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Unimolecular Decomposition Rates of Cyclobutanone, 3-Oxetanone, and Perfluorocyclobutanone. An RRKM Calculation of Internally Converted Hot Molecules¹

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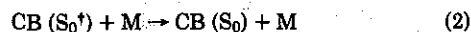
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Introduction

The RRKM (Rice–Ramsperger–Kassel–Marcus) theory has been developed to the point where it gives fairly reliable specific rate constants, $k(E)$, in many applications involving unimolecular reactions,^{1,2} although non-RRKM kinetic behavior has been found recently in several systems indicating the failure of the standard assumption of random lifetime distribution.^{3–5} We shall not be concerned presently with the latter aspect. Instead, we restrict ourselves to the former, calculation of the rates by the general RRKM computer program of Hase and Bunker which has recently become available.⁶ Because of our recent experimental studies of photoactivated molecules which undergo rapid $S_1 \rightarrow S_0$ internal conversion process to give monoenergetic, vibrationally hot, ground state molecules, we have chosen to study three model molecules, cyclobutanone (CB),⁷ 3-oxetanone (OXTN),⁸ and perfluorocyclobutanone (PFCB).⁹ Hot cyclobutanone molecules decompose to ethylene and ketene,



unless collisionally deactivated by a collision partner, M



The observed decomposition rate constants, $k_{\text{obsd}}(E)$, evaluated for various internal excitation energies (E), agreed reasonably well with the calculated rate constants,^{7a} $k_{\text{calcd}}(E)$, obtained from the semiclassical approximation procedure developed by Rabinovitch et al.¹⁰ Since the cycloreversion reaction (1) is known to be a “concerted” process (σ 2s + σ 2a) allowed by the conservation of orbital symmetry,¹¹ we expect 3-oxetanone and perfluorocyclobutanone to behave similarly. We wish to compare the specific unimolecular rate constants calculated for varying energies and activated complex models in the above three molecules featuring changes in the substituent groups and consequent changes in the vibrational frequencies. The calculation predicts that the internally converted OXTN produced by photoactivation at ~ 320 nm would have a unimolecular decomposition lifetime as short as 10^{-10} sec and the pressure quenching can only be observed experimentally above 1 atm.⁸ The calculated rates for PFCB agree well with the photochemically observed quenching rates of a PFCB intermediate which has been suggested to be the internally converted PFCB (S_0^+),^{9b} and the calculation quantitatively lends additional support for the proposed mechanism.

Unimolecular Decomposition Rates of Cyclobutanone, 3-Oxetanone, and Perfluorocyclobutanone. An RRKM Calculation of Internally Converted Hot Molecules¹

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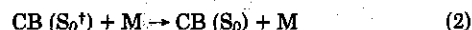
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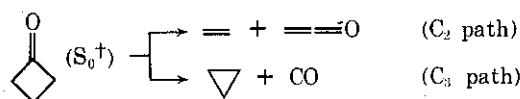


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We define C_2 and C_3 path for cyclobutanone to be as shown below:

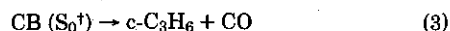


Computational Procedure

Cyclobutanone (CB). Figure 1 shows a simplified energy diagram for the unimolecular decomposition of cyclobutanone. The notations used by Robinson and Holbrook are adopted here for convenience.^{3b} The version of the general RRKM program employed in this study requires postulation of an activated complex (or critical configuration) model for which the principle moments of inertia (I_a , I_b , and I_c), the vibrational frequencies, and E_0 , the difference in zero point energies between the molecule and the complex (i.e., the activation energy at 0°K) are specified. The principle moments of inertia were calculated from the atomic masses and coordinates by a program supplied by Hase. The ground state of cyclobutanone is planar. Four of the activated complex models used are shown along with the bond length used in calculating the atomic coordinates in Figure 2. The frequencies for the complex were then calculated to fit the thermal A factor as experimentally determined¹² ($E_a = 52.0$ kcal/mol and $A = 3.6 \times 10^{14}$ sec⁻¹ at 641°K) using the absolute rate theory (ART). A computer program of W. L. Hase calculates the A factor by ART for a set of estimated frequencies and also computes the difference between the activation energy (E_a) and E_0 . The known experimental frequencies for the CB molecule¹³ and the calculated frequencies for the four activated complex models are listed in Table I, together with each set of three moments of inertia. Two other "trial models" were studied, both using the same moments of inertia as the hot molecule and both allowing the b_2 ring mode, ν_{19} (see Table I), to become zero as the "reaction coordinate"; one called "upper limit" case (UL) reduced all of the frequencies except the ring puckering vibration, ν_{27} (see Table I), by a constant factor of 14.79% while the other, "lower limit" case (LL), reduced only the ring puckering frequency to 8.8 from 71.8 cm⁻¹. The b_2 ring vibration mode has been chosen, somewhat arbitrarily, as the reaction coordinate. The program is largely insensitive to the mode chosen.

