Product distributions were determined after >99% disappearance of cyclohexyl bromide by extraction of the N$_{2226}$B$_{2226}$ solution with 5–6 portions of 1–2 ml of pentane and glpc analysis of the pentane extracts. Cyclohexene and cyclohexyl phenyl sulfide were determined using octane and tetradecane as internal standards on matched 6.5 ft × 0.25 in. 11% Apiezon L columns with temperature programming to obtain both analyses from a single injection. In control experiments the sum of products determined by this method accounted for 97% of the initial cyclohexyl bromide when the reaction was carried out in sealed glass ampoules, but some cyclohexene was lost when the reaction was carried out in septum-capped flasks. In the latter cases cyclohexyl phenyl sulfide was determined by the glpc method and the cyclohexene was assumed to account for the remainder of the cyclohexyl bromide consumed. Control experiments showed that this assumption gave results within 2% of those obtained by glpc analysis of both products.

Acknowledgment. We thank the U. S. Public Health Service (GM 16909) and the National Science Foundation (GP 38493) for support of this research.

Mercury ($^3P_1$)-Sensitized Decomposition of *cis*- and *trans*-3,4-Dimethyl-1-pyrazoline. The Kinetics of Highly Vibrationally Excited Triplet 1,2-Dimethyltrimethylene Biradicals

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Abstract: The Hg($^3P_1$)-photosensitized decomposition of both *cis*- and *trans*-3,4-dimethyl-1-pyrazoline was studied from 0.2 to 4 and 5 Torr, respectively, and in the presence of Ar at pressures up to 1 atm. The major products are nitrogen, *cis*- and *trans*-dimethylcyclopropane, *cis*- and *trans*-2-pentene, 3-methyl-1-butene, and ethane. The product distributions from both reactant isomers are nearly identical. For the cis reactant $\Phi_{N_2} = 0.93 \pm 0.05$ at 4 Torr, and for the trans reactant $\Phi_{N_2} = 0.95 \pm 0.05$ at 5 Torr. Total hydrocarbon quantum yields are independent of pressure from ~1 to 760 Torr (pressurized with Ar). Highly vibrationally excited triplet 1,2-dimethyltrimethylene biradicals are formed by N$_2$ elimination from both pyrazolines. The hot biradicals either dissociate to methyl and methallyl radicals or cyclize to dimethylcyclopropanes, which are also sufficiently excited to experience geometrical and structural isomerization, the latter only being observed at pressures below about 1 Torr. Pentenes and ethane are formed by radical–radical combination reactions.

Direct and triplet-sensitized photodecomposition of 1-pyrazolines has frequently been postulated to proceed *via* nitrogen elimination to yield 1,3 biradicals.[1-9] The spin multiplicity of the intermediates and their subsequent reactions depend on the primary photophysical processes occurring in the precursor, though in general direct photolysis is thought to yield singlet biradicals while triplet photosensitizers are thought to produce triplet biradicals.

Direct photolysis of 1-pyrazolines yields cyclopropanes, presumably *via* biradical cyclization, and olefins as the major products both in vapor and condensed phases.[3,7,9] Olefins and cyclopropanes are also formed in two vapor phase systems which are thought to involve triplet 1,3 biradicals as the olefin precursor. These are the addition of CH$_2$($^3B_1$) to double bonds[10,11] and the triplet photosensitization of dimethylcyclobutanone vapors.[12,13] In contrast, triplet photosensitization of 1-pyrazolines in solution yields cyclopropanes but no olefins.[3,8,9] If triplet biradicals are important intermediates in these reactions, there is an unexplained effect of phase on the reaction products. On the other hand, triplet biradicals may not be involved in all cases, or the biradicals may have different properties, dependent upon their mode of formation. In this work we have investigated the reasons for the above noted differences in behavior.

No one mechanism can explain the results of the photolytic or pyrolytic decomposition of all the compounds in which diradical intermediates are thought to play a role. The diverse modes of reaction can be attributed to different structures and/or electronic states of the intermediates. We initiated an investigation of the vapor phase triplet-sensitized decomposition of 1-pyrazolines in order to compare and contrast behavior with that obtained by triplet sensitization in solution and with direct photolysis. *cis*- and *trans*-3,4-dimethyl-1-pyrazoline were chosen for study since the expected triplet biradicals would be similar to those obtained by adding CH$_2$($^3B_1$) to *cis*- or *trans*-2-butene[10,11] or by the triplet-sensitized decomposition of *cis*- and *trans*-2,3-dimethylcyclobutanone.[12,13] The investigation was expected to reveal whether the triplet biradicals produced

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from pyrazolines can yield olefins in the gas phase, and whether their behavior can be related to that of triplet biradicals generated from other sources.

