the trans conformation in *n*-butane[40] is also shown. The second minimum corresponding to $\phi = 112.5°$ (close to cis conformation) occurs ~0.6 kcal/mol above the trans conformation ($\phi = 0$), and the Boltzmann factor at 300°K for the ratio of trans conformer/cis conformer is 2.7. Since the relaxed triplet 1,2-DMTM biradical (**8**), which lives long enough to achieve rotational (internal) equilibrium at room temperature, gives the *trans*-DMCP/*cis*-DMCP ratio of 2.4, it is likely that the conformer ratio for the DMTM biradical determines the *trans*-DMCP/*cis*-DMCP ratio, on the assumption that the biradical conformational and the *n*-butane conformational interactions are similar. It is also clear that steric interference between the two CH_3 groups in the *trans,trans*-1,3-DMTM biradicals (**9**) is nearly nonexistent, and hence the *trans*-DMCP/*cis*-DMCP ratio is near unity, ~1.23. We believe similar arguments apply also in the case of triplet dimethyltetramethylene biradicals **16** and **17**. We should, however, note that the trans/cis ratio obtained for the cyclized dimethylcyclobutane from the biradical **16** is 3.9, indicating the possibility that an additional instability exists for the cis conformer of the 1,2-dimethyltetramethylene.

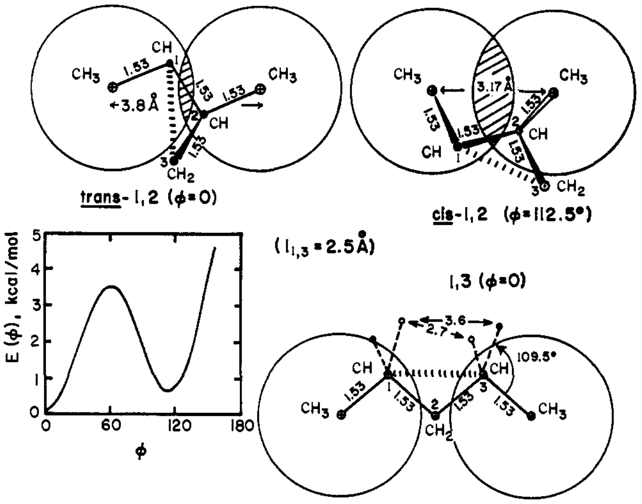

Figure 7. Projections of various geometries of model dimethyltrimethylenes having normal C–C and C–H bond distances. Steric interference between the two CH_3 groups is indicated by 2.1-Å circles corresponding to the van der Waals radius of the CH_3 group. Conformational energies of *n*-butane *vs.* the angle of deviation from the plane of the trans conformer is shown after Flory (ref 40).

In conclusion, we emphasize that the most important difference between the singlet and triplet biradicals is the short and long lifetime, respectively, with respect to cyclization. The long lifetime (~10^{-8} sec)[4c] of the triplet biradicals (slow ring closure) may be due to the slow spin-forbidden T $\rightsquigarrow$ S intersystem crossing which may precede the final act of coupling of the two radical centers.

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[40] P. J. Flory, "Statistical Mechanics of Chain Molecules," Interscience, New York, N. Y., 1969, pp 51, 141.

Decomposition of *cis*- and *trans*-2,3- and -2,4-dimethylcyclobutanones from the Vibrationally Excited Ground States. Thermal and Photochemical Activation[1]

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Abstract: The unimolecular decomposition pathways of vibrationally hot cis and trans isomers of 2,3- and 2,4-dimethylcyclobutanone (DMCB) have been studied. Effects of geometric isomerism, position of CH_3 group substitution, and internal excitation energies (50–104 kcal/mol) on the decomposition rates are measured. Rates are significantly enhanced by high excitation, α,β rather than the α,α' substitution, and cis geometry of the 2,3-DMCB isomers. An attempt is made to rationalize these and other rate variations, by assuming steric interference in the critical configurations of the twisted cyclobutanone ring. It is found that specific rate constants calculated from the RRKM unimolecular rate theory agree well with the observed rate values. Collisional efficiencies (relative) of Ar, O_2, C_2H_4, and *trans*-2,3-DMCB in deactivating vibrationally hot *trans*-2,3-DMCB (S_0*, 91 kcal/mol) have been found to be 0.22, 0.26, 0.62, and 1.00. The probable mechanism of a minor thermal decarbonylation process (<0.2%) and its implication in cyclobutanone chemistry are briefly discussed.

It has been recently shown that vibrationally hot ground state cyclobutanones (S_0*) decompose in a concerted manner.[2] Likewise, the reverse reaction of cycloaddition of ketene and olefins has been found to be stereospecific (with retention of the configuration of the olefin) in several cases.[3] The present work on the *cis*- and *trans*-2,3- and -2,4-dimethylcyclobutanones (DMCB) was undertaken to investigate further the unimolecular rate processes involved in the decomposi-

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[1] This research has been supported by National Science Foundation Grant GP-28010X.

[2] (a) H. A. J. Carless and E. K. C. Lee, *J. Amer. Chem. Soc.*, **92**, 4482, 6683 (1970); (b) *ibid.*, **94**, 1 (1972).

[3] (a) R. Huisgen, L. Feiler, and G. Binsch, *Angew. Chem., Int. Ed. Engl.*, **3**, 753 (1964); (b) J. C. Martin, V. W. Goodlett, and R. D. Burpitt, *J. Org. Chem.*, **30**, 4309 (1965); (c) R. Montaigne and L. Ghosez, *Angew. Chem., Int. Ed. Engl.*, **7**, 221 (1968); (d) G. Binsch, L. A. Feiler, and R. Huisgen, *Tetrahedron Lett.*, 4497 (1968); (e) T. Do Minh and O. P. Strausz, *J. Amer. Chem. Soc.*, **92**, 1766 (1970).

