nitro-4-methoxybromobenzene used) of slightly brownish-yellow plates, m. p. 110–112°. A further recrystallization from alcohol after long boiling with charcoal gave pale yellow plates, m. p. 112–113°.

*Anal.* Calcd. for $C_{16}H_{17}O_6N$: C, 60.16; H, 5.37. Found: C, 59.73; H, 5.41.

**2,3,4,4′-Tetramethoxy-2′-aminobiphenyl (XVIII).**—The nitro compound (8.15 g.) was reduced with hydrogen and Raney nickel at 115° and 800 lb.; the product (6.6 g., 90%) after crystallization from alcohol, formed slightly tan plates, m. p. 107.5–109°. Recrystallization from alcohol gave white plates, m. p. 109.5–110°.

*Anal.* Calcd. for $C_{16}H_{19}O_4N$: C, 66.40; H, 6.62. Found: C, 66.13; H, 6.64.

An acetyl derivative, **XIX**, after crystallization from dilute methyl alcohol and petroleum ether–benzene, gave fine, white needles, m. p. 98–99°.

*Anal.* Calcd. for $C_{18}H_{21}O_5N$: C, 65.22: H, 6.39. Found: C, 65.02; H, 6.30.

**2,3,4,4′-Tetramethoxy-2′-iodobiphenyl (XX).**—A solution of 2.89 g. of 2,3,4,4′-tetramethoxy-2′-aminobiphenyl in 25 cc. of 3.6 *N* sulfuric acid, diluted after the amine had dissolved to 45 cc., was diazotized at 0° by adding slowly a solution of 0.7 g. of sodium nitrite in 5 cc. of water. The diazonium solution was then poured with stirring into an ice-cold suspension of 15 g. of copper powder in 25 cc. of 50% potassium iodide solution. Slow evolution of nitrogen took place, and the decomposition of the diazonium iodide was completed by leaving the mixture in the ice-box overnight, then slowly heating up to 100°. The copper powder, on which the organic material was adsorbed, was collected by filtration, washed with water and dried, and extracted with several portions of hot benzene. The extracts were evaporated to dryness with a stream of air. The residue, after it had been taken up in hot methanol and boiled with charcoal, filtered and cooled, deposited 1.40 g. (a 35% yield) of white granular crystals of the iodobiphenyl, m. p. 102–103° after a second crystallization from methanol. A 25% yield was obtained when no copper was used to disperse the diazonium complex, which then formed a viscous dark red oil, from which the product was purified only with difficulty.

*Anal.* Calcd. for $C_{16}H_{17}O_4I$: C, 48.00; H, 4.28; I, 31.7. Found: C, 48.06; H, 4.61; I, 31.9 (Parr bomb).

**3,4,7-Trimethoxydibenzofuran (XXI).**—On diazotizing the above amine under the same conditions, and allowing the diazonium solution to warm up slowly to room temperature, a reddish oil was deposited on the sides of the flask. After boiling with charcoal in methanol solution, a neutral compound crystallized on diluting with water, m. p. 75–76°.

*Anal.* Calcd. for $C_{15}H_{14}O_4$: C, 69.75; H, 5.46. Found: C, 69.73; H, 5.54.

## Summary

1. Deaminoiodocolchinol methyl ether has been shown to contain a seven-membered ring by oxidation to a dibasic acid. The dimethyl ester of the acid undergoes an ester condensation with sodium methoxide to form a phenanthrol, proving the presence of $\alpha$-hydrogens in the ester.

2. 2,3,4,4′ - Tetramethoxy - 2′ - nitrobiphenyl has been prepared by a crossed Ullmann reaction between 4-iodopyrogallol trimethyl ether, and 2-nitro-4-methoxybromobenzene, and has been converted into the corresponding amino and iodo compounds. 3,4,7-Trimethoxydibenzofuran is formed from diazotized 2,3,4,4′-tetramethoxy-2′-aminobiphenyl in acid solution.

ROCHESTER, NEW YORK RECEIVED DECEMBER 17, 1945

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

# The Thermal Decomposition of Tetrahydrofuran

BY CHARLES H. KLUTE[1] AND W. D. WALTERS

It has been observed that the homogeneous thermal decomposition of the cyclic ether, dioxane, proceeds mainly by a chain reaction.[2] However, other studies[3] have indicated that saturated cyclic compounds such as cyclopentane, methyl cyclopentane, cyclohexane and succinic anhydride, thermally decompose chiefly by non-chain processes. In certain instances, in addition to decomposition into compounds with fewer carbon atoms, dehydrogenation of the ring appears to occur as a homogeneous reaction. The earlier work on the thermal behavior of the cyclic ether, tetrahydrofuran, was concerned with the production of butadiene by catalytic dehydration, particularly over phosphate catalysts having an acid reaction.[4] The present investigation of the products as well as the kinetics of the decomposition was undertaken in order to obtain more information concerning the homogeneous thermal decomposition of cyclic compounds.

