

versely, triplet benzene molecules should give triplet methylenes.

Since  $^1\text{CH}_2$  and  $^3\text{CH}_2$  apparently yield the same products upon reaction with benzene, it will be necessary to use other reactions to determine the ratio  $[^1\text{B}_{2u}]/[^3\text{B}_{1u}]$ .

If propane is added to the ketene-benzene system in a region where absorption is almost solely by the benzene, one can assume that  $^1\text{CH}_2$  and  $^3\text{CH}_2$  react with the propane by their previously discussed reactions 21-24. It is now possible to use ratios of certain products, particularly  $[n\text{-C}_4\text{H}_{10}]/[i\text{-C}_4\text{H}_{10}]$ , which are closely related to the fraction of triplet methylenes to determine the ratio  $[^1\text{B}_{2u}]/[^3\text{B}_{1u}]$ .

At 2800 Å in ketene-propane mixtures one finds  $[n\text{-C}_4\text{H}_{10}]/[i\text{-C}_4\text{H}_{10}] = 1.93$  and  $\alpha_T$  is 0.20. At 3800 Å the figures are 0.37 and  $\alpha_T = 0.77$ . From the data one can make a plot of  $[n\text{-C}_4\text{H}_{10}]/[i\text{-C}_4\text{H}_{10}]$  vs.  $\alpha_T$ .

At constant total pressure the fraction of triplet methylenes may increase as the mole fraction of ketene decreases in the ketene-benzene-propane system since the ratio  $[n\text{-C}_4\text{H}_{10}]/[i\text{-C}_4\text{H}_{10}]$  goes down at 2520 Å (where ketene does not absorb). The limiting ratio is 0.30. This gives 0.87 for the fraction of triplet methylenes.

The fluorescent yield of benzene is 0.18,<sup>29</sup> and at zero ketene pressure 0.82 is the fraction of benzene molecules free to engage in other processes. If the fraction of  $^3\text{CH}_2$  is equated to the fraction of  $^3\text{B}_{1u}$  radicals, one obtains  $0.82 \times 0.87 = 0.71$  as the apparent quantum yield of triplet benzene. This figure is based on data from the ketene-propane system.

The value 0.71 agrees as well as could be expected with the values obtained by the method of Cundall, *et al.*,<sup>30</sup> and by the use of biacetyl.<sup>31</sup> In a forthcoming article C. Burton and the senior author have reviewed data on triplet benzene formation in the gas phase at about 2530-2590 Å and conclude that  $0.72 \pm 0.07$  is about the best value based on presently available information.

These calculations are not stressed but are presented as interesting support for the order of magnitude of the yield of triplet benzene.

(30) R. B. Cundall and A. S. Davis, *Trans. Faraday Soc.*, **62**, 1151 (1966); W. A. Noyes, Jr., and D. A. Harter, *J. Chem. Phys.*, **46**, 674 (1967).

(31) *Cf.* W. A. Noyes, Jr., and I. Unger, *Pure Appl. Chem.*, **9**, 461 (1964).

## Mechanistic Consequences of Curved Stern-Volmer Plots. The Photolysis of Cyclobutanone.

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**Abstract:** Mechanistic determinations of photochemical mechanisms are often based on a steady-state analysis of a simplified mechanism, which then often predicts straight-line behavior for reciprocal pressure plots, etc. For the special case of fluorescence processes this leads to the well-known Stern-Volmer plots. If one of the steps of this mechanism involves an energy-dependent rate constant, then such a quasi-Stern-Volmer plot may no longer be linear and hence is not useful as a test of the mechanism, let alone give numerical values for the individual constants of the mechanism. Conversely, however, a linear Stern-Volmer plot is no guarantee against these complications since the pressure curvature may set in at pressures higher than investigated. This complication is extremely severe in the present example and has its origin in the spread in internal energy of one of the intermediates as the result of strong photopartitioning, even though the irradiation was carried out with monochromatic light. For nonfiltered photo-experiments one would expect this complication to be aggravated. The mechanism of the photolysis of cyclobutanone is considered in light of this complication, forcing one to perform more elaborate experiments to elucidate the nature of the primary steps. It is shown here that propylene is not formed in a primary process anywhere within the first absorption band of cyclobutanone. Although this has been suggested before, the conclusion was based on inadequate evidence. A simple quasi-Stern-Volmer plot would easily have led one to the opposite conclusion.

