independent hydroquinones) sitting on centers of symmetry (Figure 4). Bond lengths and angles are shown in Figure 6. There is excellent agreement between the molecular dimensions of the two independent hydroquinone "half-molecules". An interesting feature of the geometry of the dimethylbenzoquinone molecule is the significantly greater length of the C(12)–C(9) ($-CH_3$) bond as compared to the C(12)–C(10) (–H) bond and the smaller C(12)–C(9)–C(13) angle as compared to C(10′)–C(9)–C(13). Both hydroquinone rings are planar within the accuracy of the analysis, and the hydroxyl oxygen atoms lie 0.003 and 0.019 Å from the respective planes. The ring of the quinone molecule is also planar, with O(11) and C(13) lying 0.027 and –0.035 Å from the plane.

One set of independent hydroquinone molecules of the complex forms an infinite chain in the [101] direction with the quinone molecules by OH---O hydrogen bonding. The quinone and hydroquinone molecules forming this chain lie in the ($\bar{1}$01) plane. The O(1)–H hydroxyl group acts as a donor to O(11) of the quinone molecule. The O(1)---O(11) distance is 2.732 (2) Å, the H(1)---O(11) distance is 1.77 (2) Å, and the O(1)–H(1)---O(11) angle is 172 (2)°. Sandwiched between chains separated by the *b*-axis parameter lie the other set of hydroquinone molecules. These molecules are inclined at almost right angles to the first set and are linked to them by O(5)–H---O(1)(–H) hydrogen bonds. The O(5)---O(1) distance is 2.775 (2) Å, the H(5)---O(1) distance is 1.95 (3) Å, and the O(5)–H(5)---O(1) angle is 167 (2)°. Inspection of the structure suggests that the nonstoichiometric amounts of benzene found upon crystallization from that solvent result from partial replacement of the cross-linking hydroquinone molecules by benzene molecules.

The structure of the 1:2 complex of 2,5-dimethylbenzoquinone **5** with hydroquinone **4a** thus differs in a most interesting way from that[5b] of the 2:1 complex of **5** with 2,5-dimethylhydroquinone (**6**). Each structure is layered with a basic unit of hydroquinones hydrogen bonded to quinone molecules. The unusual stoichiometries in the two structures have as a common origin the steric repulsion of the methyl groups of adjacent molecular strips. However, the extra molecule is incorporated in a quite different manner here than in the previous structure[5b] where the normal quinhydrone chains were reduced to triplets, each hydroquinone being hydrogen bonded to two quinone molecules but with the hydrogen-bonded chains not continuing beyond that point. It has not yet been possible to obtain single crystals of the unstable isomer **6**/**3a** suitable for structure determination but it is most interesting that the unstable isomers formed by both the 2-methyl- and 2,5-dimethyl-substituted hydroquinones with unsubstituted benzoquinone have, unlike the stable isomers, the more usual 1:1 stoichiometry.

Conclusions

In spite of the extensive structural change required for redox reactions of unsymmetrically substituted quinhydrones in the solid state, it has been found that such reactions may, in favorable cases, proceed essentially quantitatively under relatively mild conditions; the equilibrium lies in the direction predicted from earlier redox measurements in solution. In those cases where the 1:1 complex of the product quinone and hydroquinone is unstable with respect to the 1:2 complex, the latter is formed, and the product obtained appears to be a mechanical mixture of the 1:2 complex with the superfluous quinone which has separated into its own microcrystallites. The products of these reactions thus are controlled by the energetics of crystal packing rather than by the stoichiometry of the starting quinhydrone.

Acknowledgment. We are indebted to the National Science Foundation for support of this work. The computer program MULTAN 80 and RANTAN employed in the structure determination were written by members of Professor M. M. Woolfson's group at the University of York, England, and the refinements were carried out using SHELX (G. M. Sheldrick, Cambridge University, England).

Registry No. Benzoquinone/naphthohydroquinone 1:1 complex, 87970-33-0; phenylbenzoquinone/naphthohydroquinone 1:1 complex, 87970-35-2; benzoquinone/2,5-dimethylhydroquinone 1:1 complex, 87970-32-9; benzoquinone/2-methylhydroquinone 1:1 complex, 55836-33-4; naphthoquinone/hydroquinone 1:1 complex, 60706-28-7; naphthoquinone/phenylhydroquinone 1:1 complex, 87970-34-1; 2,5-dimethylbenzoquinone/hydroquinone 1:2 complex, 87970-37-4; 2-methylbenzoquinone/hydroquinone 1:2 complex, 87970-36-3.

