

methane and methyl iodide quantum yields at both $\lambda 3130$ and $\lambda 2600$. Obviously, the results given in this paper and in the preceding one¹ are not in agreement with this. However, in spite of that fact, we concur in one important conclusion reached by him, namely, in the photolysis of acetaldehyde there must be two primary dissociation processes.

Summary

1. At $\lambda 2654$, with 200 mm. acetaldehyde and with a temperature of 60° , it has been found that over the iodine pressure range of 1 to 2.5 mm., Φ_{CO} is 0.66, Φ_{CH_3I} is 0.35 and Φ_{CH_3} is 0.28.

2. Under similar conditions except for wave length, Φ_{CO} increases from 0.21 at $\lambda 3130$ to 0.66 at $\lambda 2654$, then appears to become slightly less at $\lambda 2380$; Φ_{CH_3I} increases from 0.20 at $\lambda 3130$ to a maximum at 0.43 at $\lambda 2804$, decreasing somewhat at shorter wave lengths; and Φ_{CH_3} increases linearly from 0.013 at $\lambda 3130$ to 0.39 at $\lambda 2380$.

3. At $\lambda 2654$, in the absence of iodine, Φ_{CO} increases from 0.78 at 60° to 5.85 at 150° . Over the same temperature range, but with ample

iodine present, Φ_{CO} , Φ_{CH_3I} and Φ_{CH_3} remain constant at the values given above.

4. In all experiments having sufficient iodine present to suppress secondary reactions, Φ_{CO} was found to be approximately equal to the sum of Φ_{CH_3I} and Φ_{CH_3} .

5. From the results obtained in the absence of iodine, an activation energy of 9.6 kcal. has been calculated for the photolysis chain process. It is postulated that $CH_3CO + M \rightarrow CH_3 + CO + M$ is the reaction which requires this energy of activation.

6. The conclusions given in the previous paper of this series have been verified. In addition, it has been shown that two primary photodecomposition processes must occur in the region of absorption usually attributed to the carbonyl group. At $\lambda 3130$ the dissociation is almost entirely into methyl and formyl radicals. With shorter wave lengths a second decomposition, directly into methane and carbon monoxide, becomes increasingly more important, until at $\lambda 2380$ the two processes have equal probability of occurrence.

LOS ANGELES, CALIF.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

The Thermal Decomposition of Five-Membered Rings

BY F. O. RICE AND MARY THOMAS MURPHY¹

From the point of view of the principle of least motion,² ring compounds would be expected to decompose ordinarily through rupture of a C-C bond in the ring; this primary decomposition would then be followed by a very rapid decomposition of the divalent radical directly into molecules. In a recent paper³ it was shown that cyclohexene undergoes a change of this nature on heating and actually decomposes quantitatively into 1,3-butadiene and ethylene when the pyrolysis is conducted under conditions such that the products do not react with each other or with the substrate.

It seemed worth while to extend this study to other ring systems and accordingly we prepared a number of five-membered ring compounds and made a complete over-all analysis of the products formed on thermal decomposition. We shall dis-

cuss the behavior of a group of four acid anhydrides which can conveniently be considered first because the experimental results are readily predictable from the principle of least motion.

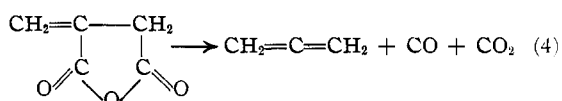
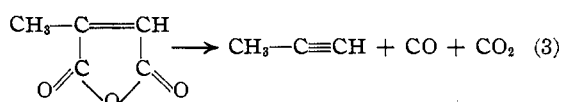
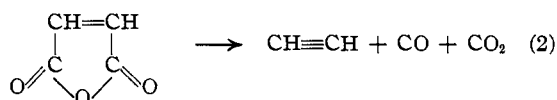
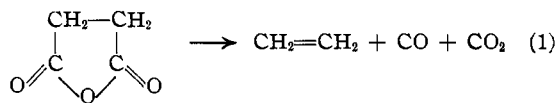
In any organic decomposition, the atoms of the original molecule must take up new positions to give products and it is desirable that there be as little motion of the atoms as possible in passing from the old to the new configurations. This is a statement of the first part of the principle of least motion. The second part of the principle states that a reaction will be favored which involves least change of the electronic configuration of the reacting system. It is of course understood that the principle applies only to elementary or single step reactions which from the thermodynamic standpoint are approximately equally probable.

In the light of the preceding paragraph we may now write the products to be expected in the decomposition of the following acid anhydrides

(1) Present address, College of Chesnut Hill, Philadelphia, Pa.

(2) Rice and Teller, *J. Chem. Physics*, **6**, 489 (1938).

