Photochemically Activated Cyclopropane Produced from the Photolysis of 1-Pyrazoline

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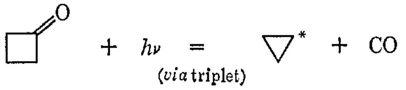
Abstract: 1-Pyrazoline has been photolyzed in the gas phase with light of 3130 Å. Cyclopropane, propylene, and ethylene were among the products. The ratio of propylene to cyclopropane depended on the pressure; the ethylene was only slightly dependent. Propylene is formed from at least two sources, only one of which is pressure dependent. The photolysis has been interpreted in terms of a singlet biradical trimethylene which forms "hot" cyclopropane and can then isomerize to propylene or be deactivated to cyclopropane. The "hot" cyclopropane is not monoenergetic but has energy distributed around 75 kcal/mole.

During the last 10 years many chemically activated reactions[2] have been studies, especially in conjunction with tests of the Marcus formulation of the Rice, Ramsperger, Kassel (RRKM) theory. In these reactions the energy left in a product is in excess of that needed for the product to undergo subsequent unimolecular reaction. The energies of these excited products are determined by the ways they are made. In principle, photochemical activation, in which this energy is acquired from the excess photon energy, can give species with ranges of energy limited only by the absorption bands of the parent molecule. The energy of the primary product can be varied by altering the wavelength of photolysis. In practice, the excess photon energy from the primary reaction has been found to be distributed over the products so that the species formed have a range of energies shown in the systems eq 1,[3–6] 2,[7] and 3.[8]



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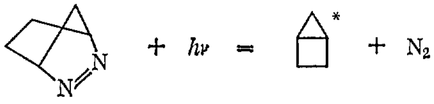

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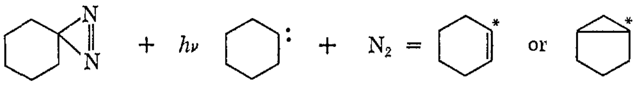

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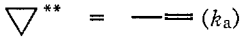
Cyclopropane from the photolysis of cyclobutanone[3–6] possesses enough energy to isomerize to propylene unless deactivated by collisions. The reactions have been interpreted as



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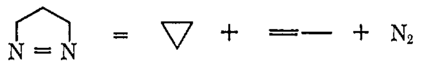
If (a) the strong collision assumption applies, as has been found to be valid up to 100 kcal/mole of energy for reasonably complex deactivating gases,[9] and (b) the cyclopropane molecules are formed within a narrow energy range, then a plot of propylene/cyclopropane *vs.* reciprocal pressure should give a straight line of slope k_a/k_s where k_a = average rate constant for isomerization and k_s = rate of deactivation of the "hot" cyclopropane per Torr. This kind of relationship holds for chemically activated systems, but it does not hold for photoactivated ones.[3–8] The curvature has been attributed to a broader spread of energies in photoactivation caused by either the range of wavelength used for photolysis[8] or the partitioning of the excess energy between the initial fragments.[3–7]

For cyclobutanone, the partitioning of the excess photon energy has been interpreted in terms of a statistical distribution[4] between the number of energy levels available in the two fragments. In the 2,3-diazobicyclo[2.2.1]hept-2-ene photolysis,[7] the spread of energies has been explained in terms of a Gaussian function for the number of molecules formed at each energy. The upper limit of the energy available was determined by the thermochemistry and photon energy.

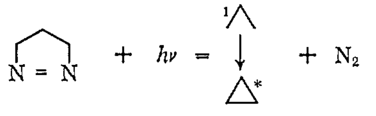
1-Pyrazoline decomposes thermally[10] through a trimethylene intermediate to propylene, cyclopropane, and nitrogen (eq 6). Photolysis[11] of 1-pyrazoline also



(6)

$$\log k\,(\mathrm{sec}^{-1}) = 15.9 - (42{,}400/2.3RT)$$

yields propylene, cyclopropane, and nitrogen *via* a singlet trimethylene intermediate which undergoes rapid ring closure to cyclopropane (eq 7).