Supplementary Material Available: Tables of thermal parameters, details of plane calculations, and observed and calculated structure factors for the 1:2 complex (12 pages). Ordering information is given on any current masthead.

Comparative Photophysics of Platinum(II) and Platinum(IV) Porphyrins

Dongho Kim,[†] Dewey Holten,*[†] Martin Gouterman,[‡] and Johann W. Buchler[⊥]

Contribution from the Department of Chemistry, Washington University, St. Louis, Missouri 63130, Department of Chemistry, University of Washington, Seattle, Washington 98195, and Institut für Anorganische Chemie, Technische Hochschule, D-6100 Darmstadt, Federal Republic of Germany. *Received January 25, 1984*

Abstract: Absorption changes and kinetic behavior produced by excitation of Pt^{II}(TPP) and Pt^{IV}(TTP)Cl_2 with 35-ps flashes at 355 and 532 nm are reported. (TPP is tetraphenylporphyrin; TTP is tetratolylporphyrin.) The transient difference spectrum obtained for the Pt(II) compound persists for >10 ns and is assigned to the lowest ring triplet, $^3T(\pi,\pi^*)$. Similar results were found for Pd^{II}(TPP). On the other hand, the absorption changes obtained for the Pt^{IV} compound decay rapidly, with a time constant of 45 ± 10 ps. This transient behavior is ascribed to a low-lying ring-to-metal $[a_{2u}(\pi),d_{x^2-y^2}]$ charge-transfer state predicted by theory.

Extensive experimental and theoretical investigations of the electronic structure of metalloporphyrins, their excited states, and interconversion processes have been carried out over the past 3 decades.[1] Much of the experimental work has focused on the ground-state absorption, fluorescence emission from the lowest excited singlet, $^1Q(\pi,\pi^*)$, and phosphorescence emission from the lowest excited triplet, $^3T(\pi,\pi^*)$. However, there are a rather large number of transition-metal porphyrins that can be characterized

[†] Washington University.
[‡] University of Washington.
[⊥] Institut für Anorganische Chemie.

(1) Gouterman, M. In "The Porphyrins"; Dolphin, E. Ed.; Academic Press: New York, 1978; Vol. III, Chapter 1.

0002-7863/84/1506-4015$01.50/0

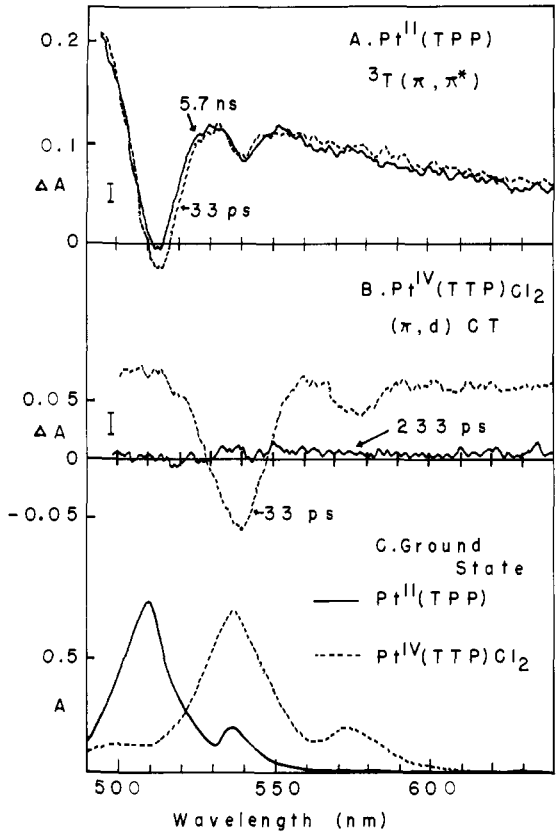


Figure 1. Transient difference spectra in toluene at various delay times following excitation of $Pt^{II}(TPP)$ (A) and $Pt^{IV}(TTP)Cl_2$ (B) with 35-ps, 300-μJ, 355-nm flashes. Each spectrum is the average of approximately 300 spectra, with a maximum standard deviation for ΔA of 0.01 across the wavelength region shown, as indicated on the left of each panel. Ground-state absorption spectra in toluene are shown in C.

as "nonemitters". It is thought that in these compounds the normally emissive (π,π^*) states decay rapidly via low-lying (d,d) or charge-transfer (CT) excited states, (π,d) or (d,π^*), predicted by iterative extended Hückel (IEH) theory.[1,2]

Picosecond transient absorption measurements on several transition-metal porphyrins have been undertaken to help characterize these predicted low-lying excited states, both spectrally and kinetically.[3-8] Examples include $(d_{z^2},d_{x^2-y^2})$ in Ni^{II} porphyrins,[4] (π,d_{z^2}) in Co^{II},[5] (d_π,d_{z^2}) in Co^{III},[5b,c] (d,π^*) in some Os^{II} and Ru^{II} porphyrins,[6,7] and $(\pi,d_{x^2-y^2})$ in Cu^{II} porphyrin complexed with a basic axial ligand.[8] In this paper we report on picosecond studies of the lowest excited states in $Pt^{II}(TPP)$ and $Pt^{IV}(TTP)Cl_2$. (TPP^{2-} and TTP^{2-} are the dianions of tetraphenylporphyrin and tetratolylporphyrin, respectively.)

