Since the energy of the polar CT state is reduced by the solvent, we obtain significant increase in $\Delta E_{\text{overlap}}$ due to solvent effect. Obviously, when the $p_\sigma$ overlap between the monomers is small ($Z > 4$ Å) this contribution to the red shift disappears. It is important not to confuse this overlap effect with the previously proposed solvent shift[2,3] (which is attributed to change of the *monomer*, rather than the dimer, dipole moment upon excitation). In fact, as seen from Table I, the solvent shift is zero in the present calculation in the absence of overlap interaction.[16]

In contrast to previous suggestions[2,3] the hydrogen bonds between the water and the V ring keto carbonyls are found to contribute a negligible red shift (6 $\text{cm}^{-1}$).

Recently, it was found that dimeric chlorophyll derivatives in which the macrocycles are bound by two covalent links do not display any appreciable red shifts.[17] However, in these dimers the monomers are held face to face ($Y \sim 0$, according to the notation of Figure 1). In such a system the allowed electronic transition is expected to be blue shifted rather than red shifted.

The observations that anhydrous dimers do not display large red shifts[2] was used as evidence that the water molecules in the $(\text{Chl } a\cdot\text{H}_2\text{O})_2$ are responsible for a significant part of the observed red shift. We feel that the main contribution of the water is indirect, holding the dimer in a configuration with large excimer shift.

In summary, the present calculations demonstrate that the observed red shift in P700 can be reproduced by a dimer in a nonpolar solvent if the interaction between the monomer units is similar to that in the crystalline stack. In such a case, the red shift is primarily due to $p_\sigma$ overlap and exciton interactions. We believe that the calculations are reliable since they also reproduce the observed red shift in a well-defined crystal of chlorophyll derivative.

Of course, our calculations do not exclude the possibility that in P700 or other reaction centers the monomers interact weakly and that the observed red shift is due to other factors (e.g., interaction with charged groups similar to that proposed for the red shift of retinal in rhodopsin[13]). However, it is clear now that, if the red shift of P700 is due to the same type of excimer interaction as that in the crystalline stack, then the distance between the monomers must be <4 Å; otherwise the overlap would be too small to account for the observed red shift. It is intriguing to note that excimer interactions are associated with extremely large Franck–Condon factors (see Table 2 of ref 9). A large Franck–Condon factor for the transition between the positively charged dimer and the neutral dimer might explain why the electron transfer in the photosynthetic process is so efficient.[18]

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**Arieh Warshel**[20]
*Department of Chemistry, University of Southern California*
*Los Angeles, California 90007*

*Received July 11, 1978*

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## Picosecond Studies of Excited-State Protonation and Deprotonation Kinetics. The Laser pH Jump†

*Sir:*

Among the most important and general chemical concepts are the acid–base properties of molecules. The Lewis definition of acids and bases, that an acid is an electron pair accepting species while a base is electron pair donating,[1] serves to demonstrate the link between the acid–base properties of a molecule and its electronic structure. Thus a change in electronic structure, e.g., by electronic excitation, should produce a concomitant change in acid–base properties. Such an effect was first observed by Weber,[2] who found a spectral shift in the fluorescence spectrum of 1-naphthylamine-4-sulfonate which occurred at a much different pH than the spectral shift in the absorption spectrum. Subsequent development by Förster[3] and Weller[4] has produced an active field of chemical research.[5] Such studies typically combine spectroscopic data on absorption and/or fluorescence with a Förster cycle[6] calculation to predict excited-state $\text{p}K_\text{a}$ values. Because of the exceedingly rapid times scales involved, few direct determinations of the kinetics of excited-state proton-transfer reactions in solution have been made.[7,8]

By virtue of its extremely high time resolution, picosecond laser spectroscopy provides a general technique[9,10] for the study of excited-state proton-transfer reactions. We report here direct measurements of the kinetics of excited-state deprotonation and protonation for 2-naphthol-6-sulfonate and its anion in aqueous solution. In addition, a general method which utilizes the difference in ground- and excited-state $\text{p}K_\text{a}$ values to provide a means for rapid initiation of acid- or base-catalyzed reactions, the laser pH jump, is described.