Table I. Product Distribution from Pyrolysis

					Product yield, %			
Run	Temp, °C	Pressure, Torr[a]	Time, min	Conversion, %	PR	*t*-2B	*c*-2B	*t*-DMCP + *c*-DMCP
				Parent = *cis*-2,3-DMCB				
5[b]	325	53.8	5.5	8	85.8	<0.3	13.8	
6[b]	325	26.9	10.5	28	84.9	<0.4	14.6	<0.5
7[b]	325	53.8	7	17	85.2	0.2	14.6	
8	325	3.8	4	22	84.8	0.2	15.0	<0.5
Av of four runs					85.2	0.2	14.5	
				Parent = *trans*-2,3-DMCB				
3	350	27.9	7.5	13	52.2	45.1	2.7	
4	375	8.8	30	~100	53.2	41.4	5.4	<0.5
5[c]	325	8.1	15	35	51.8	47.2	0.9	<0.7
Most reliable[d]					52	47	0.9	
				1:1 Mixture of *trans*- and *cis*-2,3-DMCB				
2M	350	56	5	19	81.1	5.3	13.6	
3M	325	54	5	8	82.3	4.5	13.2	
Av of two runs					81.7	4.9	13.4	

[a] Pressure at pyrolysis temperature. [b] Thermal conductivity detection. [c] Repurified by preparative vpc to 99.5% trans isomer. [d] Runs 3 and 4 excluded, because of the presence of *cis*-2,3-DMCB impurity.

tion of vibrationally hot ground state DMCB (S_0*) isomers. Effects of geometric isomerism, position of CH_3 substitution, and internal excitation energies on unimolecular decomposition rates will be considered for systematic analysis. Since thermal activation gives the excited molecules with a broad energy distribution and photochemical activation gives approximately monoenergetic excited molecules with a narrow energy distribution, these systems offer an ideal opportunity for studying various unimolecular rate parameters and some aspects of collisional energy transfer processes.

Experimental Section

cis- and *trans*-2,3- and 2,4-DMCB's were prepared as described previously.[4] Cyclobutanone was obtained from Aldrich Chemical Co., and was used without further purification, as the impurities found by vpc were less than 0.005%. After degassing and pyrolyzing, analysis was carried out in the same way as described in the preceding paper,[4] except that no glc analysis with an $AgNO_3$ column was used to separate *cis*-2-pentene from *cis*-dimethylcyclopropane.

Pyrolyses were carried out in a quartz vessel (8.3 ml) equipped with a greaseless, Viton A diaphragm valve (Springham). While in use the valve was heated above 50° with a heat gun in order to reduce the amount of parent ketones absorbed by the Viton A diaphragm. The pyrolysis cell was inserted into a tubular furnace in which temperature fluctuations and gradients were large. Pyrolyses of the DMCB isomers were performed at ~560 and 590°K using cyclobutanone as an internal standard, as its thermal decomposition has been studied previously.[5] Typical conversions for these pyrolysis were about 40% decomposition with ~2.0 Torr each of the DMCB and cyclobutanone. Another series of pyrolyses were carried out at ~6 Torr of the DMCB, pyrolyzed to higher conversion to determine the yields of the minor C_5 products.

Results

Cyclobutanone decomposes thermally to give mainly ring fission products (>99%),[5] and it was found in the present study that the DMCB isomers decompose mainly by ring fission (see Table I). It was possible to determine the relative rates of the ring fission processes in the different isomers using cyclobutanone as an internal standard for thermolysis. These results are shown in Table II for the two ring fission modes (a and b) possible as illustrated.

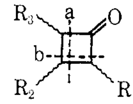
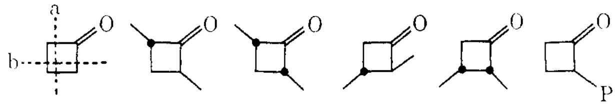


Table II. Relative Rates of Pyrolysis of the DMCB Isomers (560–590°K; DMCB: CB = 1:1)



1 2 3 4 5 6[a]

	Parent					
	1	2	3	4	5	6
Mode a	(0.25)	1.0	1.1	4.4	98	1.6
Mode b	(0.25)	1.0	1.1	4.0	17	0.4

[a] 2-*n*-Propylcyclobutanone was pyrolyzed under the same condition as the DMCB's, and it was prepared as described in ref 2b.

The product distributions for the minor products resulting from ring cleavage are shown in Table III. Because of the low yields of these products, the data show a large random error, as can be seen by comparison between runs on the same isomer. These pyrolyses do, however, indicate the approximate values of the trans/cis ratio in DMCP (1,2-dimethylcyclopropane).

The other important data on the decomposition/stabilization of the hot ground state DMCB's (S_0*) were obtained from the Stern–Volmer plots of the photolysis runs. The procedure by which the half-quenching pressures ($P_{1/2}$) of the collisional deactivator molecules (M) had been obtained was described briefly in the preceding paper,[4] and graphical illustrations of it are given in Figures 1 and 2 for the 2,4-DMCB isomers. The corrected values from the experimental $P_{1/2}$ values are listed in Table IV.

From the results shown in Table IV for *trans*-2,3-DMCB at 325 nm, the following relative values of deactivating efficiencies β_p (pressure/pressure) for the quenching gases are obtained: DMCB = 1.00; C_2H_4

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(4) H. A. J. Carless, J. Metcalfe, and E. K. C. Lee, *J. Amer. Chem. Soc.*, 94, 7221 (1972).