## Experimental

**Materials.**—Tetrahydrofuran was prepared by the hydrogenation of furan over a Raney nickel catalyst at room temperature under a gage pressure of 60 psi. Prior to hydrogenation the absolute alcohol under which the Raney nickel had been stored was completely removed from the catalyst by evacuation with a diffusion pump and then dry furan was distilled under vacuum into the flask containing the catalyst. The furan was obtained either from the Eastman Kodak Company or from the Quaker Oats Company. After hydrogenation the tetrahydrofuran was dried with fused sodium hydroxide pellets and separated into three fractions by distillation in a stream of nitrogen through a vacuum-jacketed fractionating column. The middle fraction was dried over freshly cut metallic sodium and then tested for peroxides by means of the ferric ion–thiocyanate test.[5] If peroxides

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(1) Fellow of the Sherman Clarke Fund for Chemical Research, University of Rochester. Present address: Shell Development Company, Emeryville, California.

(2) Kuchler and Lambert, *Z. physik. Chem.*, **B37**, 285 (1937).

(3) (a) Frey, *Ind. Eng. Chem.*, **26**, 198 (1934); (b) Kazanskii and Plate, *Ber.*, **67**, 1023 (1934); (c) Rice and Murphy, THIS JOURNAL, **64**, 898 (1942); (d) Kuchler, *Trans. Faraday Soc.*, **35**, 874 (1939); (e) Kuchler, *Z. physik. Chem.*, **B53**, 307 (1943); (f) Pease and Morton, THIS JOURNAL, **55**, 3197 (1933).

(4) Ostromyslenskii, *J. Russ. Phys.-Chem. Soc.*, **47**, 1472 (1915); U. S. Patent 2,241,792; British Patent 506,038, *C. A.*, **33**, 9328 (1939); French Patent 844,893, *C. A.*, **34**, 7931 (1940).

(5) Yule and Wilson, *Ind. Eng. Chem.*, **23**, 1254 (1931).

were present, the tetrahydrofuran was shaken with mercury in the dark for twenty-four hours. The peroxide-free material was fractionated twice in a stream of nitrogen, only the middle fraction being retained for the subsequent operation. The samples which were prepared during this study had refractive indices of $n^{20}\text{D}$ 1.4073 ± 0.0003 and boiling points of 64.6 ± 0.2° at 741 mm.

The methods used for the preparation of nitric oxide(6) and the purification of biacetyl(7) have been described previously. Propylene, 99.5%, propane, 99.9%, and ethane, 95%, were used directly from the cylinders supplied by the Ohio Chemical Company. Acetaldehyde from the Eastman Kodak Company was purified by fractionation.

**Apparatus and Method.**—The reaction vessel and furnace were the same as the apparatus already described.(6) The mercury manometer and capillary tubing connected to the reaction vessel were wound with resistance wire and heated electrically to prevent condensation of any liquid. The experiments for the determination of the effect of increased surface were carried out in a bulb packed with thin-walled Pyrex tubes, about 2.5 mm. in diameter.

Gas samples were obtained by allowing the gases in the reaction vessel to expand into an evacuated bulb. The analysis of the gaseous products other than aldehydes was carried out in a modified constant volume apparatus.(8) Ordinarily the total percentage of unsaturates was determined by means of activated sulfuric acid, but in four experiments a solution of 87% sulfuric acid was employed for the absorption of propylene and a solution of activated sulfuric acid for ethylene. The samples being analyzed were diluted with nitrogen to prevent the absorption of some of the ethylene in the 87% sulfuric acid.

