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

The Effect of Added Gases upon the Thermal Decomposition of Tetrahydrofuran[1]

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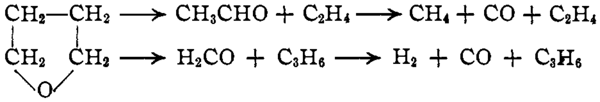
The rate of decomposition of tetrahydrofuran is not increased appreciably by the addition of nitrogen, carbon monoxide, methane or hydrogen. With 200 mm. of tetrahydrofuran reacting for 20 minutes at 546°, the change in the pressure increase produced by the addition of 100 mm. of hydrogen, which appears to have the largest effect of the four gases, is about +13%. Propylene under similar conditions raises the pressure increase at least 130%. Analyses for carbon monoxide, acetaldehyde and formaldehyde have shown also that the amount of tetrahydrofuran reacting is increased by the addition of propylene. Ethylene which is an important product of the decomposition of tetrahydrofuran has a similar accelerating influence upon the decomposition. Other unsaturated hydrocarbons, such as allene, cyclopentadiene and diallyl, have been found to accelerate the rate of pressure increase of tetrahydrofuran.

Introduction

In a previous investigation[2] the homogeneous thermal decomposition of tetrahydrofuran was found to proceed according to the reactions



$$CH_2\text{—}CH_2 \longrightarrow CH_3CHO + C_2H_4 \longrightarrow CH_4 + CO + C_2H_4$$

$$CH_2 \quad CH_2 \longrightarrow H_2CO + C_3H_6 \longrightarrow H_2 + CO + C_3H_6$$

the first reaction being the more important. Moreover, it was observed that the addition of propylene to tetrahydrofuran at 550° results in a rate of pressure increase greater than that for tetrahydrofuran alone. The observed acceleration is considerably greater than the slow rate of pressure increase which propylene itself undergoes at 550°. This behavior is in marked contrast to the inhibiting effect of propylene upon the thermal decompositions of many other compounds in the same temperature range,[3] but in the case of another five-membered ring compound, cyclopentane, Küchler[4] reported that propylene accelerates the ring cleavage reaction. From the preliminary pressure measurements[2a] obtained with mixtures of tetrahydrofuran and propylene it was not possible to decide whether the greater rate of pressure increase is due to an accelerated decomposition of tetrahydrofuran or due to some other cause, such as a promoted decomposition of propylene. However, the presence of any product molecule which contains an atom of oxygen indicates that a molecule of tetrahydrofuran has reacted; therefore, in the present study an analysis for the oxygen-containing products has been made in order to measure the amount of tetrahydrofuran which has reacted. Since ethylene and presumably propylene are found in the products of the decomposition of tetrahydrofuran, it appeared that further investigation of the effect of propylene and also ethylene might provide information concerning the importance of these products in contributing to the S-shaped nature of the pressure–time curve found in the normal decomposition of tetrahydrofuran. In addition, it was of interest to study not only the influence of unsaturated hydrocarbons, but also the effect of other added gases upon the decomposition.

Experimental

Materials.—The tetrahydrofuran employed in almost all of the experiments was obtained from the Eastman Kodak Company and was usually purified in a manner similar to that employed in the previous study.[2] Similar results have been obtained with tetrahydrofuran (after purification) from the du Pont Company and with samples prepared by hydrogenation of furan. The tetrahydrofuran, which was peroxide-free, was kept under vacuum at −78° until used.

C.P. propylene and ethylene, each with a stated purity of 99.5%, were obtained from the Ohio Chemical and Manufacturing Company and were used in the majority of the experiments. However, samples of propylene obtained from several other sources and subjected to various methods of purification gave comparable results.

Electrolytic hydrogen from the Air Reduction Sales Company was purified by passage through a Baker Chemical Company Deoxo-Purifier. Dry nitrogen with a stated purity of 99.99% was obtained from the Linde Air Products Company. Carbon monoxide from the Matheson Company was used after the removal of any condensable gases. Nitric oxide which had been prepared by the method already described[5] was further purified by four distillations between −160° and −196°.

