

of tenths of a microsecond, by examining absorption changes during the 2- μ sec. pulse. An indication was found of 10–20% more ions under these conditions. This appears to be consistent with the model of Free-

man and Fayadh.²⁵ Any yield of ions with still shorter lifetimes could only be observed using pulses with durations in the nanosecond range.

(25) G. R. Freeman and J. H. Fayadh, *J. Chem. Phys.*, **43**, 86 (1965).

Photoinitiation of Unimolecular Reactions. The Photolysis of 2,3-Diazabicyclo[2.2.1]hept-2-ene

Timothy F. Thomas and Colin Steel

Contribution from the Department of Chemistry, Brandeis University,
Waltham, Massachusetts. Received June 14, 1965

The gas-phase photolysis of 2,3-diazabicyclo[2.2.1]hept-2-ene (I) with 337-m μ light has been investigated in the pressure range 10–1000 μ . The variation in the yields of hydrocarbon products, bicyclo[2.1.0]pentane (II), cyclopentene (III), and 1,3-cyclopentadiene (IV), with pressure is consistent with the initial formation of "hot" II which can either be deactivated or isomerize to "hot" III. The latter can either undergo unimolecular decomposition to yield IV or be deactivated. Changing the wave length of irradiation from 313 to 334 m μ changed the relative yields of the products in a manner consistent with this "hot" molecule mechanism.

Introduction

It has been recognized for some time that unimolecular reactions which have been photoinitiated should provide more specific information for energy transfer and rate studies than the corresponding thermal systems. Preliminary work¹ indicated that the photodecomposition of cyclic azo compounds such as 2,3-diazabicyclo[2.2.1]hept-2-ene (I) might prove to be a convenient source of vibrationally excited strained ring hydrocarbons which would undergo unimolecular reaction. These systems have the advantage that the nitrogen produced acts as a monitor of the hydrocarbons formed so that the over-all stoichiometry can be checked. Also the unimolecular reactions of the hydrocarbons formed have been studied in conventional thermal systems.^{2–4}

Experimental Section

Procedure. The azo compound I, whose preparation has been previously described,⁵ was vaporized into the reaction vessel and the pressure measured by means of both a quartz spiral gauge (Texas Instruments) and, where applicable, by a Pirani gauge which had been calibrated for I. The pressure range covered was limited by the vapor pressure of I at room temperature, viz., 2.5 mm.

(1) C. Steel, *J. Phys. Chem.*, **67**, 1779 (1963).

(2) M. L. Halberstadt and J. P. Chesick, *J. Am. Chem. Soc.*, **84**, 2688 (1962).

(3) C. Steel, R. Zand, P. Hurwitz, and S. G. Cohen, *ibid.*, **86**, 679 (1964).

(4) D. W. Vanas and W. D. Walters, *ibid.*, **70**, 4035 (1948).

(5) S. G. Cohen, R. Zand, and C. Steel, *ibid.*, **83**, 2895 (1961).

Most photolyses were carried out to completion in a reactor at 44° equipped with 16 "black light" lamps (General Electric F8-T5-BLB). A 500-mm. grating monochromator (Bausch and Lomb) and a high-pressure mercury arc (PEK 110) were used for the experiments requiring monochromatic light.

All absorption spectra were obtained on a Cary 14 spectrophotometer, while a Zeiss spectrofluorometer was used for obtaining fluorescence spectra.

Analyses for bicyclo[2.1.0]pentane (II), cyclopentene (III), and 1,3-cyclopentadiene (IV) were effected by a flame ionization gas chromatograph equipped with a 25-ft. glass column packed with 10% SF-96 on Chromosorb W 60/80. We originally employed a silver nitrate column as in our earlier work, since this is a common column for the separation of olefins,⁶ but we found that the fraction of injected IV which passed through this column depended drastically on both the size of the sample and the past history of the column. This is probably the reason why we did not originally observe this compound since the early studies,¹ with the exception of two runs, were carried out at pressures above 1 mm. where we now know IV is only a minor product. The identities of the compounds II, III, and IV were confirmed by mass spectral analyses. A small amount of 1,4-pentadiene ($\leq 2\%$), as identified by gas chromatography, was also formed. Total hydrogen and nitrogen were estimated by conventional gas analyses employing a gas buret and Toepler pump. The relative amounts of the two gases were determined by gas chromatography using a molecular sieve column and a thermal conductivity detector. Good agreement between the yields of H₂ and IV was obtained. Thus at 35 μ and for a 2-l. reaction vessel we found H₂/N₂ = 0.379 and IV/(II + III + IV) = 0.396.

