

generated DIM, either neat or diluted with DMF, was added to a DMF solution (1 mL) of the metalloporphyrin under Ar and the total volume was adjusted to 5 mL. The temperature of the porphyrin solution was maintained at  $18 \pm 0.5$  °C. In general, the spectra were recorded at the 350–750 nm range.

**Carbon Monoxide Affinity Measurements.** The experimental procedures used for these studies were similar to those described before for oxygen affinity measurements, but special precautions were necessary to avoid air-oxidation of the Fe(II)-porphyrins. Because of the very high oxygen affinity of the Fe(II)-porphyrins in solution, Fe(II)-porphyrins were freshly prepared in a carefully deaerated condition and used immediately. In a typical experiment, a mixture of a 5 mL benzene solution of 2.0 mg ( $1.6 \times 10^{-6}$  mol) of Fe(III)<sub>2</sub>-gale-Cl<sub>2</sub> and 0.5 mL of aqueous buffer solution (0.1 M phosphate, pH 6.86) was deoxygenated by three freeze-pump-thaw cycles ( $2 \times 10^{-6}$  torr). To the mixture 20 mg ( $1.1 \times 10^{-4}$  mol) of solid Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> was added, and the mixture was stirred vigorously for 30 min. The resulting orange-red solution of crude bis-ferrous gable porphyrin was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and applied to a specially prepared alumina column (vide infra). The column was eluted with oxygen-free methanol (1%) in benzene to afford the fractions containing Fe(II)<sub>2</sub>-gable alone. The fractions were combined and evaporated to dryness, and the residue was redissolved in 10 mL of deoxygenated DMF. Into the 1-cm quartz cell was placed 0.1 mL of the stock solution of Fe(II)<sub>2</sub>-gable. To the solution, 3 mL of deoxygenated DMF containing an appropriate amount of an axial ligand was added. Into the quartz cell was introduced by means of a vacuum line a premixed Ar-CO gas, deoxygenated by either procedure A or procedure B described below, by a vacuum line into the quartz cell. Then the mixture was kept standing at the fixed temperature until the equilibrium was attained, as indicated by reaching constant absorbance. This procedure was repeated several times under different CO partial pressure. The slow equilibration is inevitably accompanied with some minor O<sub>2</sub> oxidation, leading to the Fe(III)-porphyrins. Concentration of Fe(III) species was determined spectrophotometrically at 630 nm absorption. Data were only recorded when less than 5% of total Fe-porphyrin was converted to the corresponding Fe(III) complex.

**Deoxygenation Procedure A.** MnO<sup>17</sup> was freshly prepared by pyrolysis of Mn(C<sub>2</sub>O<sub>4</sub>) at 350 °C,  $1 \times 10^{-2}$  torr. The freshly prepared MnO was packed into a column (1 cm o.d.  $\times$  20 cm) and a mixed Ar-CO gas was introduced.

**Deoxygenation Procedure B.** A THF solution of sodium anthracenide (0.01 M) was prepared<sup>18</sup> in a vacuum line. Mixed Ar-CO gas was bubbled through the solution by applying a vacuum.

For the present deoxygenation purpose, the MnO method was found more effective than the sodium anthracenide method.

**Preparation of Alumina Column.** A suspension of 4 g of neutral alumina (Wolem activity I) and 0.15 g of Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> in 20 mL of deoxygenated H<sub>2</sub>O was stirred for 30 min under Ar. Alumina was collected by decantation, washed with deoxygenated H<sub>2</sub>O ( $6 \times 10$  mL), and dried in vacuo ( $1 \times 10^{-3}$  torr, at room temperature) for 12 h. The pretreated alumina was placed into a column and used for the purification of bis-ferrous gable porphyrin. To remove trace oxygen adsorbed on alumina, 1 mL (ca.  $1 \times 10^{-4}$  M) of benzene solution of bis-ferrous gable porphyrin was passed through the column by use of benzene-methanol (100:1) as an eluent, just before use. All of the procedures above were carried out in a carefully deoxygenated glovebox.

**Acknowledgment.** We are grateful to Professor J. Sessler for his helpful discussion. We are also grateful to Mr. Mano for his kind assistance in some of the spectroscopic measurements.