Diallyl (1,5-hexadiene), 99.89 ± 0.08 mole per cent., was obtained from the National Bureau of Standards. Allene, 99.9% pure, was generously furnished by Dr. F. O. Rice of Catholic University. Cyclopentadiene was prepared and purified as in a previous investigation.[6] Baker C.P. thiophene-free benzene was dried over anhydrous calcium sulfate and outgassed before use. The following C.P. gases from the Matheson Company were used without purification: methane, isobutene, butene-1, butene-2 and butadiene-1,3.

Apparatus and Method.—The Pyrex reaction bulb was kept at the elevated temperature by means of an electrically heated furnace of the same type as that used in earlier investigations.[5,6] The temperature was measured by the use of a calibrated[7] platinum, platinum–13% rhodium thermocouple. For experiments with increased surface a packed reaction bulb filled with thin-walled Pyrex tubes was used. In all of the experiments in which carbon monoxide and aldehyde analyses were performed a Warrick–Fugassi valve[8] was used to separate the tetrahydrofuran supply bulb from the remainder of the vacuum line. In these experiments the added gas was introduced into the reaction vessel, and then the tetrahydrofuran which vaporized from the warmed supply bulb was allowed to pass into the reaction vessel. In this procedure the added gas remained in the reaction vessel 1 or 2 minutes before the tetrahydrofuran could be introduced. However, in the other experiments the apparatus and procedure were modified so that the added unsaturated hydrocarbon could be introduced either simultaneously with the tetrahydrofuran or at a definite time prior to the introduction of the tetrahydrofuran.

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(2) (a) C. H. Klute, Doctoral Thesis, University of Rochester, 1942; (b) C. H. Klute and W. D. Walters, THIS JOURNAL, **68**, 506 (1946).

(3) (a) F. O. Rice and O. L. Polly, *J. Chem. Phys.*, **6**, 273 (1938); (b) R. N. Pease, THIS JOURNAL, **61**, 1024 (1939); (c) J. R. E. Smith and C. N. Hinshelwood, *Proc. Roy. Soc.* (*London*), **180A**, 237 (1942); **183A**, 33 (1944).

(4) L. Küchler, *Z. physik. Chem.*, **B53**, 307 (1943).

(5) C. H. Klute and W. D. Walters, THIS JOURNAL, **67**, 550 (1945).

(6) D. W. Vanas and W. D. Walters, *ibid.*, **70**, 4035 (1948).

(7) W. F. Roeser and H. T. Wensel, *J. Research Natl. Bur. Standards*, **14**, 247 (1935).

(8) E. L. Warrick and P. Fugassi, *Ind. Eng. Chem., Anal. Ed.*, **15**, 13 (1943).

Analyses.—Carbon monoxide was determined by means of Cosorbent reagent after the removal of condensable materials and olefins. The procedure for the separation of carbon monoxide from the condensable products and its analysis was checked in the following manner. A gas mixture consisting of carbon monoxide, nitrogen, ethylene, propylene, ethane and tetrahydrofuran and contained in the cold reaction vessel was removed, separated and analyzed. In three such determinations of simulated reaction products, the average volume of carbon monoxide obtained by analysis agreed with the volume of carbon monoxide introduced to within 3%. The determination of aldehydes in the products was made polarographically.[9] Reference solutions were run with each determination of aldehydes.