(5) (a) M. N. Das, F. Kern, T. D. Coyle, and W. D. Walters, *ibid.*, 76, 6271 (1954); (b) A. T. Blades, *Can. J. Chem.*, 47, 615 (1969).

Table III. Relative Yields of Products[a] from the Pyrolysis of DMCB Isomers (~610°K)

Run no.	DMCB	P, Torr[b]	PR[c]	*t*-2B	*c*-2B	2M1B	2M2B	*c*-2P	*t*-2P	*t*-DMCP	*c*-DMCP	DMCP *t*/*c*
B29	*t*-2,4-	6.1	(1000)			0.19	0.81	<0.01	<0.01	1.00	1.32	0.76
B34	*t*-2,4-	6.0	(1000)			0.13	0.72	0	0	0.45	1.04	0.43
B28	*c*-2,4-	6.0	(1000)			0.25	0.80	0.01	<0.01	0.91	0.46	1.95
B31	*c*-2,4-	6.5	(1000)			0.20	0.56	0	0	0.59	0.30	1.96
B37	*t*-2,3-	6.1	505	489	6.3	0.02	0.11	0.02	0.01	0.20	0.36	0.56
B39	*t*-2,3-	6.1	496	497	6.0	0.02	0.09	0.02	0.01	0.18	0.42	0.43
B36	*c*-2,3-	6.2	823	12.7	164	0.01	0.06	<0.01	<0.01	0.22	0.70	0.32
B40	*c*-2,3-	5.8	829	14.1	156	<0.01	0.03	0	0	0.14	0.64	0.21

[a] Pyrolysis was carried out to ~70% conversion. [b] Pressure measured at pyrolysis temperature. [c] The sum of the ring fission products = 1000.

Table IV. Corrected Half-Quenching Pressures ($P_{1/2}$, Torr)[a] of the Hot DMCB (S_0^*) by Parent DMCB Isomer, C_2H_4, O_2 and Ar at Various Excitation Wavelengths

λ_{ex}, nm	Colliding gas (M)	DMCB (S_0^*)			
		trans-2,4	*cis*-2,4	*trans*-2,3[a]	*cis*-2,3[a]
325	DMCB	0.95 ± 0.15	1.10 ± 0.15	(a) 2.2 ± 0.2 (b) 2.6 ± 0.7	(a) 4.8 ± 0.6 (b)
325	C_2H_4[b]	2.1 ± 0.2	1.9 ± 0.3	(a) 3.9 ± 0.3 (b) 3.6 ± 0.4	(a) 11 ± 1 (b) 10 ± 2
325	O_2[b]			(a) 11.7 ± 1.2 (b) 11.5 ± 1.6	
325	Ar[b]			(a) 14.5 ± 1.5 (b) 16.2 ± 1.6	
313	DMCB			(a) 3.4 ± 0.5 (b) 3.8 ± 0.5	(a) 7 ± 1 (b) 8 ± 1
281	Ar[b]			(a) 75 ± 10 (b) 78 ± 10	

[a] As determined by both decomposition modes "a" and "b." [b] When the quenching gas was other than DMCB, it was necessary to correct the value of $P_{1/2}$(DMCB; M) observed from the Stern–Volmer plot in order to obtain the value of $P_{1/2}$(M) applicable at zero pressure of DMCB: $P_{1/2}(\mathrm{M}) = P_{1/2}(\mathrm{DMCB; M})[1 + P_{\mathrm{DMCB}}/P_{1/2}(\mathrm{DMCB})]^{-1}$. Typical pressures of DMCB in the mixture were fixed at 0.1–0.5 Torr.

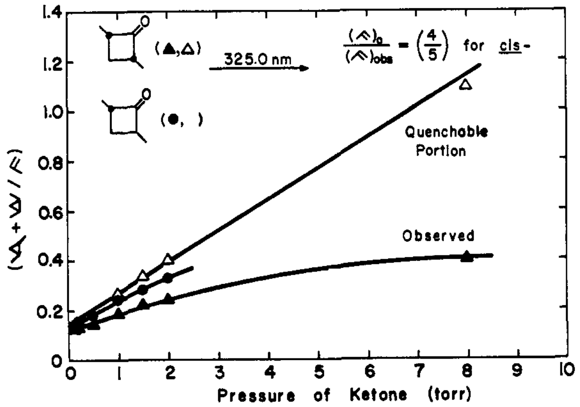

Figure 1. Stern–Volmer plots of reciprocal yield of propylene *vs.* parent ketone pressure for the 2,4-DMCB isomers. The filled points represent observed yields, comprising both quenchable and unquenchable portions. The open points for *cis*-2,4-DMCB represent the corrected data on only the quenchable portion, which is about four-fifths of the total.

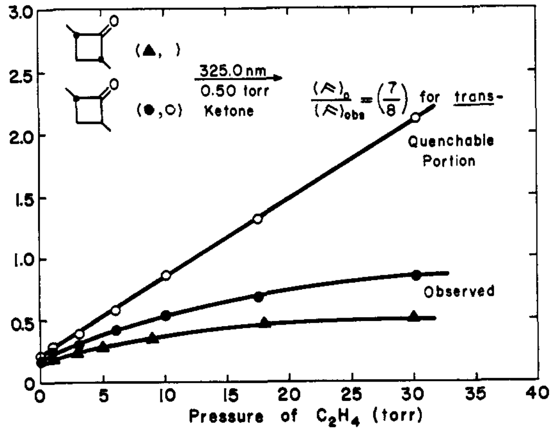

Figure 2. Stern–Volmer plots of reciprocal yield of propylene *vs.* C_2H_4 deactivator pressure. The filled points represent observed yields, comprising both quenchable and unquenchable portions. The open points for *trans*-2,4-DMCB represent the corrected data on only the quenchable portion, which is about seven-eights of the total.

