be accounted for by any simple viscosity correction, and waits interpretation. The phenomenon is the more interesting in that it is not observed with mean diffusion coefficients, nor with conductance mobilities.

It is of interest to compare qualitatively the self-diffusion data with mean diffusion coefficients for the salt, and for this purpose a "mean" diffusion coefficient for sodium chloride has been calculated from the ion self-diffusion coefficients by means of the limiting Nernst equation, $\mathfrak{D}_{\pm} = \dfrac{2}{\dfrac{1}{\mathfrak{D}^{+}} + \dfrac{1}{\mathfrak{D}^{-}}}$. The results are given as curve 3, Fig. 2, and the measured mean diffusion coefficients[9] by curve 4. The gross discrepancy at high concentrations is in large part due to the fact that mean diffusion coefficient measurements, being made in a constant volume system, yield an average of the values for the salt and for the *solvent*, an effect not present in self-diffusion. By use of the equation

$$\mathfrak{D}_{\text{obs.}} = F_{H_2O}\mathfrak{D}_{\text{Salt}} + F_{\text{Salt}}\mathfrak{D}_{H_2O}$$

for a binary system, where F_{H_2O} and F_{Salt} are the volume fractions, and of the value 2.28 cm.^{2}/day for $\mathfrak{D}_{H_2O}$,[19] the point for 3.5 N sodium chloride on curve 4 may be brought to agreement with that on curve 3, providing the not unreasonable value of 50 cc. is taken for the molar volume of sodium chloride.

Acknowledgment.—Support of the above work by a grant-in-aid from The Research Corporation is gratefully acknowledged.

[19] W. J. C. Orr and J. A. V. Butler, *J. Chem. Soc.*, 1273 (1935).

LOS ANGELES, CALIFORNIA RECEIVED JUNE 15, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ROCHESTER]

The Thermal Decomposition of Cyclopentane[1,2]

BY DON W. VANAS, NANCY M. LODGE AND W. D. WALTERS

The homogeneous thermal decomposition of cyclopentane has been investigated in the neighborhood of 555°. Addition of nitrogen, hydrogen or a small quantity of nitric oxide does not alter appreciably the rate of pressure rise during the initial stages of the decomposition. In the presence of a mixture of products, or in the presence of added ethylene, propylene or cyclopentadiene, an increase in the rate of pressure rise is observed. Small amounts of diallyl or allene accelerate the rate. Analyses for cyclopentadiene and hydrogen indicate that the dehydrogenation of cyclopentane is accelerated by the addition of ethylene or propylene.

Introduction

Earlier studies[3] have shown that the homogeneous thermal decomposition of cyclopentane in the neighborhood of 600° proceeds mainly by two reactions: (a) a dehydrogenation reaction to yield cyclopentadiene and hydrogen probably by way of cyclopentene as an intermediate and (b) a ring-cleavage reaction to form propylene and ethylene. However, the products formed at 900° under a pressure of 10 mm., were found to contain the substances mentioned above and also an appreciable quantity of C_3H_4, either allene or methylacetylene.[3d]

Küchler studied the kinetics of the cyclopentane decomposition in a static system by means of pressure measurements and by analyses for hydrogen, ethylene and propylene.[3e] In the over-all pressure–time curve for cyclopentane, as in the cases of cyclohexane[4,5] and methylcyclopentane,[5] an induction period was observed. Although the dehydrogenation was assumed to proceed in two steps, the first of these, loss of one molecule of hydrogen to form cyclopentene, was regarded as the rate-determining step in the dehydrogenation. On the basis of the analytical data the ring cleavage reaction seemed to have an induction period, but the dehydrogenation appeared to be a first-order reaction. Küchler reported that the rate of the ring cleavage could be accelerated by the addition of propylene. He postulated that the ring cleavage is autocatalytic and that another product ethylene would be twice as effective as propylene in accelerating the reaction. The present study was undertaken to investigate further the possible effects of the products upon the decomposition of cyclopentane. Moreover, the rate of formation of cyclopentadiene during the decomposition appeared to warrant additional attention.

Experimental

Materials.—The cyclopentane used in the majority of the experiments was National Bureau of Standards Sample No. 219-5s which had a stated purity of 99.95 ± 0.02 mole per cent. Another source of cyclopentane was the hydrogenation of cyclopentadiene. The cyclopentane after fractionation showed no test for unsaturation with bromine. The sample used was taken from a fraction which had a corrected boiling point of 49,3° and n^{21}D 1.4064 compared with the values of the Bureau of Standards,[6] 49.262° and 1.4059 (interpolated).