In the previous work[2] it was found that carbon monoxide, acetaldehyde and formaldehyde are the principal oxygen-containing products from the homogeneous decomposition of tetrahydrofuran. No evidence was obtained for the formation of any other product containing oxygen, such as furan, carbon dioxide, water or acrolein. In the present study the possibility that ketene might be a product was investigated by two methods: (a) The reaction products were allowed to come into contact with water and any acetic acid formed was titrated. (b) The products from five runs were separated into several fractions by means of differences in volatility and infrared absorption curves were obtained for each fraction. These analyses showed that the amount of ketene present in the decomposition of 200 mm. of tetrahydrofuran after 20 minutes at 550–555° would not exceed 0.3–0.4 mm. Therefore, it has been assumed that analyses for carbon monoxide, acetaldehyde and formaldehyde would be sufficient to determine the amount of tetrahydrofuran reacted. In agreement with the findings of the earlier study[2] the infrared absorption curves indicated that, in addition to ethylene, at least one other unsaturated hydrocarbon, such as propylene or butene-1, is present, propylene being the more likely.

Results and Discussion

Effect of Nitrogen.—In order to find out whether an inert gas influences the rate of decomposition of tetrahydrofuran, experiments with added nitrogen were carried out at 546°. The results are shown in Table I. The amount of decomposition in 20 minutes, as measured by the pressure increase, ΔP_{20}, appears to be about 5% greater in the presence of nitrogen, but this observed increase is of the order of magnitude of the experimental error. Likewise 40 mm. nitrogen added to 80 mm. tetrahydrofuran produces no significant change in rate.

TABLE I

EFFECT OF NITROGEN UPON THE DECOMPOSITION OF TETRAHYDROFURAN AT 546°

ΔP_{20} is the pressure increase during the first 20 minutes

Run no.	$P^0_{C_4H_8O}$, mm.	$P^0_{N_2}$, mm.	ΔP_{20}, mm.
152	203	0	79
154	202	0	78
151	203	101	81
153	202	105	83

Effect of Propylene.—The previous observations that the addition of propylene substantially increases the rate of pressure rise of tetrahydrofuran have been confirmed. Moreover, the accelerating effect of propylene is neither inhibited by the addition of a small amount of nitric oxide nor appreciably altered by a thirty-fold increase in the surface to volume ratio. In order to relate the results of the pressure measurements to the quantities of tetrahydrofuran decomposed, the amounts of the principal oxygen-containing products, namely, carbon monoxide, acetaldehyde and formaldehyde have been determined. As shown in Table II, with 100 mm. propylene and 200 mm. tetrahydrofuran at 546° the amount of tetrahydrofuran reacted after 20 minutes is about 2.2 times the amount of pure tetrahydrofuran which would be decomposed under similar conditions. The carbon monoxide content is increased about threefold, but the pressures of aldehydes after 20 minutes are approximately the same with and without added propylene. However, the results at shorter periods of reaction (Table III) show that the concentrations of aldehydes build up more rapidly in the presence of propylene than in the normal reactions.

TABLE II

CARBON MONOXIDE AND ALDEHYDES FROM THE DECOMPOSITION OF TETRAHYDROFURAN

Time of reaction, 20 minutes; temperature, 546°; ΔP_{20} is the pressure increase during the first 20 minutes; P_{CH_3CHO} is given to the nearest 0.5 mm., other pressures to the nearest mm.

$P^0_{C_4H_8O}$, mm.	$P^0_{C_3H_6}$, mm.	ΔP_{20}, mm.	P_{CO}, mm.	P_{H_2CO}, mm.	P_{CH_3CHO}, mm.	$P_{CO+ald.}$, mm.
200	0	76	35			53
201[a]	0	76		6[a]	12[a]	
200	100	180	99			116
199	101	183		6	10	
199	101	191		6	11	
201[a]	0	65[a]	29[a]			47
202	0	68		6[b]	11.5[b]	
201	100	168[a]	90[a]			107
199	101	182		6[b]	11[b]	

[a] Average of two nearly identical runs. [b] Aldehyde analysis bulb cooled to −78°; in other runs cooled to −196°.

