cals by some process. A quantitative method of determining ethyl alcohol was not available when these experiments were performed. In any case the most logical chain stopping step is reaction 8. For (8) to be important at 150° and not at 35 and 70°, the concentration of ethoxy radicals must be far greater even at the lowest intensity used. This is so because (5) and (7) must have appreciable activation energies whereas (8) would probably have a low activation energy. This may mean that the intermediate steps preceding ethoxy formation (such as (6) and (3)) proceed far more rapidly at 150° than at lower temperatures.

(e) The Reaction of Ethyl Radicals with Oxygen.—The rapid reduction of the quantum yield of C_2 hydrocarbons with increase in oxygen pressure is an indication of the speed with which ethyl radicals react with oxygen and provides a means whereby the method of competing reactions may be used to measure the rate of reaction 9.

The C_2 hydrocarbons are formed along with butane by the well characterized reactions 10, 11 and 12,[4-6] at a rate given by

$$R_{C_2} = 2k_{10}(C_2H_5)^2 + k_{12}(K)(C_2H_5) \qquad (21)$$

The total number of ethyl radicals introduced into the system may be assumed to be the sum of those introduced by reactions 1, 2, 2a and 6. Thus from the yields of CO and CO_2 and the number of quanta absorbed, one can estimate the number of ethyl radicals formed. They may now be assumed to disappear only by reactions 9, 10, 11 and 12. Since those which disappear by reactions 10, 11 and 12 can be calculated from Φ_{C_2}, the number which disappear by reaction 9 can be calculated. If one uses k_{10}, k_{11} and $k_{12}/k_{11}^{1/2}$ from previous work,[5,24] the instantaneous value of (C_2H_5) can be calculated from eq. 21. Hence all of the information necessary for calculation of k_9 is available. The results are shown in Table II. Considerable scatter is to be expected due to uncertainties in Φ_{C_2}, but the activation energy of (9) must be very low, and the steric factor is of the same order as that of (12), *i.e.*, about 10^{-3}. The steric factor for the corresponding methyl radical reaction has a similar order of magnitude.[15,25,26]

The initial product of (9) must be $C_2H_5O_2$ radicals but no definite conclusions about their subsequent reactions can be drawn from the present work although some suggestions can be made. At 35°, for example, since the formations of CO, CO_2 and CH_3CHO have been accounted for by the mechanism, these products may not result in appreciable quantities from reactions of $C_2H_5O_2$ radicals. Decomposition, either directly or following hydrogen abstraction to form a hydroperoxide, would almost certainly produce acetaldehyde in much larger amounts than observed at all temperatures. It seems probable that reaction 13 takes place[23] although reaction with oxygen to form C_2H_5O and ozone cannot be eliminated. From the mechanism the expression $2(\Phi_{CO} + \Phi_{CO_2}) - \Phi_{O_2}$ should be zero if none of the oxygen consumed by the radicals is returned to the system. The values for this expression show considerable scatter but are about 0.4 (35°), 0.7 (70°), 1.0 (100°), and at 150° there are about as many negative as positive values. Support is obtained therefore for a reaction which returns some oxygen to the system.

Further speculation about reaction mechanism does not seem to be warranted.

Thus the photochemical diethyl ketone–oxygen reaction may be described in much the same terms as the acetone–oxygen reaction.[11,25,27,28] Many important questions remain to be answered, particularly as regards the detailed behavior of the RO_2 intermediates. It seems fairly evident that their main fates are not the formation of hydroperoxides.

Acknowledgment.—The author wishes to acknowledge use of part of the doctoral thesis of R. B. Martin for some of the preliminary results of this investigation and to thank Professor W. A. Noyes, Jr., and his group for many helpful discussions and suggestions.

ROCHESTER, NEW YORK

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

The Thermal Decomposition of Ethylcyclobutane[1]

BY RUSSEL E. WELLMAN AND W. D. WALTERS

RECEIVED NOVEMBER 9, 1956

The thermal decomposition of ethylcyclobutane has been studied over the pressure range 7–400 mm. at 450° and at 420–460° for pressures of 10 to 200 mm. The products were found to be almost exclusively ethylene and 1-butene. The decomposition is a homogeneous, first-order reaction which is not inhibited by nitric oxide, propylene or toluene. The temperature dependence of the experiments with initial pressures of 10–200 mm. gave an activation energy of 62 ± 1 kcal./mole. The first-order rate constant can be expressed as $k = 3.6 \times 10^{15} e^{-62000/RT}$ sec.$^{-1}$.

