Intramolecular Energy Relaxation in the Photodissociation of 1-Pyrazolines

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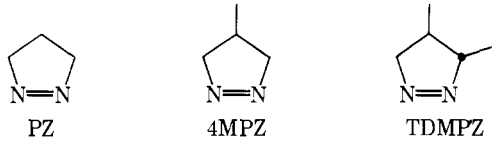
Abstract: The energy dependence and absolute magnitude of the nonradiative lifetimes of 4-methyl-1-pyrazoline and *trans*-3,4-dimethyl-1-pyrazoline excited to their first singlet ($n \rightarrow \pi^*$) state at low pressures in the gas phase do not effectively differ from the corresponding singlet state lifetimes of 1-pyrazoline. These data combined with quantum yield, product composition, and energy partitioning results indicate that on excitation by wavelengths near the onset of absorption, 1-pyrazolines dissociate principally from their first singlet excited state, likely by rupture of a single C–N bond, to form an intermediate which undergoes subsequent decomposition with random intramolecular energy relaxation of all of the available energy to the internal degrees of freedom of the reaction products. In the case of the *trans*-3,4-dimethyl-1-pyrazoline, about 40% of the decomposition does appear to arise from fragmentation of the vibrationally excited ground electronic state, but the $S_1 \rightarrow S_0$ internal conversion process is most likely a result of some recyclization of the intermediate that is formed by single C–N rupture from the S_1 state. On photolysis at shorter wavelengths in the first singlet band, methyl substitution has little or no effect on the energy partitioned to the internal degrees of freedom of the hydrocarbon fragments, and the resulting energy distribution indicates that the 1-pyrazolines fragment by simultaneous rupture of both C–N bonds.

The photochemical decomposition of 1-pyrazoline produces vibrationally excited ground electronic state cyclopropanes that contain enough of the photolysis energy such that they may undergo subsequent isomerization to olefins unless they are collisionally deactivated by the diluent.[1] Consequently, the 1-pyrazoline system offers an additional opportunity to characterize intramolecular energy relaxation in a photofragmentation reaction of a relatively complex molecule in considerable detail.[2] In a previous report[1a] it was illustrated that the singlet state lifetime of 1-pyrazoline is dependent on the energy of excitation to its first singlet ($n \rightarrow \pi^*$) state. In addition, the amount of the energy partitioned to the internal degrees of freedom of the cyclopropane fragment depended on the excitation energy in such a fashion as to indicate that the dynamics of the dissociation process is wavelength dependent.

We have now extended this work to include characterization of the energy dependence of the nonradiative lifetimes and the energy partitioning of 4-methyl-1-pyrazoline (4MPZ) and *trans*-3,4-dimethyl-1-pyrazoline (TDMPZ). The measurements were carried out to ascertain the effect of added vibrational degrees of freedom remote from the chromophore on these quantities and, in addition, to elucidate the electronic state from which pyrazolines actually dissociate when excited near the onset of absorption to their first singlet state. The results also illustrate that energy partitioning measurements can yield insight about the mechanistic details of photofragmentation reactions. They also provide an additional example of a system in which intramolecular vibrational energy relaxation of highly excited ground state polyatomic molecules is on a time scale shorter than 10^{-10} to 10^{-11} sec.

In order to make comparisons of the internal energy distribution functions of the vibrationally excited cyclopropanes formed on photolysis of 1-pyrazoline (PZ), 4MPZ, and TDMPZ, the measurements were carried out under



PZ 4MPZ TDMPZ

identical conditions of diluent deactivating collider (cyclohexane) and excitation radiation wavelength distribution. In addition, energy partitioning subsequent to 313-nm excitation was characterized at sufficiently low pressures such that collisional perturbations of the initially prepared state of the electronically excited pyrazoline were negligible. Consequently, some of the previous measurements with 1-pyrazoline[1a] and 4-methyl-1-pyrazoline[1e] were redetermined under conditions appropriate for comparison with the results contained in this report.

Experimental Section

Materials. The preparation of 1-pyrazoline and 4-methyl-1-pyrazoline have been described.[3] The *trans*-3,4-dimethyl-1-pyrazoline was prepared by the method described by Crawford and Ali.[4] The azo compounds were purified by GLC and stored at −78°. All materials were handled in greaseless vacuum lines and carefully degassed by freeze-thaw-pump cycles at 78°K. Where appropriate, precautions were taken to ensure complete mixing of the reactants in the fluorescence and photolysis cells.

Apparatus. Gas handling and pressure measurements were carried out on the previously described equipment[1a] with the exception that a Texas Instruments quartz spiral gauge was used in place of a Pyrex spiral gauge for the pressure measurements in the quantum yield and simple photolysis experiments. Product analyses were carried out on a Hewlett-Packard Model 5750 chromatograph with flame ionization detection using dimethylsulfolane, silver nitrate–dibutyl phthalate, and silver nitrate–dimethylsulfolane column combinations.

The excitation and fluorescence emission spectra were recorded by use of the Hitachi Perkin-Elmer MPF-2A spectrophotofluorimeter described earlier.[1a] The fluorescence emission lifetime measurements were measured directly by the single photon counting, time correlation technique on the apparatus that has also been described in detail.[1a,5] The fluorescence and decomposition quantum yield measurements and the simple photolysis experiments were carried out with a 200-W Osram super pressure mercury lamp in conjunction with a Bausch and Lomb high intensity grating monochromator as the excitation source. Stray radiation in the excitation beam was eliminated by use of combinations of Corning CS7-51 and CS7-54 filters. The bandpass of the excitation source was 8 nm at 313 nm and 10 nm at 334 nm. Also mounted on the Gaertner optical bench was a 0.25 m Jarrell-Ash scanning grating monochromator to view fluorescence emission. An EMI 9783B photomultiplier tube (PMT) was used to detect emission; either a RCA 1P-28 or a RCA quartz jacketed GA-As PMT was used to monitor excitation intensity during the experiments.