Experimental Section

Details of the dual-beam picosecond transient absorption spectrometer have been described elsewhere.[4c] Basically, a pump pulse of ~35-ps duration at 532 or 355 nm excites a small region in a 2-mm-pathlength optical cell through which the sample is flowed. At a time "delay" adjustable from about −500 ps to about 10 ns a weaker ~35-ps "white-light" (450–900-nm) probe pulse passes through excited and unexcited regions of the sample and is dispersed by a polychromator onto two 500-channel tracks of a vidicon detector coupled to a computer-controlled optical multichannel analyzer. The digitized information is used to construct a "transient difference" spectrum, the difference in absorption (ΔA) between the excited or transient state and the ground state, at the preset pump-probe time delay. The system operates at a 10-Hz repetition rate.

$Pt^{II}(TPP)$ was purchased from Porphyrin Products (Logan, Utah) and its purity checked by thin-layer chromatography. $Pt^{IV}(TTP)Cl_2$ was prepared, purified, and characterized as described elsewhere.[9] Spectral grade toluene was employed. The ground-state absorption spectra of the two compounds in this solvent are identical with those published in the literature (Figure 1C).[2c,9,10] All measurements were carried out at room temperature.

Results and Discussion

Figure 1A shows transient difference spectra for $Pt^{II}(TPP)$ in toluene at two time delays following excitation with 35-ps flashes at 355 nm. The spectra reveal strong absorption to the blue of 510 nm and bleaching of the ground-state Q bands at 510 and 540 nm (Figure 1C). The difference spectra at the short and long time delays are the same within experimental error. From these data and spectra at other time delays not shown, we place a time constant of >10 ns on the relaxation of the excited state. Such a long decay time was found in previous picosecond measurements on platinum(II) and palladium(II) protoporphyrin(IX) dimethyl ester[4a] and on platinum(II) octaethylporphyrin.[6b] The latter study, which employed 7-ps flashes, also revealed an initial 15-ps step to the relaxation that was attributed to intersystem crossing $^1Q(\pi,\pi^*) \rightarrow {}^3T(\pi,\pi^*)$.[6b] In both previous studies, the long-lived absorption changes were ascribed to the $^3T(\pi,\pi^*)$. These assignments are consistent with the observation that Pt^{II} porphyrins phosphoresce, but do not fluoresce.[1,2c,10] Thus, on the basis of these kinetic arguments, we also assign the transient difference spectra of Figure 1A to the $^3T(\pi,\pi^*)$. In fact, the transient absorption (positive ΔA) in Figure 1A appears to be characteristic of (π,π^*) excited states of TPP compounds, exhibiting strong absorption below 510 nm increasing in strength to shorter wavelengths and a weak tail between 530 and 650 nm.[4,5,8,11] We obtained similar spectral and kinetic results for $Pd^{II}(TPP)$, not shown.

Figure 1B shows the absorption changes observed following excitation of $Pt^{IV}(TTP)Cl_2$ with 355-nm flashes. The difference spectrum at a 33-ps delay exhibits bleaching of the ground-state Q bands near 540 and 575 nm (Figure 1C). The transient absorption across the range 480 to 630 nm (and to 700 nm) is relatively featureless. This is clearly different from the spectrum assigned to the $^3T(\pi,\pi^*)$ in Figure 1A. The kinetic behavior is drastically different as well. The transient absorption and ground-state bleachings have completely recovered at the 233-ps time delay shown in Figure 1B. Measurements at intermediate delays yield a time constant of 45 ± 10 ps for the relaxation. Previous work on this compound has shown that it does not emit.[2c] It was suggested on the basis of IEH calculations on Ni^{IV} and Pd^{IV} porphyrins that the emission is quenched by a low-lying ring-to-metal $[a_{2u}(\pi),d_{x^2-y^2}]$ CT state. The weak, featureless transient absorption in Figure 1B is similar to spectra assigned previously to CT states in Co^{II} and Co^{III} porphyrins.[5b,c] Thus, on the basis of these spectral comparisons, the short lifetime, and the theoretical prediction,[2c] we assign the transient behavior ob-