**Aldehyde Analyses.**—Since the use of Schiff reagent showed that aldehydes are present as intermediates during the decomposition, the products from ten experiments were combined into a sample which could be used for the identification of the intermediate aldehydes. Formaldehyde was detected by the Schryver–Rimini reaction.(9) Acrolein was found to be absent by the test described by Pritzker.(10) A test with Lewin's reagent(11) showed that an aldehyde other than formaldehyde is present. Modification of the Lewin test together with other tests for aldehydes indicated that a mixture of acetaldehyde and formaldehyde is contained in the reaction products. In order to identify the second aldehyde with greater certainty, a derivative with dimedon(12) was prepared. The product was cyclicized to the anhydride which was recrystallized and dried *in vacuo*. Formaldehyde did not interfere in the test since formaldimethone was removed by treatment with alkali. The anhydride of pure acetaldehyde was prepared in a similar manner. Two preparations of the unknown derivative had uncorrected melting points of 174° and 172–173°, respectively, and the melting point of the acetaldehyde derivative was 173–174°. The mixed melting point of the acetaldehyde derivative with the second unknown derivative was 173–174°. These results indicate that acetaldehyde is present and that no appreciable quantities of other aldehydes except formaldehyde are present.

For the measurement of total aldehyde concentration during the course of the reaction, most of the charge was removed from the reaction vessel and to this sample was added distilled water and then bisulfite reagent stabilized with ethyl alcohol. This method of analysis which involved the use of excess standard iodine solution and titration with thiosulfate(13) was calibrated against gaseous acetaldehyde and the total amount of aldehyde could be determined with an accuracy of about 5%.

## Results and Discussion

**Products.**—The analyses of the gaseous products other than aldehydes are summarized in Tables I and II. The analyses show that at the lower percentages of decomposition the chief products are ethylene, carbon monoxide and methane, together with smaller amounts of higher unsaturated compounds, hydrogen and ethane. As the reaction approaches completion, the percentage of unsaturates decreases markedly, indicating that they are undergoing further reaction, and the percentages of saturated hydrocarbons and carbon monoxide increase. The fact that the percentage of hydrogen is low indicates that dehydrogenation of tetrahydrofuran to dihydrofuran or to furan does not occur to any significant extent. Moreover, it was found that no furan could be detected in the reaction products using the antimony chloride(14) reaction. The analytical results together with a measurement of the fraction of the products condensable at −78° indicate that the decomposition of tetrahydrofuran into water and butadiene does not occur as a homogeneous reaction to more than a small extent, if at all.

TABLE I

GASEOUS PRODUCTS FROM THE DECOMPOSITION OF TETRAHYDROFURAN

| Temp., °C. | $P_0$, mm. | $\Delta P/\Delta P_f$, % | Mole% Unsatd. | $H_2$ | CO | $CH_4$ | $C_2H_6$ |
|---|---|---|---|---|---|---|---|
| 546 | 217 | 24 | 40.0 | 3.2 | 28.2 | 26.9 | 1.4 |
| 546 | 215 | 24 | 39.5 | 3.5 | 29.2 | 25.5 | 2.3 |
| 550 | 205 | 27 | 39.4 | 4.7 | 27.6 | 23.3 | 4.3 |
| 551 | 191 | 30 | 39.1 | 2.7 | 32.3 | .. | .. |
| 550 | 202 | 57 | 31.7[a] | 4.2[a] | 32.3[a] | 25.1[a] | 6.3[a] |
| 551 | 196 | 89 | 25.7 | 3.8 | 35.0 | 28.5 | 7.6 |
| 538 | 129 | 100 | 6.8 | 5.1 | 35.9 | 39.9 | 12.3 |
| 539 | 192 | 100 | 6.7 | 4.0 | 36.9 | 40.0 | 12.4 |

[a] Average of two analyses.

TABLE II

ANALYSES OF UNSATURATES IN GASEOUS PRODUCTS

| Temp., °C. | $P_0$, mm. | $\Delta P/\Delta P_f$, % | Mole % Total unsatd. | $C_2H_4$ | $C_3H_6$ and higher unsatd. |
|---|---|---|---|---|---|
| 550 | 203 | 21 | 40.9 | 32.3 | 8.6 |
| 551 | 198 | 23 | 40.5 | 32.0 | 8.5 |
| 551 | 204 | 33 | 38.4 | 29.4 | 9.0 |
| 550 | 225 | 43 | 34.6 | 27.8 | 6.8 |

The ratios of the final pressure to the initial pressure were measured at different initial pressures and temperatures, and the results are shown in Fig. 1. A small "dead" space correction has been applied to the observed values in order to obtain those given in Fig. 1. The amounts of aldehydes existing as intermediates during the course of the decomposition at 550° are shown in Fig. 2. From a calculation of the

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(6) Klute and Walters, THIS JOURNAL, **67**, 550 (1945).

(7) Walters, *ibid.*, **62**, 880 (1940).

(8) Gantz and Walters, *ibid.*, **63**, 3412 (1941).

