

creasing concentration of sodium acetate. In the case of plumbic acetate, the solubility is *decreased* by the addition of the sodium salt. There is no evidence for the existence of compounds corresponding to the plumbates of the aqueous system. The absence of amphoteric properties of plumbic acetate would, by itself, be difficult to reconcile with the generally analogous behavior of corresponding compounds of the water and the acetic acid systems. In view of the other facts here presented, however, the decrease in solubility of plumbic acetate in the presence of sodium acetate appears merely as an instance of the "salting out" of a non-electrolyte.

### Summary

1. The solubility of plumbic acetate in acetic acid over a wide range of temperature was determined. No solvate was isolated.

2. The conductivities of solutions of plumbous and plumbic acetates in acetic acid at 30°, over a range of concentrations, were measured. The former was found to behave as a typical weak base, the latter as a non-electrolyte.

3. The solubility of plumbic acetate was found to decrease with increasing concentration of sodium acetate. There was no evidence of amphoteric behavior.

LAWRENCE, KANSAS

RECEIVED MARCH 20, 1942

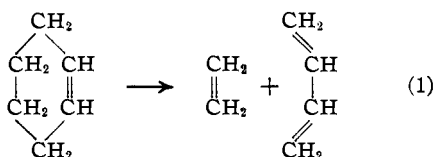
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE CATHOLIC UNIVERSITY]

## The Decomposition of Cyclohexene Oxide and 1,4-Cyclohexadiene from the Standpoint of the Principle of Least Motion<sup>1</sup>

BY FRANCIS OWEN RICE AND ADRIAN L. STALLBAUMER

(I) **Cyclohexene Oxide.**—In this paper we propose to discuss the homogeneous thermal decomposition of organic compounds in the gaseous state, more particularly with reference to two compounds which we have investigated experimentally. The principle of least motion which we use to interpret our results has been discussed in a recent paper.<sup>2a</sup>

Before taking up in detail the decomposition of cyclohexene oxide, we should like to point out that under certain conditions<sup>2b</sup> cyclohexene decomposes according to the following equation, in which ethylene and butadiene are the sole products



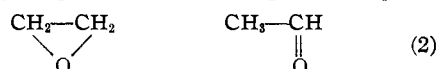
This decomposition illustrates the value of the principle of least motion because this reaction obviously requires less motion of the constituent atoms and involves less disturbance of the electronic system than any other thermodynamically possible reaction that can be written.

(1) This is taken from the dissertation presented by Adrian L. Stallbaumer for the Degree of Doctor of Philosophy in the Catholic University.

(2a) Rice and Teller, *J. Chem. Physics*, **6**, 489 (1938); **7**, 199 (1939).

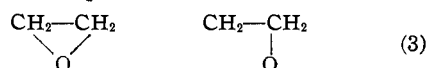
(2b) Rice, Ruoff and Rodowskas, *THIS JOURNAL*, **60**, 955 (1938).

A second reaction that we wish to discuss in this connection is the decomposition of ethylene oxide.<sup>3</sup> The decomposition is obviously complicated yielding methane and carbon monoxide as the final products presumably produced from the decomposition of acetaldehyde which appears as an intermediate product. We exclude a direct migration of a hydrogen atom according to the equation



both from the principle of least motion (attack of a hydrogen atom on a shielded carbon atom) and also on the experimental basis that ethylene oxide produces free radicals (Paneth effect) under conditions<sup>4</sup> where acetaldehyde is stable. Accordingly we are forced to assume that the change of ethylene oxide into acetaldehyde is not a single step reaction merely involving the migration of a hydrogen atom.

The first step of the decomposition of ethylene oxide may occur in two ways. The first way represented by the equation

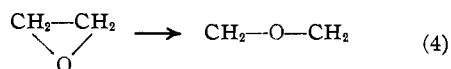


seems unlikely because migration of a hydrogen atom to the exposed end carbon atom could read-

(3) Heckert and Mack, *ibid.*, **51**, 2706 (1929).