= 0.59; O_2 = 0.20; Ar = 0.16. The last value is particularly useful, since the $P_{1/2}$(Ar) values at 281 nm for the hot 2,3-DMCB (S_0^*) listed in Table IV can be converted to give a value for $P_{1/2}(\mathrm{DMCB}) = P_{1/2}(\mathrm{Ar})[\beta_p(\mathrm{Ar})/\beta_p(\mathrm{DMCB})]$ at 281 nm. Furthermore, using the strong collision assumption, the unimolecular decomposition rate constants $k(E) = \omega_{1/2}(\mathrm{DMCB})$ are calculated accordingly,[6] and the results are tabulated in Table V.

Discussion

Thermal Decomposition of DMCB. The rates of ring fission (modes a and b) of 2-*n*-propylcyclobutanone (2PCB) from the vibrationally excited, ground state seem to indicate a concerted mechanism of decomposition rather than a biradical (ring-opened) mechanism.[2b] Similarly, the stereoretention found in the ring-fission

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(6) The ring fission rate $k(E)$ is $\omega(\mathrm{M})[\mathrm{D/S}]$, and $k(E) = \omega_{1/2}(\mathrm{M})$ for [D/S] = 1, where one-half of the quenchable products is quenched out and the half-quenching collision rate $\omega_{1/2}(\mathrm{M})$ can be calculated from the $P_{1/2}$ value (in Torr) by $\omega_{1/2}(\mathrm{M}) = 1.75 \times 10^7 P_{1/2}$ sec^{-1}. The gas kinetic collision diameter of 7 Å for the DMCB isomers was taken to be a reasonable estimate, and M is DMCB here.

Scheme I

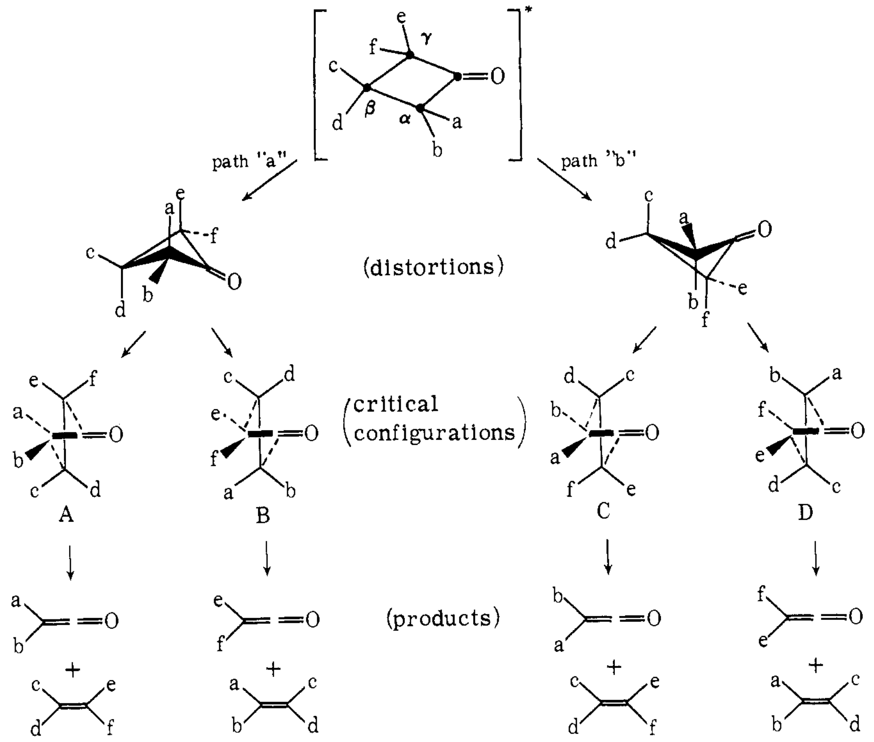

Table V. Unimolecular Rates of the Ring Fission Processes $k(E)$ at Different Photoexcitation Energies for the DMCB Isomers[6]

		$k(E)$, 10^6 sec^{-1}			
λ_{ex}, nm	E, kcal/mol	*trans*-2,4	*cis*-2,4	*trans*-2,3	*cis*-2,3[a]
325[b]	90.8	(a) 8.3	9.6	24	59
		(b) 8.3	9.6	18	25
313[b]	94.1	(a)		36	9.1
		(b)		27	4.0
281[c]	104.5	(a)		120	
		(b)		94	

[a] The true values are probably ~10% higher, since as much as 24% of the S_0^* species in the photoactivation of *cis*-2,3-DMCB could be *trans*-2,3-DMCB (S_0^*).[4] [b] Determined from the DMCB runs in Table IV. [c] Determined from the Ar runs in Table IV.

products (*cis*- and *trans*-2-butene) from thermal decomposition of *cis*- and *trans*-2,3-DMCB isomers also indicate the presence of a concerted process;[2a] ~99% stereoretention is observed at 325° (see Table I). As the concerted break-up of the cyclobutanone ring must be a $[_\sigma 2_s + {}_\sigma 2_a]$ process,[3,7] distorted ring structures as depicted in Scheme I can be envisaged as the possible critical configurations. The sp^3 C atoms on the cyclobutanone ring are labeled α, β, and γ, and six possible substituents on these carbon atoms are labeled a–f. The ketene and olefin products resulting from each of the four possible critical configurations (A–D) are shown also.