Results and Discussion

Radiative and Nonradiative Lifetimes. Nonradiative relaxation of the S_1 state of 1-pyrazoline primarily, if not ex-

clusively, results in dissociation.[1a] This work contains measurements of the nonradiative lifetimes (τ_{nr}) of the 1-pyrazoline system as a function of methyl substitution for hydrogen on the pyrazoline ring. The energy dependence of τ_{nr} has been suggested to result from an increase in the dissociative rate of a singlet state in addition to enhanced intersystem crossing to a dissociative triplet state as the energy of excitation is increased in the first singlet band.[1a,6] Whereas the rates of intersystem crossing to the T_1 state and internal conversion to the S_0 state are expected to be energy dependent, the effect of adding vibrational degrees of freedom by substitution of methyl for hydrogen on these rates is less predictable.[7] The effect on nonradiative relaxation would depend on how methyl substitution would perturb the promoting, optical, and accepting modes, the "effective" density of states in the lower energy manifold, and if intramolecular vibrational energy relaxation occurs in the initially prepared excited state.[8] The results from the well-studied benzene system[9a] have shown that methyl substitution can have no effect on intersystem crossing rates. The effect of methyl substitution on the rate of $S_1 \rightarrow T_1$ intersystem crossing in acetone is more likely a result of perturbations caused to the promoting mode rather than an effect due to altering the density of states in the triplet or singlet vibronic manifold.[9b]

If dissociation occurs directly from the initially excited singlet state, the effect on the dissociative rate due to increasing the vibrational complexity of the molecule will depend on the relative magnitude and the nature of the coupling between the excited singlet state, the dense vibrational manifold of the ground state, and the dissociative continuum.[10] If the extreme of constant coupling[10b] were to exist between the initial state, manifold, and continuum, the following characteristics should be observed. In the limit of weak coupling of the dense manifold of vibrational states of the ground state to the dissociative continuum, the probabilities of dissociation and emission would depend upon the density of states in the S_0 manifold; consequently, methyl substitution for hydrogen should alter the lifetime of the excited state. Conversely, if there is strong coupling of the dense manifold of vibrational states of the ground state to the dissociative continuum, the relative dissociative and radiative probabilities would be independent of the density of vibrational states in the ground state manifold. If the opposite extreme, random coupling[10a] between the initial state, the manifold, and the continuum, actually existed, the excited singlet state lifetime would always be dependent on the density of states in the manifold, and sequential behavior should be observed. Increasing the vibrational complexity of the reactant should decrease the probability of direct dissociation and increase the probability that dissociation from the vibrationally excited S_0 state will occur. The experimental results (vide infra) indicate that near the onset of absorption 1-pyrazolines dissociate directly from the S_1 state. Consequently, interpretation of the low excitation energy lifetime data given below is likely more appropriately carried out within the framework of the theoretical model for dissociation[10] rather than by use of the theoretical models that describe nonradiative relaxation by intersystem crossing.[7] It is also likely that on excitation to higher energies the relaxation processes are more complex and less able to be understood within one theoretical framework. Although the data contained in this work are not of high enough resolution to affect single vibronic excitation, the qualitative features of the data should be appropriate for interpretation.

Figure 1 illustrates the energy dependence of the fluorescence emission lifetimes of PZ, 4MPZ, and TDMPZ. The PZ data[1a] are reproduced here for comparison. In all of the measurements, the pressure is sufficiently low that the average time between collisions is at least a factor of 4 greater than the excited state lifetime.

Table I. The Emission and Nonradiative Lifetimes of *trans*-3,4-Dimethyl-1-pyrazoline (TDMPZ)

λ_{ex}, nm	Excitation bandpass, nm	Pressure, Torr	τ_F, nsec	τ_{nr},[a] nsec	τ_{nr},[b] nsec
345	1.6	0.015	380	529	458
337	0.3	0.015	308	398	346
337	0.2	0.030	296		
334	2.4	0.035	250	307	281
323	2.4	0.035	116	128	122
316	1.6	0.015	85	91	88
337	0.3	10[c]	260	322	294

[a] Assuming that the radiative lifetimes of TDMPZ and PZ are the same and both are equal to 1350 nsec.[1a] [b] Assuming that τ_r(TDMPZ) = 1.66τ_r(PZ). [c] Cyclohexane is the buffer gas.

In order to obtain the nonradiative lifetimes (τ_{nr}), we measured the relative fluorescence emission quantum yields of PZ and TDMPZ under conditions for which τ_F was well documented (334 nm excitation, 7.5 ± 0.1 Torr total pressure, cyclohexane diluent, τ_F(PZ) = 320 nsec,[1a] τ_F(TDMPZ) = 260 nsec). The result Φ_F(TDMPZ)/Φ_F(PZ) = 0.82 indicates that the radiative lifetimes, τ_r, are the same for these two molecules. The ratio of the radiative lifetimes calculated from the Strickler-Berg expression[11] and the integrated absorption coefficients indicates, however, that τ_r(TDMPZ)/τ_r(PZ) = 1.66. The approximate nature of the calculation of absolute values of radiative lifetimes is known; the cause of the discrepancy in the calculated relative radiative rates of isomers such as these examples is less well understood. The experimental results for 1-pyrazoline do indicate that τ_r is essentially independent of λ_{ex} to wavelengths as short as 316 nm.[1a] We have, therefore, displayed the data for TDMPZ in Table I using two values for τ_r. In Figure 2, we illustrate the energy dependence of the nonradiative lifetimes of the three pyrazoline systems assuming that their radiative lifetimes are the same and energy independent.

