Distribution and Exchange of Excess Vibrational Energy Produced in the Photolysis of 2,3-Diazabicyclo[2.2.1]hept-2-ene[1]
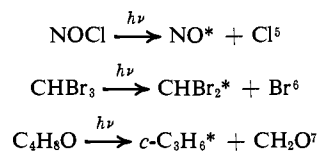
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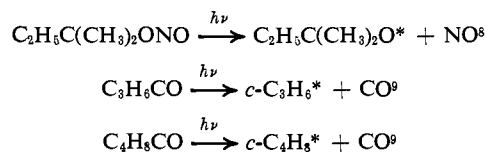
Abstract: 2,3-Diazabicyclo[2.2.1]hept-2-ene (I) has been photolyzed with monochromatic light, and the effects of pressure and wavelength of irradiation on the relative yields of the products—bicyclo[2.1.0]pentane (II), cyclopentene (III), cyclopentadiene (IV), and 1,4-pentadiene (V)—have been analyzed in detail. The initial hydrocarbon product, vibrationally excited bicyclo[2.1.0]pentane, appears to be produced with a distribution of energies having a standard deviation of 6.65 kcal mole^{-1}. Models for rationalizing the distribution and location of the excess energy are proposed. Wavelength dependence studies indicate that the Kassel theory gives a satisfactory fit to the energy dependence of rate constants for the excited hydrocarbon molecules. Relative efficiencies of several added gases with respect to vibrational deactivation have been determined.

The production of vibrationally excited molecules and radicals by chemical activation has recently been comprehensively reviewed by Rabinovitch and Flowers and by Rabinovitch and Setser;[3,4] other methods include thermal and photochemical production. In the latter case vibrationally excited species are formed in the primary, photodissociative step. In principle the photochemical method has several advantages: the excess energy may be varied by simply varying the exciting wavelength and, since the reactions may be run at low temperatures, complicating side reactions can be kept to a minimum.

The basic requirement for application of the direct photochemical method is that the energy of the light quantum absorbed less the endothermicity of the primary photochemical step be significantly greater than the activation energy for some unimolecular reaction of a primary product. Several of the systems meeting this requirement which have been studied in some detail are

$$NOCl \xrightarrow{h\nu} NO^* + Cl[5]$$

$$CHBr_3 \xrightarrow{h\nu} CHBr_2^* + Br[6]$$

$$C_4H_6O \xrightarrow{h\nu} c\text{-}C_3H_6^* + CH_2O[7]$$

and

$$C_2H_5C(CH_3)_2ONO \xrightarrow{h\nu} C_2H_5C(CH_3)_2O^* + NO[8]$$

$$C_3H_6CO \xrightarrow{h\nu} c\text{-}C_3H_6^* + CO[9]$$

$$C_4H_8CO \xrightarrow{h\nu} c\text{-}C_4H_8^* + CO[9]$$

In two cases, $CHBR_2^*$ and cyclo-$C_3H_6^*$, estimates were made of the excess energy of the reacting species. Also, in the systems $CHBr_2^*$ and $C_2H_5C(CH_3)_2O^*$ it was noted that the vibrational excitation was not monoenergetic. But in no case has detailed knowledge of the kinetic parameters, available only for cyclopropane among the previous examples, been combined with a systematic treatment of the dispersion of the excess energy which may be a general feature of all primary dissociative steps (see Discussion).

As has previously been reported[10] the photolysis of 2,3-diazabicyclo[2.2.1]hept-2-ene (DBH) leads to the formation of a cyclic hydrocarbon with sufficient vibrational excitation to undergo a series of unimolecular reactions. In this case all the required kinetic parameters are known, and preliminary indications of the spread in vibrational energies have been reported. In the present study highly monochromatic light has been employed in an attempt to reduce the spread of vibrational excitation energies, and an explicit distribution function has been used to fit the pressure dependence results. In addition the effect of wavelength of irradiation (and thus of the average excess vibrational energy) on the unimolecular reaction rates has been evaluated, and the relative efficiencies of various additive molecules in removing the excess vibrational energies from the reactive products have been determined.

Experimental Section

Materials. The preparation of 2,3-diazabicyclo[2.2.1]hept-2-ene has already been reported.[11] Possible trace decomposition products were removed by selective vaporization under vacuum prior to each photolytic run, and gas chromatographic analysis of "zero-time" photolysis samples revealed less than 0.1% of volatile impurities. Carbon dioxide used in the added gas experiments was Matheson 99.8% minimum, argon was Matheson 99.998% minimum, and propylene was Matheson 99.0% minimum. The "isooctane" was Fisher reagent grade 2,2,4-trimethylpentane, 99% pure, used without further purification except for routine degassing on the vacuum line. The presence of impurities in the added gases was checked by analyzing small samples from the gas mixtures before photolysis.

Samples for photolysis were vaporized into optical cells on a greaseless, mercury-free vacuum line which had been evacuated to less than 10^{-5} torr before filling. Mixtures of DBH and an inert gas were made up by first filling the reaction vessel (a 2-l. spherical

(1) Research sponsored by Directorate of Chemical Sciences, Air Force Office of Scientific Research, Grant 583-66. C. I. S. also acknowledges support from the American Cancer Society through Institutional Grant IN-29.

(2) Author to whom inquiries should be addressed.

(3) B. S. Rabinovitch and M. C. Flowers, *Quart. Rev.* (London), **18**, 122 (1964).

(4) B. S. Rabinovitch and D. W. Setser, *Advan. Photochem.*, **3**, 1 (1964).

(5) N. Basco and R. G. W. Norrish, *Proc. Roy. Soc.* (London), **A268**, 291 (1962).

(6) J. P. Simons and A. J. Yarwood, *Trans. Faraday Soc.*, **57**, 2167 (1961).

(7) B. C. Roquitte, *J. Phys. Chem.*, **70**, 1334 (1966).

(8) D. Durant and G. R. McMillan, *ibid.*, **70**, 2709 (1966).

(9) R. F. Klemm, D. N. Morrison, P. Gilderson, and A. T. Blades, *Can. J. Chem.*, **43**, 1934 (1965).

(10) T. F. Thomas and C. Steel, *J. Am. Chem. Soc.*, **87**, 5290 (1965).

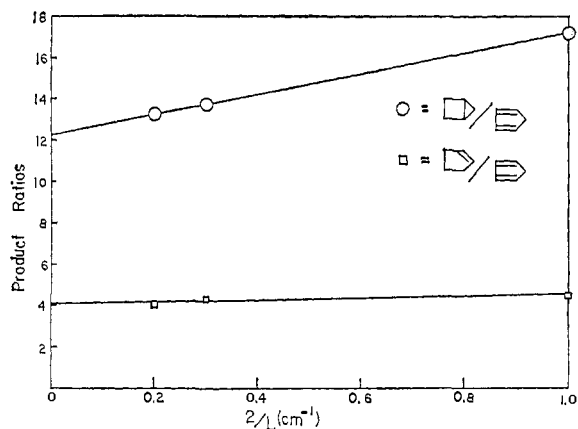(11) S. G. Cohen, R. Zand, and C. Steel, *ibid.*, **83**, 2895 (1961).