Ethylene, propylene and cyclopropane were obtained in cylinders from the Ohio Chemical and Manufacturing Company and had a stated purity of 99.5% in each case. All of these gases were subjected to thorough degassing before use. In two experiments propylene prepared from *n*-propyl alcohol and purified by chemical treatment and distillation was used as a check. Hydrogen and nitrogen obtained from

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[1] Abstracted from the Ph.D. thesis of Don W. Vanas, du Pont Fellow in Chemistry, 1945–1946, and the M.S. thesis of Nancy M. Lodge. A portion of this work was supported by the Office of Naval Research under Contract N6onr-241, Task Order I.

[2] For data supplementary to this article, order Document 3350 from the American Documentation Institute, 1719 N Street, N. W., Washington 6, D. C., remitting $1.00 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or $1.00 for photocopies (6 × 8 inches) readable without optical aid.

[3] (a) F. E. Frey, *Ind. Eng. Chem.*, **26**, 198 (1934); (b) B. A. Kazansky and A. F. Plate, *Ber.*, **67**, 1023 (1934); (c) P. P. Borisov, E. M. Shaknazarova and E. I. Margolis, *J. Gen. Chem.* (*U. S. S. R.*), **4**, 1385 (1934); (d) F. O. Rice and M. T. Murphy, THIS JOURNAL, **64**, 896 (1942); (e) L. Küchler, *Z. physik. Chem.*, **B53**, 307 (1943).

[4] R. N. Pease and J. M. Morton, THIS JOURNAL, **55**, 3190 (1933).

[5] L. Küchler, *Trans. Faraday Soc.*, **35**, 874 (1939).

[6] C. B. Willingham, W. J. Taylor, J. M. Pignocco and F. D. Rossini, *J. Research Natl. Bur. Standards*, **35**, 219 (1945).

cylinders were purified by a train similar to that described by Michaelis.[7] Nitric oxide which had been prepared by the method already described[8] was purified by several distillations between traps at −160 and −196°.

Cyclopentadiene was prepared, purified and stored in the manner previously described.[9] Diallyl (1,5-hexadiene, Standard Hydrocarbon Sample No. 553-5s) of stated purity 99.89 ± 0.08 mole per cent. was obtained from the National Bureau of Standards. Allene (99.9%) was generously furnished by Dr. F. O. Rice of the Catholic University.

Apparatus and Method.—The reaction vessel, furnace and method of temperature regulation have been described in a previous publication.[9] The temperatures were measured by the use of calibrated[10] chromel–alumel or platinum, platinum–13% rhodium thermocouples. The investigation of surface effects was carried out in a reaction bulb which was filled with Pyrex tubes and which had a thirty-fold larger surface to volume ratio. The cyclopentane and diallyl storage bulbs were separated from the rest of the system by Warrick–Fugassi valves[11] and the bulb for preparing vapor mixtures of cyclopentane and other gases was separated from the vacuum-manifold by a graphite-lubricated, mercury-sealed stopcock of the type described by Echols.[12] Mixtures of cyclopentane with other gases were prepared in three ways: (a) vapor mixtures were prepared and mixed before introduction into the evacuated reaction bulb, (b) samples of the two substances were condensed in a cold finger and then the entire mixture was vaporized into the reaction vessel, (c) the added gas was allowed to remain in the reaction bulb for various time intervals before the cyclopentane was added.

Analyses.—Two different analytical procedures were employed for the determination of cyclopentadiene in the products. In one procedure which utilized ultraviolet absorption, cyclopentadiene was determined by measurement of the optical density of an alcoholic solution at 240 mμ with a Beckman spectrophotometer.[13a,b] The other procedure[13a,c] involved the reaction of cyclopentadiene with benzaldehyde in alcoholic alkali to form the highly colored phenyl fulvene which was determined spectrophotometrically at 400 mμ. In a number of experiments the amounts of the product gases non-condensable at −196° were determined and in some of these runs the samples were sent to the National Bureau of Standards for mass spectrometric analysis so that the quantities of hydrogen could be ascertained. At the time of the latter experiments a silica reaction vessel was in use in place of the usual Pyrex bulb. Mass spectrometric analyses have been carried out also on the entire reaction mixture.