Mechanistic analyses of photochemical systems frequently employ pressure plots of the observed species as a means of interpreting the mechanism. These analyses implicitly assume that the reactive species can be divided into reactive and unreactive states only. In particular, such a two-level mechanism yields a linear plot if relative concentrations are appropriately plotted against reciprocal pressures, the Stern-Volmer plot, in the case of a quenching process. If such a plot

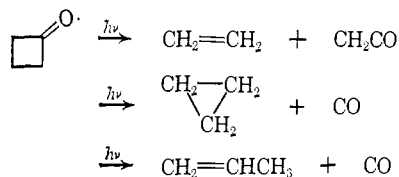
has pronounced curvature, this can be attributed to a variety of causes,<sup>2</sup> hence making any mechanistic conclusions difficult at best. The opposite has, however, not been clearly emphasized; that is, even linear (or nearly linear) plots may not be a sufficient guarantee against this type complication, hence invalidating conclusions based on this apparently linear plot. One should probably look for special features of a mechanism before accepting results derivable from a linear Stern-Volmer plot. The photolysis of cyclobutanone

(1) (a) Abstracted from the Ph.D. thesis of R. J. Campbell; (b) Alfred P. Sloan Research Fellow; (c) National Science Foundation Undergraduate Participant.

(2) H. M. Frey and I. D. R. Stevens, *J. Chem. Soc.*, 4700 (1964); T. F. Thomas and C. Steel, *J. Am. Chem. Soc.*, **87**, 5290 (1965).

constitutes a case for which the two-level approximation breaks down completely, such that the mechanistic analysis based on this approximation becomes invalid, even though over a range of pressures the system appears to give linear quasi-Stern-Volmer plots.

The following reactions have been suggested as the primary processes.<sup>3</sup>



It was reported that the ethylene to carbon monoxide ratio was a function of temperature and wavelength and that the ratio of cyclopropane to propylene was 15.5 at 3130 Å and independent of temperature and pressure although the same ratio was about 2 at 2537 Å and was a function of pressure.<sup>4</sup> When the photolysis was done in a large excess of ethylene (E), an increase in the yield of pentenes was observed.<sup>5</sup> This was attributed to a gettering mechanism by ethylene of the trimethylene biradical which occurs as an intermediate in the primary step. In work done recently by Klemm, Morrison, Gilderson, and Blades (KMGB)<sup>6</sup> it was reported that the E/CO ratio was  $1.7 \pm 0.1$  at both 3130 and 2537 Å with only a slight temperature dependence at 3130 Å. They tried the ethylene-gettering experiments but were unable to find evidence for increased pentene formation. They also did pressure studies at both wavelengths at 100° and over a pressure range of 10–200 torr. From the sharp pressure dependence of the cyclopropane to propylene ratio they concluded that the propylene was formed in a secondary reaction from vibrationally hot cyclopropane. The basis for this conclusion does not appear clear and it was felt that there still was not sufficient evidence to decide whether propylene is a primary photolytic product. Since we were interested in studying the detailed energy-transfer processes, it was important to definitely establish whether or not any propylene was formed directly.

### Experimental Section

Greaseless stopcocks, diaphragm pressure gauges, and oil pumps were used in a conventional high-vacuum system to ensure a completely mercury-free system, in order to avoid complication of the results with a possible photosensitized decomposition of the cyclobutanone. The cyclobutanone was obtained from Aldrich Chemical Co. and was double distilled through Dry Ice-acetone baths before each run. Research grade ethylene was obtained from Phillips Petroleum Co. and was pumped through an isopentane slush to remove traces of impurities which would interfere with the analysis. No impurities were detected by glpc after this treatment. The pressure-study experiments and the ethylene-gettering experiments were done with a GE-UA-2 mercury lamp with appropriate solution filters<sup>7</sup> to isolate the 2537-Å line. Runs were typically for 5–10 min after which all the products were sent through the thermal conductivity detector, after separating them from the ethylene used as a pressurizing gas.

