Unimolecular Isomerization of Chemically Activated Methylcyclopropane Formed by Cyclopropyl Plus Methyl Radical Combination
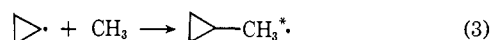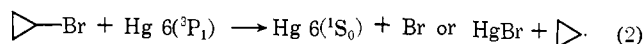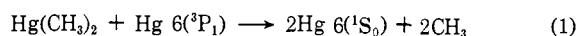
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Abstract: The unimolecular isomerization of chemically activated methylcyclopropane, formed from the combination of methyl and cyclopropyl radicals, to isomeric butenes has been studied at low substrate pressures in a fast-flow system. The rate constant for the overall isomerization reaction has been measured against collisional deactivation by helium. Using the RRKM formulation of unimolecular reaction rate theory and a stepladder model for the deactivation process, it is concluded that an effective collision of He with vibrationally excited methylcyclopropane (initially containing 89 kcal/mol of energy) removes 7–13 kcal/mol. The collisional transition probability of vibrational–translational energy transfer is quite small, however, being $\sim$0.02–0.03. Some mechanistic details of the reaction have also been investigated by deuterium-labeling techniques, and the results are discussed.

Collisional energy transfer between highly vibrationally excited species and inert gases is one of the fundamental problems of gas-phase chemical kinetics. Information concerning various techniques used and some of the results obtained have been discussed by Cottrell and McCoubrey[1] and Stevens.[2]

The present study is concerned with the reactions of chemically activated methylcyclopropane (MCP) produced by the combination of methyl and cyclopropyl radicals generated by a mercury-sensitization technique.

$$Hg(CH_3)_2 + Hg\ 6(^3P_1) \longrightarrow 2Hg\ 6(^1S_0) + 2CH_3 \qquad (1)$$

$$\triangleright\!\!-Br + Hg\ 6(^3P_1) \longrightarrow Hg\ 6(^1S_0) + Br\ or\ HgBr + \triangleright\cdot \qquad (2)$$

$$\triangleright\cdot + CH_3 \longrightarrow \triangleright\!\!-CH_3^* \qquad (3)$$

The MCP* thus produced contains an estimated 89 kcal/mol of energy and either undergoes rearrangement to isomeric butenes or is deactivated in a stepwise manner by collision with inert helium molecules. By measuring the product distribution as a function of carrier gas pressure, we have obtained unimolecular rate constants for the overall isomerization process.

Rabinovitch and coworkers[3] have shown that knowledge of the variation with pressure of the stabilization (S) to decomposition (D) ratio, S/D, in the chemically activated systems can provide information regarding the average amount of energy transferred per effective collision and its probability. Using the procedure outlined by the above authors, we have carried out theoretical calculations based on a simple stepladder energy-degradation model with various step sizes for comparison with experimental results.

Experimental Section

The apparatus used consisted of a fast-flow system attached to the sampling inlet of a mass spectrometer, the description and

operation of which have been given in a previous publication.[4] Only the features pertinent to this study are given here.

Reactants at partial pressures of a few millitorr were mixed in a stream of helium used as a carrier. The mixture was saturated with mercury vapor at 57° ($\sim$20 mTorr) before passing through the reactor which consisted of a length of Vycor tubing of 9-mm i.d. surrounded by an annular low-pressure mercury resonance lamp thermostated at 55–60°. At 10 Torr of helium the residence time of the reactants in the illuminated zone was about 1.5 msec. A sampling leak located just below the reaction zone allowed mass spectrometric monitoring of the reaction mixture during operation. The major portion of the reaction mixture was collected at −196° for analysis by gas chromatography. In experiments where the pressure of the carrier gas was increased beyond the vapor pressure of the reactants it was necessary to ballast the reactant volumes with helium in order to force the flow of reactants into the system. Gas chromatographic separation of the isomeric butenes was achieved using a tandem column consisting of two 20-ft sections of 30% glutaronitrile–propylene carbonate on 60/80 mesh Diatoport-S, one operated at room temperature and the other at 0°, and a final 20-ft length of 15% mineral oil on 60/80 mesh firebrick kept at room temperature. Helium was employed as carrier gas at a flow rate of 60 cm³ min⁻¹.

The cyclopropyl bromide used was from Aldrich Chemicals and was purified by preparative gas chromatography. Dimethylmercury (Eastman Organic) and dimethylmercury-d_6 (Merck) were degassed and collected at −98° before use. Research grade hydrocarbons were used as standards for the calibration of the gas chromatograph.