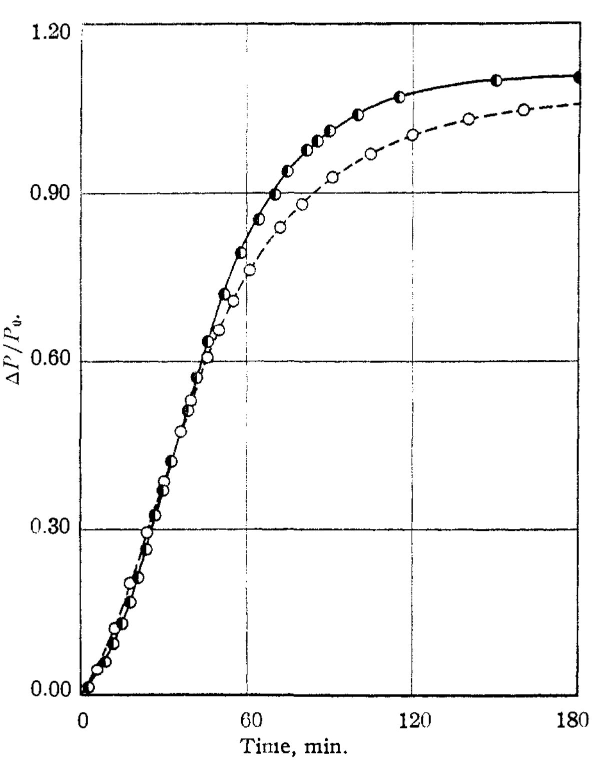

Fig. 1.—Decomposition of cyclopentane: ◐, P_0 = 101 mm. at 558° in the unpacked bulb; ○, P_0 = 111 mm. at 557° in the packed bulb.

Results and Discussion

Products.—In agreement with the results of earlier studies ethylene, propylene and hydrogen have been found by mass spectrometric analysis to be important gaseous products of the thermal decomposition of cyclopentane. The analyses showed that hydrogen accounts for 95–96% of the gas fraction volatile at −196° from experiments carried to not more than 15% pressure increase at 555° with initial pressures near 100 mm. The remainder of the non-condensable fraction was chiefly methane. The analyses mentioned in the previous section indicated the presence of cyclopentadiene in the condensable products. On the basis of the observed products the principal over-all reaction at 550° appear to be

$$C_5H_{10}\begin{cases}\rightarrow C_2H_4 + C_3H_6 & (1)\\ \rightarrow C_5H_6 + 2H_2 & (2)\end{cases}$$

Rate of Pressure Increase.—Experiments in the packed and unpacked Pyrex vessels gave curves of the type shown in Fig. 1. The ratio of the final to the initial pressure for each of these experiments was 2.18 (corrected for "dead space"). These results are not far different from those obtained by Küchler in vessels of Jena Supremax glass empty ($P_f/P_0 \cong 2.1$) and with packing to give an eleven-fold increase in $S/V(P_f/P_0 < 2)$. Our experiments at 557° with initial pressures from 50 to 200 mm. were found to follow approximately the relationship $(dP/dt)_{max} = kP_0^{3/2}$ which Küchler had first observed. The average values of the maximum rate of pressure increase for our experiments at 100 mm. at 555 and 558° were found to be 1.48 ± 0.05 and 1.68 ± 0.03 mm./min., respectively, compared with 1.44 and 1.63 mm./min. calculated from Küchler's expression for k.

Experiments at 556° showed that the addition of 15–30 mm. nitrogen or hydrogen to 110 mm. cyclopentane has no effect upon the maximum slope of the pressure–time curve or upon the pressure increase during the first twenty minutes. Nitric oxide (Table I) does not appear to inhibit the rate of pressure increase or alter significantly the induction period.

Dehydrogenation.—In order to obtain additional information about the dehydrogenation portion of the cyclopentane decomposition, analyses for cyclopentadiene were made near the start of the reaction. The results are shown as curve 1 in Fig. 2. This curve does not have the appearance of a simple first order reaction which might have been expected from Küchler's results and assumptions about the reaction. Since cyclopentadiene appears to decompose only slowly, as indicated by earlier work[3d] and by other experiments in the present study, the loss of cyclopentadiene by decomposition will probably not be large during the initial stages of the reaction. Moreover, the disappearance of cyclopentadiene by reaction would tend to produce a curve different in shape from curve 1 in Fig. 2 (*i.e.*, concave downward instead of upward). Preliminary results indicate that at longer reaction times the cyclopentadiene concentration reaches a maximum and then decreases slowly.