Experimental Section

Materials. *cis*-3,4-Dimethyl-1-pyrazoline (CDMP) and *trans*-3,4-dimethyl-1-pyrazoline (TDMP) were prepared by the stereospecific cycloaddition of diazomethane to *cis*- and *trans*-2-butene, respectively, according to the method of Crawford and Ali.[14] Positive identification was made by means of nmr, ir, and uv spectra. The uv spectrum of TDMP is reported in Figure 1. The purity of both CDMP and TDMP was determined by glc on a 2.5-m Ucon insoluble on Fluoropak column. The impurities were 1-pyrazoline, found in maximum amount of 3.6% in TDMP and in varying amounts up to 50% in CDMP. Small amounts of C_6–C_9 hydrocarbons were also present, but these did not interfere with product analysis. Samples of CDMP and TDMP were purified by preparative glc with a Ucon on Fluoropack column. The product distributions from Hg-sensitized decomposition of purified samples of either CDMP or TDMP were identical with the product distributions of the same products from either CDMP or TDMP in samples containing 1-pyrazoline impurity. The results were therefore independent of whether glc purified samples were used. Argon of 99.995% stated purity and USP oxygen were taken directly from NCG cylinders. Matheson CO, N_2O, and n-C_4H_8 were used, the former after several fractionations.

Apparatus. Gas handling and photolyses were done in grease-free sections of a glass vacuum system routinely evacuated to 10^{-5} Torr. The entire apparatus was light shielded with a black cloth cover. A G.E. G8T5 germicidal lamp was used with a 3-compartment quartz filter containing 2.5 cm of 2.0 M $NiSO_4$, 2.5 cm of 0.6 M $CoSO_4$, and 5 cm of Cl_2 at 1 atm. The emission spectrum of the filter-lamp combination consisted almost entirely of the 2537-Å line with a 0.06% contribution by the 2652-Å line and 0.05% at 2654 Å. The filtered radiation passed through a 3.8 cm i.d. × 18.8 cm photolysis cell, which was provided with a gas circulating pump[15] and contained beads of Hg. The total volume of the cell and pump was 329 cm^3. Reactants were decomposed to at most 5%. The hydrocarbon products were frozen out at −195.6°, the noncondensibles pumped away, and a measured amount of n-butane added to serve as an internal standard. In runs without additive gases nitrogen was pumped into a measuring buret. Absolute yields of condensible products were measured *via* glc and the n-butane standard. All work was done at ambient temperature, 25 ± 4°.

Analysis. Products were analyzed on a Barber-Coleman Model 5000 gas chromatograph with flame ionization detector. The three part column used consisted of:[16] (1) 6.1 m 20% benzyl ether on Firebrick, (2) 6.1 m 20% 2,4-dimethylsulfolane on firebrick, (3) 3.1 m 20% diisodecyl phthalate on Chromosorb P. The column was immersed in a water bath at 36 to 38° and operated at 25 cc/min of He. It did not separate ethane and ethylene nor 1-butene and isobutene. The former separation was achieved on a silica gel column. Reaction products were identified by comparison with authentic samples or literature values. Their relative sensitivities in the flame ionization detector were determined with prepared mixtures.

Nitrous oxide actinometry was performed by photolyzing N_2O at 100 Torr plus about 10% n-butane in the reactor.[17] Yields of N_2 were measured on the gas buret. Periodic checks during experimentation revealed that the effective flux decreased from 0.054 to 0.034 μeinsteins min^{-1} over the several month period. The pressure dependence of absorbed radiation was also measured. N_2O was photolyzed in the presence of 10% n-butane at total pressures from 500 to 2.8 Torr. At pressures below about 30 Torr the amount of absorbed radiation started to decrease and at 2.8 Torr had fallen to 32% of its value at 100 Torr. The effect of pressure is most likely due to pressure broadening of the absorption line. The Doppler breadth of the emission line of our source is greater than that of the Hg absorption line in the cooler reactor, but at higher pressures pressure broadening will serve to diminish the mismatch. Radiation imprisonment effects at low pressures were absent. Using $\tau/\tau_0 = 177$, at 2×10^{-3} Torr of Hg,[18] where τ is the effective lifetime of Hg($^3P_1$) in the absence of quenching, and τ_c, the radiative lifetime, equals 1.14×10^{-7} sec, gives $\tau = 2 \times 10^{-5}$ sec. If $k_q = \sigma_{N_2O}{}^2[8\pi kT(M_{Hg} + M_{N_2O}/M_{Hg}M_{N_2O})]^{1/2}$, where $\sigma_{N_2O}{}^2 = 25.4$ Å^2,[18] $k_q[N_2O] = 1.1 \times 10^7$ sec^{-1} at 1 Torr. Thus even at pressures as low as 1 Torr of N_2O the radiative process cannot compete with chemical quenching processes.