In the RRKM program, semiclassical state counting¹⁴ was employed because of the high energies and relatively low frequencies involved in the calculation. No correction was made for anharmonicity in the vibrations. The program then calculates the specific rate constant as a function of total vibrational excitation energy ($E = E_{h\nu} + E_{th}$) and also the total translational energy of the decomposition products, assuming no exothermicity from the activated complex.

In addition to the C_2 decomposition channel (1), there is a C_3 decomposition channel (3) which involves the decarbonylation process



This C_3 decomposition process is known to be two orders of magnitude slower than the primary C_2 decomposition process in pyrolysis.^{12b} Hase's ART program was used to fit frequencies of the activated complex to give the observed thermal rate constant^{12b} $k = 2.34 \times 10^{14} \exp(-58,000/RT)$ sec⁻¹ at 641°K, assuming no change of the moments of inertia in the activated complex. Three "models" were used

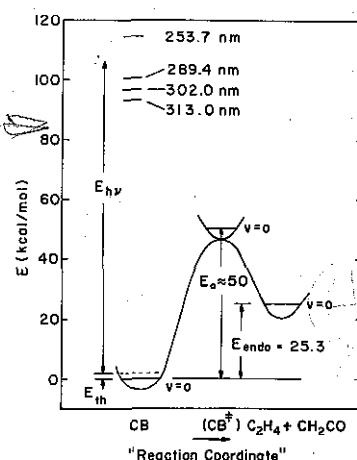


Figure 1. Simplified energetics diagram for CB (S_0^+).

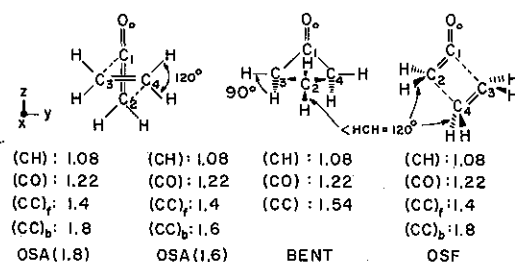


Figure 2. Assumed structures for four activated complexes of CB. OSA refers to "orbital symmetry allowed" and OSF refers to "orbital symmetry forbidden". Bond lengths are in Ångström units.

here; in all three, as before, the frequency of the b_2 mode ring vibration (no. 19) at 850 cm⁻¹ was assumed to become zero as the "reaction coordinate". It is, of course, not necessary and is indeed unlikely that the same mode would be the reaction coordinate for both C_2 and C_3 decomposition pathways; as noted before the choice is not particularly important in terms of the calculated results. In the "upper limit" case, all of the vibrational frequencies except the ring puckering vibration (ν_{27}) at 71.8 cm⁻¹ were decreased by a constant factor of 12.1%. In the "lower limit" case, the ring puckering frequency only was reduced to 13.6 cm⁻¹. In the "most probable" case, perhaps better called the intermediate case, the five ring vibration frequencies, with the exception of the sixth mode corresponding to the "reaction coordinate", were reduced by a constant factor of 32.9%. For the C_3 decomposition process, the RRKM program as described above for the C_2 decomposition rate calculation was used to compute the rates as a function of the vibrational excitation energy.

Perfluorocyclobutanone (PFCB) and 3-Oxetanone (OXTN). As it will be shown later, it was found in the rate calculation for cyclobutanone that various values of the moments of inertia corresponding to different activated complex geometries yielded only minor variations of the unimolecular rate constants, within a factor of 2. Because of this insensitivity, the same moments of inertia were used for the activated complex as for the hot molecule for the PFCB and OXTN calculation.

Three moments of inertia of PFCB were calculated assuming geometries similar to the planar ground state of CB,^{13b} since neither an infrared nor microwave analysis is presently available. For the same reason, the molecular vi-

TABLE I: Frequencies (cm^{-1})^a and Moments of Inertia ($\text{amu } \text{\AA}^2$)^b for Cyclobutanone C_2 Path