(3) S. W. Benson and G. B. Kistiakowsky, *J. Am. Chem. Soc.*, **64**, 80 (1942); F. E. Blacet and A. Miller, *ibid.*, **79**, 4327 (1957).

(4) R. Srinivasan, *Advan. Photochem.*, **1**, 83 (1963).

(5) M. C. Flowers and H. M. Frey, *J. Chem. Soc.*, 2758 (1960).

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

(7) E. J. Bowen, "The Chemical Aspects of Light," 2nd ed, Clarendon Press, Oxford, 1948.

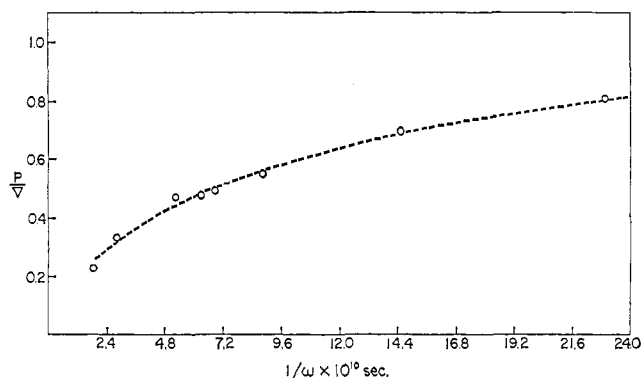


Figure 1.  $P/\nabla$  vs.  $1/\omega$  (reciprocal pressure) for the 2537-Å photolysis using ethylene as the pressurizing gas. The collision diameters used were: ethylene, 4.95 Å; cyclopropane, 4.92 Å; cyclobutanone, 6.5 Å.

The continuous wavelength studies were done with a monochromator (Diffraction Products, Inc.) with 1-mm slits in combination with a 5-kw high-pressure xenon lamp (Hanovia Model 966c). A hydrogen flame detector was used to analyze the products after separating them from cyclobutanone. All the products are reported as ratios in order to avoid inaccuracies inherent in absolute actinometry.

### Results

The results shown in Figure 1 are for the 2537-Å photolysis of cyclobutanone using ethylene as the pressurizing gas.

Several runs were also performed using 10% oxygen, 70% nitric oxide, and *cis*-butene-2<sup>8</sup> as tests for a triplet intermediate. All such tests gave negative results. In the case of oxygen and nitric oxide, there was no significant change in the ratio of the results, and in the presence of *cis*-butene-2 no *trans*-butene-2 was detected resulting from a possible triplet photosensitization of the *cis*-butene-2. Tests for heterogeneous effects were made by packing the vessel with quartz wool as well as by attempting to season the cell walls with very long full-arc runs. All these tests showed no effect within experimental error on the product yields.

The results in Figure 2 show the ratio of  $P/\nabla$  vs. the wavelength for 14.3 torr of cyclobutanone. These experiments were performed with the 5-kw xenon lamp in combination with the monochromator. The half-width of the band pass was approximately 50 Å as determined by actual measurement with another spectrometer. The results in Figure 2 correspond to the adsorption band from 2400 to 3200 Å, with a peak around 2800 Å. There is also a band from 1900 to 2050 Å with a maximum around 1930 Å.<sup>9</sup> Photolysis was also done at 2000 Å using the edge of this band, giving a  $P/\nabla$  ratio of  $2.4 \pm 0.2$ . The results shown in Figure 3 are of the ethylene vs. (total  $C_3$  + ethylene) yield,  $C_2/(C_2 + C_3)$ .

