V, was accomplished by heating it under reflux for 70 minutes with 100 ml. of γ-collidine. The cooled mixture was treated with 300 ml. of ether and with 300 ml. of cold, dilute (1:2) hydrochloric acid. The ether solution was washed with water and sodium bicarbonate solution, and dried with sodium sulfate. Distillation gave 13.4 g. (68.5%) of the dienone, b. p. 147° (2 mm.); n^{25}_{D} 1.5987.

Anal. Calcd. for $C_{14}H_{14}O$: C, 84.81; H, 7.12. Found: C, 84.34; H, 7.35.

1,2,3,4-Tetrahydro-9-phenanthryl Acetate (VII).—A solution of 4.95 g. of the dienone, VI, in 50 ml. of acetic anhydride was treated with a solution of 0.50 g. of sulfuric acid in 25 ml. of acetic anhydride. After four hours at room temperature, the acetic anhydride was hydrolyzed with ice water. Filtration of the resulting suspension, gave 5.69 g. (95%) of 1,2,3,4-tetrahydro-9-phenanthryl acetate (VII), m. p. 78.5–81°. Crystallization from aqueous methanol gave 5.25 g. of the acetate, m. p. 80–81.5°.

Anal. Calcd. for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 79.68; H, 6.88.

1,2,3,4-Tetrahydro-9-phenanthrol (VIII).—Hydrolysis of 4.51 g. of the acetate, VII, by refluxing with 100 ml. of 5% methanolic potassium hydroxide for one hour gave (after acidification of the solution and crystallization of the compound from aqueous ethanol) 3.25 g. of 1,2,3,4-tetrahydro-9-phenanthrol (VIII), m. p. 104–106°. Crystallization of the compound from a mixture of carbon tetrachloride and petroleum ether (b. p. 60–68°) raised the melting point to 105.5–106.5°.

Anal. Calcd. for $C_{14}H_{14}O$: C, 84.81; H, 7.12. Found: C, 84.77; H, 7.16.

By crystallization from benzene, 1,2,3,4-tetrahydro-9-phenanthryl 3′,5′-dinitrobenzoate (IX), m. p. 221–222°, was obtained as lemon-yellow leaflets. This compound is reported[7] to melt at 220°.

1,2,3,4-Tetrahydro-9-phenanthrol (VIII) from 9-Acetylamino-1,2,3,4-tetrahydrophenanthrene.[9]—9-Acetylamino-1,2,3,4-tetrahydrophenanthrene[6] (1.50 g.) and 20 ml. of 15% sulfuric acid were placed in a Carius tube. Air was displaced with carbon dioxide, and the sealed tube was shaken thoroughly. The tube was heated at 240–260° for 3.5 hours; the contents of the tube were extracted with ether; the ether layer was dried with sodium sulfate, and the solvent evaporated. Distillation of the residue at a bath temperature of 200–220° (2 mm.) yielded 1.03 g. of an oil which solidified rapidly. Crystallization of the distillate from a mixture of carbon tetrachloride and petroleum ether (b. p. 60–68°) gave 0.85 g. of colorless crystals, m. p. 105–106.5°. A mixture of this compound with the tetrahydrophenanthrol from the preceding experiment showed no depression of melting point.

1,2,3,4-Tetrahydro-9-phenanthryl acetate, m. p. 80–81.5°, was prepared from the above tetrahydrophenanthrol with acetic anhydride. It did not depress the melting point of the acetate, VII, obtained by the dienone–phenol rearrangement.

2-Bromo-1,2,3,4-tetrahydro-9-phenanthrol (X).—(a) A solution of 594 mg. of the tetrahydrophenanthrol, VIII, in 10 ml. of acetic acid was treated with a solution of 480 mg. of bromine in five ml. of acetic acid. The resulting solution was poured into 75 ml. of water containing a trace of sodium bisulfite; the product solidified slowly. Crystallization from aqueous ethanol yielded 631 mg. of tan needles, m. p. 99–100°.

(b) An identical bromotetrahydrophenanthrol was obtained from an attempted preparation of the bromodienone, XI.