Absorption on Glass. It was established that in the pressure range accessible for study, viz., 10–1000 μ , the azo compound I was strongly adsorbed on Pyrex glass surfaces. This was first observed by noting that the hydrocarbon product ratios were sensitive to the surface to volume ratio of the photolysis vessel employed when the latter was changed from a 2-l. bulb to a coiled length of 6-mm. tubing. The effect was confirmed by measurement of the fraction of I absorbed. To do this a given pressure of azo compound, as read

(6) B. Smith and R. Ohlson, *Acta Chem. Scand.*, **13**, 1253 (1959).

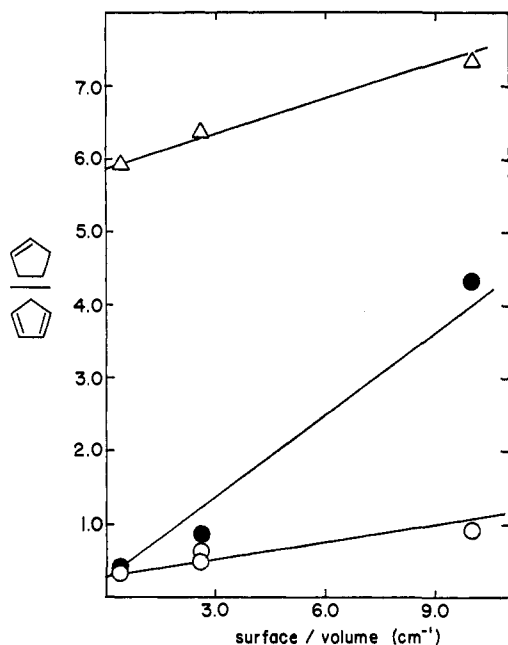


Figure 1. Effect of surface on product ratios: Δ , $p = 890 \mu$, aged surface; O , $p = 10 \mu$, aged surface; \bullet , $p = 10 \mu$, fresh surface.

by the absolute spiral gauge, was allowed to equilibrate in the reaction vessel. The pressure gave a measure of the number of azo molecules in the gas phase. Pyrolysis of the azo sample and subsequent determination of the nitrogen formed gave a measure of the amount of total azo, since we had established in earlier studies that the thermal reaction $I \rightarrow N_2 + II$ goes cleanly to completion.⁵ At 10μ , for example, in a vessel of surface to volume ratio 0.40 cm^{-1} , the fraction of I on a clean Pyrex surface at 25° is 0.29. The hydrocarbon product ratios were also very dependent on the condition of the glass used. Figure 1 shows typical product ratio plots using both fresh vessels and those which had been "seasoned" by carrying out several photolyses. Seasoning certainly reduces the effect of the surface and appears to give a surface which is more reproducible than a fresh one. It will also be seen from Figure 1 that extrapolation back to zero surface to volume ratio, to get product ratios for the homogeneous reaction, is subject to most uncertainty at the lowest pressure where relatively the effect of surface is most serious. It is this uncertainty and not the analytical accuracy which is reflected in the larger size of the low-pressure experimental points shown in Figure 2.

Results and Discussion

Product Yields as a Function of Pressure. For each photolysis, product analyses for bicyclo[2.1.0]pentane (II), cyclopentene (III), and 1,3-cyclopentadiene (IV) were carried out. In order to separate the gas-phase and the surface-phase contributions, product ratios for II/IV and III/IV were obtained as a function of surface to volume ratio (see Figure 1). These functions were used because it was found that although II and III were formed both on the surface and in the gas phase, IV was formed predominantly by a gas-phase reaction.