Typical runs with the GE-UA-2 mercury lamp were for 5–10 min for the pressure studies at 2537 Å. The tests for ethylene gettering were done with the full arc for periods of 0.5–2 hr, and under these conditions traces of several other products were observed. The addition of a large excess of ethylene should produce a

(8) R. B. Cundall and D. G. Milne, *J. Am. Chem. Soc.*, **83**, 3902 (1961).

(9) A. Udvarhazi and M. A. El-Sayed, *J. Chem. Phys.*, **42**, 3335 (1965).

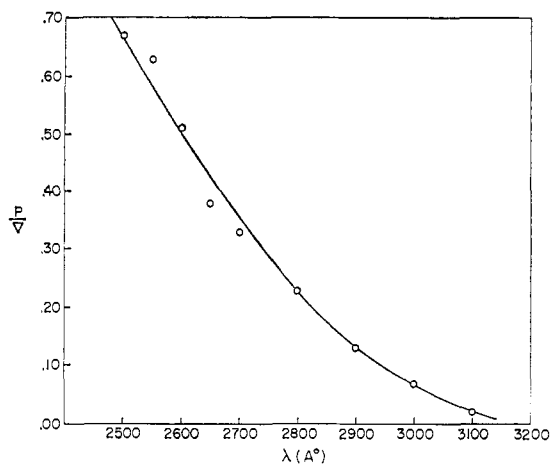


Figure 2.  $P/\nabla$  vs. wavelength ( $\lambda$ ) using the 5-kw xenon lamp.

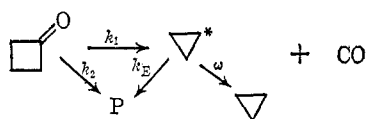
linear increase in some of these products if a simple gettinger mechanism is occurring. However, a 20-fold increase in the ethylene pressure had no apparent effect on the yield of these other products.

At 3000 Å, near the long-wavelength side of the first absorption band, it was observed that the total yield ( $C_2 + C_3$ ) as well as the fractionation between the two primary processes ( $C_2/C_3$ ) were not functions of pressure, at least up to 28.6 torr. This corresponds to an effective gas kinetic collision frequency of about  $6 \times 10^8 \text{ sec}^{-1}$ . The onset of the first absorption band is near 3300 Å. Fluorescence was observed in EPA at 77°K with a short-wavelength limit near 3200 Å, indicating 3250 Å as a reasonable assignment for the 0-0 absorption.

## Discussion

**a. Trimethylene Intermediate Experiments.** It has been suggested that the trimethylene biradical is an intermediate in this system, based on the evidence that the addition of a large excess of ethylene produced significant increases in the yield of various pentene isomers.<sup>5</sup> As mentioned above (see Results) the results of this work do not support this contention, even for data taken for extended periods with the full mercury arc. This appears to be confirmed by other recent work on this question,<sup>6</sup> and hence there is no direct evidence for a trimethylene species being an intermediate in this photolysis. If trimethylene is an intermediate in the photolysis of cyclobutanone, the lack of any direct formation of propylene in a nonpressure-dependent step would indicate that at least in this system the biradical is incapable of reacting directly to propylene.

**b. Pressure Studies.** The mechanism which considers the possible suggested ways of producing the observed species (for this discussion ignoring ethylene) is



where  $\omega$  is the collision frequency. In any such scheme it is implicitly assumed that cyclopropane is divided into reactive and unreactive states only, with the transition rate given by  $\omega$ . In such a two-level model the

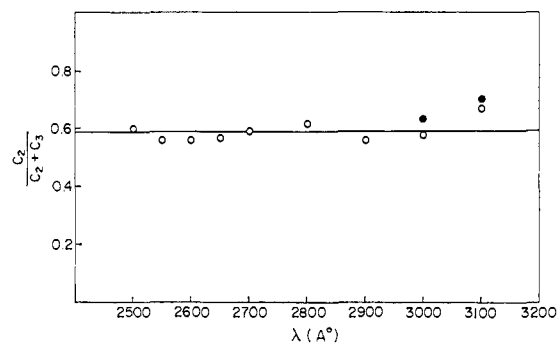


Figure 3.  $C_2/(C_2 + C_3)$  (ethylene/(total  $C_3$  + ethylene)) vs. wavelength for photolysis using 5-kw xenon lamp.