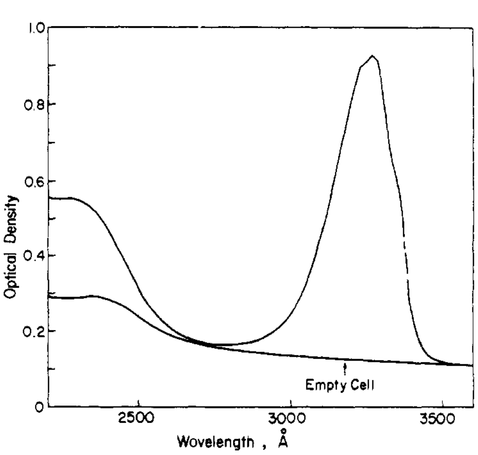

Figure 1. Uv spectrum of *trans*-3,4-dimethyl-1-pyrazoline: l = 10 cm; p = 5.3 Torr.

Results

Reaction Products. The major products of the mercury-photosensitized decomposition of either isomer of 3,4-dimethyl-1-pyrazoline are nitrogen, *cis*- and *trans*-2-pentene (C2P and T2P), 3-methyl-1-butene (3M1B), and ethane. Minor quantities of 2-methyl-1-butene (2M1B), 2-methyl-2-butene (2M2B), propylene, cyclopropane, 1-butene (or isobutene), and methane are also formed. In addition, trace amounts ($\lesssim$1%) of ethylene, propane, *cis*- and *trans*-2-butene, and butadiene are present. Blank runs and other evidence indicate that some of the trace products may be due to a "dark" surface-sensitized decomposition of DMP. Significant amounts of unidentified higher molecular weight compounds with glc retention times approximately equivalent to C_8 hydrocarbons are formed. No geometrical isomerization of CDMP or TDMP could be detected by glc. Propylene, cyclopropane, and 1-butene yields were greatly reduced in experiments with glc-purified DMP samples. These three products could be attributed to the mercury photosensitized decomposition of 1-pyrazoline. The relative yields of C_5 hydrocarbons and ethane were unaffected by varying amounts of 1-pyrazoline impurity.

Some reaction product quantum yields from CDMP and TDMP are given in Table I. They are independent of the starting isomer at any arbitrary experimental condition, within experimental error. The quantum yields are reproducible, on the average, to about 10%.

Extent of Decomposition. A series of experiments on mixtures of 3.7 Torr of DMP in approximately 20 Torr Ar was done to test whether the observed products resulted from secondary reactions of stable reaction products. The rates of formation of *all* the major and minor products are independent of the extent of photodecomposition from 0.06 to 11%, the

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Table I. Product Quantum Yields from the Hg-Sensitized Decomposition of *cis*- and *trans*-3,4-Dimethyl-1-pyrazoline

Pressure, Torr			Quantum yield								
CDMP	TDMP	Additive	N_2	C_2H_6	TDMC	CDMC	3M1B	T2P	C2P	2M2B	2M1B
0.2			(1.0)[a]	0.11	0.096	0.064	0.060	0.087	0.065	0.018	0.016
0.4			(1.0)[a]	0.10	0.14	0.088	0.072	0.10	0.077	0.016	0.013
0.8			(1.0)[a]	0.12	0.15	0.088	0.066	0.090	0.066	0.013	0.010
3.7			0.93	0.13	0.17	0.099	0.070	0.088	0.063	0.009	0.009
3.7		4.6 (Ar)		0.13	0.17	0.093	0.061	0.075	0.055	0.010	0.008
3.7		17.0 (Ar)		0.12	0.16	0.085	0.052	0.062	0.047	0.009	0.007
3.0		16.1 (10% O_2–Ar)		<0.002	0.16	0.10	<0.001	<0.001	<0.001	0.009	0.007
3.4		36.5 (Ar)		0.11	0.16	0.096	0.047	0.058	0.045	0.008	0.006
3.7		95.6 (Ar)		0.11	0.17	0.10	0.053	0.068	0.049	0.009	0.006
3.1		209 (Ar)		0.12	0.20	0.13	0.059	0.075	0.056	0.007	0.005
2.7		438 (Ar)		0.10	0.27	0.15	0.043	0.055	0.039	0.010	0.005
3.7		728 (Ar)		0.03	0.35	0.17	0.011	0.012	0.011	0.008	0.006
	0.2		(1.0)[a]	0.12	0.13	0.080	0.070	0.094	0.071	0.071	0.016
	5.3		0.91	0.14	0.19	0.11	0.080	0.093	0.068	0.011	0.009
	5.0	14.9 (Ar)		0.12	0.17	0.097	0.066	0.084	0.062	0.009	0.007
	4.4	15.2 (10% O_2–Ar)		<0.002	0.15	0.088	<0.001	<0.001	<0.001	0.009	0.007
	4.9	96 (Ar)		0.098	0.18	0.10	0.064	0.079	0.057	0.008	0.006
	5.1	309 (Ar)		0.054	0.21	0.11	0.056	0.066	0.048	0.007	0.006
	5.3	519 (Ar)		0.075	0.20	0.098	0.038	0.044	0.031	0.005	0.004
	5.3	740 (Ar)		0.051	0.26	0.13	0.035	0.045	0.034	0.006	0.005
	2.7	737 (10% O_2–Ar)		<0.002	0.26	0.11	<0.001	<0.001	<0.001	0.005	0.005

