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PHOTOREACTIONS OF TETRAKIS(μ-PYROPHOSPHITO)DIPLATINATE(II) WITH ALCOHOLS AND HYDROCARBONS

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SUMMARY

Hydrogen-atom transfer has been established as an important reaction pathway for the $d\sigma^*p\sigma$ triplet excited state of $[Pt_2(P_2O_5H_2)_4]^{4-}$ (Pt_2). Substrates that serve as H-atom donors include alcohols with α(C-H) bonds and benzyl hydrocarbons. These substrates react photochemically with Pt_2 (370-nm irradiation) in acetonitrile solution to give ketones (from alcohols) and dimers (from benzyl hydrocarbons). The reactions of alcohols with $^3Pt_2{}^*$ involve a pre-equilibrium complex, [$^3Pt_2{}^*$-alcohol]; the excited-state complex deactivates through intramolecular H-atom transfer. Rates of stable product formation (k_p) generally parallel the rates of excited-state deactivation (k_q), with k_p/k_q approximately 0.1.

INTRODUCTION

The triplet excited state of tetrakis(μ-pyrophosphito)diplatinate(II) [$Pt_2(P_2O_5H_2)_4{}^{4-}$ = Pt_2; triplet excited state, $^3Pt_2{}^*$] is deactivated by reaction with a variety of hydrogen-donor organic species (refs. 1, 2), including alcohols (refs. 3-5), benzyl hydrocarbons (ref. 4), alkenes (refs. 3, 6), and main-group hydrides (ref. 7). The initial photoproducts are organic radicals and the monohydride Pt_2H (refs. 3, 5, 8); subsequent, poorly understood steps lead to formation of the stable axial dihydride Pt_2H_2 (ref. 9) and typical organic radical products (e.g., dimers from alkanes, ketones from alcohols) (ref. 4). In contrast to other hydrogen abstraction reactions, the hydrogenated product Pt_2H_2 is efficiently photoconverted back to Pt_2 with the evolution of H_2, thereby completing a catalytic cycle (eqns. 1-4, refs. 9, 10).

The wide range of rate constants (ref. 3) for the C-H activation step eqn. (2) suggests that Pt_2 may be useful in selective functionalization of organic substrates. The utility of Pt_2 as a photodehydrogenation catalyst

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depends on factors that are not well understood, such as dehydrogenation selectivity and overall reaction efficiencies.

$$Pt_2 \xrightarrow[370\ nm]{h\nu} {}^3Pt_2^{*} \qquad (1)$$

$${}^3Pt_2^{*} + RH \xrightarrow{k_q} Pt_2H + R\cdot \qquad (2)$$

$$Pt_2H \xrightarrow{\bigcirc} 1/2\ Pt_2H_2\ (+1/2\ Pt_2?) \qquad (3)$$

$$Pt_2H_2 \xrightarrow[313\ nm]{h\nu} Pt_2 + H_2 \qquad (4)$$

In an effort to address these questions, we have examined in detail the reactions of alcohols and hydrocarbons with ${}^3Pt_2^*$ in acetonitrile solution. Our work has included determination of the rates of product formation as well as the rates of initial H-atom abstractions.

EXPERIMENTAL SECTION

Materials

The tetra-*n*-butylammonium (TBA) salt of Pt_2 was prepared from the potassium salt as described previously (ref. 11). The tetra-*n*-octylammonium (TOA) salt was prepared by vigorous mixing of ethyl ether with an aqueous mixture of K_4Pt_2 and TOABr (Aldrich 98%), followed by drying and evaporation of the ether phase. $[TOA]_4Pt_2$ is a yellow, viscous oil that resisted attempts at crystallization. Calculated 54.1%C, 9.88%H, 2.0%N. Found 54.4%C, 9.81%H, 1.55%N. $[TOA]_4Pt_2$ dissolves in diethyl ether, toluene, methylene chloride and acetonitrile, but not in water.