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Experimental Section

1-Pyrazoline was prepared according to the method of Crawford, Mishra, and Dummel[12] and purified by gas chromatography using a 10-ft column of 20% dinonyl phthalate on 30–40 mesh Supasorb. (We are grateful to Professor Crawford for an initial supply of this material.) The uv spectrum of 1-pyrazoline has an absorption band between 280 and 340 MHz with a maximum at 340 MHz.

The work was carried out in a conventional high-vacuum system fitted with greaseless stopcocks. Typically the experimental procedure was as follows. The Pyrex cell was filled with 5 Torr of 1-pyrazoline and 50 Torr of nitrogen at room temperature. After an 8-min photolysis with a 125-W medium-pressure mercury arc, the reaction mixture was transferred to a pump-down trap for injection into the gas chromatograph (Gas Chromatography Ltd. flame ionization detector). Separation of the products was achieved with a 6-ft column of 30–60 mesh Phase Sep P maintained either at room temperature or temperature programmed. Monochromatic radiation was supplied by a Bausch and Lomb grating monochromator.

Results and Discussion

Photolysis of 1-pyrazoline in the gas phase gave ethylene, propylene, and cyclopropane as products. The amount of ethylene produced was much less than propylene or cyclopropane. With 5 Torr of pyrazoline the yields (based on total hydrocarbon products) were 8, 41, and 51%, respectively. The ratio of propylene to cyclopropane varied with the total pressure while the ratio of ethylene to propylene plus cyclopropane was only slightly dependent on pressure.

A limited pressure range is available at room temperature using only pure 1-pyrazoline owing to its low volatility; consequently, the higher pressure region was studied by adding inert gas. Nitrogen was established to have a deactivating efficiency of 0.1 (compared to pyrazoline) by observing that 50 Torr of nitrogen added to 5 Torr of pyrazoline gave the same propylene to cyclopropane ratio as 10 Torr of pyrazoline. (In the thermal isomerization of cyclopropane,[13] nitrogen has been found to be 0.07 as efficient in transferring energy *to* cyclopropane as cyclopropane itself.) Butane was found to have an efficiency of ~1 in the same way.

The ratio of propylene to cyclopropane *vs.* the reciprocal effective pressure of nitrogen and butane is shown in Figure 1. The features of this graph which merit comment are the following.

(1) The plot is not linear and suggests that the intermediate cyclopropane is formed with a range of energies.

(2) An appreciable amount of propylene was detected even in the presence of 200 Torr of butane. Crawford's liquid-phase ratio of propylene to cyclopropane (0.18) is shown in Figure 1 as the point at infinite pressure.[11a] Since no cyclopropane will isomerize at infinite pressure, an additional source of propylene is inferred.

(3) Figure 1 also shows the ratio of propylene to cyclopropane obtained when oxygen is the bath gas (oxygen was assumed to have the same efficiency as nitrogen, 0.1). The ratio of propylene to cyclopropane is shifted to lower values compared to the nitrogen and butane case. If the curve obtained with oxygen is assumed to have zero intercept at infinite pressure, the amount of propylene formed by the secondary source can be compared with the total C_3 products from the major process.