A solution of 3.96 g. of 1-keto-4,4-tetramethylene-1,4-dihydronaphthalene (VI) in 50 ml. of carbon tetrachloride was treated with a solution of 3.2 g. of bromine in 30 ml. of carbon tetrachloride. When the solvent was evaporated on the steam-bath, hydrogen bromide was evolved, but attempts to crystallize the residue failed. The residue was then treated with 150 ml. of ether and 150 ml. of water. Extraction of the ether layer with 80 ml. of 3% sodium hydroxide solution, followed by acidification of the alkaline solution, gave an oil that solidified rapidly. Crystallization from aqueous ethanol yielded 1.18 g. of 2-bromo-1,2,3,4-tetrahydro-9-phenanthrol, m. p. 99–100.5°.

Anal. Calcd. for $C_{14}H_{13}BrO$: C, 60.67; H, 4.73. Found: C, 60.60; H, 4.90.

Evaporation of the ether solution gave an oil, which was probably the bromodienone, XI. Attempts at crystallizing this oil failed.

Summary

1. 1-Keto-4,4-tetramethylene-1,4-dihydronaphthalene has been rearranged with sulfuric acid in acetic anhydride to 1,2,3,4-tetrahydro-9-phenanthryl acetate.

2. The rearrangement of spirodienones represents a new method, free of inhibiting steric factors, for the preparation of rings containing six or more carbon atoms.

MINNEAPOLIS, MINNESOTA RECEIVED JANUARY 23, 1950

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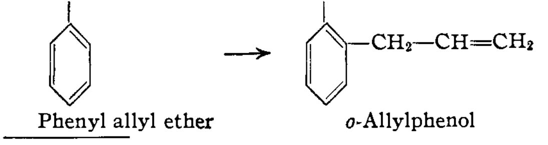
[9] We are indebted to Dr. John Richter for this experiment.

[CONTRIBUTION FROM CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF WISCONSIN]

The Kinetics of the Rearrangement of Vinyl Allyl Ether[1]

BY FREDERIC W. SCHULER[2] AND GEORGE W. MURPHY

The rearrangement of aryl allyl ethers to yield allyl phenols, as illustrated by the rearrangement of phenyl allyl ether



Phenyl allyl ether o-Allylphenol

is known as the Claisen rearrangement.[3] The essential skeleton involved in the rearrangement has been demonstrated to be

C=C—O—C—C=C

for Hurd and Pollack[4] have synthesized the simplest compound with this skeleton structure, vinyl allyl ether, and have shown that it rearranges in the gas phase to give allylacetaldehyde.

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(1) An abstract of a thesis presented by Frederic W. Schuler to the faculty of the University of Wisconsin in partial fulfillment of the requirements for the degree of Doctor of Philosophy, October, 1949.

(2) National Research Corporation, Cambridge, Massachusetts.

(3) See, for example, Tarbell in "Organic Reactions," Vol. II, Ch. 1, John Wiley and Sons, Inc., New York, N. Y., 1942.

(4) Hurd and Pollack, THIS JOURNAL, **60**, 1905 (1938).

$$\underset{\text{Vinyl allyl ether}}{CH_2{=}CH{-}O{-}CH_2{-}CH{=}CH_2} \xrightarrow[250°]{} \underset{\text{Allylacetaldehyde}}{CH_2{=}CH{-}CH_2{-}CH_2{-}CHO}$$

with apparently no other products formed. The only kinetic studies of the Claisen rearrangement have been made with aryl allyl ethers in solution. Kincaid and Tarbell[5] have made rate measurements on the rearrangement of allyl *p*-tolyl ether in diphenyl ether solution. The kinetics of the rearrangement of vinyl allyl ether was of interest because the rearrangement occurs in the gas phase and Hurd and Pollack had shown that there were no side reactions. The mechanism is simpler than that of the aryl allyl ethers, as there is no keto–enol shift following the primary rearrangement. In the present study the order of the reaction, the effect of pressure upon the order, the effect of increased surface area on the reaction rate, and the energy and entropy of activation are reported.

