These acids have been identified as dihydronaphthalene-1,4-dicarboxylic acid and an acid having adjacent carboxyl groups, one of which is in the 2-position. The latter acid is probably dihydronaphthalene-1,2-dicarboxylic acid.

A new procedure for converting dihydroaromatic dicarboxylic acids to monocarboxylic aromatic acids by oxidation with alkaline ferricyanide is described.

Naphthalene-1,4-dicarboxylic acid has been prepared in high yield by the oxidation of the dihydronaphthalene-1,4-dicarboxylic acid with bromine in glacial acetic acid.

NIAGARA FALLS, N. Y. RECEIVED DECEMBER 7, 1937

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

The Thermal Decomposition of Alicyclic Compounds. I. The Decomposition of Cyclohexene and Some Simpler Hydrocarbons

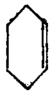
BY F. O. RICE, P. M. RUOFF[1] AND EDWARD L. RODOWSKAS

1. Introduction

In contrast to the thermal decomposition of open chain paraffin hydrocarbons to which the free radical chain mechanism may be applied successfully,[2] consideration of the decomposition of cyclic compounds indicates that an entirely different mechanism may be involved since a rupture of the ring does not cause the immediate formation of two radicals.

This difference in behavior may be ascribed to a fundamental difference between open chain and ring compounds; both may be regarded as being built up of small unsaturated molecules joined together by the opening of double or triple bonds; in ring compounds the two free valences are joined to form the ring and, thus, when a cyclic compound is ruptured, it can fall apart into its constituent molecules;[3] on the other hand, when an open chain compound is ruptured, the two free radicals fly apart and cannot undergo internal rearrangement into molecules.

Therefore, when a molecule such as cyclohexene is thermally decomposed, a primary rupture of a C–C bond may be postulated according to the equation



$$\longrightarrow -CH_2CH_2CH_2CH{=}CHCH_2- \qquad (1)$$

This particular rupture of a C–C bond rather than one of the two alternative scissions[4] has been selected because a resonating radical is formed which may also be written in the form

$$-CH_2-CH_2-CH_2-\overset{|}{C}H-CH{=}CH_2 \qquad (2)$$

but since neither of these forms represents the true formula, it is preferable to represent it as

$$-CH_2-CH_2-CH_2-CH{=}CH{=}CH_2 \qquad (3)$$

It seems reasonable to assume that the formation of this resonating radical will lower the activation energy required, and, therefore, the primary C–C rupture would be expected to occur in the beta-position to the double bond rather than at some other position which would not yield a resonating radical. It is, of course, possible that the intermediate radical, $-CH_2CH_2CH_2CH{=}CH{=}CH_2$, may have no appreciable stability so that the decomposition into ethylene and butadiene may occur in a single elementary act.[5]

The primary formation, then, of the radical (3) may be followed by a simple electronic rearrangement to give ethylene and butadiene according to the equation

$$-CH_2-CH_2-CH_2-CH{=}CH{=}CH_2 \longrightarrow CH_2{=}CH_2 + CH_2{=}CH-CH{=}CH_2 \qquad (4)$$

Since this decomposition of the radical (3) probably requires only a relatively small activation energy and involves nothing more than a change in electronic configuration, the reaction represented by equation (4) may be assumed to predominate and any attack of the radical (3) on the substrate such as

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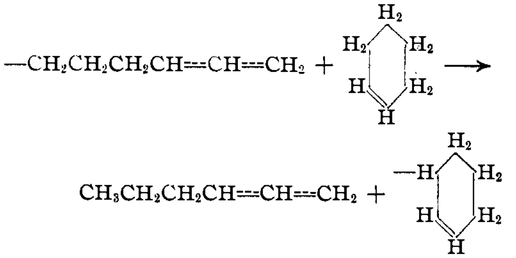
[1] Hormel Foundation Fellow, 1934–1938.

[2] (a) Rice, THIS JOURNAL, 53, 1959 (1931); (b) Rice and Rice, "The Aliphatic Free Radicals," the Johns Hopkins Press, Baltimore, Md., 1935; (c) Frey, *Ind. Eng. Chem.*, 26, 200 (1934).