The basic experimental apparatus used in these experiments has been described in detail elsewhere[11] and is shown schematically in Figure 1. Briefly, a single 30-ps, 1060-nm pulse is extracted from the pulse train of a mode-locked Nd:YAG laser. A second harmonic, 532-nm pulse is generated in a KDP crystal and is in turn frequency doubled in ADP to produce the fourth harmonic at 266 nm. The 532- and 1060-nm pulses are removed by spectral filters. The 266-nm excitation pulse is directed onto the sample which is contained in an optical quality quartz cuvette of 2-mm path length. Fluorescence from the sample is imaged through the slit of a streak camera (Electrophotonics ICC-512, S-20 response) having a demonstrated resolution of 3 ps. The width of the 266-nm pulse was

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† Work performed under the auspices of the U.S. Department of Energy.

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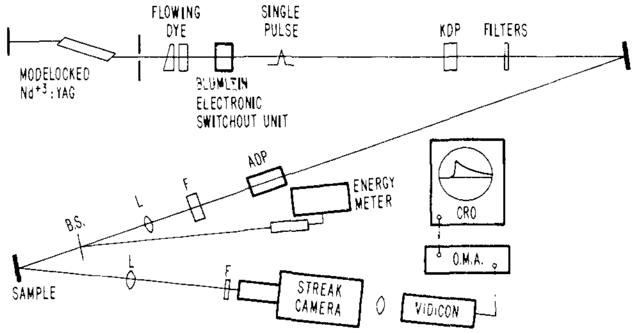

**Figure 1.** Schematic diagram of the experimental apparatus used for measurement of excited-state proton-transfer kinetics: L = lens, F = spectral filter, B.S. = beam splitter.

found to be 20 ps. The streaks are recorded via an optical multichannel analyzer (PAR 1205D detector) and displayed on an oscilloscope or X-Y recorder. Narrow band pass filters placed between the sample and the camera slit allowed the fluorescence from the various emitting species to be isolated.

The sodium 2-naphthol-6-sulfonate (Eastman) was used without further purification. For $H_2O$ as the solvent, identical results were obtained both for deionized, distilled $H_2O$ which was carefully degassed in a $N_2$ atmosphere and for regular distilled water. The latter was used throughout these experiments. For all the experiments described here, the 2-naphthol-6-sulfonate concentration was $1.0 \times 10^{-3}$ M. The pH of the solutions was adjusted by addition of reagent grade HCl or NaOH and was measured on a pH meter accurate to ~0.1 pH unit (Fisher Model 230). The samples were typically used shortly after preparation. However, the results obtained with freshly prepared and day-old solutions were identical.

The goal of these experiments was to obtain the rates of excited-state protonation and deprotonation $k_b$ and $k_f$, respectively, for the reaction

$$\mathrm{AH(S_1)} + \mathrm{H_2O} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \mathrm{A^-(S_1)} + \mathrm{H_3O^+} \qquad (1)$$

2-Naphthol-6-sulfonate ($pK_a = 9.1$)[5] is a weak acid in its ground electronic state. Hence the only ground-state species present at pH $\leq 7$ will be 2-naphthol-6-sulfonate. As long as the solution is not so acidic as to make the protonation reaction fast (pH $\geq 3$), the rate of excited-state proton transfer is simply determined from the rise time of the anion emission. Since the fluorescence of 2-naphthol-6-sulfonate ($\lambda_{max} \simeq 360$ nm) is considerably shifted from that of its anion ($\lambda_{max} \simeq 430$ nm), only the anion emission will be recorded when a 450 ± 10 nm spectral filter is placed between the cell and the streak camera slit. Figure 2 is a plot of the rise time (10–90%) of the emission from 2-naphtholate-6-sulfonate vs. the initial pH of the solution. As the solution becomes more acidic, the rise time becomes more rapid owing to bimolecular prontonation of the excited anion. At very high acidities, the protonation rate becomes so rapid that the temporal profile of the excited anion emission follows that of the protonated species. By measuring the time history of both anionic and acidic species under a variety of experimental conditions and using a kinetic scheme which includes terms for the fluorescence lifetimes and quenching, the complete kinetics of excited-state protonation and deprotonation have been obtained for 2-naphthol-6-sulfonate in $H_2O$.[12] For 2-naphthol-6-sulfonate, $k_f = (1.02 \pm 0.2) \times 10^9\ \mathrm{s^{-1}}$ and $k_b = (9.0 \pm 3) \times 10^{10}\ \mathrm{L\ mol^{-1}\ s^{-1}}$. The excited-state $pK_a$ obtained from the ratio of these rates agrees well with that of Weller.[13] Thus, picosecond techniques have allowed direct determination of previously unmeasurable proton-transfer rates.[7] By systematic variation of substituents and chromophores, such measurements provide the basis for modeling the detailed chemistry of the proton in condensed media.