Vibrn no. ^c	Molecule	Activated complex			
		OSA (1.8)	OSA (1.6)	Bent	OSF
18 ring (b_2)	1124	766	748	774	791
24 CH_2 rock (b_1)	1073	1073	1073	1073	1073
7 ring (a_1)	956	598	580	606	623
13 CH_2 rock (a_2)	902	902	902	902	902
8 ring (a_1)	850	492	474	500	517
19 ring (b_2)	850	0	0	0	0
12 CH_2 twist (a_2)	829	829	829	829	829
25 CH_2 rock (b_1)	735	735	735	735	735
9 ring (a_1)	670	312	294	320	337
20 CO wag (b_2)	454	454	454	454	454
26 CO wag (b_1)	395	395	395	395	395
27 ring (b_1)	71.8 ^d	43.7	42.4	44.0	45.7
I_{xx}	142.06 ^b	93.55	90.10	110.80	149.00
I_{yy}	105.17 ^b	103.70	92.18	86.54	117.00
I_{zz}	46.87 ^b	49.51	41.40	56.35	42.57
$(I_a I_b I_c)^{1/2}$	836.86	693.04	586.38	735.06	861.46

^a Vibration numbering and fundamental frequencies given in ref 13a. ^b Moments of inertia given in ref 13b. ^c Frequencies which remain unchanged above 1200 cm^{-1} with vibrational number in parentheses are 3004 (21), 2978 (22), 2978 (1), 2975 (10), 2933 (2), 2933 (4), 1816 (3), 1479 (4), 1470 (5), 1402 (6), 1402 (15), 1332 (16), 1242 (17), 1209 (23), and 1200 (11). ^d A harmonic frequency which gives the same vibrational partition function (at 641°K) as with the observed anharmonic frequencies.

TABLE II: Frequencies (cm^{-1}) and Moments of Inertia ($\text{amu } \text{\AA}^2$) for Perfluorocyclobutanone and 3-Oxetanone C_2 Path

PFCB ^d			OXTN ^e		
Vibrn no. ^a	Molecule	Complex	Vibrn no. ^b	Molecule ^b	Complex
8 ring (a_1)	(950)	612	6 ring (a_1)	832	444
9 ring (a_1)	(700)	450	7 ring (a_1)	683	363
11 CH_2 twist (a_2)	(935)	435	14 ring (b_2)	1076	573
18 ring (b_2)	(660)	425	15 ring (b_2)	955	0
19 ring (b_2)	(1000)	0	21 ring (b_1)	140	75
27 ring (b_1)	(50)	32.3			
I_{xx}	431.72	431.72	I_{xx}	137.08 ^c	137.08
I_{yy}	372.00	372.00	I_{yy}	101.97 ^c	101.97
I_{zz}	532.34	532.34	I_{zz}	41.66 ^c	41.66
$(I_a I_b I_c)^{1/2}$	9246	9246	$(I_a I_b I_c)^{1/2}$	763.10	763.10

^a Vibration numbering given in ref 13a. ^b Vibration numbering and fundamental frequencies given in ref 17. ^c Moments of inertia given in ref 16. ^d Frequencies which remain unchanged with vibrational number in parentheses are 1434 (1), 1366 (2), 1820 (3), 700 (4), 567 (5), 293 (6), 364 (7), 1250 (10), 435 (12), 200 (13), 1250 (14), 435 (15), 270 (16), 260 (17), 450 (20), 1250 (21), 1250 (22), 337 (23), 200 (24), 200 (25), and 350 (26). ^e Frequencies which remain unchanged with vibrational number in parentheses are 2931 (1), 1847 (2), 1457 (3), 1134 (4), 979 (5), 2962 (8), 111 (9), 1102 (10), 2924 (11), 1430 (12), 1250 (13), 488 (16), 2956 (17), 1284 (18), 1049 (19), and 401 (21).

brational frequencies of PFCB were estimated from those assigned for CB and perfluorocyclobutane.¹⁵ Fortunately, the moments of inertia¹⁶ and vibrational frequency assignments¹⁷ of OXTN were available for the planar ground state.

The frequencies of the activated complex were calculated to fit the experimental A factor of CB¹² using Hase's ART program, since again no thermal A factors for PFCB and OXTN are presently available. The frequencies and moments of inertia used are listed in Table II. Since the thermochemical and thermal kinetic data for either of these molecules are not experimentally available, we decided to use the same E_0 value used for CB (see Figure 1).

