for all lifetime measurements involving allyl alcohol. Stern–Volmer plots of both the intensity quenching and the lifetime data were found to be linear (Figure 1) in accord with the following equations

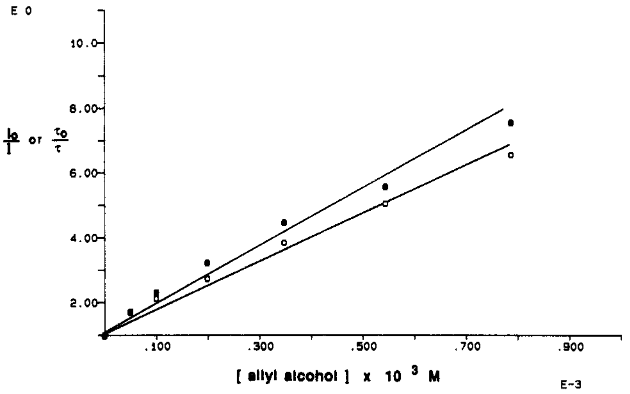

Figure 1. Representative Stern–Volmer plots for allyl alcohol quenching of $^3Pt_2^*$ in methanol. The open circles represent emission lifetime measurements and the solid circles represent emission intensity data.

$$\tau_0/\tau = 1 + K_{SV}[Q] = 1 + k_q\tau_0[Q] \tag{1}$$

$$I_0/I = 1 + K_{SV}[Q] = 1 + k_q\tau_0[Q] \tag{2}$$

where τ_0 is the lifetime in the absence of added quencher and I_0 is the emission intensity in the absence of added Q.

The quenching constants k_q calculated from the experimental Stern–Volmer constants and τ_0 ($k_q = K_{SV}\tau_0^{-1}$) for the lifetime and intensity measurements in methanol are (7.6 ± 0.5) × 10^8 and (9.3 ± 0.9) × 10^8 L mol^{-1} s^{-1}, respectively, in reasonable agreement with each other. In aqueous solution at room temperature, the measured τ_0 was 9.7 ± 0.2 μs and the k_q values were (1.8 ± 0.1) × 10^9 and (1.9 ± 0.1) × 10^9 L mol^{-1} s^{-1}, determined from lifetime and intensity measurements, respectively. The k_q values determined here for allyl alcohol are considerably larger than those reported previously[4a] as 3 × 10^8 (aqueous solution) and 1 × 10^6 L mol^{-1} s^{-1} (methanol solution).

Benzyl Alcohol. In aqueous solution Stern–Volmer plots proved to be linear for $^3Pt_2^*$ quenching by benzyl alcohol at concentrations below 0.02 M. At higher concentrations limiting k_q values were found, the likely result of self-aggregation of this substrate in the aqueous medium; similar behavior has been described.[4a] By using only the points below that concentration limit, a value of 4 × 10^7 L mol^{-1} s^{-1} was measured by emission intensity quenching, about an order of magnitude greater than the k_q previously reported.[4a] No such difficulties were encountered for methanol solutions in which emission intensity quenching and repeated measurements of the lifetime quenching gave a k_q value of (1.6 ± 0.2) × 10^6 L mol^{-1} s^{-1} for benzyl alcohol.

Other Substrates. Quenching rate constants for all of the substrates investigated here are tabulated in Table I. All other k_q values are in approximate agreement with published values.[4,12]

B. Pressure Effects on k_q Values. The volume of activation for any dynamic excited-state process is defined by

$$\Delta V^{\ddagger}_i = -RT\left(\frac{\mathrm{d}\ln k_i}{\mathrm{d}P}\right)_T \tag{3}$$

where k_i is the rate constant at a particular pressure. The activation volume can be determined from the slope ($-\Delta V^{\ddagger}/RT$) of the plot of ln (k_i) versus P at constant temperature. In the absence of quenchers, the phosphorescence lifetime of $^3Pt_2^*$ in

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(12) Harvey, E. L. Ph.D. Dissertation, California Institute of Technology, Pasadena, CA, 1990.