[a] At pressures less than 1 Torr, hydrocarbon quantum yields were calculated from hydrocarbon yields (by glc) and N_2 yields (by gas buret) and assuming $\Phi_{N_2} = 1.0$.

maximum conversion attempted, confirming the absence of such complications.

Quantum Yields. Nitrogen was not determined in added Ar experiments. At 3.7 Torr Φ_{N_2}(CDMP) = 0.93 ± 0.05, while at 5.3 Torr Φ_{N_2}(TDMP) = 0.95 ± 0.05. These values are somewhat uncertain because of uncertainties in corrections for the N_2 produced by a background reaction, which in dark runs amounted to 10–15% of the N_2 produced under identical photolytic conditions. The N_2 quantum yields do show that the predominant process is production of N_2 and a hydrocarbon fragment. Total hydrocarbon quantum yields, Φ_{HC}, were calculated by summing individual product quantum yields. They showed no significant variation with pressure over the entire interval, 0.2 mm to 1 atm (added Ar), for either CDMP or TDMP, and have the average values Φ_{HC}(CDMP) = 0.73 ± 0.06 and Φ_{HC}(TDMP) = 0.69 ± 0.07. Some of the discrepancy in mass balance can be attributed to the formation of the unidentified higher molecular weight products. If the C_2H_6 yield is multiplied by two, for reasons to be discussed later, the measured hydrocarbon quantum yields increase to within 90% of the N_2 quantum yields.

Effect of Pressure. All of the hydrocarbon reaction products reported in Table I exhibit pressure dependencies. The yields of 3MB1, T2P, and C2P decrease monotonically with increasing pressure over the entire range, while TDMC and CDMC show the opposite behavior. Ethane quantum yields have maxima in the vicinity of 3–5 Torr, while 2M1B and 2M2B are independent of pressure above 3–5 Torr and have slight increases at lower pressures. Furthermore, TDMC/CDMC increased from approximately 1.8 at low pressures to 2.1 at 1 atm (3–5 Torr of pyrazoline pressurized to 1 atm with Ar). The dimethylcyclopropane ratio was independent of the starting geometrical isomer of dimethylpyrazoline.

Experiments with Added O_2. Addition of small quantities of oxygen, about 10% of either CDMP or TDMP, suppressed the formation of ethane, 3M1B, T2P, and C2P, while the yields of CDMC, TDMC, 2M1B, and 2M2B were unaffected. The quantum yields of ethane were reduced to less than 0.002, while the 2-pentenes and 3M1B were reduced to less than 0.001.

Discussion

Mechanism. The nitrogen quantum yields determined in pure pyrazoline samples (Φ_{N_2} = 0.93 ± 0.05 from CDMP and 0.95 ± 0.05 from TDMP) show that the principal path of the sensitized reaction is dissociation of dimethylpyrazoline by nitrogen elimination. Also, since the total quantum yields of the measured hydrocarbon products are independent of Ar pressure up to 1 atm, quenching or vibrational relaxation of an excited N_2 precursor to energies below the dissociation threshold must not occur. These observations suggest the formation of a short lived dimethylpyrazoline (most probably a triplet) *via* energy transfer from Hg($^3P_1$), which dissociates primarily (>90%) to N_2 plus a hydrocarbon fragment in a pressure-independent process at least up to 1 atm of Ar.