Results and Discussion

Cyclobutanone (C_2 Path). Figure 3 shows a plot of cal-

culated values of the specific rate constant (k_{RRKM}) as a function of total molecular excitation energy for six different activated complex models. Also, experimental values^{7a} of the mean collision frequency at the half-quenching pressure ($\omega_{1/2}$) obtained at 313.0, 302.0, 289.4, and 253.7 nm are shown for comparison. In the energy ranges covered, the values of k_{RRKM} for all six models come within a factor of 2 for a given energy, indicating relative insensitivity to the choice of the activated complex models used here. There is an agreement at high energies between the values of $k(E)$ calculated from the semiclassical approximation formulation^{7a} and the values of k_{RRKM} calculated for OSA (1.8) which can be regarded as the "most probable" (MP) one. OSA (1.8) refers to the "orbital symmetry allowed" model, 1.8 Å separation of nascent double bond centers, and OSF refers to the "orbital symmetry forbidden" model in Figure

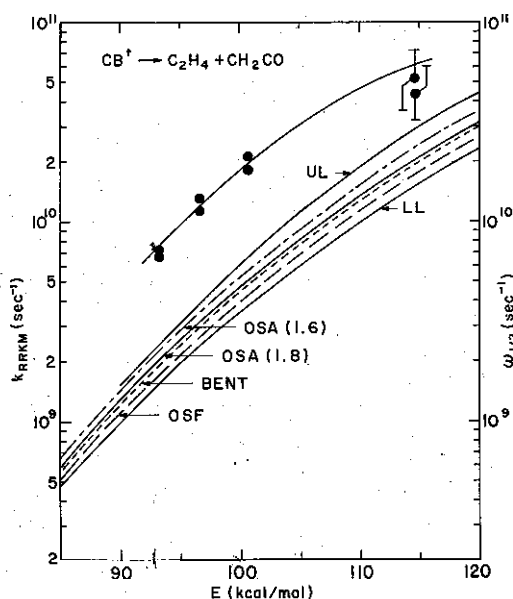


Figure 3. (Left) Calculated specific rate constants of the C₂ path of CB for various activated complex models vs. excitation energy. (Right) Observed mean collision frequencies at the half-quenching pressure ($\omega_{1/2}$) vs. excitation energy (ref 7a).

2. We can certainly regard the "upper limit" (UL) and the "lower limit" (LL) values to represent the two extreme cases. For this reason we chose to limit our activated complex models to the MP, UL, and LL cases in subsequent calculations.

Assuming that the factor of 2~3 discrepancy between the observed values of $\omega_{1/2}$ and the calculated values of k_{RRKM} is due to the inefficient collisional deactivation by propylene which was used as the collision partner (M), we have calculated the values of average energy loss per collision (Δ) for the multistep deactivation scheme given in Appendix. Keeping many terms in the kinetic analysis (stepladder model) and numerically fitting the experimental points of $\omega_{1/2}$ to k_{RRKM} , the values of Δ at 313.0- and 253.7-nm excitation have been obtained for the three models, and they are shown in Table III. These values are reasonable and are in agreement with similar values calculated for other systems.¹⁸ the average energy loss per collision, however, is not constant for both 253.7- and 313.0-nm excitation, 6 and 3 kcal/mol per collision, respectively. It should be noted that we have neglected the possibility of activating collisions in this model, since they should be less probable for these high photoactivation energies and large collision partners¹⁹ (and therefore large Δ 's). Calculations on other systems show a decreasing effect of deleting activating collisions as more complex collision partners are involved, although there may be a factor of 2 or 3 difference in Δ when helium is used.^{18b}

The general RRKM program also calculates the amount of internal energy of the complex which is converted to translational energy during the reaction. This is accomplished for a given initial energy by determining the probability that various quantities of energy are contained in the vibrational mode which becomes the reaction coordinate. Figure 4 shows the relative translational energy distribution for the three models, MP, UL, and LL, at two wavelengths, 253.7 and 313.0 nm. The plots are somewhat curved on semilogarithmic paper, but are fairly closely approximated by a simple exponential function. Thus an ex-

TABLE III: Energy Loss per Collision (Δ) for CB† (M = Propylene)

λ_{ex} , nm	$E = E_{hv} + E_{th}$, kcal/mol	Δ , kcal/mol/collision	Condition
313.0	93.2	3.7	Upper limit
313.0	93.2	3.1	OSA (1.8)
313.0	93.2	2.4	Lower limit
253.7	114.6	9.2	Upper limit
253.7	114.6	5.9	OSA (1.8)
253.7	114.6	4.1	Lower limit

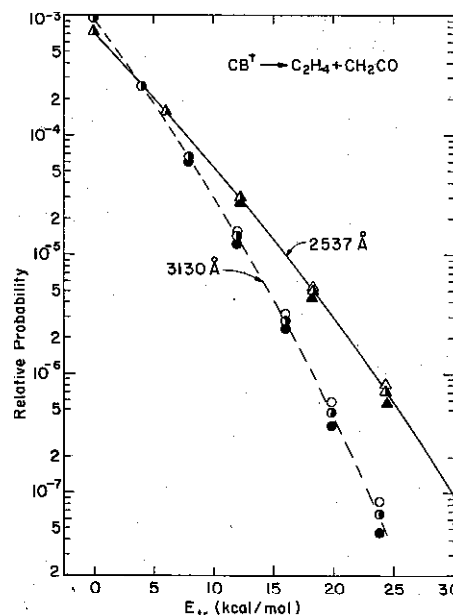


Figure 4. Relative probability for the translational energy distribution for the C₂ path of CB: (filled symbols) upper limit; (half-filled symbols) OSA (1.8); (open symbols) lower limit.