Analysis of the butene-1-d_3 product was carried out on a Varian HR100 instrument.

Results and Discussion

The products detected and their variation with helium pressure are presented in Table I. In order to elucidate certain aspects of the product-forming reactions, in some experiments the CH₃ radicals were replaced by CD₃ radicals from the decomposition of Hg(CD₃)₂. These results are tabulated in Table II. Finally, the yield of some minor C₄–C₅ products are reported in Table III.

Product Formation and Reaction Mechanism. The experimental results indicate that the "hot" MCP formed in reaction 3 undergoes structural isomerization to various butenes unless collisionally deactivated. This rearrangement is presumed to involve a singlet-state 1,3-diradical-like intermediate as outlined in eq 4–7. Figure 1 is a schematic energy diagram for the

(1) T. L. Cottrell and J. C. McCoubrey, "Molecular Energy Transfer in Gases," Butterworths, London, 1961, Chapter 7.
(2) B. Stevens, "Collisional Activation in Gases," Pergamon Press, London, 1967, Chapters 4 and 6.
(3) R. E. Harrington, B. S. Rabinovitch, and M. R. Hoar, J. Chem. Phys., 33, 744 (1960); G. H. Kohlmaier and B. S. Rabinovitch, ibid., 38, 1692, 1709 (1963); 39, 490 (1963); B. S. Rabinovitch and M. C. Flowers, Quart. Rev., Chem. Soc., 18, 122 (1964).
(4) E. Jakubowski, P. Kebarle, O. P. Strausz, and H. E. Gunning, Can. J. Chem., 45, 2287 (1967).

Table I. Products[a] from the Photosensitized Decomposition of 0.5–1.0 mTorr of Cyclopropyl Bromide and 15 mTorr of $Hg(CH_3)_2$ as a Function of He Carrier Gas Pressure

|	P_{He}, Torr								
	4.5	9	11	18	40	72	110	145	190
	ω, sec^{-1} ($\times 10^{-7}$)								
	0.9	1.8	2.2	3.6	8.0	14.4	22.0	29.0	38.0
Butene-1	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
cis-Butene	0.21	0.31	0.28	0.34	0.22	0.28	0.34	0.37	0.26
trans-Butene	0.29	0.41	0.36	0.40	0.22	0.24	0.31	0.32	0.21
Isobutylene	0.23	0.35	0.38	0.26	0.20	0.16	0.17	0.21	0.15
Σ(butene)	1.73	2.07	2.02	2.00	1.64	1.68	1.82	1.90	1.61
MCP		0.04	0.05	0.08	0.18	0.30	0.61	0.98	1.00
Cyclopropane + acetylene	0.19	0.64	0.80	0.40	0.76	0.29	0.44	0.59	0.61
Propylene	0.41	0.27	0.33	0.20	0.37	0.12	0.17	0.23	0.25
Allene	0.05	0.24	0.22	0.10	0.14	0.19	0.13	0.20	0.22
Propane	0.14	0.06	0.05	0.04	0.03	0.08	0.07	0.08	0.02
Ethylene	0.06	0.18	0.16	0.14	0.06	0.13	0.08	0.02	0.08
Butene-1/Σ(butene)	0.58	0.48	0.50	0.50	0.60	0.60	0.55	0.53	0.62
cis-Butene/trans-butene	0.72	0.76	0.78	0.85	1.00	1.16	1.09	1.15	1.24
MCP/Σ(butene) (S/D)		0.019	0.025	0.040	0.110	0.180	0.330	0.510	0.620

[a] Relative yields compared to butene-1 taken as unity.

Table II. Product Yields from the Photosensitized Decomposition of 0.5–1.0 mTorr of Cyclopropyl Bromide and 15 mTorr of $Hg(CD_3)_2$ at 10 Torr of He Pressure

| Product[a]	Yield	Product[a]	Yield
HC≡CH	0.03	c-C_3H_5D	0.12
HC≡CD	0.03	c-C_3H_5D	0.18
DC≡CD	0.20	CH_3—C≡CH	0.09
H_2C=CH_2	0.01	H_2C=C=CH_2	0.26
D_2C=CD_2	0.12	CH_2=CH—CH_2—CD_3	1.00
CH_3—CH=CH_2	0.05	trans-CH_3CH=$CHCD_3$	0.49
CDH_2—CH=CH_2	0.06	cis-CH_3CH=$CHCD_3$	0.34
CD_3—CH=CH_2	0.02	CH_3—C(=CH_2)CD_3	0.30
CD_3—CD=CD_2	0.10	c-C_3H_5—CD_3	0.06
C_3D_8	0.01		

[a] Average of three determinations; normalized to butene-1 yield.