We will consider steric interactions due to CH_3 groups in the configurations A–D as considered for the *n*-propyl group in 2PCB.[2b] For the sake of simplifying the evaluation of the steric interactions, let us group the interactions to be either strong (s), medium (m), weak (w), or nil (n). If a CH_3 group on the nascent ketene moiety projects toward the twisted ring (a in configuration A) the interaction is *strong*, and if it projects away from the twisted ring (b in configuration A) the interaction is *nil*. If a CH_3 group on the nascent olefin moiety points away from the C=O group on the twisted ring (c and e in configuration A) the interaction is *medium*, and if it is on the same side of the C=O group (d and f in configuration A) the interaction is *weak*. With this assumed classification of the individual CH_3-group interactions, the over-all steric interactions (hindrance) are evaluated for four possible critical configurations resulting from each of the four DMCB isomers. The results are tabulated in Table VI.

The steric interaction at the α position for path a or the γ position for path b is the most crucial one, and the formation of the twisted critical configuration would be favored if the interaction is nil (but not if strong). Additional interactions at β and γ (or α) positions could somewhat hinder its formation. The number of the favorable formations (for which the interaction at α position is nil) of the critical configurations leading to paths a and b are shown in lines 4 and 8 of Table VI. So far, stabilities of the critical configurations have been considered, and now stabilities of the parent and the product molecules should be considered. The 2,4-DMCB isomers and the resulting products probably have small CH_3:CH_3 interactions. But *cis*-2,3-DMCB and the resulting *cis*-2-butene should certainly suffer from steric instability. Thus, the rate of decomposition of *cis*-2,3-DMCB *via* path a could be greatly enhanced by this energetic consideration.

From the above considerations of the summary in Table VI, one expects a slightly greater rate for the thermal decomposition of *cis*-2,4-DMCB than for *trans*-2,4-DMCB and it is found as shown in Table II. Furthermore, the data in Table II confirm the expectation that the rate for path a to be *cis*-2,3-DMCB > *trans*-2,3-DMCB and the rate for path b to be *cis*-2,3-DMCB ⩾ *trans*-2,3-DMCB and *cis*-2,4-DMCB ⩾ *trans*-2,4-DMCB. However, the expectation contra-

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(7) R. B. Woodward and R. Hoffmann, "Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970.

Table VI. Steric Interactions[a] due to Methyl Substituents for the Four Critical Configurations Shown in Scheme I

DMCB isomer Two Me groups	*cis*-2,3- a, c	*trans*-2,3- a, d	*cis*-2,4- a, e	*trans*-2,4- a, f
	(i) Critical Configuration for Path a (in order α, β, γ)			
A	s; m; -	s; w; -	s; -; m	s; -; w
C	n; w; -	n; m; -	n; -; w	n; -; m
α interaction	1n, 1s	1n, 1s	1n, 1s	1n, 1s
β, γ interactions when α interaction is nil (n)	1w-	1m-	1-w	1-m
	(ii) Critical Configuration for Path b (in order γ, β, α)			
B	-; m; m	-; w; m	s; -; m	n; -; m
D	-; w; w	-; m; w	n; -; w	s; -; w
γ interaction	2-	2-	1n, 1s	1n, 1s
β, α interactions when γ interaction is nil (- or n)	1ww, 1mm	1wm, 1mw	1-w	1-m

[a] Steric interactions due to the CH_3 group substituents are given in the order of the α, β, and γ carbon positions for path a (dominant interaction at α) and the order γ, β, and α for path b (dominant interaction at γ): s = strong; m = medium; w = weak; n = nil. Interactions of the H atoms at the unsubstituted positions are considered to be nil and shown by a hyphen (-).

dicts the observation that (a/b) ≫ 1 for *cis*-2,3-DMCB, (a/b) ≈ 1 for *trans*-2,3-DMCB, and *trans*-2,3-DMCB > *trans*-2,4-DMCB for path a. It might be possible to take into consideration the stability of the vibrational ground state for resolving the difficulty, but additional elaborations at this time may not be fruitful. Furthermore, it suffices to show in Figure 3 that rate variations found in the DMCB (S_0*) isomers generated by photoactivation at 325 nm are considerably less than those found in their thermolysis, as expected.

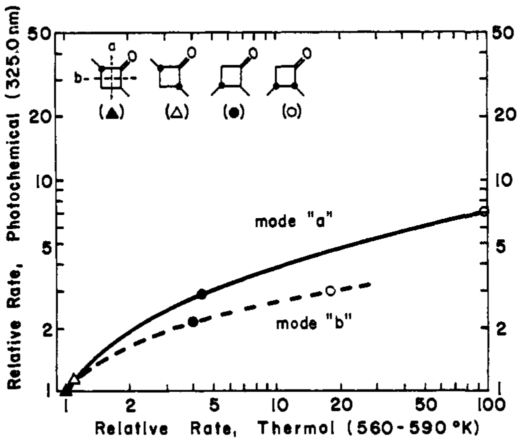

Figure 3. Comparison of relative rates (modes a and b) of ring fission processes in photolysis *vs.* thermolysis.

Thermal Activation Rates. The approximate activation energy (E_a) for thermal decomposition of *cis*-2,3-DMCB was estimated from the data given for run 7 in Table I, assuming that its Arrhenius preexponential factor (A) is equal to $A = 10^{14.56}$ sec^{-1}, that for cyclobutanone.[5] $E_a \approx 50$ kcal/mol was obtained. However, according to the data in Table II, *cis*-2,3-DMCB decomposes ~230 times faster than cyclobutanone at 560–590°K. From these more reliable competition data, we obtain $E_a \approx 46$ kcal/mol for *cis*-2,3-DMCB, if $A = 10^{14.56}$, and similarly E_a = 51 kcal/mol for the 2,4-DMCB isomers and $E_a \approx 49$ kcal/mol for *trans*-2,3-DMCB. Of course, choice of a higher value of A factor should increase the above value of E_a. Clearly, a more accurate temperature dependence study is required in order to determine experimentally the A factors and E_a's for all four isomers.