The results clearly indicate that in this low-pressure region the fluorescence emission lifetime and the nonradiative lifetime of the 1-pyrazoline system is relatively insensitive to the vibrational complexity of the reactant on excitation by shorter wavelengths in the first singlet band. Near the onset of absorption to the first singlet TDMPZ appears to exhibit a longer nonradiative lifetime than does PZ. At first glance, the results might indicate that increased vibrational complexity is actually increasing τ_{nr}, opposite to the effect predicted by the model proposed by Rice and coworkers.[10] However, an alternate explanation is possible. It is likely that the excited state equilibrium geometry of 1-pyrazoline[1a] differs somewhat from that of its ground state. The onset of the absorption spectrum of TDMPZ[12] is red shifted from that of PZ by ~10 nm, presumably because of hot band transitions. It is therefore possible that on excitation in the low energy end of the spectrum a significantly greater proportion of the TDMPZ contain less vibrational energy in their excited singlet state than they would if they were in thermal equilibrium with the bath; whereas, for PZ, the opposite is certainly true.[1a] This becomes more plausible in view of the fact that the nonradiative lifetime of PZ excited near its onset of absorption, 333 nm, and at high enough pressures such that the collisional relaxation time with the bath molecules is much shorter than its excited state lifetime, is 400 nsec,[1a] whereas under similar circumstances τ_{nr} of TDMPZ is ~300 nsec (Table I). Under these conditions, the excited state of PZ is coming into thermal equilibrium with the bath molecules by losing internal vibrational ener-

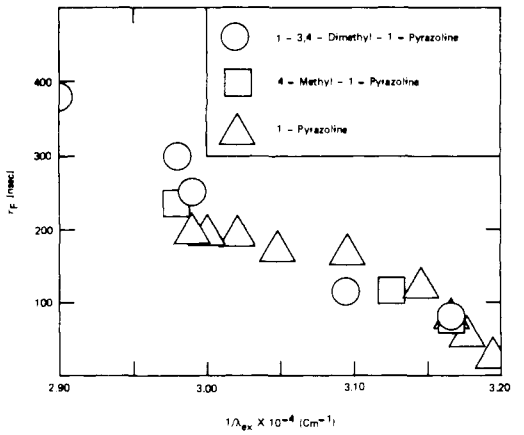


Figure 1. The measured fluorescence decay lifetimes of PZ, 4MPZ, and TDMPZ. The data for PZ from ref 1a are reproduced here for comparison.

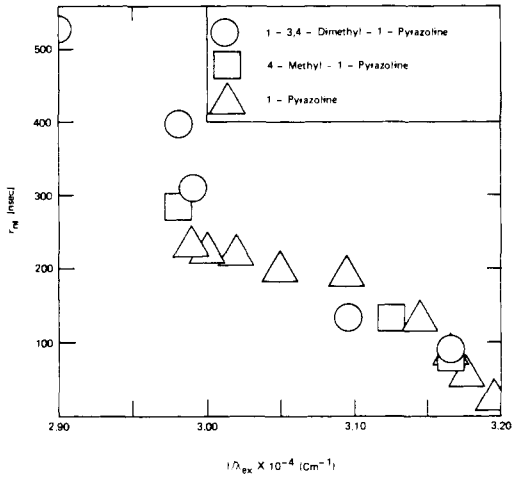


Figure 2. The nonradiative lifetimes of PZ, 4MPZ, and TDMPZ.

gy, and τ_{nr} increases, whereas TDMPZ gains internal energy and τ_{nr} decreases.

The results then indicate that increasing the vibrational complexity of the reactant does not effectively alter the nonradiative lifetime of the excited singlet state in this system. In the formulation of Rice and coworkers[10] this would imply that either the dense manifold of states belonging to the ground state is strongly coupled to the dissociation continuum, or that all vibrational modes of the ground state should not be considered as contributing to the effective density of states. Since intermolecular energy exchange with the bath molecules has the same effect on lifetimes as does changing the wavelength of excitation, when working near the onset of absorption to the first singlet, the results do indicate that intramolecular energy relaxation occurs in the excited state prior to fragmentation or emission.