Burdick and Jackson high purity, UV grade acetonitrile was used as received as solvent for all experiments. Isopropanol and 2-butanol (Aldrich Gold Label 99+%), 3-methyl-2-butanol (Aldrich 99%), toluene (Burdick and Jackson High-Purity Solvent) and ethylene glycol (Aldrich 99+%) were used as received. Benzyl alcohol, 1-phenyl-1-ethanol (α-methylbenzyl alcohol), 1-phenyl-1-propanol and diphenylmethane were obtained from Aldrich (reagent grade); 2-methyl-1-phenyl-1-propanol was Wiley 99%. Purification of ethylbenzene, cumene and *tert*-butylbenzene is detailed elsewhere (ref. 12). The liquid alcohols and hydrocarbons were purified by fractional distillation under vacuum or a nitrogen atmosphere and stored under nitrogen or argon. The solid quencher 2,2-dimethyl-1-phenyl-1-propanol (Wiley 97%) was sublimed under vacuum two times immediately prior to use. The monodeuterated alcohol $PhCD(OH)CH_3$ was synthesized by reducing acetophenone with $NaBD_4$ and quenching the reaction with H_2O.

Quenching experiments

Acetonitrile solutions containing $[TBA]_4Pt_2$ (1-3 $\times 10^{-4}$ M) plus incrementally varied quencher concentrations were degassed with at least 5 freeze-pump-thaw cycles on a vacuum line with a limiting pressure of $\sim 10^{-5}$ torr. Quenchers were added directly to the quenching cell (roundbottomed flask connected by two arms to 1-mm and 1-cm cuvettes and sealed by Teflon vacuum valves) using a syringe of the appropriate volume (between 10 µL and 1 mL); the solution was opened to air for the addition of each quencher aliquot. Alternatively, relatively concentrated quencher solutions were successively diluted by additions of acetonitrile. Excited-state lifetimes (τ) were measured with a Quanta Ray Nd:YAG (8-ns fwhm; 355-nm excitation) laser system described elsewhere (ref. 13). Emission was monitored at 518 nm. Quenching rate constants and the quantities derived from them have estimated errors of 5-10%.

The lifetime τ of $[TOA]_4Pt_2$ phosphorescence in toluene is 7.3 µs. An unquenched τ_o of 10.3 µs in toluene is calculated if k_q for toluene is assumed to be the same as that found in CH_3CN solutions ($k_q=4.2\times10^3 M^{-1}s^{-1}$). Therefore, τ_o is approximately invariant in acetonitrile, methanol and toluene! In studies that employ high quencher concentrations, the quenchers may begin to alter the properties of the solvent medium and therefore change the excited-state lifetime, which may be sensitive to solvent viscosity or other properties. Since changes in the solvent medium do not significantly alter the natural lifetime τ_o of Pt_2, however, such effects are negligible and lifetime changes can be attributed solely to changes in reaction rates.

Bulk photolyses

Acetonitrile solutions of $[TBA]_4Pt_2$ ($\sim 3\times10^{-4}$M) were degassed with at least 5 freeze-pump-thaw cycles. Solutions were irradiated in a 1-cm cell, and the absorbance changes were measured in an attached 1-mm cell. Cary 14 (modified by Olis Instrument Systems) and Shimadzu UV-260 absorption spectrometers were used. For the irradiation source, a 1000W Hg-Xe lamp with cutoff and band pass optical filters provided a photon flux of $\sim 10^{-7}$ Ei s^{-1} for the wavelength range 340-400 nm. Actinometry was performed with Aberchrome 540, or *trans*-2-(2,5-dimethyl-3-furanyl)ethylidene-3-(1-methylethylidene)succinic anhydride, dissolved in degassed toluene (Burdick and Jackson High-Purity Solvent). Absorbances of both the actinometer and Pt_2 solutions are sufficiently high that all photons reaching the solutions are absorbed.

Product identification

Products were identified by gas chromatography and their retention times compared to those of authentic samples. In some cases the products were also identified through ^1H NMR. Prior to GC analysis, KPF_6 was added to photolyzed solutions to precipitate the platinum complex. Both Carbowax and glass columns were used with a flame ionization detector on a Hewlett-Packard 8410 GC. GC peak areas are proportional to moles of carbon detected; this relationship was verified for the bibenzyl/biphenyl system. Biphenyl was used as the internal standard. Although the k_q for the reaction of biphenyl with $^3Pt_2^*$ is $\sim 10^5 M^{-1}s^{-1}$, quenching does not lead to product formation and biphenyl is present at such low concentrations (less than 0.01 M) that its quenching is not significant.