[3] See ref. 2b, Chapter XIII.

[4] Presumably the rupture of a C–H or a C=C bond may be omitted from consideration, since they are far stronger than the C–C bond.

[5] For a discussion of resonance see Pauling and Sherman, *J. Chem. Phys.*, 1, 606 (1933); Ingold, *Chem. Rev.*, 15, 225 (1934); see also Harkness, Kistiakowsky and Mears, *J. Chem. Phys.*, 5, 682 (1937), who have proposed resonating free radicals for the association of dienes.


(5)

may be neglected.(6)

This reasoning appears to be well supported by our experimental results. When cyclohexene is decomposed at low pressures, almost theoretical yields (90–95%) of ethylene and butadiene are obtained. The dehydrogenation reaction

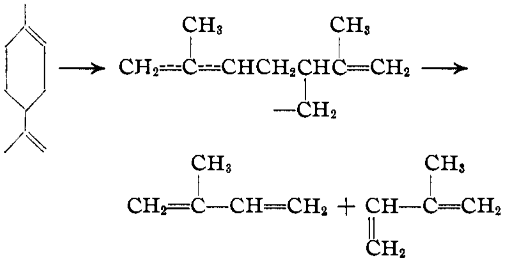
$$C_6H_{10} \longrightarrow C_6H_6 + 2H_2 \qquad (6)$$

occurs at most to the extent of 1 or 2%, and the same is true for a decomposition such as

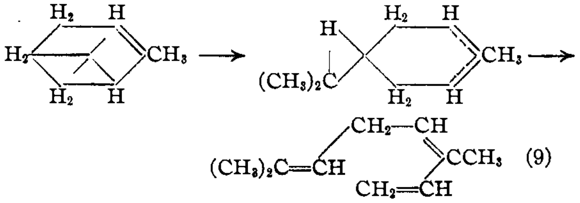
$$C_6H_{10} \longrightarrow 2C_2H_4 + C_2H_2 \qquad (7)$$

which produces acetylene. The most striking thing is the complete absence of tar or heavy oily products; at the end of a series of runs in which several moles of cyclohexene were decomposed, the exit end of the cracking furnace was perfectly transparent.

This manner of decomposition as illustrated in the case of cyclohexene seems to be characteristic of a number of cyclic compounds. It is interesting to note how frequently isoprene arises in the decomposition of monocyclic terpenes.(7) The decomposition of dipentene,(8) for instance, into isoprene may be pictured as


(8)

With some compounds, this picture must be modified slightly because the primary rupture of a C–C bond is followed by an electronic rearrangement and formation of a single product molecule. Thus the thermal isomerization of alpha-pinene would yield ocimene as earlier suggested.(3)


(9)

Rupture of the beta C–C bond in the four-membered ring would give a radical which would rearrange immediately to give ocimene. It is reported that ocimene isomerizes into alloocimene upon heating,(9) and the latter has been found recently in the thermal treatment of alpha-pinene.(10)

By following the principles illustrated in these examples, it would seem possible to predict the products formed in the pyrogenic decomposition of a great variety of unsaturated cyclic compounds.

2. Experimental Considerations

As a large number of procedures have been recommended for the thermal decomposition of organic compounds,(11) it is necessary to consider first the principles involved in relation to the various processes previously suggested.

Presumably the decomposition of a molecule such as cyclohexene consists of a primary unimolecular decomposition yielding two olefinic molecules. In general, it is the object of an experiment to preserve these product molecules unaltered and to recover the undecomposed part of the substrate. Certainly, if we wish to understand the mechanism of a decomposition it is necessary, as far as possible, to avoid (a) any unimolecular decomposition of the products or (b) any bimolecular reactions of the products with themselves or with the substrate.

The products which we have to consider are such compounds as acetylene, ethylene, ketene, allene, butadiene and their homologs. Previous work(12) gives but little precise information concerning the unimolecular decomposition of these compounds because they are all extremely reactive and polymerize easily to larger molecules. In order to test their stability, it is necessary to heat them at high temperatures and low pressures (5–15 mm.) since unimolecular decompositions

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(6) See, however, Egloff, "Reactions of Pure Hydrocarbons," Reinhold Publishing Co., 330 West 42d St., New York, N. Y., 1937, p. 694.