Figure 1. Effect of cell length L on product ratios. The pressure of I was 1 mm and the photolysis wavelength 334 mμ: ○, [II]/[IV]; □, [III]/[IV]. The size of the points represents the spread in the ratios obtained for a series of analyses of each sample.

flask in the case of the added gas runs) to the desired azo pressure, then quickly expanding a much higher pressure of the added gas into the same vessel. The sudden pressure surge served to mix the two gases thoroughly at the pressures employed. In some cases the azo compound was frozen into a small tip of the reaction vessel (at 78°K) and then a known amount of the inert gas added by freezing into the same tip. Pressures were measured by means of a Texas Instruments quartz spiral pressure gauge calibrated throughout the range 2×10^{-3} to 5×10^2 torr. When filling vessels with DBH the pressure in the system was monitored for 10–20 min before closing off photolysis vessels, in order that equilibrium between the vapor and surface-adsorbed phases might be closely approached.[10] The ultimate vacuum of the sampling line was checked with a cold cathode vacuum ionization gauge (N.R.C. Equipment Corp.).

The reaction vessels used were cylindrical Pyrex optical cells of 19-mm o.d. and lengths ranging from 2.0 to 20 cm. They were sealed either by fusing the glass connecting tubing (while the sample was kept at 77°K) or by closing a greaseless bellows valve (Hoke 480). Leak rates as low as 5×10^{-4} torr in 24 hr into a 25-cc vessel were attained with the latter.

Optics and Light Sources. Samples were irradiated with the output of a Bausch and Lomb 500-mm grating monochromator, using both a high-pressure mercury arc and a xenon arc as light sources (P.E.K. 110 and 75). Slits were set at 1.0 mm for the mercury arc and 0.7 mm for xenon arc giving band widths (total width at half-intensity) of 3.3 and 2.3 mμ, respectively. The wavelength settings of the monochromator were calibrated by means of a low-pressure mercury "Pen-Ray" source.[12] An optical train consisting of a quartz condensing lens and an adjustable diaphragm was used to collimate the light emitted by the monochromator so that the beam passed through the 20-cm cell without striking its sidewalls. This condition was necessary to reduce the contribution to product formation from photolysis of DBH adsorbed on the cell walls.[10] With only the end faces of the cells illuminated, the ratio of irradiated surface to reaction volume decreased in inverse proportion to the cell lengths. Use of cells of different lengths thus permitted extrapolation of experimental results to the limiting case of zero surface reaction. An example of this extrapolation procedure is shown in Figure 1, where results from cells of length 10, 6.7, and 2.0 cm, DBH pressure 1 torr, and λ_{irr} 344 mμ are plotted. Cells used for these extrapolations were preconditioned by several photolyses at high pressures of DBH (~2 torr) and kept sealed when not in use in an effort to maintain the same surface history for all of them. Inert gas–DBH mixtures were photolyzed in a Rayonet Photochemical reactor in order to accommodate the 2-l. bulb used. The output of the F8T5-BLB lamps used in this reactor superimposed on the DBH absorption spectrum results in an effective irradiation wavelength of 337 mμ in this case.

Photolysis Conditions. When the high-pressure mercury arc was used as the light source, photolyses were carried out until approximately 40% of the DBH had decomposed; this required 10 to 12 hr of irradiation by either 313- or 334-mμ light with the
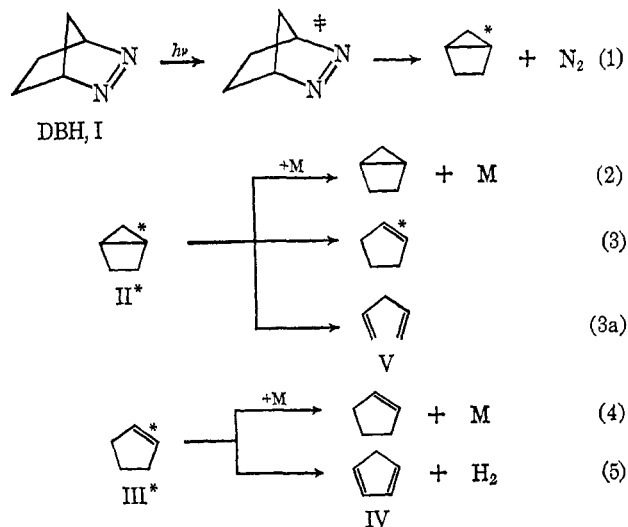
(12) C. B. Childs, *Appl. Opt.*, **1**, 711 (1962).

operating conditions described previously. The continuous emission of the xenon arc was considerably weaker in the range 345 to 313 mμ, so that extents of photolysis between 5 and 15% required irradiation times of from 12 to 65 hr. Extent of photolysis was found to affect the relative product yields only slightly, however. For example, photolysis of 0.109 torr of DBH at 313 mμ (mercury arc) in a 10-cm cell yielded the product ratios II/IV = 0.614 and 0.623, and III/IV = 0.685 and 0.719 after 6 and 21 hr of photolysis, respectively. This effect may result from an increase in the contribution of photolysis at the surface as the reaction progresses, since as the pressure of DBH decreases the fraction of total DBH which is adsorbed on the Pyrex windows increases. No correction of the experimental results back to 0% photolysis was deemed necessary, in view of the smallness of this time effect.

All photolyses were carried out at room temperature, which varied from 23 to 28°. The products were analyzed by gas chromatography, using a 25 ft by $^1/_8$ in. column of 10% SF-96 on Chromosorb W 60-80. Samples for analysis were taken from the optical cells by expansion into a gas-sampling valve, thus avoiding any problems of incomplete freezing out or transfer of products. The identification of N_2, H_2, II, III, and IV as the principle photolysis products has been described previously.[10] In addition 1,4-pentadiene (V) appears to be formed in yields as high as 5%; its identification as a product is based on comparison of retention times with known samples on several different gas chromatographic columns and is supported by mass spectral analysis of the appropriate gc fraction. Because of its low yield, which decreased with increasing pressure, the product could not be collected in large enough quantity to obtain a definitive mass spectrum; however, the parent peak was clearly shown to be 68.

Pyrolysis of Cyclopentene. The pyrolysis of cyclopentene was carried out in a conventional static reaction system similar to that described previously[13] except that the greased stopcocks were replaced by bellows valves (Hoke 480). Pressures above 10 torr were read on a mercury manometer; lower pressures were read on a capacitance manometer (Granville Phillips) which had been calibrated against the quartz spiral manometer. The reaction was carried out to about 10% completion, and then a sample was removed by expansion into an evacuated bulb for gas chromatographic analysis. The first-order rate constant k was then determined from the equation ln [(III + IV)/III] = kt. Beyond 20% decomposition significant amounts of side products appear in the gas chromatograms.[14]

Results and Discussion

Mechanism. The irradiation of DBH (I) in its n–π^* absorption band (*ca.* 300–350 mμ) initiates the sequence of reactions as shown in eq 1–5. In this pro-

cess the slight exothermicity of the primary process (1), estimated to be about 14 kcal mole^{-1},[10] added to the

(13) E. Leventhal, C. R. Simmonds, and C. Steel, *Can. J. Chem.*, **40**, 930 (1962).

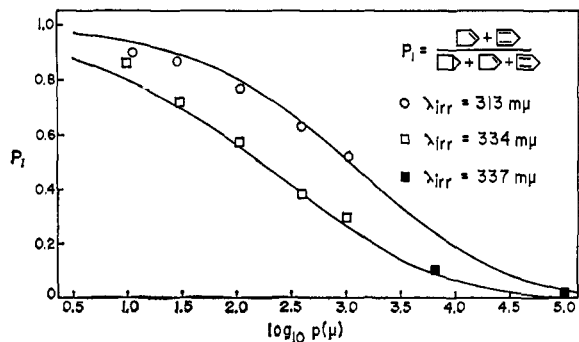(14) Values of A and E_0 for step 5 are from D. W. Vanas and W. D. Walters, *J. Am. Chem. Soc.*, **70**, 4035 (1948).

