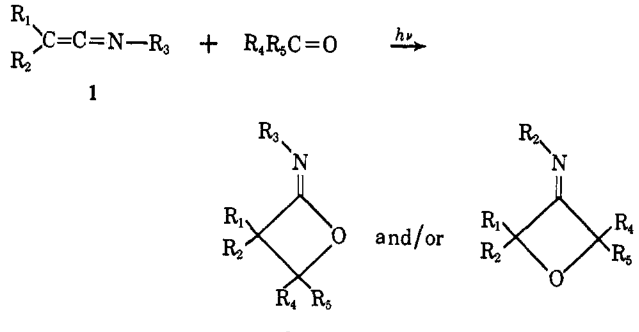
Quenching of the Excited Singlet State of Fluorenone by a Ketenimine. Consequences for the Photocycloaddition Reaction

Sir:

Recently,[1] we demonstrated that the Paterno–Buchi reaction[2] can be extended to ketenimines (Chart I).

Chart I



1

2(α)

3(β)

Adducts result from both possible directions of addition of the carbonyl group across the carbon–carbon double bond (**2** called α, and **3** called β). The mechanism of the benzophenone–ketenimine reaction[1b] has been shown to involve triplet benzophenone in competing reactions of cycloaddition and energy transfer to ground-state ketenimine. A relative rate study on the fluorenone–ketenimine reaction revealed that energy transfer in that system was not competitive with cycloaddition.[1c] We now wish to report the results of a kinetic study of the fluorenone–dimethyl-N-(cyclohexyl)ketenimine (**4**) reaction which illustrates *the operational importance of complexation between singlet fluorenone and ground-state* **4**.

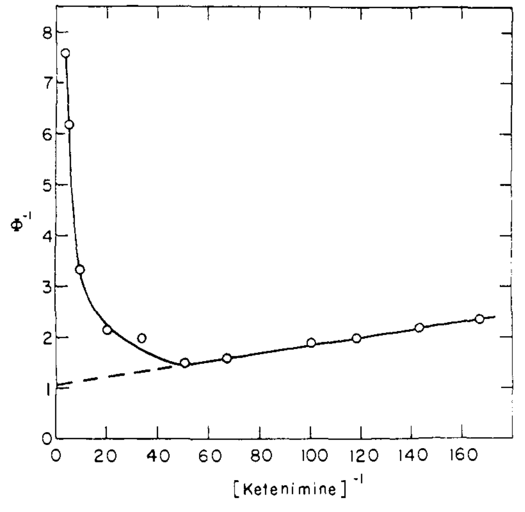


Figure 1. Dependency of the reciprocal of the quantum yield for adduct formation on ketenimine concentration in the fluorenone–dimethyl-N-(cyclohexyl)ketenimine reaction. Slope = 0.006 *M;* intercept = 1.08.

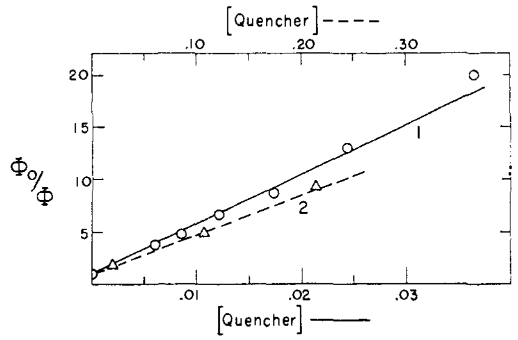


Figure 2. Effect of added triplet quenchers on the fluorenone–dimethyl-N-(cyclohexyl)ketenimine reaction at 1.0 *M* fluorenone and 0.01 *M* ketenimine. Curve 1, di-*t*-butyl nitroxide, slope = 473 l. mole^{-1}. Curve 2, pyrene, slope = 44 l. mole^{-1}.

Figure 1 shows the dependency of the reciprocal of the quantum yield for adduct formation on the reciprocal of ketenimine concentration.[3–5] At concentrations of **4** below 0.02 *M*, this plot is linear. The *triplet* nature of the reaction in this region is demonstrated by the results of quenching studies with pyrene and di-*t*-butyl nitroxide[6] at 0.01 *M* **4** (Figure 2). A Stern–Volmer plot of the quenching efficiency is linear out to $\Phi_0/\Phi = 9$ with the former and out to $\Phi_0/\Phi = 19$ with the latter. The smaller quenching constant with pyrene is probably due to inefficient quenching (less than a diffusion-controlled k_q) as compared to efficient quenching with di-*t*-butyl nitroxide (a diffusion-controlled k_q).[7]

The simplest scheme necessary to accommodate these results is shown in Scheme I where (1) is excitation, (2) is intersystem crossing of singlet fluorenone to triplet fluorenone, (3) includes all deactivation processes of triplet fluorenone excluding quenching by added quencher, (4) is adduct formation, and (5) is quenching by added quencher.

