termined by a Volhard titration (43 mg.). The amount of ammonium chloride which underwent reaction was therefore 388 mg.

The methyl chloride was determined in both solutions as methyl iodide.[6] A total amount of 195 mg. of methyl chloride was found. Ammonia was determined by direct titration, 85 mg. was found. The yield of methyl chloride calculated on the basis of ammonium chloride which underwent reaction was 53%; that of ammonia 69%.

The authors acknowledge the assistance of Miss H. Berliner.

Summary

Diazomethane was allowed to react with di-ammonium malonate, di-ammonium succinate, di-ammonium phthalate, di-(methylammonium) phthalate, di-(ethylammonium) phthalate, di-(dimethylammonium) phthalate, and di-(triethylammonium) phthalate.

In all cases the dimethyl esters of the corresponding dibasic acids were obtained.

Reaction of diazomethane with ammonium chloride yielded methyl chloride.

During these esterifications ammonia, methylamine, ethylamine, dimethylamine and triethylamine were evolved from the corresponding ammonium and N-substituted ammonium salts.

JERUSALEM, PALESTINE RECEIVED JANUARY 24, 1944

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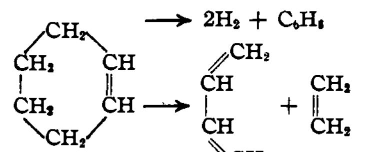
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE JOHNS HOPKINS UNIVERSITY]

The Thermal Decomposition of Substituted Cyclohexenes[1]

BY F. O. RICE[2a] AND MARY THOMAS MURPHY[2b]

1. **Introduction.**—If cyclohexene is heated above its decomposition point, at low pressures and for a time sufficiently short that only a small fraction is decomposed, it undergoes a simple dissociation into smaller molecules. The particular conditions mentioned have been selected in order to avoid as far as possible bimolecular reactions of the products with each other or with the substrate. Several thermodynamically possible decompositions may occur such as



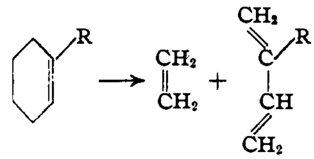
(1)

(2)

Reactions of these types have been discussed in a recent paper[3] in the light of a principle called the principle of least motion. In the case of several reactions such as those listed above which are all thermodynamically possible, the principle states that that reaction is favored which involves as little motion of the atoms as possible in passing from the old to the new configuration. The second half of the principle states that a reaction will be favored which involves least change of the electronic configuration of the reacting system. From both these standpoints, it is plausible to assume that the reaction will be favored which involves breaking or making as few bonds as possible.

On the basis of this principle we would predict with some confidence that reaction (2) would be greatly favored over reaction (1) and this has actually been found experimentally[4]; no benzene is found in the products but butadiene and ethylene are formed in almost theoretical yield. An investigation, therefore, of the decomposition of substituted cyclohexenes would provide not only a further test of the principle of least motion but also a method of preparing substituted butadienes.

2. **1-Methylcyclohexene.**—We found that this compound decomposes to the extent of about 80% according to the equation ($R = CH_3$)



(3)

As might be expected, secondary reactions occur to a larger extent than in the decomposition of cyclohexene. For every 100 molecules of methylcyclohexene decomposed, about 40 molecules of hydrogen and 30 molecules of methane are formed in subsidiary reactions. Since separate experiments showed that isoprene itself is decomposed to the extent of only a few per cent. under the experimental conditions, doubtless the secondary reactions are due in greater part to attack of free radicals on the substrate.

Zelinski and co-workers[5] pyrolyzed a number of substituted cyclohexenes both alone and diluted with water vapor. They obtained a yield of 75% ethylene and 35.3% isoprene by heating 1-methylcyclohexene at 690°.

3. **1-Ethylcyclohexene.**—There seems to be extensive decomposition which produces much methane and hydrogen; presumably there must be highly unsaturated C_8 or C_6 hydrocarbons formed although we could not identify anything in the higher fractions in spite of a careful search for ethylbutadiene which would be expected ac-

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(1) Original manuscript received June 28, 1943.

(2) (a) Present address, Catholic University, Washington, D. C. (b) Present address, College of Chestnut Hill, Philadelphia, Pa.

(3) Rice and Teller, *J. Chem. Phys.*, **6**, 489 (1938).