collision frequency,  $\omega$ , leads to complete removal of active molecules, since there are no other types of active molecules to which transport can take place. Hence, such a simplified formulation implicitly contains the strong collision assumption. This will be retained here for simplicity, but could be readily removed as shown by Serauskas and Schlag.<sup>10</sup> A conventional steady-state analysis of this mechanism yields

$$\frac{\nabla}{P} = \frac{k_1 \omega}{\omega k_2 + k_2 k_E + k_1 k_E} \quad (1)$$

In the low-pressure limit this expression reduces to a linear function of pressure (or  $\omega$ ), and at high pressures it approaches a constant value of  $k_1/k_2$ . The latter is the case when all cyclopropane is collisionally stabilized rather than reacting to form propylene. A plot of this ratio for all pressures, including the transition region, therefore predicts curvature as the reaction goes from the low- to the high-pressure region. If instead the propylene is formed entirely *via* the hot cyclopropane route, this mechanism predicts a straight line for the  $\nabla/P$  vs.  $\omega$  plot. Such a plot was made by KMGB and curvature was observed which they interpreted as being due to a large internal energy spread in the hot cyclopropane rather than due to two competitive processes forming propylene. Such an energy spread has not yet been included in the above simplified mechanism but would also produce curvature as shown below. This plot then cannot distinguish between curvature produced by the mechanism and that produced by an energy spread in the hot cyclopropane.

A plot of the inverse of eq 1, a quasi-Stern-Volmer plot, does, however, offer a method for distinguishing between these two effects. Such linear plots are often employed to answer mechanistic questions in photochemistry and to determine the separate rate constants in eq 1. The results from the photolysis of cyclobutanone at 2537 Å using ethylene as the inert gas are plotted in this manner in Figure 1. The simplified mechanism is now predicting a straight line. The data in the low-pressure region seem to fit such a straight line quite well, and it was not until the advent of the higher pressure points that this notion had to be abandoned. A larger experimental error could easily be misleading here. The curvature, in fact, becomes so pronounced at higher pressures that the graph may well extrapolate to

(10) R. V. Serauskas and E. W. Schlag, *J. Chem., Phys.* **42**, 3009 (1965); R. V. Serauskas and E. W. Schlag, *ibid.*, **43**, 898 (1965).

the origin. Hence a more elaborate mechanistic analysis was needed.

A number of causes have been discussed<sup>2</sup> to explain curvature of Stern–Volmer plots. Generally one would expect these complications whenever chemical species are produced with a range of internal energy such that the corresponding  $k_E$ 's vary strongly and hence are differently affected by pressure. Such complications can be avoided for primary processes by using monochromatic radiation. Conversely, for a nonmonochromatic light source one can expect such behavior for primary processes for which the quantum yield is pressure dependent, hence emphasizing the need for monochromatic light sources for mechanistic analyses. In the reactions carried out with cyclobutanone, curvature was still produced, even though monochromatic sources were employed. This could be due to the fact that the monochromatic energy absorbed by the cyclobutanone is partitioned among all the products. Hence, care must be taken, even in monochromatic experiments, in the analyses of secondary species which may not be monoenergetically excited. A further, though usually negligible, effect can come from the initial thermal distribution in the molecules. All the effects discussed above are present even in the strong collision region of pressures. At very low pressures and high energies, and in the presence of simple inert gases, further curvature can be caused by an excited species surviving a single collision, and hence more shots are required to deactivate it. Such many-shot effects could also be important in producing curvature in photochemical experiments, though not under the conditions studied here. In cases of monoenergetically excited molecules one can often attribute all low-pressure curvature to this effect.<sup>11</sup> However, at higher pressures these molecules would give a linear Stern–Volmer plot.