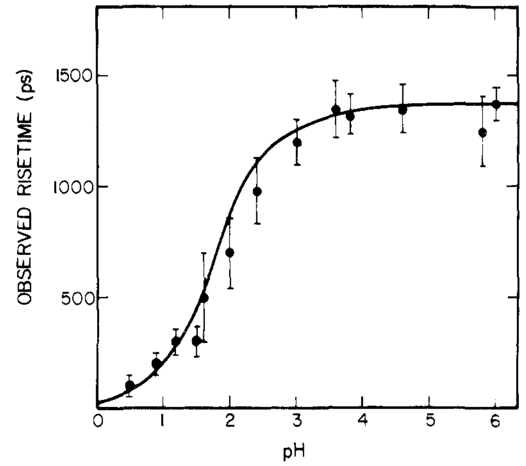

**Figure 2.** Experimentally observed risetime (10–90%) of 2-naphtholate-6-sulfonate emission vs. solution pH. Individual points represent the average of four-six separate streak camera exposures. The solid line is a fit using a kinetic model with $k_f = 1.02 \times 10^9\ \mathrm{s^{-1}}$ and $k_b = 9.0 \times 10^{10}\ \mathrm{L\ mol^{-1}\ s^{-1}}$.

Previously it has been suggested and purportedly demonstrated[14] that excited-state $pK_a$ shifts could be used to initiate ground-state reactions. Unfortunately, a simple calculation shows that the light flux used in those experiments was many orders of magnitude too low to produce any meaningful change in pH.[15] It is well known that laser sources produce extremely high light fluxes. For example the pulses employed in this work had a flux on the order of $10^{27}$ photons $\mathrm{cm^{-2}\ s^{-1}}$, while the lamp sources previously employed[14] had a flux of $\sim 10^{16}$ photons $\mathrm{cm^{-2}\ s^{-1}}$. Lasers with even higher flux are readily available.

From reaction 1 it is seen that one hydronium ion, $H_3O^+$, is produced for each proton transfer. Since the excited-state lifetime of 2-naphtholate-6-sulfonate is ~10 ns, while the proton-transfer time is <1 ns, excited-state acid–base equilibrium is achieved. Knowing the 2-naphthol-6-sulfonate absorption coefficient is 266 nm, its excited-state $pK_a$ value, the UV pulse energy, and the excitation geometry, we calculate that the $H_3O^+$ concentration was increased by $>10^{-4}$ M. Thus, the solution had a pH of 7 before excitation, and was rapidly modulated, or jumped, to pH $\leq 4$ on a time scale given by the subnanosecond proton-transfer rate. The pH will return to its previous value on a time scale greater than or equal to the excited-state lifetime ($\tau \sim 10$ ns), since it is the protonation rate of ground-state anions which determines how rapidly the ground-state acid–base equilibrium is reestablished. Choice of a more appropriate proton-transfer species could allow both a faster jump and a slower decay.[5] The ability to change rapidly the pH of solutions offers interesting kinetic and synthetic possibilities. Furthermore, since the majority of solution phase reactions are either acid or base catalyzed, including most reactions of biological importance, this pH jump technique offers a general, widely applicable method for rapid initiation of solution-phase chemistry. Once initiated, the reaction kinetics can be followed by picosecond spectroscopic techniques. This combination provides a means with which heretofore inaccessible aspects of the mechanisms and kinetics of reactions in solution can be unraveled, bringing a more detailed understanding to broad areas of chemistry and biochemistry.