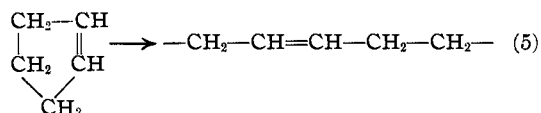
(3) Rice, Ruoff and Rodowskas, *This Journal*, **60**, 955 (1938).



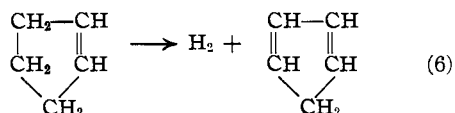
As will be described in the experimental section we obtained the expected products⁴ in theoretical yield when the experimental conditions were such as to preserve the products from further degradation.

We then examined the effect of heat on various hydrocarbons containing a five-membered ring. Cyclopentadiene proved to be astonishingly stable and was not affected appreciably by conditions which caused extensive decomposition in all the other five-membered ring systems examined.

The thermal decomposition of cyclopentene is especially interesting because the present state of our knowledge of elementary reactions does not permit us to state unequivocally the course of the decomposition. Rupture of a carbon-carbon bond according to the equation



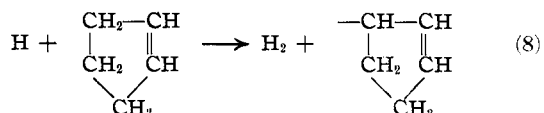
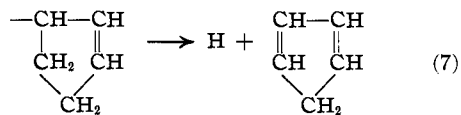
would presumably lead to a complicated mixture of products. On the other hand, if molecular hydrogen separates in a single elementary step according to the equation



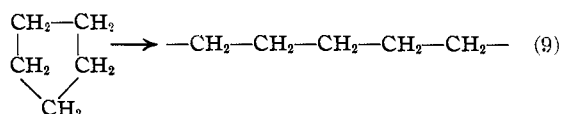
we would obtain cyclopentadiene and hydrogen as the only products. Actually we obtained these in 95% yield. However, this result does not prove that Eq. (6) represents an actually occurring single step reaction; the products shown in Eq. (6) may actually be formed by a hydrogen atom

(4) Itaconic anhydride is an exception because we obtained methylacetylene as well as allene (see experimental part).

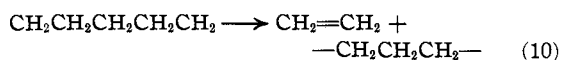
chain initiated by radicals produced according to Eq. (5).



Cyclopentane, as might perhaps be expected from the principle of least motion, undergoes a more complicated decomposition. If we assume that direct loss of hydrogen as H₂ does not occur to an appreciable extent we may write the following equation for the first step



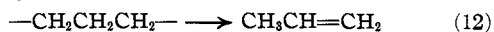
This would be followed by



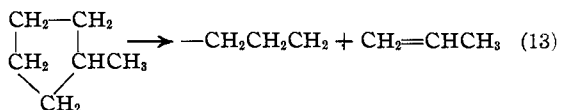
The divalent radical CH₂CH₂CH₂ might decompose into ethylene and CH₂ which would attack the cyclopentane and build up to CH₄, at the same time starting a hydrogen atom chain in the cyclopentane leading to cyclopentene. A puzzling feature of this decomposition lies in the appearance of appreciable quantities of a C₃ hydrocarbon having the equivalent of two double bonds. We did not determine whether this was methyl acetylene or allene. If it was allene possibly the direct separation of H₂ from one carbon atom may occur under favorable circumstances



However, it seems also possible that a hydrogen atom in this divalent radical might migrate according to the equation



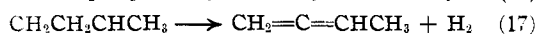
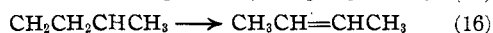
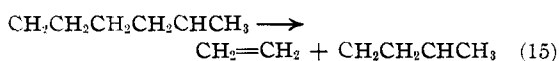
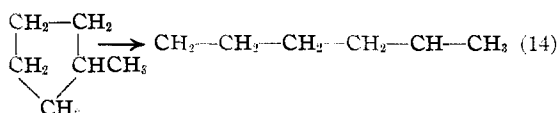
The decomposition of methylcyclopentane is, as might be expected, quite complicated. Rupture of one of the ring bonds attached to the tertiary carbon atom would lead to the following



The radical CH₂CH₂CH₂ would then change according to Eq. (11) or (12). About 40% of the

methylcyclopentane appears to decompose into propylene.

