Since the interactions between the phosphorus lone pair AO's do not alter their total energy, the average lone pair binding energy in a polyphosphine should be equal to *minus* the average of the corresponding IP's. The values found in this way (allowing for the degeneracy of I_2 in 1) are shown in Table I. It will be seen that those for 1–4 can be quite well explained in terms of a simple inductive effect by the CF_3 groups. Thus the average values rise in the order $(1 \sim 4) < 2 < 3$, and while extrapolation of the values for 1, 2, and 4 leads to an estimate (12.06 eV) for 3 which is larger than that (11.70 eV) observed, the difference is small and could very well be due to increased bond angles at phosphorus, and consequent increase in lone pair s character, in 3. If $p\pi:d\pi$ bonding were important, it would increase the lone pair binding energy in 1, 2, and 4 relative to 3. Our results therefore indicate that such bonding must be relatively unimportant.

The mean lone pair binding energies of the other compounds listed in Table I also seem to follow a simple inductive pattern. Thus the values for 1 and 5 are almost identical, as would be expected on this basis, and that for 6 is close to the mean (10.07 eV) of the values for 2 and 7. It is interesting that only one lone pair signal was obtained from 5. This could be due to orthogonality of the two phosphorus lone pair orbitals (P_1 and P_3), combined with a negligible coupling to the $C=C$ π MO. Alternatively the splitting by mutual interaction between P_1 and P_2 into a lower antisymmetric (to C_2) combination ($P_1 + P_2$) and a higher symmetric one ($P_1 - P_2$) could be just balanced by an equal interaction between the former and the antisymmetric bonding $C=C$ π MO.

Acknowledgment. The authors are grateful to the National Science Foundation (Grant GP 38027X), the Air Force Office of Scientific Research (Contract F44620-71-C-0119), and the Robert A. Welch Foundation (Grants F-126 and F-135) for generous financial support.

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Nonlinear Quenching and Variable Excited State Lifetimes in the Photochemistry of Mixed Chromophores[1]

Sir:

The classic Stern–Volmer (S-V) quenching technique[2] remains the simplest, most widely used method of determining excited state lifetimes when a single quenchable excited state is involved. If two or more excited states of a compound are reactive and/or are quenched, S-V quenching plots usually curve. Extracting excited state lifetimes in such cases is nontrivial, since both the initial and final slopes of such curved plots are composite functions of the decay kinetics of both states.[3–5]

Only one paper has been published exemplifying such complications, in compounds displaying irreversible singlet → triplet intersystem crossing.[6]

Excitation transfer within "bichromophoric" compounds[7] is attracting increased attention as photochemists expand their studies to polyfunctional systems. On the other hand, mixtures of different molecules with similar absorbances have received little, if any, quantitative study, despite the excellent possibility that this situation may be widespread in biological and environmental systems. Both mixtures and bichromophores are obvious candidates for the complicated quenching kinetics which can attend the presence of more than one quenchable excited state. We have recently described a nonconjugated diketone in which excitation is rapidly equilibrated between the lowest triplets of both chromophores.[8] In such cases S-V quenching plots are linear (slopes proportional to equilibrium lifetimes) at quencher concentrations sufficiently low that thermal interconversion of the states is not impeded.[5] We now report the first example of nonlinear quenching due to interference with excited state interconversion in systems containing two independent absorbing chromophores.

We have studied various combinations of the benzoyl and p-methoxybenzoyl (anisoyl) chromophores, either as mixtures of two ketones or as α,ω-diaroylalkanes. These two chromophores were chosen since they have similar triplet excitation energies[6] and very different triplet lifetimes.[9] For example, with mixtures of nonanophenone (NB) and p-methoxynonanophenone (NA), 313-nm[10] irradiation of degassed benzene solutions produces both acetophenone and p-methoxyacetophenone, indicating that each chromophore undergoes Norrish type II photoelimination.[11] Relative quantum yields of these products in the presence of various concentrations of 2,5-dimethyl-2,4-hexadiene (an efficient quencher of triplet ketones)[12,13] were determined by glc analysis following the usual parallel irradiation of samples.[12] Figures 1 and 2 exemplify the kind of S-V quenching plots obtained in such systems. Figure 1 plots acetophenone formation from NB both in the absence and presence of 0.01 M NA. The measured $k_q\tau$ value for nonanophenone alone is 31 M^{-1}.[14,15]

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(8) P. J. Wagner and T. Nakahira, *J. Amer. Chem. Soc.*, 95, 8474 (1973).