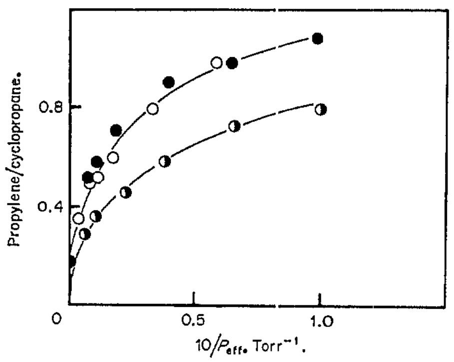
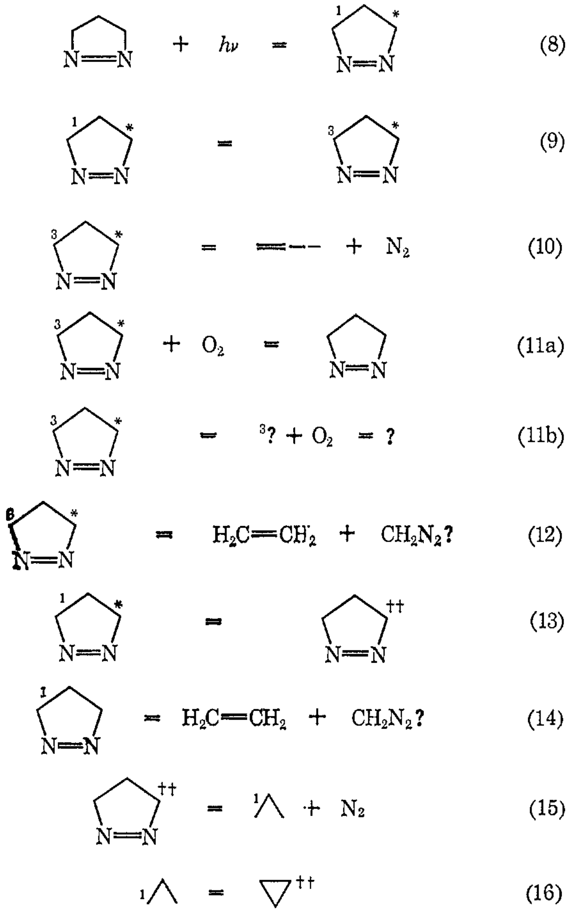


Figure 1. Propylene/cyclopropane *vs.* reciprocal pressure. Point at infinite pressure is the result obtained by Crawford[11] in solution (personal communication). The effective pressure for nitrogen and oxygen was calculated using 1/10 for the collision efficiency. Butane taken to have an efficiency of 1: ●, nitrogen; ○, butane; ◑, oxygen.

The secondary propylene is taken as the difference between the two curves in Figure 1. These results for various pressure are shown in Table I. The extra propylene is seen to be essentially constant over a considerable pressure change and must be formed by a pressure-independent process.

The mechanism for the photodecomposition of 1-pyrazoline can be interpreted in terms of steps 8–16,



followed by eq 4 and 5. The formation of the pressure-independent propylene is shown in the mechanism to originate through reactions 9 and 10 from triplet pyr-

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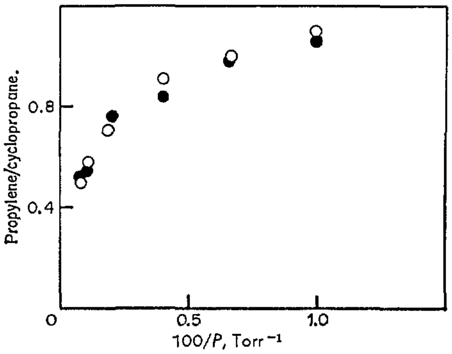


Figure 2. Variation of propylene/cyclopropane as a function of reciprocal nitrogen pressure in the photolytic decomposition of 1-pyrazoline: ○, full mercury arc; ●, monochromatic radiation of wavelength 3126 Å. $I_{\text{arc}}/I_{\text{monochromatic}}$ = *ca.* 2000.

azoline. The effect of oxygen on the propylene yield is what would be expected if oxygen were acting as a triplet quencher and accounts for reactions 11a and 11b in the mechanism. A mass balance of reactant and products failed to disclose any trapping of radical fragments by oxygen, so oxygen probably acts as a physical quencher rather than as a chemical one.

Table I

Pressure (Torr)	— = from secondary source[a]/ — = plus *c*-Pr from *c*-Pr* [b]
50	0.16
93	0.15
200	0.16
450	0.17
1950	0.14
∞ [c]	0.18

[a] "Extra" amount of propylene formed with nitrogen or butane as the bath gas. [b] Amount of propylene plus cyclopropane (*c*-Pr) formed with O_2 as the deactivating gas. [c] Reference 11a.