Photoactivation Rates. The values of $k(E)$ for the oscillator number $s = 45$ in the DMCB isomers were obtained from an approximate calculation based on the RRKM formulation.[8,9] It was assumed that the values of $A = 10^{14.56}$ sec^{-1} and $E_a = 52.0$ kcal/mol determined in the thermal unimolecular decomposition of cyclobutanone[5] and the estimated values[10] of $E_z = 93$ kcal/mol, $E_{th} = 2.8$ kcal/mol, and $a = 0.87$ could be adapted for use in the calculation. The experimentally obtained values of $k(E)$ are compared with the calculated values[11] in Figure 4. It was not possible to take into account the stereochemical effects of two CH_3 groups on the specific rate constants in the calculation, because no requisite information was readily available. Probably, *trans*-2,3-DMCB represents most closely the model molecule for which the rate calculation was carried out, and the agreement between the observed and calculated rates is remarkably good[12] at four excitation energies studied.

A rough experimental value of the $P_{1/2}$ at 254 nm using Ar as the colliding gas, but obtained by ignoring the curvature in the Stern–Volmer plot, is 220 Torr for *trans*-2,3-DMCB. This corresponds to k(mode a) = 3.5×10^8 sec^{-1} and k(mode b) = 2.8×10^8 sec^{-1}. Although this value fits well with the calculated value

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(8) (a) R. A. Marcus and O. K. Rice, *J. Phys. Colloid Chem.*, **55**, 894 (1957); (b) R. A. Marcus, *J. Chem. Phys.*, **20**, 355 (1952); (c) see an RRKM calculation on cyclobutanone in N. E. Lee and E. K. C. Lee, *ibid.*, **50**, 2094 (1969).

(9) (a) See for a review, B. S. Rabinovitch and D. W. Setser, *Advan. Photochem.*, 3, 1 (1964). (b) $k(E) = A'[(E - E_0 + a^+E_z^+)/(E + aE_z)]^{s-1}$ used by D. W. Setser and B. S. Rabinovitch, *Can. J. Chem.*, **40**, 1425 (1962), was taken with further approximations of $A' = A$,[5] $E_0 = E_a$,[5] $a = a^+$ and $E_z = E_z^+$.

(10) (a) E_z of DMCB was estimated as E_z of cyclobutanone (57.8 kcal/mol)[8] plus the contribution due to two (CH_2) substituents, 2 × 17.6 kcal/mol. (b) E_{th} of DMCB was estimated as the average vibrational energy content at a 296°K thermal bath; and $E = E_{h\nu} + E_{th}$. (c) $a' \approx 0.87$ at $\epsilon' = E/E_z = 0.4$–0.7 (λ_{ex} 325.0–253.7 nm) was chosen from G. Z. Whitten and B. S. Rabinovitch, *J. Chem. Phys.*, **38**, 2466 (1963).

(11) Values of $k(E)$ for $E = 90$ kcal/mol calculated at different choices of parameter a are as follows: 1.7×10^7 sec^{-1} at $a = 0.8$ and 1.3×10^8 sec^{-1} at $a = 1.0$. The value of $k(E)$ is the sum of the rates for modes a and b.

(12) We regard the agreement by a factor of 2–3 to be sufficient in this kind of RRKM calculation.

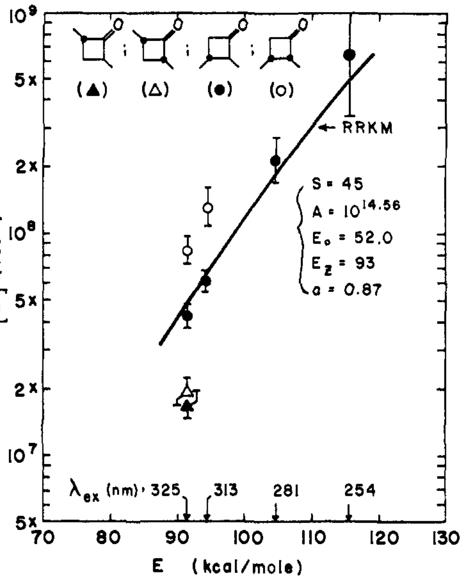

Figure 4: Comparison of observed and calculated (RRKM theory) specific rate constants (modes a + b) as a function of excitation energy

in Figure 4, no reliance can be placed upon it due to the inaccuracy of measurement.

The values of $k(E)$ at $E \cong 92$ kcal/mol obtained are 4×10^9 sec^{-1} for cyclobutanone (S_0*)[13] and 4×10^6 sec^{-1} for 2-*n*-propylcyclobutanone (S_0*)[2b] as compared with the value of 4×10^7 sec^{-1} for *trans*-2,3-DMCB (S_0*). It is significant that each (–CH_2–) group addition to cyclobutanone lowers on the average the specific rate constant by a factor of 10 at an excitation energy of 92 kcal/mol. A similar incremental decrease in the unimolecular decomposition rates for a homologous series has been observed for the chemically activated alkyl radicals at 300°K:[14] 2-butyl, 2×10^7; 2-pentyl, 1.2×10^7; 2-hexyl, 1.85×10^6; 2-heptyl, 3.9×10^5, and 2-octyl, 4.8×10^4 sec^{-1}.

