$$SiH_4 + Cl\cdot \underset{-1}{\overset{1}{\rightleftarrows}} (H_4Si\cdot Cl)^* \xrightarrow{2} H_3Si\cdot + HCl$$

If the Cl in the complex has a significantly different absorption or fluorescence spectrum, then the rate measurement is that of complex formation and not the rate of reaction. Since many derivatives of disilane are known to decompose via mechanisms which involved pentavalent silicon,[14] this type of adduct formation must be considered. In principle the extent of complex formation could be determined by isotopic scrambling on labeled chlorosilanes or by isotope effects in SiD_4 if the error limits could be reduced. This adduct formation may also be related to the third-order behavior of the phosphine reaction.

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Multistep Collisional Stabilization of Chemically Activated Alkylcyclopropanes

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The kinetics of alkylcyclopropanes, chemically activated to energies at least 40 kcal/mol above their decomposition or isomerization thresholds, have been investigated at low pressures in the presence of large, polyatomic bath gases. The homologous series cyclopropane, methylcyclopropane, and ethylcyclopropane has been examined. The activated molecules were formed by the room temperature photolysis of ketene in the presence of appropriate 1-alkenes, C_5 or C_6 alkanes, and oxygen. The ratio of isomerization rate to collisional stabilization rate, D/S, was measured for each activated molecule as a function of pressure. All data plots of D/S vs. reciprocal collision frequency were concave upward, indicating multistep collisional deactivation. Using RRKM theory and a stepladder deactivation scheme the experimental data were adequately fit by computer models. The collisional energy transfer results are discussed and compared with earlier results on activated alkylcyclobutanes and other chemical activation systems. Evidence for a dependence of collisional deactivation stepsize on size of chemically activated species is presented.

Introduction

Intermolecular exchange of energy is an inherent part of almost every gas phase reaction. Despite its significance to chemistry, energy exchange from highly excited polyatomic molecules to polyatomic collision partners is a poorly understood process. Two reviews of the subject have recently been published,[1,2] and two comprehensive experimental studies have made a significant contribution.[3,4] Chan et al.[3] examined the thermal isomerization of methylisocyanide in the presence of various bath gases and determined the relative collisional activation–deactivation efficiencies of over 100 different gases. Luu and Troe[4] used the photoactivated isomerization of cycloheptatriene to toluene to measure the relative collisional deactivation efficiencies of 43 different bath gases. Both studies showed the collisional energy transfer efficiency was strongly dependent upon the number of atoms in the collider molecule. At least up to a size of 10 atoms per collider molecule, the collisional efficiency increases with increasing molecular size. Quasi-statistical theories[5] of energy transfer provide an explanation of this trend. It should be noted that these models imply a dependence on the size of the excited molecule as well as on the size of the bath gas.

There are few data on the effect of the size of the excited molecule on intermolecular energy transfer. A systematic study has been reported by Tardy and Rabinovitch,[6] who studied the decomposition of hot alkyl radicals created by H atom addition to the homologous series of alkenes: *cis*-butene-2, pentene-1, hexene-1, 2-methylbutene-1, and

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octene-1. On formation the alkyl radicals had approximately 10 kcal/mol of internal energy in excess of their threshold for decomposition. Bath gases used in the experiments were H_2, N_2, CH_4, and CF_4. Analysis of these systems, using Rice–Ramsparger–Kassel–Marcus theory and a stepladder deactivation model, gave the results that the average energy transfer increased with the size of the bath gas molecule but was independent of the complexity of the hot radical.

We have recently reported work on the average collisional energy transfer from chemically activated methylcyclobutane[7] and ethylcyclobutane.[8] Despite having principal collision partners of comparable collisional efficiency, defined according to ref 3 and 4, the average energy transfer from methylcyclobutane was greater than that from ethylcyclobutane. This caused us to speculate that the amount of vibrational energy transferred may decrease with increasing size of the excited molecule.

This paper concerns our subsequent experiments on the multistep deactivation of chemically activated molecules in the homologous series cyclopropane, methylcyclopropane, and ethylcyclopropane. In all cases the activated molecule was produced by addition of singlet methylene to the double bond of an alkene. All of these reaction systems have been studied previously, though never in a comparative manner with the aim of examining the characteristic vibrational energy transfer.

The activated cyclopropane system was first examined by Setser and Rabinovitch,[9] and then by Simons, Rabinovitch, and Setser.[10] No oxygen was present to scavenge triplet methylene radicals. More importantly none of the bath gases utilized may have been a truly strong collider. From the work of Chan et al.,[3] ethylene, the largest bath gas, has a collisional energy transfer efficiency only 60% that of *n*-pentane.

Rowland, McKnight, and Lee[11] studied the reaction of methylene-*t* with ethylene at high pressure, in both the presence and absence of oxygen. Irradiation of ketene at 313 nm was used. A 30:1:1 mixture of C_2H_4, CHTCO, and O_2 gave a high pressure rate constant for cyclopropane decomposition of 5.1×10^{10} s^{-1} on the basis of the collision diameters of this study.

Activated methylcyclopropane has been examined by Butler and Kistiakowsky,[12] by Dorer and Rabinovitch,[13] and by Topor and Carr.[14] The first two studies were not concerned with intermolecular energy transfer. Topor and Carr reported the multistep nature of the collisional deactivation, however their data did not extend far enough into the low pressure region for an accurate determination of the average vibrational energy transfer.

