the valence band position) of the semiconductor employed. These observations suggest to us that radical cation formation may be required,[24] i.e., that the (oxidant + adsorbed olefin) complex alone cannot account for the observed reactivity.

This method offers the synthetic chemist interested in olefin oxidations significant advantages over alternate methods for oxidative olefin cleavage. The use of TiO_2 and atmospheric oxygen is cheaper, safer, and more selective than the use of ozone or conventional inorganic oxidants. The workup is particularly easy, the sensitizer being removed by filtration and/or a neutral water wash. We note that a nonaqueous solvent is required for these reactions: further nonselective oxidation is observed in water, presumably because of the generation of the very reactive·OH radical[26] in water.

Clearly, application of the principles of photoelectrochemistry to organic conversions will open a new area of profitable research. Such investigations are continuing in our laboratory.

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Time-Resolved Determinations of Deuterium Isotope Effects on $O_2(^1\Delta_g)$ Lifetimes in Solution

G. Peters and M. A. J. Rodgers*

Center for Fast Kinetics Research
The University of Texas at Austin
Austin, Texas 78712

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The natural lifetime (τ_Δ) of the lowest excited singlet state of molecular oxygen, $O_2(^1\Delta_g)$, as a function of the solvent and its isotopic composition has been the subject of experimental and theoretical interest over the past decade. Until recently it appeared that the wide range of observed lifetimes[1-10] could be satisfactorily rationalized in terms of a theory based on energy transfer between the electronic levels of O_2 and ground-state vibrational levels of the solvent. New data, however, has appeared which indicate that a reappraisal, especially of the isotope effect, is necessary. Direct, time-resolved[11-13] measurements of the weak $^3\Sigma_g \leftarrow {}^1\Delta_g$ luminescence at 1270 nm have been used to confirm earlier less direct values of τ_Δ in several solvent media and have additionally shown a ratio $\tau_\Delta{}^D/\tau_\Delta{}^H = 3.4$ in chloroform, markedly different from earlier values. Furthermore, recent steady-state photooxidation measurements[14] using diphenylisobenzofuran (DPBF) and rubrene (R) as monitoring substrates lead Ogilby and Foote[14] to report unusually high values for $\tau_\Delta{}^D/\tau_\Delta{}^H$ for the solvents benzene, acetonitrile, acetone and chloroform (fully protiated and fully deuterated species). In this laboratory a time-resolved technique was used[15] for directly monitoring the loss of optical absorption of DPBF owing to the elementary process

$$O_2(^1\Delta_g) + M \xrightarrow{k_m} -M \qquad (1)$$

(M = monitoring substance). These experiments showed that the value $\tau_\Delta(D_2O)$ was 53 μs—significantly higher than hitherto reported. Confirmation of this higher value has been subsequently provided by Matheson and Massoudi.[16] In view of the differences in τ_Δ and $\tau_\Delta{}^D/\tau_\Delta{}^H$ values brought to light by the new data,[11-14] it was considered worthwhile to apply the time-resolved substrate bleaching method to the problem. We have examined the four solvents (protio and deuterio analogues) studied by Ogilby and Foote and have found in only one case good agreement with their data.

In the absence of additional quenching substances, the natural decay of singlet oxygen competes with the process which causes bleaching of the monitor (reaction 1):

$$O_2(^1\Delta_g) \xrightarrow{k_d} O_2(^3\Sigma_g) \qquad (2)$$

Under first-order conditions ($[M]_0 > 10[O_2(^1\Delta_g)]_0$) it follows that

$$k_{obsd} = k_d + k_m[M]$$

where k_{obsd} is the observed first-order rate constant for the bleaching of M. A linear plot of k_{obsd} against [M] shows consistency with the scheme and allows k_d ($= 1/\tau_\Delta$) and k_m to be evaluated from the intercept and the slope, respectively.

