# Barriers to Decomposition of Ground and Excited State 1-Pyrazolines

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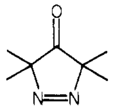
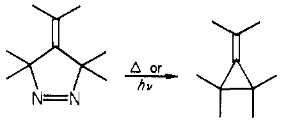
**Abstract:** 3,3,5,5-Tetramethyl-4-isopropylidene-1-pyrazoline (**2**), 3,3,5,5-tetramethyl-1-pyrazoline (**3**), and 3-acetoxy-3,5,5-trimethyl-1-pyrazoline (**4**) exhibit barriers to triplet sensitized deazatization of about 7 kcal mol$^{-1}$. Because these barriers are in general higher than those found for direct irradiation, loss of nitrogen from the singlet state is more efficient than from the triplet state. Quantum yields and singlet lifetimes determined here provide rate constants and partitioning ratios for both excited states; however, it is not yet clear whether radiationless decay of the singlet state proceeds via the triplet. The heat of formation of gaseous **2** has been measured as 18.2 ± 0.6 kcal mol$^{-1}$. This figure is used to show that the high thermal stability of **2** is due to severe steric interactions which develop in the transition state for stepwise deazatization.

Following their clever but unsuccessful attempt to prepare a cyclopropanone from compound **1**, Corey and Mock[1] found that analogue **2** could be converted thermally or photochemically to the isopropylidenecyclopropane. The importance of compounds similar to **2** as trimethylenemethane precursors has led a number of workers[2-9] over the past 15 years to investigate the decomposition of such pyrazolines.



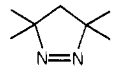
**1**



**2**

We have reported previously[10] that the singlet excited state of **2** encounters a sizable barrier to decomposition in acetonitrile and that **2** undergoes thermal deazatization with great difficulty. Presently, we show that (a) the barrier to triplet-sensitized loss of nitrogen from **2** and two other pyrazolines is at least as large as in the singlet state, resulting in lower triplet quantum yields, (b) the singlet lifetime of **2** varies more than fivefold over a 50 °C temperature range, and (c) the unexpectedly high thermal stability of **2** is not due to ground state stabilization but is instead attributable to steric interactions which develop in the transition state.

Quantum yields for benzophenone-sensitized deazatization of pyrazolines **2**–**4** are shown in Table I. These data were fitted to eq 1,[11] giving activation energies for excited state decomposition ($\Phi_r$ = nitrogen yield, $k_d$ = radiationless decay rate constant).



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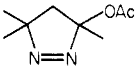

**4**

$$\ln (1/\Phi_r - 1) = \ln (k_d/A) + E_a/RT \qquad (1)$$

Taking advantage of the intense and long-lived fluorescence of **2**, we studied its lifetime $\tau_f$ as a function of temperature. The results are included in Table II along with nitrogen quantum yields ($\Phi_r$) in benzene and fluorescence quantum yields ($\Phi_f$) in acetonitrile. Fitting the experimentally measured $\Phi_r$'s to eq 1 (where $k_d$ now includes fluorescence) gave $E_a$ = 6.1 ± 0.6 kcal mol$^{-1}$ and an intercept of −10.7 ± 0.9. These values were then used to derive

Table I. Benzophenone-Sensitized Deazatization of 1-Pyrazolines

| compd | $\Phi_r$[a] (temp, °C) | $E_a$(sens)[b] | $E_a$(direct)[b] |
|---|---|---|---|
| **2** | 0.034 (6.7), 0.088 (26.3), 0.231 (56.0), 0.346 (76.2) | 7.6 | 6.1,[c] 8.7[d] |
| **3** | 0.107 (6.5), 0.225 (25.1), 0.498 (55.0), 0.652 (75.4) | 7.8 | 0[e] |
| **4** | 0.081 (6.7), 0.148 (26.3), 0.338 (56.0), 0.502 (76.2) | 6.8 | 2.2[e] |

[a] 0.05 M pyrazoline in benzene with 366-nm irradiation. [b] kcal mol$^{-1}$. [c] Calculated from eq 1. [d] Using the $\tau_f$ values and calculated $\Phi_r$'s in Table II. [e] Reference 10.