(7) Egloff, Herman, Levinson and Dull, *Chem. Rev.*, **14**, 287 (1934).

(8) Staudinger, *Ber.*, **44**, 2212 (1911).

(9) Enklaar, *Rec. trav. chim.*, **26**, 174 (1907).

(10) Arbusov, *Ber.*, **67B**, 563 (1934); see, however, Charlton and Day, *Ind. Eng. Chem.*, **29**, 92 (1937).

(11) Hurd, "Pyrolysis of Carbon Compounds," The Chemical Catalog Company, New York, N. Y., 1929, p. 117, contains a discussion of the different methods for terpene decomposition including pressure, vacuum and hot wire methods.

(12) Egloff and Parrish, *Chem. Rev.*, **19**, 150 (1936).

are unaffected by pressure change but bimolecular reactions are retarded. We have proved experimentally that ethylene and butadiene are extremely stable under these conditions.

The unimolecular decomposition of such products as these may be disregarded, since from this standpoint the products are more stable than the original substance. However, in certain cases, when the products are more complex and, consequently, less stable, the extent of decomposition of the original substance must be kept relatively small, within the range of 5–20%. This condition would apply, for example, to the decomposition of alpha-pinene but not to dipentene.

On the other hand, the second of these considerations, the polymerization or condensation of the olefinic product molecules, must be taken into account in all cases. At atmospheric pressure or higher, ethylene, for instance, gives chiefly olefins,[13] while butadiene readily undergoes a Diels–Alder reaction[14] with itself[15] and with ethylene[16] giving cyclic olefins.

But, as has been mentioned previously, ethylene and butadiene are very stable at conditions where these bimolecular reactions may be prevented, but where cyclohexene may still be decomposed. Thus, we found that neither ethylene nor butadiene polymerized or decomposed when passed through a quartz tube at 10 mm. pressure and at 855 and 750°, respectively. The time of contact was of the order of 0.03 and 0.01 second, respectively. At 970° and 4 mm. pressure, with 0.03 second contact, only about 2% of the ethylene decomposed to give acetylene and hydrogen. No condensation products were formed.

It is quite evident, then, that all pyrolytic reactions of cyclic compounds should be conducted at relatively low pressures; in the case of some of the larger molecules it may be necessary, in addition, to decompose to a small extent per pass in order to diminish the unimolecular decomposition of the product. Decomposing to a small extent also would diminish the bimolecular reactions of the products with themselves, and, to a lesser extent, the bimolecular reactions of the products with the substrate; however, by conducting the pyrolysis at low pressures, all of these bimolecular reactions may be rendered negligible without affecting the unimolecular reactions that give the desired products.

In addition to requiring proper experimental conditions, a study of the mechanism of decomposition reactions depends also largely upon the development of accurate methods of analytical separation and identification of the products formed.

3. The Decomposition of Cyclohexene

(a) Previous Work.—Except for the studies of Zelinsky,[17] the non-catalytic decomposition of cyclohexene at low pressures and temperatures above 300° has not been studied extensively. Generally, the experiments[18] have been conducted in the presence of catalysts and at normal pressures. Under these conditions either appreciable dehydrogenation to benzene or contamination with secondary products have been reported.[19]

Zelinsky, however, found that passing steam and cyclohexene through an empty silica tube at 650°, under conditions of considerable reduction of the partial vapor pressure of the hydrocarbon, ethylene and butadiene were obtained in yields of 78.3 and 65.2%, respectively. Hydrogen composed about 10% of the gaseous products while acetylene and propylene each were represented to the extent of 2–3%.

We have found that it is desirable to reduce the partial vapor pressure of the hydrocarbon to about one hundredth of an atmosphere and this is not practicable using an inert gas since over 2000 liters would be required per mole of substrate.

Our experiments show that at low pressures (7–15 mm.) and at 700–800°, cyclohexene decomposes practically quantitatively (90–95%) into ethylene and butadiene. Dehydrogenation occurs at the most to the extent of 1–2% while no propylene is found and acetylene is present in traces. One mole of substrate can be passed through the apparatus in about forty minutes.