RESULTS AND DISCUSSION

H-atom transfer quenching of $^3Pt_2^*$

The reaction between $^3Pt_2^*$ and organic substrates has typically been monitored by determining the rate with which the organic compound (Q) quenches the luminescence of the $^3Pt_2^*$ excited state. The Stern-Volmer equation (eqn. 5) describes the dependence of the excited-state lifetime on the quencher concentration when deactivation of the excited state occurs via bimolecular reaction with a quencher.

$$1/\tau - 1/\tau_o = k_q[Q] \tag{5}$$

The quenched and unquenched lifetimes of the luminescent excited state are given by τ and τ_o, respectively; k_q is the Stern-Volmer quenching rate constant determined from the slope of a plot of $(1/\tau - 1/\tau_o)$ versus [Q].

The rates of hydrogen-atom abstraction by $^3Pt_2^*$, as measured by quenching rates (k_q), are given for a variety of organic H-atom donors in Table 1. Benzyl alcohols quench $^3Pt_2^*$ mainly through H-atom transfer, as demonstrated by the large kinetic isotope effect observed for quenching with α-methylbenzyl alcohol ($k_H/k_D = 5$) and the observation of ketones and Pt_2H_2 as photolysis products in reasonably high yields (*vide infra*). Also, k_q tends to decrease with increasing D(C-H) for the alcohols, as observed in photoabstraction reactions by the $n\pi^*$ excited states of ketones (refs. 14-16).

TABLE 1
$^3Pt_2^*$ Stern-Volmer quenching rate constants for organic H-atom donors in acetonitrile solution at room temperature (ref. 17).

Alcohols RR'CHOH			
R	R'	k_q ($M^{-1}s^{-1}$)	D(C-H) (kcal/mol)
Ph	H	4×10^6	85
Ph	CH_3	1.8×10^6	84
Ph α-D	CH_3	3.6×10^5	
Ph	CH_2CH_3	1.2×10^6	84
Ph	$CH(CH_3)_2$	5×10^5	84
Ph	$C(CH_3)_3$	3×10^4	84
CH_3	CH_3	$\sim 10^4$	91
CH_3	CH_2CH_3	$\sim 10^4$	91
CH_3	$CH(CH_3)_2$	3×10^5	91
CH_2OH	H	1.6×10^4	93
Benzyl hydrocarbons			
$PhCH_3$		4.2×10^3	88
$PhCD_3$		2.8×10^3	
$PhCH_2CH_3$		6.4×10^3	85
$PhCH(CH_3)_2$		5.0×10^3	84
$PhC(CH_3)_3$		7.4×10^3	100

Benzyl hydrocarbons also quench $^3Pt_2^*$ through H-atom abstraction, as confirmed by the formation of Pt_2H_2 and radical coupling products (e.g., bibenzyl from toluene). The yield of radical coupling products is low (*vide infra*) and the isotope effect for toluene (k_H/k_D = 1.5) is much lower than for the alcohols. It is particularly striking that the atom-transfer quenching rates for the reactions of $^3Pt_2^*$ with benzyl alcohols are much higher than the rates for hydrocarbons with comparable benzylic C-H bond strengths.

The reactivity differences between benzyl hydrocarbons and alcohols can be explained by polar interactions. The presence of OH groups in alcohols gives rise to the possibility of H-bonding interactions between the substrate and the H-bonded terminal oxygens on the Pt_2 ligands. In forming the triplet excited state of Pt_2 responsible for H-atom-transfer reactions, an electron is promoted from a dσ* orbital directed out along the Pt-Pt axis to a pσ orbital localized between the two platinum atoms (ref.

11, 18). This leaves a hole in the dσ* orbital, localized in the axial site. The situation is similar to the hole left in the oxygen-localized n orbital in the $n\pi^*$ states of organic ketones, which also abstract H atoms from suitable substrates (ref. 14). Polar interactions may specifically facilitate the approach of alcohol substrates to the axial sites of the metal complex, leading to H-atom abstraction by the metal center (Figure 1).