Table I. Quenching Raie Constants Determined at Ambient Pressure

quencher	solvent	k_q,[a] L mol^{-1} s^{-1}	method of measurement[b]
$C_6H_5CH_2OH$	CH_3OH	1.6×10^6 (6)	τ, I, K_{sv}
	CH_3CN	6.3×10^6 (2)	τ
	H_2O	$\geq 4 \times 10^7$ (4)[c]	I, K_{sv}
$(C_6H_5)_2CHOH$	CH_3OH	7.1×10^5 (4)	τ
$C_6H_5CH(OH)C_2H_5$	CH_3OH	4.6×10^5 (1)[c]	τ
$C_6H_5CH(OH)CH_3$	CH_3OH	9.4×10^5 (3)	τ
$C_6H_5CD(OH)CH_3$	CH_3OH	2.6×10^5 (4)	τ
$C_6H_5CH_2OCH_3$	CH_3OH	1.4×10^6 (4)	τ
tetrahydrofuran	CH_3OH	1.2×10^5 (2)	τ, I, K_{sv}
benzophenone	CH_3OH	1.9×10^8 (2)[c]	τ
cyclohexene	CH_3OH	2.4×10^6 (2)[c]	τ
allyl alcohol	CH_3OH	8.4×10^8 (9)	τ, I, K_{SV}
	H_2O	2.1×10^9 (12)	τ, I, K_{SV}
	CH_3CN	1.5×10^9 (1)[c]	τ
4-methyl-1-penten-3-ol	CH_3OH	2.6×10^8 (1)[c]	τ
$(n\text{-}Bu)_3SnH$	CH_3OH	5.8×10^7 (5)	τ, I, K_{SV}
	CH_3CN	2.8×10^7 (3)	τ
O_2	CH_3OH	3.3×10^9 (2)	τ

[a] Number of independent experiments is given in parenthese following the quenching constant; the estimated uncertainty is ±10% except where noted otherwise. [b] "τ" indicates the measurement of k_q by phosphorescence lifetime quenching; "I" indicates the measurement of k_q by phosphorescence intensity quenching; "K_{WV}" indicates that linear Stern–Volmer plots were obtained over four to seven [Q] values. [c] Estimated uncertainty is ±20%.

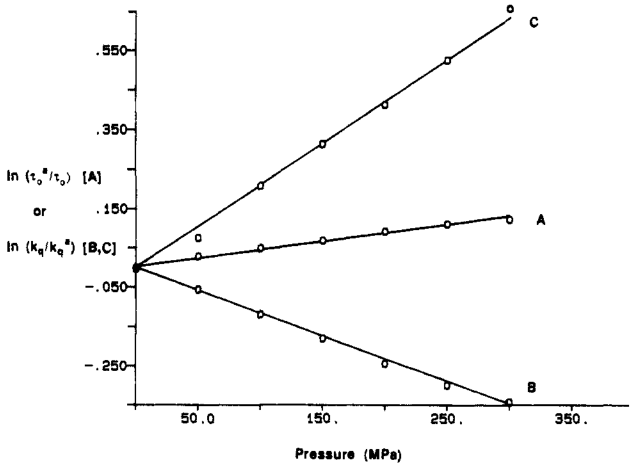

Figure 2. (A) Plot of ln (τ_0^a/τ_0) vs pressure for the phosphorescence lifetime of $(TBA)_4[Pt_2(POP)_4]$ in deaerated methanol at 25 ± 1 °C in the absence of quenchers. (The superscript "*a*" represents values measured at ambient pressure.) (B) Plot of ln (k_q/k_q^a) vs pressure for the quenching of $^3Pt_2^*$ by O_2 at 21 ± 1 °C. $[O_2] = 2.12 \times 10^{-3}$ M in methanol; k_q is corrected for solvent compressibility. (C) Plot of ln (k_q/k_q^a) vs *P* for benzyl alcohol quenching of $^3Pt_2^*$ in acetonitrile at 20 ± 1 °C. The benzyl alcohol concentration is 0.060 M; k_q is corrected for solvent compressibility.