Activated methylcyclopropane formed by methylene radical insertion into cyclopropane[15] and by combination of methyl and cyclopropyl radicals[16] has also been investigated. The latter study gave evidence of multistep deactivation, though the only collision partner examined was the weak collider helium.

The only previous study of the activated ethylcyclopropane system was by Dorer and Rabinovitch.[13] Their interest was to compare ethylcyclopropane decomposition with trifluoroethylcyclopropane. No attempt was made to measure the energy transfer characteristics of the excited molecule.

Experimental Section

The vacuum apparatus, light source, and experimental techniques have been previously described.[8] The gas chromatographic separations were performed using a variety of columns and conditions. Helium flow rate was always maintained at approximately 140 cm^3/min. For single column operation a pressure of 40 psig was used; for two columns in series the column pressure was raised to 75 psig. The cyclopropane system was analyzed using a 7 m by 0.65-cm o.d. 3% Squalane on firebrick column held at 0 °C. The methylcyclopropane system was analyzed initially using a 6 m by 0.65 cm o.d. 20% benzyl ether on firebrick column at room temperature. It proved impossible to analyze low pressure reaction products this way because of the proximity of the methylcyclopropane and butene-2 peaks. These analyses were made using a 6 m by 0.65-cm o.d. 40% $AgNO_3$ ethylene glycol (saturated solution) on firebrick column in series with the 7-m 3% Squalane column. The $AgNO_3$ column was kept at room temperature while the squalane column was held at 0 °C. The same two column series was used for the ethylcyclopropane system. The $AgNO_3$ column was kept at 10 °C and the squalane column was maintained at room temperature.

Research grade ethylene, propylene, and 1-butene were used as purchased from the Phillips Petroleum Co. *n*-Pentane (98% purity) and 2-methylpentane (99^+% purity) were used as received from the Aldrich Chemical Co. Impurities, as determined by gas chromatography, did not interfere with the reaction or product analyses. Oxygen was Chemtron industrial grade. Ketene was prepared by pyrolysis of acetic anhydride[17] and purified by several trap-to-trap distillations prior to use.

An Osram HBO 500 Hg arc lamp, the output of which was filtered through Pyrex, was used. Photolyses were performed on mixtures prepared in the following ratios: 10:2:1:1 of *n*-pentane:ethylene:ketene:oxygen; 10:2:1:1 of *n*-pentane:propylene:ketene:oxygen; 10:2:1:1 butene-1:2-methylpentane:ketene:oxygen. A mixture of 10:2:1:1 2-methylpentane:1-butene:ketene:oxygen did not produce enough stabilized ethylcyclopropane for analysis at low pressure.

Reaction Mechanism

The general reaction mechanism may be written

$$CH_2CO + h\nu \rightarrow CH_2(^1A_1) + CO \tag{1}$$

$$CH_2(^1A_1) + \text{1-alkene} \rightarrow \text{alkylcyclopropane*} \tag{2}$$

$$CH_2(^1A_1) + \text{1-alkene} \rightarrow \text{miscellaneous alkenes*} \tag{3}$$

$$CH_2(^1A_1) + \text{alkane } (C_{m-1}) \rightarrow \text{alkane } (C_m) \tag{4}$$

$$C_nH_{2n}^* \xrightarrow{\omega} C_nH_{2n} \tag{5}$$

$$C_nH_{2n}^* \rightarrow \text{decomposition products} \tag{6}$$

$$CH_2CO + h\nu \rightarrow CH_2(^3B_1) + CO \tag{7}$$

$$CH_2(^3B_1) + O_2 \rightarrow CO, CO_2, H_2, H_2O,... \tag{8}$$

Photolysis, reactions 1 and 7, produces electronically excited ketene having an energy content slightly in excess of its decomposition threshold. The singlet radical formed in reaction 1 may thus carry some excess energy into its subsequent reaction. The activating reaction of interest here, reaction 2, leads to formation of excited alkylcyclopropane. Singlet methylene undergoes other side reactions with the 1-alkene giving a variety of activated products (reaction 3). Any activated molecule will either be collisionally stabilized (5) in a many step process or react (6), either by isomerization or by decomposition. Our concern was with the fraction of activated alkylcyclopropane molecules that stabilize at any given pressure. While the amount of collisionally stabilized alkylcyclopropane may be monitored, the extent of isomerization

TABLE I: Lennard-Jones Parameters[a]

molecule	σ, Å	ϵ/k, K
cyclopropane	4.81	249
methylcyclopropane	5.04	278
ethylcyclopropane	5.27	310
ethylene	4.23	205
propylene	4.67	303
1-butene	5.09	310
n-pentane	5.77	325
2-methylpentane	6.14	325

[a] All of the above constants were obtained from ref 3 except for the methylcyclopropane values which were calculated from those for cyclopropane and ethylcyclopropane. From ref 28, $\sigma_{\text{ketene}} = 5.45$ Å and $\sigma_{O_2} = 3.60$ Å. Oxygen was assigned a collisional efficiency of 0.25.

