the sonochemical production of hydrogen peroxide. It appears that there are differences between peroxide formation due to ionizing radiation and that due to ultrasonic cavitation, but further work is required to clarify the differences.

Acknowledgments.—The author wises to thank Drs. Robert L. Bowman and Charles R. Maxwell for their helpful discussions and Mr. B. Burr for mass spectrometer analyses.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON]

The Isomerization of Vibrationally Excited Cyclopropane-d_2 Produced from Methylene plus Ethylene-d_2[1]

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RECEIVED SEPTEMBER 3, 1958

Vibrationally excited cyclopropane-d_2 molecules have been produced at 25° by addition of methylene radicals, arising from photolysis of ketene at 3600 and 3100 Å., to *trans*-ethylene-d_2. The addition is stereospecifically *cis*. The geometric and structural isomerization of the hot cyclopropane molecules has been studied at pressure up to 36 atm. Comparison of these results with thermal studies, and between themselves, provides support for similarity of activation steps for the two isomerization processes.

trans-Cyclopropane-d_2 has been observed to isomerize thermally to *cis*-cyclopropane-d_2 as well as to propylene.[2] The former reaction has been shown to occur as a unimolecular process while the latter is known to be such.[3] The mechanisms of the geometric *cis-trans* isomerization and structural isomerization to propylene may involve either of the two molecular reaction coordinates suggested originally by Chambers and Kistiakowsky[3a]; namely a C–C extension, or an approach of a hydrogen on one carbon atom to an adjacent carbon.[4] Whatever mechanism may apply, the results of Rabinovitch, Schlag and Wiberg suggest that the activated complexes for both geometric and structural isomerization are similar, particularly energy-wise. The present study was undertaken to test this point in another way, by measuring the relative rates of the two isomerization processes at a range of energies appreciably different (higher) from those accessible in the thermal study.

Kistiakowsky and Sauer[5] pointed out that vibrationally excited cyclopropane is formed on addition of methylene to ethylene. Frey[6a] reported the isolation of cyclopropane and propylene as principal products of the photolysis of ketene–ethylene mixtures, and Frey and Kistiakowsky[6b] presented quantitative studies of the variation of product proportions with total pressure. In the present work, by use of *trans*-ethylene-d_2 the stereochemistry of the addition process has been determined and the rate of geometric *cis–trans* isomerization of the vibrationally excited cyclopropane-d_2 has been measured and compared with that of the concomitant structural isomerization to propylene.

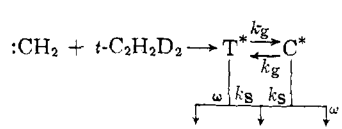
Experimental

trans-Ethylene-d_2 was of 99.3% isotopic purity with 0.7% ethylene-d_1. Ketene was purified by repeated bulb-to-bulb distillation. Mass spectrometric analysis showed the ketene to be essentially pure with negligible amounts of the dimer.

Photolysis of ketene–ethylene-d_2 mixtures was carried out in sealed reactors at 25°. A General Electric AH-6 high pressure mercury arc lamp served as the light source. The bands at 3100 and 3600 Å. were employed. A Corning glass filter No. 5330 was employed to isolate the 3600 Å. region and a solution filter, made by dissolving $NiSO_4 \cdot 6H_2O$ and $CoSO_4 \cdot 7H_2O$ in water,[7] was used at 3100 Å. The solution was circulated through a Corex D glass envelope in front of the lamp. The reactor was of Corex glass as well for the study at 3100 Å., while Pyrex vessels were employed at 3600 Å. A range of pressures of 0.14 to 36.6 atm. was covered. In each case the ratio of ketene/ethylene-d_2 was close to 1/7. The amount of ketene varied from 2–20 cc. per run, while the ketene decomposition varied from 1–20% in most cases, and up to 40% in a few cases. Some polymerization was observed which, however, only became appreciable for the runs at the highest pressures which necessitated the longest exposure times (up to 35 min.). At the end of each run the excess ethylene-d_2 was pumped off at −160°. The remaining gases were then distilled through a column of brick-dust covered with a saturated solution of $AgNO_3$ in ethylene glycol and Kel-F alkane oil. This effectively removed the remaining ketene. The cyclopropane–propylene mixture was analyzed and separated by gas chromatography, and the cyclopropane was analyzed for the percent *cis* and *trans*-cyclopropane-d_2 on a Beckman IR-2 spectrophotometer by methods used previously.[2]

Results and Discussion

Relevant processes are represented by the scheme where T, C and P refer to *trans*-cyclopropane-d_2, *cis*-cyclopropane-d_2 and propylene, respectively.



