

Flowers and Frey¹² on similar cyclopropane derivatives. Their data for the geometrical isomerization of 1,2-dimethylcyclopropane gave a value of 1.07 kcal./mole for the ΔH of the *trans* to *cis* isomerization, with an equilibrium constant of 0.41 at 399°. A structural isomerization yielding four C₅ olefins was found to be slower than the geometrical isomerization. The greater proportion of 2-pentenes in the products from *cis*-1,2-dimethylcyclopropane compared to the products from the *trans* isomer was attributed to the repulsion of the methyl groups.

Although the activation energies of the *cis-trans* isomerization reactions of the 1,2-dimethylcyclobutanes are almost the same or slightly lower than the activation energies for the symmetrical ring cleavage reactions 1 and 4, the rates of isomerization are smaller than the rates of the ring cleavages. The slower rates of isomerization appear to be caused by the fact that the pre-exponential factors for the isomerizations are approximately an order of magnitude smaller than those of the ring cleavages. The apparent entropies of activation for the geometrical isomerizations at 430° were estimated from the relationship $A = \kappa e(k_B T/h) \exp(\Delta S^*/R)$. If κ is taken as 1, the apparent entropy of activation, ΔS^* , is 5.5 e.u. for reaction 3 and 4.4 e.u. for reaction 6.¹³ The lower apparent entropies of

(12) M. C. Flowers and H. M. Frey, *Proc. Roy. Soc. (London)*, **A257**, 122 (1960); **A260**, 424 (1961).

activation for the *cis-trans* isomerizations (3 and 6) compared to the ring cleavage reactions (1, 2, 4, and 5) may be the result of a situation where any activated complex for isomerization has a somewhat lower entropy than the type of activated complex required for ring cleavage. On the other hand, if a biradical were formed as a very short-lived intermediate¹⁴ in both isomerization and ring cleavage, the differences in rates of the subsequent steps leading to isomerization or ring cleavage could produce differences in the observed over-all rates. It should be noted that depending on the C-C bond broken initially more than one type of biradical could conceivably be formed.

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(13) With $\kappa = 0.5$, the values of ΔS^* would be 6.9 and 5.8 e.u. for reactions 3 and 6, respectively.

(14) In a consideration of the 1,2-dideuteriocyclopropane isomerization data (see E. W. Schlag and B. S. Rabinovitch, *J. Am. Chem. Soc.*, **82**, 5996 (1960)) recently S. W. Benson, *J. Chem. Phys.*, **34**, 521 (1961), has discussed such a mechanism for the pyrolysis of cyclopropane and suggested it for cyclobutane. F. T. Smith, *ibid.*, **29**, 235 (1958), has postulated an internal rotation (rather than a ring opening) for the geometrical isomerization of 1,2-dideuteriocyclopropane.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER, ROCHESTER, NEW YORK]

The Vapor Phase Decomposition of 2,5-Dihydrofuran¹

BY C. A. WELLINGTON AND W. D. WALTERS

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The decomposition of 2,5-dihydrofuran between 342 and 409° has been found to be a first order homogeneous process yielding equal amounts of hydrogen and furan as the only products. Addition of nitric oxide, propylene or toluene had no effect upon the rate of decomposition. The calculated first order rate constants were observed to remain unchanged, in this study, over the pressure range 5–46 mm. and at pressures from 57 to 270 mm. in earlier work in this Laboratory. From experiments with initial pressures of 10–12 mm. the rate constant was calculated to be $5.3 \pm 0.1 \times 10^{12} \exp.(-48,500/RT)$ sec.⁻¹.

Experiments² conducted some years ago in this Laboratory showed that the thermal decomposition of 2,5-dihydrofuran takes place at 400–470° and that furan is an important product. Furan was detected first² by the Liebermann-Burchard reaction,³ and its presence was confirmed by infrared absorption measurements.^{2,4} In a series of exploratory experiments⁴ near 400° with initial pressures of 125–270 mm. the reaction mixture was removed after 50–60% pressure increase and the gas, non-condensable at –195°, was measured. The measured amounts of this gas averaged within 4% of the values expected from the observed pressure increase on the basis that the reaction yields only furan and hydrogen. No evidence was obtained

for the presence of aldehydes in the products. Pressure-time curves for the decomposition in a constant volume system indicated that the reaction is a first order process over the pressure range 57–270 mm. and experiments at 370–410° gave a value of about 48 kcal./mole for the activation energy.⁴

Recently α -alkyl-2,5-dihydrofurans have been passed over broken silica and activated charcoal at 470–480° and have been found to give α -alkylfurans and hydrogen.⁵

In order to determine the stoichiometry of the decomposition and to ascertain the kinetic parameters more accurately, a study of the decomposition of a highly purified sample of 2,5-dihydrofuran has been undertaken.