TABLE II: Thermochemical Parameters

compd	C_v,[a] kcal/(mol K)	$\Delta H_f{}^\circ{}_0$, kcal/mol
$CH_2(^1A_1)$	0.006	98 ± 4[b]
C_2H_4	0.0064	14.5
C_3H_6	0.0087	8.5
$1\text{-}C_4H_8$	0.012	5.0
cyclopropane		16.8
methylcyclopropane		12.5[c]
ethylcyclopropane		8.4[d]

[a] Heat capacity. [b] Reference 19. [c] Reference 14. [d] Based upon $\Delta H_c(\text{l})_{\text{ECP}} = 805.9$ kcal/mol[30] and an assumed value of $\Delta H_{\text{vap}} = 7.2$ kcal/mol.

cannot be monitored because of secondary decomposition of the isomerization products. Therefore an internal standard technique was used to obtain a measure of the amount of activated alkylcyclopropane generated by reaction 2. The internal standard was a large alkane which reacts with singlet methylene to give a stable product, reaction 4. The amount of alkane product is proportional to the extent of singlet methylene reaction.

Oxygen was always present in the reactant mixture at a concentration of roughly 7%. This ensured that the triplet methylene was scavenged via reaction 8.

Results

The ratio of decomposition to stabilization rate (D/S) was obtained from the relative amount of stabilized alkylcyclopropane (S) and the internal standard product (ISP).

$$D/S = \frac{D + S}{S} - 1 = \frac{(S/\text{ISP})_{p=\infty}(\text{ISP})}{S} - 1 \quad (9)$$

The proportionality factor relating the amount of internal standard product to the total alkylcyclopropane created, ($D + S$), is the ratio of stabilized alkylcyclopropane to ISP at high pressure where the extent of decomposition is negligible.

The bimolecular collision frequency (ω) was calculated as the product of collision number and pressure.[18] The molecular collision diameters were found by multiplying the Lennard-Jones constants, given in Table I, by the square root of the collision integral, $r^{(2,2)}(kT/\epsilon)$.

The experimental data are presented as plots of D/S vs. ω^{-1} in Figures 1–7. All of the plots show upward curvature, indicative of a multistep deactivation process.

Theoretical Calculations

Microcanonical decomposition rate constants for the alkylcyclopropanes were computed using Rice–Ramsperger–Kassel–Marcus theory of unimolecular reactions.[18] The harmonic oscillator models for the excited molecules and their activated complexes are listed in Tables II and III.

TABLE III: RRKM Frequency Assignments (cm^{-1})

Cyclopropane[a]

▽	▽$^+$	▽ → $CH_2 + C_2H_4$
740 (2)	550 (3)	400 (2)
870 (3)	900 (5)	830 (3)
1080 (7)	1100 (4)	1040 (5)
1460 (3)	1430 (3)	1410 (4)
3050 (6)	3020 (5)	3050 (6)

Methylcyclopropane

motion	▽[b]	▽$^{+b}$ (model I)	▽$^{+c}$ (model II)	▽$^+$ → $CH_2 + C_3H_6$
torsion	225			225
skeletal bend	291, 349			291, 349
HCC ring	*756, 804*	670, 680	350 (2)	400 (2)
	810, 911			650, 756
	983, 1016			810, 1016
	1111, 1387			1072, 1387
HCH ring	1419, 1488			1419, 1488
ring def	*889, 1047*	640, 930	640, 930	804, 889
	1202	1300	1300	1380
CC stretch	968			968
HCC methyl	1021, 1072			0, 1072
HCH methyl	1380, 1465			1380, 1465
	1474			1474
CH stretch-ring	3017 (2), 3055 3079, *3100*	0	0	3017 (2), 3055 3079, 3100
CH stretch-methyl	2898, 2976 (2)			2898, 2976 (2)

Ethylcyclopropane[b]

motion	▽	▽$^+$	▽$^+$ → CH_2 + $n\text{-}C_4H_8{}^{-1}$
torsion	150, 225		150, 225
skeletal bend	290, 370 441		290, 370 441
HCC ring	*747, 768*	670, 680	400 (2)
	817, 918		650, 747
	957, 1012		768, 1012
	1107, 1329		1108, 1329
HCH ring	1427, 1460		1427, 1460
ring def	*890, 1029*	640, 930	817, 941
	1198	1300	1380
CC stretch	983, 1088		983, 1088
HCC methyl	941, 1041		0, 1041
HCH methyl	1383, 1460 (2)		1383, 1460 (2)
HCC methylene	1273, 1310		1273, 1310
CH_2-CCH	768		768
HCH methylene	1444		1444
CH stretch-ring	3006 (2), 3069 (2)		3006 (2), 3069 (2)
	3080	0	3080
CH stretch-methyl	2909, 2965 (2)		2909, 2965 (2)
CH stretch-methylene	2936, 2965		2936, 2965

[a] Reference 9. [b] Reference 13. [c] Reference 14.

The calculation of the energy distribution functions and the solution to the steady state matrix equation were carried out as previously described for the activated ethylcyclobutane system.[8] The matrix grain size was 200 cm^{-1}.