Here k_g and k_s refer to the observed rate constants and the above scheme carries no further implication

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(1) This research was supported by the National Science Foundation. Abstracted from the M.S. Thesis of E. Tschuikow-Roux, University of Washington, Feb., 1958.

(2) Rabinovitch, Schlag and Wiberg, *J. Chem. Phys.*, **28**, 504 (1958).

(3) (a) T. S. Chambers and G. B. Kistiakowsky, THIS JOURNAL, **56**, 399 (1934); (b) H. O. Pritchard, R. G. Sowden and A. F. Trotman-Dickenson, *Proc. Roy. Soc.* (*London*), **A217**, 563 (1953); (c) N. B. Slater, *ibid.*, **A218**, 224 (1953).

(4) These are extremes, and an intermediate type of coördinate could also be considered. See also F. T. Smith, *J. Chem. Phys.*, **29**, 235 (1958).

(5) G. B. Kistiakowsky and K. Sauer, THIS JOURNAL, **78**, 5699 (1956).

(6) (a) H. M. Frey, *ibid.*, **79**, 1259 (1957); (b) H. M. Frey and G. B. Kistiakowsky, *ibid.*, **79**, 6373 (1957).

(7) W. A. Noyes and P. A. Leighton, "Photochemistry of Gases," Reinhold Publ. Corp., New York, N. Y., 1941, p. 69; E. J. Bowen, *J. Chem. Soc.*, 76 (1935).

concerning mechanism. Then

$$k_g = \frac{\omega(P + T + C)C}{(T + C)(T - C)}, \text{ and } k_s = \omega P(T + C)$$

where ω is the specific rate of collisional deactivation. That the addition reaction of methylene to *trans*-ethylene-d_2 is stereospecifically *cis* as written above is shown below.

The pressure dependence of cyclopropane formation is shown in Fig. 1 and that of *cis*-cyclopropane-d_2 in Fig. 2. It is evident that methylene carries excess energy arising from the photolysis process since the lifetime of the hot cyclopropane with respect to propylene formation declines, and the rate of geometric isomerization increases, with increase of light energy. This result further signifies that methylene must add to the olefin before it is "thermalized" by collisions. This accords with Frey and Kistiakowsky's conclusions.[6b]

In Fig. 1, the high pressure limit of the cyclopropane/propylene ratio is $\simeq$0.85, somewhat higher than that of Frey and Kistiakowsky. The extra propylene arises from addition of methylene across the C–H bond, rather than to the C=C bond.[6] The invariance of the limiting ratio with photolysis light energy indicates independence of the relative addition rates on methylene energy, at least at these energies.

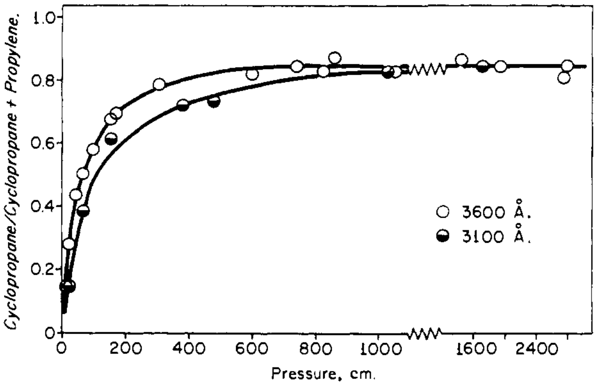

Fig. 1.—Cyclopropane formation as function of pressure.

The monotonic decline of *cis* percentage toward zero with increasing pressure (Fig. 2) shows that methylene addition is stereospecifically *cis* and is stereochemically similar to the addition of methylene to disubstituted ethylenes such as butene-2.[8]

A summary of calculated rate constants is given in Table I. At pressures larger than 3 atm. a correction was applied to the calculated value of the gas kinetic collision constant ω to take into account the molecular volume and the partially compensating shielding factor.[9] The total correction factor is $1 + 0.626nb$, where n = number of molecules/cc. and b = van der Waals constant. Evaluation of k_s could be made accurately only in the lower pressure region since $P \rightarrow 0$ above total pressures of 300 cm.; evaluation of k_g was more inaccurate at lower pressures because of the smaller amounts of cyclopropane isolated for analysis; it was not done in every instance, since the lower pressures only encompassed a small portion of the accessible pressure range for geometric isomerization.