Table II. Temperature-Dependent Excited-Singlet Parameters for **2**

| temp, °C | $\Phi_r$[a] | $\Phi_f$[b] | $\tau_f$,[c] ns | $k_r$,[e] $10^6$ s$^{-1}$ |
|---|---|---|---|---|
| −78 | (0.0062) | | 570[d] | 0.011 |
| −6.1 | | 0.30 | | |
| 5.3 | (0.41) | | 207 | 2.0 |
| 6.3 | 0.41 | | | |
| 12.9 | (0.49) | | 156 | 3.1 |
| 16.7 | (0.52) | | 147 | 3.5 |
| 22.9 | (0.58) | | 117 | 5.0 |
| 25.4 | | 0.15 | | |
| 30.0 | 0.66 | | | |
| 32.0 | (0.65) | | 84 | 7.7 |
| 40.0 | (0.71) | | 66 | 10.8 |
| 44.9 | | 0.08 | | |
| 51.7 | (0.77) | | 39 | 19.7 |
| 59.9 | 0.80 | | | |
| 60.2 | | 0.05 | | |

[a] Values in parentheses are calculated as described in the text. The others are the average of three runs in benzene. [b] In Acetonitrile from ref 12. [c] Average of two values in benzene. [d] In toluene. [e] Rate constant for singlet deazatization.

Table III. Nitrogen Quantum Yields in Benzene at 25 °C

| compd | $\Phi_r$-(direct) | sensitizer | triplet energy[a] | $\Phi_r$(sens) |
|---|---|---|---|---|
| **2** | 0.59[b] | xanthone | 74.2 | 0.036 |
| | | *p*-MAP[c] | 72.4 | 0.043 |
| | | acetophenone | 73.6 | 0.054 |
| | | benzophenone | 68.5 | 0.081 |
| | | thioxanthone | 65.5 | 0.056 |
| | | 2-acetonaphthone | 59.3 | 0.0044 |
| | | benzil | 53.7 | 0.0083 |
| **3** | 0.98 | benzophenone | 68.5 | 0.23 |
| **4** | 0.50 | benzophenone | 68.5 | 0.14 |

[a] kcal mol$^{-1}$. [b] The quantum yield of $N_2$ was shown to equal that for pyrazoline disappearance. [c] *p*-Methoxyacetophenone.

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$\Phi_r$ at the temperatures where $\tau_f$ was measured. Finally, deazatization rate constants ($k_r = \Phi_r/\tau_f$) were fit to the Arrhenius equation, yielding the more reliable values of $E_a = 8.7$ kcal $mol^{-1}$ and $A = 1.4 \times 10^{13}$. This procedure exploits the fact that $\tau_f$ has a far stronger temperature dependence than $\Phi_r$ (cf. Table II). Unfortunately, it cannot be applied to azo triplet states because they do not emit.

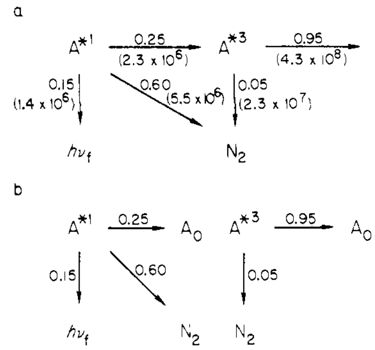
Quantum yields for direct and sensitized deazatization of **2**, **3**, and **4** are summarized in Table III. To investigate the source of the anomalously low sensitized $\Phi_r$ values for **2**, we have performed independent nanosecond laser transient absorption studies of the quenching of benzophenone triplets by **2** in benzene solution at 23 °C. In these measurements, a 355-nm pulse generated triplet benzophenone molecules via rapid intersystem crossing from the $^1$n,$\pi$* state. A time-delayed 532-nm laser pulse was then used to monitor the decay of the benzophenone $T_1 \rightarrow T_n$ visible absorption. The variation of this exponential decay rate with the concentration of **2** gave a value of $5.7 \times 10^8$ $M^{-1}$ $s^{-1}$ for the triplet-quenching constant. This indicates that the photosensitization experiments were indeed performed under conditions of efficient energy transfer and that the low photochemical quantum yields reflect an inherent property of the triplet state of **2**. Using the data of Table III, we estimate that the energy of this triplet is in the range 59–65 kcal $mol^{-1}$, comparable to the value reported for a related 4-alkylidene-1-pyrazoline.[4] The observation that $k_q$ is below the diffusion-controlled limit is most likely a manifestation of steric hindrance to energy transfer, because the experimental value is close to that found for azo-*tert*-butane.[13]

Comparing $E_a$'s calculated by using eq 1, we find that the barrier is lower for direct irradiation than for triplet sensitization, in accord with expectations based upon the energy surfaces for one-bond homolysis.[10] The magnitude of the difference varies considerably, compounds **2** and **3** representing the two extremes. Although the reasons for the observed variations in $E_a$ are obscure, the present data indicate that $\Phi_r$ of pyrazolines is not enhanced by triplet sensitization. Whether retro-1,3-dipolar cycloaddition to a diazo compound[14] can be avoided by this technique remains to be seen.

