solvent distilled, last traces *in vacuo* at 100°. There remained 1.53 g. (93%) of amber oil, $[\alpha]^{25}D$ −89.8° (*c* 3.68, ether). Because of the small quantity of material at hand, no attempt was made at distillation or analysis.

Ethyl (−)-2-Phenyl-2-benzenesulfonylpropionate.—The above product (1.53 g.) was dissolved in acetic acid (15 ml.) and treated with 30% hydrogen peroxide (6 ml.). After 30 minutes at 100° an additional 6 ml. of hydrogen peroxide was added. After another 30 minutes on the steam-bath the solution was cooled and thrown into water, and the mixture extracted twice with benzene. After being washed with water, 5% sodium hydroxide solution, and water, then dried, the extract was evaporated to leave 1.14 g. (67%) of a thick glass, $[\alpha]^{27}D$ −15.5° (*c* 2.78, ethanol). No attempt at purification was made.

Reductive Desulfuration of Ethyl 2-Phenyl-2-benzenesulfonylpropionate.—The above product (1.14 g.) and Raney nickel (10 g.) in ethanol (30 ml.) were heated under reflux for four hours. Customary processing gave 0.40 g. (63%) of ethyl (−)-2-phenylpropionate, $[\alpha]^{25}D$ −40.9° (*c* 4.24, ether). Although the quantity on hand was too small to permit ready purification, the crude product gave a fair analysis.

Anal. Calcd. for $C_{11}H_{14}O_2$: C, 74.2; H, 7.92. Found: C, 73.3; H, 7.80.

On the basis of a rotation of −51.0° for the optically pure substance,[16] the present sample is about 90% stereochemically homogeneous.

***p*-Phenylphenacyl 2-Phenyl-2-phenylmercaptopropionate.**—2-Phenyl-2-phenylmercaptopropionic acid (2.0 g.) was dissolved in ethanol (10 ml.) and neutralized to phenolphthalein with 10% sodium hydroxide solution. *p*-Phenylphenacyl bromide (2.3 g., 10% excess) was suspended in ethanol (30 ml.), and treated with the previous solution. The mixture was boiled under reflux for two hours, cooled and poured into water. The oil was extracted with benzene, and the extract washed with water, dried over anhydrous sodium sulfate and decolorized by filtration through Norit. Solvent evaporation left 3.3 g. (94%) of sirup. This was crystallized in a mixture of benzene (10 ml.) and boiling ligroin (25 ml.). Another recrystallization gave the pure material, m.p. 119–119.5°.

Anal. Calcd. for $C_{29}H_{24}O_3S$: C, 77.00; H, 5.35; S, 7.07. Found: C, 77.25, 77.13; H, 5.61, 5.58; S, 6.73.

***p*-Phenylphenacyl 2-Phenyl-2-benzenesulfonylpropionate.**—The above ester (1.0 g.) was dissolved in acetic acid (15 ml.) and treated with 30% hydrogen peroxide (4 ml.). The solution was heated on the steam-bath for 20 minutes, cooled and thrown into water. The mixture was extracted with ether, and the extract washed with water, 5% sodium hydroxide solution and water. After drying and decolorization through Norit, the solvent was distilled to yield 0.93 g. (87%) of sirup. This was crystallized from benzene (10 ml.) and ligroin (40 ml.) to produce 0.54 g. of solid, m.p. 154–156°. Another recrystallization gave the pure product, m.p. 162°.

Anal. Calcd. for $C_{29}H_{24}O_5S$: C, 72.00; H, 5.00; S, 6.61. Found: C, 72.45, 72.39; H, 5.07, 5.13; S, 6.36.