Table III. C_4 and C_5 Products from the Photosensitized Decomposition of 0.6 mTorr of Cyclopropyl Bromide and 20 mTorr of $Hg(CH_3)_2$ at 10 Torr of He Pressure

Product[a]	Yield	Product[a]	Yield
⌐\	1.00	CH≡C—CH_2—CH_3	0.01
⌐\	0.38	CH_3—C≡C—CH_3	0.02
_/	0.31	CH_2=CH—CH(CH_3)$_2$	0.01
⌐⌐	0.30	CH_2=C(CH_3)C_2H_5	0.01
▷—CH_3	0.04	trans-Pentene-2	0.04
⌐\	0.06	cis-Pentene-2	0.01
⌐\	0.01		

[a] Average of two determinations; normalized to butene-1 yield.

reactions. From the diagram it is noted that $E_{-5} = E_6$, resulting in $N(E_{-5}) = N(E_6)$, where $N(E_{-5})$ and $N(E_6)$ are the total number of energy states per unit energy for
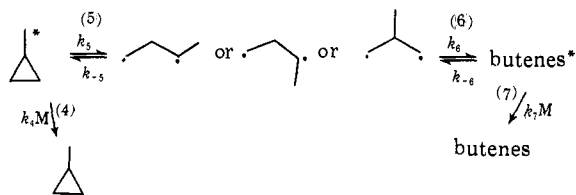
the activated diradical with energies E_{-5} and E_6. On this basis it has been shown that if $k_5k_6 \gg k_{-5}k_{-6}$, the RRKM equation implies that the structural isomerization can be considered a single-step process.[5] For
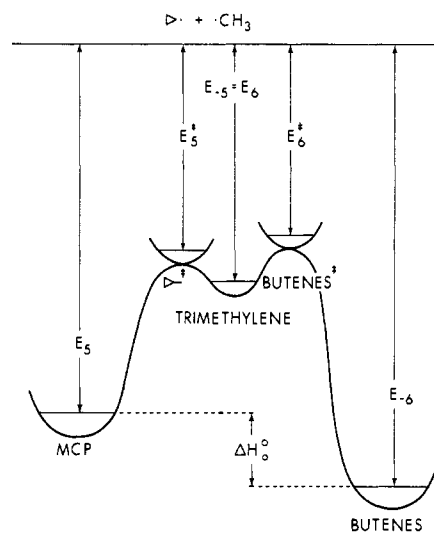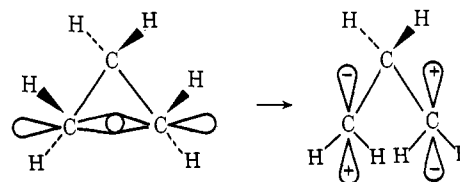

Figure 1. Schematic energy diagram for the chemically activated unimolecular isomerization of MCP.
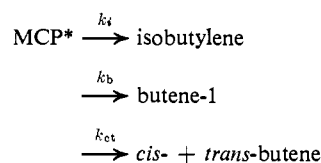
cyclopropane, it has been estimated[5] that $k_5k_6/k_{-5}k_{-6} \sim 40$ when $E_6{}^{\ddagger} = 30$ kcal/mol. The ring opening presumably is via a conrotatory mechanism, yielding an antisymmetric singlet-state trimethylene intermediate.[6,7]


Based upon these considerations, we are assuming that the structural rearrangement of MCP* can be

(5) M. C. Lin and K. J. Laidler, Trans. Faraday Soc., 64, 927 (1968).
(6) R. J. Crawford and A. Mishra, J. Amer. Chem. Soc., 87, 3768 (1965).
(7) R. Hoffmann, ibid., 90, 1475 (1968).

treated as a series of competing unimolecular reactions.

$$MCP^* \xrightarrow{k_i} \text{isobutylene}$$

$$\xrightarrow{k_b} \text{butene-1}$$

$$\xrightarrow{k_{ct}} cis\text{-} + trans\text{-butene}$$

An interesting facet of the isomerization is its stereochemistry. The intermediate diradical can exist in two conformational structures, **1** and **2**, each forming
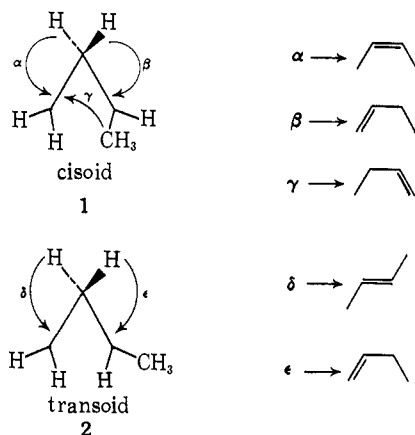

specific butenes upon hydrogen migration, the cisoid form giving cis-butene and butene-1 and the transoid form trans-butene and butene-1. (That hydrogen migration from the methyl group (step γ) does not occur will be shown below.)