Of all the above causes, the only significant contributor in the work reported here would be expected to be curvature due to energy spread in the secondary species, cyclopropane.

If in eq 1,  $k_2 = 0$ , the ratio reduces to

$$\nabla/P = \omega/k_E \quad (2)$$

and a plot of this ratio *vs.* pressure should give a straight line. This is, in general, however, only true if the implicit two-level division of cyclopropane into hot and cold states is a justified assumption. This has been pointed out by Slater,<sup>12</sup> with particular reference to the Hinshelwood theory of unimolecular reactions. If, in fact, the cyclopropane is produced in many vibrational energy states, then one may write<sup>13</sup>

$$\frac{P}{\nabla} = \frac{\sum_E f_E k_E / (\omega + k_E)}{\sum_E f_E \omega / (\omega + k_E)} \quad (3)$$

where  $f_E$  is the probability that the cyclopropane will be produced with a given vibrational energy  $E$ , characterized by a microscopic rate constant  $k_E$ . This equation could be derived by simple induction or from more general considerations<sup>10</sup> in which it should be noted that

(11) D. W. Setser and B. S. Rabinovitch, *Can. J. Chem.*, **40**, 1425 (1962); G. H. Kohlmaier and B. S. Rabinovitch, *J. Chem. Phys.*, **38**, 1692 (1963).

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

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

this equation still assumes the validity of the strong collision approximation, as well as some approximations regarding the form of the absolute reaction probability.<sup>12</sup> These approximations can, however, be removed by the inclusion of many shot terms in eq 3.<sup>10</sup> Such terms become important at very low pressures, particularly for higher energy species. For the particular case of all cyclopropane being produced in a very narrow range of vibrational energy (monoenergetic excitation), eq 3 reduces to eq 2. If an energy distribution is present, eq 3 no longer predicts a straight line in a  $P/\nabla$  *vs.* reciprocal pressure plot (unless one is in the high- or low-pressure limiting regions). Furthermore, this curvature becomes particularly acute in the high-pressure section of the plot and hence aggravates any extrapolation to  $\omega^{-1} = 0$ . Furthermore, as one increases the photolysis energy, one would expect this high-pressure falloff to shift to higher pressures; hence, particularly photolysis at shorter wavelengths may give false linear Stern–Volmer plots in the conventional pressure region.

Exceptions to this difficulty may be found in fluorescence studies where the excited species may well have a wide range of internal energies but a very narrow range in the corresponding microscopic rate constants. This might be the case for collisional quenching studies of fluorescence in which one might have nearly linear Stern–Volmer plots in spite of a fairly wide range of the emitting species.

**c. Wavelength Studies.** It was decided to study the yields as a continuous function of wavelength and to investigate the  $P/\nabla$  ratio at a fixed pressure in the long-wavelength limit of the absorption band. This was possible in view of the high intensity (5-kw) xenon arc which was used in conjunction with a monochromator. This method should also provide information as to whether the reaction is well behaved over the entire absorption band, *i.e.*, whether the yields of cyclopropane and propylene are simply determined just by the internal energy content of the cyclopropane, except for the possible side reaction to form propylene directly.

It can be seen from Figure 2 that in the long-wavelength limit the ratio of  $P/\nabla$  approaches zero, indicating that within experimental error propylene is not formed in this region in a primary process, but cyclopropane is. This in itself does not preclude propylene becoming a primary process at shorter wavelengths. It can be seen, however, from Figure 3, that if one combined the total  $C_3$  yield (cyclopropane and propylene) and used the ethylene yield as an internal actinometer, then the  $C_2/(C_2 + C_3)$  yield is independent of wavelength over the entire range of the absorption band. Hence, since cyclopropane is the sole primary process in the long-wavelength region, no new primary process to form  $C_3$  appears to start up at higher energies, the entire appearance of propylene being accounted for by a loss of cyclopropane. Similarly there appears to be no measurable evidence for the further decomposition of propylene<sup>14</sup> either on the basis of this mass balance or on the basis of any other new peaks in the glpc analysis.