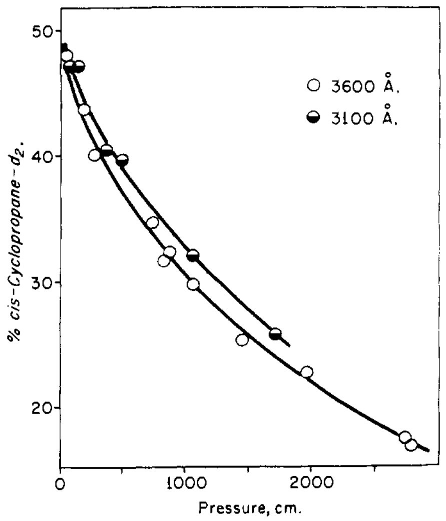

Fig. 2.—*cis*-Cyclopropane-d_2 formation as function of pressure.

Table I

Summary of Rate Constants Determined at Different ω

Total press., cm.	ω^a 10^{10} sec.$^{-1}$	k_g 10^{10} sec.$^{-1}$	k_s 10^{10} sec.$^{-1}$
	3600 A.		
10.9	0.17		0.80
20.1	0.31	10.8	.60
41.9	0.64		.61
64.1	0.97		.67
94.8	1.44		.67
154	2.34		.58
166	2.53		.55
300	4.36	9.5	.54
594	9.27		Av. .63
738	11.5	13.0	
819	12.9	11.1	
855	13.4	12.2	
1047	16.6	12.1	
1440	23.1	11.8	
1938	31.7	13.1	
2730	46.0	12.4	
2780	46.8	11.9	
		Av. 11.8	
	3100 A.		
19.7	0.30		1.39
66.4	1.01	18.8	1.21
149	2.27	(27.5)	0.87
377	5.74	14.4	0.01
472	7.17	16.2	1.07
1036	16.4	14.8	
1700	27.5	14.6	
		Av. 15.8	Av. 1.11

[a] These molecular diameters in 10^{-8} cm. were used in the calculation of ω: cyclopropane, 4.92; ethylene, 4.95; ketene, 6.40. Collisional deactivation efficiency arbitrarily set equal to unity.

The average rate constant ratios are k_g/k_s = 18.7 at 3600 A. and 14.2 at 3100 Å. This *ratio*

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(8) P. S. Skell and A. Y. Garner, This Journal, **78**, 3409 (1956).

(9) S. Chapman and T. G. Cowling, "The Mathematical Theory of Non-Uniform Gases," Cambridge University Press, 1952, p. 274.

tends to be less affected by any complexities of the reaction system, such as dimerization of ketene, formation of small amounts of higher hydrocarbons, etc., than are the individual constants.

A rough estimate is now desired of the internal energy of the cyclopropane molecules formed in this process and we speculate as follows. The energies of the 3100 and 3600 Å. radiation correspond to 92 and 78 kcal./einstein, respectively. The photolysis reaction has a heat of 55 kcal./mole at room temperature

$$\mathrm{CH_2CO} \xrightarrow{h\nu} :\mathrm{CH_2} + \mathrm{CO}$$

where $\Delta H_f(\mathrm{CH_2}) = 67$ kcal. is computed by adopting $D(\mathrm{CH_2{-}H}) = 87$ kcal. as a possible value[10] (and assuming the same electronic state, presumably ground singlet, of methylene in both processes) and with other heats of formation as tabulated.[11] At 3100 Å., the excess light energy is 37 kcal./mole of which 12/19, *i.e.*, 23 kcal., is arbitrarily assumed to reside with the methylene (if 3/4, the ratio of vibrational degrees of freedom of the products, were used instead,[12] this number would become 27 kcal.). The exact value is of no consequence.

