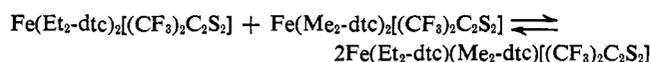


conveys three key features: basically octahedral coordination about iron producing a chiral complex; partial double-bond character in the dithiocarbamate C-N bonds; the presence of methylene groups rendered diastereotopic by the chirality of the molecular configuration. At -9° the two diastereotopic methylene resonances H_a and H_b separated by 0.98 ppm are observed together with a single methyl triplet. With increasing temperature these signals undergo broadening and collapse to a single line, signifying increasingly rapid racemization of the complex. Indication that the averaging process is intramolecular follows from observations of the equilibrium



which is established immediately upon mixing. Ligand exchange is not observed under conditions where racemization of the $R = \text{Et}$ complex is rapid. Decreasing the temperature below -9° results in broadening of both the methylene and methyl signals followed by a sharpening of these signals at -72° . At this temperature H_a has split into two signals (H_a and H_a') and the methyl resonance has separated into two well-defined peaks. These changes are entirely consistent with a slowing down and eventual freezing of rotation about the C-N bonds. Such frozen conformations will result in two nonequivalent methyl groups and four nonequivalent methylene protons; only three of the latter could be resolved. These stereochemical processes are reversible with temperature and are exhibited by the $R, R = (\text{CH}_2)_{4,5}$ complexes also. The ethyl and pentamethylene species show remarkable diastereotopic splittings of 1.76 and 1.87 ppm, respectively, in CD_2Cl_2 at 30° . The $R = \text{Me}$ complex manifests only the restricted rotation process in its pmr spectrum since it lacks the diastereotopic protons required for detection of racemization. Approximate lifetimes for racemization and C-N bond rotation obtained from coalescence temperatures for **1** in CD_2Cl_2 solution are 1.3×10^{-3} (56°) and 3.9×10^{-3} sec (-60°).

The pmr work has produced two observations of some general importance. First, these results demonstrate the utility of diastereotopic groups in following racemization reactions of metal complexes, at least in those cases where isotropic interactions effect suitable chemical shift differences. Second, the direct observation of restricted rotation about C-N bonds of coordinated bidentate dithiocarbamates provides additional evidence for the contention founded on infrared data¹¹ and supported by structural determinations^{3,11a,12} that such bonds generally have a multiplicity exceeding one, and proves that the activation energy for rotation is within convenient thermal range.

Further investigations of the structural and electronic properties of the group $\text{M}(\text{R}_2\text{-dtc})_2[(\text{CF}_3)_2\text{C}_2\text{S}_2]^{0,-}$ and related complexes, and of restricted rotation about C-N bonds in dithiocarbamates are continuing, and the results will be reported in a subsequent publication.

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Quenching of Alkyl Ketone Fluorescence by 1,3-Dienes

Sir:

A commonly used technique¹⁻⁸ for detecting the involvement of the triplet state in a photochemical reaction of a carbonyl compound is the quenching of the reaction by 1,3-dienes. In particular 1,3-pentadiene has been extensively used in this manner. The diolefin is presumed to accept energy from the triplet state of a given donor excited molecule but not from the donor's excited singlet state.² The reduction in the overall quantum yield (ϕ) for the reaction at high diolefin concentration ($\sim 10 M$) is taken as a measure of the quantum yield from the triplet state, ϕ_T^0 , while the unaffected portion of ϕ is equated to the quantum yield from the singlet state, ϕ_S^0 ; thus, if all the reaction is quenched at high diolefin concentration, the reaction is assumed to arise only from the donor's triplet state. In addition, Stern-Volmer plots of the quenching of a reaction by diolefins are used to evaluate the reaction rate constants from the triplet state. Slopes of these plots have been found to vary from rather large values to very small values, and, correspondingly, the lifetimes of the triplet state involved are concluded to be either long ($\sim 10^{-6}$ sec) or very short ($\sim 10^{-10}$ sec), as a result of the Stern-Volmer analysis.

If singlet energy transfer (or chemical reaction) between the molecule under study and the diolefin occurs, the conclusions of studies such as those described above are obviously open to question.

We wish to report that the fluorescence of 2-pentanone, norcamphor, *t*-butyl methyl ketone, and acetone is quenched by 1,3-pentadiene at high pentadiene concentrations, indicating that the singlet state of the carbonyl is affected by the diolefin. As a result, accurate measurements of the relative singlet-triplet quantum yields for reactions of alkyl ketones should not be made by the above-mentioned technique without corrections for singlet quenching. In addition, the quenching of a photoreaction of an alkyl ketone by high concentrations of diolefin should no longer be considered sufficient evidence to assign the reaction to an excited triplet state. This, unfortunately, makes the problem of distinguishing between very rapid triplet reactions and singlet reactions of alkyl ketones considerably more difficult. Furthermore, care must be taken in the use of triplet-sensitized *cis-trans* isomerization of diolefins,⁹ such as