We used a previously described laser flash photolysis system[15] comprising a pulsed (8 ns) nitrogen gas laser excitation source coupled with computer controlled kinetic spectrophotometric detection.[17] Acetonaphthone ($\sim 10^{-3}$ mol L^{-1}) was employed as sensitizer to generate $O_2(^1\Delta_g)$ via its triplet state. Singlet oxygen kinetics were monitored by subsequent removel of the chromophores DPBF (415 nm, protio solvent) or rubrene (500 nm, deuterio solvent). Rubrene was preferred over DPBF as monitor in the solvents exhibiting large τ_Δ values owing to its lower rate constant for reaction. This meant that larger monitor concentrations could be used and hence larger bleaching signals (still <10% removal) could be observed. This ensured good signal-to-noise ratios and kept the value of k_m[M] near k_d to lessen the need for extended extrapolation for obtaining the intercept value (k_d).

Experiments were undertaken in aerated solutions at varying monitor concentrations (DPBF, 1–7 × 10^{-5} mol L^{-1}; rubrene, 1.5–13 × 10^{-5} mol L^{-1}) up to a limit governed by monitor concentration at which no more than 30% of the 337-nm excitation light was being directly absorbed by monitor. Neutral density filters were employed to attenuate the laser beam in order to ensure that less than 10% of the monitor was removed. Photolysis by the xenon monitoring arc was prevented by allowing light through the spectrometer for only ca. 10 ms during which time the experiment was conducted. Under the prevailing conditions, the removal of monitor was strictly first order.

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Table I. Summary of τ_Δ Values

solvent	τ_Δ,[a] ms	$10^{-7}k_m$,[b] L mol^{-1} s^{-1}	$10^{-3}k_d$,[c] s^{-1} (τ_Δ)	$k_d(H)/k_d(D)$[d]	$10^{-3}k_d^0$, s^{-1} (τ_Δ)	$k_d^0(H)/k_d^0(D)$[f]	$k_d(H)/k_d(D)$[g]
benzene	23.8,[4] 25.6,[8] 24.3,[8] 27,[2,9] 24.4[10]	67.0[i]	37.5 (27)	14.6	35.4 ± 0.5 (28)	35 ± 13	13.8-18.0
benzene-d	35.7[2]	2.8[i]	2.6 (385)		1.0 ± 0.35 (1000)		
benzene-d[h]		4.3[j]	1.5 (670)		1.5 ± 0.51 (670)	25 ± 9	
acetonitrile	30.3,[3] 55.5[2]	128.0[i]	13.0 (77)	5.7	10.8 ± 0.5 (92)	13.4 ± 6	5.6-9.7
acetonitrile-d		8.0[j]	2.3 (435)		0.8 ± 0.33 (1250)		
acetone	26.3,[4] 41.6,[2] 51[13]	102.0[i]	20.0 (50)	7.0	18.1 ± 0.4 (55)	13.8 ± 4	13.2-21.2
acetone-d		2.8[j]	2.9 (345)		1.31 ± 0.35 (760)		
chloroform	58.8,[1] 227,[2] 111,[3] 250[11,13]	49.0[i]	4.5 (220)	1.6	2.41 ± 0.45 (415)	2.13 ± 1	8.9-10.6
chloroform-d	303,[1] 840[11]	3.9[j]	2.8 (360)		1.13 ± 0.37 (885)		

[a] Literature values. [b] Bimolecular rate constants of $O_2(^1\Delta_g)$ quenching by monitor (this work). [c] k_d values, this work–uncorrected for $O_2(^1\Delta_g)$ by sensitizer (ACN). [d] Ratios $k_d(H)/k_d(D)$, this work–uncorrected for $O_2(^1\Delta_g)$ by sensitizer (ACN). [e] Values of k_d, this work–corrected for quenching of $O_2(^1\Delta_g)$ by sensitizer. [f] Corrected ratios. [g] $k_d(H)/k_d(D)$ ratios obtained by Ogilby and Foote, maximum range of ratios reported. [h] Data obtained in C_6D_6 with CB sensitizer. [i] DPBF as monitor. [j] Rubrene as monitor.

Representative linear plots of k_{obsd} as a function of monitor concentration are shown in Figure 1. Values of τ_Δ (= $1/k_d$) and k_m were extracted and a summary of these data is contained in Table I. The values of k_{obsd} in Figure 1 are averaged from a minimum of six data points from freshly replenished samples at each monitor concentration. The values of τ_Δ are estimated to be accurate to ±15%. For the protiated solvents our τ_Δ values are in reasonable agreement with the most reliable literature values. Our data for C_6D_6 and $CDCl_3$ disagree with the published values. These discrepancies cause particular concern where the literature values are derived from the time-resolved luminescence measurements ($CDCl_3$). Previous published work on acetonitrile-d_3 and acetone-d_6 was not found.