methanol solution is 9.3 ± 0.1 μs. Increasing the hydrostatic pressure on a methanol solution of $^3Pt_2^*$ to 300 MPa caused a small, but reproducible, reduction in the lifetime to about 8.1 μs. The emission decay is strictly exponential at all pressures. From a linear plot of ln (τ^{-1}) versus *P* at seven different pressures between 0.1 and 300 MPa (Figure 2A), an apparent activation volume $\Delta V^{\ddagger}_d$ of −1.0 ± 0.2 cm^3 mol^{-1} was calculated. This result is of similar magnitude to the previously reported pressure effects on $^3Pt_2^*$ in both aqueous ($\Delta V^{\ddagger}_d = -1.6$ cm^3 mol^{-1}) and acetonitrile ($\Delta V^{\ddagger}_d = -0.2$ cm^3 mol^{-1}) solution.[9c]

When a quencher is present, the deactivation rate constant k_d is defined as

$$k_d = \tau^{-1} = k_r + k_n + k_q[Q] = \tau_0^{-1} + k_q[Q] \qquad (4)$$

Table II. Volumes of Activation Measured for the Quenching of $^3Pt_2^*$ in Methanol by Benzylic Quenchers[a] ($\Delta V^{\ddagger}$ values in cm^3 mol^{-1})

quencher	[Q][b]	$\Delta V^{\ddagger}_d$[c]	$\Delta V^{\ddagger}_q$[d]	k_q,[e] L mol^{-1} s^{-1}
$C_6H_5CH_2OH$	0.060	−4.2	−5.4	1.6×10^6
$C_6H_5CH_2OH$[f]	0.060	−5.6	−5.7	6.3×10^6
$(C_6H_5)_2CHOH$	0.10	−2.3	−2.8	7.1×10^5
$C_6H_5CH(OH)C_2H_5$	0.045	−1.5	−2.6	4.6×10^5
$C_6H_5CH(OH)CH_3$	0.10	−3.6	−4.4	9.4×10^5
$C_6H_5CD(OH)CH_3$	0.051	−1.7	−4.7	2.6×10^5
$C_6H_5CH_2\text{-}O\text{-}CH_3$	0.039	−2.8	−4.1	1.4×10^6

[a] 21 ± 1 °C. [b] Quencher concentration in mol L^{-1} at ambient pressure. [c] Apparent volume of activation calculated from eq 4; the estimated uncertainty is <±1 cm^3 mol^{-1}. [d] $\Delta V^{\ddagger}$ for the quenching process (k_q is corrected for solvent compressibility); estimated uncertainty is <±1 cm^3 mol^{-1}. [e] k_q calculated at ambient pressure according to eq 5. [f] Values determined in acetonitrile solution.

where τ_0 is the lifetime for a specific set of conditions in the absence of quencher. Thus, for any [Q] at any pressure, the value of k_q can be calculated from the measured lifetime τ according to[10b]

$$k_q = (\tau^{-1} - \tau_0^{-1})[Q]^{-1} \qquad (5)$$

For pressure runs with a compressible solvent, [Q] needs to be corrected for compressibility-induced changes from the ambient pressure value. For methanol, compressibility accounts for a 14% decrease in volume[13] between 0.1 and 300 MPa with a corresponding increase in [Q] from 0.060 M at ambient pressure to 0.068 M at 300 MPa. Here, the apparent volume of activation $\Delta V^{\ddagger}_d$ was determined from plots of ln (k_d) (i.e. ln τ^{-1}) versus pressure, and $\Delta V^{\ddagger}_q$ was determined from plots of ln (k_q) (corrected for solvent compressibility) versus pressure.

O_2 Quenching. Oxygen quenches $^3Pt_2^*$ via energy transfer with a k_q value of 1.4×10^9 L mol^{-1} s^{-1} in methanol solution.[2] In air-saturated methanol at room temperature, $[O_2] = 2.12 \times 10^{-3}$ M.[14] The measured lifetime under these conditions was 140 ns; from these values a k_q value of 3.3×10^9 L mol^{-1} s^{-1} was calculated. Notably, increasing the pressure to 300 MPa leads to a longer τ (about 168 ns). Since the lifetime of $^3Pt_2^*$ shortens somewhat upon increasing pressure in the absence of quenchers, this result indicates that $\Delta V^{\ddagger}_q$ for O_2 must be positive. This is confirmed by the linear plot of ln (k_q) (where k_q was corrected for methanol compressibility) versus *P* for oxygen quenching in Figure 2B. The calculated $\Delta V^{\ddagger}_q$ is +2.8 ± 0.5 cm^3 mol^{-1}.