Figure 2. Variation in product function $P_1 = ([III] + [IV])/([II] + [III] + [IV])$ with pressure p (μ): O, λ_{irr} 313 mμ; □, λ_{irr} 334 mμ; ■, λ_{irr} 337,mμ (effective); O and □, I and no added gas; ■, I and CO_2 as added gas. See text for method of calculating effective pressure in latter case. Full-line curves are theoretical curves derived from model.

Figure 3. Variation in product function $P_2 = [IV]/([III] + [IV])$ with pressure p (μ): O, λ_{irr} 313 mμ; □, λ_{irr} 334 mμ; ■, λ_{irr} 337 mμ (effective); O and □, I and no added gas; ■, I and CO_2 as added gas. See text for method of calculating effective pressure in latter case. Full-line curves are theoretical curves derived from model.

energy of the absorbed light quantum supplies the products II* and III* with vibrational energy well in excess of the activation energies of steps 3, 3a, and 5. Let us first assume that the rate coefficients of these reactions can be represented by a simple Kassel-type equation.[15] Bunker,[16] on the basis of trajectory calculations, has shown that this form is a good approximation over a reasonable energy range. Furthermore this expression will allow us to use the thermal kinetic parameters which are available. Later we shall consider the effect of using a more sophisticated model. We therefore have[14,17]

$$k_3(E_m) = 10^{14.1}\left(1 - \frac{45.6}{E_m}\right)^{s-1} \quad (6)$$

$$k_5(E_m + \Delta H_3) = 10^{13.04}\left(1 - \frac{58.8}{E_m + \Delta H_3}\right)^{s'-1} \quad (7)$$

$$k_{3a}(E_m) = 10^{14.35}\left(1 - \frac{52.3}{E_m}\right)^{s''-1} \quad (8)$$

Here E_m represents the vibrational energy of a particular II*, not including "fixed" or zero-point energy; ΔH_3 in eq 7 is the exothermicity of reaction 3 which equals 28.2 kcal mole^{-1}.[18,19] The values to be chosen for the "number of effective oscillators," s, s', and s'', require some explanation. Halberstadt and Chesick's[20] finding of $s = 18 \pm 2$ seems somewhat low compared to results obtained over a wider pressure range for the homologous ring compound cyclobutane ($s = 18 \pm 1$),[21] methylenecyclobutane ($s = 20 \pm 1$),[22] and methylcyclobutane ($s = 25 \pm 1$).[23] Consequently an assignment of $s = 20.0$ has been made for bicyclo[2.1.0]pentane. The other two assigned values were $s' = 20.8$ and $s'' = 20.0$. The latter choice was made because the same molecule II* is involved in reactions 3 and 3a;

(15) L. S. Kassel, *J. Phys. Chem.*, **32**, 225 (1928).
(16) D. L. Bunker, *J. Chem. Phys.*, **40**, 1946 (1964).
(17) The values of A and E_0 for both steps 3 and 3a are taken from C. Steel, R. Zand, P. Hurwitz, and S. G. Cohen, *J. Am. Chem. Soc.*, **86**, 679 (1964).
(18) M. A. Dolliver, T. L. Gresham, G. B. Kistiakowsky, and W. E. Vaughn, *ibid.*, **59**, 831 (1937).
(19) R. B. Turner, "Kekule Symposium on Theoretical Organic Chemistry," Butterworth & Co., Ltd., London, 1959, p 67.
(20) M. L. Halberstadt and J. P. Chesick, *J. Am. Chem. Soc.*, **84**, 2688 (1962).
(21) R. W. Vreeland and D. F. Swinehart, *ibid.*, **85**, 3349 (1963).
(22) P. J. Burkhardt, Ph.D. Thesis, University of Oregon, 1962.
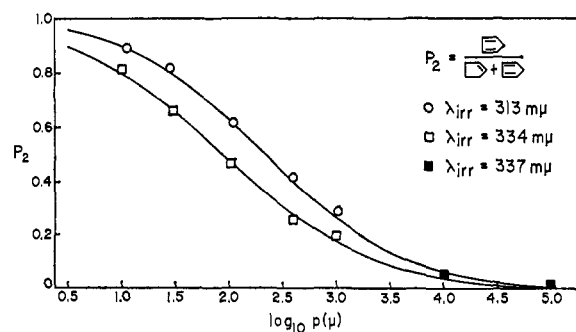(23) T. F. Thomas, Ph.D. Thesis, University of Oregon, 1964.

the former choice was originally made to give more exact agreement with the relative yields of III and IV, but it does in fact agree with our experimental determination of s' (see below). It should be borne in mind that because we are dealing with a linked series of unimolecular reactions only one energy, E_m, has to be assigned; that is, there is only one adjustable parameter to define the rate constants of three reactions. Therefore, this system should provide a more stringent test than do systems in which only one unimolecular reaction is initiated. Rate coefficients for the vibrational deactivation steps 2 and 4 are estimated by assuming a collision diameter of 6.3 A for DBH and by making the simplifying approximation that both II* and III* are deactivated on every collision with a DBH molecule. The resulting values of the rate coefficients at 300°K are

$$k_2 = k_4 = 2.076 \times 10^4 \, \mu^{-1} \, sec^{-1} \quad (9)$$

Pressure Dependence of Product Yields. If the initial hydrocarbon molecules II* are all formed with the same vibrational energy content E_m, then solution of the rate equations for steps 1 through 5, assuming steady-state concentrations of the excited species, leads simply to eq 10–12. The product function P_1 is simply

$$P_1 = \frac{III + IV}{II + III + IV} = \frac{1}{1 + \dfrac{k_2 p}{k_3(E_m)}} \quad (10)$$

$$P_2 = \frac{IV}{III + IV} = \frac{1}{1 + \dfrac{k_4 p}{k_5(E_m + 28.2)}} \quad (11)$$

$$P_3 = \frac{V}{II + III + IV + V} = \frac{1}{1 + \dfrac{k_2 p + k_3}{k_{3a}(E_m)}} \quad (12)$$

the probability that II* undergoes isomerization to III*, while P_2 and P_3 are the probabilities that III* and II* undergo reaction to IV and V, respectively.

The experimental results for the product distribution ratios P_1, P_2, and P_3 are plotted in Figures 2–4 as functions of the pressure. These results were obtained using the mercury arc light source and irradiation wavelengths of 313 and 334 mμ; each point represents at least three photolyses, in vessels of different lengths, and an extrapolation to $2/L = 0$ (see Figure 1). To best fit
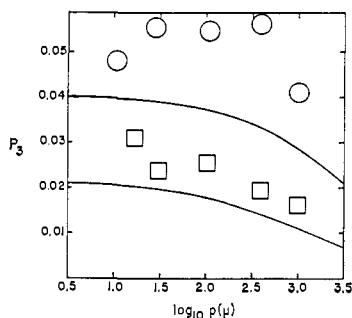
Figure 4. Variation in product function $P_3 = [V]/([II] + [III] + [IV] + [V])$ with pressure p (μ): O, λ_{irr} 313 mμ; □, λ_{irr} 334 mμ. Full-line curves are theoretical curves.

both the experimental values of $P_1 = 0.574$ and $P_2 = 0.468$ at 106 μ of pressure and 334 mμ by eq 10 and 11 requires $E_m = 76.3$ kcal mole^{-1}. Since 334 mμ corresponds to 85.3 kcal/einstein and step 1 is approximately 14 kcal mole^{-1} exothermic, this result indicates that 77% of the excitation energy available to the primary photolysis products goes into the vibrational modes of II*.