Alcohols exhibit unusual quenching behavior when present at high concentrations. The rate of quenching, $1/\tau - 1/\tau_0$, reaches a limiting value as more alcohol is added (Figure 2). The initial linear region is used to extract k_q.

A hydrogen-bonded intermediate alters the previously assumed bimolecular reaction model by dividing the quenching reaction into two steps. The first step (eqn. 6) is formation of an H-bonded precursor complex between ${}^3Pt_2^*$ and the alcohol substrate, followed by intramolecular H-atom transfer (eqn. 7).

$$ {}^3Pt_2^{*} + RR'CHOH \overset{K_{eq}}{\rightleftharpoons} {}^3[Pt_2 \cdots HCOHRR']^{*} \qquad (6)$$

$$ {}^3[Pt_2 \cdots HCOHRR']^{*} \xrightarrow{k_H} Pt_2H + RR'\dot{C}OH \qquad (7)$$

The kinetic treatment of the pre-equilibrium mechanistic model [eqns. (6) and (7)] leads to eqn. (8):

$$1/\tau - 1/\tau_0 = K_{eq}k_H/(K_{eq} + 1/[ROH]) \qquad (8)$$

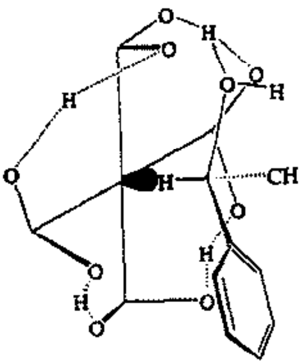

Fig. 1. View of an alcohol molecule docking with the Pt2 ligands.

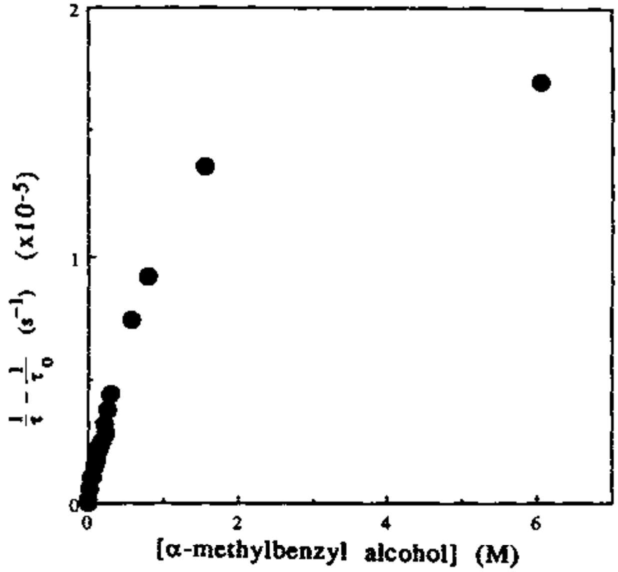

Fig. 2. Stern-Volmer plot for the quenching of $^3Pt_2^*$ phosphorescence by α-methylbenzyl alcohol in acetonitrile solution at room temperature.

At high alcohol concentrations, the Stern-Volmer plot should plateau, as observed (Figure 2). Rearrangement of eqn. (8) gives eqn. (9):

$$(1/\tau - 1/\tau_0)^{-1} = 1/k_H + 1/K_{eq}k_H[ROH] \qquad (9)$$

Such a double-reciprocal plot of the alcohol quenching data is linear (Figure 3).

Values of K_{eq} and k_H can be extracted from both Stern-Volmer and double-reciprocal plots. The slope of the Stern-Volmer plot at low alcohol concentrations is equal to $K_{eq}k_H$, which corresponds to the k_q reported previously. At high concentrations, k_q reaches a limiting value equivalent to the intramolecular H-atom abstraction rate constant, k_H. The slope of the double-reciprocal plot equals $(K_{eq}k_H)^{-1}$; the high-concentration limit is k_H^{-1}.