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

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TABLE I

PYROLYSIS DATA

	1-Methylcyclohexene	1-Ethylcyclohexene	1-Phenylcyclohexene	3-Vinylcyclohexene	Dipentene	3-*p*-Menthene
Moles used	0.516	0.664	0.493	1.05	0.98	0.50
% decomposed	10	14	23	61	33	6
Pressure in mm.	8	10	5–10	12	10	5
Furnace temp., °C.	750 ± 20	700 ± 10	750 ± 10	700 ± 10	700 ± 10	655 ± 10
Contact time, sec.	0.02	0.02	0.04	0.03	0.06	0.03
			Moles of product per mole of substrate decomposed			
H_2	0.42	0.21	0.17	0.06	0.13	0.36
CH_4	0.29	0.35	0.08	0.05	0.15	0.49
C_2H_2	..	..	..	0.02	..	..
C_2H_4	1.00	0.52	0.87	0.11	0.14	0.15
C_2H_6	..	0.02	..	..	..	0.0[illegible]
C_3H_4	..	..	..	..	0.02	..
C_3H_6	0.08	0.05	..	..	0.10	0.73
C_4H_6	0.06	..	..	1.60	0.02	0.03
C_5H_8	0.81	..	..	..	1.62	..
C_4H_n	..	..	..	0.08	0.14	..
$C_{10}H_{10}$	..	..	0.41	..	..	..

cording to equation 3 ($R = C_2H_5$). The large amount of methane formed indicates that there is a considerable amount of chain decomposition.

We must remember, however, that in a previous discussion of the principle of least motion[6] it was pointed out that a molecule having a long carbon skeleton, when ruptured by heat, could coil around and react with itself to produce an isomer. Considerations of this kind from the principle of least motion suggest as possibilities isomerization of 1-ethylcyclohexene to 3-vinyl-2-hexene or decomposition of ethylbutadiene into ethylene and 1,2-butadiene. We would have missed 1,2-butadiene if it had been formed in our experiment. There does not seem to have been any previous work published on the pyrolysis of ethylcyclohexene.

4. **1-Phenylcyclohexene.**—We did only one experiment and obtained 41 molecules of phenylbutadiene for every 100 molecules of phenylcyclohexene decomposed. It is possible that the low yield is due to polymerization of the phenylbutadiene during distillation. The pyrolysis of 1-phenylcyclohexene does not appear to have been studied previously.

5. **3-Vinylcyclohexene.**—We have proved that this compound decomposes from 80–85% into 1,3-butadiene. In view of the fact that this molecule would produce a radical having a long carbon skeleton which could react with itself and isomerize, it is not surprising that there are some side reactions. From the principle of least motion, we would predict the formation of 1,3,6-octatriene caused by the radical, $CH_2CHCHCH_2CH_2CHCHCH_2$, coiling around and reacting with itself.

The gas phase dimerization of butadiene has been studied by several workers[7,8] but the reverse reaction does not seem to have been investigated experimentally although Kistiakowsky has made some calculations on the rate of dissociation.

6. **Dipentene.**—The yield of isoprene was 81% of the amount of dipentene decomposed. From some other work we estimate that 3–4% of the isoprene formed decomposed under our experimental conditions so that the small amounts of methylacetylene and butadiene found probably come from decomposition of the isoprene. It seems plausible also that dipentene can isomerize into 3,7-dimethyl-1,3,6-octatriene by coiling around itself in such a way as to make this isomerization possible with a minimum of atomic motion.

In 1911 Harries and Gottlob[9] developed the isoprene lamp for the conversion of terpenes to isoprene. Staudinger and Klever[10] obtained a 60% yield of isoprene by passing the vapors of dipentene, diluted with nitrogen, over a hot platinum coil at 20–30 mm. pressure.

7. **3-*p*-Menthene.**—This material gave a good yield of propylene on pyrolysis but the expected 2-isopropylbutadiene could not be detected. The only previous work relating to this compound that we could find[11] is that 3-*p*-menthene is a product of the pyrolysis of menthol and is stable at 500°.

8. **Experimental.**—Our sample of 1-methylcyclohexene (b. p. 108–109°, $n^{20}D$ 1.4510) was prepared by Dr. J. Greenberg from 1-methylcyclohexanol. The 1-ethylcyclohexene used was prepared by Dr. P. M. Ruoff according to the method of Signaigo and Cramer[12] and had a b. p. 135.5–136.8° and $n^{20}D$ 1.4577. 1-Phenylcyclohexene was prepared by Dr. J. Greenberg, using cyclohexanone and phenyl bromide as starting points.[13] It had b. p. (5 mm.) 102–103°, m. p. 10–11°.

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(10) Staudinger and Klever, *Ber.*, **44**, 2212 (1911).

(11) Isikawa, Tosimitu, Miyata, Araki and Someno, *Science Repts., Tokyo Bunrika Daigaku*, **A3**, 273 (1939); *C. A.*, **34**, 3240^1 (1940).

(12) Signaigo and Cramer, THIS JOURNAL, **55**, 3326 (1933).

(13) Sabatier and Mailhe, *Compt. rend.*, **138**, 1322 (1904); Noller and Kaneko, THIS JOURNAL, **57**, 2442 (1935).