Taking $E_m = 76.3$ kcal mole^{-1} and using eq 10 and 11, one may predict $P_1 = 0.124$ and $P_2 = 0.080$ at 1011 μ for λ_{irr} 334 mμ, in contrast to the experimental values $P_1 = 0.294$ and $P_2 = 0.196$. Similarly, the predicted values at 19.9 μ of $P_1 = 0.895$ and $P_2 = 0.838$ disagree with the experimental finding that $P_1 = 0.826$ and $P_2 = 0.745$. Clearly a treatment which assumes that all II*'s are produced with the same degree of vibrational excitation (the basis for using a single E_m in eq 10 and 11) following irradiation of DBH with highly monochromatic light does not accurately predict the data obtained. Therefore, a model which considers the II* to be produced with an explicitly stated distribution of energies must be considered.

It seemed reasonable to assume (see below) that the molecules produced in the primary photolytic process (step 1) would have vibrational energies distributed more or less symmetrically about a single most probable value; hence the following Gaussian-like distribution function was chosen for the II*(E_i).

$$f_{II}(E_i) = \frac{e^{-1/2\left(\frac{E_{mp}-E_i}{\sigma}\right)^2}}{\sum_i e^{-1/2\left(\frac{E_{mp}-E_i}{\sigma}\right)^2}} \quad (13)$$

Here the upper limit on the energies E_i is the total excitation energy available to the products and the lower limit is zero. The most probable value of E_i is E_{mp}, and σ, the standard deviation from E_{mp}, measures the width of the energy spread. Regardless of the form assumed for f_{II}, its fundamental definition is the probability that II* will be produced with a vibrational energy E_i. Applying steady-state conditions to the concentrations of excited molecules in each energy level E_i yields eq 14

$$II^*(E_i) = \frac{f_{II}(E_i)I_a\phi_d}{k_3(E_i) + k_2p} \quad (14)$$

$$III^*(E_i + 28.2) = \frac{f_{II}(E_i)I_a\phi_d\left(\frac{k_3(E_i)}{k_3(E_i) + k_2p}\right)}{k_3(E_i + 28.2) + k_4p} \quad (15)$$

and 15. In eq 14 the effect of step 3a on the steady-state concentration of II*(E_i) has been ignored, this being a reasonable approximation since 1,4-pentadiene never constitutes more than 5% of the total products and its relative yield varies only slowly with pressure and wavelength. I_a is the rate of absorption of quanta by DBH and ϕ_d the quantum yield of dissociation. To obtain the product distribution functions analogous to eq 10–12, it is only necessary to sum the instantaneous rates of steps 2, 3a, 4, and 5 over all the available energy levels of the excited intermediates and combine these total rates as indicated in the definitions (eq 10–12) of P_1, P_2, and P_3.

The results, after some simplification, are

$$P_1 = \sum_i \frac{f_{II}(E_i)k_3(E_i)}{k_3(E_i) + k_2p} \quad (16)$$

$$P_2 = \sum_i \frac{f_{III}(E_i + 28.2)k_5(E_i + 28.2)}{k_5(E_i + 28.2) + k_4p} \quad (17)$$

$$P_3 = \sum_i \frac{f_{II}(E_i)k_{3a}(E_i)}{k_{3a}(E_i) + k_3(E_i) + k_2p} \quad (18)$$

In eq 17 ($f_{III}E_i + 28.2$) is the probability that a III* molecule will be produced with an energy of ($E_i + 28.2$) kcal mole^{-1} and is related to the primary energy distribution function by

$$f_{III}(E_i + 28.2) = \left\{ \frac{k_3(E_i)/[k_3(E_i) + k_2p]}{\sum_i k_3(E_i)/[k_3(E_i) + k_2p]} \right\} f_{II}(E_i) \quad (19)$$

We call the factor in braces the "chemical filter factor," since it results from the fact that more energetic II*'s have a greater chance of escaping collisional deactivation than their less energetic counterparts, thus skewing the distribution of III*($E_i + 28.2$) to higher energies.

The smooth (theoretical) curves appearing in Figures 2–4 are generated from eq 13 through 19 with the vibrational energy spread measured by $\sigma = 6.65$ kcal mole^{-1} and the center of the energy distribution given by $E_{mp} = 76.3$ kcal mole^{-1} for irradiation at 334 mμ and $E_{mp} = 82.04$ kcal mole^{-1} for 313 mμ. These most probable values for the vibrational excitation energy of II* were obtained from

$$E_{mp} \text{ (kcal mole}^{-1}) =$$
$$\left[\frac{28.6 \times 10^3}{\lambda_{irr}(m\mu)} - \Delta H_1\right] - 23.3 \quad (20)$$

The factor in brackets represents the total available excitation energy. We discuss later what may happen to the remaining 23.3 kcal. The summations were evaluated by taking increments in E_i equal to the spacing of the vibrational energy levels in nitrogen, 6.65 kcal mole^{-1}, with the series limited by $E_i \leq [28.6 \times 10^3/\lambda_{irr}$ (mμ)] $+ 14.0$. Original calculations were done with $\Delta E_i = 1$ kcal mole^{-1}, but the larger grid size was employed to save computation time when it was found that increasing to 6.65 kcal did not significantly affect the fit of the theoretical curves to the experimental data.

Inspection of Figures 2 and 3 shows that the procedure just described gives product distribution functions P_1 and P_2 in reasonably good agreement with the experimental values over the pressure range 10^1 to 10^5 μ. The results at the two highest pressures were obtained by adding CO_2 to low pressures of DBH and calculating
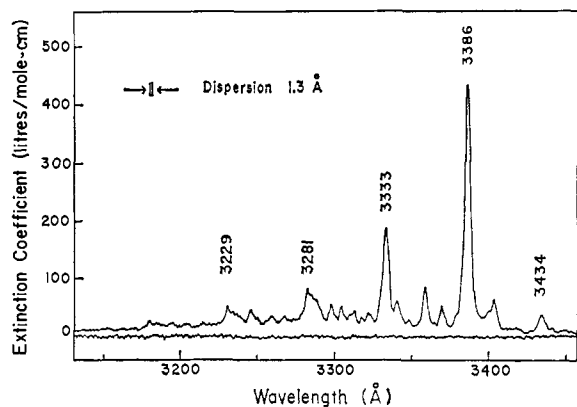
Figure 5. Gas-phase absorption spectrum of 2,3-diazabicyclo-[2.2.1]hept-2-ene (I).

effective pressures from the relative collisional deactivation efficiencies given for CO_2 in Table I. These results show that both P_1 and P_2 go to zero at "high" pressures, as required by the simple hot molecule mechanism. Results at low pressures are subject to greater error in the $2/L \rightarrow 0$ extrapolations, so that it is not possible to state conclusively whether both P_1 and P_2 approach the required limit of unity at sufficiently low pressures, although this appears to be so. The displacement along the log p axis between the experimental results for λ_{irr} 313 and 334 mμ corresponds closely to the spacing between the theoretical curves in the case of both P_1 and P_2, indicating that the degree of vibrational excitation of II* varies with wavelength of irradiation as stated in eq 20.