Experimental

Materials.—Three different samples of 2,5-dihydrofuran were used in these experiments. Samples A and B were kindly given to us by Dr. Raymond Paul, Société Des Usines Chimiques, Rhone-Poulenc, Paris. Sample A, which

(1) Financial support was received during a portion of this work from a Shell Research Grant to the Department of Chemistry.

(2) Performed by H. I. Machoukin as part of his senior research problem for the B.S. degree, 1955.

(3) V. E. Levine and E. Richman, *Proc. Soc. Exptl. Biol. Med.*, **31**, 582 (1934).

(4) Results of Anna Morlang in connection with her senior research problem for the B.S. degree, 1956.

(5) I. F. Bel'skii, N. I. Shulkin and R. A. Karakhanov, *Doklady Akad. Nauk S.S.S.R.*, **132**, 585 (1960).

was used in the previous experiments^{2,4} without purification, had been prepared by the dehydration of 1,4-butanediol.⁶ Samples B and C were obtained recently; the latter was supplied by Aldrich Chemical Co. To remove the impurities of furan and tetrahydrofuran, revealed by gas chromatographic analysis, the samples were purified by the following procedure. The samples were distilled from bulb to bulb *in vacuo* and then were purified by means of gas chromatography using a 3 m. tetraiso-butylene-firebrick column at room temperature. The purified material was dried over Linde Molecular Sieve 4A. All samples after purification showed the same kinetic behavior. The mass spectrometric analysis (Consolidated Model 21/620 instrument) of a purified sample of A gave peaks consistent with the expected spectrum of pure 2,5-dihydrofuran; the masses and observed intensities (for peaks amounting to at least 2% of the highest peak) were: 12(3.0), 13(3.3), 14(6.4), 15(9.1), 26(7.2), 27(17.1), 28(3.1), 29(8.7), 31(3.2), 37(8.0), 38(13.1), 39(92.1), 40(28.1), 41(100.0), 42(64.4), 43(5.5), 44(3.3), 68(2.7), 69(19.0), 70(64.4P), 71(3.0).

The infrared spectrum from 2 to 15 μ at about 3 mm. pressure in a 1 m. gas cell showed significant absorptions at the following wave lengths (microns) 3.28w, 3.42w, 3.54s, 6.35w, 7.43w, 9.18s, 9.72m-w, 9.87m, 9.90m, 10.11m, 11.04m, 12.5-7w, 13.46w, 14.83m, 15.20. Published traces⁷ of the spectrum, although small, show the same general absorption pattern. There is also reasonable correspondence between certain infrared frequencies and published Raman data.⁸ That sample A after purification has the structure corresponding to 2,5-dihydrofuran was confirmed by determination of the nuclear magnetic resonance spectrum⁹ of a 25% solution in carbon tetrachloride. Cyclohexane was used as a standard. The spectrum showed only two peaks at 4.14 and 5.46 τ ; the peak areas were in the ratio 1:2.0. Such a spectrum is in accord with the structure of 2,5-dihydrofuran and quite different from that of a sample of 2,3-dihydrofuran which had two singlets (showing some interaction) at 3.74 and 5.13 τ and two triplets, one with its center at 5.81 τ showing little interaction and the second with its center at about 7.48 τ showing more interaction.

The furan (Eastman) which was used as a standard in the analysis of the products was purified by means of gas chromatography and dried as in the purification of the 2,5-dihydrofuran. Nitric oxide (99%, Matheson) was purified by two vacuum distillations from -159 to -195° . Propylene (99.5%, Ohio) was distilled four times under vacuum from -112 to -150° . Toluene (Mallinckrodt A.R.) was distilled from trap to trap under vacuum; the middle portion (after it was dried) was retained for use. All of the materials were degassed.