The average internal energy on formation of the activated alkylcyclopropane is given by[19]

$$\langle E \rangle = -\Delta E_0(\text{reaction 2}) + \int_0^T \{(^1CH_2) + C_v(\text{1-alkene})\}\, dT + E_{xs} + E_a - \langle E_{tr} + E_r \rangle \quad (10)$$

where $-\Delta E_0(\text{reaction 2}) = \Delta H_f{}^\circ{}_0(^1CH_2) + \Delta H_f{}^\circ{}_0(\text{1-alkene}) - \Delta H_f{}^\circ{}_0(\text{alkylcyclopropane})$; $\int_0^T\{C_v(^1CH_2) + C_v(\text{1-alkene})\}\, dT$ = the thermal energy of the reactants; E_{xs} is the average excess photolysis energy carried by $CH_2(^1A_1)$ at the time of reaction; E_a is the activation energy for reaction 2, assumed to be 1 ± 1 kcal/mol; and $\langle E_{tr} + E_r \rangle$ is the average translational and rotational energy of the alkylcyclopropane on formation. This was taken to be 2 ± 1 kcal/mol. The maximum possible E_{xs} may be estimated by assuming all of the excess photon energy is carried by methylene into the addition reaction. The thermochemistry specific to each activating reaction is discussed in Tables II and III.

The D/S ratio was found as a function of reciprocal collision frequency from the steady state matrix equation. The transition probabilities employed were those for the stepladder model. The average energy on formation, $\langle E \rangle$, and the average vibrational energy transfered per collision, ΔE, were treated as adjustable parameters. $\langle E \rangle$ was kept within the bounds set by eq 10. Only those calculations matching the experimental results over the entire range to within ±20% and giving agreement with $k_{a\infty}$ were considered an acceptable data fit.

Activated Cyclopropane

The important reactions for this system were as follows:

$$CH_2(^1A_1) + C_2H_4 \rightarrow c\text{-}C_3H_6^* \quad (11)$$

$$CH_2(^1A_1) + C_2H_4 \rightarrow C_3H_6^* \quad (12)$$

$$CH_2(^1A_1) + n\text{-}C_5H_{12} \rightarrow n\text{-}C_6H_{14}\text{, 2-methylpentane, 3-methylpentane} \quad (13)$$

$$c\text{-}C_3H_6^* \rightarrow C_3H_6^* \quad (14)$$

$$C_3H_6^* \rightarrow H\cdot + \cdot CH_2CH{=}CH_2 \quad (15)$$

An asterisk implies an excited species; any excited molecule may be collisionally stabilized.

The maximum reaction pressure, 630 torr, was limited by the room temperature vapor pressure of n-pentane. n-Hexane was monitored as the internal standard product. At this pressure, the n-hexane to cyclopropane ratio had not become linear in ω^{-1}, so the value of $(n\text{-hexane}/c\text{-}C_3H_6)_{p=\infty}$ could not be determined experimentally. Also, $k_{a\infty}$ could not be measured. The value for the determined ratio was calculated from the corresponding ratio for the activated methylcyclopropane system, $(n\text{-hexane/methylcyclopropane})_{p=\infty}$, and knowledge of the relative reactivity of singlet methylene with ethylene and propylene.[20] The D/S ratio may then be found from the relative yields of n-hexane and cyclopropane at any pressure by use of eq 9.

The D/S ratio was also determined using the propylene concentration as a measure of D, the rate of decomposition of cyclopropane. The procedure described by Simons, Rabinovitch, and Setser[10b] was used to correct for propylene formation via reaction 12. This method assumed the decomposition of hot propylene is negligible.

The data are shown in Figure 1 as a plot of D/S vs. ω^{-1}. The D/S ratios computed by each method are seen to be in reasonable agreement. The data points obtained from the propylene/cyclopropane ratio lie below those from the n-hexane/cyclopropane ratio, as expected, due to reaction 15. Moreover, the difference is greatest at low pressure, and least at high pressure, which is in agreement with reaction 15 competing with collisional deactivation of hot propylene.

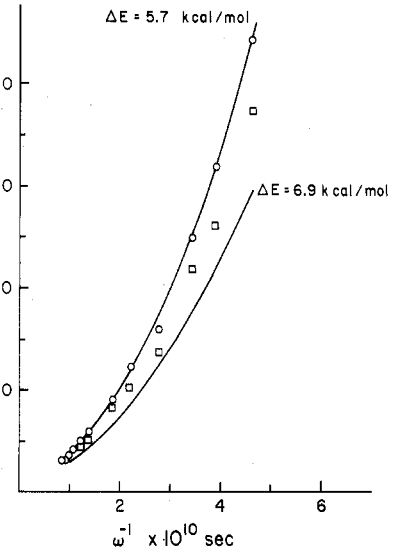

Figure 1. Activated c-C_3H_6 experimental data: (O) data points based upon the hexane/c-C_3H_6 ratio; (□) data points based upon the propylene/c-C_3H_6 ratio. The solid lines are calculated curves for $\langle E \rangle$ = 102.2 kcal/mol with ΔE = 5.7 and 6.9 kcal/mol.

As was reported by Simons, Rabinovitch, and Setser,[10b] cyclopropane appeared to form via a minor reaction pathway other than homogeneous methylene addition to ethylene. A plot (not shown) of cyclopropane/propylene vs. collision frequency gave a nonzero intercept at zero pressure. The value we obtained for the intercept, 0.006, was consistent with the room temperature data of Simons et al.[10b] Following the previous authors, this "excess stabilization" was taken into account by subtracting the intercept from the ratio of cyclopropane to propylene at each pressure. By limiting their attention to values of D/S less than 33, Simons et al. found the correction for excess cyclopropane could be kept small. This limitation to D/S < 33 was adhered to in our own analysis.