(9) P. J. Wagner, A. E. Kemppainen, and H. N. Schott, *J. Amer. Chem. Soc.*, 95, 5604 (1973).

(10) A potassium chromate filter and a Hanovia 450-W mercury arc together provide light mostly centered around 313 nm with ~10% centered around 302.5 nm. Relative extinction coefficients, $\epsilon_{NA}/\epsilon_{NB}$, are 2.25 and 2.7 at these two wavelengths.

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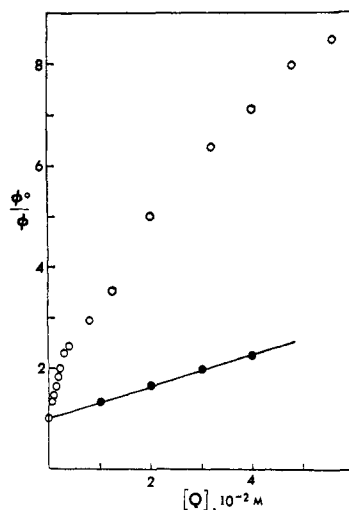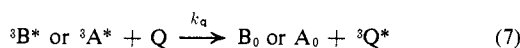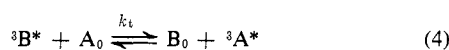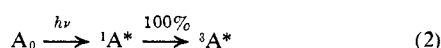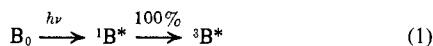Figure 1. Stern–Volmer plots for quenching by 2,5-dimethyl-2,4-hexadiene of acetophenone formation from nonanophenone (NB), solvent benzene: ●, 0.10 M NB; ○, 0.01 M NB plus 0.01 M p-methoxynonanophenone.

The initial slope in Figure 1 for NB in the presence of NA is $\sim$675 M^{-1}; the final slope is $\sim$90 M^{-1}. It is clear that the presence of a second ketone can drastically alter quenching behavior. Figure 2 plots p-methoxyacetophenone formation from NA both in the absence and presence of 0.01 M NB. Although no curvature appears in the mixed case, the slope of 1100 M^{-1} is only half that recorded in the absence of nonanophenone.

The changed quenching behavior caused by the presence of another chromophore can be readily interpreted. In the absence of quencher, triplet excitation is partially equilibrated between the two ketones by bimolecular energy transfer. Therefore the triplet lifetime of each ketone and the initial slopes of S-V plots are different than in the absence of the other ketone. The curvature in Figure 1 must correspond to quenching by the diene of energy transfer from NA and NB. The final linear portion involves reaction only from the shorter-lived triplet NB.

Scheme I summarizes the relevant rate processes,

Scheme I

$$B_0 \xrightarrow{h\nu} {}^1B^* \xrightarrow{100\%} {}^3B^* \tag{1}$$

$$A_0 \xrightarrow{h\nu} {}^1A^* \xrightarrow{100\%} {}^3A^* \tag{2}$$

$${}^3B_p \xrightarrow{k_r^b} B_p \tag{3}$$

$${}^3B^* + A_0 \underset{k_{-t}}{\overset{k_t}{\rightleftharpoons}} B_0 + {}^3A^* \tag{4}$$

$${}^3A^* \xrightarrow{k_r^a} A_p \tag{5}$$

$${}^3A^* \xrightarrow{k_d} A_0 \tag{6}$$

$${}^3B^* \text{ or } {}^3A^* + Q \xrightarrow{k_q} B_0 \text{ or } A_0 + {}^3Q^* \tag{7}$$

where B_0, A_0, B_p, and A_p symbolize benzoyl and anisoyl reactants and products, respectively. A full quantitative dissection of quantum yield and quenching slope

(15) Measured $k_q\tau$ values for solutions containing only one ketone are independent of ketone concentration; therefore it is expected that 0.01 and 0.1 M nonanophenone would display the same triplet lifetime: P. J. Wagner, I. Kochevar, and A. E. Kemppainen, J. Amer. Chem. Soc., **64**, 7489 (1972).
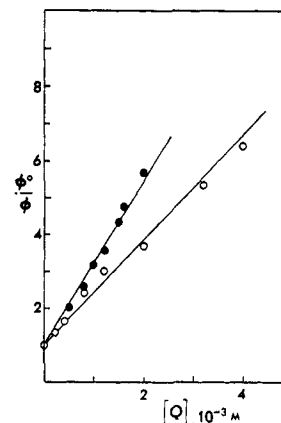