K_{eq} and k_H values were determined for a series of alcohols (Table 2). The fact that K_{eq} is relatively invariant with respect to substitution on the

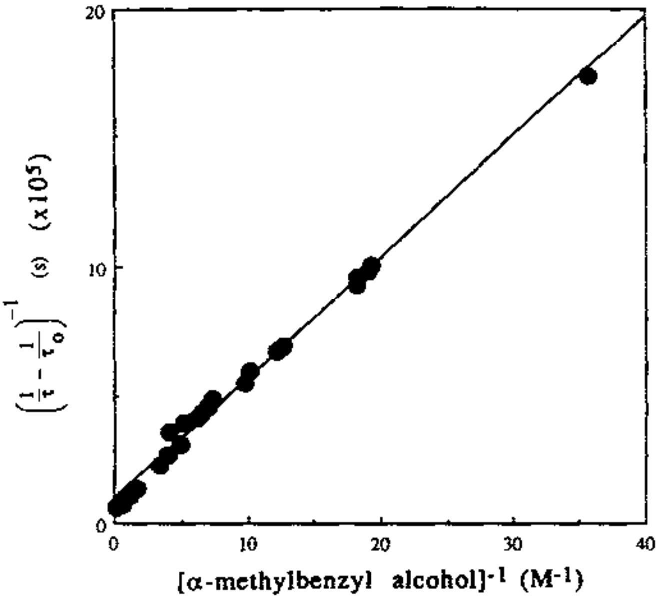

Fig. 3. Double-reciprocal plot of the quenching data for the reaction of α-methylbenzyl alcohol with $^3Pt_2^*$ in acetonitrile solution at room temperature.

TABLE 2
$^3Pt_2^*$ phosphorescence quenching parameters for selected alcohols in acetonitrile solution at room temperature.

RR'CHOH			
R	R'	K_{eq} (M^{-1})	k_H(s^{-1})
Ph	CH_3	1.0	2.1x10^6
Ph	$CH(CH_3)_2$	0.2	2.1x10^6
CH_2OH	H	0.5	3.5x10^4
CH_3	$CH(CH_3)_2$	0.5	5.0x10^5

α-carbon is consistent with a docking interaction involving only the hydroxyl group, since variation of alkyl groups on the α-carbon should not affect the hydroxyl group significantly.

For the series of aliphatic alcohols including isopropanol, 2-butanol and 3-methyl-2-butanol, an increase in substituent size dramatically increases the quenching rate (Table 1) from the lower measurement limits (10^4 $M^{-1}s^{-1}$) to rates near those of the benzyl alcohols. Within a series of benzyl alcohols (Figure 4), increasing substituent size decreases the quenching rate.

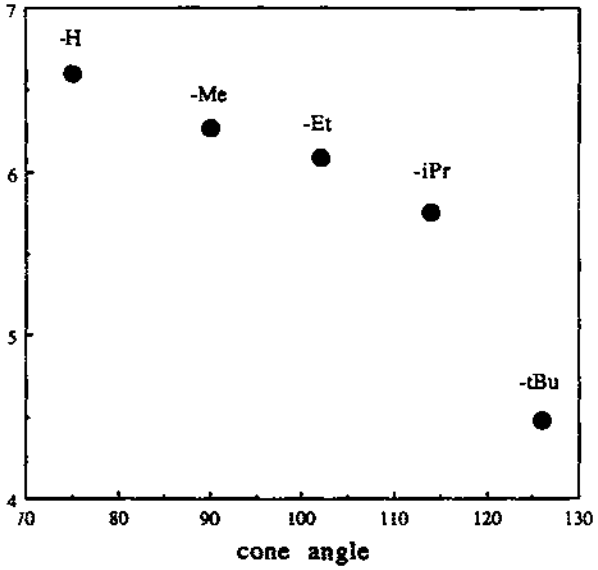

Fig. 4. The variation of the Stern-Volmer quenching rate k_q with the cone angle of α-substituents on benzyl alcohols.

Product formation rates

Stern-Volmer quenching constants provide useful information about factors that control the selectivity of the initial H-atom abstraction by $^3Pt_2^*$, but do not necessarily forecast the efficiency of formation of stable products. Although the quenching of $^3Pt_2^*$ with alcohols has been studied thoroughly, deactivation of the excited state is only the first step in a sequence of reactions that leads to the products Pt_2H_2, H_2 and ketones. The ratio of the effective rate constant for product formation (k_p) and the rate constant of the quenching step (k_q) can be expressed as an efficiency parameter Φ_p:

$$k_p/k_q = \Phi_p \qquad (10)$$

A Φ_p value of unity means that every deactivation reaction leads to the formation of one molecule of a stable atom-transfer product. The growth of the distinctive ultraviolet absorption band for Pt_2H_2 at 313 nm proved to be a useful handle for following product formation with alcohols in CH_3CN.