From the data presented in Table I it is seen that the cis- to trans-butene ratio is pressure dependent and increases to a value exceeding unity at higher pressures. Thus, cis-isomer formation must predominate in the initial hydrogen-transfer reaction. At low pressures where collisional deactivation is inefficient, isomerization to the more stable trans isomer occurs, which, in turn, is followed by either unimolecular decomposition or deactivation. These results appear to be of general validity for trimethylenes, monosubstituted in the terminal position. Thermal studies of the structural isomerization of various monosubstituted cyclopropanes have yielded the following ratios for the cis- to trans-alkene-2 products: MCP,[8,9] ~2; trifluoromethylcyclopropane,[10] ~1.4; ethylcyclopropane,[11] ~1.6; and trifluoroethylcyclopropane,[10] ~1.3. The above effect could possibly be attributed to a decrease of the stability of the Π_u molecular orbital, caused by steric repulsions, and a consequent increase in the free-radical character of the cisoid intermediate. This would presumably lead to an enhancement of the hydrogen migration in the cisoid form, resulting in the predominance of the cis-olefin product.

Formation of butene-1 can also be envisioned via a 1,4 H-atom transfer, step γ, occurring parallel to steps β and ε. This question was investigated by using CD_3 instead of CH_3 radicals in the combination reaction 3 and analyzing the resulting butene-1-d_3 from the structural isomerization of c-C_3H_5–CD_3* by nmr spectros-
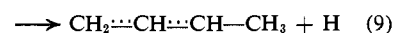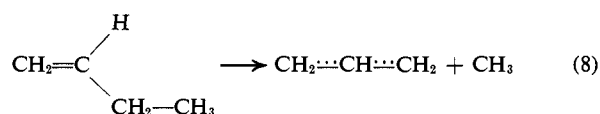
copy. Butene-1-d_3 formed via γ would yield the product
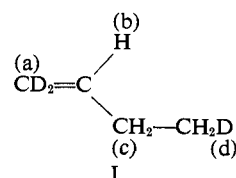
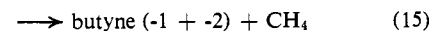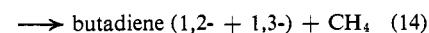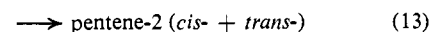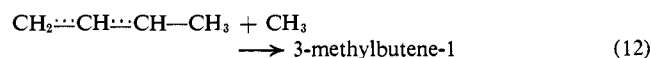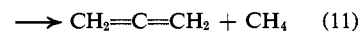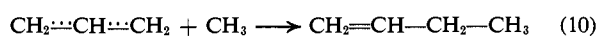while that from β or ε would give
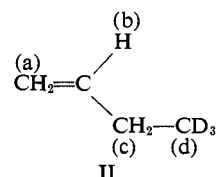
Before a conclusion can be reached as to the importance of step γ it will be noted that the initial butenes produced from MCP* isomerization will have excess energy of ~97–100 kcal/mol (vide infra). Molecules such as butene-1, cis- and trans-butene, and isobutylene possessing weak allylic C–C bonds, ~72 kcal/mol, and allylic C–H bonds, ~85 kcal/mol, as well as normal C–C bonds, ~85 kcal/mol, can undergo unimolecular decomposition by C–H or C–C bond rupture under the above circumstances. In the case of butene-1 the following decomposition processes are the most likely.

These reactions should be followed by

$$CH_2\text{⋯}CH\text{⋯}CH_2 + CH_3 \longrightarrow CH_2{=}CH{-}CH_2{-}CH_3 \quad (10)$$

$$\longrightarrow CH_2{=}C{=}CH_2 + CH_4 \quad (11)$$

$CH_2\text{⋯}CH\text{⋯}CH{-}CH_3 + CH_3$

$$\longrightarrow \text{3-methylbutene-1} \quad (12)$$

$$\longrightarrow \text{pentene-2 } (cis\text{-} + trans\text{-}) \quad (13)$$

$$\longrightarrow \text{butadiene } (1,2\text{-} + 1,3\text{-}) + CH_4 \quad (14)$$