Experimental values of product distribution functions P_3 are compared with the curves calculated by means of eq 13, 18, and 20 in Figure 4. It can be seen that the predicted values of P_3 are consistently about 30% lower when compared with the experimental P_3's at either wavelength of irradiation. Despite the considerable scatter in the determination of the relative yield of the small smounts of V, there does appear to be some correspondence between the predicted and the observed increase in P_3 with decreasing pressure. Thus it may be tentatively concluded that most or all of the V found in the products is formed via step 3a. The discrepancy between observed and calculated P_3's could be explained by slight error in any of the kinetic parameters used. Thus, both theoretical curves could be raised to pass through the experimental points by any one of the following adjustments: reducing s'' from 20.0 to 19.7, reducing E_0 for step 3a from 52.3 to 51.8 kcal mole^{-1}, or increasing the frequency factor from $10^{14.35}$ to $10^{14.50}$ sec^{-1}. Such adjustments would be very reasonable since the experimental uncertainties in E_0 (step 3a) and A_3 were ±0.6 kcal mole^{-1} and $10^{±0.23}$ sec^{-1}, respectively,[17] and s'' is known to ± 1.0 only by analogy with s. The possibility of a small contribution to formation of V by a concerted mechanism (i.e., directly from DBH) cannot be completely ruled out because of the indicated uncertainties in kinetic parameters, although such a mechanism would not show any pressure effects such as suggested in Figure 4, because of the short lifetime of DBH$^+$ which can be estimated from the known extinction coefficients and the fluorescence yield to be ~3 × 10^{-8} sec.[24]

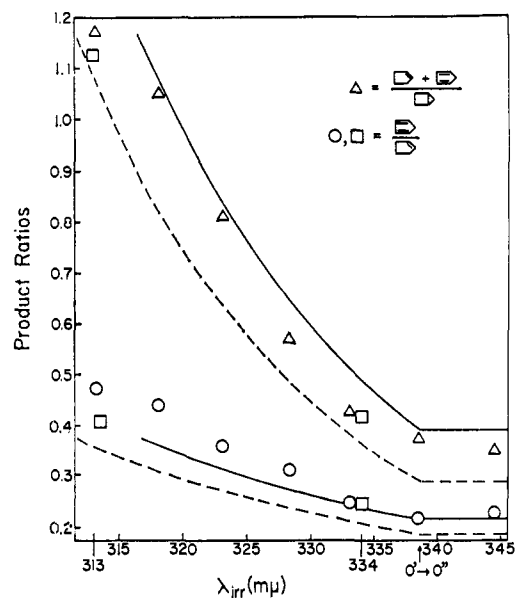Figure 6. Wavelength dependence of product ratios △ for ([III] + [IV])/[II]; □ and ○ for [IV]/[III]; △ and ○, xenon arc photolyses; □, mercury arc photolyses. The dashed- and full-line curves are theoretical curves for E_{mp} = [28.6 × $10^3/\lambda_{irr}$ (mμ)] − 9.33 and [28.6 × $10^3/\lambda_{irr}$ (mμ)] − 7.833 kcal mole^{-1}, respectively.

Wavelength Dependence of Product Yields. The n–π* absorption spectrum of DBH is shown in Figure 5, and the results of photolyses at 986 μ of DBH using a xenon arc as light source and irradiating at successive peaks in the main vibrational progression are shown in Figure 6. The plotted quantity (III + IV)/II is a measure of the ratio of the rate at which II* undergoes reaction to the rate at which it is collisionally deactivated. Since at constant pressure the latter rate is constant, (III + IV)/II is simply a measure of the rate at which II* undergoes reaction. Similarly IV/III measures the rate at which III* undergoes reaction. In detail, allowing for energy dispersion we have

$$R_1 = \frac{III + IV}{II} = \frac{\sum_i \tau_{II}(E_i)f_{II}(E_i)k_3(E_i)}{\sum_i \tau_{II}(E_i)f_{II}(E_i)k_2 p} \quad (21)$$

$$R_2 = \frac{IV}{III} =$$

$$\frac{\sum_i \tau_{III}(E_i + 28.2)f_{III}(E_i + 28.2)k_5(E_i + 28.2)}{\sum_i \tau_{III}(E_i + 28.2)f_{III}(E_i + 28.2)k_4 p} \quad (22)$$

where τ_{II} and τ_{III}, the lifetimes of II* and III*, respectively, are given by the formulas $\tau_{II}(E_i) = 1/[k_3(E_i) + k_2 p]$ and $\tau_{III}(E_i + 28.2) = 1/[k_5(E_i + 28.2) + k_4 p]$. The strong dependence of the product ratios on wavelength of irradiation is clearly shown; a change of 7.1 kcal mole^{-1} in E_λ, the irradiation energy per einstein, on going from the absorption maximum at 3386 A to the one at 3129 A changes R_1 by a factor of 3.12. Theoretical curves in Figure 6 calculated from the above equations accurately predict this strong dependence on λ_{irr}. In calculating the dotted curves, the most probable value for the vibrational energy of II* was assumed to be given by eq 20, with all other quantities the same as used to fit the pressure dependence data. Increasing

(24) C. Steel and T. F. Thomas, Chem. Commun., 900 (1966).

E_{mp} by 1.5 kcal mole^{-1} (solid curves) is seen to give a noticeably better fit to the wavelength dependence data. That this slight discrepancy between the assignments of E_{mp} required to give the best fit to the wavelength-dependence and the pressure-dependence results is not primarily the result of differences in photolysis conditions such as light intensity and extent of photolysis is indicated by the results of mercury arc photolyses displayed as squares in Figure 6 where the intensity was 20 times greater than for the xenon arc photolyses. In fact the departure of the experimental points from the dotted curves corresponds closely to the upward deviation of P_1 at 1000 μ of DBH from the theoretical curves in Figures 2 and 3. Whether these slight discrepancies —which are also observable at low pressure, especially for P_1—result from experimental artifacts such as inaccurate correction for surface photolysis or reflect minor complications not considered in the treatment of the reaction mechanism is not known.

Hot-Band Effect. A notable feature of both the experimental results and the theoretical curves is the attainment of a plateau at 3386 A. We discuss elsewhere[24,25] evidence that the (0'–0'') band is at 3386 A and that the band at 3434 A is a hot band corresponding to the (0'–1'') transition. In summary this evidence is based on the facts that (i) the short wavelength origin of the fluorescence is at 3386 A; (ii) the spacing between the band at 3386 A and that at 3434 A, *viz.* 410 cm^{-1}, corresponds exactly to a strong infrared band seen directly in absorption but is significantly different from the spacing of the main absorption progression which is 480 cm^{-1}; (iii) the intensity of the band at 3434 A relative to the intensities of the other vibronic bands is temperature dependent. These conclusions are further reinforced by the present studies which show that II*'s produced by irradiation of DBH at both 3386 and 3434 A behave as if they had the same excess energy, that is, are formed from isoenergetic DBH molecules.