Benzyl Alcohol and Other Benzylic Substrates. For the entire series of benzylic type quenchers, an increase in pressure caused a shortening of the emission lifetime. The decrease was largest for benzyl alcohol and benzyl methyl ether, but it was still significant and reproducible for the other substrates. In all cases the emission decays were exponential. For some pressure experiments, the τ measured at 0.1 MPa at the start of the experiment was not identical with that measured at the end of the experiment. This difficulty is believed to be caused by formation of photoproducts that slightly affect τ. The problem was circumvented in subsequent experiments by signal averaging 4 to 16 emission decay traces collected at about 4 Hz instead of 64 traces at 10 Hz. As a result, the sample was exposed to fewer laser pulses per τ measurement. In any case, the $\Delta V^{\ddagger}_d$ values derived from the earlier experiments were the same as those obtained from the strictly reversible runs.

From plots of ln (k_d) and ln (k_q) versus pressure for 0.060 M benzyl alcohol the respective $\Delta V^{\ddagger}_d$ and $\Delta V^{\ddagger}_q$ values −4.2 ± 0.7 and −5.4 ± 0.6 cm^3 mol^{-1} (Figure 2C) were determined for methanol solution. A nearly identical $\Delta V^{\ddagger}_q$ value (−5.7 cm^3 mol^{-1}) was determined for benzyl alcohol in acetonitrile solution. Activation volumes for all benzylic quenchers investigated are given in Table II. Notably, the $\Delta V^{\ddagger}_q$ value for benzyl methyl ether was found to be similar to that for benzyl alcohol. Furthermore, the α-protio and α-deuterio phenyl methyl carbinols both gave

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Table III. $\Delta V^{\ddagger}$ Values ($cm^3\ mol^{-1}$) for Other Quenchers[a]

quencher	[Q], M	$\Delta V^{\ddagger}_{app}$	$\Delta V^{\ddagger}$	k_q, L $mol^{-1}\ s^{-1}$
$H_2C{=}CHCH_2OH$[b]	6.0×10^{-4}	−1.6	−1.4	2.2×10^9
$H_2C{=}CHCH_2OH$	9.0×10^{-4}	−0.2	−0.2	9.6×10^8
$H_2C{=}CHCH(i\text{-}C_3H_7)OH$	6.4×10^{-3}	+0.6	+0.7	2.6×10^8
$(n\text{-}Bu)_3SnH$	9.3×10^{-3}	+0.3	+0.6[d]	5.1×10^7
$(n\text{-}Bu)_3SnH$[c]	9.3×10^{-3}	−1.8	−2.5	2.5×10^7
O_2	2.12×10^{-3}	+1.6	+2.8	3.3×10^9
cyclohexene	9.8×10^{-2}	−7.2[e]	−7.6[e]	2.4×10^6

[a] Solvent is CH_3OH at room temperature except where noted; the estimated uncertainty for all $\Delta V^{\ddagger}$ values is <±1 $cm^3\ mol^{-1}$ except where noted. [b] In H_2O. [c] In CH_3CN. [d] Estimated uncertainty is ±2 $cm^3\ mol^{-1}$. [e] Estimated uncertainty is ±3 $cm^3\ mol^{-1}$.

the same $\Delta V^{\ddagger}_q$ values despite the substantial isotope effect on k_q.

Other Quenchers. Cyclohexene efficiently quenches $^3Pt_2^*$.[6] However, emission decay traces obtained with a methanol solution of $^3Pt_2^*$ and cyclohexene were nonexponential at all pressures, although reasonable exponential decay traces were observed for about the first two lifetimes. Increased hydrostatic pressure greatly enhanced excited-state decay; the excited-state lifetime dropped sharply from 2.3 μs at 0.1 MPa to 0.6 μs at 300 MPa. From these values (and those at five intermediate pressures), a $\Delta V^{\ddagger}_d$ value of about −7 $cm^3\ mol^{-1}$ was determined.