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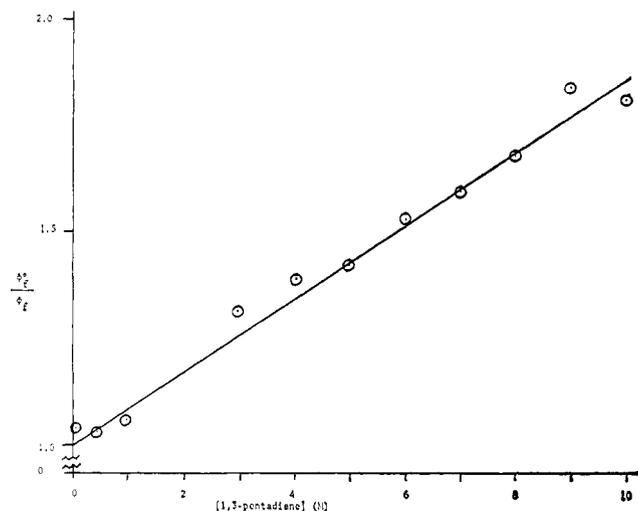


Figure 1. Stern-Volmer plot for quenching of 2-pentanone fluorescence by 1,3-pentadiene.

1,3-pentadiene, to determine intersystem crossing quantum yields of alkyl ketones. Also, alkyl ketone singlet reactivities determined by examining the residual photoreaction in the presence of high concentrations of piperylene^{8,10} may need correction since piperylene quenching will lower both the quantum yield and the lifetime of the excited singlet state.

Figure 1 presents a representative Stern-Volmer plot for the quenching of the fluorescence of 2-pentanone by 1,3-pentadiene. The slopes (${}^1k_q\tau_s$) and values of 1k_q , the rate constant for quenching of the alkyl ketone singlet state by pentadiene, determined for acetone, 2-pentanone, norcamphor, and *t*-butyl methyl ketone are summarized in Table I. Since values for 1k_q are $\sim 10^7$

Table I. Summary of Fluorescent Quenching Data

Compound	Solvent	$\tau_s^0 {}^1k_q$, M^{-1}	τ_s^0 , nsec	1k_q , M^{-1} sec^{-1}
Acetone	Hexane	0.19	2.0	9×10^7
2-Pentanone	Hexane	0.08	1.8	4×10^7
Methyl <i>t</i> -butyl ketone	Benzene	0.08	4.2	2×10^7
Norcamphor ^a	Benzene	0.26	5.2	5×10^7

^a In addition to quenching of the norcamphor fluorescence we have observed reduction in τ_s^0 in neat pentadiene. This clearly establishes that the ketone excited state is interacting with the diolefin and eliminates the possibility that competitive absorption by the diolefin (or an impurity) is the reason for the fluorescent quenching.

$M^{-1} sec^{-1}$ and singlet lifetimes for alkyl ketones are on the order of a few nanoseconds, it is clear that singlet interaction only becomes important at high concentrations of diolefin. However, since this is precisely the condition commonly used to evaluate ϕ_T^0 and ϕ_S^0 , the present results indicate that, in previous studies employing high concentrations of 1,3-pentadiene, the singlet state has been quenched in addition to the triplet state and thus that previous estimates of ϕ_S^0 and ϕ_T^0 may be inaccurate. The extent of the inaccuracy depends on the lifetimes of the singlet state and the rate constant

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for singlet quenching. For 2-pentanone the error in ϕ_S^0 may be as much as a factor of 2, while for 2-hexanone it is more like a factor of 1.25.¹¹ As a result, plots of ϕ_T^0/ϕ_T , from which numerical values for the triplet lifetime are obtained, are not strictly valid since they depend on knowledge of the relative amounts of singlet and triplet reaction.

The correct Stern-Volmer expression for the quenching of a reaction which occurs from both the singlet and triplet excited states by a quencher which can quench both excited singlets and triplets is given by the equation¹²

$$\frac{\phi^0}{\phi} = \{1 + {}^1k_q\tau_S^0[Q]\} \{1 + {}^3k_q\tau_T^0[Q]\} \times \left\{ \frac{1 + (\phi_T^0/\phi_S^0)}{1 + (\phi_T^0/\phi_S^0) + {}^3k_q\tau_T^0[Q]} \right\} \quad (1)$$

where τ_S^0 and τ_T^0 are the lifetimes of the excited singlet and excited triplet states, respectively, in the absence of quencher.

When $[1 + (\phi_T^0/\phi_S^0)]{}^1k_q\tau_S^0 < {}^3k_q\tau_T^0$, which is the case for quenching of Norrish type II reactions from 2-hexanone and 2-pentanone by piperylene, at high concentrations of quencher ($[Q]$), the plot of ϕ^0/ϕ approaches a linear asymptote with a slope of ${}^1k_q\tau_S^0 \cdot (1 + \phi_T^0/\phi_S^0)$. This slope is $0.265 M^{-1}$ for 2-pentanone,¹¹ and, hence, the ratio ϕ_T^0/ϕ_S^0 is about 2.25. Such a value implies that $\sim 70\%$ of the type II reaction emanates from the triplet state which is in agreement with the 65% observation made in the gas phase.⁵

The presence of the singlet quenching offers an explanation as to why Stern-Volmer plots of the quenching of Norrish type I and type II reactions have nonzero slopes in the region of 1–10 M pentadiene.⁴ In addition, the inefficient quenching of the singlet state may explain some of the small Stern-Volmer slopes which have been taken to indicate very short triplet lifetimes.

It should also be noted that the magnitude of 1k_q explains why fluorescent quenching was not observed in the previous gas-phase studies of 2-pentanone⁵ and acetone.¹³

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