**Registry No.** Fe(TPP)(1,2-Me<sub>2</sub>Im)(CO), 80975-58-2; (gable)[Fe(CO)]<sub>2</sub>, 97467-40-8; (gable)[Fe(1-MeIm)(CO)]<sub>2</sub>, 97467-41-9; (gable)[Fe(1,2-Me<sub>2</sub>Im)(CO)]<sub>2</sub>, 97467-42-0; (gable)[Fe(CO)]<sub>2</sub>(μ-DIM), 97486-02-7; (gable)Fe<sub>2</sub>, 96481-89-9; (gable)[Fe(1-MeIm)]<sub>2</sub>, 97486-03-8; (gable)[Fe(1,2-Me<sub>2</sub>Im)]<sub>2</sub>, 97467-43-1; (gable)Fe<sub>2</sub>(μ-DIM), 97467-44-2; CO, 630-08-0.

(17) Jampolsky, L. M.; Kaiser, M. B. S.; Sternbach, L. H.; Goldberg, M. W. *J. Am. Chem. Soc.* **1952**, *74*, 5222-5224.

(18) Brown, T. L.; Dickerhoof, D. W.; Bafus, D. A.; Morgan, G. L. *Rev. Sci. Instrum.* **1962**, *33*, 491-492.

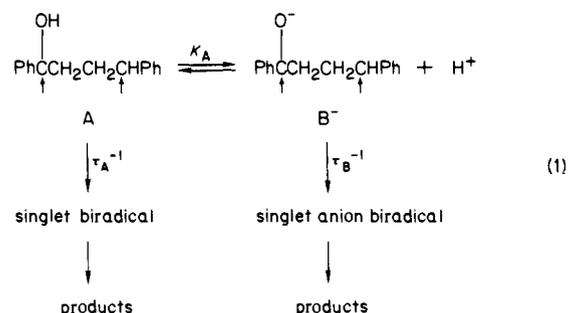
## pH Dependence of the Lifetime of a Norrish II Biradical

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**Abstract:** The transient spectroscopy of  $\gamma$ -phenylbutyrophenone in a 2:1 (v/v) methanol:water mixture has been studied as a function of pH. The lifetime of the Norrish II 1,4-biradical shows an excellent titration curve. The moderately strongly absorbing acidic form of the biradical has a lifetime of 125 ns, with  $\lambda_{\max}$  of the difference spectrum with starting material at 320 nm. The strongly absorbing basic form has a lifetime of 62 ns and  $\lambda_{\max}$  325 nm. The  $pK_a$  in the mixed solvent is 11.8. The  $pK_a$  in pure water, based on solvent dependence of  $pK_a$  values for phenols of similar acidity, is estimated as  $10.2 \pm 0.2$ , essentially identical with a value reported for the acetophenone ketyl monoradical.

The spectra, lifetimes, and properties of Norrish II biradicals are increasingly well known.<sup>1-4</sup> The OH group of the triplet biradical appears to be quite important in determining its lifetime. For example, solvent dependence of lifetime correlates with H-bond accepting ability of the solvent,<sup>5</sup> with the biradical showing much longer lifetimes in more basic solvents such as methanol, pyridine, and HMPA than in, e.g., hydrocarbons. We now report the  $pK_a$  of the biradical derived from  $\gamma$ -phenylbutyrophenone and the effect of deprotonation of the OH group on the lifetime of the biradical.



### Experimental Section

The laser flash photolysis studies were performed on a Q-switched Nd-YAG laser (fourth harmonic, 266 nm, attenuated to ca. 10 mJ per pulse, 10 ns fwhm) at the Center for Fast Kinetics Research at UT-

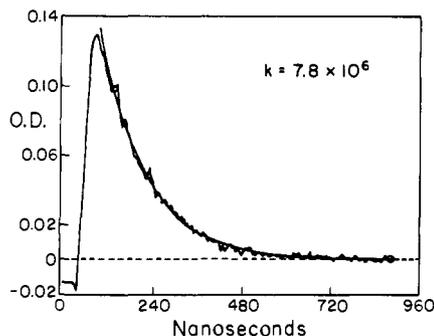
(1) Scaiano, J. C.; Lissi, E. A.; Encinas, M. V. *Rev. Chem. Intermed.* **1978**, *2*, 139.

(2) Scaiano, J. C. *Tetrahedron* **1982**, *38*, 819 and references therein.