Scheme I

$$\mathrm{F} \xrightarrow{h\nu} {}^1\mathrm{F}^* \tag{1}$$

$${}^1\mathrm{F}^* \xrightarrow{k_x} {}^3\mathrm{F}^* \tag{2}$$

$${}^3\mathrm{F}^* \xrightarrow{k_d} \mathrm{F} \tag{3}$$

$${}^3\mathrm{F}^* + \mathrm{K} \xrightarrow{k_r} \text{adduct} \tag{4}$$

$${}^3\mathrm{F}^* + \mathrm{Q} \xrightarrow{k_q} \mathrm{F} + \mathrm{Q}^* \tag{5}$$

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[1] (a) L. A. Singer and P. D. Bartlett, *Tetrahedron Letters*, 1887 (1964); (b) L. A. Singer and G. A. Davis, *J. Am. Chem. Soc.*, in press; (c) L. A. Singer and G. A. Davis, *ibid.*, in press.

[2] (a) E. Paterno and G. Chieffi, *Gazz. Chim. Ital.*, **39**, 341 (1909); (b) G. Buchi, C. G. Inman, and E. S. Lipinsky, *J. Am. Chem. Soc.*, **78**, 876 (1956); (c) D. R. Arnold, R. L. Hinman, and A. H. Glick, *Tetrahedron Letters*, 1425 (1964); (d) N. C. Yang, M. Nussim, M. J. Jorgenson, and S. Murov, *ibid.*, 3657 (1964).

[3] Ketenimine disappearance rather than adduct appearance was followed by infrared techniques. The isolated yield of α-adduct fluorenone–**4** is 74%.[1c] However, infrared analyses of crude reaction mixtures indicate the true adduct yield to be 96%.

[4] Quantum yield measurements were carried out on a rotating photochemical assembly[1b] in degassed and sealed Pyrex ampoules containing benzene solutions of **4** and 1.0 *M* fluorenone. Irradiation from a 450-w Hanovia lamp was filtered through Corning 7-39 filters. All the light is taken up by fluorenone under these conditions.

[5] Actinometry was by the benzophenone–benzhydrol system: W. M. Moore and M. Keetchum, *J. Am. Chem. Soc.*, **84**, 1368 (1962), and references therein.

[6] A. K. Hoffman, A. M. Feldman, E. Gelblum, and W. G. Hodgson, *ibid.*, **86**, 639 (1964).

[7] The triplet level of fluorenone is ~51 kcal/mole[2d,8] while that of pyrene is ~49 kcal/mole.[9]

[8] K. Yoshihara and D. R. Kearns, *J. Chem. Phys.*, **45**, 1991 (1966).

[9] W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Am. Chem. Soc.*, **86**, 4537 (1964).

Kinetic analysis of Scheme I leads to $1/\Phi = 1/a + k_d/[ak_r(\mathrm{K})]$ in the absence of quencher where a is the quantum yield of fluorenone triplets. Extrapolation of the straight-line portion of Figure 1 shows $a = 0.93$, which is in excellent agreement with the previously determined value.[10]

In the presence of quencher $\Phi_0/\Phi = 1 + k_q(\mathrm{Q})/[k_d + k_r(\mathrm{K})]$. Assuming for di-*t*-butyl nitroxide a k_q of 2×10^9 l. mole^{-1} sec^{-1}, and using the slope terms from Figures 1 and 2, provides $k_d = 1.5 \times 10^6$ sec^{-1} and $k_r = 2.7 \times 10^8$ l. mole^{-1} sec^{-1}. This value for k_r for the triplet fluorenone–4 reaction is very close to that derived for the triplet benzophenone–4 reaction (4×10^8 l. mole^{-1} sec^{-1}).[1b]

We believe the striking decrease in the quantum yield for adduct formation at higher ketenimine concentrations is due to deactivation of the fluorenone singlet state *via* complex formation with ground-state **4** as shown in Scheme II. The extent of complexation relative to emission (6) or intersystem crossing (7) increases with an increase in ketenimine concentration.

Scheme II

$$ {}^1\mathrm{F}^* \xrightarrow{k_e} \mathrm{F} + h\nu \tag{6} $$

$$ {}^1\mathrm{F}^* \xrightarrow{k_x} {}^3\mathrm{F}^* \tag{7} $$

$$ {}^1\mathrm{F}^* + \mathrm{K} \xrightarrow{k_c} {}^1\mathrm{F}^*,\mathrm{K} \longrightarrow \mathrm{F} + \mathrm{K} \tag{8} $$

Such a scheme would predict fluorescence quenching as well as a decrease in intersystem crossing efficiency at higher concentrations of **4**. Indeed, semiquantitative emission studies at room temperature show quenching of the fluorenone fluorescence in the presence of **4**.[11] There is no observable wavelength shift in the fluorenone emission in the presence of **4**,[12] nor is there any evidence for ground-state complexation from absorption spectra measurements. Classical singlet–singlet energy transfer cannot account for this quenching because of the unfavorable disposition of the energy levels in the potential donor and acceptor.

Others have reported similar observations. Hammond and co-workers report the fluorescence quenching of aromatic hydrocarbons by conjugated dienes[13] and Leonhardt and Weller describe the fluoresence quenching of perylene by amines.[14] Both groups similarly ascribe this phenomenon to complexation.