Equation 1 predicts that $\Phi_r$ for **2** will be 0.0062 at −78 °C so that fluorescence and radiationless decay are the only significant singlet processes occurring at this low temperature. The reciprocal of the lifetime (Table II) then gives the sum of these two rate constants as $1.8 \times 10^6$ $s^{-1}$. Since the intercept of eq 1 for the triplet data (−10.34) equals ln ($k_d/A$), one can calculate a triplet decay rate of $4.5 \times 10^8$ $s^{-1}$ by assuming that both decomposition modes possess the $A$ factor deduced above ($1.4 \times 10^{13}$). This assumption is not unreasonable because the different product ratios[6] from direct and sensitized photolysis of deuterium-labeled **2** show that the singlet state does not decompose to a triplet trimethylenemethane; thus, both modes are spin allowed. The short lifetime of triplet **2** (2 ns) typifies the remarkable ability of triplet azoalkanes to dispose of their energy.

The photochemical parameters measured for **2** allow construction of Scheme I, which shows two ways in which the excited states of **2** might partition themselves. In the first of these, a, $A^{*1}$ reaches the ground state by way of $A^{*3}$ whereas in the second it decays directly. Unfortunately neither quantum yields nor product studies[6] can distinguish easily between these possibilities because the triplet contribution to deazatization is so small in Scheme Ia. The rate constant for intersystem crossing ($k_{isc}$) is $2.3 \times 10^6$ $s^{-1}$ if Scheme Ia is correct and must be less than this figure if Scheme Ib makes any contribution. This slow value of $k_{isc}$ suggests[15] that the $^3(\pi,\pi^*)$ state lies above the $^1(n,\pi^*)$ state reached by absorption, in accord with several theoretical calculations.[16]

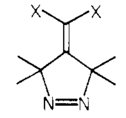
Scheme I. Partitioning of Excited States of 2 at 25 °C[a]



[a] Rate constants ($s^{-1}$) are shown in parentheses.

The structural similarity between **2** and **3** invites comparison of their rate constants for nitrogen loss, both from the excited singlet state and thermally. $k_r$ for **3** is $1.4 \times 10^{8}$[17] $s^{-1}$ whereas that for **2** is $6 \times 10^6$ $s^{-1}$. Thus the isopropylidene group lowers the rate of singlet state deazatization by a factor of 23 at 25 °C. A correlation between ground and excited state photolability has been noted[10,11] and these two compounds fall in the right order. The remaining question is, why is **2** more stable thermally than **3**?

As pointed out by one of us,[7] **2** ought to decompose thermally some $10^5$ faster than **3** because the resonance stabilization energy of trimethylenemethane is large. Bushby and Pollard[6] found only a small rate acceleration by substituents X in **5** and they suggested that initial C–N bond cleavage generates a bis-orthogonal rotamer of trimethylenemethane. Although this idea rationalizes a lack of acceleration, it does not explain why **2** thermolyzes 70 times *slower* than **3**. We sought to assess the importance of ground state stabilization and have therefore determined the heat of formation ($\Delta H_f$) of **2**. A 5-g sample was prepared 99.97% pure by recrystallization from methanol at −78 °C followed by sublimation. Five runs gave a heat of combustion of 1555.3 ± 0.6 kcal $mol^{-1}$ leading to a $\Delta H_f$ of −0.1 kcal $mol^{-1}$ for the crystalline material. Adding this value to the heat of vaporization[18] gave $\Delta H_f(g) = 18.2 \pm 0.6$ kcal $mol^{-1}$ (95% confidence level).



**5**

This figure is meaningful only by comparison with a model compound. An estimated $\Delta H_f$ for **2** can be derived from the known[7] $\Delta H_f$ of **3** by subtracting the group value for a $CH_2$ group (−4.93 kcal $mol^{-1}$) and adding an isopropylidene group (0.48 kcal $mol^{-1}$),[19] giving a total correction of 5.4 kcal $mol^{-1}$. The estimated value (14.8 kcal $mol^{-1}$) is 3.4 kcal $mol^{-1}$ below $\Delta H_f$ of **2**, showing that **2** is strained instead of stabilized. Combining these $\Delta H_f$'s with the known $\Delta H^{\ddagger}$ for thermolysis[5-7] and estimated $\Delta H_f$'s of the products allows us to construct Figure 1. To estimate $\Delta H_f$ of the transition state for **2**, we add the 5.4 kcal $mol^{-1}$ correction to $\Delta H_f$ of the transition state of **3**. The result, 53.9 kcal $mol^{-1}$, is 9.2 kcal $mol^{-1}$ below the observed value of 63.1 kcal $mol^{-1}$. The high transition state energy for **2** suggests that severe steric interactions develop between the cis alkyl substituents on the olefin as one C–N bond begins to break.[25] Crawford and Chang[20] have