Because experiments could not be done at pressures above 630 torr with n-pentane collider, a experimental value of $k_{a\infty}$ could not be determined. However, a nonlinear least-squares calculation implied $k_{a\infty} = 2.4 \times 10^{10}$ s^{-1} on the basis of a third-order fit.

Computer calculations are compared with the experimental data in Figure 1 for $\langle E \rangle_{c\text{-}C_3H_6}$ = 102.2 kcal/mol and ΔE = 5.7–6.5 kcal/mol. As $\langle E \rangle_{c\text{-}C_3H_6}$ increases, larger values of ΔE fit the experimental data equally well. However it eventually becomes impossible to fit both the high and low pressure data. This also occurs when $\langle E \rangle_{c\text{-}C_3H_6}$ is decreased. At average energies of 101.6 and 107.9 kcal/mol it was not possible to fit both the high and low pressure results to within ±20%. Acceptable matches to the experimental data were obtained for stepsizes ranging from 5.5 to 13 kcal/mol.

Activated Methylcyclopropane

Singlet methylene combination with propylene initiates the following series of reactions:

$$CH_2(^1A_1) + C_3H_6 \rightarrow MCP^*$$
$$\rightarrow n\text{-}C_4H_8\text{-}1^*$$
$$\rightarrow C_4H_8\text{-}2^* \text{ cis, trans}$$
$$\rightarrow i\text{-}C_4H_8^*$$

$$\mathrm{MCP^* \rightarrow butenes^*}$$
$$n\text{-}\mathrm{C_4H_8\text{-}1^* \rightarrow CH_3\cdot + \cdot CH_2CH{=}CH_2}$$

MCP denotes methylcyclopropane. *n*-Pentane was again used as an internal standard.

A series of nine experiments at pressures between 86 and 260 torr gave a linear relationship between the total C_6H_{14}/MCP ratio and pressure^{-1}. $(\mathrm{ISP/MCP})_{p=\infty}$ was given by the intercept of this line. Equation 9 was then used to calculate the D/S ratio at each pressure.

The experimental results are presented as a plot of D/S vs. ω^{-1} in Figure 2. At the lowest pressures (high ω^{-1}) the plot appears to become linear in ω^{-1} rather than showing continued upward curvature. Two experiments were performed using double the normal oxygen concentration. The D/S ratios from these experiments showed no deviation from the other data indicating that depletion of oxygen and subsequent triplet methylene interference was not a factor at low pressures. A possible cause is an unknown pathway for methylcyclopropane formation. This would be similar to what was observed for the activated cyclopropane system. No corrections were made to the data since an S/D vs. ω plot (not shown) passed through the origin. If excess methylcyclopropane were present the ΔE values derived below would be slightly low. To minimize this possibility the analysis was restricted to D/S ratios less than 40.

RRKM calculations were carried out using the harmonic oscillator models of both Dorer and Rabinovitch[13] (referred to as model MCP-I) and Topor and Carr[14] (hereafter called model MCP-II). At the same energy, model MCP-I gave lower values for the microcanonical decomposition rate constant than did model MCP-II. Solutions to the steady state matrix equation were obtained for both models.

Model MCP-I was able to match the experimental data over a broader range of average energy, $\langle E\rangle$, and stepwise, ΔE. For model MCP-I the acceptable range in average energy was 101.7–108.6 kcal/mol, and the corresponding range in the average energy transfer was 2.5–8.6 kcal/mol. The data fits are illustrated in Figures 3 and 4.

Model MCP-II was able to successfully match the data for average energies between 103.4 and 104.5 kcal/mol with ΔE varying between 6.3 and 8.0 kcal/mol. The experimentally determined value of $k_{a\infty}$ was 4.5×10^8 s^{-1}.

Activated Ethylcyclopropane

Singlet methylene reaction with butene-1 involves the following series of reactions:

$$\begin{aligned}\mathrm{CH_2(^1A_1) + butene\text{-}1} &\rightarrow \mathrm{ECP^*}\\ &\rightarrow \text{pentene-1*}\\ &\rightarrow \text{pentene-2* cis, trans}\\ &\rightarrow \text{2-methyl-1-butene*}\\ &\rightarrow \text{3-methyl-1-butene*}\end{aligned}$$

$$\begin{aligned}\mathrm{ECP^*} &\rightarrow \text{pentene-1*}\\ &\rightarrow \text{pentene-2*}\\ &\rightarrow \text{2-methyl-1-butene*}\end{aligned}$$

$$\text{1-pentene*} \rightarrow \mathrm{C_2H_5\cdot + \cdot CH_2CH{=}CH_2}$$

$$\text{2-pentene*} \rightarrow \mathrm{CH_3\cdot + \cdot CH_2CH{=}CHCH_3}$$

$$\text{2-methyl-1-butene*} \rightarrow \mathrm{CH_3\cdot + \cdot CH_2C(CH_3){=}CH_2}$$

$$\text{3-methyl-1-butene*} \rightarrow \mathrm{CH_3\cdot + CH_3\dot{C}HCH{=}CH^2}$$

ECP represents ethylcyclopropane, and an asterisk denotes an excited molecule.

2-Methylpentane was used an internal standard in this system. Singlet methylene reacts with 2-methylpentane to produce 3-methylhexane, 2-methylhexane, 2,4-dimethylpentane, 2,3-dimethylpentane, and 2,2-dimethylpentane. Of the five reaction products, 3-methylhexane was formed in greatest yield and was used to monitor the extent of the activation reaction.