STANFORD, CALIFORNIA RECEIVED JULY 20, 1951

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

Kinetics of the Thermal Decomposition of Vinyl Ethyl Ether[1]

BY ARTHUR T. BLADES AND GEORGE W. MURPHY

The thermal decomposition of vinyl ethyl ether has been studied at 497–586° in a flow system with toluene as a carrier gas. The toluene suppresses chain reactions which could otherwise result from the production of free radicals during the decomposition. Over most of the temperature range the data indicate an intramolecular decomposition directly into acetaldehyde and ethylene as the only reaction. The constants of the Arrhenius equation are in satisfactory agreement with those obtained by Wang and Winkler,[2] who studied the decomposition of the pure ether in a static system in the temperature range 377–448°. The nature of the activated state is discussed. Above 537° a secondary reaction, with a radical split as the probable primary step, begins to be evident.

The thermal decomposition of vinyl ethyl ether into ethylene and acetaldehyde was first studied by Wang and Winkler[2] using a static system in the temperature range 377 to 448°. Although the major reaction was believed to proceed through an intramolecular mechanism, the presence of free radicals was shown by the fact that vinyl ethyl ether catalyzed the decomposition of acetaldehyde.

The present research was undertaken as the first in a series of vinyl alkyl ether decomposition studies. It was hoped that attention could be focused unambiguously on the intramolecular decomposition, to the exclusion of free radical interference. To accomplish this, the decomposition was carried out in a flow system using toluene as a carrier gas; toluene is known to react readily with a large number of free radicals, forming stable molecules and the relatively inert benzyl radical. Two benzyl radicals eventually react to form dibenzyl. This technique has been extensively applied by Szwarc in the estimation of bond energies by pyrolytic methods,[3] and more recently in the determination of rate constants in the intramolecular decomposition of acetic anhydride.[4] By using a large excess of toluene, it was hoped that, although free radicals might be produced, they would be unable to cause chain decomposition of the acetaldehyde which results from the principal reaction.

Experimental

Vinyl ethyl ether (stabilized) was purchased from General Aniline and Film Corporation and redistilled on a 10-plate column (b.p. 35.2°, $n^{25}D$ 1.3740). The toluene was Merck and Company Reagent Grade and was distilled on the same column. Although some precautions were observed to obtain peroxide-free ether, the type of experiments performed did not require it. Any peroxide-generated radicals would quickly react with toluene.

The apparatus was similar to that reported by Szwarc.[5] Toluene was allowed to vaporize from a Pyrex reservoir maintained at 22.5°, while the ether was forced to pass through a fine capillary from a reservoir at 0°. In this way a mole ratio of toluene to ether of about fifty to one was maintained throughout the run. The pressure of about 2 cm. was measured on an oil mercury manometer with a magnification factor of ten.[6]

The reaction cell was a Pyrex glass tube 1.5 cm. in diameter and 20 cm. long, surrounded by an aluminum block

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[1] Presented at the 119th Meeting of the American Chemical Society, Cleveland, Ohio, April, 1951.

[2] S. Wang and C. A. Winkler, *Can. J. Research*, **21B**, 97 (1943).

[3] M. Szwarc, *Chem. Revs.*, **47**, 75 (1950).

[4] M. Szwarc, *Trans. Faraday Soc.*, **47**, 269 (1951).

[5] M. Szwarc, *J. Chem. Phys.*, **17**, 431 (1949).

[6] Ostwald-Luther, "Physiko-chemische Messungen," Funfte Aufgabe, Reprinted by Dover Publications, Inc., New York, N. Y., 1943, p. 200.

furnace, enclosed in a three-inch layer of magnesia insulation, and maintained within ± 0.2° by a phase-shift thyratron control circuit,[7] with a platinum resistance thermometer as the detecting element. Temperatures were monitored continuously by a triple junction chromel–alumel thermocouple feeding into a Brown Recording Potentiometer. The thermocouple was calibrated at the melting points of lead and zinc.

The effluent gases were forced to pass through the flow limiting capillary whose dimensions determined the contact time of the gases in the reaction cell. The products were then condensed in a liquid air trap from which permanent gases were removed by an automatic toepler pump and stored for analysis.