The effect of pressure on the quenching by allyl alcohol was initially investigated in aqueous solution. Emission decays were exponential for this quencher at all pressures, but the lifetime was only slightly reduced by increased pressure. For 6.0×10^{-4} M allyl alcohol in water, $\Delta V^{\ddagger}_q = -1.4\ cm^3\ mol^{-1}$. In a methanol, the activation volume was similarly small, $\Delta V^{\ddagger}_q = -0.6\ cm^3\ mol^{-1}$. A 6.4×10^{-3} M solution of 4-methyl-1-penten-3-ol in methanol also exhibited but a small change in lifetime with increasing pressure; in this case the lifetime actually increased slightly with pressure. Exponential decay traces were observed at all pressures. These results are summarized in Table III.

Both methanol and acetonitrile solutions of $^3Pt_2^*$ with added tributyltin hydride were susceptible to significant net photochemistry, as reported earlier.[5] The photoproducts did not seem to have an appreciable effect on the excited-state lifetime of $^3Pt_2^*$, but lower laser power (about 2 mJ/pulse) was used in order to limit the extent of photoproduct formation. In methanol solution the small positive activation volume is an average of two values, one of which was negative and the other positive. The effect of pressure caused a small decrease in excited-state lifetime for an acetonitrile solution.

Finally, the pressure effect on the emission lifetime of $^3Pt_2^*$ in the presence of added thallium bromide was examined in aqueous solution. Although the absorption spectrum of $Pt_2(POP)_4^{4-}$ was unaffected by the addition of TlBr (1.1×10^{-3} M), the maximum of the corrected emission spectrum was shifted to about 565 nm. This shift has been attributed[15] to formation of an exciplex between Tl^+ and $^3Pt_2^*$ (eq 6). The emission lifetime

$$^3Pt_2^* + Tl^+ \rightleftharpoons {}^3[Pt_2Tl^+]^* \qquad (6)$$

was unaffected, as reported earlier;[15] furthermore, increasing the pressure on this aqueous solution had no effect on τ. Since the lifetime of $^3Pt_2^*$ and the purported exciplex $^3Pt_2Tl^*$ are nearly identical under ambient solution conditions and τ for $^3Pt_2^*$ shows little pressure sensitivity, $\Delta V^{\ddagger}_d$ for the exciplex must also be nearly zero.

Discussion

Previous work has demonstrated that the emission quenching of the $Pt_2(POP)_4^{4-}$ triplet excited state by secondary alcohols is accompanied by hydrogen atom abstraction, as illustrated in Scheme I. Although other quenching mechanisms are undoubtedly operative, such as for O_2 and benzophenone, the kinetic isotope effect measured previously for α-methyl benzyl alcohol (k_H/k_D = 4)[12] and corroborated here (Table I) substantiates the importance of this deactivation path (eq 7) for benzylic alcohols and related quenchers,

$$^3Pt_2^* + H{-}R \rightarrow HPt_2 + R^{\bullet} \qquad (7)$$

where Pt_2 is $Pt_2(POP)_4^{4-}$ and R–H a suitable hydrogen atom donor.

Only alcohols with the benzyl or allyl moiety exhibited quenching rate constants faster than 10^5 L $mol^{-1}\ s^{-1}$. Although hydrogen atom abstraction by $^3Pt_2^*$ has also been observed for aliphatic alcohols such as isopropyl alcohol and *sec*-butyl alcohol, the rates were slow.[4a] Arenes, such as toluene and ethylbenzene, which also have benzylic C–H bonds, have also been observed to have quenching rates several orders of magnitude lower than that for benzyl alcohol.[12] These observations have been attributed to the complementary stabilization of the organic radical by the α-phenyl ring and the α-oxygen substituents. Since the quenching rate constant found for benzyl methyl ether is comparable to that for benzyl alcohol (Table I), the $O{-}CH_3$ functionality appears to be comparable to O–H in facilitating this process. Even larger k_q values were measured under comparable conditions for the allylic alcohols 1-propen-3-ol ("allyl alcohol") and 4-methyl-1-penten-3-ol (Table I), consistent with the modestly greater stabilization and smaller size of an allylic radical than of a benzylic radical.[16] The relative facility by which tri-n-butyltin hydride quenches $^3Pt_2^*$ is no doubt reflective of the weakness of the Sn–H bond.