For the reaction of interest, the heat is[11]$\sim$ 67 kcal. To this may be added the 23 kcal which

$$:\mathrm{CH_2} + \mathrm{C_2H_2D_2} \longrightarrow \text{cyclo-}\mathrm{C_3H_4D_2}$$

for *ad hoc* purposes[12] (and being associated with the lighter and smaller association partner) is assumed to appear in cyclopropane entirely as vibrational energy, plus a few kcal of thermal energy (at 25°) of the methylene and ethylene. One conceives then of an energy of the hot cyclopropane of $\sim$95 kcal./mole; since part of any error in the estimate of $\Delta H_f(\mathrm{CH_2})$ cancels out (12/19 here), this number may be valid to ± 10 kcal. The order of magnitude may also be checked in the following crude fashion. Consider one of the measured rate constants, say k_s. Since the formed cyclopropane molecules are roughly monoenergetic, in view both of their mode of formation and high energy, then assuming random energy distribution we may write with Slater[3b,c,13] for the classical theory

$$k_{s\mathrm{E}} = \text{const.}\left(\frac{E - E_0}{E}\right)^{n-1}$$

where n is the number of vibrational modes which interact with the bond-breaking coördinate, counting degenerate modes fully. Marcus and Rice[14] have given a useful representation of the classical approximation involved and the equation is better written for computational purposes

$$k_{s\mathrm{E}} = \text{const.}\left(\frac{E - E_0 + E_z{}^+}{E + E_z{}^*}\right)^{19}$$

where $E_z{}^* \simeq E_z{}^+$ is vibrational zero point energy $\simeq 35$ kcal./mole,[15] $E_0 = 65$ kcal./mole,[2,3a] $E = 95$ kcal./mole and the const. is set equal to the observed[2,3a] high pressure frequency factor, $10^{15.2}$ sec.$^{-1}$ Then $k_{s\mathrm{E}} = 3 \times 10^9$ sec.$^{-1}$; $k_{s\ \mathrm{obsd}} = 1.1 \times 10^{10}$ sec.$^{-1}$ (Table I). On the same basis for 3600 Å., $k_{s\mathrm{E}} = 9 \times 10^8$ sec.$^{-1}$, $k_{s\ \mathrm{obsd}} = 6.3 \times 10^9$ sec.$^{-1}$. The agreement is better than should be expected (the $k_{s\ \mathrm{obsd}}$ are upper limits being based on unit collisional deactivation efficiency). A still further substantiation of the high level of energy of the energized cyclopropane molecules is their essentially mono-energetic character, as supported by the constancy of values of rate constants over the pressure range studied.

Thus the energy of the vibrationally excited cyclopropane is of the order indicated, which appreciably exceeds the average energy of the reacting molecules in thermal studies of cyclopropane isomerization.[16] Frey and Kistiakowsky[6b] came to the same conclusion earlier.

From thermal studies at 445° of the geometrical and structural unimolecular isomerization of cyclopropane-d_2,[2,16] the average value of the ratio corresponding to k_g/k_s is 12. Relative to the values quoted earlier, 18.7 (3600 Å.) and 14.2 (3100 Å.), the variation is negligible and supports the similarity of transition states for both processes. There is an apparent inversion of the magnitudes at the two wave lengths which presumably reflects experimental error.

SEATTLE, WASHINGTON

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(10) See Douglas, Rabinovitch and Looney, *J. Chem. Phys.*, **23**, 315 (1955), for a summary of experimental values of $D(\mathrm{CH_2{-}H})$.

(11) F. D. Rossini, "Selected Values of Chemical Thermodynamic Properties," Circular 500, National Bureau of Standards, 1952.

(12) *Cf.* W. D. McGrath and R. G. W. Norrish, *Z. physik. Chem.* (*N. F.*), **15**, 245 (1958), and discussion of some experimental evidence on nature of energy distributions in reaction products.

(13) N. B. Slater, *Proc. Leeds. Phil. Soc.*, **6**, 259 (1955), and private communication.

(14) R. A. Marcus and O. K. Rice, *J. Phys. Colloid Chem.*, **55**, 894 (1951).

(15) Gunthard, Lord and McCubbin, *J. Chem. Phys.*, **25**, 768 (1956); B. S. Rabinovitch and R. W. Diesen, *ibid.*, in press.

(16) The high pressure average rate constant of the *reacting* cyclopropane molecules for propylene formation (not to be confused with the lesser average rate constant of the energized molecules) has been determined (by method of Johnston and White, *J. Chem. Phys.*, **22**, 1969 (1954)) by us in unpublished work to be 8×10^6 sec.$^{-1}$ in thermal fall-off studies at 445°. This compares with the significantly larger values of k_s observed in the present study. The comparison is somewhat devious since the thermal value is an average quantity and can be labelled as a kind of k_E for direct comparison only in the spirit of Kassel theory.