$$\longrightarrow \text{butyne } (\text{-}1 + \text{-}2) + CH_4 \quad (15)$$

As allylic C–H bonds are considerably stronger than allylic C–C bonds, butene-1 should decompose primarily by reaction 8. In the case of product I, the resulting butene-1 product would be
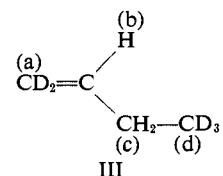
A similar mechanism for product III would result in its re-formation by combination of $CH_2\text{⋯}CH\text{⋯}CH_2$ with CD_3 radicals. $k_{\text{disproportionation}}/k_{\text{recombination}}$ for methyl with allyl radicals has not been measured. For ethyl the analogous reactions[12] give $k_d/k_r = 0.05$, thus indicating that ~95% of the butene-1 decomposed by

(8) J. P. Chesick, J. Amer. Chem. Soc., 82, 3277 (1960).
(9) D. W. Setser and B. S. Rabinovitch, ibid., 86, 564 (1964).
(10) D. W. Placzek and B. S. Rabinovitch, J. Phys. Chem., 69, 2141 (1965).
(11) M. L. Halbestadt and J. P. Chesick, ibid., 69, 429 (1965).

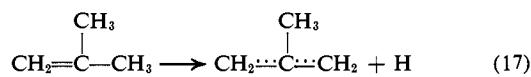(12) D. G. L. James and G. E. Troughton, Trans. Faraday Soc., 62, 145 (1966).

allyl–CH_3 cleavage is rescavenged. Analysis of the butene-1-d_3 nmr spectra showed that methyl protons (d) were not present. The average of several proton integrations gave the intensity ratios (a) 1.97, (b) 1.00, (c) 1.90, thus assigning the spectrum to II, which leads to the conclusion that 1,4-H-atom transfer by path γ does not take place. This is in agreement with the results of the benzophenone-photosensitized decomposition of 3,5-dimethyl-1-pyrazoline in which the 1,4-H-atom migration product, pentene-1, was not detected.[13]

Chemically activated 2-butenes will decompose mainly by allylic C–H rupture
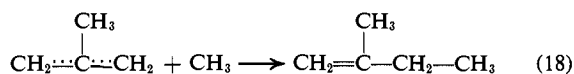
$$CH_3-CH=CH-CH_3 \longrightarrow CH_3-CH \cdots CH \cdots CH_2 + H \quad (16)$$
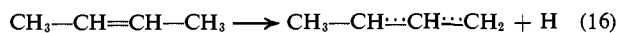
followed by reactions 12–15.

Isobutylene, containing excess energy of $\sim$100 kcal/mol can also undergo unimolecular decomposition via allylic C–H scission

$$\underset{CH_2=C-CH_3}{\overset{CH_3}{|}} \longrightarrow \underset{CH_2 \cdots C \cdots CH_2}{\overset{CH_3}{|}} + H \quad (17)$$

leading to

$$\underset{CH_2 \cdots C \cdots CH_2}{\overset{CH_3}{|}} + CH_3 \longrightarrow \underset{CH_2=C-CH_2-CH_3}{\overset{CH_3}{|}} \quad (18)$$

In order to obtain a rough estimate of the butene decomposition, experiments were carried out in which the analytical technique was altered to allow for butadiene, butyne, and pentene analysis. Table III summarizes the results of these experiments. From the data in this table, it can be estimated that $\sim$8% of the butenes* undergo allylic C–H rupture. The extent of allylic C–C rupture (8) from butene-1* cannot be estimated from the experimental data, as the recombination product with excess methyl radicals in the system is again butene-1. In a study of the unimolecular decomposition of product olefins in methylene chemical activation systems, Dorer and Rabinovitch[14] have shown that the decomposition of butene-1* from the isomerization of MCP* containing $\sim$107.9 kcal/mol of excess energy is four to five times slower than the MCP* isomerization. In our system, at 10 Torr of He, $\sim$95% of the MCP* undergoes structural isomerization; assuming similar relative rates ca. 20–25% of butene-1* should undergo allylic C–C rupture (8). The likelihood that the majority of the allyl radicals will be rescavenged by methyl (10) as butene-1 in our system probably accounts for a butene-2 ratio slightly larger than previously observed in other studies.[8,9,15]