(b) Apparatus and Materials.—A number of experiments using hot wire methods[20] and flowing methods[21]

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[13] (a) Storch, THIS JOURNAL, **56**, 374 (1934); (b) Pease, *ibid.*, **52**, 1158 (1930); (c) Frolich and Schneider, *Ind. Eng. Chem.*, **23**, 1405 (1931).

[14] Alder and Stein, *Z. angew. Chem.*, **50**, 510 (1937), give an excellent comprehensive review of this reaction.

[15] Vaughan, THIS JOURNAL, **54**, 3863 (1932); Moor, Strigaleva, Shilyaeva, *J. Gen. Chem.* (U. S. S. R.), **5**, 818 (1935); *C. A.*, **30**, 365 (1936).

[16] Wheeler and Wood, *J. Chem. Soc.*, 1819 (1930); see also ref. 13c.

[17] Zelinsky, *J. Gen. Chem.* (U. S. S. R.), **4**, 856 (1934); also Badische Anilin und Soda Fabrik, German Patent 252,499 (1912).

[18] (a) Jones, *J. Chem. Soc.*, **107**, 1582 (1915); (b) Mailhe, *Chemie et Industrie*, **29**, 757 (1933); (c) Hershberg and Ruhoff, *Org. Syntheses*, **17**, 25 (1937); (d) Wheeler and Wood, ref. 16.

[19] See Kistiakowsky, Ruhoff, Smith and Vaughan, THIS JOURNAL, **58**, 146 (1936).

[20] Herriott, *J. Gen. Physiol.*, **18**, 69 (1934); also Hershberg and Ruhoff.[18c]

[21] (a) Rice, Greenberg, Walters and Vollrath, THIS JOURNAL, **56**, 1760 (1934); (b) Rodowskas, Dissertation, Johns Hopkins University, 1935.

through hot tubes were made. It was found that the flowing method gives very satisfactory results. The substance is vaporized in a flask which is fitted with an electric heater covering its upper half. In this manner the liquid is vaporized from the surface and no bumping occurs even at the lowest pressures used. The vapor, then, at low pressures passes into the pyrolytic unit, a quartz tube to which is attached a manometer at one end and a thermocouple well at the other, then through two traps cooled to suitable temperatures, and thence to the pumping system which consists of a four-stage steel mercury vapor pump backed by an ordinary rotary pump in which the oil was replaced by glycerol. This allows the exit gases to pass through to a gas collecting bottle. The gases condensing in the traps are transferred to a low temperature Podbielniak still,[22] fractionated, and then further analyzed in a modified Shepherd gas analysis apparatus[23] augmented with a hydrogenation unit.[24] The gases passing through the pumps were also analyzed. The pyrolytic apparatus is shown in detail in Fig. 1.

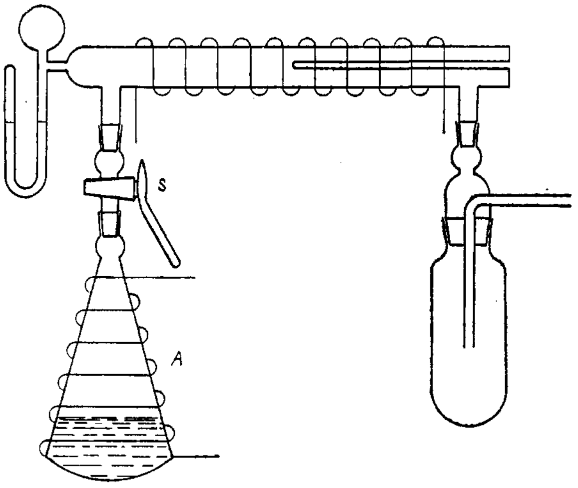

Fig. 1.—Apparatus for thermal decompositions at low pressures.

Eastman best grade of cyclohexene was used throughout these experiments. It was fractionated carefully in a 50-cm. air-jacketed Vigreux column provided with a water-cooled cold finger. The middle fraction (b. p. 82.0–82.5° at 755 mm., $n^{22.4}\mathrm{D}$ 1.4393) was checked for unsaturation by hydrogenation over Adams platinum oxide catalyst in a special apparatus designed to hydrogenate 0.1-mole quantities at constant pressure. The hydrogen consumption was within 2–3% of the theoretical.