Discrepancies could result from a contribution to $O_2(^1\Delta_g)$ quenching by the ACN sensitizer. In this case, the observed k_d would be a composite given by

$$k_d = k_d^0 + k_s[S] \qquad (3)$$

where k_d^0 is the value of k_d at zero sensitizer concentration. Such an effect would be most pronounced in deuterated solvents where $O_2(^1\Delta_g)$ is longest lived. By measuring k_d at various 2-acetonaphthone concentrations (3–30 × 10^4 mol L^{-1}), the bimolecular rate constant for sensitizer quenching was evaluated as 1.8 ± 0.4 × 10^6 L mol^{-1} s^{-1} in $CDCl_3$. Rubrene (1.46 × 10^{-4} mol^{-1}) was employed as monitor. This value of k_s (assuming no solvent dependence) allowed the calculation of corrected values $k_d^0(D)$ and $k_d^0(H)$. These data, together with the ratios $k_d^0(D)$ and $k_d^0(H)$, are contained in Table I, columns "e" and "f". As a result of the 20% error in k_s and the fact that $k_s[S]$ is the major component of k_d (~60%) for the deuterated systems, the resulting values of k_d^0 and the ratios derived therefrom are subject to substantial errors.

In order to circumvent sensitizer quenching, a further experiment was performed in C_6D_6 by utilizing 640-nm pulsed excitation from a dye laser source and a benzene-soluble analogue of methylene blue which we have named Creed Blue (CB).[18] The high extinction of CB at 640 nm allowed much lower sensitizer concentrations (2 × 10^{-5} mol L^{-1}) to be used. Rubrene (2–14 × 10^{-5} mol L^{-1}) was used as monitor. The results (Figure 1 and Table 1) show k_d = 1.5 × 10^3 s^{-1} for C_6D_6 (τ_Δ = 670 μs) in agreement, within the combined experimental error, with the value of k_d^0 obtained with ACN as sensitizer. We therefore conclude that the contribution to $O_2(^1\Delta_g)$ quenching by ACN when used as sensitizer can be significant in cases where τ_Δ is 200 μs or more. Nevertheless, appropriate corrections can be made.

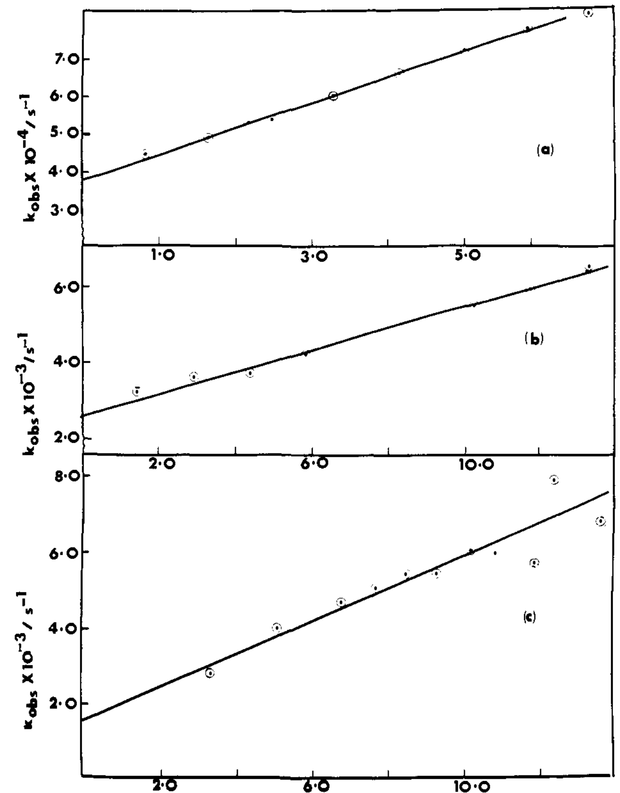

Figure 1. k_{obsd} as a function of monitor concentration: (a) C_6H_6, [ACN] = 1.15 × 10^{-3} mol L^{-1}; (b) C_6D_6, [ACN] = 8.64 × 10^{-4} mol^{-1} L^{-1}; (c) C_6D_6, [CB] = 2 × 10^{-5} mol l^{-1}.