Table I shows that nearly identical reaction product distributions are obtained from both CDMP and TDMP. Of particular importance is the fact that the ratio of dimethylcyclopropanes is independent of the starting isomer. These results rule out a concerted mechanism for the decomposition and suggest that CDMP and TDMP produce common hydrocarbon intermediates. Furthermore, the reaction product distributions are distinctly different from those obtained in the thermolysis[14] or the direct photolysis[3] of CDMP and TDMP but are similar to those obtained in the Hg(^3P)-sensitized decomposition of *cis*- and *trans*-2,3-dimethylcyclobutanone[12] and the addition of CH_2($^3B_1$) to butene-2.[11,19] In the last two cases triplet 1,3-biradical intermediates were postulated to account for the observations. The present results can also be most

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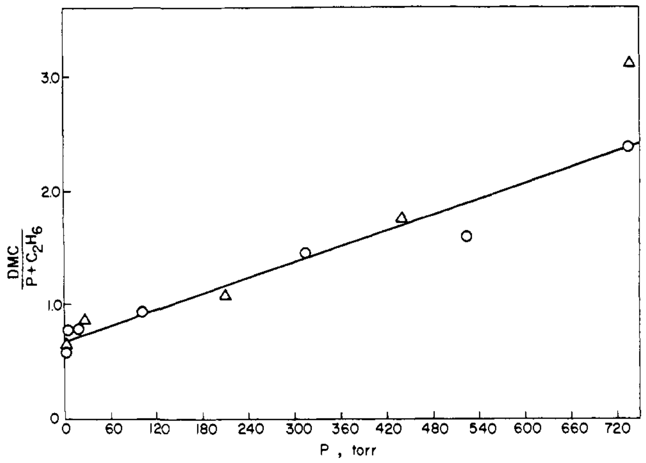
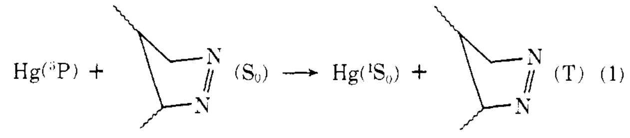


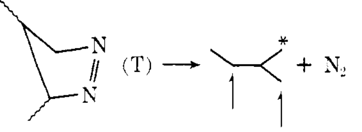
Figure 2. Ratio of dimethylcyclopropane yield to combined major C_5 olefin yield as a function of system pressure: (O) TDMP; (Δ) CDMP.

easily explained if triplet 1,2-dimethyltrimethylene (1,2-DMTM) intermediates result from N_2 elimination.

The most probable initial sequence, common to both TDMP and CDMP, is



(1)



(2)

where (T) means a triplet state of dimethylpyrazoline and the asterisk stands for vibrational excitation. The evidence for vibrational excitation lies in the effects of added Ar and O_2, as explained below.

Figure 2 shows that the ratio of the total dimethylcyclopropane yield to the sum of the yields of the major C_5 olefins plus ethane is a linearly increasing function of Ar pressure. Such a relationship requires that in the steady state 1,2-DMTM gives the major olefins and ethane by a first-order reaction which can be quenched by collisions with Ar. We interpret this to mean that 1,2-DMTM can be formed with vibrational excitation. The vibrationally excited biradicals yield the major olefins and ethane unless they are collisionally deactivated, and the only reaction of the (at least partially) deactivated biradicals is cyclization to dimethylcyclopropanes.

The mechanism of ethane, 3MB1, C2P, and T2P formation must be dissociation of vibrationally hot 1,2-DMTM to methyl plus methallyl radicals, followed by combination reactions. The relative yields of ethane, 3MB1, C2P, and T2P are independent of total pressure at pressures above 3–5 Torr, in the range where their absolute yields are decreasing, suggesting that they arise from a common intermediate. Oxygen suppresses the yields of these products, consistent with a free radical mechanism, but does not decrease the yields of dimethylcyclopropanes. Thus oxygen presumably does not react with the triplet biradicals under our conditions. Also, the observed higher molecular

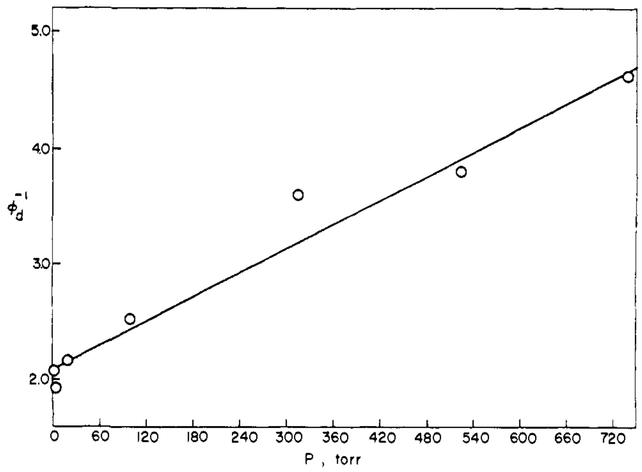
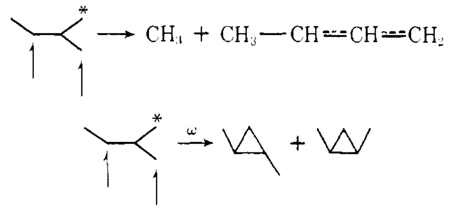