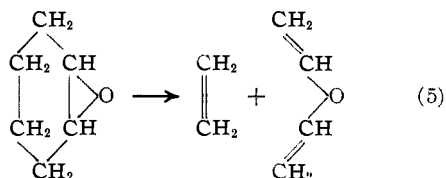
(4) Rice and Rice, "The Aliphatic Free Radicals," The Johns Hopkins Press, Baltimore, Md., 1935, p. 160.

ily occur and acetaldehyde would form in the same way that ethylene forms from diazoethane.<sup>4a</sup> The second possible method of decomposition may be represented by the equation



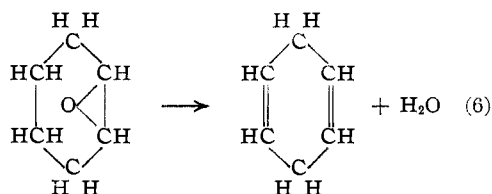
and is, we believe, followed by a radical chain decomposition leading to the formation of acetaldehyde. The radical  $\text{CH}_2-\text{O}-\text{CH}_2$  cannot isomerize to any molecule unless the constituent atoms undergo a very large amount of motion indeed.

We are now prepared to discuss the thermal decomposition of cyclohexene oxide. If we assume that the decomposition occurs by rupture of a carbon-carbon bond in a manner similar to that shown in Eq. 4, we may expect the production of ethylene and divinyl ether according to the equation



Actually no divinyl ether was found in the decomposition so that we may assume that incorporating the two carbon atoms of ethylene oxide into a six-membered ring somewhat strengthens the bond between them.

On the other hand, if the carbon-oxygen bond breaks in a manner similar to that shown for ethylene oxide in Eq. 3, we may expect that this will be followed by exceedingly rapid isomerization to cyclohexanone. Our experiments show that there is indeed extensive formation of cyclohexanone. However, this decomposition is accompanied by another because we find in the products appreciable quantities of water, acetylene, butadiene and a hydrocarbon which we believe is 1,4-cyclohexadiene. The appearance of these products would seem to indicate that the following reaction occurs



(4a) Rice and Glasebrook, *THIS JOURNAL*, **56**, 741 (1934).

The occurrence of small amounts of water and a  $\text{C}_3$  diolefin would not appear to be unreasonable in spite of the relatively large hydrogen-oxygen distances in cyclohexene oxide since these distances become smaller during the normal vibrations of the molecule. The partial decomposition of 1,4-cyclohexadiene into acetylene and butadiene is exactly parallel to the decomposition of cyclohexene into ethylene and butadiene shown in Eq. 1.

### Experimental

The cyclohexene oxide was prepared according to a method given in "Organic Syntheses."<sup>5</sup> A second sample was prepared by oxidizing cyclohexene with perbenzoic acid in chloroform solution.<sup>6</sup> The only point requiring special notice in this preparation is that after both reactants have been added, the homogeneous solution must not be allowed to rise above  $0^\circ$  and must be stirred for about ten hours. This is because the reaction is slow and exothermic and, even if kept in an ice-bath, stirring is necessary to prevent local heating. The pyrolytic apparatus used was essentially the same as that described in a preceding article.<sup>2b</sup> The cyclohexene oxide was passed through a quartz tube at a known temperature, the condensable products were caught in traps and the permanent gases were collected over saturated aqueous zinc sulfate solution after leaving the glycerol pump. Podbielniak distillations supplemented by gas analysis enabled us to make a satisfactory analysis of the products and obtain a weight balance. Table I shows the results of three experiments in which cyclohexene oxide was decomposed.

TABLE I  
THERMAL DECOMPOSITION OF CYCLOHEXENE OXIDE

	I	II	III
Moles used	1.00	1.15	0.95
Decomposed, %	25	6	27.6
Press., mm.	10	10	6
Temperature, $^\circ\text{C}$ .	780	630	735
Contact time, sec.	0.030	0.038	0.048
Water recovered, g.	2.0	1.3	3.6
"1,4-Cyclohexadiene," g.		1.1	4.9
Cyclohexanone, g.			22.3
Butadiene, moles	0.016	0.001	0.005
Acetylene	.015	.003	.016

The cyclohexanone was identified by its boiling point, refractive index and conversion into the oxime. We did not make a satisfactory identification of the material, which we assumed to be 1,4-cyclohexadiene. However, this material had two double bonds, boiled at  $88^\circ$ , was liquid at  $-80^\circ$  and its refractive index was  $n_D^{20}$  1.4680. The hydrocarbon, 1,4-cyclohexadiene, does not seem to have been very well characterized and its boiling point is variously reported<sup>7</sup> from  $84-89^\circ$  (760 mm.) and  $n_D^{20}$   $1.47 \pm 0.003$ .