Only in the case of acetone are our $k_d^0(H)/k_d^0(D)$ data in reasonable agreement with those extracted from steady-state measurements by Ogilby and Foote.[14] The reason for the discrepancy in the other three cases is not certain. In the time-resolved experiments employed here, the loss of monitor as it reacts in the elementary process 1 is being directly measured. In the steady-state case it is not always clear that type 11 photooxidation is the sole pathway for removal of monitor. Interference from type 1 and undetermined secondary processes can also contribute to loss of monitor over the extended time frame of measurement. Indeed, Ogilby and Foote[14] showed that a radical chain inhibitor was effective in changing the isotopic reaction ratio in some of their systems. Moreover, direct luminescence measurements[11-13] lead to $k_d(H)/k_d(D)$ = 3.4 in the case of chloroform. This is reasonably close to our value (2.1) but greatly different from that of Ogilby and Foote.[14] Clearly, further work is required to decide on the source of these discrepancies. As stated by Ogilby and Foote, in the solvents where large τ_Δ values are exhibited, the direct

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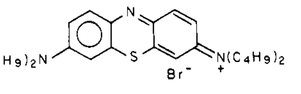
(18) The compound



was prepared and donated by Dr. David Creed of the University of Southern Mississippi to whom we are indebted.

luminescence measurement technique is to be preferred over indirect methods even when the latter, as here, have been carried out with the greatest care. Currently we are setting up for time-resolved infrared luminescence measurements in order to confirm our current indications that τ_Δ in C_6D_6, CD_3CN, and $(CD_3)_2CO$ is close to 1000 μs as shown[11] for $CDCl_3$. On the other hand, we contend that for τ_Δ values of less than ca. 200 μs, careful use of the time-resolved substrate bleaching method following flash excitation gives very reliable results.

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Synthesis, Structure, and Electrochemical Behavior of *cis*-Diammineplatinum(III) Dimers with Bridging α-Pyridonate Ligands

L. Steven Hollis and Stephen J. Lippard*

Department of Chemistry, Columbia University
New York, New York 10027

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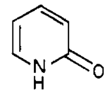
cis-Diammineplatinum α-pyridone blue, $[Pt_2(NH_3)_4(C_5H_4NO)_2]_2(NO_3)_5 \cdot H_2O$ (PPB), **1**, is a tetranuclear, mixed-valent, crystalline compound comprised formally of three Pt(II) and one Pt(III) centers linked by bridging α-pyridonate ligands, partial metal–metal bonding, and interplanar N—H···O hydrogen bonding.[1] In solution the compound is unstable, as determined by the loss of its blue color and paramagnetism with time.[2] Recently we have been studying further the reactions of α-pyridone with complexes of *cis*-diammineplatinum(II)[3] in order to provide additional clarification of the chemical and electronic spectral properties of PPB. Here we show that PPB can be oxidized to a metal–metal bonded platinum(III) dimer of which there are few well-characterized examples in the literature.[4] The crystal structure of the red-orange product reveals it to be the head-to-head isomer of *cis*-$[(H_2O)(NH_3)_2Pt(C_5H_4NO)_2Pt(NH_3)_2(NO_3)](NO_3)_3 \cdot 2H_2O$ (**2**). We also report the synthesis of the head-to-tail isomer, and electrochemical studies that reveal a quasi-reversible two-electron redox process for the $[Pt(II)]_2/[Pt(III)]_2$ couple. Concerted two-electron transfer reactions of this kind are rare for binuclear transition-metal complexes[5] and therefore of considerable interest.