Figure 3. Stern–Volmer plot of decomposition product quantum yields, $\phi_d = \phi(T2P + C2P + 3M1B + 2C_2H_6)$, from TDMP.

weight hydrocarbons can be accounted for by butenyl radical combination reactions, while the traces of 1,3-butadiene and methane arise through methallyl disproportionation and hydrogen abstraction by methyl, respectively. Evidence that ethane arises through methyl radical combination exists in the decreasing ethane quantum yields at pressures less than a few Torr. Values of the half-quenching pressure, $p_{1/2}$, for methyl combination are in the few Torr range.[20]

The following mechanism summarizes the above arguments.



(3)

(4)

$$CH_3 + CH_3\text{—}CH{=}CH{=}CH_2 \longrightarrow 3MB1 \quad (5a)$$

$$\longrightarrow C2P \quad (5b)$$

$$\longrightarrow T2P \quad (5c)$$

$$2CH_3 \longrightarrow C_2H_6 \quad (6)$$

Methyl elimination from the biradical at the former 3 position of the pyrazoline ring probably does not occur since 2MB1 is not a pressure-dependent product. Furthermore, reaction 3 is the less endothermic methyl elimination path.

Since Figure 2 has a finite intercept, 1,2-DMTM* may be capable of forming dimethylcyclopropanes before deactivation, or 1,2-DMTM* may have a wide energy distribution, with some of the biradicals being initially formed with energies below the threshold for dissociation to methyl radicals. A Stern–Volmer plot (Figure 3) of quantum yields of products arising through reactions 3, 5, and 6 permits an estimate of k_3. A steady-state treatment yields

$$\Phi_d^{-1} = (C\phi)^{-1} + \omega/k_3C\phi \qquad (I)$$

where $\Phi_d = \Phi_{C2P} + \Phi_{T2P} + \Phi_{3MB1} + 2\Phi_{C_2H_6}$, $C = [k_5 + 2\sqrt{k_6k_7}][k_5\sqrt{k_7/k_6} + 2k_7]^{-1/2}[k_5\sqrt{k_6/k_7} + 2k_6]^{-1/2}$, ϕ = quantum yield of excited biradicals which dis-

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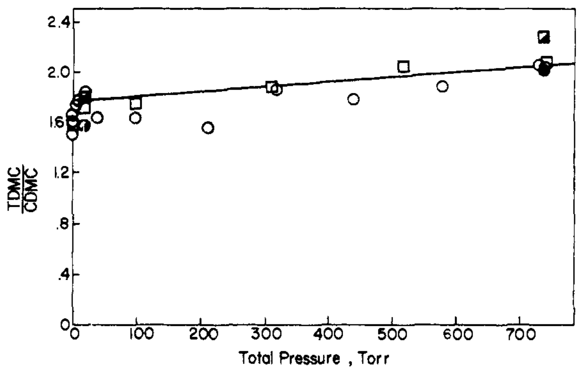


Figure 4. Pressure dependence of dimethylcyclopropane product ratios, TDMC:CDMC: (□) TDMP, (○) CDMP, (◪) TDMP with added O_2. (◑) CDMP with added O_2.

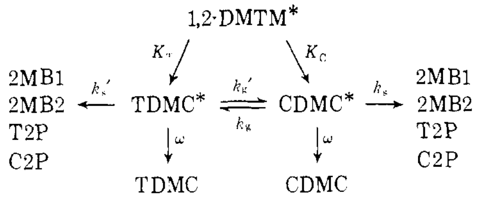
sociate as $p \rightarrow 0$, k_7 = rate constant for the combination of methallyl radicals. Although Figure 3 may be considered to show slight convex curvature with respect to the pressure axis, indicative of a broad energy distribution in 1,2-DMTM*, a reasonably satisfactory straight line can be drawn through the data. Assuming collision diameters of 3.6 Å for Ar and 7.4 Å for dimethylpyrazoline, the slope to intercept ratio yields $k_3 \sim 9 \times 10^9$ sec^{-1} for the biradical from CDMP and $k_3 \sim 7 \times 10^9$ sec^{-1} for the biradical from TDMP. We wish to emphasize that these are only approximate values because the energy distribution in 1,2-DMTM*, as well as uncertainties in the collisional deactivation efficiency of Ar, make eq I an approximation. Nevertheless, the magnitudes of k_3 demonstrate that the 1,2-DMTM* have average energy considerably in excess of the ~70–80 kcal mol^{-1} endothermicity of reaction 3. Quantitative estimates of the energy of 1,2-DMTM* are not possible since the Arrhenius parameters for (3) are not known.