Ethylene is shown as being formed both from singlet and triplet pyrazoline for the following reasons. When nitrogen was the bath gas, the yield of ethylene decreased from 8 to 6% over a 40-fold pressure increase. Addition of 25 Torr of oxygen halved the yield to 4%. Addition of a further 1525 Torr of oxygen had no further effect on the yield. Thus it is likely that both triplet and singlet pyrazoline are precursors to ethylene formation. Ethylene was always a minor product compared to C_3 hydrocarbons as is found in the photolysis of alkylpyrazolines.[11]

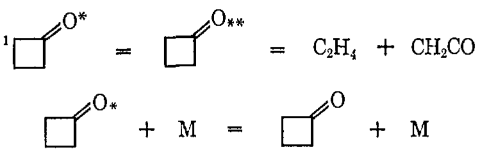
The pressure-dependent formation of propylene and cyclopropane probably occurs from the vibrationally excited ground state (rather than an electronically excited state) formed by internal conversion for the following reasons. (a) The thermal isomerization[10] of 1-pyrazoline yields the same products as the photolysis. (b) The lifetime of vibrationally excited pyrazoline (with respect to decomposition) can be calculated by the RRK theory to be ≈7 × 10^{-11} sec if the molecule contains 92 kcal/mole. This is much shorter than the time between collisions so no pressure-induced dissociation is necessary as would be for 2,3-diazabicyclo[2.2.1]-hept-2-ene.[7] The pyrazolines have been found to split directly into singlet trimethylene and nitrogen from the isotope effects in various deuterated isomers.[11] Singlet trimethylene can probably undergo ring closure to cyclopropane in less than 10^{-10} sec.

The curvature in Figure 1, caused by a spread of energies in the cyclopropane, can be explained in three ways.

(a) Nonmonochromatic Radiation. The results shown in Figure 2 indicate that this is not the cause because the curve obtained using 3130-Å monochromatic radiation is coincident with that obtained with a full mercury arc. The reason for this similarity is explained when the absorption spectrum of pyrazoline is imposed upon the spectrum of a mercury lamp. The only important radiation absorbed by the pyrazoline is the emission at 3126 and 3130 Å. The latter is twice as intense as the former and lies close to the maximum of the absorption band of pyrazoline so that at least 90% of the effective radiation with a full mercury arc is that of 3130 Å.

(b) Partial Deactivation of the Excited Pyrazoline before Decomposition. It is unlikely that much energy can be removed from the electronically excited state of pyrazoline. Comparison with 2,3-diazabicyclo[2.2.1]-hept-2-ene[7] which has nearly coincident emission and absorption spectra indicate that the minimum of the ground- and excited-state curves are at the same interatomic distances. Hence there will be little vibrational energy present in the singlet excited state which can be removed by collisions. The lifetime of the vibrationally excited ground state containing 92 kcal/mole is much too short for partial quenching by collisions at the pressures used.

(c) Energy Partitioning between Fragments of Decomposition. This has been postulated before and is the most probable cause of curvature in Figures 1 and 2. Singlet cyclobutanone[5] formed on photolysis is thought to convert to vibrationally excited ground-state cyclobutanone which then decomposes to ethylene and ketene.



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A plot of the ratio of the rates of these two reactions *vs.* reciprocal pressure is linear showing a much narrower spread of energies. In this case no partitioning between fragments has occurred.

The ratio of propylene to cyclopropane is given by[4b]

$$\frac{\text{propylene}}{\text{cyclopropane}} = \frac{k_a}{\omega} \qquad (19)$$

where

$$\omega = k_s(\text{M}) = \text{rate of deactivation}$$

and

$$k_a = \frac{\displaystyle\int_{E_{\min}}^{E_{\max}} \frac{k_E f_E}{\omega + k_E}}{\displaystyle\int_{E_{\min}}^{E_{\max}} \frac{\omega fe}{\omega + k_E}} \qquad (20)$$

where k_E (sec^{-1}) = rate constants for isomerization at energy E, f_E = fraction of molecules at energy E, and (M) = total effective concentration of deactivators.