Figure 2. Stern–Volmer plots for quenching by 2,5-dimethyl-2,4-hexadiene of p-methoxynonanophenone (NA), solvent benzene: ●, 0.02 M NA; ○, 0.01 M NA plus 0.01 M nonanophenone.

values, as well as wavelength and ketone concentration effects thereon, will be deferred to a full paper. However, present knowledge of the values of the rate constants in Scheme I allows a simple qualitative evaluation of the quenching behavior.

The halving of the triplet lifetime of NA by 0.01 M NB indicates that the rate of energy transfer from triplet NA to NB is comparable to the normal rate of decay of triplet NA, 2.3 $\times$ 10⁶ sec⁻¹.⁹ Since energy transfer from NA to NB is 1.4 kcal endothermic,⁸ the value of k_{-t} should be approximately $k_t/10^{16}$ or 5 $\times$ 10⁸ M^{-1} sec⁻¹.¹³ Thus it was to be expected that the triplet lifetime of NA would be shortened by energy transfer to NB. With much of triplet NA transferring energy to NB, much of the acetophenone production from NB involves prior excitation of NA. Efficient quenching of the long-lived triplet NA by low diene concentrations rapidly quenches out that portion of acetophenone production. The actual rate of decay of triplet NB is dominated by the long lifetime of NA, since the two triplets are partially equilibrated. At higher diene concentrations, decreases in acetophenone yield are due to direct quenching of the more reactive, shorter lived triplet NB. Plots such as in Figure 1 do attain an asymptotic linearity, but the final slope does not equal $k_q\tau$ for pure NB. Equation 8¹⁷ properly describes Stern–Volmer behavior in our system, where the τ values are the triplet lifetimes in the absence of quencher Q and the ϵ's are the molar extinction coefficients of the two chromophores. (In the extreme of complete equilibration of excitation between NA and NB, $\tau_A = \tau_B$.)

$$\frac{\Phi_B^0}{\Phi_B} = \frac{(1 + k_q\tau_B[Q])(1 + k_q\tau_A[Q]) - k_t[A]\tau_B k_{-t}[B]\tau_A}{(1 - k_t[A]\tau_B k_{-t}[B]\tau_A)\left(1 + \dfrac{k_q\tau_A[Q]}{1 + \dfrac{\epsilon_A k_{-t}[B]\tau_A}{\epsilon_B}}\right)} \tag{8}$$

$$\text{Slope (final)} = \frac{k_q\tau_B\left(1 + \dfrac{\epsilon_A}{\epsilon_B}k_{-t}[B]\tau_A\right)}{1 - k_t[A]\tau_B k_{-t}[B]\tau_A} \tag{9}$$

(16) (a) K. Sandros, Acta Chem. Scand., **18**, 2355 (1964); (b) P. J. Wagner, Mol. Photochem., **1**, 71 (1969).

(17) M. D. Shetlar, paper submitted to Mol. Photochem. Equation 8 represents a slight modification of ones in ref 4.

Communications to the Editor

It is not possible to exactly evaluate the separate factors in eq 9, since pure monochromatic irradiation was not used and the value of k_{-t} has to be estimated. However, the expression in parentheses in the numerator can be estimated to equal 2.6, while the denominator equals approximately 0.8.[18] Consequently, the final slope in Figure 1 should equal roughly three–four times the normal $k_q\tau$ value, as is actually observed.

Finally, it should be pointed out that the mixed ketone quenching plot in Figure 2 would be expected to begin curving upward at sufficiently high quencher concentrations that energy transfer from NB to NA began to be prevented.

These results specifically illustrate two predictable complications in the decay kinetics of systems containing more than one chromophore. If there is any energy transfer between chromophores, the observed decay rate of any one chromophore no longer reflects simply the reactions of one excited state. This perturbation is independent of the measuring technique, whether it be flash spectroscopy or quenching. Second, if the two excited chromophores have significantly different intrinsic lifetimes, apparent rates of their bimolecular reactions need not be linear in substrate concentration if each excited chromophore reacts with the added substrate. This perturbation is independent of the exact phenomenon being studied (quenching, sensitization, photoreduction, dimerization, cycloaddition, etc.).