(3) Caldwell, R. A.; Majima, T.; Pac, C. *J. Am. Chem. Soc.* **1982**, *104*, 629.

(4) Caldwell, R. A. *Pure. Appl. Chem.* **1984**, *56*, 1167-1177.

(5) Small, R. D., Jr.; Scaiano, J. C. *Chem. Phys. Lett.* **1978**, *59*, 246.



**Figure 1.** Time profile of decay of A at "pH" 9.36, wavelength 310 nm, incident intensity at 266 nm 14% of full power. Shown with first-order fit to data between open circles,  $k$  in  $s^{-1}$ , base line of fit shown as OD = 0.

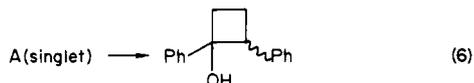
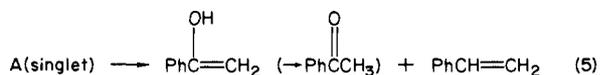
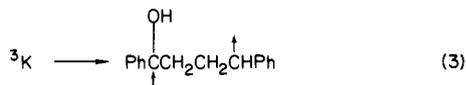
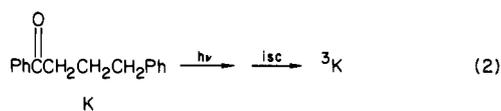
Austin. The apparatus and techniques have been previously described.<sup>6</sup> Optical densities of solutions were adjusted to about  $8\text{ cm}^{-1}$  (ca.  $9 \times 10^{-3}\text{ M}$ ) for optimum signal strength. Samples were outgassed in the cuvette in a stream of nitrogen for ca. 3–5 min before the data were taken. Transient absorbances and decay rates were stable for several times the 4–8 pulses typically averaged to obtain a decay profile. Buildup of fluorescence from styrene photoproduct, strong at 310–330 nm, was observed. Whenever necessary the emission signal above was measured after the decay measurement and was subtracted from the total signal to afford the true absorbance–time profile. Decays at all wavelengths gave consistent lifetimes.

Measurement of pH of the mixed solvent solutions (on a Beckman Expandomatic IV pH meter) was done by mixing 2 volumes of methanol (MCB Omnisolv) with 1 volume of an appropriate aqueous borate, carbonate, or phosphate buffer. Samples for kinetics were mixed identically but, owing to material limitations, were not themselves subjected to pH measurement.

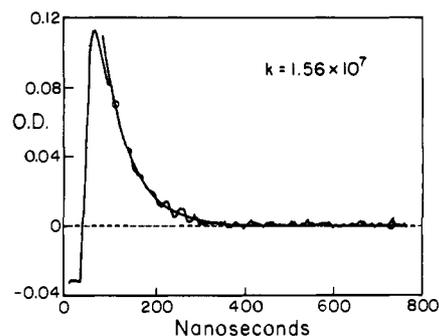
Phenols were obtained commercially (Aldrich) and used as received.  $\gamma$ -Phenylbutyrophenone was prepared by the addition of PhLi (Aldrich) in a ether:cyclohexane mixture (22 mmol) to  $\gamma$ -phenylbutyric acid (10 mmol) in ether at  $-70\text{ }^\circ\text{C}$ , mp (uncorrected)  $55\text{--}56.5\text{ }^\circ\text{C}$ , lit.<sup>7</sup> mp  $57\text{ }^\circ\text{C}$ , had the expected spectral properties, and was homogeneous to appropriate chromatographic analyses.

## Results

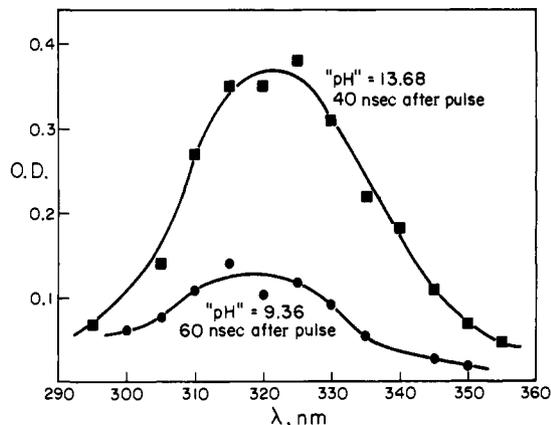
Both the photochemistry<sup>8</sup> and transient spectroscopy<sup>3</sup> of  $\gamma$ -phenylbutyrophenone have been previously reported. A short-lived ketone triplet (ca.  $2.6\text{ ns}^{8b}$ ) precedes the spectroscopically observed triplet biradical, which in turn affords the fragmentation and cyclobutanol products<sup>8c</sup> after isc to the singlet biradical. The scheme below summarizes the chemistry.