Earlier investigations[2] have indicated that the homogeneous thermal decomposition of the cyclobutane molecule produces two molecules of ethylene by a first-order reaction which is not inhibited by the presence of nitric oxide, propylene or toluene. The first-order rate constants fall off as the initial pressure is lowered (10 mm. and below) and the

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(1) This work was supported by a grant from the Celanese Corporation of America.

(2) (a) C. T. Genaux and W. D. Walters, THIS JOURNAL, **73**, 4497 (1951); (b) C. T. Genaux, F. Kern and W. D. Walters, *ibid.*, **75**, 6196 (1953); (c) F. Kern and W. D. Walters, *Proc. Natl. Acad. Sci. U. S.*, **38**, 937 (1952).

addition of inert gases raises the value of the rate constant toward the high pressure value.[2,3] It was of interest to study the thermal decomposition of ethylcyclobutane in order to ascertain whether the decomposition of a related compound would be simple, and to observe any effect of the change of structure upon the characteristics of the reaction.

Experimental

Materials and Apparatus.—The ethylcyclobutane used in the majority of these experiments (99.7 ± 0.1 mole %) was kindly furnished by the National Advisory Committee for Aeronautics.[4] This material (N) was used without further purification except for small portions which were treated in various ways as indicated later. The sample was divided into two portions by vacuum distillation. The designations N-1 and N-2 refer to the first two-thirds and the last third, respectively. The remainder of the ethylcyclobutane used was prepared from methyl cyclobutyl ketone by a Wolff–Kishner reduction as modified by Huang-Minlon.[5] The methyl cyclobutyl ketone was prepared from cyclobutanecarboxylic acid and acetic acid by a catalytic method similar to the procedure of Zelinskiĭ and Riachina.[6] The synthesis of ethylcyclobutane was carried out twice and the samples were designated as (A) and (B). Material (A) was distilled in a 15 cm. column with Heligrid packing and separated into four samples. The fractional distillation of material (B) which yielded five samples was performed in a 75 cm. Lecky–Ewell column at a reflux ratio of 10 to 1. The boiling points of the samples used for kinetic studies were: N, 70.64° at 760 mm.[7]; A-2, 69.5–69.7°, A-3, 69.7–69.8°, A-4, 69.8–69.9° at 748 mm.; B-3 and B-4, 69.4° at 741 mm. The values of $n^{20}\text{D}$ were: 1.4020 for N[7]; B-3, 1.4022 ± 0.0002; B-4, 1.4023 ± 0.0002. Values previously reported[8] are: b.p. 70.7° at 760 mm. and $n^{20}\text{D}$ 1.4023. Moreover, infrared absorption analysis of all samples used for the rate experiments gave no evidence of impurities.

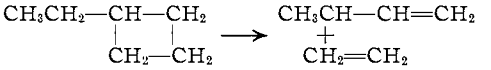
Propylene (99.5%, Ohio) and 1-butene (99%, Matheson) were degassed before use. Nitric oxide (98.7%, Matheson) was degassed at −195° and twice distilled from −158 to −195°. Toluene (Mallinckrodt Analytical Reagent) was dried over anhydrous calcium sulfate and degassed.

For experiments above 45 mm. the furnace, type of reaction vessel (350 ml., Pyrex), and the apparatus for temperature control and measurement were essentially the same as those used in the study of cyclopentanone.[9] The pressures were measured with a heated capillary mercury manometer. The experiments at initial pressures from 2 to 20 mm. were performed in a second apparatus consisting of a 500-ml. Pyrex reaction vessel connected to a 20 mm. bore mercury manometer which was read with a cathetometer. The effect of increased surface was determined by the use of a reaction bulb which was packed with thin-walled Pyrex glass tubes and had a 34-fold greater surface to volume ratio.