The absence of singlet quenching in the benzophenone–**4** reaction[1b] may simply be related to a shorter lifetime for the singlet state of benzophenone.[15] Studies are in progress to elucidate better the mechanism and generality of this type of quenching in organic photochemical reactions.

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Lawrence A. Singer, Gene A. Davis
Department of Chemistry, University of Chicago
Chicago, Illinois 60637

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[10] N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, N. Y., 1965, p 131.

[11] We thank Professor N. C. Yang for use of his emission spectrometer.

[12] At 0.2 *M* **4** the fluorenone emission is 89% quenched, and at 0.006 *M* **4** it is *ca.* 5% quenched.

[13] L. M. Stephenson, D. G. Whitten, G. F. Vesley, and G. S. Hammond, *J. Am. Chem. Soc.*, **88**, 3665 (1966).

[14] H. Leonhardt and A. Weller in "Luminescence of Organic and Inorganic Materials," H. P. Kallman and G. M. Spruch, Ed., John Wiley and Sons, Inc., New York, N. Y., 1962, p 74.

[15] The lifetime of the benzophenone singlet has been estimated at $<2 \times 10^{-10}$ sec (W. M. Moore, G. S. Hammond, and R. P. Foss, *J. Am. Chem. Soc.*, **83**, 2789 (1961)), while the lifetime of singlet fluorenone was recently estimated at $<10^{-7}$ sec.[8]

Complexes Containing the $[\mathrm{Nb_6Cl_{12}}]^{3+}$ and $[\mathrm{Nb_6Cl_{12}}]^{4+}$ Cluster Ions[1]

Sir:

Previous studies have shown that $[\mathrm{Nb_6Cl_{12}}]^{2+}$ undergoes a two-electron oxidation when titrated with iodine or oxidized polarographically.[2] However, no solid compounds of the oxidized niobium cluster ion were isolated. In the case of the related $[\mathrm{Ta_6Cl_{12}}]$ cluster, oxidation states of 2+, 3+, and 4+ have been found in aqueous solutions,[2,3] and solid derivatives of the 4+ ion have been isolated.[2] We now report the preparation and properties of some complexes containing the $[\mathrm{Nb_6Cl_{12}}]$ unit in both the 3+ and 4+ oxidation states.[4] Recently it was learned that results similar to those reported here also have been obtained by Schneider and Mackay at Stony Brook, N. Y.[5] Since the derivatives prepared and, to some extent, the results obtained are somewhat different from those of Schneider and Mackay, we are prompted to this preliminary report of our results.

The preparation of these new complexes involves the dissolution of $\mathrm{Nb_6Cl_{14} \cdot 8H_2O}$[6] in methanol or ethanol, with subsequent oxidation and crystallization. The hydrated $\mathrm{Nb_6Cl_{14}}$ is used as a starting material rather than anhydrous $\mathrm{Nb_6Cl_{14}}$ because the latter dissolves very slowly.

Preparation of $[(\mathrm{C_2H_5})_4]_x\mathrm{Nb_6Cl_{18}}$ (x = 2, 3). For the 4+ compound (x = 2) 1.5 g of $\mathrm{Nb_6Cl_{14} \cdot 8H_2O}$ was dissolved in about 200 ml of absolute ethanol. The dark green (essentially black) solution was saturated with anhydrous hydrogen chloride, oxidized with chlorine gas, and then flushed with nitrogen to remove excess chlorine. Tetraethylammonium chloride (1.12 g, 2.5 mole excess) in ethanol was added, and the dark red-brown solution was resaturated with hydrogen chloride and warmed on the hot plate for 2 hr. At this point the crystallization which had begun as soon as the tetraethylammonium chloride had been added was nearly complete. The jet black needles (1.7 g) were

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[1] Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission; Contribution No. 1920.

[2] R. E. McCarley, B. G. Hughes, F. A. Cotton, and R. Zimmerman, *Inorg. Chem.*, **4**, 1491 (1965).

[3] J. H. Espenson and R. E. McCarley, *J. Am. Chem. Soc.*, **88**, 1063 (1966).

[4] These were first reported in a more general discussion of the chemistry of the $[\mathrm{Nb_6X_{12}}]$ and $[\mathrm{Ta_6X_{12}}]$ cluster species presented before the symposium "The Metal–Metal Bond in Inorganic Chemistry," at the 151st Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966.

[5] R. F. Schneider and R. A. Mackay, State University of New York, Stony Brook, N. Y., private communication. We are grateful to these authors for a preliminary report of their results.

[6] New methods for the preparation of $\mathrm{Nb_6X_{14}}$ and $\mathrm{Nb_6X_{14} \cdot 8H_2O}$ (X = Cl, Br) are to be published. In the course of the preparative studies in this laboratory, some questions regarding the composition of various hydrate preparations have arisen. It appears as if the hydroxide group has been substituted into some of the chloride positions. Further investigation of this problem will be carried out. For a discussion of some aspects of hydroxide substitution, see R. J. Allen and J. C. Sheldon, *Australian J. Chem.*, **18**, 277 (1965).