A plot of the amounts of gas non-condensable at −196° from the experiments shown in curve 1 gave a curve which was concave upward and similar in shape to curve 1. The quantities of non-condensable gas (probably 90–95% H_2) obtained in the experiments up to 30 minutes averaged 2.3–2.4 times the amounts of cyclopentadiene. In three later

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[7] A. Weissberger, "Physical Methods of Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1946, p. 1096.

[8] C. H. Klute and W. D. Walters, This Journal, **67**, 550 (1945).

[9] D. W. Vanas and W. D. Walters, *ibid.*, **70**, 4035 (1948).

[10] W. F. Roeser and H. T. Wensel, *J. Research Natl. Bur. Standards*, **14**, 247 (1935).

[11] E. Warrick and P. Fugassi, *Ind. Eng. Chem., Anal. Ed.*, **15**, 13 (1943).

[12] L. S. Echols, *ibid.*, **10**, 527 (1938).

[13] (a) K. Uhrig, E. Lynch and H. C. Becker, *ibid.*, **18**, 550 (1946); (b) J. S. Powell and K. C. Edson, *ibid.*, **20**, 510 (1948); (c) J. S. Powell, K. C. Edson and E. L. Fisher, *ibid.*, **20**, 213 (1948).

experiments which were performed at a slightly lower temperature in a silica vessel, the amounts of hydrogen in the non-condensable fractions were determined and plotted (curve 2, Fig. 2).

In comparing the two curves in Fig. 2, curve 2 should be raised by 10–15% to compensate for the difference in temperature. The amount of hydrogen appears to be approximately twice that of cyclopentadiene.

Effect of Unsaturated Hydrocarbons upon the Pressure–Time Curve.—The effect of added ethylene upon the decomposition of cyclopentane was investigated first by observing the rate of pressure increase for mixtures of cyclopentane and ethylene.[14] The results in Table I show that the addition of ethylene increases the maximum slope of the pressure–time curve and the pressure increase during the first 20 minutes (ΔP_{20}). A comparison of the influence of ethylene with that of propylene in Table I indicates that ethylene is not twice as effective an accelerant as propylene, which had been tentatively suggested.[3e] Additional experiments in the packed bulb have shown that increased surface does not change appreciably the accelerating effect of ethylene or propylene. Moreover, the enhancement of the rate of pressure rise produced by the addition of propylene does not seem to be inhibited by nitric oxide.

TABLE I

EFFECT OF VARIOUS SUBSTANCES UPON THE DECOMPOSITION OF CYCLOPENTANE[15]

C_2H_4 = ethylene; C_3H_6 = propylene; C_5H_6 = cyclopentadiene; dec. C_5H_8 = cyclopentene allowed to decompose prior to the introduction of cyclopentane; C_3H_4 = allene; C_6H_{10} = diallyl.

Temp., °C.	$P^0_{C_5H_{10}}$, mm.	Added subst.	$P^0_{A.S.}$ mm.	$(dP/dt)_{max}$, mm./min.	ΔP_{20}, mm.
555	103	...	0	1.58[a]	18[a]
555	101	C_2H_4	15	1.70	23
555	101	C_2H_4	51	2.02	28[b]
555	104	C_3H_6	51[d]	2.32	35[c]
558	101	...	0	1.75	21
558	101	C_3H_6	22	2.06	31
558	98	C_3H_6	51	2.39	39
558	101	...	0	1.68[e]	20[e]
558	99	C_5H_6	30	2.87	54
558	98	C_5H_6	44	3.43	59[f]
557	111	...	0	1.76	20
556	111	dec. C_5H_8	11	2.15	41
556	110	dec. C_5H_8	38	2.74	51
555	105	C_3H_4	3.6[d]	1.87	32
555	99	C_3H_4	8[d]	2.30	38
555	107	...	0	..	19
555	108	C_6H_{10}	3.0[d]	..	58
555	106	C_6H_{10}	0.9[d]	..	49
557	150	...	0	~3.0	36[g]
557	152	NO	0.3	~3.0	40
557	155	NO	1.6	..	39

[a] Average of two runs. [b] Pure ethylene alone gives about 0.8 mm. pressure decrease. [c] Propylene alone produces 1.3 mm. pressure increase. [d] Mixture prepared by method (b). [e] Average of three runs. [f] Pressure change due to cyclopentadiene alone should not exceed 3 mm. [g] Average of four runs.