Experimental

Vinyl allyl ether (b. p. 65° at 733 mm.) was prepared by the method of Hurd and Pollack. Paul Kletzke, LaCrosse, Wisconsin, supplied a sample of the intermediate β-bromo ethyl allyl ether which reacted with potassium hydroxide to yield vinyl allyl ether. Allylacetaldehyde (b. p. 103° at 744 mm.) was prepared from vinyl allyl ether by passing vapor through a tube heated to 250°. The two compounds were purified by fractionation in a miniature Vigreux column, and both reproduced the physical constants reported by Hurd and Pollack. The ultraviolet absorption spectra as measured with a Beckmann Quartz Spectrophotometer showed that in 1% solutions with cyclohexane as a solvent, the vinyl allyl ether transmitted completely while the allylacetaldehyde absorbed completely at 3130 Å. It was therefore decided to employ a photometric method for following the course of the reaction.

The reaction was carried out in a quartz reaction cell mounted in a constant temperature oven and the reaction was followed using a mercury arc lamp (H-4) as a source and photomultiplier tube (RCA Electron Tube IP-28) as a detector. Filter solutions of nickel and cobalt sulfates and of potassium acid phthalate served to isolate the 3130 Å. line.[6] The evacuated reaction system was filled with vapor by warming a sample in one section of the external system and opening a stopcock in a heated line that led to the reaction cell. The per cent. transmission was interpreted in terms of the partial pressure of allylacetaldehyde from experimental calibration curves using pure allylacetaldehyde. The total pressure of the system was measured with a mercury manometer connected to the cell through a null-point glass diaphragm gage mounted in the oven. The air pressure in the manometer was adjusted until the balance point of the diaphragm was reached. By assuming that there were only the two components present, the partial pressure of the vinyl allyl ether could then be calculated.

Figure 1 is a schematic drawing of the apparatus. The oven consisted of an iron cylinder 6" in diameter and about 18" long, wound with coils of nichrome wire, and then insulated with a 2" thickness of glass wool. This was mounted in a sheet iron cylinder. The cylinder part of the oven moved on a track up against a fixed end-plate which firmly supported the reaction system. In order to obtain uniform temperature distribution in the oven it was found necessary to put in a large aluminum block of dimensions 4" × 5" × 8" drilled in such a manner that when the block and cylinder part of the oven were moved up against the end-plate the reaction cell was completely surrounded by the block, except for holes to transmit the light beam. There were also holes in the end of the oven and the fixed end-plate to permit the light from the optical system to pass through the cell. The measured temperature variation over different parts of the cell were within 0.2° as measured with single-junction copper–constantan thermocouples.

An electronic regulator of the continuous control type, similar to that described by Benedict,[7] maintained the temperature constant within 0.2° during the experimental measurements.

The reaction system consisted of a quartz reaction cell, 15 cm. long and 2.8 cm. in diameter, with plane parallel windows, connected through a graded seal to the Pyrex glass diaphragm gage and through a Kovar seal to a Hoke brass bellows-type valve mounted on the end-plate. This valve did not shut off vacuum tight under a number of experiments, so it was found necessary to use a line heated with a coil of Nichrome wire out to an external glass stopcock.

A vacuum of 10^{-6} mm. as measured with a McLeod gage could be maintained in the system with a Hy-vac mercury diffusion pump assembly. In making a rate measurement the system was evacuated and the reaction cell isolated by closing the stopcock nearest it. Air was let into the sample holder and the top end of the sample holder was opened for admission of about 0.2 cc. of vinyl allyl ether. The top end was sealed off and the air from that part of the system was removed by evacuation when the sample was frozen. The vinyl allyl ether was transferred to the evacuated reaction cell by warming with hot water and opening the stopcock in the heated line leading to the reaction cell. Readings were taken on the milliammeter in the output of the photomultiplier tube at intervals of 15 or 30 seconds. The zero reading was taken at the beginning of the experiment and checked at the end when the material was removed from the cell. A troublesome drift had been observed in the photomultiplier tube, which, however, was minimized by illuminating the tube for 20 to 30 minutes prior to each run. Initial and final zero readings checked within ± 2%. Temperature readings were taken before and after each experiment. The thermocouples were calibrated against a platinum resistance thermometer certified by the National Bureau of Standards.

