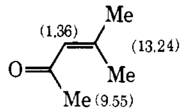
assignment of the couplings found for the mesityl oxide radical anion, *viz.*



Assignment of the coupling constants of the C$_4$ and C$_6$ methylene protons in the 2-cyclohexenone system has been made assuming pure axial and equatorial conformations for these protons and proportionality between the spin density on these centers and (a) the spin density on the contiguous carbon atom of the π system and (b) $\cos^2 \theta$, where θ is the dihedral angle between the plane of the methylene C–H bond and the axis of the $2p_z$ orbital of the carbon atom.

Figure 1 illustrates a pronounced alternating line-width effect in the esr spectrum of 2-cyclohexenone, a phenomenon becoming accentuated at higher temperatures. Similar effects were apparent in the spectra of 5,5-dimethylcyclohexenone and 3-methylcyclohexenone. In the parent molecule, time averaging of the C$_{5a}$ and C$_{5e}$ protons is found, and the lines due to C$_{4e}$ and C$_{6e}$ are broadened while those from C$_{4a}$ and C$_{6a}$ remain sharp. This implies that the precession frequencies of the electron moment about the nuclear moments due to the C$_{4e}$ and C$_{6e}$ protons are comparable with the frequency of the associated conformational change. Using an averaged value for the couplings of C$_{4e}$ and C$_{6e}$ protons affords a frequency of 14 MHz, *i.e.*, a conformational lifetime of 7×10^{-8} sec. In 5,5-dimethylcyclohexenone, line broadening is found for the protons in the C$_3$ (13.20 Oe) and C$_{6a}$ positions (12.90 Oe), leading to a flipping frequency of 3.7 MHz and a conformational lifetime of 3×10^{-8} sec. Although we have not yet completely analyzed the esr spectrum from the ketyl of 3-methylcyclohexenone, the conformational lifetime is similar to that found for 2-cyclohexenone. No line broadening was apparent in the temperature range 203–233°K for the 3,5-dimethylcyclohexenone ketyl.

The microwave spectrum of 2-cyclohexenone[6] indicates that all the heavy atoms except C$_5$ are coplanar, and the conformational change affecting the esr spectrum of the anion probably involves movement of C$_5$ above and below this plane. In the case of 3,5-dimethylcyclohexenone, an axial conformation for the C$_5$ methyl group is probably preferred.

The general pattern of spin density distribution closely follows those reported by Russell and Stevenson,[1] House, *et al.*,[3] and Harbour and Guzzo.[4] Further details of this work and its extension to a number of other α,β-unsaturated ketones and some unsaturated nitriles will be reported in due course.

Acknowledgment. The Science Research Council and Imperial Chemical Industries, Ltd., are thanked for financial report.

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Direct Observation of Triplet Exciplexes by Flash Photoconductivity and Flash Spectroscopy. Formation of Three-Component Exciplexes between Porphyrins and Nitro Aromatics

Sir:

Exciplex formation has been well documented as a mechanism for deactivation of excited singlet and triplet states for a wide variety of compounds.[1-3] Direct examination has been mostly limited to the observation of fluorescence from certain singlet exciplexes in solution and to detection of phosphorescence from certain triplet donor–acceptor pairs activated in hydrocarbon glass at 77°K.[4] We have previously found indirect chemical evidence for the formation of singlet and triplet exciplexes between excited metalloporphyrins and aromatic nitro compounds.[5,6] In the present paper we wish to report direct observation and study of triplet exciplexes for these systems both by flash spectroscopy as well as by means of a flash photoconductivity technique. A most interesting and important feature of the triplet exciplexes under investigation is the preferential formation of three-component excited complexes.

The system under investigation consists of degassed benzene solutions with zinc etioporphyrin I as excited donor and *trans-p*-nitrostilbene (PNS) and *p*-nitrotoluene (PNT) as acceptor–quenchers. Flashing of dilute ($5 \times 10^{-5} M$) solutions of porphyrin in the presence of quencher leads to transients absorbing weakly in the range 440–580 nm (λ_{max} 450 nm for zinc etio-PNS and 440 nm for zinc etio-PNT). Flashing the same solutions in a flash photoconductivity apparatus[7] also leads to production of strong transient signals having lifetimes in the millisecond range. The decay times for these transients were in all cases identical with those of the transients observed by flash spectroscopy.[8] Dark conductivity, steady-state photoconductivity, and action spectra (wavelength dependence of conductivity) were also measured; both dark and photoconductivity are higher with quencher present than for zinc etioporphyrin I alone. In a typical experiment a *ca.* tenfold increase in conductivity occurred on flashing. The relatively large increase in conductivity on exciplex formation reinforces the assumption that charge-resonance stabilization is dominant for these systems. While the two techniques are complementary, the flash photoconductivity method is simple and convenient and should prove to be of general utility for future studies.

Using both of the above techniques we have measured exciplex[9] decay times as a function of quencher concen-

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[1] B. Stevens, *Advan. Photochem.*, 8, 161 (1971).

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[6] D. G. Whitten, I. G. Lopp, and P. D. Wildes, *ibid.*, 90, 7196 (1968).

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[8] The porphyrin triplet was detected by flash photoconductivity; however, the signal was much weaker than those for exciplexes.

[9] Identity of the transient as an exciplex rather than a ground-state intermediate is supported by the observation that it is quenched by azulene as well as oxygen. At the lowest [quencher] studied triplet quenching is complete while singlet quenching is unimportant;[5,6] while exciplex multiplicity has not been determined, spin-conservation considerations suggest it is a triplet.