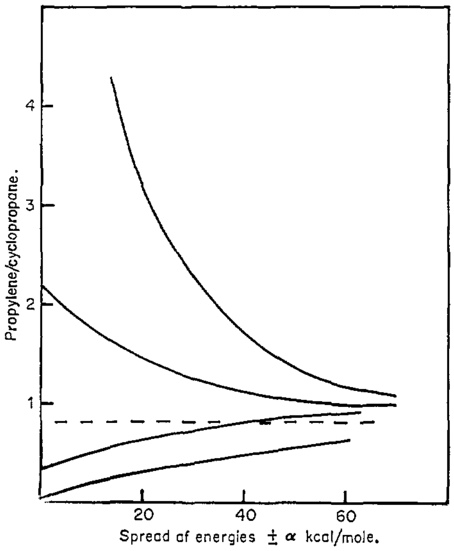


Figure 3. Plot of calculated propylene/cyclopropane *vs.* spread of energies ± α kcal/mole for triangular distributions at various peak energies and 1 Torr pressure (experimental value 0.8): bottom curve, E_{max} = 65; second, E_{max} = 70; third, E_{max} = 75; top, E_{max} = 80.

At 1 Torr, $\omega = 1.6 \times 10^7$ sec^{-1} for hard spheres (Lennard-Jones collision rates would increase the calculated energy rates by only a few kilocalories/mole). Setser and Rabinovitch[9] and also Campbell and Schlag[4b] have calculated k_E as a function of energy for the cyclopropane isomerization using RRKM theory. From the oxygen curve in Figure 1 the ratio of propylene to cyclopropane is 0.8. This gives k_a to be 1.3×10^8 sec^{-1} which corresponds to 72 kcal/mole average energy content.

At 10 Torr the ratio is 0.35 and this corresponds to 77 kcal/mole. The average energy of the reacting molecules increases with increase in pressure. The maximum possible energy available for distribution in the fragments is

$$E_{\mathrm{T}} = -\Delta H_{\mathrm{R}} + h\nu + E_{\mathrm{thermal}} \tag{21}$$

where ΔH_{R} is the heat of the reaction of pyrazoline going to cyclopropane and E_{thermal} = thermal energy of cyclopropane. To obtain ΔH_{R}, the heat of formation of pyrazoline is required. This can be estimated to be ~53 kcal/mole by comparison with ΔH_f(azomethane). The heat of the reaction pyrazoline–cyclopropane is then found to be ~−40 kcal/mole at 298°K. This gives $E_{\mathrm{T}} = 92 + 40 + E_{\mathrm{thermal}}$ (for 3130-Å photons) ≈ 130–140 kcal/mole. The average energy is therefore about half the maximum possible thermochemically.

In the photolysis[7] of 2,3-diazobicyclo[2.2.1]hept-2-ene the energy distribution in the photolysis fragments was interpreted in terms of a Gaussian function, whereas in the photolysis of cyclobutanone[4b] a statistical equilibration between all the energy levels was assumed. It was decided to try to reproduce the experimental results using various distribution functions. These were the following.

(a) Triangular Functions. This is the simplest symmetrical distribution but has no theoretical significance. The peak of the function can be placed on a particular energy and the effect of broadening the distribution on the propylene/cyclopropane ratio found. The peak of the function could then be moved to a different energy and the effect of this change on the ratio established. The fraction of molecules, f_E, at energy E was calculated as follows. The triangular function was divided into 5-kcal intervals and the height at each point found relative to each other by similar triangles. The sum of the heights, and hence fractions f_E, were then normalized to unity. There was little difference in the final calculated ratio of propylene/cyclopropane between increments of 10 kcal and those of 5 kcal. The calculated f_E's could then be inserted into eq 20 and the propylene/cyclopropane ratio calculated. The calculated values of the ratio at 1 Torr total effective pressure for various peak energies and width of spread are shown in Figure 3. At 1 Torr the experimental propylene/cyclopropane ratio is 0.8 (Figure 1). It can be seen that the only reasonable triangular distribution is that with peak at 70 kcal and width ±40 kcal, which fits the experimental value. In Figure 4 the variation of the calculated ratio with reciprocal pressure is shown. This triangular function fits quite well over the whole experimental pressure range.