The 3-vinylcyclohexene was prepared by polymerizing butadiene at 450° and 600–700 mm. The dimer was twice distilled at 2 mm. pressure, the first and last samples being rejected each time. The sample had a b. p. 128–130° and $n^{20}\mathrm{D}$ 1.4658. Our sample of limonene, b. p. (20 mm.) 67–68°, was purchased from Eastman Kodak Co. The 3-*p*-menthene was prepared by the dehydration of menthol. Sulfuric acid and aluminum oxide were both used as dehydrating agents but there was no difference in the products obtained by pyrolyzing the two samples. The material had a b. p. 168–169° and on hydrogenation gave 0.98 double bond.

The gaseous products were analyzed in a modified Shepherd[14] gas analysis apparatus containing a hydrogenation unit.[15] The products condensing in the traps were transferred to a low temperature Podbielniak still, fractionated, and then further analyzed in the gas analysis apparatus.

Isoprene was identified by its b. p., by giving two double bonds on hydrogenation and by the maleic anhydride derivative, m. p. 63°. 2-Phenylbutadiene was characterized by its b. p. and maleic anhydride derivative, m. p. 105°. 1,3-Butadiene was identified by its b. p. and hydrogenation value.

Summary

1. The thermal decomposition of a number of substituted cyclohexenes has been studied in the expectation that they would follow the pattern of the cyclohexene decomposition and yield a substituted butadiene and ethylene.

2. This was found to be the case for 1-methyl, 3-vinyl and 1-phenyl cyclohexene. In the case of ethylcyclohexene, we could not detect the expected ethylbutadiene.

3. Dipentene gave, as was to be expected, a high yield of isoprene. On the other hand, 3-*p*-menthene gave a high yield of propylene but no isopropylbutadiene could be detected.

WASHINGTON, D. C. RECEIVED FEBRUARY 19, 1944

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

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

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NEW YORK UNIVERSITY]

The Effect of Dielectric Constant and Temperature on the Catalyzed Decomposition of Azodicarbonate Ion

BY CECIL V. KING AND JESSE J. JOSEPHS

In recent years much interest in reaction kinetics in solution has centered in two factors: (1) prediction by electrostatic theory of the effects of changing dielectric constant and ionic strength and (2) the interpretation of temperature coefficients in terms of activation energy and entropy.

(1) For a reaction between ions A and B present electrostatic theory may be summarized in the well-known Christiansen–Scatchard equation[1]

$$\log k = \log k_\infty - \frac{Z_A Z_B\, \epsilon^2 N}{2.3DRT} \cdot \frac{1}{r_A + r_B} + \frac{Z_A Z_B\, \epsilon^2 N}{2.3DRT} \cdot \frac{\kappa}{1 + a\kappa} \qquad (1)$$

where the symbols have their usual significance and the last term refers to the salt effect, the next to last term to the dielectric constant effect. A similar equation has been developed by Eyring and his associates and includes a separate estimation of the radius of each ion and the critical complex.[2,3] (2) Introduction of the Eyring theory that rates may be expressed in terms of a universal frequency and an equilibrium constant K^* (reactants-critical complex) necessitates

$$k = RT/Nh \times K^*$$

defining the Arrhenius "energy of activation" as a free energy, and leads to the equation, for reactions in solution[4,5]

$$\log k = \log e \frac{RT}{Nh} - \frac{E_{\text{exp.}}}{2.3RT} + \frac{\Delta S^*}{2.3R} \qquad (2)$$

where $E_{\text{exp.}}$ is the activation energy as determined from the slope of log k *vs.* $1/T$ plots and ΔS^* has been defined as the entropy of activation. This may be compared with the corresponding "collision theory" equation

$$\log k = \log Z - \frac{E_{\text{exp.}}}{2.3RT} + \log P \qquad (3)$$

where the collision frequency Z may be calculated from the equations of the kinetic theory and P is the probability factor for effective collision.

As usually determined, in iso-composition solutions, both $E_{\text{exp.}}$ and ΔS^* contain factors due to the change in dielectric constant with temperature; and it has been suggested[6] that temperature coefficients for use in these equations should be determined in media of the same dielectric constant rather than the same composition.

Presumably there should be no entropy of activation unless the free energy of activation varies with temperature, or if the dielectric constant is kept unchanged as the temperature is varied (using rate constants at zero ionic strength).[7,8] However, since ΔS^* is deter-

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[3] Glasstone, Laidler and Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, pp. 428, 430.

[4] Ref. 3, p. 199.

[5] LaMer, *J. Franklin Inst.*, **225**, 709 (1938).

[6] Svirbely and Warner, THIS JOURNAL, **57**, 1883 (1935); Warner, *Ann. N. Y. Acad. Sci.*, **39**, 345 (1940).

[7] LaMer, *J. Chem. Phys.*, **1**, 289 (1933).

[8] Ref. 3, pp. 433–434.