(c) **Procedure.**—At the completion of a run, the first and second traps are allowed to warm up so that the ethylene and butadiene distil into a small receiver connected to the apparatus and cooled with liquid air. When the traps have warmed up to about 0°, they are heated rapidly to drive off the last traces of dissolved gases. Since butadiene is very soluble in cyclohexene and is also subject to polymerization, it is very important that this heating be rapid, and maintained until some cyclohexene distils into the receiver. The contents are then distilled in the low temperature column, collected in calibrated liter bulbs and analyzed by absorption in activated sulfuric acid and hydrogenation over nickel. The analysis by hydrogenation of the C_4 fraction showed that it consisted of 98% diolefin. It was completely absorbed by molten maleic anhydride.

The higher boiling portion is weighed and the combined liquids are then distilled in a Vigreux column. The boiling point range and the refractive index are compared with those of the original material.

The gas collected over the zinc sulfate solution after measuring, is transferred to a suitable container and then analyzed in the Shepherd apparatus. Hydrogen is determined over cupric oxide at 250°, unsaturates by absorption in activated sulfuric acid and then saturates by slow combustion. Since a small quantity of air is confined above the glycerol level in the rotary pump, oxygen must be removed first by adsorption in alkaline pyrogallol and then a correction must be applied for the residual nitrogen.

The tests for acetylene were made individually by allowing the gas sample from the C_2 fraction to expand into a small standard bulb until a pressure slightly less than atmospheric is reached. A standard amount of ammoniacal silver nitrate solution[25] is then sucked up into the bulb, which is shaken for about a minute. The amount of silver acetylide precipitate is compared with that in known mixtures of ethylene and acetylene. Hydrogenation over nickel confirmed these semiquantitative methods, while adsorption in the acetylene reagent, potassium iodomercuriate solution[25] (p. 267), was unsatisfactory for detection of very small amounts of acetylene in the presence of ethylene.

(d) Results and Discussion

Table I contains a summary of the results on the decomposition of cyclohexene; the data are incomplete in some cases because the gas analysis apparatus was under construction during part of the time these experiments were being carried out. No test for acetylene was made in these tabulated experiments; however, it was found later that, when cyclohexene is decomposed as much as 75% less than 1% of acetylene was present in the C_2 fraction. Thus it is established that acetylene was either entirely absent or present in traces only, in the earlier experiments. No acetylene was detectable in the gas collected over the zinc sulfate solution when 75% of the cyclohexene was decomposed. The Podbielniak distillation curve of the C_2 and C_4 fraction collected in traps B and C showed that no significant amount of any C_3 hydrocarbon was present.

Distillation of the liquid residue in the Vigreux column after all of the C_4 fraction had been col-

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[22] Podbielniak, *Ind. Eng. Chem., Anal. Ed.*, **5**, 119 (1933).

[23] Shepherd, *Bur. Standards J. Research*, **6**, 121 (1931).

[24] McMillan, Cole and Ritchie, *Ind. Eng. Chem., Anal. Ed.*, **8**, 105 (1936).

[25] Dennis, "Gas Analysis," The Macmillan Co., 60 Fifth Ave., New York, N. Y., 1929, p. 263.

TABLE I

DECOMPOSITION OF CYCLOHEXENE

The data in columns 1 and 2 were obtained with trial apparatus and conditions.

		1	2	3
1	Moles used	1.00	1.00	1.00
2	Moles decomposed	0.44	0.28	0.39
3	Furnace temperature, °C.	700–750	800–810	790
4	Pressure, mm.	12–15	7–10	10–13
5	Duration of run	40 min.	50 min.	40 min.
6	Time of contact, sec.	0.008	0.02	0.02
7	Gaseous products			
	a. C_2H_4 (moles)	.397	.246	.362
	b. C_4H_6	.359	.241	.359
	c. H_2	—	.021	.039
	d. Saturates	—	—	.008
	e. C_2H_2	—	—	—
8.	Yield of gaseous products, %			
	a. C_2H_4[a]	90.5	89.1	93.0
	b. C_4H_6[a]	81.6	87.1	92.2
	c. H_2[b]	—	1.0	2.0

[a] Based on moles C_6H_{10} decomposed. [b] Assuming $C_6H_{10} \longrightarrow C_6H_6 + 2H_2$.

lected, indicated no products present whose boiling points ranged from −4 to 80°. We have concluded, therefore, that there was no appreciable isomerization to the methylcyclopentenes since these have lower boiling points and would have been detected. A very slight amount of brownish oil remained in the final holdup.