ponential fit to the initial portion of the relative probability function should give an approximate value for the average value of the energy put into translation of the two decomposition fragments, neglecting the energy available between the activated complex and the products, ~24.7 kcal/mol. The data in Table IV summarize the values of the average translational energy, $\langle E_{tr} \rangle$, calculated from the probability function generated by the program.

From the results tabulated we can see that at 313.0 nm, only about 3.0 kcal/mol of the activated complex energy is put into translation of the product fragments, and at 253.7 nm only about 3.9 kcal/mol is available in translation, only 0.9 kcal/mol more than at 313.0 nm. Only about 6% of the activated complex energy is put into translation on the average, corresponding approximately to the expectation based on the internal degrees of freedom involved within the principle of equipartitioning of energy. If we assume that, in addition to the activated complex energy put into translation, all of the "exothermicity" from the complex to the products, 24.7 kcal/mol, is also converted into translational energy, then the energy distributed among the products is 33.3 kcal/mol at 313.0 nm, 36.5 kcal/mol at 302.0 nm, 40.5 kcal/mol at 289.4 nm, and 53.8 kcal/mol at 253.7 nm. Two major problems occur in the translational energy

TABLE IV: Values of Average Translational Energy (kcal/mol) vs. λ_{ex} (nm)^a for Cyclobutanone C₂ Path

Model C ₂	λ_{ex}			
	313.0 nm	302.0 nm	289.4 nm	253.7 nm
Upper limit	2.89	3.04	3.21	3.80
OSA (1.6)	3.00	3.15	3.34	3.93
OSA (1.8)	3.01	3.16	3.34	3.93
Bent	3.01	3.16	3.34	3.94
OSF	3.01	3.16	3.35	3.94
Lower limit	3.08	3.23	3.41	4.00

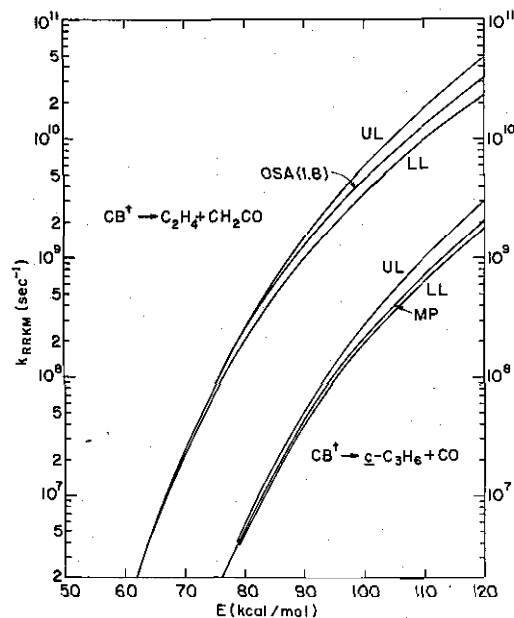
^a Internal energies of activated complex available for translation are 39.3 (313.0 nm), 42.7 (302.0 nm), 46.8 (289.4 nm), and 60.7 kcal/mol (253.7 nm).

calculations done in the program. First, when there is an "exothermicity" from the activated complex, the fraction of that energy which goes into product translation energy will depend on the shape of the potential surface in that region, an unknown quantity. Secondly, for complex molecules the reaction path does not correspond to a single vibrational mode but to a combination of modes; thus the energy from several modes may appear as translation and not just the energy contained in the single mode selected as the reaction path. It is hoped that future theoretical treatments will deal more closely with these problems in light of the importance of determining the deposition of energy in such kinetic systems.