(18) $\epsilon_A/\epsilon_B = 2.3$; $k_{-t}[B]\tau_A \approx 0.7$; $k_t[A]\tau_B = 0.25$.

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Nuclear Magnetic Resonance Spectral Studies. VIII. Titanium Tetrachloride as a Shift Reagent[1]

Sir:

Titanium tetrachloride is known to complex with polar functional groups, such as ether, ketone, and ester.[2–4] Since such complexing must affect the chemical shifts of neighboring nuclei, we have studied the effect of this easily available chemical on the nmr spectra of a variety of organic compounds. We wish to report that titanium tetrachloride induced shifts in pmr and cmr spectra can provide useful information for the elucidation of structure. Currently several lanthanide shift reagents are extensively used for the simplification of nmr spectra.[5–8]

We have observed that the addition of titanium tetrachloride to a solution of alcohols, ethers, ketones, esters, acids, amides, and nitriles causes downfield

(1) For Part VII see A. K. Bose and R. J. Brambilla, Proceedings of the 1st International Conference on Stable Isotopes in Chemistry, Biology and Medicine, Argonne, Ill., May 1973, p 431.

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shifts of protons in the vicinity of the functional group; the shift increases with increasing amounts of the shift reagent. The maximum shifts observed upon addition of titanium tetrachloride to representative compounds are shown in Table I. It can be seen that the magnitude

Table I. Titanium Tetrachloride Induced Shift[a]

Compound (CDCl₃ solution)	Downfield shift (ppm)		
	α-protons	β-protons	γ-protons
CH₃CH₂OH	1.03	0.37	
CH₃CH₂CH₂OH	1.05	0.37	0.15
(CH₃)₂CHOH	1.03	0.38	
(CH₃CH₂)₂O	0.80	0.30	
(CH₃)₂CO	0.54		
(CH₃CH₂)CO	0.56	0.30	
CH₃CO₂H	0.40		
CH₃CO₂CH₂CH₃	0.45 (CH₂)	0.20	
	0.50 (CH₃)		
CH₃CN	0.25		
CH₃CH₂CN	0.45	0.19	

[a] An excess of TiCl₄ ($\sim$0.55 equiv) was used. Shifts reached a maximum value when 0.5 equiv of TiCl₄ was added; further addition had no effect. Spectra were recorded on a Varian A-60-A spectrometer with TMS as the internal standard.

of the shift decreases with the distance from the functional group. For example, in the pmr spectrum of ethyl butyrate (Figure 1), the methyl signal of the ethyl group could be recognized by its larger shift than the other methyl group upon addition of TiCl₄. This was verified by decoupling studies.

A series of shift measurements were made on a few monofunctional compounds by adding incremental amounts of titanium tetrachloride. When the induced shift was plotted against the relative molar ratio of the shift reagent and the substrate, a linear relationship was observed. The slope of this line was determined by a standard least-squares computer analysis.[9] The "sensitivity" (defined here as extrapolated value of the shift to correspond to equimolar amounts of reagent and substrate) of various protons is listed in Table II. It

Table II. "Sensitivity"[a] to Titanium Tetrachloride

Compound (CDCl₃ solution)	Downfield shift (ppm)		
	α-protons	β-protons	γ-protons
(CH₃)₂CO	1.11		
CH₃CH₂COCH₃	1.85 (CH₃)	0.60	
	1.47 (CH₂)		
(CH₃CH₂)₂CO	1.16	0.49	
[(CH₃)₂CH]₂CO	1.46	0.51	
(CH₃CH₂)₂O	1.27	0.38	
(CH₃CH₂CH₂)₂O	0.76	0.30	0.05
CH₃CO₂CH₃	1.45 (CH₃CO–)		
	1.01 (–OCH₃)		
CH₃CO₂CH₂CH₃	1.26 (CH₃CO–)	0.41	
	0.86 (–OCH₂)		

[a] Extrapolated value of the shift to correspond to equimolar amounts of reagent and substrate (see text).

can be seen that the "sensitivity" to titanium tetrachloride follows the order of alcohol > ether > ester > nitrile. In most cases, the maximum shift observed was about one-half of the "sensitivity" values in Table II

(9) J. W. ApSimon, H. Beierbeck, and A. Fruchier, *J. Amer. Chem. Soc.*, 95, 939 (1973).