Results of the Rate Measurements

In individual runs the reaction was usually carried to between 40 and 70% completion, and a first order relationship was observed in all cases within the experimental error in the pressure range 15–40 cm. Below 15 cm. the order could not be definitely established because of rapidly increasing experimental error. Two runs were carried to completion under such conditions that the order could be checked over the entire range of concentration. In these experiments the calibration curve for obtaining the concentration of allylacetaldehyde from absorption measurements was obtained from the completely rearranged product at the temperature of the reaction. This made it possible to obtain greater precision in the computation of individual points on the curve than could be obtained in the majority of runs. The result on one of these runs is shown in Fig. 2. The reaction is seen to be first order out to 99% completion, although the agreement of the last point on the curve must be regarded as fortuitous, because of the large

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[5] Kincaid and Tarbell, *ibid.*, **61**, 3085 (1939).

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

[7] Benedict, *Rev. Sci. Instruments*, **8**, 252 (1937).

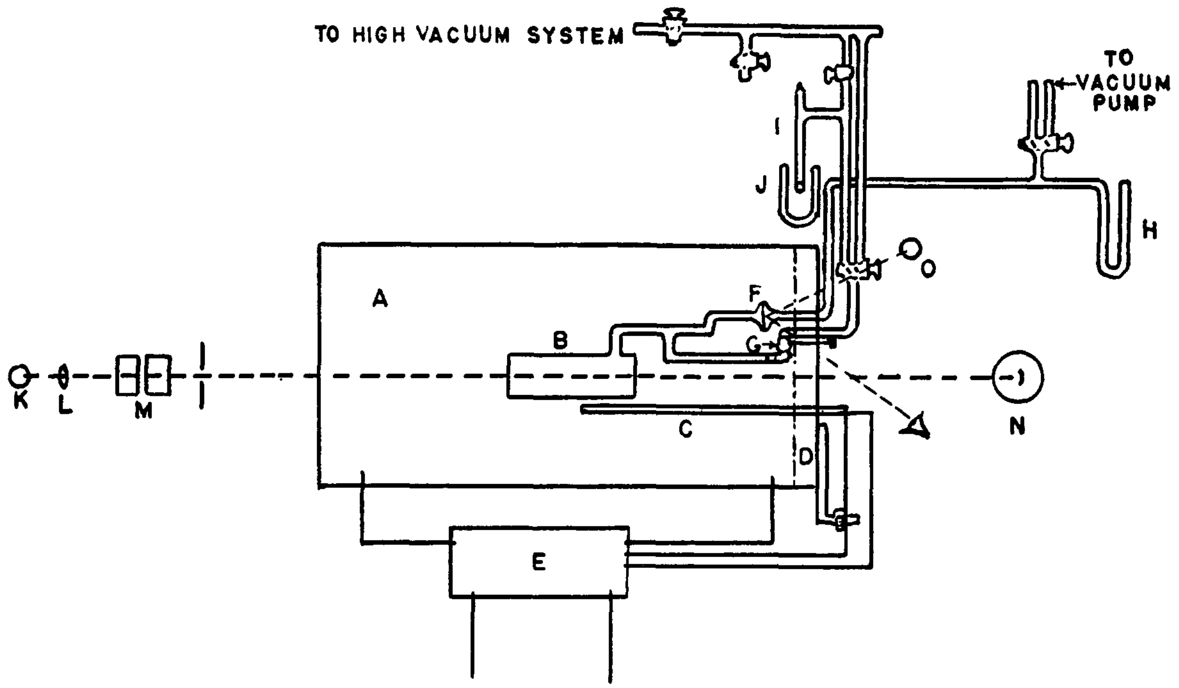

Fig. 1.—Schematic drawing of apparatus: A, oven; B, reaction cell; C, resistance element for temperature control; D, fixed end-plate; E, electronic temperature control; F, diaphragm gage; G, Hoke bellows valve; H, manometer; I, sample holder; J, cold trap; K, H-4 mercury lamp; L, lens; M, filter solutions; N, photomultiplier tube; O, light for reflection from diaphragm gage.