(5) "Organic Syntheses," Vol. V, John Wiley and Sons, Inc., New York, N. Y., 1925, pp. 31, 35.

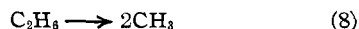
(6) Godchot and Bedas, *Compt. rend.*, **174**, 462 (1922); see also Bartlett and Bawley, *THIS JOURNAL*, **60**, 2418 (1938).

(7) Egloff, "Physical Constants of Hydrocarbons," Reinhold Publishing Corp., New York, N. Y., 1940, Vol. 2, p. 407.

(II) **1,3-Cyclohexadiene.**—We studied this compound because we hoped it would throw light on the decomposition of ethane which yields ethylene and hydrogen according to the equation

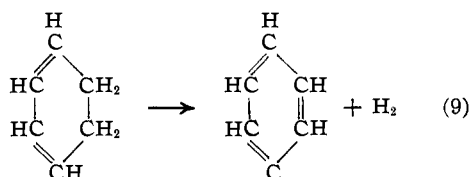


This may occur by the direct separation of molecular hydrogen in a single elementary act or it may occur by the primary separation into two methyl radicals according to the equation

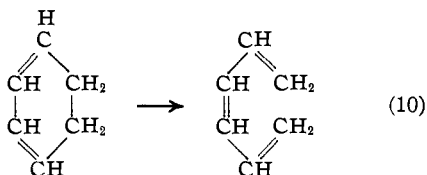


followed by a radical chain.

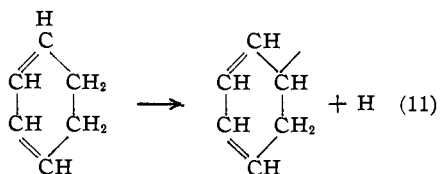
It seemed at the commencement of this investigation that we could distinguish between these two possibilities in the case of 1,3-cyclohexadiene because the final product would be different depending upon whether the process represented by Eq. 7 or that of Eq. 8 was followed. The process analogous to Eq. 7 would be



in which the separation of hydrogen occurs in a single elementary act; on the other hand, the process analogous to Eq. 8 is



Actually the experimental results showed that benzene and hydrogen are the only products and that there is no 1,3,5-hexatriene formed. However, after further consideration we concluded that our experiment is not after all decisive, and the reaction shown by Eq. 9 may not be the separation of a hydrogen molecule in a single elementary act. This is because the separation of a hydrogen atom from 1,3-cyclohexadiene according to the equation



results in a large gain of resonance energy in the ring so that the C-H bond may be as weak or even

weaker than a C-C bond. Consequently reaction 9 may also occur by a hydrogen atom chain in a manner similar to that postulated for ethane.

It is not even necessary to assume the initial separation of a hydrogen atom as shown in Eq. 11 because a trace of free radicals produced by impurities or initiated at the wall could start a hydrogen atom chain.

### Experimental

Six moles of a commercial sample of *o*-cyclohexanediol was acetylated according to standard procedure and 4.4 moles of diacetate [b. p. 240° (760 mm.) and 133° (33 mm.)] were obtained; the yield was 73%. The decomposition of the diacetate to 1,3-cyclohexadiene and acetic acid was performed in the apparatus previously described in which 820 g. (4.1 moles) was pyrolyzed at 750° and 6 mm., the time of the run being six hours; a 50% yield was obtained.

In Table II we show the results of a preliminary experiment on the decomposition of cyclohexane diacetate in which we made an over-all balance and established the fact that hydrogen is formed to the extent of less than 5% and that the main product is 1,3-cyclohexadiene.