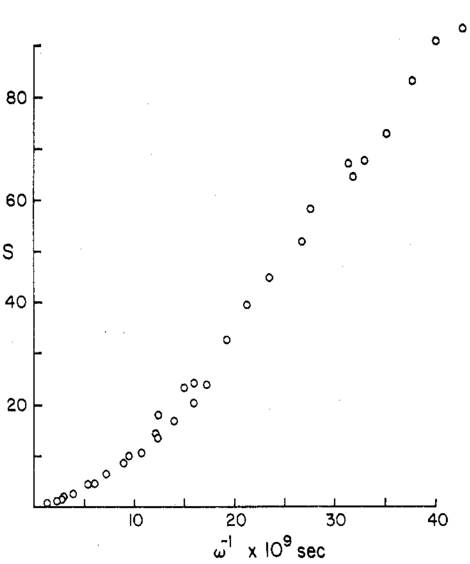

Figure 2. Experimental data for activated methylcyclopropane.

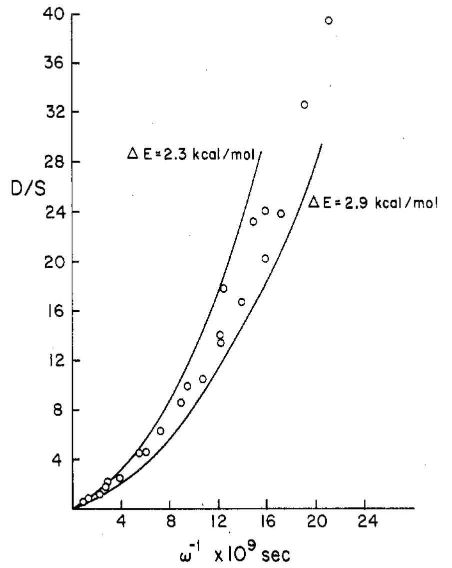

Figure 3. Experimental data for activated methylcyclopropane. The solid lines are calculated curves for $\langle E\rangle$ = 101.7 kcal/mol with ΔE = 2.3 and 2.9 kcal/mol.

The ratio of 3-methylhexane/$\mathrm{ECP}_{p=\infty}$ was obtained as the average of seven experiments in the high pressure region (225–245 torr) where ECP decomposition was negligible. The D/S ratio was then computed from eq 9.

The experimental data are shown in Figure 5. Data from both the 10:2:1:1 2-methylpentane:butene-1:ketene:oxygen and the 10:2:1:1 butene-1:2-methylpentane:ketene:oxygen mixtures are presented. The solid lines are second-order least-squares data fits, and indicate some curvature even at the low D/S ratios which limited this experiment due to lack of analytical sensitivity at the lowest pressure. The limiting high pressure slopes of these lines are the estimated high pressure rate constants, $k_{a\infty}$. For the mixture with excess 2-methylpentane, $k_{a\infty}$ = 1.4 × 10^7 s^{-1}, and for the mixture with a large excess of 2-methylpentane, $k_{a\infty}$ = 1.3 × 10^7 s^{-1}. The equality within experimental error of these rate constants reflects the similar collisional efficiencies of butene-1 and 2-methylpentane.

The computer calculations were able to match the least-squares data fit to within ±20% for values of average

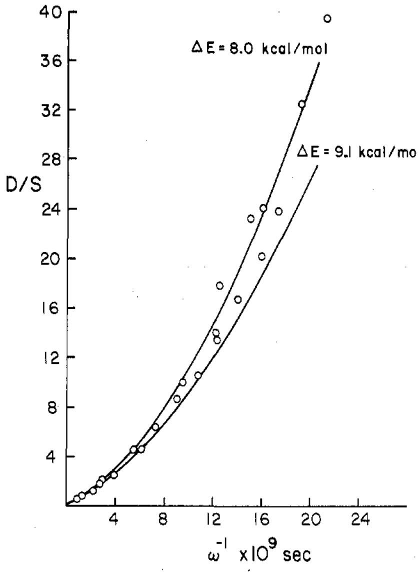

Figure 4. Activated methylcyclopropane data. The solid lines are calculated curves for ⟨E⟩ = 108.6 kcal/mol with ΔE = 8.0 and 9.1 kcal/mol.

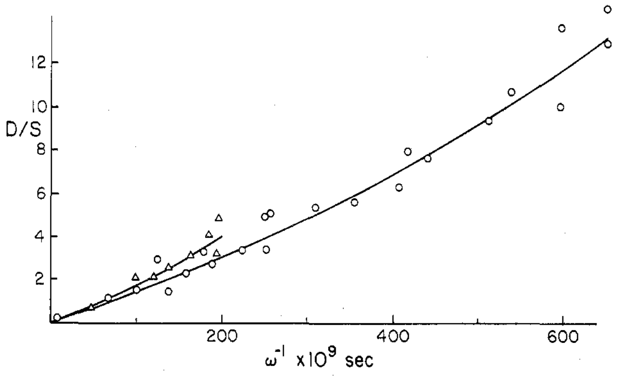

Figure 5. Experimental data for activated ethylcyclopropane: (O) data points for 2-methylpentane:butene-1:ketene:oxygen mixtures of composition 2:10:1:1; (Δ) data points for 2-methylpentane:butene-1:ketene:oxygen mixtures of composition 10:2:1:1. The solid lines are least-squares data fits.