Steric effects are also an important factor in determining the quenching rate. From the rate constants given in Table I, it is clear that benzyl alcohol and benzyl methyl ether are more effective quenchers of $^3Pt_2^*$ than the other benzyl-like H atom donors investigated. Replacing one of the benzylic hydrogens with Me, Et, or even Ph decreased k_q although the decreases did not differ greatly from the statistical factor of 2. It is conceivable that the greater efficiency of allyl alcohol as a quencher is due mostly to steric factors, the smaller allylic group allowing easier access of the reactive methylene group to the platinum metal center of $^3Pt_2^*$. However, this faster rate may reflect a contribution from a quenching pathway involving addition of the double bond to $^3Pt_2^*$ prior to H atom abstraction, since simple alkenes do quench $^3Pt_2^*$ (but more slowly than does allyl alcohol).[6] Regardless, the potential role of steric effects is evident when one considers that 1-hexene quenches $^3Pt_2^*$ 600 times faster than *trans*-3-hexene.[6]

Pressure Effects on Quenching Rates. Describing the pressure dependence of a dynamic process as an "activation volume" $\Delta V^{\ddagger}$ provides a qualitative perception of the distortions that may be occurring along the trajectory of that process. Since $\Delta V^{\ddagger}$ is a sum of both intrinsic and solvational contributions, the activation of even a unimolecular process in solution reflects not only the intramolecular changes but also the perturbations of solvent–substrate interactions. In the present case large changes in solvation would not be expected to accompany the transfer of a neutral hydrogen atom *unless* the rate-limiting step were preceded by some form of charge transfer (electron transfer). The minor role of solvational contributions appears to be confirmed by the similarities in the $\Delta V^{\ddagger}_d$ values determined in methanol and acetonitrile solutions for benzyl alcohol.

In the absence of quenchers, pressure effects on the deactivation rates of $^3Pt_2^*$ have been determined in aqueous solution,[9c] in acetonitrile,[9c] and in methanol (this work), and in each case the $\Delta V^{\ddagger}_d$ value was small and negative, −1.6, −0.2, and −1.0 $cm^3\ mol^{-1}$, respectively. (Given that the radiative rate constant k_r of $^3Pt_2^*$ is unaffected by pressure,[9c] these observations indicate that the $\Delta V^{\ddagger}$ for nonradiative deactivation is the negative contributor to the overall $\Delta V^{\ddagger}_d$.) Since it has been concluded that the Pt–Pt

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bond in $^3Pt_2^*$ is considerably shorter[17] than in the ground-state $Pt_2(POP)_4^{4-}$, there has been a tendency to suggest that $^3Pt_2^*$ represents the rare case for which the partial molar volume ($\bar{V}$) of an excited state is smaller than that of the corresponding ground state. If this were so, one would expect the deactivation from $^3Pt_2^*$ would occur with an increase in volume resulting in a positive ΔV^*_d in contrast to the negative values observed. Thus it appears likely that, as we proposed previously,[9c] compensating increases in other bonds, most likely the Pt–P bonds, give a $^3Pt_2^*$ with a total ($\bar{V}$) somewhat larger than that of the ground state. This suggestion has been recently confirmed by photoacoustic calorimetry techniques,[18] which indicated that $\Delta\bar{V}$ upon excitation of aqueous $Pt_2(POP)_4^{4-}$ to $^3Pt_2^*$ is +0.5 cm^3 mol^{-1}.[18]

The quenching of $^3Pt_2^*$ by O_2 undoubtedly occurs by energy transfer.[2] Since the rate in methanol at ambient pressure ($k_q = 3.3 \times 10^9$ L mol^{-1} s^{-1}) is within an order of magnitude of diffusion limits in methanol (1.1×10^{10} L mol^{-1} s^{-1}),[19] the positive ΔV^*_q for oxygen quenching ($+2.8 \pm 0.5$ cm^3 mol^{-1}) may simply reflect pressure-induced changes in methanol viscosity. The decreased diffusion rate is predicted from the Stokes–Einstein equation $D = k_BT/(4\pi\eta r)$, where D is the diffusion coefficient, η is the solvent viscosity, and r is the radius of a spherical particle.