TABLE II  
PYROLYSIS OF CYCLOHEXANE DIACETATE AND 1,3-CYCLOHEXADIENE

	Cyclohexane diacetate	1,3-Cyclohexadiene
Moles used	0.897	0.67
Moles recovered		None
Decomposed, %	84	100
Mm. Hg	6	4-6
Temperature, °C.	660	960
Moles permanent gas	0.123	0.518
Contact time, sec.	.186	.157
Gaseous products (moles per mole decomposed)		
Hydrogen	0.034	0.53
Methane	.054	.15
Carbon monoxide	.031	...
Ethylene	.021	.05
Carbon dioxide	.012	...
Propylene	.009	.13
Acetylenes	.004	.07
Liquid products (moles per mole decomposed)		
Cyclohexadiene	0.45	...
Benzene	Trace	0.70

In Table II we also give the results of the pyrolysis of 1,3-cyclohexadiene. We performed the experiment at high temperature because we wanted to attain 100% decomposition and thus avoid the difficulty of separating the products from undecomposed substrate; since we anticipated that all the possible products would be very stable we felt that in this particular experiment the procedure would not lead to difficulties due to decomposition of the products. Furthermore, we performed the experiment at a rather low pressure in an attempt to avoid as far as possible the initiation of chain decompositions by the adventitious formation of traces of free radicals. As will be seen in the table we ob-

tained a 70% yield of benzene and 53% of hydrogen. Since 15% of methane was formed it is evident that some sort of secondary chain reaction accompanies the main decomposition into benzene and hydrogen in spite of the low pressure. In these circumstances we feel that we cannot neglect the possibility that 1,3-cyclohexadiene may have been formed by a chain reaction in which a hydrogen atom is one of the chain carriers.

#### Summary

1. We have discussed the thermal decomposition of organic compounds from the standpoint of the principle of least motion and have pointed

out that organic decompositions may consist of a comparatively few elementary (*i. e.*, single step) reactions.

2. On heating cyclohexene oxide the main change is a rearrangement to cyclohexanone. This is accompanied by a decomposition of the cyclohexene oxide into water and a hydrocarbon, probably 1,4-cyclohexadiene.

3. 1,3-Cyclohexadiene decomposes into benzene and hydrogen.

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RECEIVED JANUARY 14, 1942

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

## Reproducible Contact Angles on Reproducible Metal Surfaces. II. Interfacial Contact Angles between Water and Organic Liquids on Surfaces of Silver and Gold

BY F. E. BARTELL AND PAUL H. CARDWELL

The angle formed at the line of contact of two liquids, such as water and an organic liquid, against a solid phase is generally referred to as an *interfacial contact angle*. Reliable data pertaining to interfacial contact angles could be of much importance, but such data as do exist are for the most part of questionable value, for seldom do data presented by different investigators show good agreement.

One difficulty which besets the investigator is that, for a given system, he may obtain different and *apparently* stable angles anywhere between two fairly wide limits. The limits of variation are the values of the angles which have usually been referred to as "advancing" and "receding" contact angles. This same variation exists also with contact angles of solid-liquid-air systems and has been discussed in an earlier paper.<sup>1</sup>

In the majority of investigations the fact that the two liquids of a solid-liquid-liquid system possess at least limited miscibility has been largely disregarded. Furthermore, it appears that no one has given much consideration to the possibility that adsorption of the dissolved material might occur at either or both of the solid-liquid interfaces, nor to the fact that highly condensed and firmly held layers might be formed which could not easily be removed and which, by their presence, would cause considerable alteration of interfacial tension.

In the present investigation it has been quite

conclusively demonstrated that all of the factors mentioned above must be taken into consideration. In addition it has been shown that time must be allowed for any given system to attain equilibrium. Moreover, in case the experimental procedure is such as to bring about a slight displacement of the liquid-liquid interface at the line of contact with the solid, there then exists a tendency for a comparatively great readjustment of conditions at and near the line of intersection of the interfaces. Such readjustment would involve partial or total removal or deposition of condensed layers as well as both adsorption and desorption processes and might require considerable time before the reattainment of equilibrium.

The solid surfaces selected for study in the present investigation were silver and gold surfaces formed by vaporization and subsequent condensation on Pyrex tips.<sup>1</sup> The liquids were "conductivity" water and purified isoamyl alcohol, *n*-butyl acetate, benzene,  $\alpha$ -bromonaphthalene and heptane. The interfacial contact angles were formed with each of these different organic liquids against water on the solids. To save time in attaining equilibrium conditions each pair of liquids (*i. e.*, water and each of the organic liquids) used in this research were mutually saturated before use and it is to be understood that when reference is made to one of the liquids it refers to that liquid as being saturated with the other liquid of the pair.

(1) Bartell and Cardwell, *THIS JOURNAL*, **64**, 494 (1942).