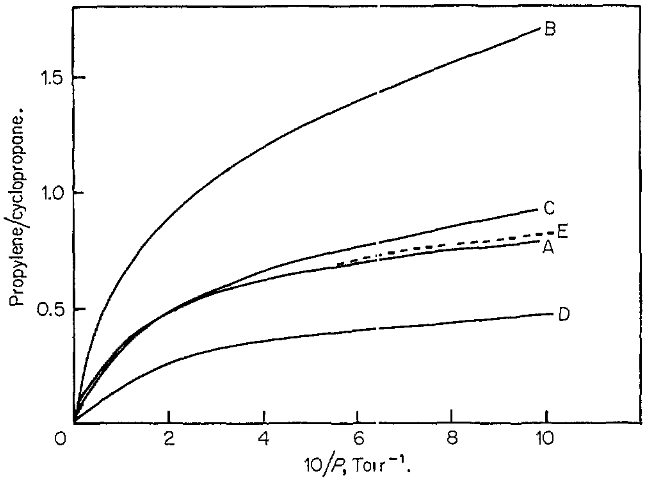


Figure 4. Plot of propylene/cyclopropane *vs.* $1/P$ for various calculated distributions: (A) best triangular function; (B) statistical distribution, E_{max} = 110 kcal/mole; (C) statistical distribution, E_{max} = 105 kcal/mole; (D) statistical distribution, E_{max} = 100 kcal/mole; (E) - - -, experimental curve.

(b) Gaussian Functions.[7]

$$f_E = \frac{e^{-\frac{1}{2}\left(\frac{E_{mp}-E_i}{\sigma}\right)^2}}{\sum_i e^{-\frac{1}{2}\left(\frac{E_{mp}-E_i}{\sigma}\right)^2}} \tag{22}$$

where E_{mp} = most probable energy and σ is related to the width of the function. The results obtained with this function were very similar to those obtained with the triangular one and are therefore not shown.

(c) Statistical Distributions.[4b] The fraction of cyclopropane molecules formed at any energy is assumed proportional to the energy level density at that energy

$$f_E = \frac{N_{\mathrm{V}}(E_i)N_{\mathrm{R}}(E_{\mathrm{T}} - E_i)}{\sum_{E_i} N_{\mathrm{V}}(E_i)N_{\mathrm{R}}(E_{\mathrm{T}} - E_i)} \tag{23}$$

where N_{V} = energy level density of the cyclopropane part of the pyrazoline, N_{R} = energy level density of the remaining degrees of freedom of the pyrazoline, and E_T = total available energy as before. The frequencies used in the calculation of the energy level densities were those assigned to cyclobutanone.[14] It was felt that as cyclobutanone and pyrazoline are similar molecules (a trimethylene part plus a diatomic of mass 28) and with all the assumptions involved, this would be a good enough approximation. The energy level densities were calculated using the semiclassical expression of Marcus and Rice[15] rather than by the method of Whitten and Rabinovitch[14] for the same reasons.