Gas analyses were carried out on a Haden and Luttropp[8] type apparatus which was modified for use with liquid absorbents. Carbon monoxide was absorbed by freshly prepared silver oxide at room temperature and hydrogen was subsequently absorbed by the same reagent at 100°. Ethylene was absorbed by Cosorbent.

Attempts were made to employ the titration methods of Zahorka and Weimann,[9] and Siggia and Maxcy,[10] for quantitative aldehyde determinations, and of Siggia and Edsberg[11] for vinyl ether analysis, but in each case difficulty was encountered in obtaining consistently reproducible results. Satisfactory aldehyde analyses were made using a Beckman spectrophotometer at wave lengths 302, 305 and 310 mμ, where acetaldehyde absorbs strongly and vinyl ethyl ether does not interfere. Rate constants were calculated on the basis of these aldehyde determinations.

For runs in which it was desired to collect the ethylene, the liquid air trap was replaced by a frozen ether bath at −120° and the ethylene collected as a gas. Analysis proved that this gas was ethylene and that it was produced in equal quantities with the acetaldehyde, within the experimental error.

At higher temperatures, small quantities of non-condensable gases were also collected, never exceeding 5% of the quantity of acetaldehyde produced. Analyses showed these gases to be approximately $^1/_3$ hydrogen, $^1/_3$ methane and $^1/_3$ carbon monoxide. A small amount of a white crystalline solid also appeared and was identified as dibenzyl by its melting point (51.2°).

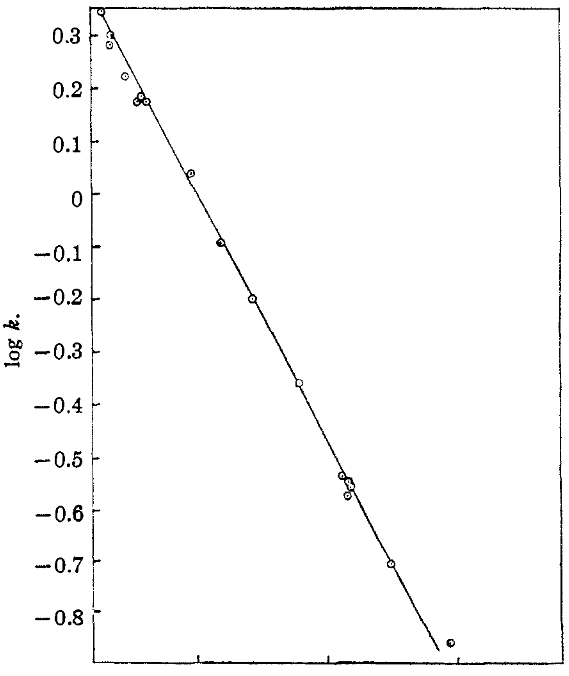

Fig. 1.—Primary reaction.

By varying the contact time between 0.28 and 0.66 sec., it was possible to confirm within experimental error the first-order character of the reaction reported by Wang and Winkler; however, because of difficulties inherent in the flow technique, our order determinations cannot be considered in themselves as conclusive.

The data conform to the Arrhenius equation as may be seen from Fig. 1, and

$$k = 2.7 \times 10^{11} \exp(-43{,}800/RT) \text{ sec.}^{-1}$$

This equation was compared with that of the Absolute Rate Theory for unimolecular gas phase reactions

$$k = \kappa(RT/Nh) \exp(\Delta S_a/R) \exp(-\Delta H/RT)$$

where κ is the transmission coefficient, ΔS_a is the entropy of activation, and ΔH_a is the heat of activation. The entropy of activation was calculated to be −10.2 e.u. at 530° assuming $\kappa = 1$.

At first it was believed that the non-condensable gases (H_2, CO, CH_4) were the result of the thermal decomposition of the acetaldehyde produced in the primary reaction. On passing acetaldehyde through the furnace in the presence of toluene, however, no non-condensable gases were produced. It appears likely that these gases result from a dissociation of the vinyl ethyl ether into radicals, followed by secondary decompositions of the fragments to form the end-products.