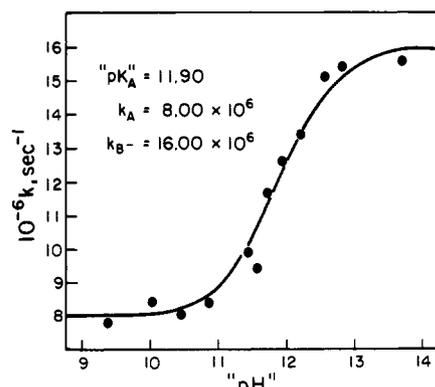
Transient spectroscopy afforded clearly different decay profiles for the triplet biradical A at high pH compared to those at neutral



**Figure 2.** Time profile of decay of B<sup>-</sup> at "pH" 13.65, wavelength 340 nm, incident intensity at 266 nm 8% of full power. Shown with first-order fit to data between open circles,  $k$  in  $s^{-1}$ , base line of fit shown as OD = 0.



**Figure 3.** Absorption spectra of acidic (A) and basic (B<sup>-</sup>) forms of the biradical.



**Figure 4.** Plot of decay rate against "pH" (glass electrode reading). The apparent  $pK_A$  value of 11.90 requires correction as described in the text.

or low pH. Figures 1 and 2 are illustrative. In neither case does the absorbance return to base line on a microsecond time scale. We ascribe this to the absorbance of the photoproducts, styrene and acetophenone enol. The higher permanent absorbance in the strongly basic media is consistent with the expected higher extinction of the acetophenone enolate. Results in  $0.1\text{ M H}_2\text{SO}_4$  are identical with those in neutral solution.

The transient absorption spectra, shown as Figure 3, document a substantially stronger absorption on the basic side than on the acidic side. The  $\lambda_{\text{max}}$  near 325 nm of the former is almost certainly real. However, the apparent weaker  $\lambda_{\text{max}}$  for the latter may or may not be a true  $\lambda_{\text{max}}$  for the neutral biradical. The observed spectrum is a difference spectrum, an observed optical density change  $\Delta\text{OD}$  being  $\epsilon_A \Delta C_A - \epsilon_K \Delta C_K$  with  $\Delta C_A = \Delta C_K$  if ketone K forms only biradical A on photolysis. Since the ketone has  $\epsilon \sim 10^2\text{ M}^{-1}\text{ cm}^{-1}$  around 320 (n- $\pi^*$ ) and  $\sim 10^3$  below 300,  $\epsilon_K \Delta C_K$  cannot be ignored unless one is certain the transient has  $\epsilon \gg 10^3$

(6) (a) Foyt, D. C. *Comput. Chem.* **1981**, *5*, 49. (b) Caldwell, R. A.; Cao, C. V. *J. Am. Chem. Soc.* **1982**, *104*, 6174.

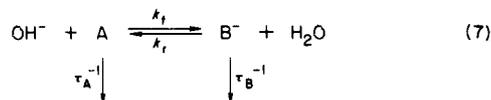
(7) "Beilstein"; 4 Auflage, E III, 7, 2193–4.

(8) (a) Wagner, P. J. *Acc. Chem. Res.* **1971**, *4*, 168. (b) Wagner, P. J.; Kemppainen, A. F. *J. Am. Chem. Soc.* **1972**, *94*, 7495. (c) Wagner, P. J.; Kelso, P. A.; Kemppainen, A. F.; McGrath, J. M.; Schott, H. N.; Zepp, R. G. *Ibid.* **1972**, *94*, 7506.

$M^{-1} \text{ cm}^{-1}$  in this region. The substantially stronger absorbance in basic media suggests that  $\epsilon$  is high and the difference spectrum a good approximation to that of the transient. We are less certain that the same holds for the cases in the more acidic media; consequently, the true  $\lambda_{\text{max}}$  may be well below 320 nm.