TABLE III

ALDEHYDES IN THE TETRAHYDROFURAN DECOMPOSITION AT 546°

$P^0_{C_4H_8O}$, mm.	$P^0_{C_3H_6}$, mm.	Time, min.	P_{H_2CO}, mm.	P_{CH_3CHO}, mm.	$P_{ald.}$ mm.
201	0	7	2.0	4.6	6.6
203	100	7	4.5	8.8	13.3
203	0	12	3.7	7.9	11.6
199	101	12	6.3	11.0	17.3

In view of the complexity of the reaction and the shape of the pressure–time curve it would appear to be difficult to determine the exact relationship between the rate of the reaction and the pressures of tetrahydrofuran and propylene. However, at 546° after about 55% pressure increase the slope of the pressure–time curve is almost constant over a considerable range. Preliminary results have indicated that with a constant large amount of propylene (150 mm.) the slope at 55% pressure increase is approximately proportional to the pressure of tetrahydrofuran. For experiments with the same initial pressure of tetrahydrofuran the increase in slope depends approximately linearly upon the propylene pressure.

When the propylene was allowed to remain in the reaction vessel for some time prior to the introduction of tetrahydrofuran, there appeared to be a difference in the pressure–time curve, particularly during the initial stages of the decomposition. To

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(9) P. J. Elving and E. Rutner, *Ind. Eng. Chem., Anal. Ed.*, **18**, 176 (1946); G. C. Whitnack and R. W. Moshier, *ibid.*, **16**, 496 (1944).

study this effect experiments were conducted at 530 and 546°, and the data are summarized in Fig. 1 and Table IV. Since the results in Table II indicate that the observed pressure increases are reasonably satisfactory measures of the relative amounts of decomposition of tetrahydrofuran, the experiments shown in Table IV have been compared on the basis of pressure increases. At 546° the accelerating effect seems to increase at first with the length of time delay and then to decrease slowly. It is to be noted that with propylene considerable reaction may have occurred at the longer times. The results from experiments carried out in the packed vessel with a thirty-fold increase in surface to volume ratio did not differ from the data shown in Table IV by more than 12%, indicating that the processes under study are homogeneous.

TABLE IV

EFFECT OF PROPYLENE AND ITS DECOMPOSITION PRODUCTS UPON THE DECOMPOSITION OF TETRAHYDROFURAN AT 546°

$P^0_{C_4H_8O}$, mm.	$P_{C_3H_6}$, mm.	Delay[b] min.	ΔP_{20},[a] mm.	$\Delta P_{20}/P^0_{C_4H_8O}$
104	0	0	21	0.20
103	51	0	57	.55
103	50	12	80	.78
101	51	38	90	.89
97	51	126	81	.84
103	50	240	83	.81

[a] ΔP_{20} is the pressure increase after 20 minutes. Each result represents the average of two or more similar experiments. [b] Delay denotes the time between the introduction of propylene into the reaction vessel and the introduction of tetrahydrofuran. A 50-mm. sample of propylene at 546° undergoes pressure changes of about 0.3, 2, 8 and 11 mm. in 12, 38, 126 and 240 min., respectively.

Effect of Ethylene.—Since ethylene is the chief unsaturated hydrocarbon found in the products, the effect of ethylene upon the rate of decomposition was studied. In experiments at 546° the carbon monoxide produced from 80 mm. tetrahydrofuran in 20 minutes in the presence of 40 mm. ethylene was at least 1.77 times the amount of carbon monoxide from pure tetrahydrofuran alone. Although aldehyde analyses were not made, it appears that the presence of ethylene increases the rate of reaction of tetrahydrofuran. The data from other experiments with added ethylene are shown in Table V.

TABLE V

EFFECT OF ETHYLENE AND ITS REACTION PRODUCTS UPON THE DECOMPOSITION OF TETRAHYDROFURAN AT 546°

$P^0_{C_4H_8O}$, mm.	$P_{C_2H_4}$, mm.	Delay, min.	ΔP_{20} mm.	$\Delta P_{20}/P^0_{C_4H_8O}$
104	0	0	21	0.20
107	51	0	43	.40
96[a]	51	12	50	.52
104	52	38	67	.64
96	51	126	67	.70

[a] Single experiment; other results are average values. At 546° a 50 mm. sample of ethylene alone gives a slow pressure decrease which does not exceed 2 mm. in 126 min.