Cyclobutanone (C₃ Path). Figure 5 shows the values of calculated RRKM rate constants of the C₃ path for three activated complex models, MP, UL, and LL, and they are compared to those calculated for the C₂ path. The ratio of the rate constants for the C₂ path to those for the C₃ path ranges from 538 at 60 kcal/mol to 15.3 at 120 kcal/mol for the "most probable" model; the ratios at other energies are 170 at 65, 90.7 at 70, 59.8 at 75, 44.3 at 80, 35.1 at 85, 29.2 at 90, 25.0 at 95, 22.0 at 100, 19.7 at 105, 18.0 at 110, and 16.5 at 115 kcal/mol. It should be noted that the C₂ path dominates the C₃ path by at least a factor of 15 for the photoactivation wavelength range of 313.0 to 253.7 nm, or $E_{hv} + E_{th}$ of 93.2 to 114.6 kcal/mol. Therefore, the calculation suggests that the quantum yield of the C₃ products resulting solely from the decomposition of CB (S_0^+) must be less than 0.03, less than $1/10$ of the total C₃ quantum yield, since the observed quantum yields of the C₂ products are ~ 0.71 at 313.0 nm ($C_3/C_2 \approx 0.4$) and ~ 0.55 at 253.7 nm ($C_3/C_2 \approx 0.8$).^{7a} This conclusion is consistent with the observations made in the photoactivation studies of alkyl-substituted cyclobutanones, 2-*n*-propylcyclobutanone and the *cis* and *trans* isomers of 2,3-dimethylcyclobutanone²⁰ and 2,4-dimethylcyclobutanone.²¹

Table V summarizes the data for the calculation of the amount of activated complex energy which goes into translation of the fragments $c\text{-C}_3\text{H}_6$ and CO. As before, these data are obtained from an exponential fit to the initial portion of the relative probability curve similar to Figure 4. These data are very similar to those for the C₂ path (see Table IV), as might be expected, particularly at these high energies. Again, about 7–8% of the activated complex energy becomes available for translation, as expected.

PFCB and OXTN (C₂ Path). Calculated specific rate constants for the C₂ path of PFCB and OXTN are com-

**Figure 5.** Calculated specific rate constants for the C₃ path of CB as compared to those for the C₂ path.**TABLE V: Values of Average Translational Energy (kcal/mol) vs. λ_{ex} (nm)^a for Cyclobutanone C₃ Path**

Model C ₃	λ_{ex}			
	313.0 nm	302.0 nm	289.4 nm	253.7 nm
Upper limit	2.65	2.81	2.99	3.58
Most probable	2.74	2.90	3.09	3.69
Lower limit	2.80	2.96	3.15	3.76

^a Internal energies of the activated complex available for translation are 33.0 (313.0 nm), 36.7 (302.0 nm), 40.8 (289.4 nm), and 54.7 kcal/mol (253.7 nm).

pared to those of CB in Figure 6. The value of k_{RRKM} for PFCB is 3 orders of magnitude smaller than that for CB at 60 kcal/mol and it is 1 order of magnitude smaller at 120 kcal/mol. One expects this kind of behavior, since the density of states ratio (activated complex/molecule) should be much higher for CB than for PFCB which has more low-frequency vibrations, although the density of states for CB should be much lower than that for PFCB. Again, as expected, the values of k_{RRKM} for OXTN is 1–1.5 orders of magnitude higher than that for CB, because OXTN has six fewer vibrational modes than CB. This suggests that the collisional deactivation of the photoactivated OXTN (S_0^+) would require about 10 times higher pressure than that required for the photoactivated CB (S_0^+).

Three experimental points for PFCB in Figure 6 were obtained using the gas kinetic collision diameter for PFCB of 6.0 Å and the "strong" collision assumption which cannot be strictly valid. Of course, the fact that these points are about a factor of 2 higher than the corresponding calculated values suggests that there is a low efficiency of collisional deactivation as has been observed in the case of CB. However, we shall not attempt a detailed comparison, because of the assumptions employed in the calculation which make the calculations for PFCB and OXTN less reliable than that for CB; (a) A factors for the decompositions

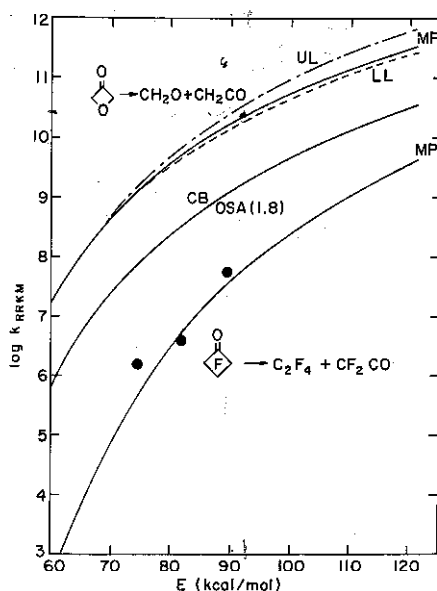


Figure 6. Calculated specific rate constants for the C_2 path of PFCB and OXTN. Three filled points are experimental values of PFCB ($E_{th} = 3.7$ kcal/mol).^{9b}

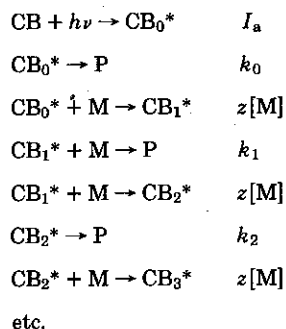
of PFCB and OXTN were assumed to be the same as the A factor for CB and (b) E_a 's for PFCB and OXTN were assumed to be the same as E_a for CB. However, since the C_2 path for CB and its isomers is allowed by the orbital symmetry conservation rules^{11,21} we should not expect much change for the values of the A factor and E_a for PFCB and OXTN.