(9) Rimini, *Bull. soc. chim.*, [3] **20**, 896 (1898); Schryver, *Proc. Roy. Soc.* (London), **B82**, 226 (1910).

(10) Pritzker, *Helv. Chim. Acta*, **11**, 445 (1928).

(11) Lewin, *Ber.*, **32**, 3388 (1899).

(12) Vorlaender, *Z. anal. Chem.*, **77**, 241 (1929).

(13) Kolthoff and Furman, "Volumetric Analysis," John Wiley and Sons, Inc., New York, N. Y., Vol. I, 1928, p. 178; Vol. II, 1929. p. 450.

(14) Levine and Richman, *J. Biol. Chem.*, **101**, 374 (1933).

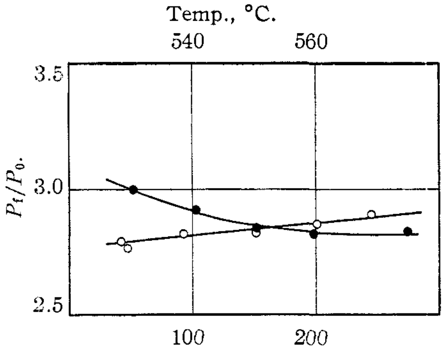


Fig. 1.—Variation of $P_f/P_0$ with initial pressure at 550° = ●; with temperature = ○ ($P_0 \sim 200$ mm.).

amount of tetrahydrofuran decomposed, based upon the observed pressure increase, the yield of aldehyde corresponding to the first point on the curve in Fig. 2 is at least 55%.

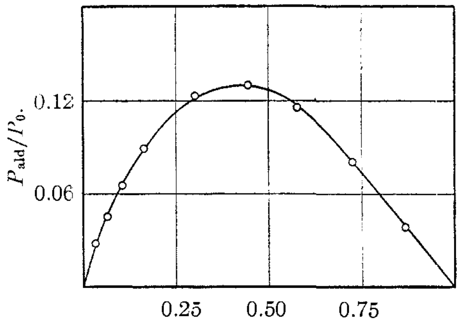
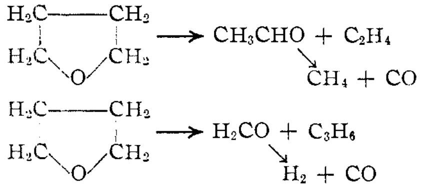


Fig. 2.—Aldehydes present during the decomposition of tetrahydrofuran at 550°, $P_0 \sim 200$ mm.

Although the results do not show that all of the decomposition proceeds by way of aldehyde formation, the analyses of the products and the measurement of pressure increase do indicate that the main reactions occurring in the decomposition are



From the gas analyses it appears that the reaction producing acetaldehyde and ethylene is considerably more important than the one yielding formaldehyde and propylene.

**Kinetics.**—In Fig. 3 are shown the results of the pressure measurements during a representative experiment at 550° and 202 mm. initial pressure. It is apparent that there is a lag in the pressure–time curve at the start of the reaction so that the rate of pressure increase during the early stages of the decomposition becomes greater as the reaction proceeds. The maximum rate of pressure increase is not attained until approximately 40% decomposition has occurred. It would seem that the shape of the pressure–time curve might be due to an induction period or autocatalysis or to the complications caused by the formation and subsequent decomposition of intermediates. Since the amounts of aldehydes present during the course of the reaction have been determined, a pressure–time curve of the type that would be observed if the aldehydes present were completely decomposed is also given in Fig. 3 (on the basis of 1 molecule of aldehyde yielding 2 molecules of products). Even for this corrected pressure–time curve the initial rate of pressure increase is not the maximum rate. However, this curve has not been corrected for the subsequent reactions which the unsaturated products may undergo.

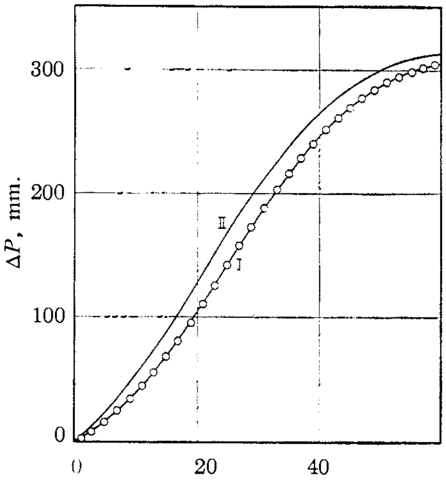


Fig. 3.—Pressure–time curve (I) for tetrahydrofuran decomposition at 550°, $P_0$ = 202 mm.; II, corrected for undecomposed aldehydes.