TABLE II

EFFECT OF CYCLOPENTANE PRODUCTS UPON THE DECOMPOSITION OF CYCLOPENTANE

Temp., °C.	P'_0, mm.	Time,[a] min.	P''_0, mm.	ΔP_{10} (1 + 2) mm.	ΔP_{10} exptl., mm.	$(dP/dt)_{max}$, exptl., mm./min.	$(dP/dt)_{max}$, calcd., mm./min.
558	54	45	49	10.0	16.0	1.74	1.76
557.5	50	48	49	9.9	15.9	1.84	1.89
556	53	50	50	8.5	13.7	1.60	1.61

[a] Time at which the second sample (P''_0) was introduced.

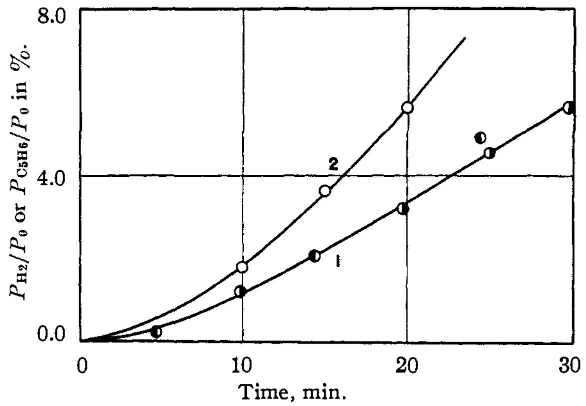

Fig. 2.—Cyclopentadiene and hydrogen present during the decomposition of cyclopentane (P_0 = 99–114 mm.): curve 1, cyclopentadiene at 557.5 ± 1°; ◑, phenylfulvene method of analysis; ◐, ultraviolet method; curve 2, ○, hydrogen at 555°.

After the initial experiments with added ethylene or propylene it was of interest to determine the effect of the cyclopentane decomposition products upon the rate of pressure increase (Table II). A 50-mm. sample of cyclopentane (P'_0) was allowed to decompose until the pressure had increased 25–30 mm. and the maximum rate of pressure rise had been reached. Then another 50-mm. sample of cyclopentane (P''_0) was added. As shown in Table II, the pressure increase observed during the ten-minute interval following the introduction of the second sample (ΔP_{10}, exptl.) is significantly greater than the sum of the pressure increases expected for the two samples decomposing independently (ΔP_{10}, 1 + 2). The maximum rate of pressure rise after the addition of the second sample [$(dP/dt)_{max}$, exptl.] is almost the same as would be calculated for a single sample equal to the sum of the two charges [$(dP/dt)_{max}$, calcd.], but this maximum rate is attained within a short time (1–4 min.) after the introduction of the second sample compared to about 25 minutes needed for the attainment of the maximum rate for a single sample. The effect of the products in accelerating the pressure rise and shortening the induction period seemed to be greater than that expected for the amounts of ethylene and propylene present in the products. Since cyclopentadiene is one of the principal substances formed when cyclopentane decomposes, experiments were performed to ascertain its influence upon the reaction. The results in Table I show that cyclopentadiene produces a greater acceleration than propylene or ethylene. The induction period is almost eliminated by the addition of 15 mm. of cyclopentadiene. That the observed acceleration is due to cyclopentadiene (or a decomposition product) and not to an impurity resulting from the particular method of preparation is indicated by experiments (Table I) in which cyclopentadiene was prepared directly in the reaction vessel by the thermal decomposition of cyclopentene (which produces cyclopentadiene and hydrogen).