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(16) J. Robert Oppenheimer Research Fellow.

**J. H. Clark,[16]* S. L. Shapiro, A. J. Campillo, K. R. Winn**
*University of California, Los Alamos Scientific Laboratory*
*Los Alamos, New Mexico 87545*

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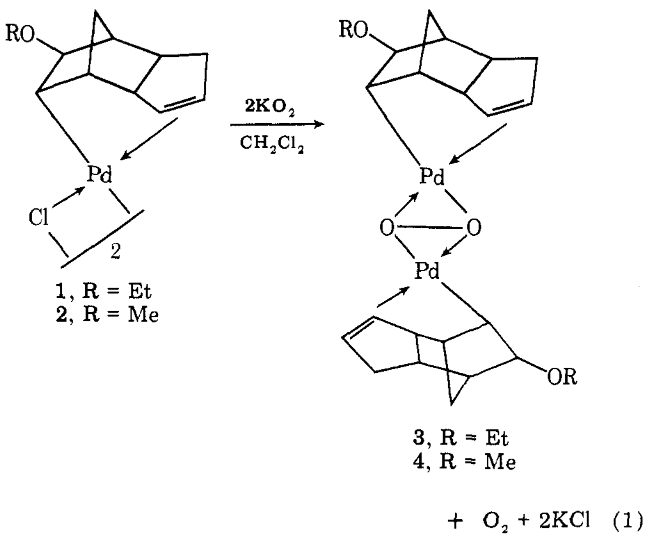
## Preparation of New Palladium Dioxygen Complexes Using Superoxide Ion

*Sir:*

Since the discovery of dioxygen complex of iridium by Vaska,[1] transition metal-dioxygen complexes have attracted the attention of many investigators.[2] The majority of these complexes have been prepared by reaction of gaseous molecular oxygen with low valent transition metal complexes. Dioxygen complexes formed by this method have inevitably phosphine or isonitrile ligand which is required for stabilization of the low valent state of the starting transition metal complexes.

We report here that reaction of superoxide ion, $O_2^-$, with binuclear palladium complexes involving chloride bridges and both a metal-carbon $\sigma$ bond and $\pi$-coordinate bond to cause anion exchange of $Cl^-$ with $O_2^-$ leads to formation of new dioxygen complexes having olefinic ligands. Experimentally, 640 mg (1 mmol) of palladium complex **1**[3] in 15 mL of $CH_2Cl_2$ was added dropwise to excess amount of finely powdered potassium superoxide (8 mmol, 4 equiv) suspended in 15 mL of $CH_2Cl_2$[4] at −40 °C and then the reaction mixture was slowly warmed to room temperature. Gradual evolution of oxygen was observed and the mixture was stirred for 4 h under 1 atm of nitrogen pressure. After removal of excess $KO_2$ and KCl by filtration, the filtrate was condensed at reduced pressure. Addition of mixed solvent of ether and petroleum ether (2:3) and cooling at 0 °C afforded a crude product as a pale yellow solid quantitatively. After repeated recrystallizations 528 mg (88%) of crystals, **3**, was obtained: mp >125 °C dec; IR (KBr) $\nu$(C—O) 1090 cm$^{-1}$; NMR ($CDCl_3$) $\delta$ 5.62 (2 H, m, olefinic), 6.21 (2 H, m, olefinic); mol wt (cryoscopy in benzene) calcd 598.8, found 606. Anal. Calcd for $C_{24}H_{34}O_4Pd_2$: C, 48.10; H, 5.72; Cl, 0.00. Found: C, 47.85; H, 6.10; Cl, 0.00.[5] Methoxy-substituted **3**, [(MeO-DiCp)PdO]$_2$, was also prepared by the reaction of **2** with an excess amount of $KO_2$ in $CH_2Cl_2$: mp >137 °C dec; IR (KBr) $\nu$(C—O) 1085 cm$^{-1}$; NMR ($CDCl_3$) $\delta$ 5.47 (2 H, m, olefinic), 6.12 (2 H, m, olefinic). Anal. Calcd for $C_{22}H_{30}O_4Pd_2$: C, 46.25; H, 5.29; Cl, 0.00. Found: C, 46.17; H, 5.29; Cl, 0.00.[5] The $^1$H NMR spectra of **3** and **4** are quite similar to those of **1** and **2**, except the peaks for olefinic protons show upfield shifts.