In order to ascertain the extent to which a heterogeneous reaction might be influencing the decomposition, experiments were carried out at 550° in the packed vessel which had 28 times the surface to volume ratio of the unpacked vessel. For an initial pressure of 100 mm. it was observed that with the packed bulb $t_{1/2}$, the time corresponding to $\Delta P/\Delta P_f = 0.5$, is only a few per cent. smaller than the value obtained in comparable experiments in the unpacked bulb. For experiments with initial pressures of 150–200 mm. the values of $t_{1/2}$ were on the average 10–12% smaller in the presence of increased surface. The over-all pressure increases were found to be essentially the same for both types of vessels, not more than 1% larger for the packed bulb than for the unpacked bulb. The initial rate of pressure increase in the packed bulb is greater than that in the unpacked bulb thus giving a pressure–time curve in which the initial rate is almost as great as the maximum rate of pressure increase. However, the fact that only a relatively small change was observed for $t_{1/2}$ even with a 28-fold increase in surface to volume ratio indicates that the amount of heterogeneous decomposition which occurs in the experiments in the unpacked reaction flask is not important.

On account of the shape of the pressure–time curve the order of the reaction was not obtained during the course of a single experiment. However, line (1) in Fig. 4 shows a plot of the logarithm of $t_{1/2}$ against the logarithm of the initial pressure, $P_0$, for different experiments at 550°. The experiments shown in Fig. 4 were carried out at very nearly the same temperature and in no case does the temperature difference between two experiments exceed 0.5°. For this type of plot, $\log t_{1/2} = -(n-1) \log P_0 + C$, where $n$ is the order of the reaction. Since the slope of line (1) is $-0.55$, an order of 1.5 is indicated for the decomposition of tetrahydrofuran. Also shown in Fig. 4 is the relationship between $\log (\mathrm{d}P/\mathrm{d}t)_{\max}$ and $\log P_0$ and in this case straight line (2) has a slope of 1.5. From these results it appears that the dependence of the maximum rate of pressure increase upon the initial rate, *i. e.*, $(\mathrm{d}P/\mathrm{d}t)_{\max} = k'P_0^{1.5}$, is similar to the relationship obtained for cyclopentane and cyclohexane.[3d,e]

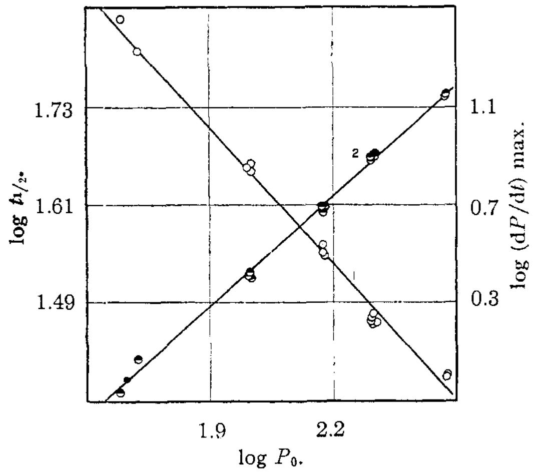


Fig. 4.—Dependence of the rate of decomposition of tetrahydrofuran at 550° upon the initial pressure: ○, log $t_{1/2}$ (min.); ●, log $(\mathrm{d}P/\mathrm{d}t)_{\max}$ (mm./min.).

The temperature coefficient of the reaction was determined from a series of experiments with initial pressures of approximately 200 mm. and at temperatures from 529 to 569°. The results of these experiments are given in Table III. Since the correction for undecomposed aldehydes indicates that $t_{1/2}$ $(\Delta P/\Delta P_f = 0.5)$ corresponds to 57% decomposition, the velocity constant $k$ can be obtained from $t_{1/2}$ by means of the rate expression for a 1.5 order reaction and on the basis that $t_{1/2}$ represents 57% decomposition of tetrahydrofuran. Fig. 5 shows a plot of log $k$ *vs.* $1/T$ from which an activation energy of 53 ± 1 kcal. is obtained. The reaction velocity constant may then be expressed as

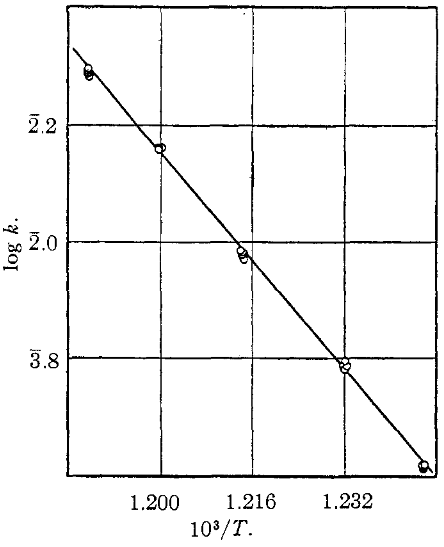


Fig. 5.