(2) (a) Antipas, A.; Buchler, J. W.; Gouterman, M.; Smith, P. D. *J. Am. Chem. Soc.* **1978**, *100*, 3015. (b) Antipas, A.; Buchler, J. W.; Gouterman, M.; Smith, P. D. *Ibid.* **1980**, *102*, 198. (c) Antipas, A.; Gouterman, M. *Ibid.* **1983**, *105*, 4896. (d) Ake, R. L. Ph.D. Dissertation, Department of Chemistry, Harvard University, Boston, MA, 1968.

(3) References to most of the previous picosecond work on transition-metal porphyrins can be found in ref 5b and 6a. References 4–8 discuss work on some of the compounds.

(4) (a) Kobayashi, T.; Straub, K. D.; Rentzepis, P. M. *Photochem. Photobiol.* **1979**, *29*, 925. (b) Chirvonyi, V. S.; Dzhagarov, B. M.; Shul'ga, A. M.; Gurinovich, G. P. *Dokl. Biophys. (Engl. Transl.)* **1982**, *259*, 144. (c) Kim, D.; Kirmaier, C.; Holten, D. *Chem. Phys.* **1983**, *75*, 305. (d) Kim, D.; Holten, D. *Chem. Phys. Lett.* **1983**, *98*, 584.

(5) (a) Dzhagarov, B. M.; Timiniskii, Yu. V.; Chirvonyi, V. W.; Gurinovich, G. P. *Dokl. Biophys. (Engl. Transl.)* **1979**, *247*, 138. (b) Tait, D.; Holten, D.; Gouterman, M. *Chem. Phys. Lett.* **1983**, *100*, 268. (c) Tait, D.; Holten, D.; Gouterman, M. *J. Am. Chem. Soc.*, submitted for publication.

(6) (a) Serpone, N.; Netzel, T. L.; Gouterman, M. *J. Am. Chem. Soc.* **1982**, *104*, 246. (b) Ponterini, G.; Serpone, N.; Bergkamp, M. A.; Netzel, T. L. *Ibid.* **1983**, *105*, 4639.

(7) Tait, D.; Holten, D.; Gouterman, M.; Barley, M.; Dolphin, D.; James, B. R., manuscript in preparation.

(8) (a) Kim, D.; Holten, D.; Gouterman, M. *J. Am. Chem. Soc.* **1984**, *106*, 2793. (b) Straub, F. D.; Rentzepis, P. M. *Biophys. J.* **1983**, *41*, 411a.

(9) (a) Buchler, J. W.; Lay, K.-L.; Stoppa, H. Z. *Naturforsch., B.: Anorg. Chem. Org. Chem.* **1980**, *35B*, 433. (b) References in ref 2c.

(10) (a) Eastwood, D.; Gouterman, M. *J. Mol. Spectrosc.* **1970**, *35*, 359. (b) Callis, J. B.; Gouterman, M.; Jones, Y. M.; Henderson, B. H. *Ibid.* **1971**, *39*, 410. (c) Hanson, L. K.; Gouterman, M.; Hanson, J. C. *J. Am. Chem. Soc.* **1973**, *95*, 4822.

(11) Pekkarinen, L.; Linschitz, H. *J. Am. Chem. Soc.* **1960**, *82*, 2407.

served for $Pt^{IV}(TTP)Cl_2$ to the (π,d) CT state. The short lifetime is consistent with the fact that the compound does not emit,[2c] since the $^3T(\pi,\pi^*)$ appears to relax to the CT in $\leq$10 ps.

Similar spectral and kinetic results were obtained for both $Pt^{II}(TPP)$ and $Pt^{IV}(TTP)Cl_2$ following excitation with 532-nm flashes. The lack of excitation-wavelength dependence to the photophysics supports the view that the spectral and kinetic behavior we have reported are due to the lowest excited states of these two compounds.

Acknowledgment. This work was supported in part by NSF grant DMR-7823958 (M.G.) and by BRSG S07RR07054-17 awarded by the Biomedical Research Grant Program, Division of Research Resources, National Institutes of Health (D.H.). Funds were also provided to D.H. by a Camille and Henry Dreyfus Foundation Grant for Newly Appointed Young Faculty in Chemistry and to J.W.B. by the Deutsche Forshungsgemeinschaft.

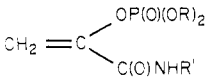
Registry No. $Pt^{II}(TPP)$, 14187-14-5; $Pt^{IV}(TPP)Cl_2$, 74194-58-4.