α-pyridone

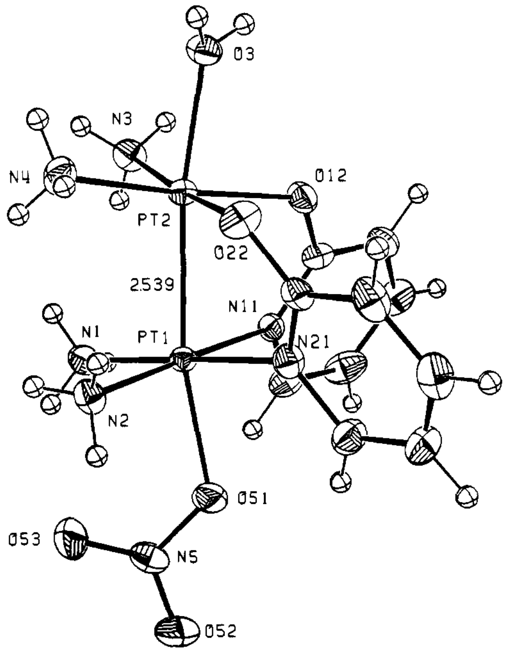


Figure 1. ORTEP drawing of the structure of the head-to-head isomer of the *cis*-$[(H_2O)(NH_3)_2Pt(C_5H_4NO)_2Pt(NH_3)_2(NO_3)]^{3+}$ cation in compound **2**, showing the 40% probability thermal ellipsoids. For clarity, hydrogen atoms are depicted as spheres with B set arbitrarily to 1 Å^2. The nitrate oxygen O(53) is intramolecularly hydrogen bonded to the ammine ligands (N1 and N2) while the coordinated H_2O (O3) is hydrogen bonded to a lattice water molecule.

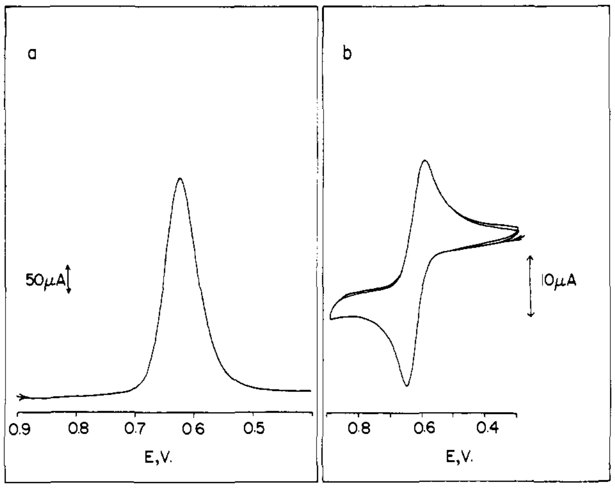


Figure 2. (a) Differential pulse voltammogram (Δi vs. V) of compound **3**, 0.4 mM. (b) Cyclic voltammogram for compound **4** (several cycles obtained at a scan rate of 20 mV s^{-1}), 0.9 mM. Experimental details are given in ref 8.

Red crystals of **2** were obtained by heating 20 mg of **1** to 80 °C in 5 mL of 5 M nitric acid for 2 min during which time the solution changed color from blue to red orange. Air evaporation of the resulting solution provided a 65–80% yield of **2**. The head-to-tail isomer, *cis*-$[(NO_3)(NH_3)_2Pt(C_5H_4NO)_2Pt(NH_3)_2(NO_3)](NO_3)_2 \cdot H_2O$ (**3**), was prepared in a similar fashion from the head-to-tail platinum(II) dimer $[Pt(NH_3)_2(C_5H_4NO)]_2(NO_3)_2 \cdot 2H_2O$ (**4**)[3] and isolated as red crystals. In addition to a complete X-ray crystal structure analysis of compound **2**,[6] both

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[6] X-ray analysis: Compound **2** crystallizes in the monoclinic system (space group $P2_1/n$) with the following cell parameters: $a = 9.709$ (1), $b = 13.779$ (2), $c = 18.655$ (2) Å; $\beta = 94.44$ (1)°; $\rho_{obsd} = 2.50$ (2), $\rho_{calcd} = 2.51$ g/cm^3; $Z = 4$. The structure was solved by standard Patterson and Fourier methods using 5715 unique reflections collected out to $2\theta = 55°$ on a Nonius CAD-4F diffractometer with Mo Kα ($\lambda = 0.7017$ Å) radiation. Refinement of the absorption corrected data with all atoms assigned anisotropic temperature parameters, except hydrogens which were refined isotropically with constraints, converged to a value of 0.032 for the discrepancy index $R_1 = \sum||F_o| - |F_c|| / \sum|F_o|$. Atomic positional and thermal parameters are provided as supplementary material. Full details will be reported at a later date.

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