$$k = 1.15 \times 10^{12} \times e^{-53{,}000/RT} \text{ mole}^{-1/2} \text{ liter}^{1/2} \text{ sec.}^{-1}$$

TABLE III

RATE OF DECOMPOSITION OF TETRAHYDROFURAN

| $P_0$, mm | $t_{1/2}$, min. | $P_0$, mm. | $t_{1/2}$, min. | $P_0$, mm. | $t_{1/2}$, min. |
|---|---|---|---|---|---|
| Temp., 529.5° | | Temp., 538.5° | | Temp., 550.5° | |
| 203 | 66.2 | 210 | 45.2 | 202 | 29.4 |
| 201 | 66.9 | 211 | 44.0 | 200 | 30.1 |
| 201 | 67.0 | 201 | 45.3 | 197 | 29.7 |
| 206 | 66.8 | 201 | 44.5 | 197 | 29.4 |
| | | 199 | 45.3 | 199 | 29.2 |
| Temp., 560° | | Temp., 569° | | | |
| 203 | 19.2 | 202 | 14.5 | | |
| 202 | 19.3 | 201 | 14.4 | | |
| 198 | 19.4 | 201 | 14.5 | | |
| 198 | 19.2 | 199 | 14.9 | | |

**Decomposition of Tetrahydrofuran in the Presence of Other Substances.**—Since acetaldehyde is one of the intermediate products of the decomposition, several experiments were carried out to ascertain the effect of acetaldehyde upon the rate of the decomposition and upon the shape of the pressure–time curve. It was observed that small amounts of acetaldehyde have very little, if any, influence upon the rate. The pressure increases in the presence of acetaldehyde during the first twenty minutes, $\Delta P_{20}$, shown in Table IV, are almost the same as those without acetaldehyde. Part of the small difference is probably due to the pressure increase produced by the decomposition of acetaldehyde itself. Moreover, the addition of acetaldehyde does not remove the concavity in the initial portion of the pressure–time curve.

In order to determine whether nitric oxide might be able to inhibit the decomposition, tetra-

TABLE IV

EFFECT OF ADDED SUBSTANCES UPON THE RATE OF DECOMPOSITION OF TETRAHYDROFURAN

| Temp., °C. | $P_{\text{TF}}$ mm. | $P_{\text{AcH}}$ mm. | $\Delta P_{20}$ mm. |
|---|---|---|---|
| 551 | 104 | 0.0 | 36.0[a] |
| 551 | 95 | 2.1 | 38.5 |
| 549 | 97 | 5.8 | 40.0 |
| 549 | 106 | 0.0 | 34.5 |
| | | $P_{\text{NO}}$ | |
| 550 | 200 | 0.0 | 115 |
| 551 | 202 | .11 | 116 |
| 550 | 205 | .33 | 109 |
| 548 | 294 | .0 | 161 |
| 548 | 295 | .88 | 206 |
| 548 | 296 | 2.35 | 241 |
| 549 | 298 | 3.37 | 259 |
| 550 | 300 | 6.75 | 290 |
| | | $P_{\text{Ac}_2}$ | |
| 549 | 80 | 0.0 | 21.0 |
| 549 | 81 | .19 | 56.0 |
| 549 | 83 | .25 | 60.5 |
| 549 | 82 | .38 | 68.5 |
| 549 | 82 | .72 | 76.5 |
| 549 | 80 | .95 | 80.0 |

[a] Values under 100 mm. given to the nearest 0.5 mm.

hydrofuran was decomposed in the presence of small quantities of nitric oxide. From the results given in Table IV it is evident that there is no appreciable inhibition. The slight decrease in rate for 205 mm. of tetrahydrofuran containing 0.33 mm. of nitric oxide is almost within the experimental error, and even if this difference does represent a small inhibition, the results do not indicate that a significant amount of the decomposition occurs by a chain process. At the higher pressures of nitric oxide, it is apparent that a catalysis occurs.