Identification of the State(s) from Which Decomposition Occurs. Although product composition studies[6] indicate that the decreases in τ_{nr} at higher energies of excitation in the first singlet band of the 1-pyrazoline system could be due to enhanced intersystem crossing and dissociation from a triplet state, little information is available that will identify the electronic state(s) from which decomposition occurs when these systems are excited near the onset of absorption. RRKM calculations[13] on the lifetimes of PZ, 4MPZ, and TDMPZ at energies isoenergetic with the S_1 state indicate that if $S_1 \rightarrow S_0$ internal conversion occurs prior to fragmentation only the dimethyl isomer would be sufficiently long lived such that its decomposition could be pressure quenched by easily accessible pressures.[14] Figure 3 illus-

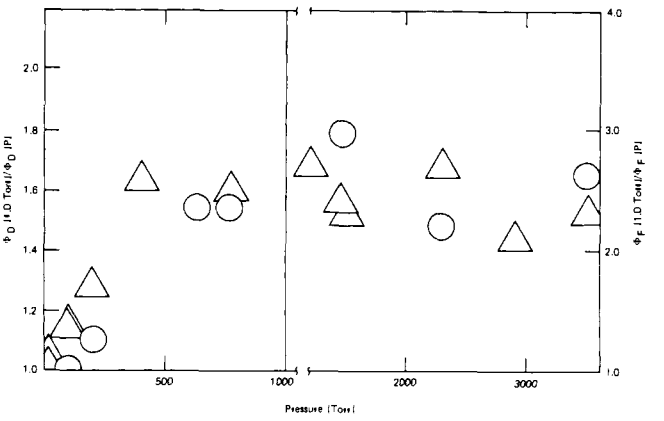


Figure 3. The pressure dependence of the relative fluorescence quantum yields (Δ) and the relative decomposition quantum yields (O) resulting from 334-nm excitation of TDMPZ. Ethane, and for a few experiments propane, was used as the pressurizing gas. The absolute magnitude of Φ_F is 0.2 at 7.5 Torr.

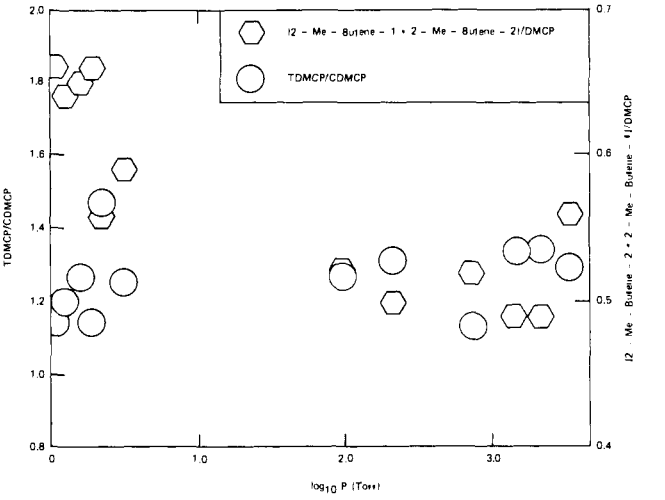


Figure 4. The pressure dependence of the product composition resulting from 334-nm photolysis of TDMPZ. At pressures ≥100 Torr ethane was used as a pressurizing gas. The lowest pressure for which product compositions are illustrated here is ~1 Torr.

trates the pressure dependence of the decomposition and fluorescence quantum yields of TDMPZ produced on 334-nm excitation of the reactant.

The decomposition quantum yield does decrease by 40% in a pressure region that is consistent with collisional deactivation of a vibrationally excited ground state TDMPZ (k_E at 90 kcal mol^{-1} for TDMPZ is 4×10^9 sec^{-1}).[14] The pressure independence of the decomposition quantum yield in the 1000 to 3500 Torr region illustrates that at least 60% of the decomposition is derived directly from an excited electronic state.

The product ratios produced by 334 nm photolysis of TDMPZ are, except at low enough pressures such that the vibrationally excited dimethylcyclopropanes isomerize, essentially pressure independent over this entire range (Figure 4). Moreover, in the pressure region in which any triplet biradicals, if formed, should be collisionally deactivated by the bath molecules, their characteristic stereochemistry and product composition is not observed.[12,15-17] The product compositions[6] (Table II) and the energy partitioning observed on photolysis of 1-pyrazolines are relatively sensitive functions of excitation energy to the first singlet state. Since pressure quenching of 40% of the decomposition quantum yield of TDMPZ results in no change in product composition, the products formed on long wavelength photolysis evidently result from a single mechanism. It seems at this

point that when the effects of vibrational frequency complexity on lifetimes, the product composition data, and the energy paritioning results (see below) are considered, the most consistent explanation of how nitrogen loss occurs is that when they are excited by wavelengths of radiation near the onset of absorption to the S_1 state, 1-pyrazolines, in addition to undergoing fluorescence emission, dissociate from the S_1 state by rupture of a single C–N bond to form an intermediate which can competitively fragment to hydrocarbon products, or recyclize to form a vibrationally excited ground electronic state 1-pyrazoline that is isoenergetic with the initially prepared S_1 state.

Direct dissociation from the S_1 state evidently also occurs when the bicyclic azo compound 2,3-diazabicyclo-[2.2.1]hept-2-ene is photolyzed in the gas phase,[18a] but nonradiative relaxation to a lower electronic state occurs prior to fragmentation when an azo compound with a less rigid ring structure, 2,3-diazabicyclo[2.2.2]oct-2-ene, is photolyzed.[18b]

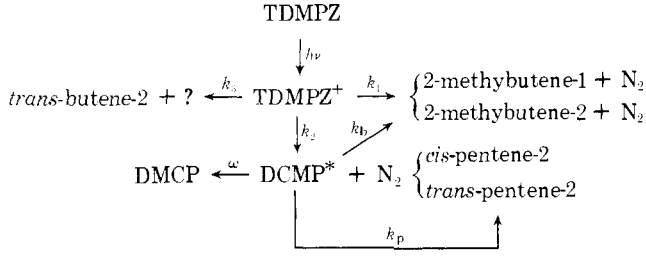
It should also be noted that the mechanism proposed here for $S_1 \rightarrow S_0$ internal conversion is very much like the mechanism that occurs in cyclobutanone photolysis:[19] that is, simple bond rupture in the excited state, and reformation of the bond to produce a vibrationally excited ground state reactant.