At high conversions to Pt_2H_2, the system appears to approach a photostationary state; i.e., the absorption spectrum shows no change upon further irradiation (Figure 5). The low-energy tail of the Pt_2H_2 band presumably absorbs some of the excitation light (λ>350 nm) and photoeliminates dihydrogen. When the growth in Pt_2H_2 due to hydrogen-atom abstraction from alcohols is exactly balanced by its photochemical decomposition, a steady-state concentration of the dihydride is established.

Long-term photolyses with benzyl hydrocarbons yield benzyl dimer products, as quantitatively analyzed by gas chromatography. The amount of product formed, the photolysis time (t), the $^3Pt_2^*$ phosphorescence lifetime (τ) and the photon flux (I) give k_p according to eqn. (11):

$$\text{mol RH consumed} = 2(\text{mol dimer } R_2 \text{ produced}) = It\tau k_p[RH] \qquad (11)$$

A small amount of Pt_2H_2 also is formed in photolyses with cumene and ethylbenzene but the k_p values for dihydride formation were not determined. Photoreactions in toluene solutions do not produce the dihydride. This may reflect the slow hydrogen-transfer rate of toluene relative to cumene and ethylbenzene.

The Φ_p values of about 0.1 reveal that the H-atom-transfer reaction is reasonably efficient for many substrates (Table 3). However, the rates of product formation span nearly three orders of magnitude among the alcohols, demonstrating remarkable reaction selectivity. From these data, we can predict that given a choice of isopropanol and benzyl alcohol in the same solution, 99.8% of the $^3Pt_2^*$ complexes will dehydrogenate benzyl alcohol.

In a test of dehydrogenation selectivity, irradiation of Pt_2 in an approximately equimolar (0.5M) solution of benzyl alcohol and cyclohexanol gave a selectivity of 15:1 in favor of benzyl alcohol. A similar experiment with 2-cyclohexen-1-ol and cyclohexanol yielded no

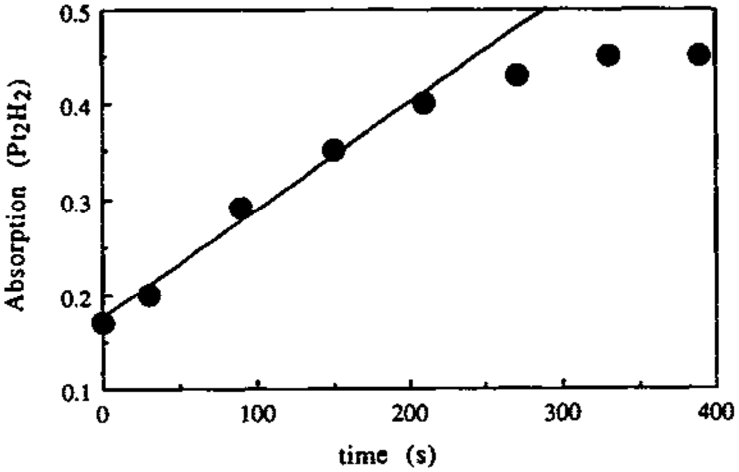

Fig. 5. Absorbance of the 313-nm Pt_2H_2 band as a function of the time of irradiation into the Pt_2 absorption band at 372 nm. The H-atom quencher is benzyl alcohol (0.077M) in acetonitrile solution.

TABLE 3
Product formation rates and reaction efficiencies for selected quenchers in acetonitrile solution.

Quencher	[ROH] (M)	k_p ($M^{-1}s^{-1}$)	Φ_p
		Pt_2H_2 product	
benzyl alcohol	0.058	5.9 x10^5	0.15
	0.077	4.0 x10^5	0.10
isopropanol	6.53	820	~0.08
		Dimer product	
toluene	4.7	25	0.006
ethylbenzene	4.1	400	0.06
cumene	3.6	600	0.1

cyclohexenone but produced 365 turnovers of cyclohexanol to cyclohexanone.

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