A review of the experimental rate data (see Benson and O'Neal)²² suggests that the A factors should be within a factor of 4 or 5 for the three molecules, CB, PFCB, and OXTN, but that the E_a values could be off as much as (but probably less than) 20%, causing larger deviations from the calculation done here. We believe that the influence of F substitution for H as well as the influence of O substitution for CH_2 in determining the values of k_{RRKM} are real.

The present calculation certainly validates the internal conversion mechanism in the photolysis of PFCB,^{9b} while it helps in designing the pressure quenching experiments so that the presence of short-lived hot ground state of OXTN can be established in the photolysis of OXTN.⁸

Appendix

The multistep deactivation scheme for the hot cyclobutanone where up transitions are neglected is



where an asterisk indicates the vibrationally hot species, the subscripts 0, 1, 2, ..., n indicate the number of colli-

sions suffered by the vibrationally hot species which loses Δ kcal/mol per collision, and P and M are the decomposition product and the collision partner, respectively. I_a , k_n , z , and $[M]$ have the usual meanings. Application of the steady state approximation to CB_0^* , CB_1^* , CB_2^* , etc., gives the following expression for the rate of product formation:

$$\frac{1}{I_a} \frac{dP}{dt} = \frac{k_0}{k_0 + zM} + \frac{k_1 z M}{(k_0 + zM)(k_1 + zM)} + \frac{k_2 z^2 M^2}{(k_0 + zM)(k_1 + zM)(k_2 + zM)} + \dots$$

At the half-quenching pressure, $M_{1/2}$, we obtain

$$\left(\frac{dP}{dt} \right)_{M_{1/2}} = \frac{1}{2} \left(\frac{dP}{dt} \right)_0 = \frac{1}{2} I_a$$

Hence, if we adopt $\omega_{1/2} = zM_{1/2}$, we obtain

$$\frac{1}{2} = \frac{k_0}{k_0 + \omega_{1/2}} + \frac{k_1 \omega_{1/2}}{(k_0 + \omega_{1/2})(k_1 + \omega_{1/2})} + \frac{k_2 \omega_{1/2}^2}{(k_0 + \omega_{1/2})(k_1 + \omega_{1/2})(k_2 + \omega_{1/2})} + \dots$$

We can find the value of Δ for a given set of k_0 , k_1 , k_2 , ..., k_n values and $\omega_{1/2}$ from the above expression, since $E_0 = h\nu$, $E_1 = h\nu - \Delta$, $E_2 = h\nu - 2\Delta$, ...