Collision Efficiencies (β_c). Collisional efficiences (β_c) of various quenching gases (M) in deactivating the photoactivated, vibrationally hot DMCB (S_0*) are tabulated in Table VII. Since some comparison of our data with the energy transfer data available from thermal CH_3NC isomerization,[15] chemically activated *sec*-butyl radical decomposition,[16] and photoactivated cyclobutanone (S_0*) decomposition[8c] should prove worthwhile, a summary is given in Table VIII. Probably, O_2 and N_2 should have approximately equal efficiency, according to the β_c *vs.* boiling point correlation established from the comprehensive study made in Professor Rabinovitch's laboratory.[15] Hence, we could compare directly the results obtained with N_2 and O_2. It is gratifying that our values of Ar and C_2H_4 show fair correspondence to the values obtained from thermal isomerization of CH_3NC. Surprisingly, however, our values of Ar and O_2 appear to be sufficiently different from the values obtained from photoactivation of cyclobutanone (S_0*) that a further study should certainly be made to understand this difference.

Table VII. Relative Collision Efficiencies (β_c) of Deactivator Molecules for *trans*-2,3-DMCB (S_0*) at λ_{ex} 325.0 nm

	Gas (M)			
	Ar	O_2	C_2H_4	DMCB
$\beta_p(M)^a$	0.16	0.20	0.59	(1.00)
σ_M, Å^b	3.42	3.43	4.23	7.0
$\beta_c(M)^c$	0.22	0.26	0.62	(1.00)

[a] $\beta_p = P_{1/2}(\text{DMCB})/P_{1/2}(\text{M})$ was obtained from the data in Table IV. [b] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids," Wiley, New York, N. Y., 1964, pp 1110–1112. Gas viscosity data fitted for the Lennard-Jones (6–12) potential. [c] $\beta_c = \omega_{1/2}(\text{DMCB})/\omega_{1/2}(\text{M})$ was obtained using $\sigma_{AM} = (\sigma_A + \sigma_M)/2$, where $\sigma_A = 7.0$ Å for DMCB (S_0*).

Minor Thermal Processes (Decarbonylation). Even though the reproducibility of the minor product distribution (or of their analysis) is rather poor for the high per cent conversion runs shown in Table III, some qualitative conclusions can be reached. Between 0.2 and 0.3% of the thermal decomposition products appear as the decarbonylation products (C_5H_{10}) from the 2,4-DMCB isomers, while only 0.1% appears as the decarbonylation products from the 2,3-DMCB isomers. Clearly, the 1,2-H migration products (*cis*- and *trans*-2-pentene from the 2,4-DMCB isomers; 2-methyl-1-butene and 2-methyl-2-butene from the 2,3-DMCB isomers) are virtually absent. It appears that 2-methyl-2-butene is, however, produced in a significant amount by a mechanism other than 1,2-H migration in the 2,4-DMCB isomers. Although some secondary isomerization of the dimethylcyclopropane isomers (also *via* 1,2-H migration) is possible, it cannot account for the predominance of 2-methyl-2-butene, since the four pentenes should be produced in roughly equal amounts when *cis*- and *trans*-dimethylcyclopropanes are thermolyzed.[17] We conclude thus that the mechanism for the branched pentene production remains a mystery. Any mechanism proposed must explain the following observations: (1) the ratio of 2-methyl-2-butene/2-methyl-1-butene is 3–5; (2) *ca.* ten times more branched pentenes are produced from the 2,4-DMCB isomers than from the 2,3-DMCB isomers; (3) *ca.* two times more branched pentenes are produced from *trans*-2,3-DMCB than from *cis*-2,3-DMCB. Observations 2 and 3 could be an indication of the possibility that the branched pentene formation step competes with the facile ring fission step (see results on Table II); the former competes better when the latter is relatively slow.

A mechanism of dimethylcyclopropane isomer formation *via* ring-opened biradicals ($C_5H_{10}CO$) in photolysis has been proposed in the preceding paper.[4] We do not

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(13) For cyclobutanone, $k(E) = 7 \times 10^9$ sec^{-1} at $E = 94$ kcal/mol was obtained assuming that C_3H_6 deactivated CB (S_0*) on every collision.[8c] In the present study, C_2H_4 is only 0.59 times as efficient (pressure/pressure) as the parent DMCB molecule or 0.62 times as efficient (collision/collision) in deactivating a DMCB (S_0*). So, it seems that the previously obtained values of $k(E)$ for CB (S_0*) are probably too high by a factor of ~1.3, if the collisional efficiency of 0.8 for C_3H_6 is taken as more reasonable. This revision brings the experimental values of $k(E)$ for CB (S_0*) even closer to the RRKM calculated values (at $a = 0.9$) in the earlier study.[8c] $k(E) = 4 \times 10^9$ sec^{-1} at $E = 92$ kcal/mol is then obtained by extrapolation.

(14) B. S. Rabinovitch and M. J. Pearson, *J. Chem. Phys.*, **41**, 280 (1964). The values of average excitation energy, $\langle\epsilon\rangle_f$, range from 44.1 for C_4 to 47.8 kcal/mol for C_8, while the decomposition threshold energies (ϵ_0) range from 33.0 to 31.2 kcal/mol. The ratio of $\langle\epsilon\rangle_f/\epsilon_0$ is 1.44–1.54 for C_5–C_8 radicals.

(15) S. C. Chan, B. S. Rabinovitch, J. T. Bryant, L. D. Spicer, T. Fujimoto, Y. N. Lin, and S. P. Pavlou, *J. Phys. Chem.*, 74, 3160 (1970).

(16) G. H. Kohlmaier and B. S. Rabinovitch, *J. Chem. Phys.*, **38**, 1692, 1709 (1963).