A comparison of the liquid residue with the original cyclohexene is as follows:

	B. p. °C. (755 mm.)	Refractive index 22.4°
Cyclohexene, C. P.	82.0–82.5	1.4393
Liquid residue	81.0–82.5	1.4408
Benzene, C. P.	78.0–79.0	1.4938

The refractive index measurements suggest that benzene may be present as much as 2%, which more or less agrees with the amount of hydrogen evolved during the pyrolysis. It is possible that some of the cyclohexene may have dehydrogenated to cyclohexadiene which may explain the slight amount of brownish oil in the liquid holdup, since cyclohexadiene is polymerized easily by heat. However, since the extent of dehydrogenation was practically insignificant as compared to the main reaction, the identification of a dehydrogenation product was not investigated further.

4. The Decomposition of Some Simpler Hydrocarbons

In connection with the work on cyclohexene, it is desirable to know something regarding the stability of some related hydrocarbons, particularly those produced in the decomposition of cyclohexene itself. We therefore made a study of the decomposition of ethylene, ethane, butadiene and butane under conditions as similar as possible to those used in the decomposition of cyclohexene. The various hydrocarbons were obtained from commercial sources; they all were distilled carefully in a Podbielniak apparatus and only the middle portion used. On analysis by catalytic hydrogenation, the ethane and butane absorbed no hydrogen and the ethylene and butadiene absorbed the theoretical amounts within ±2%. None of the gases contained any detectable quantity of acetylene.

The results for ethane and butane are shown in Table II from which it will be seen that only slight decomposition occurs under conditions such that cyclohexene undergoes very extensive decomposition. The analyses shown were obtained by a Podbielniak distillation supplemented by gas analysis, but owing to the small amounts of products the analyses are not very accurate.

TABLE II

DECOMPOSITION OF ETHANE AND BUTANE

	C_2H_6	C_4H_{10}
Moles used	0.776	0.452
Moles decomposed[a]	.003	.0183
Per cent. decomposed	.4	4.0
Temperature, °C.	795	795
Pressure, mm.	10	10
Time, min.	22	14
Contact time, sec.	0.020	0.021
Products collected over $ZnSO_4$, (N. T. P.), cc.	82	474
(a) H_2, moles	0.0026	0.0083
(b) C_2H_4, moles	.0003	.0003
(c) C_3H_6, moles	None	.0001
(d) C_nH_{2n+2} (chiefly CH_4)	0.0008	.0125
Remaining products		
(a) C_2H_2, moles	None	Trace
(b) C_2H_4, moles	0.0003	0.0102
(c) C_3H_6, moles	None	.0020
(d) C_4H_8, moles	None	(.0083)[b]
(e) Higher hydrocarbons	None	None

[a] Based on weight of products obtained. [b] Assumed to be equal to the hydrogen produced because 1,3-butadiene and acetylene were tested for and found to be absent.

Ethylene was found to be extremely stable under these conditions and even when the temperature was raised to 855°, did not decompose to any measurable extent. No hydrogen or acetylene was formed and all the ethylene was recovered unchanged after passage through the furnace.

Butadiene was also found to be very stable and decomposed at most to the extent of a few tenths of a per cent. (see Table III). No polymer of any kind was formed and practically all the butadiene was recovered unchanged. There was no trace of any tarry or oily deposit at the exit end of the furnace. In Table IV we give a comparison of the extent of decomposition of these hydrocarbons under comparable conditions.