In the experiments discussed at the beginning of this section it was observed that even in the presence of propylene or ethylene the rate of pressure rise reaches a maximum only after some minutes of reaction. This observation, as well as other results obtained in earlier work with tetrahydrofuran,[16] indicated that allowing the propylene or ethylene to remain in the reaction vessel prior to the introduction of cyclopentane might result in a greater acceleration. The data in Fig. 3 show that under these conditions the rate of pressure rise during the initial stages of the cyclopentane decomposition is increased. Two experiments with a sample of propylene prepared from propyl alcohol were in agreement with the results shown in Fig. 3 which were obtained with degassed tank propylene. A similar but somewhat less pro-

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(14) Prepared by method (a), see Experimental section.

(15) Data from other experiments are available from the American Documentation Institute.

(16) G. McDonald, N. M. Lodge and W. D. Walters, THIS JOURNAL, 73, 1757 (1951).

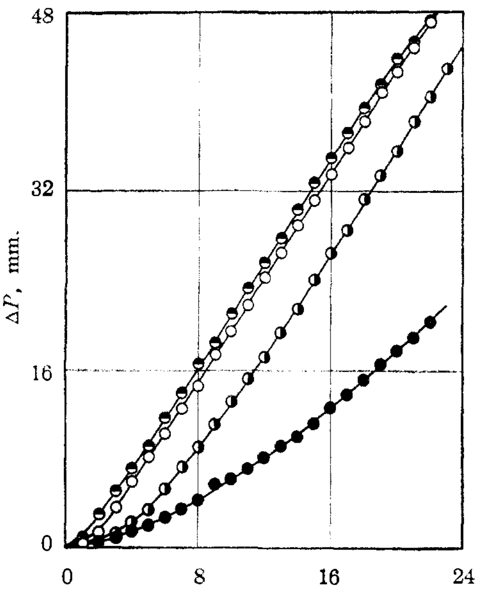

Fig. 3.—Effect of propylene and its decomposition products upon the thermal decomposition of cyclopentane at 555°: ●, 103 mm. cyclopentane; ◑, 51 mm. propylene and 104 mm. cyclopentane, simultaneous introduction; ○, 53 mm. propylene introduced into reaction bulb 10 min. before 102 mm. cyclopentane; ◓, 52 mm. propylene in bulb 30 min. before 101 mm. cyclopentane.

nounced effect was obtained in the experiments with added ethylene. Experiments in the packed reaction vessel which yielded results similar to those in the unpacked vessel give evidence that the effects observed are not appreciably heterogeneous.

One explanation for the above observations would be that the propylene (or ethylene) reacts slowly to form a molecule or radical which accelerates the decomposition of cyclopentane more than the propylene itself. Among the various products of the decomposition of propylene are allene and diallyl.[17] The results from experiments with added allene or diallyl are given also in Table I. Diallyl which decomposes rapidly at these temperatures gives a very large acceleration initially. A small quantity of added allene produces an acceleration, but the pressure–time curve still exhibits an induction period.

Preliminary results indicate that the addition of cyclopropane or isobutylene will increase the rate of pressure rise for cyclopentane, but the effect of cyclopropane is not markedly different from that of propylene which cyclopropane forms by isomerization.

TABLE III

EFFECT OF ETHYLENE OR PROPYLENE UPON THE AMOUNT OF CYCLOPENTADIENE PRESENT DURING THE CYCLOPENTANE DECOMPOSITION

Temp., 555°; time of reaction, 20 minutes; PF = phenylfulvene method; UV = ultraviolet spectrophotometric method.

$P^0_{C_5H_{10}}$, mm.	Added subst.	$P^0_{A.S.}$, mm.	Anal. method	$P_{C_5H_6}/P^0_{C_5H_{10}}$, %
101	..	0	PF	2.96 ± 0.06
104	C_2H_4	53	PF	5.67 ± .01
105	C_3H_6	52	PF	5.18 ± .07[a]
105	..	0	UV	3.0 ± .1
107	C_2H_4	52	UV	6.2 ± .1
108	C_3H_6	50	UV	6.2 ± .2

[a] Average of two experiments; in other cases, average of three experiments. Mean deviation given after each value.