Less explicable at this time is the pressure dependence of the emission quantum yield of TDMPZ (Figure 3). Over this pressure range, the fluorescence quantum yield of 4MPZ is diminished by a factor of only 1.3. The emission quantum yield of TDMPZ does decrease in the same pressure range as does its decomposition quantum yield. A possible explanation is that a sufficiently high collision rate of the bath molecules with the excited state will induce internal conversion to the ground state which in turn is vibrationally deactivated. Pressure-induced dissociation has been previously proposed to occur in the photolysis of cyclic azo compounds.[18]

Intramolecular Molecular Energy Relaxation in the Fragmentation Reaction. The kinetic schemes describing the calculation of the experimental rate constant for the structural isomerization of the vibrationally excited cyclopropane and methylcyclopropane formed on photolysis of PZ[1a,b] and 4MPZ,[1c] respectively, have been described. Moreover, for these systems the relationship between the experimental rate constant and the respective energy dependent microscopic unimolecular rate constants calculated from RRKM theory and an appropriate distribution function describing the range of internal energies of the initially formed cyclopropanes has also been illustrated.[1]

For the photolysis of TDMPZ the following scheme is appropriate to use for calculating the experimental rate constants for structural isomerization of the vibrationally excited dimethylcyclopropanes (DMCP*) formed in the primary photofragmentation reaction of excited TDMPZ (Scheme I). The rate, ω, is the rate of collisional vibrational

Scheme I



deactivation of DMCP* by the bath molecules (cyclohexane for all experiments contained in this work). Because of the ambiguity in interpretation, we have omitted from consideration the geometric isomerization of the *cis*- and *trans*-DMCP* isomers. The experimental rate constants can then be calculated from

$$k_b = \omega \frac{\{[\text{2-methylbutene-2}] + [\text{2-methylbutene-1}]\}/[\text{DMCP}] - (k_1/k_2)}{1 + (k_1/k_2)}$$

$$k_p = \omega \frac{[cis\text{-pentene-2}] + [trans\text{-pentene-2}]}{[\text{DMCP}]}$$

The rate constant ratios, k_1/k_2, are obtained by either direct measurement or extrapolation to sufficiently high pressures such that there is no cyclopropane isomerization (Table II).

Table II. The Primary Product Compositions Resulting from Pyrazoline Photolysis[a]

	Excitation, nm	Propylene	Ethylene
		Cyclopropane	Propylene + cyclopropane
PZ	334	0.30 ± 0.10[b]	0.030 ± 0.008
	313	0.19 ± 0.05[c]	0.22 ± 0.05[d]
		Isobutene[e]	Propylene
		Methylcyclopropane	Total C_4 products
4MPZ	334	0.56 ± 0.04	0.039 ± 0.004
	313	0.12 ± 0.03	0.13 ± 0.01
		2-Methylbutene-1 + 2-methylbutene-2	*trans*-Butene-2
		Dimethylcyclopropane	Total C_5 products
TDMPZ	334	0.51 ± 0.03	0.027 ± 0.010
	313	0.35 ± 0.02[b]	0.066 ± 0.005

[a] The uncertainties tabulated are standard deviations of repetitive measurements or estimates of errors in extrapolation to high pressures. [b] Measurements obtained by extrapolation of experimental measurements to high pressures where no cyclopropane structural isomerization occurs. [c] See ref 1b. [d] Data from M.A. Thesis of A. Squillace, California State University, Fullerton. [e] See ref 1e for method of calculation using experimental product ratio.

The relationship between the experimental rate constants and their respective microscopic rate constants at energy E are

$$k_b = \omega \frac{\sum_E \frac{k_E^b}{k_E^b + k_E^p + \omega} f(E)}{\sum_E \frac{\omega}{k_E^b + k_E^p + \omega} f(E)}$$

$$k_p = \omega \frac{\sum_E \frac{k_E^p}{k_E^b + k_E^p + \omega} f(E)}{\sum_E \frac{\omega}{k_E^b + k_E^b + \omega} f(E)}$$

where $f(E)$ describes the distribution of internal energies of DMCP* formed in the primary process. The frequency assignments and critical energies used in calculating the various energy dependent unimolecular rate constants,[13,14] k_E, were those parameters that were previously used in interpreting the chemical activation systems.[20]

Both Gaussian and statistical distribution functions[1a,d,2a,d,21] have been used in characterizing $f(E)$ in energy partitioning experiments. The origin of the frequency assignments of the critical configurations used in calculating the sum and density of states terms in the statistical distribution function expression is contained in ref 14. The statistical distribution function is relatively insensitive to the details of the frequency assignments. The total energy available to be distributed to the degrees of freedom of the reaction products is the sum of the thermal energy of the