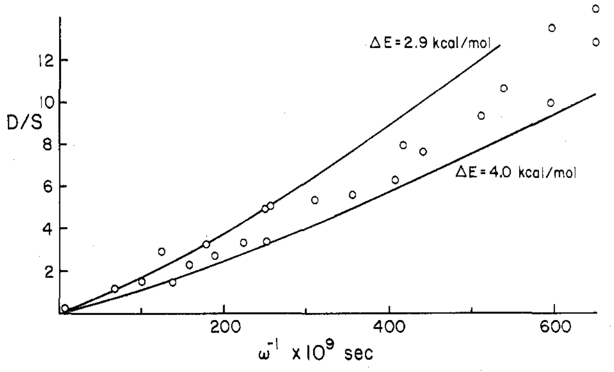

Figure 6. Activated ethylcyclopropane data. The solid lines are calculated curves for ⟨E⟩ = 101.7 kcal/mol with ΔE = 2.9 and 4.0 kcal/mol.

energy ranging from 101.7 to 106.2 kcal/mol with the stepsize varying between 3 and 11.5 kcal/mol. The computer calculations are compared with the experimental data in Figures 6 and 7.

Discussion

The homologous series of activated alkylcyclopropanes was photolyzed using the same radiation source. The principal collider was identical for the cyclopropane and methylcyclopropane systems and of almost the same collisional efficiency in the ethylcyclopropane system. Calculation of collision cross sections and thermochemistry were treated in a consistent manner. For each activated molecule a range of values for the average collisional energy transfer consistent with the experimental data was obtained. The energy transfer could be estimated more precisely if the initial energy of the activated molecule were known. The difficulty in specifying the average energy on formation of the activated molecule is chiefly because of the uncertainty in the heat of formation of singlet methylene and in the amount of excess energy carried by $CH_2(^1A_1)$ at the time of reaction. Assuming small variation in this excess energy along the homologous series, the uncertainty in the average energy on formation will be the same for each molecule. The energy transfer results may thus be compared for each activated molecule.

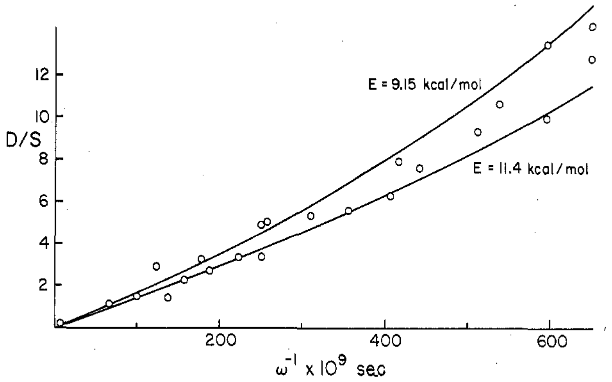

Figure 7. Activated ethylcyclopropane data. The solid lines are calculated curves for ⟨E⟩ = 106.2 kcal/mol with ΔE = 9.15 and 11.4 kcal/mol.

TABLE IV: Comparison of ΔE for the Alkylcyclopropane Series ⟨$E_{\triangledown}$⟩ = 98.4 + E_{xs} ± 6 kcal/mol, ⟨$E_{\triangledown}$⟩ = 97.4 + E_{xs} ± 6 kcal/mol, and ⟨$E_{\triangledown}$⟩ = 98.8 + E_{xs} ± 6 kcal/mol

est of (E_{xs} ± 6)	c-C_3H_6		MCP			ECP	
	⟨E⟩[a]	ΔE	⟨E⟩	ΔE (model I)[b]	ΔE (model II)[c]	⟨E⟩	ΔE
3	101.4		100.4			101.8	3.4
4	102.4	6.3	101.4	2.4		102.8	4.9
5	103.4	7.4	102.4	2.9		103.8	6.3
6	104.4	8.6	103.4	4.0	6.3	104.8	7.4
7	105.4	9.7	104.4	4.6	8.0	105.8	9.2
8	106.4	12.0	105.4	5.2		106.8	11.5
9	107.4	13.0	106.4	5.7		107.8	
10	108.4		107.4	6.9			
11	109.4		108.4	8.6			

[a] All energies are in kcal/mol. [b] Based upon $A_\infty = 7.3 \times 10^{14}\ s^{-1}$ (ref 25). [c] Based upon $A_\infty = 2.8 \times 10^{15}\ s^{-1}$ (ref 26).