In addition to the principal products already discussed and the recombination product of the methyl radicals, ethane, a number of minor products were also detected and in some experiments quantitatively measured. Since some of these, namely ethylene, propylene, propane, and acetylene also arise in the sensitization of pure dimethylmercury,[16] for the elucidation of the origin of these molecules experiments were carried out using $Hg(CD_3)_2$. The data in Table II unequiv-

ocally show that ethylene and propane come nearly entirely from dimethylmercury. C_2H_2, C_2HD, C_2H_4, and $C_3H_3D_3$, on the other hand, are rather difficult to explain in terms of specific reactions, however, their combined yield is quite minute, being less than 5% of the total attributed to the decomposition of cyclopropyl bromide. In an earlier paper dealing with the mercury-sensitized decomposition of propane under similar conditions it was calculated that $\sim$5% of the propyl radicals would undergo secondary reactions with Hg $6(^3P_1)$ atoms.[4] It thus seems likely that these products are partly coming from secondary reactions with excited mercury atoms.

Propylene (C_3H_6, C_3H_5D), which probably arises from the disproportionation reactions of allyl radicals, accounts for an average of $\sim$3% of the reaction products. The allyl radicals may arise from two processes: undoubtedly a portion comes from the cracking reaction of butene-1-d_3 (8), while another portion may come from the ring opening of the cyclopropyl radical. This latter reaction requires an activation energy[17] of 22 kcal/mol, while the cyclopropyl radicals from reaction 2 may contain excess vibrational energy up to $\sim$45 kcal/mol, the estimated exothermicity of the reaction.

The allene product can then be explained by the disproportionation of allyl with methyl or cyclopropyl with methyl. The cyclopropane from the latter reaction would end up as allene or propyne.

Now if allyl radicals were indeed produced through a unimolecular ring opening of hot cyclopropyl radicals, the pressure study should reflect this as a decrease in the butene-1/Σ(butene) ratio as the cyclopropyl radicals are stabilized. Table I shows that this ratio is essentially constant over the pressure range studied, indicating that cyclopropyl radical isomerization is unimportant.

Cyclopropane and cyclopropane-d_1 also appear as reaction products. Approximately 60% of the cyclopropane is the monodeuterated variety, which may be visualized as the product of the unusual mode of disproportionation of methyl radicals

$$\triangleright\cdot + CD_3 \longrightarrow \triangleright\!\!-\!\!D + CD_2$$
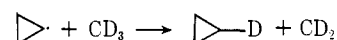
It is more difficult to propose a plausible source of the undeuterated cyclopropane.

Using the data in Table II we have calculated a secondary isotope effect $k_{aH}/k_{aD} = 1.4$ at 10 Torr of He pressure. In view of the experimental accuracy, our results are in good agreement with a value of $\sim$1.2 per D atom measured in a similar cyclopropane system with appreciably higher energetic parameters.[18]

Deactivation by Helium. It has been shown by Rabinovitch and coworkers[3] that a knowledge of the variation with pressure of the stabilization to decomposition ratio, S/D, can furnish information regarding collisional energy-transfer probabilities between excited and deactivating molecules. If a strong collision, i.e., unit collision efficiency is assumed, an apparent isomerization rate constant defined as $k_a = \omega D/S$, where ω is the hard-sphere collisional rate constant ($T = 330°K$, $\sigma_{MCP} = 5.0$ Å, $\sigma_{He} = 2.6$ Å), can be calculated for various pressures. In cases where a monoenergetic

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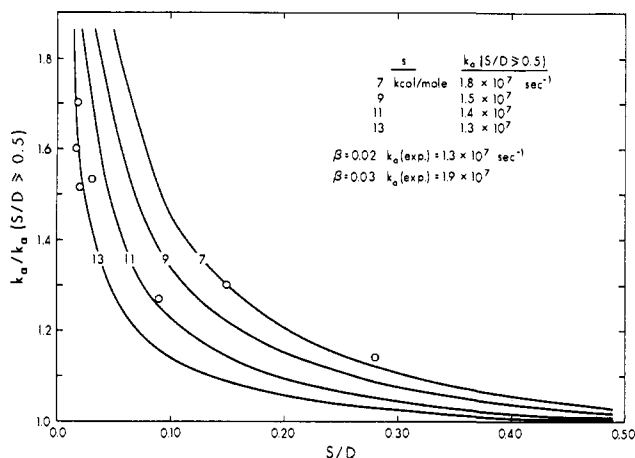(18) J. W. Simons and B. S. Rabinovitch, J. Phys. Chem., 68, 1322 (1964).