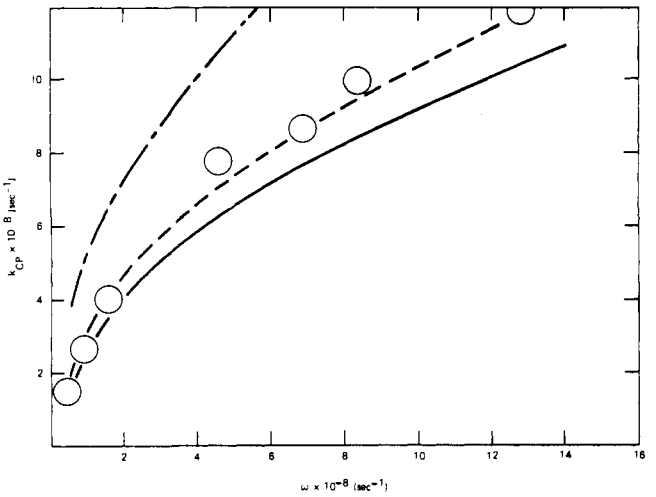


Figure 5. The experimental rate constants for the structural isomerization of cyclopropane to propylene that result from 334-nm photolysis of PZ. The solid line is a calculated curve using a statistical model for intramolecular energy relaxation (total available energy = 118.6 kcal mol^{-1}); (- - -) a calculated curve using a Gaussian distibution function for $f(E)$ with E_{mp} = 89 kcal mol^{-1} and σ = 12 kcal mol^{-1}; (- - -) a calculated curve also using a Gaussian for $f(E)$ but with E_{mp} = 93 kcal mol^{-1} and σ = 12 kcal mol^{-1}.

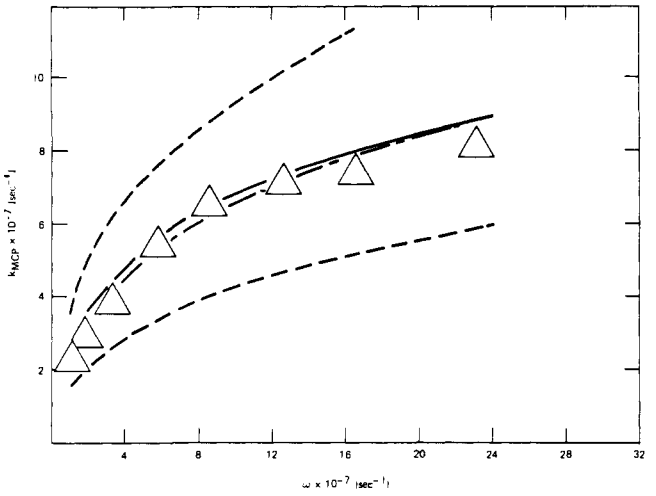


Figure 6. The experimental rate constants for the structural isomerization of methylcyclopropane formed on 334-nm photolysis of 4MPZ. The solid line is a calculated curve using a statistical model for intramolecular energy relaxation (total available energy = 119.3 kcal mol^{-1}); (- - -) calculated curves using a Gaussian distribution function for $f(E)$ with E_{mp} = 91 kcal mol^{-1} and σ = 12 kcal mol^{-1} (bottom), and E_{mp} = 99 kcal mol^{-1} and σ = 12 kcal mol^{-1} (top); (- - -) a calculated curve using a Gaussian with E_{mp} = 95 kcal mol^{-1} and σ = 12 kcal mol^{-1}.

reactant, the absorbed light energy, and the exothermicity of the reaction of 0°K (taken to be 30 kcal mol^{-1} for all of these systems[22]).

Since statistical intramolecular energy relaxation to all of the internal degrees of freedom of the hydrocarbon fragment appears to be the appropriate model for $f(E)$ when 1-pyrazolines are photolyzed by 334-nm radiation, the collisional deactivation rate, ω, for the data illustrated in Figures 5, 6, and 7 has been calculated assuming that there is statistical energy relaxation along the reaction coordinate which is partitioned to relative translation of the separating fragments.[23] This amounts to a 20 to 25% increase of ω over that value calculated assuming both collision partners have a thermal distribution of kinetic energies at the reaction temperature (296°K).

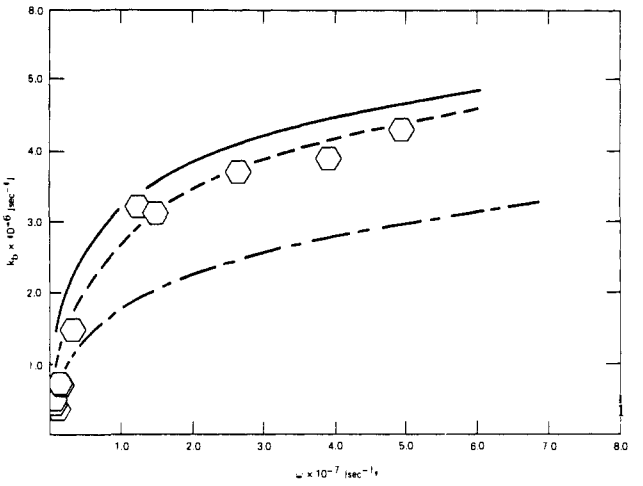


Figure 7. The experimental rate constants for the structural isomerization of dimethylcyclopropane to 2-methyl-2-butene and 2-methyl-1-butene that result from 334-nm photolysis of TDMPZ. The solid line is a calculated curve using a statistical model for intramolecular energy relaxation (total available energy = 120.1 kcal mol^{-1}); (- - -) is a calculated curve using a Gaussian for $f(E)$ with E_{mp} = 99 kcal mol^{-1} and σ = 12 kcal; (- - -) E_{mp} = 95 kcal mol^{-1} and σ = 12 kcal mol^{-1}.