The experimental results obtained at five pressures in the range $10\text{--}1000 \mu$ are shown in terms of the two prod-

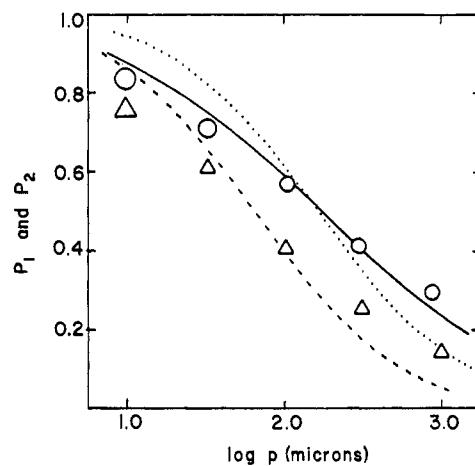


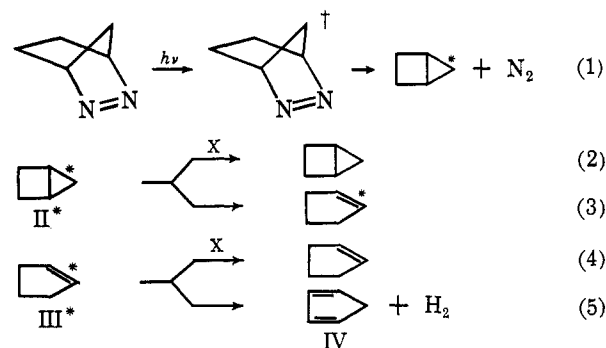
Figure 2. Variation in product functions $P_1 = ([III] + [IV])/([II] + [III] + [IV])$ and $P_2 = ([IV])/([III] + [IV])$ with pressure p of reactant I: O , experimental values of P_1 ; Δ , experimental values of P_2 ; \dots , P_1 , calculated from eq. 6 for 3.5-kcal. range of ϵ ; $---$, P_2 , calculated from eq. 7 for 3.5-kcal. range of ϵ ; $---$, P_1 , calculated from eq. 6 for 12-kcal. range of ϵ .

uct functions

$$P_1 = \frac{[III] + [IV]}{[II] + [III] + [IV]} \quad P_2 = \frac{[IV]}{[III] + [IV]}$$

where [II] = amount of II formed by the gas-phase reaction, and similar definitions apply to the other terms.

Mechanism and Kinetic Scheme. These results are consistent with the following simple scheme.



where an asterisk (*) indicates a molecule possessing sufficient vibrational energy to be capable of carrying out a unimolecular reaction, and X is a species which can deactivate such a molecule by energy transfer. A dagger (†) indicates an electronically excited molecule. This extends the mechanism which we previously suggested¹ to include reaction 5, a process which becomes important at pressures less than 1000μ . This scheme results in

$$P_1 = \int_0^\infty \frac{f_{II}(\epsilon)}{1 + \frac{\omega(p)}{k_3(\epsilon)}} d\epsilon \quad (6)$$

and

$$P_2 = \int_0^\infty \frac{f_{III}(\epsilon + \Delta H)}{1 + \frac{\omega(p)}{k_5(\epsilon + \Delta H)}} d\epsilon \quad (7)$$

On the basis of a strong collision model $\omega(p)$ is the col-

lision frequency at pressure p .⁷ $f_{II}(\epsilon)$ is the probability that when a II* molecule is produced it will have energy ϵ ; a similar definition applies for f_{III} . ΔH is the difference in enthalpy between the ground states of II and III. $k_3(\epsilon)$ and $k_5(\epsilon + \Delta H)$ are the specific rate constants for II* and III* molecules possessing energy ϵ and $(\epsilon + \Delta H)$, respectively.