Rupture of the carbon-carbon bond joining the methyl group to the ring would result in a radical reaction leading to the formation of methane and various methyl cyclopentenes. Further decomposition of these would lead to five-membered dienes. About 30% of the decomposition gives hydrogen and a mixture of cyclic mono- and di-olefins. There also seems to be a third method of decomposition represented by the equations



Unfortunately we were not able to obtain positive identification of the C₄ hydrocarbons shown in Eqs. (16) and (17).

Experimental

The decompositions were carried out in the low pressure pyrolytic apparatus described in a previous paper.⁵ In general one mole of the substrate was passed through a quartz furnace under measured conditions of temperature and pressure. The condensable products were caught in two traps kept at appropriate temperatures and the permanent gases were collected, measured, and analyzed. The contents of the traps were also analyzed by Podbielniak distillations supplemented by gas analysis and catalytic hydrogenations.

Acid Anhydrides.—Very few experimental results have been reported on these compounds. When succinic anhydride is heated at 250–280° for six hours, it gives⁶ a 41% yield of the dilactone of acetone diacetic acid. Maleic anhydride⁷ has been reported to be stable when heated at 250° and atmospheric pressure. Itaconic anhydride on distillation tends to form the more conjugated system of citraconic anhydride.⁸

The succinic and maleic anhydrides used in these experiments were Eastman Kodak Co. products and were used without further purification. Itaconic and citraconic anhydrides were prepared from citric acid according to the method given in "Organic Syntheses."⁹ The results of our experiments on all these compounds are shown in Table I. The solid material recovered in the traps was shown in each case to be unchanged substrate, by a mixed melting point. The experiment with itaconic anhydride was done under rather drastic conditions, the substrate being

(5) Rice, Ruoff and Rodowskas, *THIS JOURNAL*, **60**, 955 (1938).

(6) Volhard, *Ann.*, **253**, 206 (1889).

(7) Littmann, *THIS JOURNAL*, **57**, 586 (1935).

(8) "Organic Syntheses," **11**, 28, 70 (1931).

(9) "Organic Syntheses" **11**, 28, 70 (1931).

TABLE I
THERMAL DECOMPOSITION OF ACID ANHYDRIDES

	Succinic	Maleic	Citraconic	Itaconic
Moles used	0.284	0.163	0.517	0.193
Moles recovered	0.037	0.067	0.184	
% decomposed	87	58	64	99
Press., mm. Hg	10	10	50	3–4
Temp., °C.	880–900	820	750 ± 20	900
Contact time, sec.	0.2	0.08	0.11	0.05
Products (moles per mole of substrate decomposed) :				
CO	0.97	0.99	0.96	0.97
CO ₂	0.95	0.98	0.95	0.94
H ₂	0.06	Trace	None	..
C ₂ H ₄	0.87	Trace	None	..
C ₂ H ₂	0.05	0.96	None	..
CH ₃ —C≡CH	0.90	0.44
CH ₂ =C=CG ₂	None	0.56

practically completely decomposed. We obtained both methylacetylene and allene and cannot explain at present the formation of methylacetylene. Possibly the itaconic anhydride isomerized in the liquid state while it was being evaporated into the furnace.

Cyclopentadiene.—The explosive decomposition of cyclopentadiene has been studied at high pressures¹⁰ and a chain mechanism was suggested for its decomposition into carbon, methane, and a small amount of hydrogen. The cyclopentadiene used in this work was prepared by distilling the dimer, followed by a second distillation to remove residual traces of dimer.

The compound proved to be exceptionally stable and the amount of decomposition in our experiment was barely detectable; under the same conditions, *n*-butane would have undergone extensive decomposition. At the end of the run, the exit end of the furnace was quite clear and free from carbon and the recovered liquid had the same boiling point and refractive index as the original material. A small residue (0.3 g.) remained after distillation of a mole of product.

TABLE II
PYROLYSIS OF CYCLOPENTADIENE

Moles used	1.04
Moles recovered	1.035
% decomposed	0.5
Hg, mm.	10
Temp., °C.	900
Permanent gas, cc.	40
Contact time, sec.	0.018

The small amount of permanent gas was not analyzed.

Cyclopentene.—The thermal decomposition of this compound does not appear to have been studied. We prepared the sample used in our work by dehydrating cyclopentanol¹¹ with aqueous sulfuric acid. The material was then dried and after redistilling over sodium had a b. p. of 44.5°.

(10) Raistrick, Sapiro and Newitt, *J. Chem. Soc.*, 1761 (1939).

(11) The method used was similar to that for the preparation of cyclohexene, see "Organic Syntheses," Collected Vol. I, John Wiley and Sons, New York, N. Y., 1932, p. 177.