TABLE III

DECOMPOSITION OF BUTADIENE

Moles used	0.607
Moles decomposed[a]	.002
Per cent. decomposed	.3
Temperature, °C.	795
Pressure, mm.	10
Time, min.	22
Contact time, sec.	0.025
Products collected over $ZnSO_4$ (N. T. P.), cc.	40
(a) C_nH_{2n}, moles; chiefly C_2H_4 (some butadiene)	0.0002
(b) H_2, moles	.0009
(c) C_nH_{2n+2}, moles; chiefly CH_4	.0006
(d) C_2H_2, moles	None
Remaining products	
(a) C_2H_4, moles	0.0027
(b) C_2H_2, moles	.0003

[a] Based on weight of products obtained.

TABLE IV

SUMMARY

Hydrocarbon	Temp., °C.	Press., mm.	Contact time sec. × 10^{-2}	% decomp.
Ethylene	855	10	3.0	Stable
Ethane	795	10	2.0	0.4
1,3-Butadiene	795	10	2.5	.3
n-Butane	795	10	2.1	4.0
Cyclohexene	790	10	2.0	39.0

5. Test for Radicals

It seemed desirable to attempt to obtain more direct experimental evidence concerning the primary decomposition of cylcohexene, by making a test for free radicals by the use of metallic mirrors. The technique of this method has been described fully by Rice, Johnston and Evering.[26] In this part of the work, the vapor of an organic compound was decomposed in a free radical apparatus at a furnace pressure of 0.75 mm. Standard mirrors of antimony were placed at various distances from the furnace and the time of removal was measured with the furnace at various temperatures. The apparatus was first tested using acetone which is known to decompose into free radicals; these removed antimony and tellurium mirrors readily. Tests were then made with cyclohexane, cyclohexene and butadiene but no positive results were obtained because of the exceedingly slow rate of removal of the mirrors by these substances. There seemed to be a small amount of free radicals formed since when we used tellurium mirrors a very minute amount of some unstable telluro-organic compound formed which we were not able to identify.

When cyclohexane was passed through the furnace at 850°, the exit gases removed antimony mirrors very slowly but the rate was only about 0.05 that of acetone under the same conditions. We made a run of several hours using a tellurium mirror and obtained a very small amount of reaction products which we were not able to identify.

Cyclohexene was investigated using both antimony and tellurium mirrors. The results were identical in both cases. The following comparison gives an approximate measure of the rate of removal of a standard antimony mirror for cyclohexene and acetone. The distance of the mirror from the edge of the furnace was 20 mm.

Temp., °C.	750	850	950
Cyclohexene	2 min. (incomplete)	65 sec. (incomplete)	8 sec.
Acetone	55 sec.	6 sec.	2 sec.

We also tried to identify the fragments from cyclohexene but could not obtain any definite results. The telluro-organic compound was caught in a preliminary dry-ice trap at −80°. It was present in very small amounts mixed with some cyclohexene. The compound formed was orange-red in color and on being allowed to warm up to 0°, or on coming in contact with air, immediately decomposed depositing metallic tellurium.

Butadiene was also passed through the furnace and tested in the same way as cyclohexene. The following results were obtained

Temp., °C.	750	850	950
Butadiene	5 min. (incomplete)	55 sec.	25 sec.
Acetone	50 sec.	6 sec.	2.5 sec.

An orange-yellow highly unstable tellurium compound was isolated in the preliminary dry-ice trap. In odor, appearance and instability it clearly resembled the tellurium compound described under cyclohexene. Upon warming the liquid air trap, acetylene was identified as a decomposition product by the copper acetylide test.

Abundant deposits of carbon were found on the walls of the quartz reaction tube when both butadiene and cyclohexene were decomposed under these conditions.

Summary

1. Cyclohexene can be decomposed practi-

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(26) Rice, Johnston and Evering, THIS JOURNAL, **54**, 3529 (1932); see also ref. 2b.

cally quantitatively into 1,3-butadiene and ethylene by heating at about 10 mm. pressure and 800°.

2. The rate of decomposition of ethylene and 1,3-butadiene is negligible under these conditions as compared with cyclohexene.

3. A test for free radicals showed that the rate of removal of metallic mirrors by the fragments from cyclohexene is of a lower order as compared with the rate of removal by open chain compounds such as acetone.