Evaluation of C would allow ϕ to be estimated from the intercepts of the Stern–Volmer plots. The data used to obtain C were $k_6 = 2.4 \pm 0.2 \times 10^{13}$ cm^3 mol^{-1} sec^{-1},[21] $k_5 = k_{5a} = k_{5b} = k_{5c} = 7.9 \times 10^{12}$ cm^3 mol^{-1} sec^{-1}, and $k_7 = 7.1 \times 10^{11}$ cm^3 mol^{-1} sec^{-1}. The estimate of k_5 was obtained from the equilibrium constant for

$$\mathrm{CH_2{=}CH{-}CH{-}(CH_3)_2} \underset{5}{\overset{-5}{\rightleftharpoons}} \mathrm{CH_3 + CH_2{\cdots}CH{\cdots}CH{-}CH_3}$$

estimated from thermochemical properties[22-24] and the Arrhenius expression for (−5).[23] The value of k_7 was estimated by using the cross-combination ratio $k_5/(k_6k_7)^{1/2} = 2$. Throssell[25] has pointed out that a normal cross-combination ratio appears valid for allyl radicals. Thus $C = 0.7$ and $\phi \sim {}^2/_3$ for both TDMP and CDMP.

Figure 4 shows the pressure dependence of TDMC/CDMC. The trend can be explained by the following scheme. Similar mechanisms have been reported for the isomerizations of dimethylcyclopropanes in methylene chemical activation systems.[26] Structural isomerization to 2MB1, 2MB2, T2P, and C2P is also included here since at lower pressures their yields increase relative to 3MB1, which is not a structural isomerization product,[27] with decreasing pressure. The onset of structural isomerization at lower pressures is in accord with the results of thermal[28] and chemical activation[26] studies, which have shown that it is 10–100 times slower than geometrical isomerization.



The fact that essentially the same TDMC/CDMC ratios are observed from CDMP and TDMP implies that K_T/K_C is the same for both reactants, or even further, that 1,2-DMTM* is the same. It should be possible to obtain K_T/K_C in the limit of high pressures, *i.e.*, liquid phase, where geometric isomerization of dimethylcyclopropanes is not significant. As a first approximation structural isomerization can be neglected since k_s and k_s' are at most ~10% of k_g and k_g'. A steady-state treatment yields eq II, which predicts

$$\frac{(\mathrm{TDMC})}{(\mathrm{CDMC})} = \frac{(K_T/K_C + 1)k_g + (K_T/K_C)\omega}{(K_T/K_C + 1)k_g' + \omega} \qquad \text{(II)}$$

that as $p \rightarrow 0$, (TDMC)/(CDMC) $\rightarrow k_g/k_g'$, and as $p \rightarrow \infty$, (TDMC)/(CDMC) $\rightarrow K_T/K_C$. Assuming that $K_T/K_C = 2.7$, the value of (TDMC)/(CDMC) obtained from the benzophenone-sensitized decomposition of *cis*- and *trans*-3,4-dimethyl-1-pyrazoline in ethanol or benzene solutions,[3] k_g and k_g', as evaluated from the more convenient form of (II) by simultaneous solution

$$[(\mathrm{TDMC})/(\mathrm{CDMC})]k_g' - k_g = \frac{[K_T/K_C - (\mathrm{TDMC})/(\mathrm{CDMC})]\omega}{(K_T/K_C + 1)} \qquad \text{(III)}$$

at any two pressures. In experiments without added Ar, and assuming collision diameters of 7.0 and 7.4 Å for dimethylcyclopropane and dimethylpyrazoline, respectively, $k_g = 1.8 \times 10^8$ sec^{-1} and $k_g' = 1.2 \times 10^8$ sec^{-1}. The zero-pressure intercept of Figure 3 is in satisfactory agreement with $k_g/k_g' = 1.5$ obtained from eq III, and both fall within the range of previously reported values, 1.47 to 2.5.[26,28]

The above values of k_g and k_g', when compared with those from methylene chemical activation systems,[26,28] allow an estimate of the average energy of chemically activated dimethylcyclopropane $\langle E^* \rangle$. In the methylene work, RRKM calculations were used to obtain average excess energies. Although such calculations were not done in this study we used the literature relationships[25] between k_g, k_g', and $\langle E^* \rangle$ to estimate $\langle E^* \rangle \sim 105$ kcal mol^{-1}. The differences in energy distribution of dimethylcyclopropanes and collisional deactivation efficiency make the estimate crude, and it

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should be considered only an approximate value. Metcalfe and Lee[12] estimated that the most probable excess energies of hot dimethylcyclopropanes resulting from Hg($^3P_1$) sensitization of 2,3-dimethylcyclobutanone are 90 kcal mol^{-1}. The higher dimethylcyclopropane excess energy from TDMP and CDMP is reflected by the ratio of pentenes to dimethylcyclopropanes at 1 Torr (no Ar) = 1.8, compared with 0.2 from 2,3-dimethylcyclobutanone.