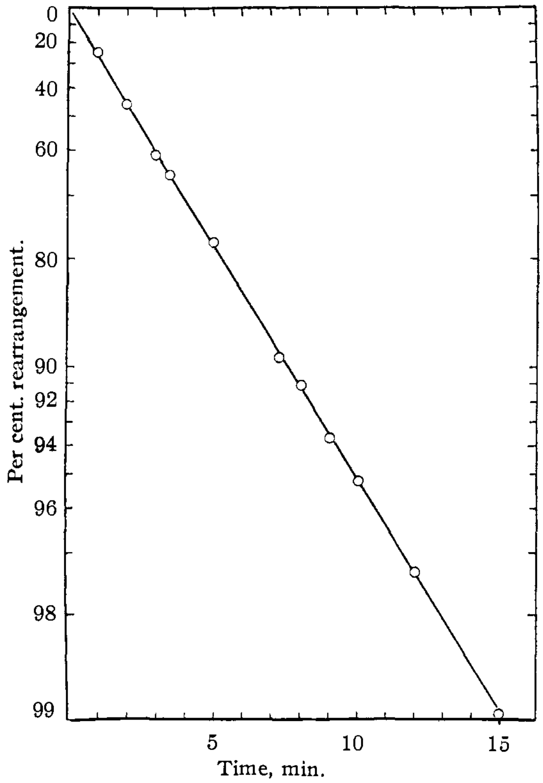

Fig. 2.—Data for high degrees of completion: T, 203°; p, 26.0 cm.

possible error. The other run under such conditions gave similar results.

Experimental results which were used for cal-

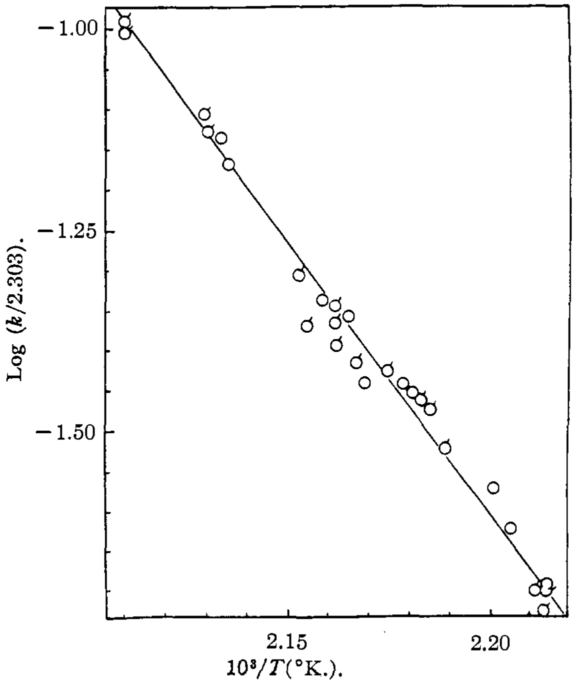

Fig. 3.—Effect of surface area on reaction rate: O, unpacked cell; ϕ, stem packed with glass wool.

TABLE I

EXPERIMENTAL RATE CONSTANTS FOR THE REARRANGEMENT OF VINYL ALLYL ETHER

Run	p^0, cm.	T in °K.	T^{-1}	$k/2.303$ (min.$^{-1}$)	k (sec.$^{-1}$)	log k
56	35.8	469.1	2.131×10^{-3}	7.49×10^{-2}	2.875×10^{-3}	−2.5413
57	38.9	469.4	2.130	7.84	3.021	−2.5199
58	33.2	473.7	2.111	10.0	3.838	−2.4160
59	29.0	473.8	2.111	9.87	3.789	−2.4215
60	30.3	427.7	2.338	0.3125	0.120	−3.9208
62	33.2	456.7	2.189	3.035	1.166	−2.9333
63	36.2	451.6	2.214	2.054	0.788	−3.1035
64	38.0	440.2	2.271	0.889	0.341	−3.4672

culation of the entropy and energy of activation are given in Table I and in Figs. 4 and 5. These results are from experiments in the later stages of the research, where the greatest precision was attained. Results shown in Fig. 3 are from earlier experiments, which are consistent with the later ones, but not so precise. The temperature in the earlier runs was somewhat uncertain because of an imperfect temperature distribution over the cell.