Apparatus and Method.—The Pyrex glass reaction vessel (319 ml.) was cylindrical with a central thermocouple well. It fitted into a steel core in an electrically heated furnace. Temperature control was achieved by use of a thermocouple-potentiometer arrangement, with the light from the mirror of a wall-type galvanometer falling on the photoelectric cell of a General Electric CR7505-N210G3 Photoelectric Relay. The Chromel-Alumel control thermocouple was situated not far from the electrical windings. The temperature at the center of the reaction bulb was measured with a platinum, platinum-13% rhodium thermocouple connected to a Leeds and Northrup Type K-2 potentiometer. The thermocouple was standardized at the melting point of pure zinc (419.5°) and a correction of $+0.15^\circ$ was applied to the observed readings. During an experiment pressures were determined by cathetometer readings of the mercury meniscus in a wide bore manometer. A two-way stopcock connected the reaction vessel either to the supply section or to the product analysis line. The latter consisted of a trap cooled in liquid nitrogen (to remove unchanged 2,5-dihydrofuran and condensable products), a Toepler pump and a gas buret in which the products non-condensable at -195° were collected and measured quantitatively. It was established that there

was no pressure decrease due to absorption in the grease of the two-way stopcock.

Analytical Procedures.—The non-condensable fraction of the reaction mixture was analyzed mass spectrometrically. The only detectable peak was that of mass 2 indicating that hydrogen is the sole constituent of this fraction. Preliminary work⁴ has shown that the non-condensable fraction gave no absorption band in the infrared region from 2.0 to 15 μ . The condensable fraction was examined gas-chromatographically by the use of a 2 m. dimethylsulfolane-firebrick column at 46° . Two peaks were obtained, one corresponding to that for pure furan and the other to that for 2,5-dihydrofuran. The substance giving the former peak was collected and was found to give a mass spectrum in agreement with that for furan and an infrared absorption spectrum which was essentially identical both with the furan spectrum in the literature¹⁰ and with that obtained for a purified sample of furan on the same Perkin-Elmer Model 21 infrared instrument with a 1 m. gas cell. The amounts of furan and 2,5-dihydrofuran in the condensable fraction were determined both by gas chromatography and by mass spectrometry. The two methods were calibrated by the use of standard mixtures similar to those found in the reaction mixtures. For the gas chromatograms the areas under the peaks were measured and for the mass spectrograms the peak heights of masses 68 and 70, after suitable corrections, were compared.

Results

Analyses.—Reaction mixtures from experiments carried to decompositions up to about 60% in the temperature range 343 – 409° were analyzed according to the procedure described above. For each experiment the pressure increase at the time of removal of the reaction mixture was determined and from this pressure increase the composition of the reaction mixture could be calculated assuming that the reaction proceeds according to the equation

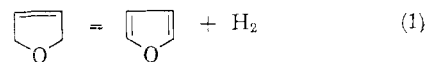


Table I presents a comparison of the observed and calculated values. Column 4 gives the ratio of the amount of hydrogen measured in the gas buret to the amount of hydrogen calculated from the pressure increase on the basis of equation 1. Column 5 gives the ratio of 2,5-dihydrofuran determined for the reaction mixture by gas chromatography to the amount computed from the observed pressure increase. The ratios for hydrogen and for 2,5-dihydrofuran are essentially equal to one over the entire range of experimental conditions used. The results give evidence that the reaction proceeds by equation 1 and that the pressure increase is a quantitative measure of the amount of decomposition of 2,5-dihydrofuran up to 60% reaction.

Order of the Reaction.—On the basis of the following observations, it was concluded that the reaction is first order for the initial pressure region 5–46 mm. Experiments at 343 – 409° with initial pressures of 5–46 mm. which were carried to about 50% decomposition gave straight lines for the plots of $\log(P_0 - \Delta P)$ vs. time. Moreover, it was found that the quarter-times for the reaction are independent of the initial pressure from 46 to 5 mm. at 392° and from 24 to 11 mm. at 355° (see Table II). At 0.9 mm. initial pressure the quarter-time was about 10% greater than that for the pressure range 5–46 mm., and this is indicative of the fall-off

(6) R. Paul, M. Fluchaire and G. Collardeau, *Bull. soc. chim. France*, **17**, 668 (1950).

(7) R. Nahum, *Compt. rend.*, **240**, 1898 (1955).