Figure 4 plots the observed transient decay time against "pH", the pH meter reading in the mixed solvent. The lifetime is significantly different at  $\text{pH} > 12.5$  from that at  $\text{pH} < 11$ . The titration curve allows the determination of the  $\text{p}K_{\text{a}}$  of the biradical if (1) the proton transfer rate is not so slow that lifetime measurements at intermediate pH are distorted and (2) the effect of base is not just a quenching (say via electron transfer) of the biradical A. We examine these assumptions in turn.

At intermediate pH, an initial rise with  $\tau_{\text{rise}} \approx 20$  ns is observed, which we associate with deprotonation of A. Assuming eq 7 to be the dominant mechanism of establishment of the acid-base equilibrium and using the standard<sup>9</sup> four-parameter fit with  $\lambda_2$



$\sim 5 \times 10^7 \text{ s}^{-1}$  and  $\tau_{\text{A}}^{-1}$  and  $\tau_{\text{B}}^{-1}$  known from the pH extremes,  $k_f$  and  $k_r$  can be calculated for each pH where both rise and decay are observed. While  $k_f$  and  $k_r$  are, of course, very sensitive to the rise, so long as  $\lambda_2 > 3 \times 10^7 \text{ s}^{-1}$  there is almost no difference in the  $K_{\text{A}}$  calculated from  $k_f$  and  $k_r$  and the  $K_{\text{A}}$  obtained (Figure 4) from the straightforward plot of  $\tau_{\text{obsd}}^{-1}$  vs. pH, which should obey eq 8 if proton transfer is rapid.

$$\tau_{\text{obsd}}^{-1} = \frac{(A)}{(A) + (B^-)} \tau_{\text{A}}^{-1} + \frac{(B)}{(A) + (B^-)} \tau_{\text{B}}^{-1} \quad (8)$$

The second assumption is easily shown to be justified. Note that the lifetime is nearly identical at "pH" 12.7 and 13.7; these values correspond to 0.033 and 0.33 M hydroxide. Were hydroxide ion acting as a quencher, a much shorter lifetime would be expected in the latter compared to the former.

We conclude that the "p $K_{\text{A}}$ " of 11.90 is a reasonable estimate of the acidity of biradical A in 2:1 (v/v) methanol:water mixture. This value is derived from the best fit to the data of Figure 4 assuming  $\tau_{\text{A}}^{-1}$  and  $\tau_{\text{B}}^{-1}$  of  $8.00 \times 10^6$  and  $1.60 \times 10^7$ , respectively. These numbers were taken as the best (visual) estimates. Data from the literature<sup>10,11</sup> permit good estimates of the liquid junction potential between saturated aqueous KCl (glass electrode) and a 2:1  $\text{CH}_3\text{OH}:\text{H}_2\text{O}$  mixture and for the free energy of proton transfer from water to this solvent. After these corrections are made, a true  $\text{p}K_{\text{A}}$  of  $11.8 \pm 0.2$  is estimated for biradical A in the mixed solvent.

This value is, however, difficult to compare to values for  $\text{p}K_{\text{A}}$ 's of model compounds because of expected variations in  $\text{p}K_{\text{A}}$  with solvent. We were restricted to a substantially nonaqueous solvent by the solubility of the reactant K and were thus forced to estimate the effect of solvent by the use of model compounds. We define  ${}^M\gamma_{\text{X}}^{\text{W}}$  as the activity coefficient of species X in the mixed solvent M relative to water (W) and presume all  ${}^{\text{W}}\gamma_{\text{X}}^{\text{W}} = 1.00$ . On this basis,

$$K_{\text{A}}^{\text{W}} = K_{\text{A}}^{\text{M}} \frac{{}^M\gamma_{\text{B}^-}^{\text{W}} {}^M\gamma_{\text{H}^+}^{\text{W}}}{{}^M\gamma_{\text{A}}^{\text{W}}} \quad (9)$$

$$\text{p}K_{\text{A}}^{\text{W}} = \text{p}K_{\text{A}}^{\text{M}} - \Delta\text{p}K_{\text{A}} \quad (9a)$$

where  $K_{\text{A}}^{\text{W}}$  is the thermodynamic acidity of A in water and  $K_{\text{A}}^{\text{M}}$  is the equilibrium constant in M in terms of concentrations,

(9) Birks, J. B. "Photophysics of Aromatic Molecules"; John Wiley and Sons Ltd.: London, 1970; pp 302-305. Note the analogy to excimer kinetics. Rate constants from eq 7 relate to parameters therein as  $X = \tau_{\text{A}}^{-1} + k_f(\text{OH}^-)$ ;  $Y = \tau_{\text{B}}^{-1} + k_r$ ;  $\lambda_1$  and  $\lambda_2$  are the observed (pseudo) first-order rate constants for decay and rise, respectively.

