

let states.^{9,10} On the other hand, the failure of piperylene to completely quench racemization of **6** or **4** (when the latter is excited directly) may imply that excited singlets can undergo rapid inversion.

Table II. Direct and Sensitized Excitation of Compound **4** in Benzene Solution at 25–27°^a

Series ^{b,c}	Concentration, <i>M</i>		Racemization, %
	Naphthalene	Piperylene	
C	0	0	8.7
C	0	1.0	5.7
C	0	10.0	4.7
C	0.1	0	35
C	0.1	1.0	0
C	0.1	10.0	0
D	0.1	0	37
D	0.1	0.01	31
D	0.1	0.10	10

^a For purposes of semiquantitative comparison, the irradiation times were 24 times as long as in experiments reported in Table I.

^b Samples in a given series were irradiated under identical conditions.

^c Concentration of **4** was 0.01 *M* in all experiments.

When compound **6** was irradiated in an MCIP glass¹¹ at 77°K., a strong emission, very similar to the phosphorescence of naphthalene, was recorded.

Consideration of all the facts and their individual implications leads to two alternative conclusions. First, one might assume that transfer of both singlet and triplet excitation from naphthalene units to arene-sulfinyl groups occurs and that both excited singlets and triplets isomerize.¹² This view would probably require that triplet excitation ultimately returns to the naphthalene unit of **6** in order to account for the phosphorescence of that compound, although it must be pointed out that isomerization and emission were observed under very different physical conditions. Alternatively, we might decline to treat the chromophores in **6** as isolated and maintain that weak coupling between two unsaturated systems effects continuous sharing of the excitation between them. This would allow increase in the intersystem crossing efficiency of **6** in comparison with other naphthalene derivatives and account for naphthalene-like emission from a triplet state of **6** which is also capable of undergoing isomerization. In a recent study of internal energy transfer,¹³ one example was found in which the action of two unconjugated chromophores was cooperative. The sensitized isomerization of **4** may involve triplets exclusively, with the rate constant for energy transfer from naphthalene to **4** being $\leq 10^{-2}$ times that for transfer from naphthalene to piperylene. It seems almost certain that direct excitation of **4** leads to isomerization by both singlet and triplet mechanisms. We prefer the second explanation since the efficient transfer of singlet excitation would require the existence of low-lying excited singlet states of tolyl sulfoxides. Careful examination of light ab-

(9) G. S. Hammond, N. J. Turro, and P. A. Leermakers, *J. Phys. Chem.*, **66**, 1144 (1962).

(10) R. Srinivasan and F. I. Sonntag, *J. Am. Chem. Soc.*, **87**, 3778 (1965).

(11) Five parts of methylcyclohexane—one part of isopentane.

(12) Evidence indicating that excited singlets and triplets of simple ketones have similar reactivity has recently been reported.³

(13) A. A. Lamola, P. A. Leermakers, G. W. Byers, and G. S. Hammond, *J. Am. Chem. Soc.*, **87**, 2322 (1965).

sorption by concentrated solutions of **4** gives no indication of weak transitions in the 3500–5000-Å. region.

(14) National Aeronautics and Space Administration Fellow, 1964 to present.

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Triplet Methylene Formation on Photolysis of Ketene and Diazomethane¹

Sir:

We present results which reconcile a recently discovered anomaly between gas phase and liquid phase behavior of diazomethane–methylene radical systems and which contrast the behavior of ketene and diazomethane systems.

It has been shown^{2a} that triplet methylene (³CH₂) arises on photolysis of ketene at ~ 3200 Å.^{2b}; the proportion *increases* with pressure from some small or zero value at low total pressures and reaches a quasi-constant plateau of $\sim 29\%$ at pressures under, and near, 1 atm.^{2a} A similar pressure dependence, although possibly lesser percentage of ³CH₂, was also found^{3,4} on photolysis of diazomethane at 4300 Å. Whitten and Rabinovitch⁴ recently pointed out a new dilemma relative to this triplet behavior; namely, it appears that only (or mainly) ¹CH₂ arises in liquid phase systems upon photolysis of diazomethane. Thus the insertion into various C–H hydrocarbon bonds is known^{5,6} to be more statistical than the usual gas phase behavior, while it has now been shown that statistical insertion is a concomitant of singlet rather than of triplet methylene which abstracts H atoms.^{3,4} Also, in unpublished work, F. H. Dorer has noted that the characteristic triplet products⁷ of reaction of ³CH₂ with *cis*-butene-2 dropped markedly when a diazomethane–butene system (4300 Å.) was liquefied at 0°.