(8) P. A. Akishin, N. G. Rambidi, I. K. Korobitsyna, G. Ya. Kondrat'eva and Yu. K. Yur'ev, *Vestnik Moskov. Univ.* **10**, No. 12, Ser. Fiz. Mat. i. Estestven., Nauk No. **8**, 103 (1955); *Chem. Abstr.*, **50**, 8330 (1956).

(9) Measurements performed on a Varian 60 Kcs. instrument by Dr. D. J. Wilson.

(10) B. Bak, S. Brodersen and L. Hansen, *Acta Chem. Scand.*, **9**, 749 (1955); A. P. Dunlop and F. N. Peters, "The Furans," Reinhold Publishing Corp., New York, N. Y., 1953, p. 11.

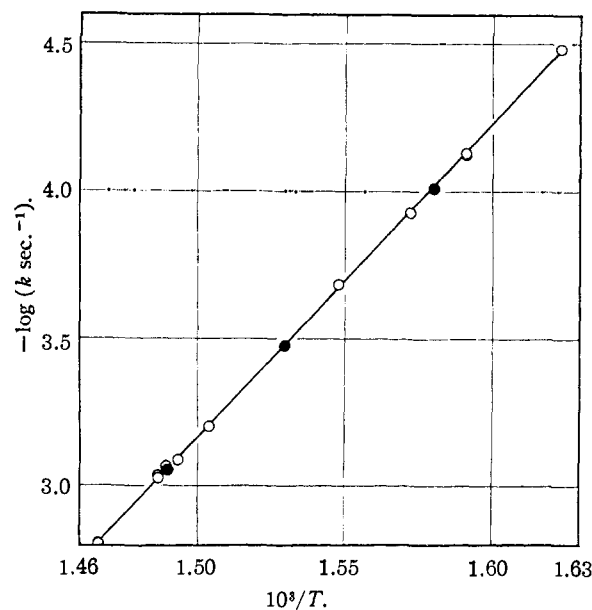


Fig. 1.—Temperature dependence of the first order rate constant for the decomposition of 2,5-dihydrofuran; O, unpacked reaction vessel; ●, packed vessel, 27-fold larger S/V .

in rate constant expected for unimolecular reactions at low pressures.

Homogeneity and Tests for Chains.—The data in Table I show that equation 1 represents the stoichiometry of the decomposition even in the presence of nitric oxide or propylene and in a vessel

TABLE I
COMPARISON OF THE ANALYZED AND CALCULATED COMPOSITIONS OF THE REACTION MIXTURE

Initial press., mm.	Temp., °C.	Spec. cond.	Ratio of anal. amt. to amt. calcd. from H_2	Ratio of anal. amt. to amt. calcd. from $C_4H_8O^a$
11.0	343	1.05	0.98
11.1	355	1.01	1.00
23.6	355	1.00	1.00
10.6	360	Packed	1.02	..
11.1	363	1.01	..
10.4	363	4.27 mm. C_3H_6	1.05	1.00
46.7	392	1.00	1.06
11.6	392	0.98	..
11.3	396	0.46 mm. NO	1.02	..
11.5	398	Packed	0.99	..
11.7 ^b	399	1.01	0.99
24.6	399	1.00	1.01
11.8	409	1.00	1.05

^a 2,5-Dihydrofuran from gas chromatographic analyses. The analysis by mass spectrometry for each experiment showed that the dihydrofuran left in the reaction mixture averaged 1.02 ± 0.02 times the amount expected from the observed pressure increase. ^b Average of two experiments.

packed with thin-walled Pyrex glass tubes to give an increase of at least 27-fold in the surface to volume ratio. The rate measurements in the packed vessel agreed well with those for the unpacked vessel under similar conditions (see Fig. 1). The effect of the additions of nitric oxide, propylene or toluene upon the rate constant are shown in Table II. These substances have been observed to inhibit various free radical chain reactions and in

