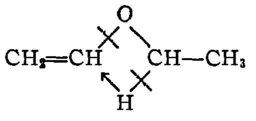
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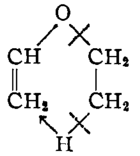
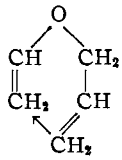

II

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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[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).

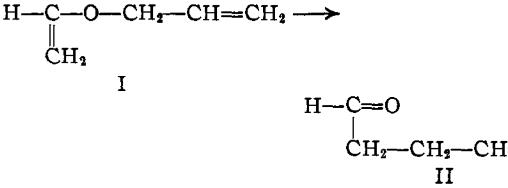
[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF WISCONSIN]

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)



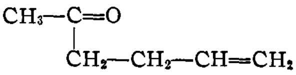
$$\mathrm{H{-}\underset{\underset{\displaystyle CH_2}{\|}}{C}{-}O{-}CH_2{-}CH{=}CH_2} \longrightarrow \quad \begin{array}{l}\mathrm{H{-}C{=}O}\\ \quad|\\ \mathrm{CH_2{-}CH_2{-}CH{=}CH_2}\end{array}$$

I 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)

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

III



$$\begin{array}{l}\mathrm{CH_3{-}C{=}O}\\ \qquad|\\ \quad\mathrm{CH_2{-}CH_2{-}CH{=}CH_2}\end{array}$$

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.

the more remote oven windings. The e.m.f. from a calibrated five-junction copper–constantan thermocouple was recorded continuously by a Brown Potentiometer; the temperature was constant within 0.1°.

(2) Filter solutions of nickel and cobalt sulfates and 2,7-dimethyl-3,6-diazicyclohepta-1,6-diene iodide[5] in Corex cells were used to restrict the mercury spectrum to lines in the vicinity of 2900 Å. The photomultiplier tube of the earlier work was replaced by a 935 phototube, the output of which was amplified by an RCA "Volt-Ohmyst" vacuum tube voltmeter and then measured by a sensitive galvanometer. A substantial gain in stability and precision was afforded by this arrangement. A number of tests showed that any photochemical action was of negligible importance under the conditions of the experiments.

(3) A diaphragm gage had been employed for pressure measurements in the original apparatus, but since this proved to be unreliable at very low pressures, a constant-level mercury monometer was substituted in the present research. The tubing between the reaction cell and the manometer was heated electrically to prevent vapor condensation. A silicone-lubricated stopcock sealed this part of the system from the vacuum line for pressures below 40 cm. Above this pressure, absorption by the grease became so troublesome that a mercury cut-off valve was substituted. In all cases, any small pressure drop during the reaction due to the absorption was taken into account in evaluating rate constants.

(4) Conversion of galvanometer readings to partial pressures was accomplished by methods similar to those previously described. We have obtained improved precision, however, by determining calibration curves experimentally at each temperature, rather than determining a single calibration curve for use at all temperatures.

Results

Graphs of log (% ether) *vs.* time at several temperatures are plotted together in Fig. 1. Most runs were carried to 70% completion, a few to 90% and precise first-order behavior was consistently found. The rate constants obey the Arrhenius equation very well, as shown in Fig. 2. Several of the points shown are averages of several runs, and the pressure range represented is 15 to 40 cm.

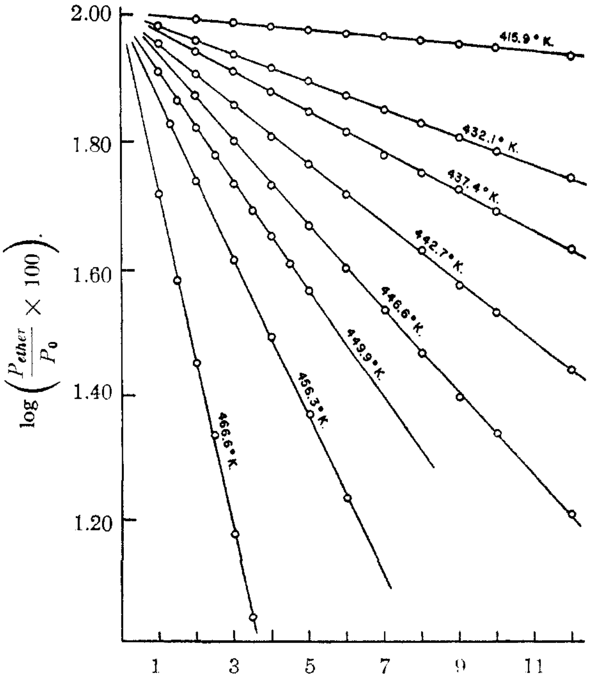

Fig. 1.

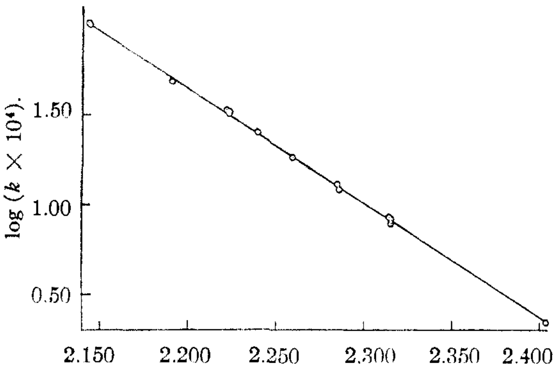

Fig. 2.