One-half mole of cyclopentene was passed through the furnace at 850°, 10 mm. pressure, and a contact time of 0.02 second. Approximately 20% decomposed under these conditions and gave the following moles of products per mole decomposed: ethylene, 0.07; propylene, 0.02; C₃H₄, 0.003; hydrogen, 0.96; cyclopentadiene, 0.93. The amount of cyclopentadiene in the product was found by distilling off all material boiling below 40° and determining the number of double bonds by hydrogenation. The result obtained by hydrogenation was checked by reacting with maleic anhydride.¹² The small C₃H₄ fraction was analyzed only for unsaturation and not for methylacetylene and allene.

Cyclopentane.—This compound has been pyrolyzed by Frey,¹³ by Kazanskii and Plate,¹⁴ and by Borisov, Shakhnazarova and Margolis.¹⁵ The main products appear to be hydrogen, ethylene, propylene, cyclopentene, and cyclopentadiene. This indicates two types of decomposition, namely, a dehydrogenation to cyclopentene and cyclopentadiene and rupture of C—C bonds leading to the formation of ethylene and propylene. The results of our work (Table III) indicate that the first reaction constitutes about one-third of the decomposition and the second reaction constitutes somewhat less than two-thirds of the decomposition. There is also an appreciable production of methane suggesting that about 10% of the decomposition is a radical chain. The cyclopentane was prepared by hydrogenating cyclopentene, prepared as described in the previous section. The purity of the cyclopentane was shown by a flat cooling curve, melting point -95.6°.

Methylcyclopentane.¹⁶—The pyrolysis of this compound has not been studied very extensively.¹⁷ Dr. Ruoff prepared this compound from cyclopentanone, making first methylcyclopentyl alcohol through the Grignard and then dehydrating and hydrogenating. The sample had a b. p. 71.5–71.8° and *n*^{20D} 1.4105. As will be seen from Table IV, a complicated decomposition occurs which may consist

(12) We wish to thank Dr. J. Greenberg, who worked out this method and made the determination.

(13) Frey, *Ind. Eng. Chem.*, **26**, 202 (1934).

(14) Kazanskii and Plate, *Ber.*, **67**, 1023 (1934).

(15) Borisov, Shakhnazarova and Margolis, *J. Gen. Chem.* (U. S. S. R.), **4**, 1385 (1934).

(16) All the experimental work on the preparation and pyrolysis of methylcyclopentane was performed by Dr. P. M. Ruoff. Preliminary work only was done on this compound and further investigation is required to establish the identity of hydrocarbons, having three or more carbon atoms, formed in the pyrolysis.

(17) See Kazanskii and Plate, *Ber.*, **67**, 1023 (1934); Ellis, "Chemistry of Petroleum Derivatives," Reinhold Publishing Corp., New York, N. Y., 1937, Vol. II, p. 90; Kuchler, *Trans. Faraday Soc.*, **35**, 874 (1939).

TABLE III

THERMAL DECOMPOSITION OF CYCLOPENTANE

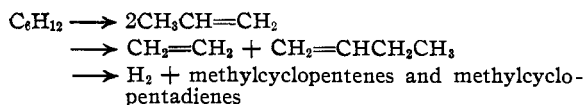
Moles used	0.475
% decomposed	11.4
Hg, mm.	10
Temp., °C.	900
Contact time, sec.	0.02

Products: (moles per mole decomposed)

H ₂	CH ₄	C ₂ H ₄	C ₃ H ₆	C ₃ H ₄ ^a	C ₅ H ₆	C ₅ H ₈
0.61	0.10	0.76	0.25	0.21		0.36

^a We did not determine whether the C₃H₄ was CH₃C≡CH or CH₂=C=CH₂.

of three reactions each occurring to a substantial extent, according to the equations



However, as our analytical results are incomplete, we have to base this conclusion on theoretical reasoning as well as on experiment.

TABLE IV

THERMAL DECOMPOSITION OF METHYLCYCLOPENTANE

Moles used	0.50					
% decomposed	10.5					
Hg, mm.	11					
Temp., °C.	900 = 50					
Contact time, sec.	0.022					
Moles of product per mole of substrate decomposed	H ₂	CH ₄	C ₂ H ₂	C ₂ H ₄	C ₃ H ₆	C ₃ H ₈
	0.75	0.44	0.02	0.33	0.65	
	C ₃ H ₄	C ₄ H ₆	C ₄ H ₈	C ₅ H ₈		
	0.16	0.13	0.15	None		

Summary

1. We have examined the thermal decomposition of certain five-membered rings from the standpoint of the principle of least motion.
2. A number of cyclic anhydrides decompose quantitatively into carbon monoxide, carbon dioxide, and an unsaturated hydrocarbon.
3. The decomposition of five-carbon rings is more complicated but the reactions occurring can be interpreted reasonably on the basis of the principle of least motion.

WASHINGTON, D. C.

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