Table III. The Internal Vibrational Energy Content of the Cyclopropane Fragments Produced on 334-nm Photolysis of 1-Pyrazolines

System	E_{mp}[a]	σ[a]	E_{mp}(RRKM)[b]
PZ	89	12	91
4MPZ	95	12	98
TDMPZ	99	12	103

[a] The most probable energy, E_{mp}, and the dispersion, σ, of the Gaussian distribution function that best fits the experimental data (units are kcal mol^{-1}). [b] The most probable energy of the statistical distribution function assuming that the sum of the reactant thermal energy, absorbed light energy, and exothermicity (0°K) are available for random relaxation.

The data illustrated in Figures 5, 6, and 7, and summarized in Table III, clearly illustrate that methyl group substitution at a site removed from the reaction center increased the amount of energy in the hydrocarbon fragment by essentially the amount predicted by a statistical model for intramolecular energy relaxation during fragmentation. Moreover, a statistical model in which all of the available energy is randomly distributed (thermal energy + light energy + exothermicity at 0°K) actually fits the experimental data well enough to allow one to conclude that this is the appropriate model for describing the long wavelength photolysis of 1-pyrazolines

The results are that although near the onset of absorption 1-pyrazolines undergo fragmentation predominantly from the S_1 ($n \rightarrow \pi^*$) excited electronic state, all of the available energy is randomly distributed to the degrees of freedom of the reaction products. This implies that the electronic excitation energy is converted to vibrational energy of an intermediate that lives sufficiently long such that there can be random intramolecular energy relaxation before separation of the nitrogen and hydrocarbon fragments. It is likely that the lifetime of the vibrationally excited intermediate is no longer than $\sim 10^{-11}$ sec since added pressures of ethane of up to 3500 Torr have no effect on the product composition derived from TDMPZ photolysis (Figure 4). These results are then an additional illustration of the applicability of the RRKM postulate of energy randomization to very short lived species.[2a,24]

Figure 8 illustrates the results for 313-nm photolysis of TDMPZ. We have carried out the energy partitioning mea-

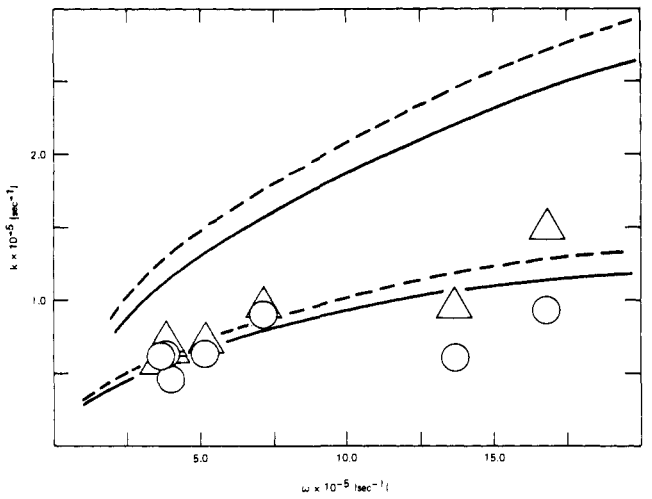


Figure 8. The experimental rate constants, k_p (△) and, k_b (○), that result from 313-nm photolysis of TDMPZ. The broken and solid curves are calculated curves for k_p and k_b, respectively, using a Gaussian distribution function for $f(E)$. The lower lines have the parameters of E_{mp} = 78 kcal mol^{-1} and σ = 12 kcal mol^{-1}, and the upper lines are using the parameters E_{mp} = 84 kcal mol^{-1} and σ = 12 kcal mol^{-1}.

surements for this system, and we have redetermined the 313-nm energy partitioning results for PZ and 4MPZ under the same conditions of excitation wavelengths and collisional deactivating bath molecules as used for TDMPZ. Moreover, the 313-nm measurements have been done at sufficiently low pressures for all three systems such that the collision rate of the excited state pyrazoline is no greater than ~0.5 of the decay rate of the excited state. We are therefore observing energy partitioning on fragmentation of the 1-pyrazoline prior to collisional perturbation of its excited state by the bath molecules. The results summarized in Table IV indicate that there is nonrandom intramolecular energy relaxation on photolysis of 1-pyrazolines by shorter wavelengths, and methyl substitution has little or no effect on the product energy distribution. The mechanism of fragmentation at shorter wavelengths of excitation is considerably changed from the mechanism that is operative at lower energies of excitation to the S_1 state.

Mechanistic Implications. The mechanism of 1-pyrazoline photolysis has been a subject of considerable study.[17,25,26] The experimental evidence[25] suggests that there may be at least two competitive pathways by which cyclopropanes are formed in these systems. One proposed mechanism is that there is simultaneous rupture of both C-N bonds to form a trimethylene biradical intermediate and nitrogen.[17] Another explanation of the mechanism is that there is sequential C-N bond rupture, which after rupture of the second C-N bond results in formation of a biradical intermediate and nitrogen. Studies with bicyclic pyrazolines support the sequential C-N bond rupturing mechanism.[25,26] In those systems, there is evidence that subsequent to initial rupture of a single C-N bond there is also formation of a diazoalkene which decomposes to nitrogen and a carbene.[25] In thermolysis, pyrazolines, as well as acyclic azo compounds,[27] are also believed to fragment in a stepwise fashion.[28]

Consideration of the geometric changes that must occur when 1-pyrazolines[29] fragment to cyclopropanes and nitrogen[30] indicates that simultaneous rupture of both C-N bonds should result in a considerable amount of the available energy being partitioned to the nitrogen vibration mode (20-60 kcal mol^{-1}, depending on the N-N bond length as the nitrogen and hydrocarbon fragments separate). Photolysis near the onset of absorption to the first singlet state results in a random distribution of the available energy to the degrees of freedom of the reaction products. It appears that when excited to lower energies in the first singlet state 1-pyrazolines decompose by first rupturing a single C-N bond, thereby allowing relaxation of the N-N bond while the fragments are still intact. The pressure dependent decomposition quantum yields of TDMPZ indicate that the intermediate formed subsequent to breaking a single C-N bond can also recyclize to some extent to form a vibrationally excited ground state pyrazoline.