The data in the literature²⁻⁴ for the thermal reactions 3 and 5 have been treated by the Kassel method⁸ and not by the more sophisticated Marcus approach.⁹ We therefore use the former and obtain

$$k_3(\epsilon) = A_3(1 - \epsilon_3/\epsilon)^{s-1}$$

$$k_5(\epsilon + \Delta H) = A_5(1 - \epsilon_5/\{\epsilon + \Delta H\})^{s'-1}$$

where A_3 and A_5 are the high-pressure A factors, ϵ_3 and ϵ_5 are the high-pressure activation energies for the corresponding thermal unimolecular reactions, and s and s' are the number of Kassel oscillators. The values $\Delta H = 28.2$ kcal. mole⁻¹,^{10,11} $A_3 = 10^{14.1}$ sec.⁻¹ and $\epsilon_3 = 45.6$ kcal. mole⁻¹,³ $A_5 = 10^{13.04}$ sec.⁻¹ and $\epsilon_5 = 58.8$ kcal. mole⁻¹,⁴ and $s = 18 \pm 2^2$ are given in the literature. The value of s' is not known but since II and III are isomeric we shall choose $s = s' = 20$.

Since there is no detailed knowledge of the mechanism for photodecomposition of azo compounds, the choice of a value of ϵ for a given wave length of irradiation is more arbitrary. The heat of formation of I is not known, but comparison with thermodynamic data for the unstrained linear analog azoisopropane¹² indicates that reaction $I \rightarrow II + N_2$ will be exothermic by an amount in excess of 14 kcal. mole⁻¹. Examination of the output of the photochemical lamps (F8-T5-BLB) and the absorption spectrum of I shows that the effective wave length for photolysis is 337 m μ (85 kcal./einstein). If we then assume that the photodissociation of I \dagger occurs before any energy is transferred by collision, the system (II* + N₂) as initially produced must have an energy of 99 kcal. or more in excess of the ground state. A value of $\epsilon = 76$ kcal. gave the best agreement with experiment. The remaining energy could be associated with translational and rotational energy of II* + N₂ and vibrational energy of N₂.

The actual distribution of the vibrational energy in II* and III*, that is, the form of the f_{II} and f_{III} functions, will be governed by several factors, the most obvious of which is the nonmonochromaticity of the light employed. Let us define $f_I(\epsilon)$ as the probability that when a I \dagger molecule is produced by photoexcitation it will have energy ϵ . This f_I function can be determined from the output curve for the lamp and the absorption curve for I since the quantum yield of reaction 1 is known to be wave length independent in this region.¹ In fact, the f_I function is rather narrow and encompasses an energy spread of only 3.5 kcal. mole⁻¹. Furthermore, since II* acquires the majority of the excess energy in the photodissociative act, it would

appear reasonable that this energy spread will also be manifested in II*; hence $f_{II} \sim f_I$. The resultant P functions obtained using the Kassel model and the above f functions are shown in Figure 2 as the dotted curve for P_1 and the dashed curve for P_2 ; they differ only very slightly from monoenergetic curves.

A photolysis which initiates a linked sequence of reactions would appear to provide a more rigorous test of the "hot" molecule mechanism than one which initiates a single reaction. It will be noted that the relative locations of the two P functions along the log p axis is correctly predicted using data from thermal systems and one arbitrary variable, ϵ . The experimental results do indicate, however, a greater spread in ϵ than can be explained by nonmonochromaticity alone. The full line curve in Figure 1 is the P_1 function for a model system in which II* is produced in three states in the ratios 1:2:1 with energies 70, 76, and 82 kcal. Other sources of vibrational dispersion have to be considered.