Phosphoenolpyruvamides. Amide–Phosphate Interactions in Analogues of Phosphoenolpyruvate

Ronald Kluger,* Jane Frances Chow, and James J. Croke

Contribution from the Lash Miller Laboratories, Department of Chemistry, University of Toronto, Toronto, Ontario, Canada M5S 1A1. *Received November 8, 1983*

Abstract: Ethyl esters of nitrogen-substituted carboxamides of phosphoenolpyruvate (**1** and **2**) were obtained from the reactions

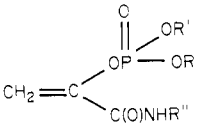


1, R = Et, R′ = *n*-Pr
2, R = Et; R′ = Ph

of triethyl phosphite with the corresponding nitrogen-substituted 3-bromopyruvamide. The hydrolysis of the ethyl ester portions of **1** and **2** occurs with an observed first-order rate constant that is 4 orders of magnitude larger than is estimated for triethyl phosphate under comparable conditions, indicating that participation by the neighboring carboxamide group is occurring. However, the enol phosphate ester substituent is cleaved much more slowly than are vinyl phosphate esters. The results are consistent with a mechanism in which the amide adds to the adjacent phosphate to form a reactive cyclic intermediate. The data support the proposal that amides can become phosphorylated during processes that involve interactions of peptides and nucleotides or during phosphate-transfer processes. The hydrolysis products of **1** and **2** may also be useful analogues of phosphoenolpyruvate in studies of enzyme mechanisms and in the design of inhibitors.

The covalent interaction of amide and phosphate functional groups has potential importance in many biochemical processes. For example, enzymic phosphate transfer may involve intermediate formation of a phosphorylated amide.[1,2] In the association complex of a nucleic acid or a phosphate ester with a protein,[3] the possibility that peptide functions can add to phosphodiester bonds is made favorable by the decreased entropic barrier provided by the macromolecular association. The chemical mechanism of such an interaction can be studied by combining the groups of interest into a single molecule.[4-7]

We have shown previously that esters of phenylphosphonic acid with an amide in the ortho position of the benzene ring undergo hydrolysis by a mechanism involving addition of the amide to the phosphonate center.[4,5] Although phosphonates share many reaction patterns with phosphates,[8,9] there are very significant differences in their interactions with enzymes.[10,11] Therefore, we sought a system that would permit the phosphorus reaction site to be a phosphate group. We also required that the amide and phosphate be in reactive proximity. Esters of derivatives of the carboxamide of phosphoenolpyruvate meet these requirements (structures **1** and **2**).



1, R, R′ = Et; R″ = *n*-Pr
2, R′, R = Et; R″ = Ph
3, R = H; R′ = Et; R″ = *n*-Pr
4, R, R′ = H; R″ = *n*-Pr

It has been shown that esters of phosphoenolpyruvate are highly reactive in hydrolysis reactions due to the participation of the carboxyl group at the phosphate ester center.[12] Amide analogues of these materials should allow facile interaction between the functional groups as well as being potentially useful for enzyme studies.[13] In this paper we report the synthesis of substituted

(1) Buchanan, J. *Adv. Enzymol.* **1973**, *39*, 91.
(2) Griffith, O. W.; Meister, A. *J. Biol. Chem.* **1981**, *256*, 9981.
(3) Schnarr, M.; Durand, M.; Maurizot, J. *Biochemistry* **1983**, *22*, 3563.
(4) Kluger, R.; Chan, J. L.-W. *J. Am. Chem. Soc.* **1973**, *95*, 2362.
(5) Kluger, R.; Chan, J. L.-W. *J. Am. Chem. Soc.* **1976**, *98*, 4913.
(6) Kluger, R.; Davis, P. P. *J. Am. Chem. Soc.* **1979**, *101*, 5995.
(7) Kluger, R.; Lam, J. C.-H. *Can. J. Chem.* **1977**, *55*, 640.
(8) Hudson, R. F.; Keay, L. *J. Chem. Soc.* **1956**, 2463.
(9) Cadogan, J. I. G.; Eastlick, D.; Hampson, F.; Mackie, R. K. *J. Chem. Soc. B* **1969**, *144*.
(10) Lazarus, R. A.; Benkovic, P. A.; Benkovic, S. J. *Arch. Biochem. Biophys.* **1979**, *197*, 218.
(11) Yount, R. *Adv. Enzymol.* **1975**, *43*, 3.
(12) Clark, V. M.; Kirby, A. J. *J. Am. Chem. Soc.* **1963**, *85*, 3705.

0002-7863/84/1506-4017$01.50/0