Preliminary experiments were also performed with mixtures of tetrahydrofuran (200 mm.) and propylene (20–80 mm.) at 550°. The results showed that the rate of pressure increase in the presence of added propylene is greater than for the tetrahydrofuran alone. Propylene itself undergoes a slight pressure increase at 550°, but the rate of pressure increase of the mixture of tetrahydrofuran and propylene is appreciably greater than the sum of the rate for tetrahydrofuran and the rate for propylene.

In the decomposition of aliphatic compounds propylene has been found to act as an inhibitor,[15] but with cyclopentane it has been observed that propylene accelerates the decomposition.[3e] Moreover, the apparent autocatalytic nature of ring cleavage in the cyclopentane decomposition has been explained on the basis of the catalytic effect of propylene and ethylene which are found in the products.[3e,16] In this connection it is of interest to note that ethylene and presumably propylene are found in the products of the tetrahydrofuran decomposition. Additional experiments are planned in order to investigate the effect of propylene and also the influence of ethylene and inert gases upon the decomposition of tetrahydrofuran.

Biacetyl has been found to promote the decomposition of a number of organic compounds[17] and this effect has been interpreted as a chain reaction initiated by free radicals produced during the decomposition of biacetyl. As indicated by the data in Table IV, small pressures of biacetyl produce a large acceleration in the rate of pressure increase during the decomposition of tetrahydrofuran. From these results it would appear that biacetyl can cause tetrahydrofuran to undergo a chain decomposition.

In order to determine whether or not tetrahydrofuran might act as a promoter for other decompositions in a manner similar to ethylene oxide, the rates of decomposition of ethane and propane containing small percentages of tetrahydrofuran were measured at 550°. Within the limits of experimental error no accelerating effect was observed in either decomposition.

**Mechanism.**—Several possible mechanisms can be written for the decomposition of tetrahydrofuran into aldehydes and unsaturated compounds. The products can be accounted for on the basis of a non-chain decomposition (ring cleavage) similar to that proposed for the decomposition of other ring compounds by Rice and Murphy[18] using the principle of least motion That a mechanism of this type is of importance in the decomposition of cyclic hydrocarbons has also been suggested by Eucken.[16] However, it is possible to account for the products by a chain mechanism involving the removal of a hydrogen atom from the tetrahydrofuran molecule followed by the decomposition of the $C_4H_7O$ radical.

The shape of the pressure–time curve and the fractional order of the decomposition would tend to indicate that the decomposition is not a simple type of reaction. Reactions obeying a 1.5-order law have often been interpreted in terms of atom or radical chain mechanisms, and in the present case the frequency factor (in terms of the same units) is of approximately the same magnitude as the values obtained in some of these chain reactions.[19] However, attempts to inhibit the decomposition of tetrahydrofuran with nitric oxide and propylene have given no positive evidence for the existence of a chain reaction.

In some cases the existence of an apparent induction period has been ascribed to the isomeriza-

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(15) Rice and Polly, *J. Chem. Phys.*, **6**, 273 (1938); Echols and Pease, THIS JOURNAL, **61**, 1024 (1939); Smith and Hinshelwood, *Proc. Roy. Soc.* (London), **180A**, 237 (1942); **183A**, 33 (1944).

(16) Eucken, *Die Chemie*, **56**, 342 (1943).

(17) Rice and Walters, THIS JOURNAL, **63**, 1701 (1941).

(18) Rice and Murphy, *ibid.*, **64**, 896 (1942); **66**, 765 (1944).

(19) Pease, "Equilibrium and Kinetics of Gas Reactions," Princeton University Press, Princeton, N. J., 1942, p. 181.

tion of the original compound into a moderately stable primary product,[3f] and this type of explanation cannot be definitely excluded at present for the case of tetrahydrofuran. In this connection it might be thought that butyraldehyde which is isomeric with tetrahydrofuran might be a possible intermediate, but the presence of butyraldehyde was not revealed in the analyses for aldehydes.

If the products of the decomposition could exhibit a sufficiently accelerating influence, as suggested by Kuchler for cyclopentane,[3e] the shape of the pressure–time curve could be due to autocatalysis. However, definite conclusions concerning the mechanism of the decomposition of tetrahydrofuran cannot be drawn until additional experimental results are obtained.

## Summary

The homogeneous decomposition of tetrahydrofuran has been investigated in the region 529 to 569° at pressures from 50 to 300 mm. Acetaldehyde and formaldehyde have been identified as intermediate products. The products found by gas analysis are chiefly ethylene, carbon monoxide and methane together with smaller percentages of higher unsaturated compounds, hydrogen and ethane.