Other Models for Rate Coefficients. In the previous discussion we have used a model in which each oscillator has at least its fixed zero-point energy and in which the excess or "nonfixed" energy[26] is distributed classically among these oscillators. The arbitrary nature of this model has long been recognized, but it possesses the advantage that the parameters can be readily determined experimentally. The Marcus theory[26] does much to remove the arbitrariness, in particular eliminating the ill-defined parameter s, and has been shown to give an excellent fit to experimental data. But for its successful application it requires a vibrational analysis of the molecules concerned and detailed knowledge of the nature of the activated state, information which we do not have for the reactions considered here. However in an elegant series of papers Rabinovitch and his co-workers[27–29] have shown that to a good approximation

$$k(E) = A\left(\frac{E - E_0 + a^+E_z^+}{E + aE_z}\right)^{n-1} \tag{23}$$

(25) B. S. Solomon, T. F. Thomas, and C. Steel, to be published.
(26) R. A. Marcus, *J. Chem. Phys.*, 20, 355, 359 (1962).
(27) D. W. Setser, B. S. Rabinovitch, and E. G. Spittler, *ibid.*, 35, 1840 (1961).
(28) B. S. Rabinovitch and J. H. Current, *ibid.*, 35, 2250 (1961).
(29) D. W. Setser and B. S. Rabinovitch, *Can. J. Chem.*, 40, 1425 (1962).

A is identified with the high-pressure frequency factor, n is the total number of vibrational modes, E_z^+ and E_z are the total zero-point energies of the activated state and the reactant molecule, respectively, and a^+ and a are arbitrary factors which made $k(E)$ equal to the "exact" value; they are weak functions of energy and generally lie between 0.83 and 0.94. We can estimate values of a^+, a, E_z^+, and E_z for II from the data given for 1,2-dimethylcyclopropane[27] since the latter is structurally similar to II. The values chosen were 0.85, 0.93, 68, and 70.3 kcal, respectively. Equation 23 fits our experimental results at 334 mμ when E = 61.8 kcal mole^{-1} compared with 76.3 kcal mole^{-1} when the simple Kassel form is used. However, eq 23 predicts a less strong energy dependence than eq 6. In the former case $k_3(67.5)/k_3(61.8)$ = 2.7 while in the latter $k_3(82.0)/k_2(76.3)$ = 6.5, and in fact our experimental data are better fitted by this model. So the interesting point emerges that the data for three reactions with different activation energies and with energies in strongly non-Boltzmann distributions are adequately accommodated by calculations using simple Kassel rate coefficients and thermal kinetic parameters.

Vibrational Energy Transfer. The production of vibrationally excited molecules II* and III* in the photolysis of I allows the study of the relative vibrational deactivation efficiencies of various added gases. The system is particularly attractive for this purpose because the photolyses may be carried out at room temperature and no free radicals are produced. Thus energy-transfer efficiencies of chemically interesting species which would react at higher temperatures, as in the usual thermal unimolecular studies,[30] or in the presence of free radicals can easily be determined. In addition, since both the degree and the range of vibrational excitation of II* and III* have been determined, the effect of these factors, as well as the effect of the chemical and physical properties of the transfer agent, on the deactivation efficiencies of the added gases may be studied. We report here on some preliminary data. If a strong collision model is assumed for deactivation, then it can readily be shown that the deactivation efficiencies of added gases (M) relative to I on a pressure-to-pressure basis are given by

$$\frac{k_2(M)}{k_2(I)} = {}^1\beta_p(M) = \frac{{}^1p_{eff} - p_{DBH}}{p_M} \tag{24}$$

$$\frac{k_4(M)}{k_4(I)} = {}^2\beta_p(M) = \frac{{}^2p_{eff} - p_{DBH}}{p_M} \tag{25}$$

Effective pressures were determined by comparing the product distribution functions obtained in the presence of M with the pressure dependence curves for pure DBH. ${}^1p_{eff}$ was obtained from P_1 curves and ${}^2p_{eff}$ from P_2 curves. The efficiencies are converted to collision-to-collision efficiencies through the equation

$$B_c(M) = \beta_p(M)\left(\frac{\mu_{MA}}{\mu_{AA}}\right)^{1/2}\left(\frac{\sigma_{AA}}{\sigma_{MA}}\right)^2 \tag{26}$$

where μ_{AA} and μ_{MA} are the reduced masses of the azo compound and the azo added-gas pair, and σ_{AA} and σ_{MA} are the corresponding mean collision diameters. Values of ${}^1\beta_p(CO_2)$ and ${}^2\beta_p(CO_2)$, for which the carbon

(30) T. L. Cottrell and J. C. McCoubrey, "Molecular Energy Transfer in Gases," Butterworth & Co., Ltd., London, 1961, p 186.

Table I. Relative Deactivation Efficiencies of Carbon Dioxide

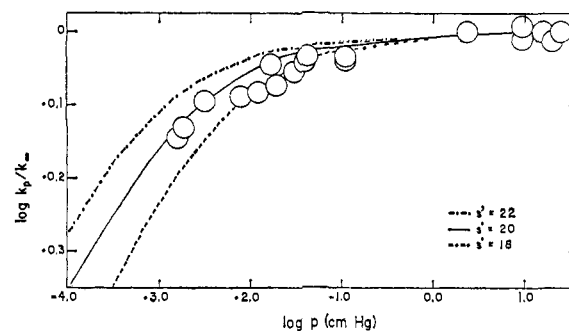| p_I, μ	p_{CO_2}, mm	P_1	P_2	$^1\beta_p(CO_2)$	$^2\beta_p(CO_2)$
156	0.496	0.437	0.292	0.117	0.137
98	0.802	0.424	0.267	0.176	0.212
95	1.017	0.411	0.235	0.172	0.240
102	2.629	0.320	0.174	0.207	0.191
16	1.178	0.458	0.225	0.114	0.204
19	1.222	0.454	0.235	0.141	0.255
82	2.640	0.346	0.148	0.142	0.237
34	0.626	0.505	0.313	0.155	0.254
171	2.074	0.347	0.183	0.138	0.215
148	0.621	0.445	0.282	0.140	0.140
164	0.591	0.405	0.262	0.234	0.246
19	3.139	0.338	0.145	0.151	0.253
22	2.111	0.392	0.188	0.147	0.256
20	584.0	0.022	0.091	...	...
199	586.0	0.031	0.019	...	...
200	600.0	0.030	<0.03	...	...
20	600.0	0.023	0.027	...	...
Average				0.16 ± 0.02	0.22 ± 0.03

Figure 7. Pyrolysis of cyclopentene (450°, reactor volume 300 cc). Falloff curves calculated using Kassel parameters given by 7, s' as shown, and collision diameter = 5.0 A.

propylene show that the deactivation efficiency varies greatly even among molecules of essentially the same molecular weight, contrary to what would be predicted for a simple transfer of excess vibrational energy into

Table II. Relative Collisional Deactivation Efficiencies of Added Gases

Added gas (M)	σ_{MM}, A[a]	$^1\beta_0(M)$	$^2\beta_c(M)$	$B_c(M)$ (pyrolysis)
Ar	3.42	0.080 ± 0.010	0.170 ± 0.020	0.07 $(c\text{-}C_3H_6)$,[b] 0.21 $(c\text{-}C_4H_8)$[c] 0.15 (N_2O_5)[d]
CO_2	4.00	0.19 ± 0.02	0.26 ± 0.03	0.39 (N_2O_5),[d] 0.23 $(C_2H_6N_2)$[e,f] 0.27 ± 0.15 $(c\text{-}C_5H_8)$[g]
C_3H_6	5.00	0.57 ± 0.08	0.38 ± 0.06	0.53 ± 0.08 (C_5H_{10})[h]
$C_5H_8N_2$ (I)	6.30	(1.00)	(1.00)	
C_8H_{18}	7.45	1.10 ± 0.19	0.87 ± 0.15	