(17) M. C. Flowers and H. M. Frey, *Proc. Roy. Soc., Ser. A*, 260, 424 (1961).

Table VIII. Comparison of Collisional Deactivation Efficiencies (β_c)

Active molecule Activation method	CH_3NC Therm	*sec*-$C_4H_9\cdot$ Chem (H+)	CB (S_0*) Photo.	*trans*-2,3-DMCB (S_0)* Photo.
Excess energy, kcal/mol	~38	~40	94	92
Temp, °K	553.7	300	296	296
Ref	15	16	8c[a]	This work
Parent	(1.00)			(1.00)
Ar	0.279	0.36	0.40	0.22
N_2	0.38	0.47		
O_2			0.36	0.26
C_2H_4	0.60			0.62
C_3H_6	0.80		(0.80)	
2-C_4H_8	0.94/0.91	(1.00)		

[a] Normalized to a value of 0.80 for C_3H_6 as in the CH_3NC deactivation.

wish to repeat the discussion here, but we will briefly discuss the energetics of the dimethylcyclopropane formation process *vs.* that of the ring fission process using Scheme II. We adapt conventions used in the RRKM thermal unimolecular reaction rate theory.[8,16–18] In the "high pressure" limit, the product ratio of [DMCP/olefin] should be equal to k_2/k_1, the ratio of thermal rate constants for the two competing reaction channels. Typical observed values of k_2/k_1 in Table III range from 0.6 × 10^{-3} to 2.3 × 10^{-3} at ~610°K. For cyclobutanone, it has been found that the ratio of Arrhenius preexponential factors is $A_2/A_1 = 0.65$ and the activation energies are $E_1 = 52.0$ and $E_2 = 58.0$ kcal/mol.[5b] Assuming that the A factors for the two reaction channels in DMCB (S_0*) are roughly equal on the basis of the cyclobutanone work,[5b] we estimate that $\Delta E = E_2 - E_1$ is 6–5 kcal/mol. Assuming also that E_1 for DMCB is approximately 50 kcal/mol, we find E_2 for DMCB is 56 ± 4 kcal/mol. We estimate the ring-expanded oxacarbene[19] obtainable from cyclobutanone has $\Delta H_f = 39 \pm 10$ kcal/mol[20] as compared to ΔH_f(ring-opened biradical) = 30 kcal/mol,[21] and ΔH_f(CB) = −20 kcal/mol[8c] at 25°. Hence, the ring-opening process is 50 kcal/mol endothermic, and the ring-expansion process is <59 kcal/mol.[22] This means that both processes are energetically feasible for the decarbonylation of the vibrationally excited cyclobutanones.

Scheme II

$$\begin{gathered}
\mathrm{K(S_0) + M \rightleftharpoons K^*(S_0{}^*)} \\
\mathrm{K^* \xrightarrow{k_1} A\dagger \longrightarrow olefin + ketene} \\
\mathrm{K^* \xrightarrow{k_2} B\dagger \longrightarrow DMCP + CO}
\end{gathered}$$

A mechanism involving a ring-opened biradical, similar to that proposed in photolyses of the DMCB isomers in the preceding paper,[4] could adequately account for much of the observed stereochemical results (trans/cis ratio in dimethylcyclopropane) in thermolysis. The trans/cis ratios obtained in thermolysis are compared to those obtained in photolysis in Table IX. It is peculiar that *trans*-2,3-DMCB decarbonylates *via stereoinversion in thermolysis* as compared with *stereoretention in photolysis.* Interestingly enough, a similar result has been obtained in thermolysis and photolysis of dimethylpyrazolines.[23] No simple explanation can be offered for these observations. So far, the present experiments shed no light on the question of oxacarbene involvement in thermolysis.

Table IX. Comparison of *trans-/cis*-Dimethylcyclopropane Ratio Obtained in Thermolysis (610°K) and Photolysis (Singlet)

	DMCB parent			
	trans-2,4-	*cis*-2,4-	*trans*-2,3-	*cis*-2,3-
Thermolysis	0.6	2.0	0.5	0.3
Photolysis	1.1[a]	2.3[a]	4.4[b]	0.7[b]

[a] 325-nm value in ref 4. [b] 313-nm value in ref 4.

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(18) (a) G. M. Wieder and R. A. Marcus, *J. Chem. Phys.*, 37, 1835 (1962); (b) D. L. Bunker, "Theory of Elementary Gas Reaction Rates," Pergamon Press, Oxford, 1966.

(19) (a) N. J. Turro and R. M. Southam, *Tetrahedron Lett.*, 545 (1967); (b) W. C. Agosta and A. M. Foster, *Chem. Commun.*, 433 (1971).

(20) $\Delta H_f = -43$ kcal/mol at 25° for tetrahydrofuran was obtained from "Handbook of Organic Structural Analysis," Y. Yukawa, Ed., W. A. Benjamin, New York, N. Y., 1965, p 570. Using a C–H bond strength of 93 kcal/mol (in cyclopentane, see J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966)), $\Delta H_f = 39 \pm 10$ kcal/mol was estimated for oxacarbene (C_4H_6O). $\Delta H_f = -20$ kcal/mol for cyclobutanone was taken.[8c]

(21) See footnote 26 in ref 4.

(22) This estimate is only an upper limit. If the ring-expansion process produces an "ylide-like" intermediate (**12** in ref 4) which might be more stable than an oxacarbene (**11** in ref 4), then the process should be less endothermic than 59 kcal/mol.

(23) R. Moore, A. Mishra, and R. J. Crawford, *Can. J. Chem.*, **46**, 3305 (1968).