Analysis of the Products.—The products of the reaction were separated on the basis of volatility and analyzed by making use of (a) infrared absorption spectra, (b) differences in absorbability in sulfuric acid and (3) mass spectrometric techniques.[10] The amount of material volatile at −195° was so small (0.1–0.5%) that it was concluded that the non-condensable gases, such as hydrogen and methane, do not constitute a significant proportion of the products. For identification of the material volatile at −139° the products from five experiments at initial pressures of about 10 mm. with reaction times of 20 min. at 450° were combined. A similar series of six experiments was performed in the packed bulb. The infrared absorption curve for the −139° fraction from the unpacked bulb and also that from the packed bulb showed absorption peaks at about 3.25, 5.2–5.3, 6.8–6.9, 7.1 and 10.5 μ (with marked absorption in the region 9.6–11.6 μ). In this work a 100-ml. gas cell with a 10-cm. path length was used. The absorptions corresponded to those of the infrared absorption spectrum of pure ethylene (a) obtained on the same Perkin–Elmer instrument (Model 12AB) in this Laboratory and (b) reported in the literature.[11] The next fraction, which was removed by volatilization at −67° in the experiments in the unpacked bulb (at −78° in the packed bulb), gave an infrared absorption in good agreement with that for 1-butene.[11] The infrared absorption of the product was compared with the literature curves[11] for *cis*-2-butene, *trans*-2-butene and isobutene and found to be quite different from these. The infrared spectrum of the remainder of the reaction mixture was obtained after volatilization of a sample into a one-liter gas cell with a path length of one meter. The results indicated that ethylcyclobutane constitutes the rest of the reaction mixture.

It was also observed that more than 97% of the −139° fraction is absorbable in activated sulfuric acid.[12] At least 93% of the −78° fraction is absorbable in 87% sulfuric acid. Some of the remainder can be absorbed in activated sulfuric acid; therefore, a small amount of ethylene is indicated. Some ethylcyclobutane is presumably present also in this fraction.

Mass spectrometric analyses were obtained for the products from a 13 mm. experiment carried to 35% pressure increase at 440°. The −139° fraction contained 99.4% ethylene and 0.6% propylene. For the −78° fraction the reported composition was 93.4% butene, 2.6% ethylene, 2.1% ethylcyclobutane, 1.5% methylacetylene and 0.4% acetylene. These findings with respect to the major products are in accord with the infrared and sulfuric acid absorption observations. The lack of a definite detection of the other possible products in the infrared measurements may be due to the smallness of the quantities, but their presence cannot be regarded as established until further evidence has been obtained. In any event the over-all reaction appears to be almost entirely



(1)

If reaction 1 is the only reaction occurring, the pressure of ethylene and the pressure of butene should be the same and should equal the pressure increase (ΔP) in a constant volume system. The results of the quantitative analyses for the amounts of the products under various conditions (calculated as mm. in the reaction vessel) are shown in Table I. Prior to the analyses the products which could be volatilized at −139° and at −78° were separated from most of the undecomposed ethylcyclobutane. In the experiments other than those analyzed mass spectrometrically ethylene was determined by absorption in activated sulfuric acid.[12] In view of the importance of butene, as shown by the results given above, the gas absorbed in 87% sulfuric acid was designated as butene. The results in Table I show that the amount of ethylene agrees well in most cases with the pressure increase which has occurred during the decomposition. In several experiments the pressure of butene is approximately the same as the pressure increase, but usually the observed amount of butene tends to be lower. The slightly smaller pressure of butene measured is probably due in part to the solubility of the butene in the undecomposed ethylcyclobutane at −78°. It is to be noted also that except in the mass spectrometric analyses (440° experiments) the rest of the −78° fraction will contain some volatilized ethylcyclobutane.

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(3) H. O. Pritchard, R. G. Sowden and A. F. Trotman-Dickenson, *Proc. Roy. Soc.* (*London*), **218A**, 416 (1953).

(4) Concerning its preparation see J. M. Derfer, K. W. Greenlee and C. E. Boord, THIS JOURNAL, **71**, 175 (1949). For the infrared absorption curve see reference 11.

(5) D. Todd in "Organic Reactions," Vol. 4, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 378; Huang-Minlon, THIS JOURNAL, **68**, 2487 (1946).