[a] Values are taken from J. O. Hirschfelder, C. F. Curtis, and R. P. Bird, "Molecular Theory of Gases and Liquids," John Wiley and Sons, Inc., New York, N. Y., 1954, p 112, or are reasonable estimates based on data given in this reference. [b] H. O. Pritchard, R. G. Sowden, and A. F. Trotman-Dickenson, *Proc. Roy. Soc.* (London), **A217**, 563 (1953). [c] H. O. Pritchard, R. G. Sowden, and A. F. Trotman-Dickenson, *ibid.*, **A218**, 416 (1953). [d] D. J. Wilson and H. S. Johnston, *J. Am. Chem. Soc.*, **75**, 5763 (1953). [e] D. V. Sideman and O. K. Rice, *J. Chem. Phys.*, **4**, 608 (1936). [f] C. Steel, Ph.D. Thesis, University of Edinburgh, 1958. [g] This work. [h] Reference 23.

dioxide pressure was varied by a factor of 60 and for which the initial pressure of I was varied from 16 to 171 μ, are presented in Table I. The data show no obvious trends in the relative efficiencies either with p_{CO_2} or p_I; in fact the average values of β have a better precision than is usually achieved by standard pyrolysis methods.

Data for other gases, together with results from pyrolysis studies, are given in Table II. A stepwise deactivation model[3] in which ΔE_{step} = 10 kcal mole^{-1} gave P_1 and P_2 curves essentially indistinguishable from those for the strong collision model. Since there is good evidence [31] that I will transfer at least this amount of energy per collision, a limiting value of β = 1 simply implies a transfer of at least 10 kcal mole^{-1} per collision. This is a relatively small amount of energy compared to the total excess energy possessed by II* and by III*, and this is undoubtedly the reason why β rapidly approaches unity with increasing molecular complexity. A value of β < 1 implies, in the two extremes, either that energy transfer does not occur on every collision but that $\Delta E_{step} \geqslant$ 10 kcal mole^{-1} when transfer does take place, or that transfer does take place on every collision with ΔE_{step} < 10 kcal mole^{-1}. The former is implicitly assumed in the derivation of eq 24 and 25, but our present data cannot distinguish between these possibilities. Our data for argon, carbon dioxide, and

translational motion. Indeed, the deactivating efficiencies increase as a smooth function of molecular complexity as measured by the degrees of freedom of the deactivating species. Our values of β may also be compared with those obtained from chemical activation studies. Kohlmaier and Rabinovitch[32] obtained the following efficiencies of M, relative to butene, in deactivating vibrationally excited *sec*-butyl radicals, $\beta_{min}(Ar)$ = 0.30 and $\beta_{min}(CO_2)$ = 0.75.

Pyrolysis of Cyclopentene. A brief investigation into the rate constant for the decomposition of cyclopentene was carried out in order to check the assignment of s' used in calculating the rate coefficient in eq 7. The results are shown in Figure 7. The curves are the familiar Kassel falloff curves; the value of σ was taken to be 5.0 A in accord with previous calculations.[20] It was found that s' = 20 ± 1 fits the observed pressure dependence which is consistent with our assigned value of 20.8. Because the change in rate constant over the experimentally accessible region was so small, the value of $\beta(CO_2)$, Table II, is of poor precision.

The Distribution of Energy. Both the pressure-dependence and the wavelength-dependence results have shown that despite the use of highly monochromatic light (energy band width of 0.7 kcal mole^{-1} when a xenon arc was used) the hydrocarbon products of the

(31) D. W. Setser, B. S. Rabinovitch, and J. W. Simons, *J. Chem. Phys.*, **40**, 175 (1964).

(32) G. H. Kohlmaier and B. S. Rabinovitch, *ibid.*, **38**, 1692, 1709 (1963).

Table III. Observed Fractions of Excess Energy in Primary Products

System	λ_{irr}, A	E_{max}^*, kcal mole^{-1} [a]	E_{mp}^*/E_{max}^*	n_p^*/n_v [b]
DBH → C$_5$H$_8^*$ + N$_2$	3341	$\sim$99.6	$\sim$0.77	33/39 = 0.85
THF → c-C$_3$H$_6^*$ + HCHO	2000	$\sim$115	$\sim$0.75	21/33 = 0.64
CHBr$_3$ → CHBr$_2^*$ + Br	2000	$\sim$87	$\sim$0.48	6/9 = 0.67
NOCl → NO* + Cl	1970	$\sim$107	$\sim$0.37	1/3 = 0.33
CH$_2$N$_2$ → CH$_2^*$ + N$_2$	4358	$\sim$67	$\sim$0.43	3/9 = 0.33
CH$_2$CO → CH$_2^*$ + CO	3200	$\sim$30	$\sim$0.67	3/9 = 0.33

[a] Source of thermochemical data are to be found in refs 5–7, 10, 29, and J. G. Calvert and J. N. Pitts, "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1966, pp 815–826. [b] n_p^* = number of vibrational modes in the excited product. $n_v = 3N - 6$, where N is the number of atoms in the original molecule.

primary photochemical step are formed with a wide range of vibrational energies, having a standard deviation of 6.65 kcal mole^{-1} from the most probable value. This factor of 10 increase in the energy dispersion must therefore occur during the primary process, following the absorption of light by I. Such an energy spread is possible in the decomposition of an isolated molecule only because not all of the excess energy available to the products of step 1 goes into the vibrational modes of II*. In fact, use of eq 20 throughout implies that 23.3 kcal mole^{-1} (23% at 334 mμ) of the available excess energy enters other degrees of freedom: N$_2$'s vibrational mode, rotational modes of either product, or translational motion of the two products with respect to each other.

That a large fraction of the excess energy goes into the vibrational modes of the more complex of the two products is not surprising when earlier results on photochemical production of hot molecules are considered. Photolysis of tetrahydrofuran at $\sim$2000 A has been reported[7] to yield vibrationally excited cyclopropane and formaldehyde. The former isomerizes to propylene with a rate constant which indicates a vibrational energy content of 86 kcal mole^{-1}, 74.8% of the estimated excess energy available to the two primary products. In this case most of the remaining energy probably energizes the vibrational modes of HCHO. In another case, flash photolysis of CHBr$_3$ with unfiltered light (λ $\sim$2000 A) produced vibrationally excited CHBr$_2$'s, 5% of which had energy in excess of the 57 kcal mole^{-1} required to eliminate HBr at sufficiently low pressures.[6] Taking the total excess energy available to CHBr$_2^*$ to be 87 kcal mole^{-1} and assuming the same general form and width for the distribution of the excess energy as found for DBH, it may be estimated that the most probable value for E^*_{vib}(CHBr$_2^*$) was roughly 42 kcal mole^{-1}. This is only 48% of the available energy, perhaps reflecting the fact that CHBr$_2$ has only six vibrational modes to absorb the excess energy, although the reliability of this estimate is reduced by the several assumptions made in obtaining it.[33]