The pressure measurements indicate that a slight induction period is present and that the reaction is 1.5 order. The rate constant can be expressed as

$$k = 1.15 \times 10^{12} \times e^{-53{,}000/RT} \text{ mole}^{-1/2} \text{ liter}^{1/2} \text{ sec.}^{-1}$$

The rate of decomposition is not retarded to any appreciable extent by either nitric oxide or propylene.

ROCHESTER, NEW YORK RECEIVED NOVEMBER 15, 1945

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[CONTRIBUTION FROM SUN OIL COMPANY]

# Effect of Side Reactions on Experimental Isomerization Equilibria

BY JOHN R. BATES

Isomerization of one hydrocarbon compound to produce another almost universally involves the use of catalyst to promote the reaction. In most cases the extent of the reaction is governed by an apparent equilibrium or stationary concentration of the two isomers. It is also true that in every instance of the use of catalyst for such purposes, side reactions other than those of pure isomerization occur. It has been generally accepted that the equilibrium reached would be governed by purely thermodynamic considerations if the same apparent equilibrium concentration were obtained when starting with each of the two isomers, irrespective of any side reactions that might occur. Kinetics of some such process are here evaluated and show that values far from calculated true equilibrium can be obtained, and confirmed by starting with either of the two isomers as the reactant.

It should be observed that these results are obviously not in contradiction with thermodynamic theory inasmuch as isomerization equilibria calculated from free energy of the isomers do not necessarily represent the lowest energy state of the system when all the possible reactions which the isomers may undergo, in addition to their transformation one to another, are considered.

Consider the reaction

$$\mathrm{A} \underset{kb_1}{\overset{ka_1}{\rightleftarrows}} \mathrm{B}$$

with side reactions

$$\mathrm{A} \longrightarrow \mathrm{M} + \mathrm{N}\ (ka_2)$$
$$\mathrm{B} \longrightarrow \mathrm{X} + \mathrm{Y}\ (kb_2)$$

If all the reactions involved are first order, which is the case in a number of reactions of hydrocarbons,[1] the following differential equations will hold and must be solved simultaneously.

$$-\mathrm{dA}/\mathrm{d}t = \mathrm{A}ka_1 - \mathrm{B}kb_1 + \mathrm{A}ka_2 \qquad (1)$$
$$-\mathrm{dB}/\mathrm{d}t = \mathrm{B}kb_1 - \mathrm{A}ka_1 + \mathrm{B}kb_2 \qquad (2)$$

Using the well-known methods of a particular integral and auxiliary equation, the following values for A and B as a function of time are obtained.

$$ka_1\mathrm{A} = \mathrm{C}(kb_1 + kb_2 - \alpha - \beta)e^{-(\alpha + \beta)t} + \mathrm{D}(kb_1 + kb_2 - \alpha + \beta)e^{-(\alpha - \beta)t} \qquad (3)$$
$$\mathrm{B} = \mathrm{C}e^{-(\alpha + \beta)t} + \mathrm{D}e^{-(\alpha - \beta)t} \qquad (4)$$

where

$$\alpha = (ka_1 + kb_1 - ka_2 + kb_2)/2$$
$$\beta = [(ka_1 + ka_2 - kb_1 - kb_2)^2 + 4ka_1kb_1]^{1/2}/2$$

C and D can be evaluated in terms of the initial quantities of A and B as follows

$$\mathrm{C} = \frac{-ka_1\mathrm{A}_0 + \mathrm{B}_0\,(kb_1 + kb_2 - \alpha + \beta)}{2\beta} \qquad (5)$$
$$\mathrm{D} = \frac{ka_1\mathrm{A}_0 - \mathrm{B}_0\,(kb_1 + kb_2 - \alpha - \beta)}{2\beta} \qquad (6)$$

The ratio of B to A, which should yield the equilibrium $K_c$ at $t = \infty$, is given by

$$\mathrm{B/A} = \frac{ka_1[Ce^{-2\beta t} + D]}{C(kb_1 + kb_2 - \alpha - \beta)e^{-2\beta t} + D(kb_1 + kb_2 - \alpha + \beta)} \qquad (7)$$

which at $t = \infty$ becomes

$$\mathrm{B/A} = \frac{2ka_1}{kb_1 + kb_2 - ka_1 - ka_2 + [(ka_1 + ka_2 - kb_1 - kb_2)^2 + 4ka_1kb_1]^{1/2}} \qquad (8)$$

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(1) Rosen (Talicheev), *Oil Gas J.*, **39**, No. 41 (1941); also, see Burk and Laskowski, paper presented before Petroleum Division, Boston Meeting, A. C. S., 1939, for references.