Effect of Unsaturated Hydrocarbons upon the Dehydrogenation.—The results above, obtained by pressure measurements, do not show whether the reaction being accelerated is the ring cleavage or the dehydrogenation, or both. As a result of two experiments in which 4–5% propylene was added, Küchler[3e] reported that propylene accelerates the ring cleavage, but does not increase the amount of hydrogen formed during the first five minutes at 551°. In the present study the cyclopentadiene formed from 100 mm. of cyclopentane after 20 minutes of reaction at 555° was determined by analysis. The data are given in Table III. The results obtained by both methods of analysis indicate that the addition of ethylene or propylene increases the amount of cyclopentadiene present after 20 minutes.[18] Ethylene or propylene pyrolyzed at 555° in the absence of cyclopentane will produce some absorption at 400 mμ in the phenylfulvene method and at 240 mμ by the direct ultraviolet technique. Therefore, corrections amounting to 1.4–2.6% in the case of ethylene and 11–12% in the case of propylene were applied in obtaining the results in Table III. For the experiments with cyclopentane alone the values from the two methods are in good agreement, but with added ethylene or propylene the phenylfulvene method, which should be the more specific, gives values slightly lower than the ultraviolet method.

In view of the increase in the cyclopentadiene from cyclopentane in the presence of added ethylene, an increase in the hydrogen also might be expected. However, the amount of hydrogen might not show the increase expected on the basis of the cyclopentadiene if (a) ethylene were reacting with hydrogen to form ethane or (b) if some of the cyclopentane were reacting with ethylene to form cyclopentene and ethane. Therefore, analyses for hydrogen were made after 15 and 20 minutes of reaction at 555° (Table IV).[19] The addition of ethylene raises the amount of hydrogen after 20 minutes to about 1.7 times the value for pure cyclopentane in comparison to a 1.9-fold increase in cyclopentadiene by the phenylfulvene method. Thus, both the cyclopentadiene and the hydrogen analyses indicate that ethylene accelerates the dehydrogenation of cyclopentane. In a comparison of the data in Tables III and IV it should be noted that the rate of the over-all reaction, as measured by the pressure increase, appeared to be about 10% slower in the case of the hydrogen experiments which were carried out at a later time in a silica vessel.

TABLE IV

HYDROGEN PRESENT DURING THE DECOMPOSITION OF CYCLOPENTANE AT 555°

$P^0_{C_5H_{10}}$, mm.	Added subst.	$P^0_{A.S.}$, mm.	Time, min.	$P_{H_2}/P^0_{C_5H_{10}}$, %
99	...	0	20	5.6
106	C_2H_4	53	20	9.8[a]
106	...	0	15	3.7
107	C_2H_4	52	15	6.2
102	...	0	10	1.82
105	C_6H_{10}	1.9	10	11.0[b]

[a] The total amount of non-condensables obtained in 20 min. from 49 mm. of C_2H_4 alone at 555° was only 1.3% of the hydrogen obtained in this experiment. [b] The amount of the hydrogen from the decomposition of 1.9 mm. of diallyl (C_6H_{10}) amounts to only 4% of this value.

Since diallyl has a marked influence upon the rate of pressure increase of cyclopentane, the amounts of hydrogen

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(17) F. O. Rice and O. L. Polly, *J. Chem. Phys.*, **6**, 273 (1938); M. Szwarc, *ibid.*, **17**, 284 (1949); V. Schneider and P. K. Frolich, *Ind. Eng. Chem.*, **23**, 1405 (1931).

(18) Experiments carried out by Mr. H. D. Batha in this Laboratory with (a) 52 mm. ethylene and 8 mm. propylene and (b) 52 mm. propylene and 7 mm. ethylene for 20 minutes at 555° show that under the present experimental conditions the increased amount of cyclopentadiene is not due to a reaction between the added ethylene and the propylene in the products (or *vice versa*) to form cyclopentadiene and hydrogen. The occurrence of this reaction at 650° has been postulated by S. Kato and F. Someno, *Bull. Inst. Phys. Chem. Research (Tokyo)*, **21**, 256 (1942).

(19) The experiments in Table IV and shown in curve 2, Fig. 2 were performed by Mr. Carl Garland of this Laboratory as part of his senior research problem for the B.S. degree.

produced with and without added diallyl were measured also. The data given in Table IV show that diallyl increases considerably the quantity of hydrogen formed during ten minutes at 555°.

Discussion.—The results indicate that the acceleration resulting from the presence of the products accounts to a considerable extent for the S-shaped nature of the pressure–time curve for the decomposition of cyclopentane. The mechanism by which ethylene, propylene or cyclopentadiene (or their decomposition products) can bring about the increase in rate has not been established from the existing experimental data. Küchler[3e] and Eucken[20] have suggested that the acceleration of the ring cleavage is due to the assistance which propylene renders in the process of transfer of a hydrogen atom from one carbon atom to an adjacent one.