(10) Bates, R. G.; Paabo, M.; Robinson, R. A. *J. Phys. Chem.* **1963**, *67*, 1833.

(11) Popovych, O.; Dill, A. J. *Anal. Chem.* **1969**, *41*, 456.

Table I. Acidities of Some Ketyl Monoradicals

ketyl	$\text{p}K_{\text{a}}$	ref
$\text{Ph}_2\dot{\text{C}}\text{OH}$	9.2	13
	$9.25 \pm 0.1$	14
$\text{Ph}\dot{\text{C}}(\text{CH}_3)\text{OH}$	$10.0 \pm 0.2$	14
$\text{CH}_2\text{OH}$	10.7	15
$\text{CH}_3\dot{\text{C}}\text{HOH}$	11.5	15
$(\text{CH}_3)_2\dot{\text{C}}\text{OH}$	12.0-12.2	15, 16

$({}^M\text{C}_{\text{B}^-})({}^M\text{C}_{\text{H}^+})/({}^M\text{C}_{\text{A}})$ . It is not necessary to estimate activity coefficients separately, merely to estimate how the last term in eq 9 will vary between water and a 2:1  $\text{CH}_3\text{OH}:\text{H}_2\text{O}$  mixture.

The acidity of phenols is a good choice for a model because the  $\text{p}K_{\text{a}}$ 's are roughly in the range of interest. Also, A resembles a phenol in that both are essentially oxygen acids, with -OH bonded to an  $\text{sp}^2$  carbon, with modest extents of delocalization of the negative charge over a 6 or 7 carbon system. While it is not likely that  ${}^M\gamma_{\text{A}}^{\text{W}} = {}^M\gamma_{\text{PhOH}}^{\text{W}}$  because of the extra carbon chain in A, it is likely that the effect of the carbon chain in A relative to PhOH will be very similar to that of the same chain in  $\text{B}^-$  relative to  $\text{PhO}^-$ . Measurement of the acidity of phenols in M relates to their acidity in water by an analogue of eq 9, with  $\Delta\text{p}K_{\text{PhOH}}$  thus ascribable to an activity term expected to be a good approximation the same as for  $\Delta\text{p}K_{\text{A}}$  for biradical A.

Determination of  $\text{p}K_{\text{PhOH}}$  in the mixed solvent was carried out for *p*-cresol, *p*-chlorophenol, and *p*-nitrophenol and compared to literature values. Values of  $\Delta\text{p}K$  ( $=\text{p}K^{\text{M}} - \text{p}K^{\text{W}}$ ) were the following: *p*-cresol, 1.7 ( $=11.87 - 10.22^{12a,b}$ ); *p*-chlorophenol, 1.5 ( $=10.82 - 9.37^{12c}$ ); and *p*-nitrophenol, 1.0 ( $=8.15 - 7.15^{12d}$ ). Reasonably, the anion best able to stabilize itself internally through interaction with electronegative substituents affords the smallest  $\Delta\text{p}K$ . Since *p*-cresol has a  $\text{p}K$  almost exactly that of the biradical A, we take its  $\Delta\text{p}K$  as the proper one to use to estimate the acidity of A in pure water. That estimate is thus  $10.2 \pm 0.2$ .

## Discussion

The aqueous  $\text{p}K_{\text{A}}$  of biradical A,  $10.2 \pm 0.2$ , may then be compared to that for the monoradical ketyls  $\text{RR}'\dot{\text{C}}\text{OH}$ . They are



relatively well studied and provide good models. Table I summarizes some data from the literature.<sup>13-16</sup> Clearly, A resembles (as it should) the aryl-alkyl analogue, acetophenone ketyl,<sup>14</sup> strongly in its acidity. In all other properties studied to date, including spectra as well as kinetic properties (hydrogen abstraction, electron transfer, rearrangements, elimination, and addition to olefins), a 1,4-biradical terminus appears to be well modeled by correspondingly substituted monoradicals.<sup>17</sup> It is, of course, necessary not to include properties requiring interaction of both termini (spin flips, cyclization, scission, internal disproportionation, etc.) in such a list.