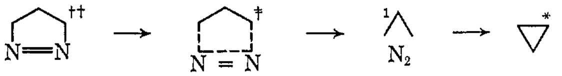
$$N(E) = \frac{(E + E_z)^{s-1}}{\Gamma(s) \prod_{i}^{s} h\nu_i} \qquad (24)$$

The frequency groupings assigned to cyclobutanone[14] were used with 21 vibrations similar to cyclopropane assigned to the C_3H_6 part and the remainder assigned to the nitrogen part of pyrazoline. The values of f_E obtained using eq 24 and 23 were then inserted into eq 20, and the propylene to cyclopropane ratio was calculated as before. With E_t = 130 kcal (from photon energy and thermochemistry above), the value of the calculated ratio at 1 Torr was 9.2 which is much greater than the experimental value of 0.8. Values the ratio with $E_T <$ 130 kcal are plotted *vs.* reciprocal pressure in Figure 4. If E_T = 105 kcal/mole the calculated curve fits the experimental one very well over the experimental pressure range. There is little difference between the best triangular function of E_T = 110 kcal/mole and the statistical curve with E_T = 105 kcal/mole.

These results suggest that the maximum energy available to the cyclopropane is much less than that calculated by thermochemical considerations. Errors in the calculation of ΔH_R are unlikely to be as high as 30 kcal/mole needed to match the E_T with thermochemical energies. There could, of course, be nonequilibration of the energy between the various vibrational degrees of freedom in pyrazoline. The lifetime of the pyrazoline molecule containing 92 kcal is $\sim 10^{-10}$ sec in which about 10^3 vibrations can occur so this effect is unlikely to be very large.

It seems as though all the excess energy is *not available* to the cyclopropane. In the cyclobutanone photolysis[4b] the statistical distribution of energies was an underestimate of the experimental propylene to cyclopropane ratio except at the highest photon energies, in contrast to pyrazoline. A considerable fraction of cyclopropane molecules must be formed with less than 65 kcal of energy because extrapolation of the propylene to cyclopropane ratio to zero pressure in Figure 1 would only give a value of $\sim$0.9–1; *i.e.*, about half the cyclopropane molecules are unable to isomerize. This is substantiated by the fact that the average energy of the system is only 75 kcal/mole.

If the mechanism of cyclopropane formation is



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42.4 kcal (thermal activation energy) of the 92 kcal of photon energy will reside in the reaction coordinate. This will probably be a combination of C–N stretch and N–N compression in the transition state. The heat of formation of trimethylene has been estimated to be about 67 kcal/mole[16] which is 55 kcal above cyclopropane. Combination of this figure with the thermal activation energy (42.4 kcal) and the exothermicity of (25) gives a value of about 28 kcal/mole released (eq 25) in passing from the transition state to the trimethylene. Little of this energy will probably appear as vibrational energy in the trimethylene as the bond angle change is not large but is probably in the relative translational modes of the fragments and in the vibrational mode of nitrogen. The trimethylene will, therefore, have available only about 92–42.4 ≈ 50 kcal/mole from the excess photon energy. The cyclopropane which is subsequently formed can have an extra 55 kcal/mole due to ring closure and so have a maximum of about 105 kcal/mole. This is near the maximum energy found from Figure 4. Only 50 kcal of the energy on this model can be distributed between the two decomposition fragments of pyrazoline. The statistical distribution of 50 kcal between the vibrational modes of pyrazoline was used to calculate the values of f_E as before, and then the distribution function f_E was shifted 55 kcal/mole to higher energies. From eq 19 and 20 the calculated propylene to cyclopropane ratio was obtained and found to be 5 at 1 Torr, disagreeing with the experimental value of 0.8. More experimental studies are necessary before any conclusion can be drawn regarding the photopartioning of energy, especially where the photon energy can be varied. The narrow uv absorption band of pyrazoline did not allow photolysis over a range of energies.

Conclusion

A reasonable fit of the experimental variation of the propylene to cyclopropane ratio is obtained if the maximum energy of the "hot" cyclopropane molecules is $\sim$105–110 kcal/mole and this energy can be distributed between the photolysis fragments of pyrazoline. Either a triangular function or a function obtained by statistically distributing the energy among the vibrational degrees of freedom of pyrazoline fits the experimental results. More information is necessary before these functions can be distinguished although there is theoretical justification for the latter.

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