**1**, R = Et
**2**, R = Me

**3**, R = Et
**4**, R = Me

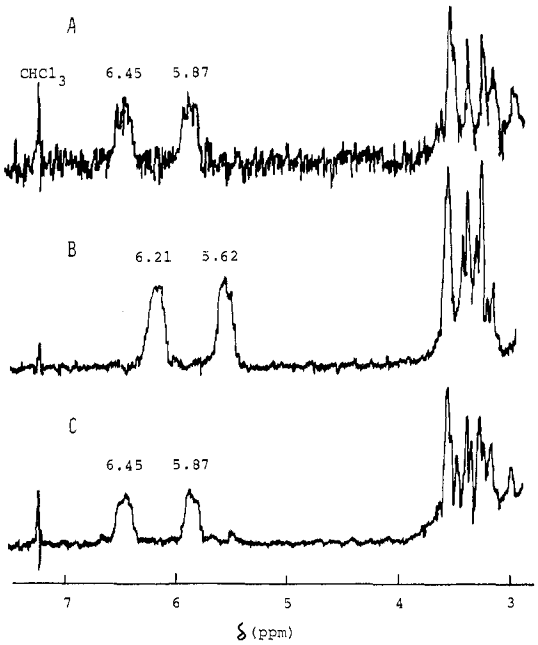
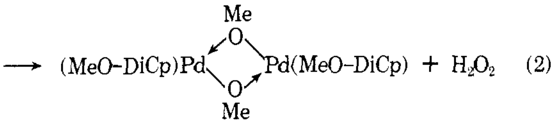


**Figure 1.** $^1$H NMR spectra of palladium complexes in $CDCl_3$: (A) [(EtO-DiCp)PdCl]$_2$ freshly prepared; (B) [(EtO-DiCp)PdO]$_2$; (C) recovered complex after warming of [(EtO-DiCp)PdO]$_2$ at 50 °C for 10 h in $CHCl_3$.

The dioxygen bridged structure[6] was further confirmed by the reactions of **3** and **4**. It was found that the dioxygen bridge in the complexes is fairly labile. Warming of **3** and **4** in $CH_2Cl_2$ or $CHCl_3$ caused exchange of the dioxygen bridge to chloride ones and gave the starting complexes **1** and **2** quantitatively.[7]

4 + 2MeOH



$$\longrightarrow (\text{MeO-DiCp})\text{Pd}\begin{matrix}\text{Me}\\ \text{O}\\ \\ \text{O}\\ \text{Me}\end{matrix}\text{Pd}(\text{MeO-DiCp}) + \text{H}_2\text{O}_2 \qquad (2)$$

**5**

Treatment of **4** by MeOH at room temperature afforded hydrogen peroxide[8] and methoxy-bridged complex **5**: mp >155 °C dec; IR (KBr) $\nu$(C—O) 1082, 1053 (bridging) cm$^{-1}$; NMR ($CDCl_3$) $\delta$ 3.18 (6 H, s, OMe), 3.40 (6 H, s, OMe), 5.16 (2 H, m, olefinic), 5.63 (2 H, m, olefinic); mol wt (cryoscopy in benzene) calcd 600.8, found 645. Anal. Calcd for $C_{24}H_{36}O_4Pd_2$: C, 47.94; H, 5.99. Found: C, 47.81; H. 6.02. The reaction is also quantitative and suggests that dioxygen is coordinated as $O_2^{2-}$ in the complex. Coordination bonds of oxygen to palladium are easily cleaved by treatment of the stronger ligand. When **4** is dissolved in $CH_3CN$ at room temperature, a new complex (**6**) is formed. Ivory needles are re-

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