Rate constants were calculated on the assumption of a first-order rate equation. The rate constants were fitted to the Arrhenius equation (Fig. 2) yielding

$$k = 8 \times 10^{15} \exp(-70{,}000/RT) \text{ sec.}^{-1}$$

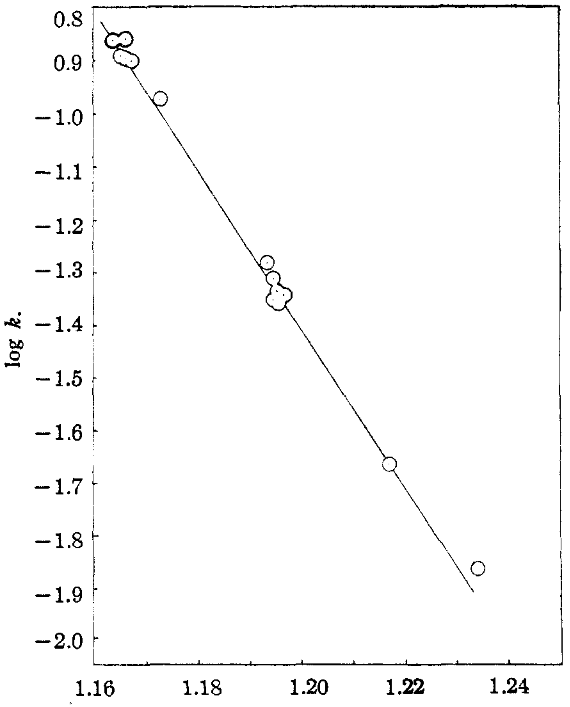

Fig. 2.—Secondary reaction.

Discussion

Two types of cyclic intermediate have been proposed for the intramolecular decomposition of vinyl ethyl ether. Wang and Winkler[2] have theorized on the energy required for the formation of I and conclude that it is energetically feasible. Their arguments do not seem to rule out the second intermediate, which is favored on the basis of the

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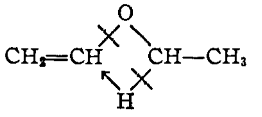
(7) J. M. Sturtevant, in Weissberger, "Physical Methods of Organic Chemistry," Part I, Interscience Publishers, Inc., New York, N. Y., 1949, p. 43.

(8) W. L. Haden and E. S. Luttropp, *Ind. Eng. Chem., Anal. Ed.*, **13**, 571 (1941).

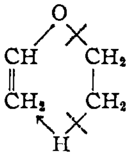
(9) A. Zahorka and K. Weimann, *Monatsh.*, **71**, 229 (1938).

(10) S. Siggia and W. Maxcy, *Anal. Chem.*, **19**, 1023 (1947).

(11) S. Siggia and R. Edsberg, *ibid.*, **20**, 762 (1948).

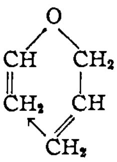


I



II

entropy of activation. Such evidence should be applied with caution in the state of our present knowledge, but the uncertainty in its interpretation should be minimized when the entropies of activation of two or more very similar reactions are considered. The evidence that the rearrangement of vinyl allyl ether to allylacetaldehyde proceeds through the intermediate



is reasonably conclusive[12,13]; entropy of activation is -7.7 e.u. at 180°, and interpreted as due to the conversion of three internal rotational degrees of vibrations. Our value of -10.2 e.u. at 530° for the entropy of activation in the decomposition of vinyl ethyl ether may be taken as consistent with this if the intermediate is II, which involves three internal rotations, instead of I, which involves only two. The fact that the entropy of activation for the vinyl ethyl ether decomposition is 2.5 e.u. more negative than for the vinyl allyl ether rearrangement is possibly due to the widely different temperatures at which these values were computed.

We do not feel that sufficient information is at hand to establish a mechanism for the secondary reaction. It appears likely that the primary step is a radical split between the $CH_2{=}CH{-}O{-}$ and C_2H_5 groups. These radicals could either decompose or react with toluene to produce the final products. Experiments on the decomposition of other vinyl ethers will probably help in establishing a mechanism for this reaction.