4. We assume that the primary step consists of rupture of a C–C bond in the beta-position to the double bond, followed by decomposition into ethylene and butadiene. No radical chain mechanism occurs as in the case of open chain compounds.

Baltimore, Maryland Received January 31, 1938

[Contribution from the Chemical Laboratory, Washington Square College, New York University]

The Mechanism of the Photodecomposition of Methyl and Ethyl Iodides[1]

By W. West and Leo Schlessinger

The investigations of the photodecompositions of the alkyl iodides hitherto reported have been concerned chiefly with the value of the quantum yield in terms of the relation between the amount of iodine produced and the number of photons absorbed. But a detailed comparison between the carbonaceous products and the iodine formed is essential to an understanding of the reaction, as, obviously, estimates of the quantum yield based solely on the iodine produced will be completely fallacious if, as is conceivable, substantial amounts of iodated hydrocarbons are also formed. Emschwiller[2] has indeed described in considerable detail the carbonaceous and other products in the photodecomposition in the liquid phase, and Spence and Wild[3] have investigated the gaseous products of the decomposition of methyl iodide. These were found to consist mostly of methane, in an amount several times more than equivalent to the iodine formed, showing the production of iodated products. In the experiments to be described, we have sought to determine quantitatively the decomposition products of the two lower alkyl iodides, both in the region of continuous absorption centered round λ 2500 Å. and in the second region of ultraviolet absorption beginning at about λ 2000 Å.

Experimental Procedure

The photolyses were carried out statically. Quartz vessels attached to the vacuum line by graded seals, were filled to the desired pressure with alkyl iodide vapor and detached, with strict precautions to eliminate traces of oxygen and mercury vapor, by the procedure previously described.[4] Illumination in the region of continuous absorption was effected by placing the vessels, 25-cc. cylinders, 1.5 cm. in diameter, as close as possible to two or four low pressure high voltage mercury arcs, emitting most of their radiation at λ 2537 and 1849 Å. The latter radiation was mostly excluded by wrapping the cell in two layers of cellophane, or, in certain experiments, in which the elimination of even traces of the short wave radiation became essential, by immersing lamps and cell in a solution of 1 *N* acetic acid. Cells with plane windows, exposed to an intense zinc spark from which the radiation at λ 2026 to 2100 Å. was isolated by differential focusing, were used in the second region of absorption.

In collecting the products, arrangements were made to avoid the passage of material through stopcocks by means of the well-known device of breaking a capillary tube by a magnetic hammer: at the same time this absence of stopcocks during illumination prevented the possibility of small air leaks. After exposure, the reaction cell was sealed to the collecting system, consisting of various traps and a Töpler pump. By appropriate cooling, the capillary separating the reaction cell from the traps having been broken by the hammer, the products volatile at −180° (hydrogen and methane) were collected and examined separately from those volatile at −80° and the residue was examined for iodine and other non-volatile products. Pressure gages on the high and low pressure sides of the Töpler allowed the removal of the gas to be followed; usually 0.5 to 1.5 cc. (at one atm.) was collected, and this represented about 95% of the total gaseous product.

The micro-analytical technique for gases developed by Leighton, Blacet and Macdonald[5] proved highly satisfactory for the examination of the gaseous products. A few operations specific to the analyses performed here should perhaps be alluded to. Small amounts of alkyl iodide vapors were removed by sintered glass beads impregnated with dimethylaniline, the absorption requiring ten to fifteen minutes at 70°. Ethane and ethylene, however, are appreciably soluble in dimethylaniline, and in order to avoid errors due to loss of these gases, the sample of gas to be analyzed was divided into two portions, one of which was used to saturate the bead, which was then transferred to the sample to be analyzed, saturated with

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(1) Presented in part at the meeting of the American Chemical Society, April, 1937, at Chapel Hill, N. C.

(2) G. Emschwiller, *Ann. chim.*, **17**, 413 (1932).

(3) R. Spence and W. Wild, *Proc. Leeds Phil. Soc.*, **3**, 141 (1936).

(4) W. West and E. Ginsburg, This Journal, **56**, 2626 (1934).

(5) Leighton, Blacet and Macdonald, *Ind. Eng. Chem., Anal. Ed.*, **3**, 266 (1931); **6**, 344 (1934).