Flash photolysis of nitrosyl chloride in quartz vessels, with effective wavelength of photolysis presumably close to the absorption maximum at 1970 A, has been found to produce NO* with up to 55 kcal ($v'' = 11$) of vibrational excitation.[5] Because vibrational relaxation of the upper levels was faster than decay of the exciting

(33) In particular the authors assumed $k(E^*) = 10^{13}[(E^* - 57)/E^*]^5$, reasonable enough in the absence of experimental values for the Kassel parameters, but potentially leading to k's in error by factors of 10, E^*'s by 5 to 10 kcal mole^{-1}. Also, the assumption of $\sigma = 6.6$ kcal for this system is purely speculative.

flash, it is not possible to determine whether the observed distribution of vibrational energies among product NO*'s was a result of stepwise collisional deactivation or was produced initially in the primary process. Assuming the latter source and a similar magnitude of energy spread as used for CHBr$_2^*$, it can be estimated that the E^*_{mp} $\sim$ 40 kcal mole^{-1} for the NO*, or 37% of the total excess energy available. Estimates of the fraction of the excess energy which appears in methylene produced by the photolysis of both diazomethane and of ketene have been made by Setser and Rabinovitch.[29] These estimates have a considerable range because of the uncertainty in the heats of formation of methylene and of diazomethane.

A summary of the fraction of excess energy which appears as vibrational excitation in the indicated product for the systems just discussed is given in Table III. There is seen to be a fairly good correlation between the fraction of the total excess energy appearing in the n_p^* vibrational modes of the starred products and the ratio of n_p^* to the total number of degrees of freedom of the original molecule less modes corresponding to translation of and rotation about its center of mass. These latter six modes (five when the original molecule is linear) must be excluded to conserve the linear and angular momentum of the total, isolated system. Table III indicates that a classical approach, assuming all involved degrees of freedom to receive equal portions of the available excess energy, gives a useful first approximation to the extent of vibrational excitation that may be expected in the product of a primary photodecomposition step.

For quantitative prediction of how excess energy will be apportioned among the various available modes it is necessary to consider specific factors that may favor one mode over another. As Simons and Yarwood[6] have pointed out, either an increase in any equilibrium bond distance between the ground and the electronically excited state of a molecule or a decrease in some equilibrium bond distance upon dissociation from the excited state may lead to preferential excitation of vibrational modes involving the affected bond. Thus the relatively high degree of vibrational excitation observed in NO* produced from NOCl probably results from the larger equilibrium N–O distance in COCl‡ than in the ground-state NOCl, for the N–O distance is only slightly different in NO and NOCl (both ground state). On the other hand the c-C$_3$H$_6^*$ produced on photolysis of tetrahydrofuran has a greater fraction of the excess energy than would be predicted from a classical equipartition of energy. Here the most significant change

in geometry is a sharp reduction in the C-C-C bond angle in the formation of c-C_3H_6*. These factors would be expected to lead to preferential excitation of the ring vibrational modes of the cyclopropane, giving this product an increased fraction of the excess energy.

In the formation of N_2 from I the N-N bond distance decreases from approximately 1.24 to 1.09 A.[34] Because of the rather rigid structure of I we expect that the electronic state from which dissociation occurs will have essentially the same geometry as the ground state and that consequently most of the change in the N-N distance occurs between the former state and N_2 leading to excitation of the vibrational mode of N_2. The extent of this vibrational excitation may be estimated by calculating the potential energy of a N_2 molecule extended to 1.24 A using the appropriate Morse equation. The value turns out to be 23.0 kcal mole^{-1}. Quantitative significance cannot be claimed for this calculation; for one thing some of the "potential energy stored in the nitrogen-nitrogen bond" may be transferred to the hydrocarbon ring before dissociation is complete. Nevertheless, the result suggests that N_2* is likely to be produced with up to four vibrational quanta (26.6 kcal mole^{-1}), which would account for the large amount of "unassigned" energy appearing in eq 20 and for the smaller than predicted fraction of the excess energy which II* receives ($cf.$ Table III). On the other hand methylene produced by photolysis of diazomethane acquires a large fraction of the excess energy. If we again assume that the N-N distance in the excited state of diazomethane from which dissociation occurs is the same as that of the ground state, 1.18 A, this results in the formation of N_2* with only 9.5 kcal mole^{-1} of excess vibrational energy. The change in the C-O bond distance in going from ketene to CO is even less, 1.15 to 1.13 A, and in this case we would expect methylene to acquire most of the excess energy.

We can also use this model to rationalize the form of energy distribution function used previously, eq 13. If we assume that the N=N stretching mode in I‡ is a harmonic oscillator in its lowest energy level, the distribution of X's (the internitrogen distances) about their equilibrium value will be of the Gaussian form $P_0(X) = (\beta/\pi)^{1/2}e^{-\beta(X_0 - 1.24)^2}$ where β depends upon the reduced mass and the force constant of the oscillation. Substituting a reasonable value, 13.3×10^5 dynes cm^{-1}, for the force constant[35] allows us to calculate the standard

deviation σ ($= 1/\sqrt{2\beta}$) from the equilibrium value as 0.04 A. This may also be taken to be the deviation in the interatomic distances of the excited nitrogen molecules when they are initially formed, and from the Morse equation, for $r_{mp} = 1.24$ A, this corresponds to a σ of 9.5 kcal mole^{-1}, somewhat greater than the experimental value of 6.7 kcal mole^{-1}. The good fit achieved between the Gaussian distribution function and the experimental product distribution functions ranging in value from 0.01 to 0.90 rules out the production of any significant ($>10\%$) fraction of vibrationally "cold" molecules, such as was recently proposed to explain results in the t-pentyl nitrite system.[8] It should be interesting in the latter case to see whether the pressure dependence of the $CH_3COCH_3/CH_3COC_2H_5$ ratio (products from decomposition of $C_2H_5C(CH_3)_2O$*) could be reproduced by using a simple Gaussian distribution function or whether in fact a bimodal distribution is necessary.

Other factors in addition to excitation of N_2* which may contribute to the energy dispersion observed in II* will be mentioned briefly. Concentration of energy in excess of any activation energy for step 1 into the critical (decomposition) mode of I would convert a portion of the total excess energy into relative translational energy of the two products. This possibility has been considered in a previous paper,[10] but probably does not account for most of the "missing" excess energy. Another possible cause of the energy dispersion, stepwise collisional deactivation, was considered. As mentioned previously this assumption for $\Delta E_{step} = 10$ kcal mole^{-1} led to pressure-dependence curves virtually indistinguishable from those based on a strong collision assumption, because a 10-kcal mole^{-1} energy loss makes eventual deactivation much more likely than reaction in the pressure regions of interest. Energy dispersion by partial vibrational relaxation of DBH‡ is also probably not significant. In the first place photolysis at 334 mμ only excites the molecule to $v' = 2$; secondly, the short lifetime of DBH‡ ($\sim 3 \times 10^{-8}$ sec) precludes pressure effects below 10^4 μ.

It would therefore appear that because of energy dispersion in the primary step the direct photochemical method of producing vibrationally excited molecules may not be too useful as a sophisticated test of unimolecular theory. However, if this dispersion can be determined and quantitatively allowed for, the method will retain some of its hoped for usefulness. In particular, information about the mechanism of photochemical dissociation may be a valuable by-product of knowledge of the form and width of this dispersion.

(34) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, pp 228–230.
(35) E. B. Wilson, J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill Book Co., Inc., New York, N. Y., 1955, p 175.