A previous determination of the  $\text{p}K_{\text{A}}$  of a biradical, that derived from intramolecular photochemical electron transfer from the dimethylamino group to the carbonyl group of  $\beta$ (dimethylamino) propiophenone, reported a value of 10.0 for the  $\text{p}K_{\text{a}}$  associated with eq 12.<sup>18</sup> Since that value differs from ours only by  $-0.2 \pm 0.2$ , it appears that the charged  $\text{N}^+\text{Me}_2$  moiety may have a surprisingly small effect on  $\text{p}K_{\text{A}}$ . Note that the first  $\text{p}K$  of protonated  $\beta$ -alanine, in which the protonated (charged) N is the same

(12) The  $\text{p}K_{\text{a}}$  value for *p*-cresol is the average from the following: (a) West, R. C., Ed. "CRC Handbook of Chemistry and Physics", 62nd ed.; CRC Press, Inc.: Boca Raton, FL, 1981; p D-142. (b) Dean, J. A., Ed. "Lange's Handbook of Chemistry", 12th ed.; McGraw-Hill: New York, 1979; pp 5-23. (c) Reference 12b, pp 5-22. (d) Reference 12c, pp 5-35. All  $\text{p}K_{\text{a}}$  values are at 25 °C.

(13) Porter, G.; Wilkinson, F. *Trans. Faraday Soc.* **1961**, *57*, 1686.

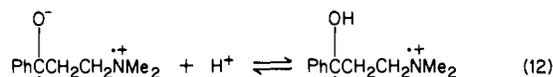
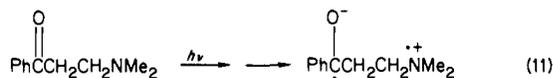
(14) Hayon, E.; Ibata, T.; Lichtin, N. N.; Simic, M. J. *Phys. Chem.* **1972**, *76*, 2072.

(15) Lawff, G. P.; Fessenden, R. W. *J. Phys. Chem.* **1973**, *77*, 1283.

(16) Asmus, K. D.; Henglein, A.; Wigger, A.; Beck, G. *Ber. Bunsenges. Phys. Chem.* **1966**, *70*, 756.

(17) See ref 2 and its ref 2, 13, and 16-21.

(18) Encinas, M. V.; Scaiano, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 2146.



number of bonds away from the acidic OH as in the present case, is some 1.28 pK units more acidic than the isoelectronic uncharged butyric acid.<sup>19</sup> Alternatively, intramolecular proton transfer to form one of the possible neutral ketyl-aminoalkyl biradicals might precede the electron-transfer measurement on which the reported pK<sub>a</sub> is predicted. While the pK<sub>a</sub> of such nonzwitterionic biradicals would indeed be near 10, this explanation would suggest more photolability than is the case.<sup>18</sup> We regard the pK<sub>a</sub> of this biradical as anomalously high, by at least 1 pH unit, and deserving of further study.

The lifetime of the basic form B<sup>-</sup> (62 ns) is a factor of 2 shorter than that of the neutral A (125 ns). The ratio is similar to that reported by Encinas and Scaiano<sup>18</sup> for the biradical from β-dimethylaminopropiophenone. Why Norrish II biradicals should behave this way is not clear. Small and Scaiano<sup>5</sup> have shown that the lifetime of Norrish II biradicals increases with increasing basicity of the solvent molecules. Assuming this to result from hydrogen bonding, i.e., partial loss of the acidic hydrogen, one would expect that complete deprotonation would increase the biradical lifetime still further, which is opposite to the present observation.