From the measured molar extinction coefficients of CDMP and TDMP at 2537 Å, an estimated 3 to at most 6% of the decomposition products may be due to direct photolysis. The compounds 2M1B and 2M2B, both of which are formed in direct photolysis,[3,29] and which have a yield (Table I) of about 1% of N_2, are most likely formed in this way. The trace amounts of C2B and T2B, which we observe as stereospecific products as in direct photolysis, are also consistent with 2–3% of decomposition from a singlet pyrazoline. The correspondence between observed yields of products which arise through singlet pathways and the expected amounts of direct photolysis suggests this mechanism rather than $T_1 \rightarrow S_1$ intersystem crossing. Thus the Hg-sensitized decomposition probably proceeds entirely through triplet states, in contrast to the Hg(^3P)-sensitized decomposition of 2,3-dimethylcyclobutanone, which also yields triplet 1,2-DMTM biradicals but where 16–19% of the singlet products are formed as a direct consequence of energy transfer from Hg(^3P).[12]

Triplet biradicals react in significantly different ways than singlet biradicals. The cyclization of triplet 1,2-DMTM occurs at a slower rate than internal rotation, leading to loss of stereospecificity of dimethylcyclopropanes[3,10,11] in contrast to the predominant retention or inversion of configuration in singlet biradicals from the photolysis[3] or thermolysis,[14] respectively, of CDMP and TDMP. This result, presumably due to the slowness of triplet–singlet intersystem crossing (spin inversion) in triplet biradicals, is reconfirmed by the TDMC/CDMC values reported here. Another significant, but previously unexplained, difference is the olefin-producing reaction. Olefins are produced in the direct photolysis of cyclic azo compounds both in the gas and liquid phase, with little or no difference in their relative yields. But in the sensitized photolysis of cyclic azo compounds in solution olefin yields are greatly reduced compared with the gas phase. This difference in behavior can be understood in terms of decomposition reactions of hot triplet biradicals. In the vapor phase, hot biradicals are formed with sufficient energy to dissociate into alkyl- plus allyl-type radicals, unless collisionally deactivated, and olefin products are formed by radical–radical combination reactions. In condensed media rapid collisional deactivation processes predominate, producing triplet biradicals whose only reaction channel is cyclization (after spin inversion) to form cyclopropanes. The mechanism of olefin formation is apparently significantly different in singlet 1,3 biradicals. The formation of olefins in condensed media indicates that intramolecular rearrangements, perhaps H or CH_3 shifts, with low energy requirements, are possible in singlet species. An intramolecular migration route is absent in triplet 1,3 biradicals.

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π,π-Biradicaloid Hydrocarbons. The Pleiadene Family. I. Photochemical Preparation from Cyclobutene Precursors

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Abstract: Arynes add to acenaphthylene and give the cyclobutenes IV–VI. Irradiation of rigid dilute solutions of IV–VI gives the pleiadenes I–III, believed to have singlet ground states. Of these, I and II are stable only in rigid media, while very dilute fluid solutions of III survive brief warm-up to room temperature. The extreme ease with which I–III dimerize raises interesting questions concerning the nature of pericyclic reactions and these are discussed. It is proposed that orbital symmetry rules are of little use for the characterization of reactions of biradicaloid species. Irradiation of fluid solutions of IV–VI causes different and much slower reactions. A rationalization of this difference is proposed. Electronic absorption spectra of the pleiadenes I–III, as well as four other related hydrocarbons, are well accounted for by π-electron calculations. This gives credence to the novel yet not completely unexpected assignments of bands to doubly excited configurations in I and II, which can be described as borderline biradicaloids. The results are of potential conceptual importance not only in spectroscopy but also in photochemistry and even thermal chemistry (orbital symmetry rules). The calculations are also used as a basis for a discussion of other aspects of the electronic states of the pleiadene family of hydrocarbons.

We shall use the term *biradicaloid hydrocarbons* for those whose ground state, in the MO description, has two approximately nonbonding orbitals occupied by a total of two electrons, regardless of the details of the prevalent electron configuration in this state (singlet or triplet, etc.). The adjective, biradicaloid, is chosen so as to indicate close similarity to what is

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