Effect of Other Products.—In the tetrahydrofuran decomposition carbon monoxide and methane are important products and hydrogen is a relatively minor product. In order to ascertain the effect of these products upon the rate of decomposition, experiments with 200 mm. of tetrahydrofuran and 100 mm. of added gas were carried out at 546°. The pressure increase during the first 20 minutes in the presence of any one of these gases was only slightly larger than that for pure tetrahydrofuran alone. The increments in rate produced by carbon monoxide, methane and hydrogen amounted to 8, 10 and 13%, respectively; under similar conditions 100 mm. of propylene would produce an increase of at least 130%.

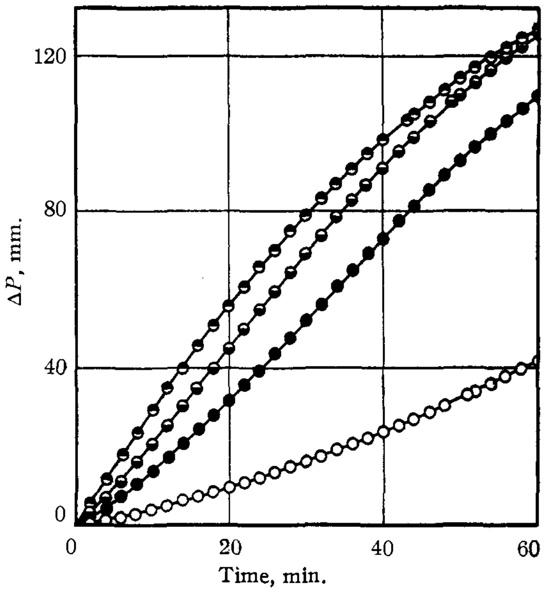

Fig. 1.—Effect of propylene and its decomposition products upon the thermal decomposition of tetrahydrofuran at 530°: O, 99 mm. tetrahydrofuran; ●, 51 mm. propylene and 101 mm. tetrahydrofuran, simultaneous introduction; ◒, 51 mm. propylene introduced into reaction bulb 23 min. before 103 mm. tetrahydrofuran; ◓, 53 mm. propylene in bulb 130 min. before 99 mm. tetrahydrofuran.

Effect of Various Substances.—In view of the fact that propylene is probably decomposing to some extent under the experimental conditions it was of interest to examine the influence of some of the substances reported as products of the thermal decomposition of propylene. Methane, hydrogen and ethylene had been studied. Allene[10] and diallyl,[3a,10] which are found among the products from the pyrolysis of propylene, had not been investigated. Allene has been found to accelerate markedly the rate of pressure increase (see Table VI), but the initial rate does not seem to be as great as the subsequent rate. The decomposition produced by diallyl is so rapid initially that it is difficult to obtain accurate pressure measurements. Diallyl itself decomposes very rapidly at this temperature.

Several other compounds have been studied, also, and the data are summarized in Table VI.

Discussion.—From the results obtained in this work it is evident that tetrahydrofuran reacts more readily in the presence of added propylene or ethylene. This behavior of propylene and ethylene (or their decomposition products) toward a

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[10] (a) V. Schneider and P. K. Frolich, *Ind. Eng. Chem.*, **23**, 1405 (1931); (b) M. Szwarc, *J. Chem. Phys.*, **17**, 284 (1949).

TABLE VI

EFFECT OF VARIOUS SUBSTANCES UPON THE DECOMPOSITION OF TETRAHYDROFURAN AT 546°

C_3H_4 = allene; C_6H_{10} = diallyl (1,5-hexadiene); C_6H_6 = benzene; C_5H_6 = cyclopentadiene; i-C_4H_8 = isobutene.