References and Notes

- (1) This research has been supported by NSF Grant GP 41407X. The earlier support by the Office of Naval Research is gratefully acknowledged.
- (2) (a) R. A. Marcus and O. K. Rice, *J. Phys. Colloid. Chem.*, **55**, 894 (1951); (b) R. A. Marcus, *J. Chem. Phys.*, **20**, 355 (1952).
- (3) See for recent reviews (a) B. S. Rabinovitch and D. W. Setser, *Adv. Photochem.*, **3**, 1 (1964); (b) P. J. Robinson and K. A. Holbrook, "Unimolecular Reactions", Wiley-Interscience, New York, N.Y., 1972; (c) W. Forst, "Theory of Unimolecular Reactions", Academic Press, New York, N.Y., 1973.
- (4) D. L. Bunker and W. L. Hase, *J. Chem. Phys.*, **59**, 4621 (1973).
- (5) (a) H. H. Harris and D. L. Bunker, *Chem. Phys. Lett.*, **11**, 433 (1971); (b) D. L. Bunker, *J. Chem. Phys.*, **57**, 332 (1972); (c) C. T. Ting and F. S. Rowland, *J. Phys. Chem.*, **74**, 4080 (1970); (d) J. D. Rynbrandt and B. S. Rabinovitch, *J. Chem. Phys.*, **54**, 2275 (1971); (e) Y.-N. Tang and Y. Y. Su, *ibid.*, **57**, 4048 (1972); (f) J. G. Moehlmann, J. T. Gleaves, J. W. Hudgens, and J. D. McDonald, *J. Chem. Phys.*, **60**, 4790 (1974).
- (6) The program of D. L. Bunker and W. L. Hase is available through Quantum Chemistry Program Exchange (No. QCPE-234), Department of Chemistry, Indiana University.
- (7) (a) N. E. Lee and E. K. C. Lee, *J. Chem. Phys.*, **50**, 2094 (1969); (b) J. C. Hemminger and E. K. C. Lee, *ibid.*, **56**, 5284 (1972); (c) J. Metcalfe, H. A. J. Carless, and E. K. C. Lee, *J. Am. Chem. Soc.*, **94**, 7235 (1972).
- (8) G. M. Breuer and E. K. C. Lee, unpublished work.
- (9) (a) R. S. Lewis and E. K. C. Lee, *J. Chem. Phys.*, **61**, 3434 (1974); (b) *J. Phys. Chem.*, **79**, 187 (1975).
- (10) (a) D. W. Setser and B. S. Rabinovitch, *Can. J. Chem.*, **40**, 1425 (1962); (b) G. Z. Whitten and B. S. Rabinovitch, *J. Chem. Phys.*, **38**, 2466 (1963).
- (11) (a) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969); (b) H. A. J. Carless and E. K. C. Lee, *J. Am. Chem. Soc.*, **92**, 4482 (1970).
- (12) (a) M. N. Das, F. Kern, T. D. Coyle, and W. D. Walters, *J. Am. Chem. Soc.*, **78**, 6271 (1954); (b) A. T. Blades, *Can. J. Chem.*, **47**, 615 (1969); (c) T. H. McGee and A. Schleifer, *J. Phys. Chem.*, **76**, 963 (1972); (d) A. T. Blades and H. S. Sandhu, *ibid.*, **77**, 1316 (1973); (e) T. H. McGee and A. Schleifer, *ibid.*, **77**, 1317 (1973).
- (13) (a) K. Frel and H. H. Gunthard, *J. Mol. Spectrosc.*, **5**, 218 (1960); (b) L. H. Scharpen and V. W. Laurie, *J. Chem. Phys.*, **49**, 221 (1968).
- (14) (a) G. Z. Whitten and B. S. Rabinovitch, *J. Chem. Phys.*, **38**, 2466 (1963); **41**, 1883 (1964); (b) D. C. Tardy and B. S. Rabinovitch, *ibid.*, **48**, 1427 (1968).
- (15) W. C. Harris and D. B. Yang, *J. Chem. Phys.*, **60**, 4175 (1974).
- (16) J. S. Gibson and D. O. Harris, *J. Chem. Phys.*, **57**, 2318 (1972).
- (17) J. R. Durig, A. C. Morrissey, and D. O. Harris, *J. Mol. Struct.*, **6**, 375 (1970).
- (18) (a) R. Atkinson and B. A. Thrush, *Proc. Roy. Soc. (London), Ser. A*, **316**, 131 (1970); (b) B. S. Rabinovitch, H. F. Carroll, J. D. Rynbrandt, J. H. Georgakakos, B. A. Thrush, and R. Atkinson, *J. Phys. Chem.*, **75**, 3376 (1971); (c) M. G. Toper and R. W. Carr, Jr., *ibid.*, **58**, 757 (1973); (d) S. W. Orchard and B. A. Thrush, *Proc. R. Soc. (London), Ser. A*, **329**, 233 (1972).

- (19) (a) D. C. Tardy and B. S. Rabinovitch, *J. Chem. Phys.*, **45**, 3720 (1966);
(b) D. C. Tardy and B. S. Rabinovitch, *J. Chem. Phys.*, **48**, 1282 (1968).
- (20) H. A. J. Carless and E. K. C. Lee, *J. Am. Chem. Soc.*, **94**, 1 (1972).
- (21) (a) H. A. J. Carless, J. Metcalfe, and E. K. C. Lee, *J. Am. Chem. Soc.*, **94**, 7221 (1972); (b) J. Metcalfe, H. A. J. Carless, and E. K. C. Lee, *ibid.*, **94**, 7235 (1972).
- (22) S. W. Benson and H. E. O'Neal, *Nat. Stand. Ref. Data Ser.*, Natl. Bur. Stand., **21** (1970). We have compared the values of A factor and E_a for the hydrocarbons and their perfluoro analogs, ethane, cyclobutane, cyclobutene, and vinylcyclopropane. Also, the cyclopropane-ethylene oxide, cyclobutane-oxetane, and cyclopentene-2,5-dihydrofuran pairs were compared.