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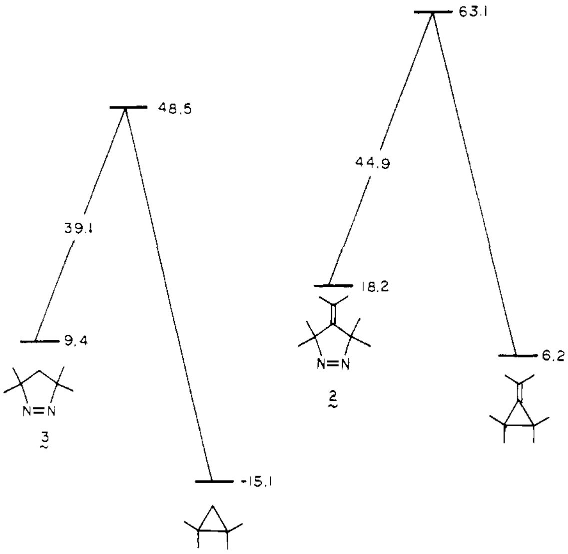
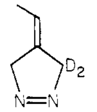
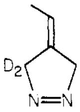


**Figure 1.** Enthalpy diagram for pyrazoline thermolysis. Values given are heats of formation and activation in kcal $mol^{-1}$.

recently arrived at the same conclusion based on secondary deuterium isotope effects in compounds **6** and **7**. Bond breaking



6



7

was found to occur preferentially at the $\alpha$ carbon anti to the methyl group. Steric repulsion between the methyl groups in **2** is inevitable in the one-bond cleavage mechanism unless opening of the C—N=N angle is the only manifestation of bond breaking. This is unlikely, however, because the diazenyl radical is calculated to be bent.[21] Any twisting[22] about the ring C–C bonds during homolysis will further increase methyl–methyl repulsion. Since the force constant for $sp^3$–$sp^2$–$sp^3$ bending is the same as that for $sp^3$–$sp^3$–$sp^3$,[23] strain relief at the expanding angle of C-4 is about the same for **2** and **3**. However, the strain introduced by a *tert*-butyl group cis to a methyl on an olefin is 4 kcal $mol^{-1}$ and is expected to vary sharply with distance.[19] The observation[20] that 4-methylene-3,3,5,5-tetramethyl-1-pyrazoline decomposes at nearly the same rate as **3** lends support to this explanation because *cis-tert* hydrogen interactions are negligible (on the order of 0.5 kcal $mol^{-1}$, an alkene gauche correction). Finally we note, in agreement with Crawford,[20] that simultaneous two-bond cleavage is not appealing because nitrogen should be able to depart from **2** without forcing the methyl groups together and raising the energy.

In summary, the deazatization quantum yield of several 1-pyrazolines seems to be governed by an activation barrier in the excited state potential energy surfaces. The long singlet lifetime of **2** (~100 nsec) contrasts with its short estimated triplet lifetime (~2 nsec), making it difficult to assess the role of the triplet state. The 4-isopropylidene group unexpectedly inhibits deazatization of both the ground and excited singlet state, an effect attributed to methyl–methyl interactions present in the transition state for one-bond C–N cleavage.

## Experimental Section

All of the compounds studied here have been reported previously.[1,5] The solvent in all cases was reagent grade benzene which had been irradiated with chloranil, chromatographed on alumina, and distilled from $P_2O_5$. Quantum yields were determined in a photochemical merry-go-round using a Hanovia 450 W medium pressure mercury arc and filters to isolate the desired wavelength (313 or 366 nm). Solutions were degassed and sealed in quartz tubes, nitrogen evolution being measured with a Toepler pump and gas buret. The initial absorbance was arranged to be about 3 and conversions were kept below 20%. A solution of 2,3-diazabicyclo[2.2.1]hept-2-ene plus benzophenone was employed as the actinometer ($\Phi_r$ = 1.0).[7] The temperature of the merry-go-round water bath was regulated to ±0.1 °C with an RFL Industries proportional temperature controller.

Fluorescence lifetimes were determined with a nitrogen laser and a Tektronix 7912 transient digitizer. The sample was contained in a jacketed cell attached to a Lauda K-2/RD circulating bath and the temperature was monitored with a Digitec 590TC type T thermocouple made by United Systems Corp. Nitrogen was bubbled through the benzene solution continuously throughout the course of the experiment.

Bomb calorimetry was carried out as described previously.[24]

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**Registry No. 2**, 55204-47-2; **3**, 2721-31-5; **4**, 37696-47-2.

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