Table IV. The Internal Vibrational Energy Content of the Cyclopropane Fragments Produced on 313-nm Radiation of 1-Pyrazolines[a]

System	E_{mp}	σ	E_{mp}(RRKM)
PZ	78	12	95
4MPZ	≤82	12	103
TDMPZ	78	12	108

[a] See footnotes to Table III.

Excitation at shorter wavelengths, where τ_F is becoming short and the decomposition quantum is approaching unity, results in nonrandom energy relaxation to the reaction products. Less energy appears in the hydrocarbon fragment, and the internal energy distribution function is independent of methyl substitution on the ring. It is of interest to note that vinyl substitution on the ring[1d] also does not affect the product energy distribution to any degree that might indicate a mechanistic change in fragmentation, or any effect of added degrees of freedom on intramolecular energy relaxation. That there is a large difference between the total available energy and the energy that appears in the internal degrees of freedom of the hydrocarbon fragment, 47 kcal mol^{-1}, is likely a result of nitrogen being produced with a large amount of vibrational energy. The most plausible explanation is that when excited to higher energies in the first singlet state 1-pyrazolines undergo fragmentation by simultaneous C-N bond rupture on a time scale short relative to the rate of intramolecular vibrational energy relaxation.

Acknowledgment. We wish to thank Professor E. K. C. Lee for extending his hospitality in allowing F.H.D. the use of the facilities in his laboratory at the University of California, Irvine in order to carry out the fluorescence lifetime measurements. Professor Lee and Professor Colin Steel of Brandeis University also provided helpful comments concerning this work. We also wish to thank Ms. Kerry Wadey for aid with the computer calculations. This work was supported in part by the National Science Foundation.

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Solution and Complexing Studies. I. Gas–Liquid Chromatographic Investigation of Supposed Complexing Systems

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Abstract: GLC measurement of the infinite dilution liquid–gas partition coefficients (K_R) of chloroform, 1,2-dichlorethane, benzene, toluene, ethylbenzene, and the three xylenes in each of the electron acceptor (A)/inert solvent (S) systems, di-*n*-octyl ether/*n*-heptadecane and di-*n*-butyl tetrachlorophthalate/squalane over the whole range $x_A = 0$–1 reveals that plots of K_R against molarity (C_A) or volume fraction (ϕ) of A are strictly linear. Thus $K_R = \phi_A K_{R(A)}^0 + \phi_S K_{R(S)}^0$ where a K^0 designates a liquid–gas partition coefficient for a solute at infinite dilution in either pure A or S. Since the conventional GLC equation for the stability constant (equilibrium quotient) of a 1:1 complex (K_1) is $K_R = K_{R(S)}^0(1 + K_1 C_A)$, it follows that $K_1 = \bar{V}_A(K_{R(A)}^0 - K_{R(S)}^0)/K_{R(S)}^0$ where $\bar{V}_A$ is the molar volume of A. It is possible through this equation to calculate nominal stability constants from data relating solely to pure A and S. The remarkable generality of this observation is demonstrated by comparison of calculated and published data for more than seventy charge-transfer or hydrogen-bonding systems described in the literature. The general equation described above can be derived on the basis of any model of solution in which A and S do not interact. Thus, for example, they can be immiscible, or ideal, or nonideal provided the interaction of a solute with A in S is the same as in pure A. Since there is spectroscopic evidence of interaction of the solutes used with both pure A components and, further, none of the solutes provide ideal solutions in either the A or S components used, it is suggested that in the solvent mixtures used there is a high degree of aggregation such that on dilution of A by S the local concentration of A is still that of the pure liquid. Whatever the explanation, it is clear that the conventional dilution approach to determination of stability constants, at least in systems such as these, does not provide a meaningful measurement of K_1. Further, the solvent systems used show such conformity of behavior, which we are unable to describe on the basis of existing theories, that a re-evaluation of theory is indicated.

Evidence for the existence of weak molecular complexes can be derived inferentially via studies based on a variety of techniques, but quantitative evaluation of the associated stability (formation) constants or, more correctly, equilibrium quotients, almost always involves the use of partition or spectroscopic (uv-visible or NMR) data deriving from experiments involving variation of component concentrations. More than 10 years ago the formal analogy between the classical partition method and an alternative GLC approach was pointed out and placed on a quantitative basis[1-3] and shortly afterwards[4] a general theory of the GLC approach to complexing studies was developed. These observations catalyzed interest in the GLC method since among its numerous practical advantages[4] it is ideally suited for nonaqueous systems, and weak complexing largely involves organic systems of very limited aqueous solubility.

With few exceptions, GLC studies have been concentrated on reactions of the type

$$D(g) \overset{K_{R(S)}^0}{\rightleftharpoons} D(l)$$

$$D(l) + A(l) \overset{K_1}{\rightleftharpoons} AD(l)$$