In the present work a systematic examination was made of the possible dependence of rate constant upon pressure. Runs were made at pressures ranging from 2.0 to 76.0 cm., and, as shown in Table II, no significant change in *k* was found. Runs at still lower pressures would have been desirable in order to check theories of collisional activation, but the apparatus did not permit this extension. It is remarkable, however, that the data show no change in rate constant over the 38-fold change in pressure here investigated.

TABLE I

EFFECT OF PRESSURE ON RATE CONSTANTS

Pressure, cm.	Temperature, °K.	k, sec.$^{-1}$
22.2	432.1	8.42×10^{-4}
28.8	432.0	8.36
76.5	432.0	8.38
2.0	442.5	1.7×10^{-3}
4.5	442.5	1.8
21.1	442.6	1.90
28.8	442.6	1.84
66.9	442.6	1.87
71.8	442.5	1.89
2.6	456.1	4.7×10^{-3}
6.8	456.1	4.9
24.0	456.3	4.86
76.0	456.2	4.81

Surface effects were also examined, both by baking the reaction cell in an oven at 500° to clean the walls and by packing the cell with glass helices to increase the surface area. It was found that in each of these cases the rate constants were abnormally high at first, but dropped progressively with succeeding runs until the normal values were reached. For example, three runs made at 442.5° K. after cleaning the cell walls by baking yielded the following constants: 2.24, 2.00 and 1.84×10^{-3} sec.$^{-1}$. Four runs made after adding glass helices which increased the surface area by a factor of 4.3 to 1 yielded rate constants of 3.8, 2.10, 1.93 and 1.82×10^{-3} sec.$^{-1}$. (The first of these conformed poorly to a first-order rate equation.) There was also evidence that the material formed in these first packed-cell runs was not pure allyl acetone; the optical properties were somewhat different. This can be interpreted by assuming that a competing reaction occurs at a fresh glass

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[5] M. Kasha, *J. Optical Soc. Am.*, **38**, 929 (1948).

surface and that the product is not allyl acetone. The reaction which does form allyl acetone is homogeneous, however, as shown by the fact that the normal rate constant is obtained once the walls become coated, even though the surface-to-volume ratio has been greatly changed. The competing reaction can perhaps be considered to be eliminated or made negligibly slow by the coating which builds up on the cell surfaces. Schuler and Murphy[2] found that packing the stem of their reaction cell with glass wool did not lead to abnormal rate constants in the case of vinyl allyl ether. However, vinyl allyl ether and isopropenyl allyl ether are such similar compounds that it is believed this difference may be due only to a greater sensitivity of the present technique.

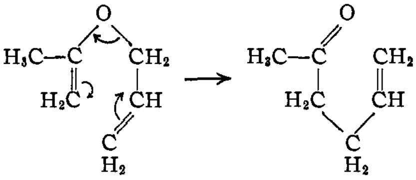
Discussion

The rate constants were fitted to the Arrhenius equation, $k = s \exp(-E_a/RT)$, by a least squares treatment; the constants found were $s = 5.4 \times 10^{11}$ sec.$^{-1}$ and $E_a = 29.3$ kcal., with a probable error in E_a of less than 1%. The entropy of activation was computed with the aid of the absolute rate equation, $k = \kappa e\,(RT/Nh) \exp(\Delta S_a/R) \exp(-E_a/RT)$, assuming that the transmission coefficient, κ, was unity, and found to be -7.7 e.u. (The symbols used here are: s, frequency factor; E_a, experimental energy of activation; ΔS_a, entropy of activation; N, Avogadro's number; h, Planck's constant; R, gas constant; T, absolute temperature.)

In comparing the rearrangements of vinyl allyl ether and isopropenyl allyl ether, we find that the entropies of activation are the same within our experimental error; on the other hand the energy of activation is 1.3 kcal. less for isopropenyl allyl ether than for vinyl allyl ether.

The first-order rate dependence and the negative entropies of activation are consistent with the assumption of a cyclic transition state. We have made a rough calculation of the entropy due to the three internal rotational degrees of freedom in vinyl allyl ether and in isopropenyl allyl ether based on the geometry of the molecule and the assumption of free rotation. The results are 24.9 and 26.0 e.u., respectively. They can be regarded as high theoretical limits for the negative entropies of activation. The rotation must be considerably restricted around each bond, a factor which, if it could be properly evaluated, would reduce the calculated values substantially. Furthermore, some entropy will be associated with the torsional vibrations of the transition state which replace the internal rotations of the initial state. If both these factors are considered, the experimental entropies of activation seem to us quite reasonable. The extra methyl group in isopropenyl allyl ether leads to greater moments of inertia for the internal rotations, and hence a greater entropy than for vinyl allyl ether. A slightly larger entropy of activation would be expected for the former compound but, as pointed out above, no difference was actually found.

The 1.3 kcal. difference in energies of activation for the two ethers is outside the probable error. The lower value obtained for isopropenyl allyl ether suggests that the supply of electrons at the $=CH_2$ end of the vinyl group is an important factor in determining the energy of the transition state, which probably involves electron shifts as shown



The methyl group has a directing influence on electrons to this point, which leads to a lower activation energy than for vinyl allyl ether.

The authors are grateful to the University Research Committee for a grant from funds supplied by the Wisconsin Alumni Research Foundation. They also wish to acknowledge the helpful suggestions of Professors Harlan L. Goering and Paul D. Bartlett in discussions on this subject.

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