Radicals II are also formed in the reactions of TCNE with the cyclopentadienyl carbonyl dimers of Cr, Mo, W, and Fe as well as with the corresponding benzyl derivatives (Table I), but not with $Re_2(CO)_{10}$, $Co_2(CO)_8$, and $[\eta^5\text{-}C_5H_5Ni(CO)]_2$ which give $TCNE\cdot^-$ as the only detectable paramagnetic species in solution. Radical II with M = $\eta^5\text{-}C_5H_5Cr(CO)_3$ is the most labile and decays rapidly above −25°. At similar low temperatures, the same radical can also be produced (together with $TCNE\cdot^-$) from $[\eta^5\text{-}C_5H_5Cr(CO)_3]_2Hg$ and TCNE underscoring the generality of the oxidative homolytic scission of metal–metal bonds. The esr spectra of these species are simpler than that of I, since the corresponding metal nuclei in largest natural abundance have no nuclear spin. However, satellite lines due to ^{53}Cr and ^{95,97}Mo have been observed. The metal–metal bonds of main-group organometallic compounds can also undergo oxidatively promoted homolysis judging by the ready formation of radical II with M = $(n\text{-Bu})_3Sn$ in the reaction of TCNE and hexa-*n*-butylditin (Table I).[16] This radical is extraordinarily stable, and it appears to have been isolated in pure form, although not recognized as II, in a recent preparative study.[17] The hexaphenyl derivative and the silicon analogs do not give II but only $TCNE\cdot^-$ as was already reported.[18] The details of this work together with additional radical reactions of TCNE and other organic electron acceptors with organometallic compounds will be reported elsewhere.

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Spin Selectivity in Low Temperature Solid State Photochemistry

Sir:

A few years ago it was suggested[1] that microwave radiation capable of changing the direction of the unpaired spins of a photochemically active triplet state (*i.e.*, microwaves in resonance with its zero-field (zf) transitions) could affect the rate and yield of solid state photochemical reactions involving this state. In this communication we report on the observation that the rate of the biphotonic photochemistry of pyrimidine[2] in benzene at 1.6°K is found to decrease when the system is exposed to microwaves in resonance with its zf transitions or to a static magnetic[3] field. The theoretical treatment of this problem given in this communication reveals that this could arise from having unequal intersystem crossing (ISC) rates, unequal decay rates, or unequal photochemical reaction rates for the three zf levels of the triplet state. In the system studied, in addition to unequal ISC and decay rates, *the different spin levels are found to have different photochemical reaction rates.*

The phosphorescence intensity of pyrimidine in benzene at liquid helium temperatures decreases as a function of time under 3130 Å excitation.[2] A new uv absorption band with an optical density of >0.10 that of the unreacted pyrimidine is found to appear at 3600 Å upon melting an irradiated thin sample for 12 hr. The overall rate of the reaction (determined from the decrease in the phosphorescence intensity with uv exposure time) is found to be first order in optically clear crystals. (Nonlinear effects due to scattering of the exciting light are found when polycrystalline samples are used.) At low intensity, the rate constant of the reaction is found to be second order in the exciting light intensity, suggesting a biphotonic reaction as was found for other systems.[4,5]

The effect of resonant microwaves[6] and static magnetic field (10 kG) on decreasing the rate of the photochemical disappearance of pyrimidine is shown in Figure 1. These perturbations cause a decrease in the value of the rate constant of the observed photochemical change by a factor of $\frac{1}{2}$–$\frac{1}{3}$.

In the absence of spin–lattice relaxation between the three zero-field (zf) levels, a set of rate equations may be derived for the following biphotonic mechanism.

$$S_0 \underset{\beta_i}{\overset{\alpha_i I}{\rightleftarrows}} T_i \xrightarrow{\gamma_i I} \text{product}$$

The rate equations for populating any zf level *i* of the triplet state (T) and the ground state (S_0) are given by