Figure 2. Plot of k_a/k_a (S/D $\geqslant$ 0.5) vs. S/D: (O) experimental, (——) calculated curves for various step sizes.

initial energy distribution is present in the excited molecules experimental k_a values have been found to be essentially constant at S/D values greater than 0.5.[19-21] When plots of k_a/k_a (S/D $\geqslant$ 0.5) vs. S/D are constructed, a turnup at low S/D values (low pressures) is observed. The reason for this curvature is apparent from the form of the theoretical D/S relationship in the low-pressure region ($\omega \ll k_t$)

$$(D_T/S_T) = (1/\beta\omega)^T \prod_{t=1}^{T} k_{t'} \tag{19}$$

where T is the number of transitions in the active region $E_6{}^{\ddagger}$, β is an efficiency factor which accounts for elastic collisions, and k_t is the specific unimolecular rate constant from the level $E_6{}^{\ddagger}/T$ obtained using RRKM theory (see the Appendix). By fitting calculated curves based upon step-ladder degradation models to the experimental turn-up, information concerning the step size (s) for deactivation and the probability of energy transfer has been obtained. Detailed descriptions of the step-ladder model and computational procedures used can be found in the articles cited in ref 3.

Comparison of Calculated and Experimental k_a. Figure 2 contains plots of the experimental k_a ratios vs. S/D obtained from the data in Tables I and III. The experimental k_a values have not been corrected for butene loss owing to cracking of the "hot" butenes formed in the isomerization reaction. At 10 Torr of He this correction would increase k_a by about 20%. Assuming that butene decomposition is consistently four to five times slower than MCP* isomerization would require that the experimental D/S ratios be multiplied by a constant factor of 1.2–1.25 and thus cancel out when k_a/k_a (D/S $\geqslant$ 0.5) ratios are taken.

In order to match the calculated ratios with the experimental, $\beta = 0.02$–0.03 and $s = 7$–13 kcal/mol are required. This step size is in good agreement with that reported by Rabinovitch and coworkers (4–8 kcal/mol) in a study of the collisional deactivation of vibrationally excited cyclopropane by helium.[20] When the efficiency factors are compared, however, the present value is an order of magnitude smaller than that found by the

above authors and is in agreement with values of 0.05–0.07 reported by Chesick[8] in the thermal isomerization of MCP and 0.04 derived by Atkinson and Thrush[22] for the collisional deactivation of vibrationally excited cycloheptatriene produced by a photochemical method. The high-pressure isomerization rate constant k_a (S/D $\geqslant$ 0.5) can be obtained with $\beta = 0.3$ if the step size, s, is reduced to a value of $\sim$0.4 kcal/mol; however, the turnup in the calculated k_a ratios appears at much higher S/D values than the experimental results indicate.
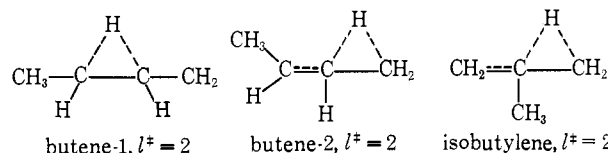
Appendix

RRKM Calculations. In this treatment k_E, the specific unimolecular rate constant at the energy E, is given by the expression

$$k_E = l^{\ddagger}\left(\frac{I_A{}^{\ddagger}I_B{}^{\ddagger}I_C{}^{\ddagger}}{I_A I_B I_C}\right)^{1/2} \frac{\sum P(E^{\ddagger})}{hN(E_0 + E^{\ddagger})}$$

which represents the probability that the energized molecule of energy $E = E_0 + E^{\ddagger}$ crosses the barrier of energy E_0; $\sum P(E^{\ddagger})$ is the total number of energy states of the activated complex having energy $E^{\ddagger}$, and N ($E_0 + E^{\ddagger}$) is the total number of energy states per unit energy of the active molecules having energy $E = E_0 + E^{\ddagger}$. The $I^{\ddagger}$'s and I's are the moments of inertia of the activated complex and reactant, $l^{\ddagger}$ is the reaction path degeneracy, and h is Planck's constant.

Dorer and Rabinovitch[23] have carried out RRKM calculations for the isomerization of chemically activated MCP ($\langle E \rangle = 107.9$ kcal/mol) to butenes employing various models for the reactant and the activated complex. However, k_E for the energy range of present interest has not been reported. In these calculations the methyl torsion was taken either as a free rotation or as a libration in both the active molecules and the activated complex: the former treatment increases the value of k_E by only 20%. An overall activated complex was constructed for the formation of butenes. Thermal data[9] for the structural isomerization of MCP was used to assign the frequencies to the activated complex.