The present work shows that the dehydrogenation portion of the decomposition is increased in the presence of ethylene or propylene. This acceleration and also the shape of the curve showing the amount of cyclopentadiene or hydrogen *vs.* time for the decomposition of pure cyclopentane give evidence that the dehydrogenation of cyclopentane probably does not proceed as a simple first order reaction. On the basis of the hydrogen formed during the early stages of the reaction Küchler[3e] reported that the hydrogen-forming reaction was first order. Moreover, the rate of pressure increase during the induction period in his experiments seems to have been greater than in the present study. In view of these differences during the initial stage, but agreement in the subsequent period, the possibility of the presence of an impurity in the cyclopentane has been given consideration. In the present study samples of cyclopentane from several different sources[21] have been found to give similar results. Although no definite conclusion can be reached, several experimental observations have indicated that at least part of the difference could be explained if the cyclopentane used in the previous study[3e] contained a small amount of cyclopentene.

Since analyses for ethylene and propylene were not performed in the presence of added substances, no direct evidence for the acceleration of the ring cleavage has been obtained in this work. However, the increase in the rate of pressure rise in the presence of propylene appears to be greater than can be accounted for on the basis of the measured increase in the dehydrogenation reaction. This observation gives an indication that the addition of propylene increases the rate of ring cleavage, in agreement with Küchler's experiments; but ethylene appears to be considerably less effective.

Acknowledgment.—We wish to thank Dr. F. L. Mohler and the staff of the Mass Spectrometry Section of the National Bureau of Standards for performing the mass spectrometric analyses.

ROCHESTER 3, NEW YORK RECEIVED JULY 25, 1951

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[20] Eucken, *Die Chemie*, **56**, 342 (1943).

[21] Mr. H. D. Batha of this Laboratory has observed that the rate of pressure rise during the induction period at 555° for a sample of cyclopentane (99.95%) from the Phillips Petroleum Co. is the same as that for the two kinds of cyclopentane described in the Experimental section.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF CALIFORNIA, LOS ANGELES]

The Vapor-phase Photolysis of Acetone–Iodine Mixtures

BY JAMES N. PITTS, JR.,[1] AND F. E. BLACET

The quantum yield of methyl iodide formation, Φ_{CH_3I}, is temperature dependent and much less than unity in the vapor-phase photolysis of acetone–iodine mixtures at 3130 Å. At constant acetone concentration and 3130 Å., Φ_{CH_3I} increased from 0.12 at 80° to 0.28 at 177°. Φ_{CH_3I} is also a function of wave length, and at 100° it increases from 0.17 at 3130 Å. to 0.50 at 2654 Å. Only small amounts of carbon monoxide and methane were formed, but no ethane was detected. The significance of these results in terms of the various primary processes postulated for acetone photolysis is discussed.

The nature and extent of the primary processes occurring in the vapor phase photolysis of acetone have been the subject of numerous investigations, the results of which have been reviewed by Davis[2] and again critically discussed by Noyes and Dorfman.[3] The latter authors present a mechanism for the photochemical decomposition in the pressure region where wall effects can be neglected. This includes the following primary processes

$$CH_3COCH_3 + h\nu \longrightarrow \begin{cases} CH_3 + CH_3CO & (1) \\ 2CH_3 + CO & (2) \\ CH_3COCH_3' & (3) \end{cases}$$

and excludes the concerted intramolecular process (4).

$$CH_3COCH_3 + h\nu \longrightarrow C_2H_6 + CO \qquad (4)$$

In addition to these primary processes, Noyes and Dorfman include reaction (5) to account for the fraction, *a*, of the acetyl radicals produced by process (1) that immediately dissociate as a result of excess energy remaining after (1).

$$a\ CH_3CO' \longrightarrow a\ CH_3 + a\ CO \qquad (5)$$

In this investigation acetone–iodine mixtures were irradiated in order to obtain quantitative information as to the extent of processes (1), (2), (4) and (5), and to examine carefully the photolysis products by chemical and mass spectrometric methods.

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[2] W. Davis, Jr., *Chem. Revs.*, **40**, 201 (1947).

[3] W. A. Noyes, Jr., and L. M. Dorfman, *J. Chem. Phys.*, **16**, 788 (1948).