This appears to put the mechanism of this photolysis on firm ground as one that does not involve a (measurable) primary formation of propylene, rather all propylene being formed as the results of the decomposition

(14) J. W. Simons, B. S. Rabinovitch, and F. H. Dorer, *J. Phys. Chem.*, **70**, 1076 (1966).

of vibrationally excited cyclopropane. This appears to be so over the entire first absorption band. The mechanistic analysis had to be based on actual measurements in the limiting regions, since extrapolations were at best risky in view of the strong curvature of the plot caused by the internal energy distribution of cyclopropane. Now that one can assign all the observed curvature in the Stern–Volmer plot (Figure 1) unequivocally to a distribution of the internal energy of cyclopropane, it is tempting to evaluate this distribution. Unfortunately, this demands de-convoluting eq 3 which is not straightforward. High- and low-pressure limiting forms of (3)<sup>13</sup> give one only a qualitative assessment of the energy spread.

The numerical value of 1.5 for  $C_2/C_3$  agrees well with the value 1.7 observed by KMGB. Such a small value appears to be good evidence that both primary processes have essentially the same activation energy. The slightest difference in activation energies would lead not only to a much different value, but also to a pronounced wavelength dependence of this ratio, contrary to what was observed (Figure 3). A few points were also taken on the next higher energy absorption band which appear to lie on the same line as the points from the first band. The second excited electronic state probably undergoes rapid intersystems crossing such that the species have the same apparent behavior. It is probably unlikely here that reaction of ground-state cyclobutanone is involved, since the thermal decomposition does not show any  $C_3$  products,  $C_2$  being the exclusive path.<sup>15</sup> The  $C_3$  path would have to lie at least 3 kcal above this not to have been observed, though this energy difference is larger than tolerable in the photochemical reaction, in view of the wavelength independence and absolute magnitude of the observed  $C_2/C_3$  ratio.

The total products as well as the ratio  $C_2/C_3$  were pressure independent for cyclobutanone excited at 3000 Å, which is only 7–8 kcal above the 0–0 transition for this first singlet state. It is not sufficient from this alone to decide that there is negligible activation energy in this state since these low excited states probably can-

not be collisionally relaxed much further by simple gases. However, a simple picture of reaction occurring from a thermalized first excited state with some activation energy seems to be negated by the strong energy dependence of the  $P/\nabla$  ratio down to lowest energies. This indicates that the reaction still remembers its initial mode of activation and does not just occur from an equilibrated first excited state with appreciable activation energy.

The most reasonable mechanism then appears to involve internal excitation of the first excited electronic state undergoing reaction with virtually no activation energy, both modes,  $C_2$  and  $C_3$ , involving the same activation energy, maybe due to a common slow step such as ring opening of the excited cyclobutanone.

### Conclusion

Linear Stern–Volmer plots can still be pathological due to undiscovered curvature in the ultrahigh-pressure region. Such complications can be expected in any mechanism involving several excited states of the same species for which there exists a mechanistic choice depending on this excitation energy. Such problems can arise even if irradiation is monochromatic.

Cyclobutanone is proposed to undergo photolytic rupture *via* only two different, but isoenergetic pathways; hence, these two paths may well proceed by way of the same slow step. The reactions from both of the first two excited electronic states proceed by a common path, probably by way of the first singlet, excited electronic state. The strong energy dependence of the product yield (Figure 2) over the entire absorption band seems to preclude the possibility of any appreciable activation energy for reaction from the first excited singlet state. The cyclopropane is formed in its ground electronic state with large amounts of internal energy proportional to the photolytic energy absorbed by the cyclobutanone precursor, but with an energy distribution due to photopartitioning between all the products of the photolysis.

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(15) M. N. Das, F. Kern, T. D. Coyle, and W. D. Walters, *J. Am. Chem. Soc.*, **76**, 6271 (1954).