The uncertainty in the average energy given by eq 1 is E_{xs} ± 6 kcal/mol. This range encompasses the spread in literature values for $\Delta H_f°_0\{CH_2(^1A_1)\}$. Table IV lists the average vibrational energy transferred from each molecule at the average energy given by chosen values for E_{xs} ± 6 kcal/mol. An acceptable computer fit to the experimental data was obtained for all three systems at values of this uncertain term of 4–8 kcal/mol. At any given value the largest stepsize occurs with cyclopropane and the smallest with methylcyclopropane. The variation of stepsize which results from change in the Arrhenius parameter on which the RRKM models are based is seen in the results for methylcyclopropane models MCP-I and MCP-II. Table IV also illustrates how the value deduced for the stepsize is dependent upon the assumptions made regarding

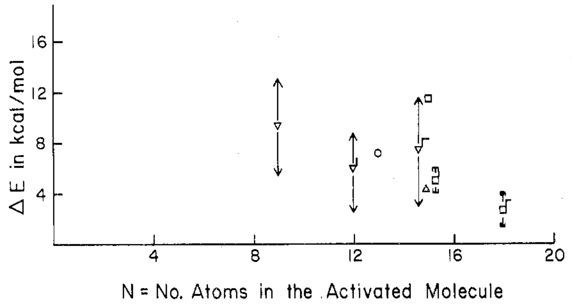

Figure 8. ΔE vs. N (number of atoms in the activated molecule): (○) activated spiropentane, (□) activated dimethylcyclopropane, (△) photoactivated cycloheptatriene, (⬍) stepsize range found for the alkylcyclobutanes, (↕) stepsize range found for the alkylcyclopropanes. For all the data points, $\langle E \rangle - E_0 \geq 40$ kcal/mol and $N_{\text{Collider}} \geq 10$ atoms.

thermochemistry if the average energy is not treated as an adjustable parameter.

The deactivation stepsizes for ethylcyclopropane must be regarded as uncertain. There could be error in the ethylcyclopropane RRKM model I since it is based upon estimated rather than measured values of the thermal Arrhenius parameters.[13] The heat of formation could also be inaccurate since it was necessary to estimate a heat of vaporization; inspection of Table IV shows that a decrease of only 1 kcal/mol would make the stepsize results for ethylcyclopropane similar to those for methylcyclopropane. A serious shortcoming is due to the small range of D/S which was experimentally accessible. Lower pressure data would have provided greater curvature and a more accurate assessment of ΔE.

In two recent experiments, values of the $\tilde{a}^1A_1$–X_3B_1 splitting in methylene have been reported to be 6.3 ± 0.8[21] and 8.3 ± 1 kcal/mol.[22] The latter implies $\Delta H_f{}^\circ{}_0\{CH_2(^1A_1)\} = 101.5$ kcal/mol. If this is used in eq 10, the following results are obtained: cyclopropane, $\langle E \rangle = 106$ kcal/mol, $k_{a\infty}$(calcd) $= 2.9 \times 10^{10}$ s^{-1}, $\Delta E = 10$ kcal/mol; methylcyclopropane model I, $\langle E \rangle = 105$ kcal/mol, $k_{a\infty}$(calcd) $= 4.5 \times 10^8$ s^{-1}, $\Delta E = 6$ kcal/mol; methylcyclopropane model II, $\langle E \rangle = 105$ kcal/mol, $k_{a\infty}$(calcd) $= 7.6 \times 10^7$ s^{-1}, $\Delta E = 8$ kcal/mol; ethylcyclopropane model I, $\langle E \rangle = 106$ kcal/mol, $k_{a\infty} = 1.5 \times 10^7$ s^{-1}, $\Delta E = 12 \pm 2$ kcal/mol. No fit could be obtained with ethylcyclopropane model II.

Summary of Results for the Alkylcyclobutane and Alkylcyclopropane Homologous Series

The results of these studies show that multistep deactivation is a general phenomenon in methylene radical chemical activation systems. D/S vs. ω^{-1} plots exhibited upward curvature in five distinct chemical systems with activated molecules ranging in complexity from cyclopropane to ethylcyclobutane. An RRKM analysis coupled with a stepladder deactivation model was capable of predicting the behavior of each system.

The analysis of the alkylcyclobutanes was more straightforward than that of the alkylcyclopropanes. Methyl- and ethylcyclobutane each undergo essentially a unique decomposition reaction, whereas methyl- and ethylcyclopropane decompose into a variety of butenes and pentenes. Consequently RRKM analysis of the alkylcyclopropanes requires construction of an average or overall activated complex. Secondly, an unexplained "excess" stabilized product was noticed in the cyclopropane and methylcyclopropane systems, but there was no hint of this in the methylcyclobutane system. Finally, only one experimental value of the high pressure Arrhenius parameter has been reported for methyl- and ethylcyclobutane;[23,24] for methylcyclopropane two different experimental values of the Arrhenius parameter have been found;[25,26] and for ethylcyclopropane the experimental Arrhenius activation energy was rejected in favor of an estimate based upon values for similar molecules.[13]

The energy transfer results are summarized in Figure 8, which shows the average vibrational energy transfer plotted vs. the number of atoms in the activated molecule. Also shown on the plot are the results from chemically activated spiropentane,[27] chemically activated dimethylcyclopropane,[28] and photoactivated cycloheptatriene.[29] The data chosen for presentation in Figure 8 were restricted to hydrocarbon systems activated to energies at least 40 kcal/mol above the unimolecular reaction threshold energy, and for which energy transfer took place primarily to molecules having at least 10 atoms. Only the data point for cycloheptatriene is for a non-methylene chemical activation system. This point fits well with the rest of the data, and concern that photoactivation and chemical activation systems give differing results may be unwarranted.

Figure 8 suggests that a decrease in the average amount of energy transferred per gas kinetic collision occurs with increasing size of activated molecule. However, this should be taken only as a tentative conclusion because of the wide range of data fits for the activated cyclopropanes. The trend suggested by Figure 8 is consistent with predictions from quasi-statistical models of energy transfer.[5]

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