If several vibrational and rotational levels of an electronic ground state are occupied, even monochromatic light can result in the formation of an excited state having a finite energy spread. However, at room temperature such broadening should be minor, causing an effective spread of not more than 2 kcal. More important may be the differing amounts of energy which each dissociating molecule may have associated with its photochemical reaction coordinate. There is no generally accepted model for the photodissociation of azo compounds; those which have been proposed are open to criticism. But certainly in a general sense, it can be visualized that one requirement may be the location of a certain critical energy in a particular coordinate. Simple models, which are admittedly gross approximations, indicate that not all molecules which photodissociate will have exactly the same energy localized in this coordinate. Consider the case in which a photoexcited molecule can be represented by a system of 20 identical coupled harmonic oscillators among which are distributed 50 quanta, each of energy 2 kcal.; then the relative probabilities that a particular oscillator has 16, 18, 20, 22, 24, 26 kcal. associated with it is 1.00:0.70:0.49:0.34:0.23:0.15. This suggests that if 16 kcal. is the critical energy that must be associated with the photochemical coordinate, there can be an effective 10 kcal. spread in the energy associated with this coordinate for molecules which actually photodissociate. This could result in a corresponding dispersion in the vibrational energy associated with the products.

Lifetimes of Excited Molecules. For monoenergetic molecules II* and III*, eq. 6 and 7 become

$$P_1 = \frac{k_3(\epsilon)}{k_3(\epsilon) + \omega(p)}$$

and

$$P_2 = \frac{k_5(\epsilon + \Delta H)}{k_5(\epsilon + \Delta H) + \omega(p)}$$

Thus, for the pressures at which $P_1 = 0.5$ and $P_2 = 0.5$, p' and p'' , respectively, we have $k_3(\epsilon) = \omega(p')$ and $k_5(\epsilon + \Delta H) = \omega(p'')$. This allows us to estimate the lifetimes of II* and III* at 3.0×10^{-7} and $7.6 \times$

(7) N. B. Slater, "Theory of Unimolecular Reactions," Cornell University Press, Ithaca, N. Y., 1959, p. 17.

(8) L. S. Kassel, "The Kinetics of Homogeneous Gas Reactions," Reinhold Publishing Corp., New York, N. Y., 1932, Chapter 5.

(9) R. A. Marcus, *J. Chem. Phys.*, **20**, 359 (1952).

(10) M. A. Dolliver, T. L. Gresham, G. B. Kistiakowsky, and W. E. Vaughan, *J. Am. Chem. Soc.*, **59**, 831 (1937).

(11) R. B. Turner, "Kekulé Symposium on Theoretical Organic Chemistry," Butterworth & Co. Ltd., London, 1959, p. 67.

(12) G. E. Coates and L. E. Sutton, *J. Chem. Soc.*, 1187 (1948).

10^{-7} sec., respectively, in our system when 337-m μ light is employed.

The Effect of Wave Length. Despite the above-mentioned dispersion in the vibrational energy associated with II* and III*, changing the wave length of irradiation should result in a corresponding shift in the band of vibrational energies. If for simplicity we take only a single energy, we have shown that the results for both P_1 and P_2 at $p = 100 \mu$ are best fitted by $\epsilon = 76$ kcal. when $\lambda_{\text{irr}} = 337$ m μ (Figure 2). However, because of the energy dispersion the best fit to experimental data at 1000 μ is given by $\epsilon = 79$ kcal. It would appear that about 80% of the excitation energy appears as vibrational energy in II*. Thus for $\lambda_{\text{irr}} = 334$ and 313 m μ we obtain $\epsilon = 79.6$ and 84.1 kcal., respectively. Some preliminary results showing the effect of wave length are given in Table I. The cal-

Table I. Effect of Wave Length on Product Functions P_1 and P_2 ^a

λ_{irr} , m μ	P_1 , exptl.	P_2 , exptl.	P_1 , calcd.	P_2 , calcd.
313	0.49 \pm 0.02	0.25 \pm 0.02	0.65	0.28
334	0.28 \pm 0.05	0.13 \pm 0.02	0.37	0.14

^a Pressure of reactant I = 1005 μ .

culated values for P_1 and P_2 were obtained by substituting the above values for ϵ in eq. 6 and 7. The other parameters had the literature values quoted above.