The liquid behavior is not necessarily at odds with the gas phase results. One explanation might attribute the liquid phase decline in ³CH₂ proportion to effects on the mechanism arising from ternary, rather than binary, interactions. However, a second possible explanation⁴ is that collisional processes play a crucial role in inhibiting the formation of ³CH₂ in the liquid and that the proportion of ³CH₂ could pass through a maximum in the gas phase. Thus, consider in Scheme I a modified (and abbreviated) version of the mechanism described by Porter and Connelly⁸ for ketene photolysis;

(1) This work was supported by the Office of Naval Research.

(2) (a) J. W. Simons and B. S. Rabinovitch, *J. Phys. Chem.*, **68**, 1322 (1964). (b) ³CH₂ has now been shown to be produced at other wave lengths as well with ketene; see S. Ho, I. Unger, and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, **87**, 2297 (1965).

(3) F. H. Dorer and B. S. Rabinovitch, *J. Phys. Chem.*, **69**, 1952, 1964 (1965).

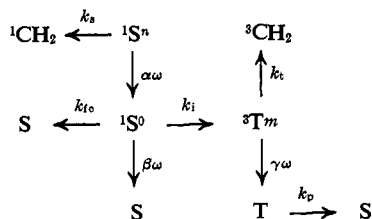
(4) G. Z. Whitten and B. S. Rabinovitch, *ibid.*, in press.

(5) W. E. Doering, R. G. Buttery, R. G. Laughlin, and N. Chaudhuri, *J. Am. Chem. Soc.*, **78**, 3224 (1956).

(6) D. B. Richardson, M. C. Simmons, and I. Dvoretzky, *ibid.*, **83**, 1934 (1961).

(7) F. J. Duncan and R. J. Cvetanović, *ibid.*, **84**, 3593 (1962).

Scheme I



we will accept it as a useful basis for discussion of diazomethane also. Here ${}^1\text{S}^n$ is the lowest excited singlet at the level n of vibrational excitation; intersystem crossing occurs from lower vibrational levels; S and T are unreactive states; α , β , and γ are efficiency factors which could be unity. The original mechanism⁸ has been modified by addition of the collisional stabilization rate,⁹ $\beta\omega$. A maximum ratio [${}^3\text{CH}_2/{}^1\text{CH}_2$] is predicted from a steady-state treatment

$$[{}^3\text{CH}_2/{}^1\text{CH}_2] = \frac{\alpha k_i k_t \omega}{k_s(k_t + \gamma\omega)(k_i + k_{tc} + \beta\omega)} \quad (1)$$

Equation 1 has the limiting value zero, for $\omega \rightarrow 0$, ∞ . Also, $\omega_{\max} = (k_i k_t)^{1/2}$ and

$$[{}^3\text{CH}_2/{}^1\text{CH}_2]_{\max} = \frac{k_i k_t}{k_s(k_i^{1/2} + k_t^{1/2})^2} < (k_i/k_s), (k_t/k_s) \quad (2)$$

where, for simplicity, k_{tc} was omitted and α , β , and γ set at unity.

The present study was designed to test the two explanations. Experiments with ketene, diazomethane, and *cis*-butene-2 have been conducted at pressures above the highest previously used.^{2,3} Since butene cannot be taken above 2 atm. at room temperature, ethylene was used in one experiment as an inert gas with respect to diazomethane. However, it is not an inert gas with respect to methylene and should not bring about collision-induced¹⁰ intersystem crossing of the methylene itself, ${}^1\text{CH}_2 + \text{M} \rightleftharpoons {}^3\text{CH}_2 + \text{M}$. Obviously, however, the noninterfering side products, cyclopropane and propylene were formed.

Some results for diazomethane are summarized in Figure 1. A maximum in proportion of ${}^3\text{CH}_2$ is achieved at ~ 1 atm. pressure; it drops markedly at higher pressures. Similar behavior was confirmed with ethylene diluent. The behaviors of diazomethane systems in the gas and liquid phases are thus to be reconciled by the second explanation. The temperature dependence of the triplet proportion, found both here and in the ketene system, merits further investigation.