In the present calculation we have assumed a "rigid" model for the activated complex and only vibrations are considered active in the reactant and the complex. All vibrations are taken to be harmonic. The product of the moments of inertia of the activated complex is taken to be the same as that of the reactant molecule. Vibrational frequencies used in the calculations are those of Dorer and Rabinovitch,[23] and the reaction path degeneracy is based on the following models[5,23]

butene-1, $l^{\ddagger} = 2$ butene-2, $l^{\ddagger} = 2$ isobutylene, $l^{\ddagger} = 2$

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In view of the present experimental data the energetically more favorable model proposed by Lin and Laidler,[5] *i.e.*, 1,4-H-atom migration, for the formation of butene-1 is not considered here.

Using the values of $l^{\ddagger} = 10$ and $E_0 = 61.4$ kcal/mol for the overall structural isomerization of MCP*, k_E's were calculated as a function of energy. The quantities $\Sigma P(E^{\ddagger})$ and $N(E_0 + E^{\ddagger})$ were evaluated by the method of Whitten and Rabinovitch[24] on an IBM 360/67 computer.

Thermochemistry. The energy content of the "hot" MCP molecule $E = E_{exo} + E_{ther}$, the exothermicity of the reaction plus the thermal contributions of the reactants. In the case of radical–radical combinations, the exothermicity is equal to the strength of the bond being formed, which, unfortunately, is unknown for MCP. Using an estimated value[25] of $\Delta H_f^{298}(\text{MCP}) = 8.1$ kcal/mol and 34.0 and 61.0 kcal/mol for ΔH_f^{298} of methyl and cyclopropyl radicals, respectively,[26] D-(c-C_3H_5–CH_3) $= 86.9$ kcal/mol. At $57°$, E_{ther} is estimated to be ~ 2 kcal/mol, with the result that $E \simeq 89$ kcal/mol.

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Chemiluminescence in Oxidation Reactions. The Oxidation Mechanism of Dimedone

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Abstract: The detailed mechanism whereby organic molecules chemiluminesce during autooxidation (oxyluminescence) has not been completely determined. Particularly, the reasons for the low luminescence quantum yield observed in such reactions have remained largely unexplained. In this paper the detailed mechanism of oxyluminescence is examined in the case of dimedone (1,1-dimethyl-3,5-cyclohexanedione) oxidation. This proceeds by formation of the 4-peroxydimedone radical which disproportionates with a rate constant of $(4.5 \pm 0.5) \times 10^8 M^{-1} \sec^{-1}$ and propagates with a rate constant of $(7 \pm 1) \times 10^2 M^{-1} \sec^{-1}$ at $22°$ and with an activation energy of 5 ± 1 kcal. The disproportionation reaction leads to two chemiluminescent products, one of which, a precursor, is believed to be either the first excited single state of 1,1-dimethyl-3,4,5-cyclohexanetrione (D=O) or a complex between triplet D=O and adjacently formed singlet oxygen. If the precursor is the complex then triplet D=O is initially formed by an adiabatic transition from the vibrationally excited triketone molecule in its electronic ground state. The other chemiluminescent species, shown to be a product of the first, is triplet D=O. The observed chemiluminescence efficiency is $(2.5 \pm 0.5) \times 10^{-10}$. The lifetime of the precursor is estimated to be 10^{-7} sec and its emission efficiency $(3.6 \pm 0.2) \times 10^{-3}$. The efficiency with which the precursor decomposes (or intersystem crosses) to give triplet D=O is >0.12, and the efficiency with which it is initially formed is $(4.5 \pm 0.5) \times 10^{-8}$. The low oxyluminescence quantum yield is attributed to the low excitation efficiency of the precursor which, whether its formation depends on an adiabatic transition from the ground state or directly on the efficiency of formation of the first excited singlet state, is a statistically unlikely process.

The oxidation mechanism of simple organic compounds has been extensively studied.[1] Detailed mechanisms of the oxidation of aromatic and aliphatic hydrocarbons such as tetralin,[2-4] cumene,[2,3] and ethylbenzene[1b,3,5] have been proposed by Ingold and coworkers; methyl oleate[6] and benzaldehyde oxidation[7] have also been extensively studied. This study presents an initial attempt to investigate the oxidation of compounds with reactive methylene groups, such as dimedone[8] which forms secondary 4-peroxydimedone radicals during oxidation. The disproportionation of such peroxy radicals is exothermic by 115–150 kcal,[9] and is assumed to proceed *via* the decomposition of a tetroxide intermediate as proposed by Russell.[10] The ketone produced in this reaction has been shown to chemiluminesce from its triplet state.[11,12] There is, however, much evidence[11,13] that some portion of this luminescence is oxygen insensitive. Kellogg[11] ascribes

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