The explanation more recently suggested by Scaiano<sup>2</sup> for the solvent effect, that H-bonding to solvent creates a bulky terminus which causes an increase in population of a longer-lived *anti* conformation at the expense of a short-lived *gauche*, is also of no help in the present case. We would expect the ionic (basic) form

(19) Edsall, J. T.; Wyman, J. "Biophysical Chemistry"; Academic Press: New York, 1958; Vol. 1, pp 452-3 and 458.

of the biradical B<sup>-</sup> to be the more heavily solvated and thus by the same reasoning have the higher fraction of *anti* conformation. Again, this suggests the longer lifetime for B<sup>-</sup>, still contrary to observation. In any case, for one clear example, *gauche* and *anti* conformations of a Norrish II biradical have similar lifetimes.<sup>20</sup> Consequently, conformational arguments need not necessarily even apply to all Norrish II biradicals.

Ruling out reasonable explanations which do not fit is, unfortunately, easier than deriving convincing ones which do. At present, our only potentially useful thought is to consider the effect as a polar effect. In that connection, we note that Norrish II biradical lifetimes are, in most of the few cases so far studied, shortened by electron donating polar groups.<sup>4</sup> The O<sup>-</sup> group is clearly a better donor than the OH group and the observation thus in this regard consistent with precedent. However, we have more recently noted a case in which the opposite is true.<sup>21</sup> The best generalization we can now make is apparently that these biradical lifetimes are determined by several subtle and delicately balanced factors, with their intersystem crossing possibly subject to more than one electronic mechanism.

**Acknowledgment.** This work was supported by NSF Grant CHE8213637 and partially (fellowship to D.E.M.) by Robert A. Welch Foundation Grant AT-532. The Center for Fast Kinetic Research at The University of Texas at Austin, at which all flash kinetic work was performed, is supported by NIH Grant RR-00886 from the Biotechnology Branch of the Division of Research Resources and by The University of Texas at Austin. Assistance of Dr. Steven Atherton is gratefully acknowledged. S.N.D. thanks the authorities of Kurukshetra University (Kurukshetra, India) for granting study leave.

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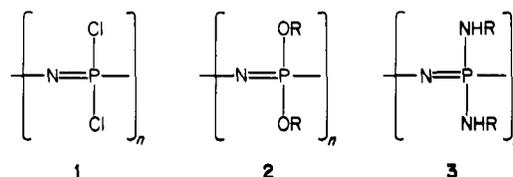
## Conformation, Bonding, and Flexibility in Short-Chain Linear Phosphazenes

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**Abstract:** A number of linear, short-chain phosphazenes have been prepared as structural models for three classes of phosphazene linear high polymers. X-ray diffraction results from studies of OP(Cl)<sub>2</sub>NPCl<sub>3</sub> (7), OP(Cl)<sub>2</sub>NP(Cl)<sub>2</sub>NPCl<sub>3</sub> (10), [Cl<sub>3</sub>PNP(Cl)<sub>2</sub>NP(Cl)<sub>2</sub>NPCl<sub>3</sub>]<sup>+</sup>PCl<sub>6</sub><sup>-</sup> (14), OP(OPh)<sub>2</sub>NP(OPh)<sub>3</sub> (8), OP(NHPh)<sub>2</sub>NP(NHPh)<sub>3</sub> (9), and OP(NHPh)<sub>2</sub>NP(NHPh)<sub>3</sub> (12) suggest different values for the bond angles and bond lengths than have been used in the past in structural studies of the high polymers. The P-N bond lengths in the short-chain species differ by 0.07 Å or less within each molecule, and planar skeletal conformations are preferred, especially cis-trans planar. The evidence suggests that, although the molecules are stabilized by electron delocalization, the conformations originate from intramolecular nonbonding interactions. The short phosphazene chains stack in the crystal lattice in a parallel arrangement analogous to that expected in polymer microcrystallites. Comparisons between the <sup>31</sup>P NMR shifts of the short chain species and the corresponding high polymers revealed a close similarity between the electronic and structural environments of the middle units in the short chain species and in the repeating units of the high polymers.

The availability of new high polymer systems based on a polyphosphazene backbone provides an opportunity for the exploration of the influence of inorganic elements and different side groups on the conformations and bond torsional mobility of macromolecular chains. Typical high polymeric phosphazene structures are shown in 1-3.<sup>1-4</sup> Those species with organic side



(n ≈ 15 000; R = alkyl or aryl)

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groups are derived from poly(dihalophosphazenes), such as 1, by nucleophilic-type substitution reactions.<sup>5,6</sup>