On the basis of Scheme I, which is a reasonable, if not proven, basis of discussion, there can be no collision-induced intersystem crossing as originally tentatively suggested^{2a,3}: if k_i is replaced or supplemented by a collision process, characterized by rate constant $\delta\omega$, then no maximum in the ratio [${}^3\text{CH}_2/{}^1\text{CH}_2$] can arise. In addition, both collision processes $\beta\omega$ and $\gamma\omega$ must be assumed to occur and to be dominant at high pressures.

The situation is somewhat different for ketene

(8) (a) G. B. Porter and B. T. Connelly, *J. Chem. Phys.*, **33**, 81 (1960); (b) G. A. Taylor and G. B. Porter, *ibid.*, **36**, 1353 (1962).

(9) Such a possibility is considered reasonable on the basis of existing information by Professor Porter (private communication). The internal conversion process, k_{tc} , is not definitely established; a phosphorescence process has not been seen for ketene.

(10) H. M. Frey, *J. Am. Chem. Soc.*, **82**, 5947 (1960).

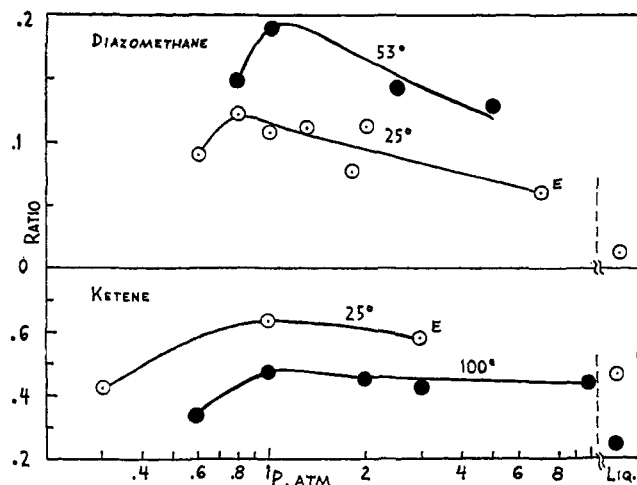


Figure 1. Plot of [*trans*-dimethylcyclopropane/*cis*-pentene-2] vs. pressure. The *trans* compound is the principal diagnostic product of ${}^3\text{CH}_2$ reaction. The use of *cis*-dimethylcyclopropane in the ratio, in place of *cis*-pentene-2, gives a curve of the same shape. Other diagnostic triplet products, 3-methylbutene-1 and *trans*-pentene-2, give similar, but inaccurate, trends. E stands for ethylene and Liq. for liquid.

(actually, for other reasons, ketene- d_2 was used). Here, only a moderate maximum in the ratio [${}^3\text{CD}_2/{}^1\text{CD}_2$] and only a modest further drop in liquid butene were found. We know of no prior liquid phase results bearing on these matters for ketene. Insofar as a maximum ratio effect exists, it militates against the likelihood of a collisional intersystem crossing process¹¹ (even though such a process is compatible with a plateau in ${}^3\text{CH}_2$ proportion). Whether a plateau or a maximum in the ratio exists (a study of the effect of variation of λ would be of interest), it is necessary to invoke at least one of the collisional processes, $\beta\omega$ or $\gamma\omega$, in I. For a plateau, the limiting ratio, as $\omega \rightarrow \infty$, becomes either $< k_i/k_s$ or $< k_t/k_s$, depending on whether $\beta\omega$ or $\gamma\omega$ is retained. Porter⁸ has given k_s as 2×10^9 sec.⁻¹, which places the present phenomena in the proper pressure region. Scheme I is not necessarily complete. For example, collisional excitation of T could be included; this would modify the above discussion regarding the optional roles of $\beta\omega$ and $\gamma\omega$ in an obvious way.

The present type^{2a} of chemical evidence is a powerful complement to quantitative spectroscopic-photocatalytic studies on these systems. Further details and extension will be submitted shortly.

(11) C. S. Parmenter, *J. Chem. Phys.*, **41**, 658 (1964), has found no evidence for such collisional processes with other carbonyl-containing compounds, which supports, but does not prove, our present conclusion with respect to ketene.

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Molecular Weight and Molecular Weight Distribution of Unfractionated Yeast Transfer Ribonucleic Acid¹

Sir:

The marked functional similarities of the different amino acid specific s-RNA's² suggest that this class of

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