Despite the increase in viscosity engendered by increased pressure, the quenching rates between $^3Pt_2^*$ and the organic substrates are enhanced by higher pressure, in direct contrast to quenching by O_2 (Table II). If one considers that the measured ΔV^*_q for the quenching process may be partially offset by a positive contribution due to increased viscosity, then the pressure effect on k_q is qualitatively even larger. These results are consistent with a significant amount of organization in the transition state and a mechanism involving the intimate association between the H atom donor R–H and the $^3Pt_2^*$. Activation enthalpies and entropies determined by Harvey[12] from the temperature dependence of the quenching show that the rates are largely governed by the negative ΔS^* for the reactions. Activation enthalpy and entropy values measured were +2.5 kcal mol^{-1} and −33 eu for isopropyl alcohol, +2.4 kcal mol^{-1} and −19 eu for benzyl alcohol, and +1.6 kcal mol^{-1} and −26 eu for α-methylbenzyl alcohol. The substantially negative ΔS^*_q values are consistent with the negative ΔV^*_q values for the latter two substrates and point to a significant amount of organization in the formation of the transition state.

For allyl alcohol, k_q approaches the diffusion-control limit. Therefore the very small ΔV^*_q of about −1 cm^3 mol^{-1} may be interpreted as a cancellation of two opposing contributions, a positive ΔV^* caused by the increase in viscosity and a negative one from the increased organization of the quenching reaction, although an alternative quenching mechanism such as addition of the double bond to a Pt center may be dominant. The quenching of $^3Pt_2^*$ by cyclohexene is much slower than the diffusion-control limit, so any positive contribution to ΔV^* would be smaller, and coordination of the olefin moiety to the axial site of the platinum dimer may be responsible for the ΔV^*_q of −7.6 cm^3 mol^{-1}. The small ΔV^*_q determined for Bu_3SnH may simply reflect the bulkiness of this substrate. This is certainly consistent with the results for the benzylic quenchers; the sterically bulkier quenchers gave less negative ΔV^*_q values.

In summary, a positive ΔV^* was observed for $^3Pt_2^*$ quenching by O_2, which almost certainly occurs by energy transfer. This effect is the probable result of pressure-induced viscosity changes in the solution. In contrast, ΔV^* values determined for quenching by the hydrogen atom donors benzyl alcohol and benzyl methyl ether are substantially negative. This implies a transition state formed by an associative interaction between the benzylic H atom donor and a site on the excited-state complex $^3Pt_2^*$, presumably one of the metal atoms. Such a mechanism would also be consistent with the strongly negative ΔS^* values determined previously[12] for similar reactions of $^3Pt_2^*$. The pressure effects are attenuated for the faster quencher allyl alcohol. While a less negative ΔV^* would be a likely consequence of an earlier transition state for H atom transfer, it may also reflect the compensating pressure effect on solvent viscosity for these reactions which more closely approach the diffusion limit.

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Steric Effects on Geminate Recombinations

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Abstract: Steric effects on the binding of isonitrile ligands to iron(II) porphyrins were investigated by picosecond flash photolysis. Two different types of steric effects were distinguished and characterized: (1) steric restrictions to porphyrin planarity and (2) blocking of the pathway for ligand approach. Heme planarity was restricted by coordinating 1,2-dimethylimidazole trans to the ligand binding site being investigated. Blocking of the binding site was explored by using adamantane heme 6,6-cyclophane, in which the adamantane moiety forms a "cap" over the binding site. Results of picosecond kinetic measurements demonstrate that the first effect, heme nonplanarity or "trans strain", influences the bond-making step, whereas the second effect, ligand blocking, involves a conformational preequilibrium prior to bond making. Relevance of these findings for contact pair recombination, in general, and for heme protein ligation, in particular, are discussed.

How chemical bonds are formed is a fundamental question that has attracted interest for decades and is being actively investigated today. Since the bond making itself is very fast, inferences drawn from mixing reagents can only be indirect. Consequently, "perturbation methods" are popular, in which one investigates the reforming of bonds following homolysis or heterolysis.

Geminate recombination of free radicals after homolytic photolysis or thermolysis was first considered[1] for simple diatomics