$$\frac{dT_i}{dt} = \alpha_i IS - \beta_i T_i - \gamma_i IT_i \qquad (1)$$

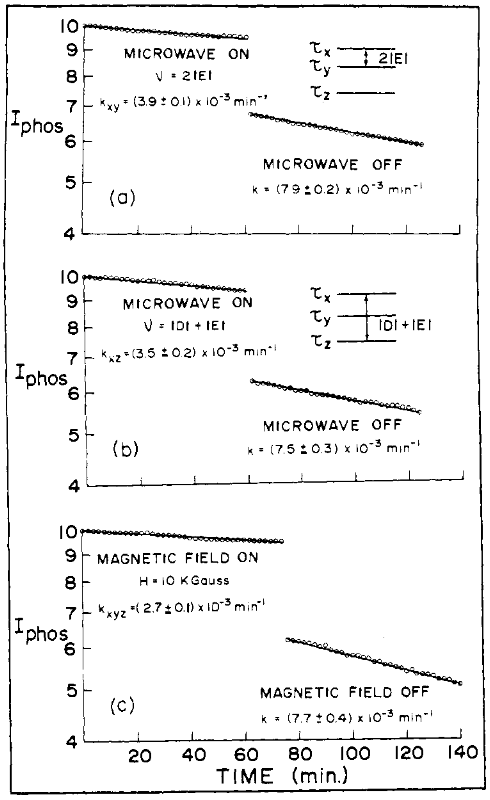

Figure 1. The effect of microwaves in resonance with zero-field transitions or 10 kG static magnetic field on the rate of photochemical reaction of the triplet state of solid pyrimidine in benzene at 1.6°K. At this temperature, the spin–lattice relaxation between the zf levels is slow and the system exists in a state of spin alignment.

$$\frac{dS_0}{dt} = \sum_{i=x,y,z} (\beta_i T_i - \alpha_i I S_0) \tag{2}$$

where x, y, and z are the three orthogonal zf states. The dependence on the intensity of the exciting light (I) is included explicitly in the ISC ($\alpha_i I$) as well as the photochemical reaction ($\gamma_i I$) rates. β_i is the decay rate of the sublevel i to the ground state.

Since the reaction is slow compared with photophysical processes, these rate equations can be solved under a pseudo-steady-state approximation. The rate constant for this photoreaction at certain light level, $k(I)$, is found to be

$$k(I) = \frac{YI^2}{1 + XI} \tag{3}$$

where $Y = \Sigma_i n_i \gamma_i$, $X = \Sigma_i n_i = \Sigma_i \alpha_i / \beta_i$.

If a microwave field in resonance with the $x \leftrightarrow y$ zf transition is applied, the population of the two levels tend to equalize. Under this condition, the quantities k_{xy}, Y_{xy}, and X_{xy} are obtained by substituting the new steady-state population[7] $n_{xy} = (\alpha_x + \alpha_y)/\beta_x + \beta_y)$ for n_x and n_y in eq 3. Notice that resonant microwaves could affect the rate of the photochemical reaction if either the populations or the photoreactivities (measured by γ_i) of its zf levels are unequal or both. The question most interesting to chemists would be whether the rate of the photochemistry of a triplet state depends on the initial direction of the unpaired spins in the molecular framework, *i.e.*, $\gamma_x \neq \gamma_y \neq \gamma_z$.

The relative population of the zf levels (known for pyrimidine)[8] is related to the γ_i's as follows.

$$\frac{Y_{xy}}{Y} = \frac{k_{xy}(1 + X_{xy}I)}{k(1 + XI)} = \frac{n_{xy}(\gamma_x + \gamma_y) + n_z\gamma_z}{n_x\gamma_x + n_y\gamma_y + n_z\gamma_z} \tag{4}$$

The relative values of γ_i can be determined by simultaneously solving this and a similar equation involving, *e.g.*, Y_{xz}/Y, if I is calculated by determining k at two different light intensities.

In five different experiments, using different exciting light intensities, the above method gave γ_x:γ_y:γ_z the ratio 1:0.70 ± 0.13:0.5 ± 0.1; *i.e.*, the rate of the photochemistry induced by an absorption of a second photon by the lowest triplet state depends on the orientation of the spins in the molecular framework.

γ contains the product of the probabilities of both the absorption of the second photon and the nonradiative process(es) leading to the observed photochemistry. Spin selectivity could arise if the different zf levels have different probabilities for either or both of these two processes. For example, the second photon could excite the molecule to a higher energy triplet state which, *via* spin-orbital coupling, radiationlessly and spin selectively crosses to a photochemically active singlet state or to a singlet state of product. It should be emphasized that this is a tentative explanation. However, in any mechanism postulated, the coupling between the spin motion and the orbital motion (responsible for the chemical reaction) must be invoked.

The details of the photochemistry involved are now being worked out and the complete work will be published at a later date.

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Modification of the Cavity of β-Cyclodextrin by Flexible Capping

Sir:

The cyclodextrins (cycloamyloses) have generated great interest[1] because of their ability to bind substrates into their cavity utilizing hydrophobic interactions in aqueous solution. In this respect they mimic binding sites in enzymes, and cyclodextrins have been utilized accordingly in a number of enzyme models. Simple cyclodextrins themselves are