TABLE II
RATE OF DEHYDROGENATION OF 2,5-DIHYDROFURAN UNDER VARIOUS CONDITIONS

Temp., °C.	Initial press., mm.	Added subs.	$P_{a.a.}^a$, mm.	$10^4 k$, sec. ⁻¹
355.4	23.58	7.53
355.4	16.78	7.49
355.4	10.98	7.47
362.9	10.43	C_3H_6	4.27	11.9
362.9	11.13	11.8
368.0	10.26	C_3H_6	20.44	15.4
368.0	10.44	C_7H_8	10.28	16.0
368.0	11.33	15.9
381.5	11.23	NO	0.27	33.8
381.5	11.55	33.4
391.8	46.65	61.2
391.8	11.63	63.1
391.8	5.82	61.5
396.5	11.34	NO	0.46	80.2
396.5	10.94	81.5

^a $P_{a.a.}$ denotes the pressure of the added substance; C_3H_6 is propylene and C_7H_8 is toluene.

the case of the chain dehydrogenation of ethane at 600° an appreciable decrease in rate has been found upon addition of nitric oxide.¹¹ None of the three additives had a significant influence on the rate of the dehydrogenation over the temperature range studied. It may be concluded that there is no chain reaction of importance occurring under the present conditions and that the hydrogen seems to be split off as a molecule.

Temperature Dependence.—An Arrhenius plot of $(-\log k)$ against $(1/T)$ for the experimental data over the temperature range 342–409° is shown in Fig. 1. A straight line can be drawn to fit the experimental results; no point lies more than 2% from the line. The activation energy for the dehydrogenation at initial pressures between 10 and 12 mm. was determined graphically and also by the method of least squares on an IBM 650 computer. The value obtained was 48.5 ± 0.3 kcal./mole. With $E = 48.5$, then $A = 5.3 \pm 0.1 \times 10^{12}$ sec.⁻¹. Equating the experimental pre-exponential factor to $\kappa e(kT/h) \exp(\Delta S^*/R)$ and assuming κ to be unity, one obtains a value of -3.9 e.u. for the entropy of activation at 400°.

Discussion

From the observed kinetics and the findings in the experiments with free radical inhibitors, it appears that the decomposition of 2,5-dihydrofuran proceeds by way of the loss of molecular hydrogen in a unimolecular process. On the basis of the model of Robles,¹² the electron diffraction work of Beach¹³ and the results of the present study it is not likely that the hydrogen atoms eliminated are either those of the two C–H groups or one of those of a CH_2 group with one hydrogen from one of the C–H groups. Likewise there is no evidence that in the present instance two hydrogen atoms come off the same carbon atom. It seems most probable that

(11) L. A. K. Staveley and C. N. Hinshelwood, *J. Chem. Soc.*, 1568 (1937).

(12) H. de Vries Robles, *Rec. trav. chim.*, 59, 189 (1940).

(13) J. Y. Beach, *J. Chem. Phys.*, 9, 54 (1941).

the hydrogen in the products involves one hydrogen atom of each of the two CH_2 groups. From the structure proposed for 2,5-dihydrofuran, the distance between the position of the carbon atoms of the two CH_2 groups (approx. 2.34–2.36 Å.) might seem large for the elimination of H_2 from these groups. It is possible to envisage, as a conceivable mechanism, an initial migration of hydrogen in the ring to produce two adjacent CH_2 groups (2,3-dihydrofuran). However, this mechanism seems to be ruled out because the thermal decomposition of 2,3-dihydrofuran^{14,2} results mainly in the disappearance of the five-membered ring rather than a dehydrogenation to form furan (and hydrogen).

In the case of the dehydrogenation of 2,5-dihydrofuran, the route to the transition state may be a ring deformation in which the oxygen atom and the CH_2 groups move out of a planar arrangement and the H atoms of the non-adjacent CH_2 groups move closer together. Such a vibration may bring the hydrogen atoms into sufficiently close proximity to make the formation of molecular hydrogen possible. Formation of a transition state of this sort implies the loss of some vibrational freedom and results in a more rigid structure. This is con-

(14) C. L. Wilson, *J. Am. Chem. Soc.*, **69**, 3002 (1947).

sistent with the negative entropy of activation for the reaction. The somewhat analogous unimolecular decomposition of cyclopentene¹⁵ also has a negative entropy of activation, (-2.7 cal./deg. mole at 500°) and the transition state may be formed by an analogous mechanism. In the decomposition of cyclopentene it is possible that the hydrogen molecule is produced from hydrogen atoms of adjacent methylene groups, but the possibility of formation of hydrogen from non-adjacent methylene groups has not been ruled out on the basis of the existing experimental results. Compared with the observed activation energy (58.8 kcal./mole) for the dehydrogenation of cyclopentene to cyclopentadiene, the activation energy for the dehydrogenation of 2,5-dihydrofuran is 10.3 kcal./mole lower. This may be the result of the greater resonance energy of furan (about 17.2 kcal./mole)¹⁶ compared with that of 1,3-cyclopentadiene (2.9 kcal./mole).¹⁶

Acknowledgment.—The authors wish to thank Mr. Carl Whiteman, Jr., for making the infrared measurements and least squares calculations.