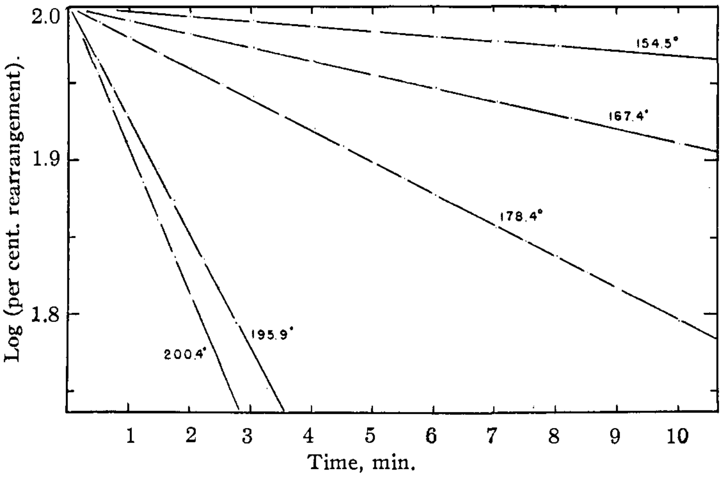

Fig. 4.—Rate data of Table I plotted according to first order relation, temperatures on graph are in °C.

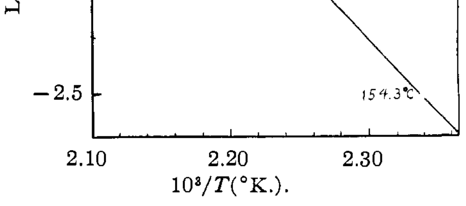

Fig. 5.—Rate of rearrangement as a function of temperature, data from Table I.

Rate constants obtained when the stem of the reaction cell was packed with glass wool were the same as without packing, within the experimental error, as can be seen in Fig. 3, so that the reaction is seen to be homogeneous. The stem of the cell was about 4 cm. long and 1.5 cm. in diameter with a volume about one-tenth that of the reaction cell. This test could be expected to show up gross surface effects only. It was also observed that the same rate constants were obtained in a cell which had been used for several runs without cleaning, and in a cell which was baked for several hours prior to a run at 475°. The latter treatment removed a slight discoloration in the cell which became apparent after several runs, indicating that side reactions were not completely absent.

From the results of Table I the frequency factor and the energy of activation of the Arrhenius equation were evaluated by the method of least squares, and the equation was found to be

$$k = 5.0 \times 10^{11} \exp(-30{,}600/RT) \text{ sec.}^{-1}$$

in the pressure range 25–40 cm. and the temperature range 154–200°. This equation was compared with that of Eyring for unimolecular gas phase reactions[8]

$$k = \kappa\, e(k'T/h) \exp(\Delta S^{\ddagger}/R)\exp(-\Delta E/RT)$$

where κ is the transmission coefficient, k' is Boltzmann's constant, $\Delta S^{\ddagger}$ is the entropy of activation, $\Delta E = RT^2(\mathrm{d}\ln k/\mathrm{d}t)$ is the experimental energy of activation, and the other symbols have their usual significance. The entropy of activation was calculated at 180°, assuming that the transmission coefficient was unity. The value obtained was −7.7 cal. deg.$^{-1}$ mole^{-1}.

Discussion of Results

A cyclic mechanism has been proposed for the Claisen rearrangement on the chemical evidence of the intramolecular nature of the rearrangement and the inversion of the allyl group.[3,9] The

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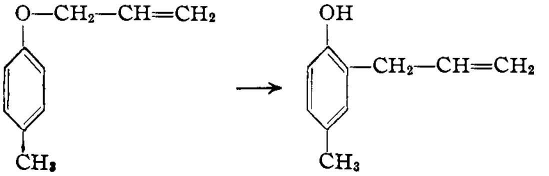
(8) Glasstone, Laidler and Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 199.

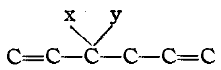
(9) Hurd and Pollack, *J. Org. Chem.*, **3**, 550 (1939).

negative value for the entropy of activation of the vinyl allyl ether rearrangement is consistent with this interpretation. Three internal rotational degrees of freedom in the initial state would become vibrational degrees of freedom in the activated complex, and such a change would be accompanied by a decrease in entropy associated with the greater restriction of movement.