$P^0_{C_4H_8O}$, mm.	P^0_{added}, mm.	Subst. added	ΔP_{20}, mm.	P_{CO}, mm.
108	0	....	23	...
99	4.1	C_3H_4	70	...
100	13.3	C_3H_4	100	...
~105	2.9	C_6H_{10}	>110	...
~115	3.4	C_6H_{10}	>120	...
103	51	C_6H_6	25	...
101	51[a]	C_6H_6[a]	26	...
200	0	....	76	35
197	50	C_5H_6	241[b]	133
198	50	C_5H_6	234[b]	132
251	0	....	121	...
207	102	i-C_4H_8	262[b]	...

[a] Time delay of 22 minutes. [b] The tetrahydrofuran was introduced 1 or 2 minutes after the added substance; in cases other than (*a*) or (*b*), simultaneous introduction. The pressure change for 50 mm. pure cyclopentadiene is about +3 mm. in 20 minutes.[11]

ring compound is of particular significance because unsaturated hydrocarbons, such as propylene and ethylene, are the products of decomposition of many cyclic compounds. In a number of these decompositions, namely, those of cyclopentane, cyclohexane and methylcyclopentane, the S-shaped pressure–time curves have been attributed to an acceleration by the products.[4,12] In the case of S-shaped pressure–time curve observed in the tetrahydrofuran decomposition, the present study indicates that autocatalysis by the unsaturated hydrocarbons is a contributing factor. In addition, as shown in the earlier work,[2] the shape of the curve is influenced by the fact that near the beginning of the reaction the rate of decomposition of the aldehydes is not as great as their rate of formation.

The observation that allowing the propylene to remain in the reaction bulb increases the acceleration indicates that some substance, either molecule or radical, is formed which is more effective than the original compound. Likewise, in the experiments with simultaneous introduction of propylene and tetrahydrofuran, the shape of the pressure–time curve near zero time suggests that a large part of the observed acceleration may be caused by a substance formed by the pyrolysis of propylene. That propylene by itself can decompose slowly under the experimental conditions is indicated by the slow pressure rise and by the appearance of ethylene and methane in the infrared absorption spectrum of propylene pyrolyzed for 20 minutes at 555°.[13] To establish the cause of the increased effectiveness of pyrolyzed propylene will require additional studies, but it may be of significance that allene and diallyl, possible products of the propylene decomposition, seem to produce considerable acceleration of the tetrahydrofuran reaction.

In the case of ethylene, exploratory experiments have shown that some of the reported products[10a,13a,b,d,14] from the reaction of ethylene, namely, butenes, butadiene and acetylene, as well as propylene, accelerate the decomposition of tetrahydrofuran to a greater extent than ethylene.

For an explanation of the accelerating effect of propylene upon the decomposition of cyclopentane, Küchler[4] and Eucken[12] have suggested that during a properly oriented collision the unsaturated hydrocarbon assists in the transfer of a hydrogen atom from one carbon atom to an adjacent carbon atom, thereby enabling the reactant to reorganize more readily into stable product molecules. A similar explanation might be applied to the influence of unsaturated hydrocarbons upon the decomposition of tetrahydrofuran. At the present time no experimental evidence for this mechanism has been reported and further investigation will be needed before a decision concerning the mechanism can be made.

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[11] For other data on the thermal behavior of cyclopentadiene see F. O. Rice and M. T. Murphy, THIS JOURNAL, **64**, 896 (1942).

[12] A. Eucken, *Die Chemie*, **56**, 342 (1943).

[13] For other data concerning the pyrolysis of propylene see (a) F. E. Frey and D. F. Smith, *Ind. Eng. Chem.*, **20**, 948 (1928); (b) R. V. Wheeler and W. L. Wood, *J. Chem. Soc.*, 1819 (1930); (c) C. D. Hurd and R. N. Meinert, THIS JOURNAL, **52**, 4978 (1930); (d) G. Egloff and E. Wilson, *Ind. Eng. Chem.*, **27**, 917 (1935).

[14] R. N. Pease, THIS JOURNAL, **52**, 1158 (1930); R. E. Burk, B. G. Baldwin and C. H. Whitacre, *Ind. Eng. Chem.*, **29**, 326 (1937).