There is an experimental difficulty in obtaining vessels with a very small surface-to-volume ratio which can be satisfactorily irradiated with light from a monochromator. Because of the optical requirements, fairly small vessels with a reasonably large surface-to-volume ratio (2.5 cm.⁻¹) had to be employed. The discrepancy between the calculated and experimental P values may be due to surface effects. However, the ratios $P_1(313)/P_1(334)$ and $P_2(313)/P_2(334)$, which have values 1.75 and 1.93, should be less sensitive to these effects and are in reasonably good agreement with the calculated values, 1.76 and 2.00. It is of interest to note that Frey¹³ has reported similar wave length effects for the unimolecular rate constants of various "hot" molecules formed by addition and insertion reactions of methylene produced by the photolysis of diazomethane.

Other Mechanism. Srinivasan¹⁴ has proposed that the pressure dependence of the yields of the hydrocarbons formed by the photodissociation of cyclopentanone arises because photodissociation from different vibrational levels of the electronically excited

(13) H. M. Frey, *Trans. Faraday Soc.*, **56**, 1201 (1960); **57**, 951 (1961); **58**, 516 (1962).

(14) R. Srinivasan, *J. Am. Chem. Soc.*, **83**, 4344 (1961).

state gives different products. This mechanism has to be considered for our system in view of the rather large calculated value of the lifetime for spontaneous emission of I \ddagger (*viz.*, 3×10^{-6} sec.). However, it should be noted that since I has not been observed to fluoresce this time can only be regarded as an upper limit for the dissociative lifetime, thus $\tau_{\text{diss}} \ll 3 \times 10^{-6}$ sec. Other arguments suggest that a Srinivasan-type mechanism does not contribute significantly in our system. Such a mechanism would require that the product ratio obtained on excitation to the low-lying vibrational levels of I \ddagger should be pressure insensitive and close to that for photolysis in solution (II:III:IV = 0.98:0.02:0.00). Irradiation with an effective wave length of 337 m μ , which is close to the long wave length limit of absorption (344 m μ) should populate only the lowest vibrational levels of I \ddagger , yet the yields are strongly pressure dependent (Figure 1) and at the lowest pressures of 1,3-cyclopentadiene (IV), not bicyclo[2.1.0]pentane (II), is the major product. Therefore only the possibility that the long wave length limit does not correspond closely to a $0' \rightarrow 0''$ transition would allow a Srinivasan-like mechanism to apply in this case, although this seems unlikely for a rigid structure such as I.¹⁵ In an attempt to shed more light on this problem, we examined the fluorescence spectrum of I and of its next higher homolog, 2,3-diazabicyclo[2.2.2]oct-2-ene (V).¹⁶ Compound I fluoresces so weakly that we are uncertain if the emission is above the noise level of our spectrofluorometer. On the other hand, V, which has a similar absorption spectrum to I,^{5,16} fluoresces strongly. The short wave length limit of this emission corresponds closely to the long wave length limit of absorption with some overlap. This indicates¹⁷ that the long wave length limit of absorption does indeed correspond closely to $0' \rightarrow 0''$ excitation.

Finally, it may be noted that, since we observed pressure effects at the lowest experimental pressures (10 μ), if a Srinivasan-type mechanism were operative in our case the lifetime of I \ddagger with respect to photodissociation would have to be greater than 10^{-5} sec. This seems somewhat high for a molecule which does not fluoresce (thus $\tau_{\text{fluor}} \gg 10^{-5}$ sec.) and which has a quantum yield for dissociation of 1.0 in solution, where the time between collisions is about 10^{-12} sec.

Acknowledgment. This work was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research Grant 583-64. We are also indebted to Dr. G. O. Dudek (Harvard University) for aid in obtaining the mass spectra.

(15) K. B. Wiberg, "Physical Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1964, p. 174.

(16) S. G. Cohen and R. Zand, *J. Am. Chem. Soc.*, **84**, 586 (1962).

(17) P. Pringsheim, "Fluorescence and Phosphorescence," Interscience Publishers, Inc., New York, N. Y., 1949, p. 302.