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MADISON, WISCONSIN RECEIVED AUGUST 20, 1951

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[12] C. D. Hurd and M. W. Pollack, *J. Org. Chem.*, **3**, 550 (1939).

[13] F. W. Schuler and G. W. Murphy, THIS JOURNAL, **72**, 3155 (1950).

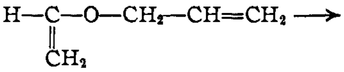
[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF WISCONSIN]

Kinetics of the Rearrangement of Isopropenyl Allyl Ether[1]

BY LAWRENCE STEIN AND GEORGE W. MURPHY

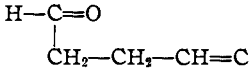
The kinetics of the gas phase rearrangement of isopropenyl allyl ether to allyl acetone has been studied over the pressure range 2 to 76 cm. and temperature range 143 to 194°. The reaction is first order, with rate constants independent of pressure in the range studied. The entropy of activation is virtually the same as that reported previously for vinyl allyl ether, while the energy of activation is 1.3 kcal. lower. These observations are discussed in terms of the supposed cyclic transition states.

The kinetics of the gas phase rearrangement of vinyl allyl ether (I) to allyl acetaldehyde (II)



$$H-\underset{\underset{\displaystyle CH_2}{\|}}{C}-O-CH_2-CH=CH_2 \longrightarrow$$

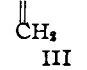
I



$$H-\underset{\underset{\displaystyle CH_2-CH_2-CH=CH_2}{|}}{C}=O$$

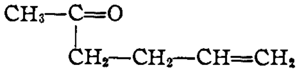
II

has been studied recently by Schuler and Murphy.[2] This type of rearrangement possesses a number of interesting features which make it particularly suitable for fundamental kinetics studies. In a continuation of this research we have employed a greatly improved apparatus to study the kinetics of the rearrangement of isopropenyl allyl ether (III) to allyl acetone (IV)



$$CH_3-\underset{\underset{\displaystyle CH_2}{\|}}{C}-O-CH_2-CH=CH_2 \longrightarrow$$

III



$$CH_3-\underset{\underset{\displaystyle CH_2-CH_2-CH=CH_2}{|}}{C}=O$$

IV

Experimental

Isopropenyl allyl ether (III) was prepared by the method of Hurd and Pollack.[3] A total of 18 g. of the ether was made (b.p. 87.5–88.0° at 745 mm.; n^{20}_D 1.4190) and sealed into glass ampoules, which were then kept in a refrigerator at 0° until used.

Allyl acetone (IV) was prepared by the reaction of allyl bromide with acetoacetic ester to form allyl acetoacetic ester, and the subsequent ketone cleavage of the latter to the desired product. The preparation of *n*-amyl methyl ketone by this method is described in "Organic Syntheses,"[4] and we have followed this technique except for the substitution of allyl bromide for *n*-butyl bromide in the initial step. Starting with one mole of acetoacetic ester, 38.5 g. of allyl acetone was obtained, b.p. 128–128.5° at 745 mm., n^{20}_D 1.4200.

The apparatus of Schuler and Murphy[2] was adapted to this problem, with the following principal modifications and improvements: (1) Temperature control was improved by employing a Western Electric 14A thermistor as the sense element for the electronic regulator and by direct application of controlled heat to the aluminum block instead of to

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[1] Presented at the 119th Meeting of the American Chemical Society, Cleveland, Ohio, April, 1951.

[2] F. W. Schuler and G. W. Murphy, THIS JOURNAL, **72**, 3155 (1950).

[3] C. D. Hurd and M. A. Pollack, *ibid.*, **60**, 1905 (1938).

[4] "Organic Syntheses," Coll. Vol. I, Second Ed., John Wiley and Sons, Inc., New York, N. Y., 1941, p. 248, 351.