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

(16) G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, p. 80 and p. 85.

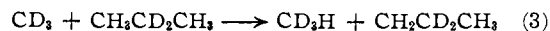
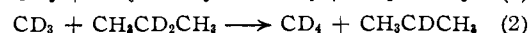
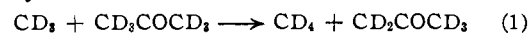
[CONTRIBUTION FROM THE NATIONAL BUREAU OF STANDARDS, WASHINGTON, D. C.]

Photolysis of Acetone- d_6 in the Presence of Propane-2,2- d_2 . Decomposition of the n -Propyl Radical

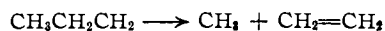
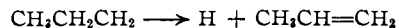
BY WILLIAM M. JACKSON AND J. R. MCNESBY

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Methyl- d_3 radicals generated by photolysis of acetone- d_6 react with acetone- d_6 and propane-2,2- d_2 to produce methane by the reactions



Ratios of rate constants obtained are approximately temperature independent and $k_1/k_3 = 1.10$; $k_2/k_3 = 0.58$. Analogous ratios for CH_3 radicals are indistinguishable from those for the CD_3 species. Decomposition of n -propyl to H and propylene is found to proceed at a much lower rate than suggested by Kerr and Trotman-Dickenson. Consideration of kinetic and thermochemical evidence suggests the best values for the rate constants k_{3a} and k_{4a} are

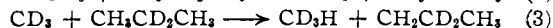
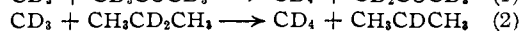
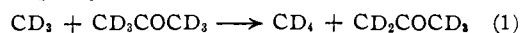


$$k_{3a} = 10^{14.1} \exp(-37,000/RT) \text{ sec.}^{-1} \quad (5a)$$

$$k_{4a} = 10^{13.9} \exp(-31,000/RT) \text{ sec.}^{-1} \quad (4a)$$

Introduction

The present work was undertaken for the purpose of measuring the kinetics of abstraction reactions and to investigate reactions of propyl and isopropyl radicals. The methane producing reactions when acetone- d_6 is photolyzed in the presence of $\text{CH}_3\text{CD}_2\text{CH}_3$ are



The n -propyl radical produced in (3) decomposes to CH_3 radicals and ethylene, but the former do not affect the CD_4 and CD_3H . In the early stages of reaction

$$[\text{CD}_4]/[\text{CD}_3\text{H}] = k_1[\text{Ad}_6]/k_3[\text{Pd}_2] + k_2/k_3 \quad 1$$

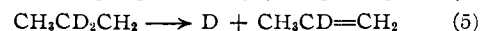
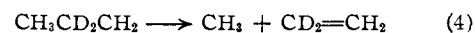
where $[\text{Ad}_6]$ and $[\text{Pd}_2]$ refer to the concentrations of acetone- d_6 and propane-2,2- d_2 , respectively.

The measurement of $[\text{CD}_4]/[\text{CD}_3\text{H}]$ provides a means of evaluating k_1/k_3 and k_2/k_3 . These ratios may be reduced further by carrying out the measurements at different temperatures.

$$k_1/k_3 = (A_1/A_3) \exp[(E_3 - E_1)/(RT)] \quad 2$$

$$k_2/k_3 = (A_2/A_3) \exp[(E_3 - E_2)/(RT)] \quad 3$$

The problem of the kinetics of the decomposition of n -propyl to form propylene has been studied by examination of the relative rates of the two decomposition reactions.



Experimental

I. Apparatus.—The light source was the full arc of a medium pressure mercury lamp. A filter was used to remove radiation below 2200 Å. The apparatus consisted of a cylindrical quartz reaction vessel, of 40 cc. capacity,