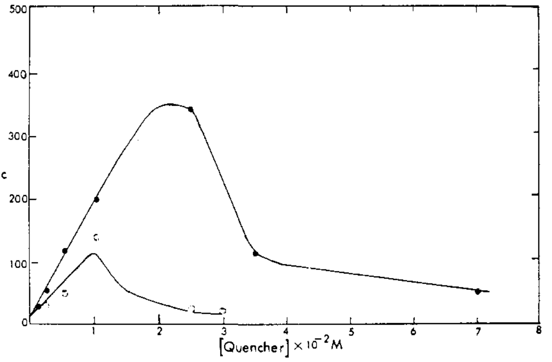

Figure 1. Exciplex lifetime (τ) as a function of [quencher]. Each value of τ determined both by flash photoconductivity and flash spectroscopy: ●, *trans-p*-nitrostilbene as acceptor–quencher; ©, *p*-nitrotoluene as acceptor–quencher.

tration in the range 0.001–0.07 *M*. While transient absorption is constant in both initial intensity and dispersion over this quencher concentration range, the lifetimes[10] first increase linearly with increasing quencher concentration and then decrease with increase in [quencher] as indicated in Figure 1. Quenching of the zinc etioporphyrin I triplet by the nitro compounds is fast ($kq = 3 \times 10^9$ l. mol^{-1}sec^{-1} for PNT and $kq = 1.6 \times 10^9$ [5] for PNS) and therefore complete over the quencher concentration range studied.[11] Consequently the increase in lifetime cannot be due to reversible or incomplete formation of the triplet exciplex $(DA)^{3*}$ (eq 1), where D = zinc etioporphyrin I and A = acceptor-quencher. The increase in lifetime with [quencher] is evidently due to the participation of a second species $(DAA)^{3*}$ whose formation competes with decay of $(DA)^{3*}$ such that the predominant species monitored is $(DAA)^{3*}$.[12] This situation is described by eq 1–3. Using the steady-state as-

$$D^{3*} + A \xrightarrow{k_1} (DA)^{3*} \qquad (1)$$

(complete under the experimental conditions)

$$(DA)^{3*} + A \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} (DAA)^{3*} \qquad (2)$$

$$(DA)^{3*} \xrightarrow{k_3} D + A \qquad (3)$$

sumption for $(DA)^{3*}$, the following relationship can be derived

$$\text{rate of decay} = k_{\text{obsd}}[(DAA)^{3*}] = \frac{k_{-2}k_3[(DAA)^{3*}]}{k_2[A] + k_3} \qquad (4)$$

or

$$\tau = \frac{1}{k_{\text{obsd}}} = \frac{1}{k_{-2}} + \frac{k_2[A]}{k_{-2}k_3} \qquad (5)$$

Equation 5 predicts a linear increase in τ with [A] with a slope equal to $k_2/k_{-2}k_3$ and intercept of $1/k_{-2}$. The slope/intercept ratio k_2/k_3 reflects competition between decay of $(DA)^{3*}$ and formation of $(DAA)^{3*}$; the large observed values listed in Table I are consistent with the proposed mechanism.

Table I. Data from Linear Plots of τ *vs.* [A]

Quencher	Slope	Intercept	Slope/intercept
PNT	1.1×10^{-2} sec M^{-1}	1×10^{-5} sec	1.1×10^3 M^{-1}
PNS	1.8×10^{-2} sec M^{-1}	1×10^{-5} sec	1.8×10^3 M^{-1}

The decrease in τ observed at higher quencher concentration is not predicted by eq 1–3; it does not appear possible to make a simple modification or correction in the kinetic scheme to incorporate this reduction in τ.[15] Since there is evidence that singlet exciplexes with charge-resonance character have reduced lifetimes in polar media,[16,17] it appeared possible that the observed results might be due in part to an increase in medium polarity with an increase in [A]. To test this possibility we investigated the effect of low concentrations of acetonitrile, ethanol, and *N*-methylformamide on exciplex lifetime. These small polar molecules do not form triplet exciplexes with zinc etioporphyrin I but have dielectric constants close to those of the nitro aromatics. In each case we observed reduction of decay time comparable to the reduction caused by an increase in [A]. For example, for 0.01 *M* PNT the lifetime decreased from 134 to 46 μsec on the addition of 0.01 *M* *N*-methylformamide, while for 0.01 *M* PNS the lifetime dropped from 194 to 67 μsec on the addition of 0.05 *M* acetonitrile.

In summary, these experiments on direct observation of triplet exciplexes show that for the porphyrin–nitro aromatic system a three-molecule complex $(DAA)^{3*}$ is probably the dominant species produced at moderate acceptor concentration. Exciplex lifetimes are reduced by increases in medium polarity. This can be effected either by increasing [A] above 0.01 *M* or by the addition of polar solutes to benzene solutions of the exciplex. We are extending our flash photoconductivity studies to other systems to determine factors affecting exciplex decay and to investigate additional reactions of exciplexes.

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(10) Good first-order decay was observed in every case. More precise data were obtained *via* the flash photoconductivity technique.

(11) Fluorescence quenching becomes significant (>10%) for PNS at concentrations >0.003 *M* (fluorescence quenching slope is 35.8 M^{-1}).[5] However, no new transients or additional components in decay are observed at these or higher concentrations. Our inability to observe singlet exciplexes, even at high concentrations, by either technique suggests their lifetimes are shorter than the duration of the flash (10–15 μsec).

(12) This apparently is the first observation of the formation of a 1:2 exciplex between nonassociating (in the ground state) molecules, although Chandross and Thomas[13] have recently found that three-component singlet complexes form by reaction of intramolecular exciplexes with acetonitrile, and Lumry, *et al.*,[14] have reported fluorescent 1:2 exciplexes from indole and associating solvents such as alcohols.

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(15) For example, the observed points (Figure 1) do not fit a simple expression $\tau = c_1 + c_2(A) + c_3(A)^2$ where c_3 is negative.

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