Assuming that the transmission coefficient was unity, Kincaid and Tarbell[5] obtained a value of −8.1 cal./deg./mole for the entropy of activation for the rearrangement of allyl *p*-tolyl ether in diphenyl ether solution



Foster, Cope and Daniels[10] studied the rearrangement of allyl groups in three carbon systems of the type



$$\mathrm{C{=}C{-}C(x)(y){-}C{-}C{=}C}$$

where the x and y are $-CN$ or $-COOC_2H_5$ groups and obtained values of −11 to −14 cal./deg./mole for the three different compounds studied. This rearrangement is analogous to the Claisen rearrangement, also showing inversion of the allyl group, and is thought to have the same cyclic mechanism.

Acknowledgments.—The authors gratefully acknowledge the assistance of L. Lincoln and T. R. Lloyd of the departmental machine shop in the construction of the furnace and optical bench, W. R. Rowe in the construction of the temperature control system, L. Stein in many different phases of the experimental work, and the University Research Committee for a grant from funds supplied by the Wisconsin Alumni Research Foundation.

Summary

1. The gas phase rearrangement of vinyl allyl ether to allyl acetaldehyde has been studied and found to be a homogeneous, first order reaction in the pressure range 15–40 cm.

2. The energy of activation is 30,600 cal. mole^{-1} and the entropy of activation at 180° is −7.7 cal. deg.$^{-1}$ mole^{-1}. The large negative entropy of activation indicates that the reaction proceeds by a cyclic mechanism.

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[10] Foster, Cope and Daniels, THIS JOURNAL, **69**, 1893 (1947).

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

Complexes of Ferric Iron with 8-Hydroxyquinoline-5-sulfonic Acid

BY J. P. PHILLIPS

The method of continuous variations[1] when applied to the green, soluble complex formed between ferric iron and 8-hydroxyquinoline in perchlorate solution at low *p*H values shows that the complex contains one mole of iron per mole of 8-hydroxyquinoline.[2] These results have been duplicated by this writer and others[3] for both 8-hydroxyquinoline and the related 8-hydroxyquinoline-5-sulfonic acid; with both compounds the 1:1 mole ratio of iron to reagent was observed in perchlorate solutions at various *p*H values. These facts were somewhat surprising because Molland has stated,[4] without citing sufficient experimental detail for duplication, that the complex between ferric iron and 8-hydroxyquinoline-5-sulfonic acid (referred to as HOs) has the formula $FeOs_3$, and Yoe and Hall have shown that the similar compound 7-iodo-8-hydroxyquinoline-5-sulfonic acid forms a complex containing a 1:3 mole ratio of iron to reagent.[5]

The investigation reported here was undertaken to establish whether a 1:3 complex can be formed between ferric iron and 8-hydroxyquinoline-5-sulfonic acid, and, if so, to determine under what conditions this complex exists.

Experimental

All measurements were made with a Beckman Model DU quartz spectrophotometer using 1.00-cm. cells and sensitivities such that the slit widths were less than 0.1 mm.

Standard solutions of 8-hydroxyquinoline-5-sulfonic acid were prepared by dissolving weighed samples of the reagent in water or the appropriate dilute acid. The compound was prepared by a known method,[6] recrystallized several times from dilute hydrochloric acid and dried at 110°. Calcd.: N, 6.24. Found: N, 6.09, 6.18. Standard solutions of ferric iron were prepared from ferric ammonium sulfate dissolved in dilute sulfuric acid, from pure ferrous ammonium sulfate oxidized with nitric acid, and from pure iron wire dissolved in hydrochloric acid and oxidized with hydrogen peroxide, giving, respectively, solutions of ferric sulfate, nitrate and chloride. (The small

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[1] Vosburgh and Cooper, THIS JOURNAL, **63**, 437 (1941).

[2] Sandell and Spindler, *ibid.*, **71**, 3806 (1949).

[3] Merritt, Huber and Phillips, unpublished observations.

[4] Molland, THIS JOURNAL, **62**, 541 (1940).

[5] Yoe and Hall, *ibid.*, **59**, 872 (1937).

[6] Matsumura, *ibid.*, **49**, 813 (1927).