(6) N. Zelinskiĭ and E. Riachina, *Ber.*, **57B**, 1932 (1924); see also B. A. Kazanskiĭ, *ibid.*, **69B**, 952 (1936), and reference 8.

(7) The physical constants for (N) are those reported for the material before it was sent to us. A measurement of the last few drops of this material gave a value of $n^{20}\text{D}$ 1.4025 ± 0.0002.

(8) J. Wibaut, H. Hoog, S. L. Langedijk, J. Overhoff and J. Smittenberg, *Rec. trav. chim.*, **58**, 329 (1939).

(9) E. R. Johnson and W. D. Walters, THIS JOURNAL, **76**, 6266 (1954).

(10) The mass spectrometric analyses were performed by the Consolidated Engineering Corp.

(11) Infrared Spectral Data, American Petroleum Institute Research Project 44, Carnegie Institute of Technology, Pittsburgh, Pennsylvania, Curves 18 and 530 for ethylene, Curve 901 for 1-butene, and Curve 891 for ethylcyclobutane.

(12) W. J. Gooderham, *J. Soc. Chem. Ind.* (*London*), **57**, 388T (1938).

TABLE I

ANALYSES OF THE PRODUCTS OF THE DECOMPOSITION OF ETHYLCYCLOBUTANE

P_0, mm.	ΔP,[a] mm.	C_2H_4,[b] mm.	C_4H_8, mm.	Non-cond., mm.	Rest of $-139°$ fract., min.	Rest of $-78°$ fract., mm.
Temp., 420°						
67.3	23.2	23.3	22.3	0.03	0.7	1.1
Temp., 430°						
10.68	5.30	5.31	5.25	0.02	0.16	0.74[c]
Temp., 440°[d]						
12.67	4.57	4.38	4.20	0.02	0.03	0.08[e]
76.8	27.5	26.7 ± 0.2	26.1	0.1	0.6 ± 0.2	0.03[f]
Temp., 450°						
16.34	5.75	5.78	5.26	0.04	0.22	0.32
45.3	26.6	25.6	25.3	.27	.6	0.7
68.8	36.5	38.2	33.0	.27	.4	5.4
9.44[g]	5.25[g]	5.45	4.68	.05	.18	0.58
Temp., 460°						
66.7	61.8	56.0	55.2	3.0	1.5	1.4[c]

[a] Corrected for dead space. [b] Usually includes C_2H_4 from $-78°$ fraction as well as $-139°$ fraction. [c] May include a small amount of C_2H_4. [d] Both experiments at 440° were analyzed mass spectrometrically. [e] Does not include 0.09 mm. ethylcyclobutane. [f] Does not include 1.2 mm. ethylcyclobutane. [g] Packed bulb used.

The data in Table I indicate that over approximately the first-half of the reaction the decomposition is represented satisfactorily by equation 1 and that pressure measurements may be used to follow the rate as long as high percentages of decomposition are avoided. It also appears that an increase in the surface does not alter the products formed or the stoichiometry of the reaction. It has been observed that for 25–50 mm. of 1-butene the pressure increase occurring in 10 min. at 450° is only 0.5%. From this result together with previous observations in this Laboratory on ethylene under similar conditions it was concluded also that until 50% decomposition there will not be sufficient reaction of the primary products to disturb the pressure measurements appreciably. However, in the experiment at 460° (Table I) kept until the decomposition was almost complete there is evidence that in the last stages of the decomposition the products initially formed undergo subsequent reactions. In consideration of this result the significance of the ratio of the final pressure to the initial pressure will not be as great as that of data in the earlier stages of the reaction, but it is of some interest that for four experiments at 450–460° with initial pressures ranging from 6.5 to 66 mm., the pressure after a time corresponding to approximately six half-lives averaged 2.00 times the initial pressure and for a 196 mm. experiment allowed to proceed for about thirteen half-lives the value for ratio of the maximum pressure to the initial pressure was 1.94. These observations in agreement with the data presented above indicate that essentially two molecules of products are formed from one molecule of ethyl cyclobutane.

Results and Discussion

Pressure-Time Curve and Homogeneity.—Since the pressure increase was found to be a reliable measure of the amount of ethylcyclobutane decomposed, pressure–time curves were used to determine the rates of reaction under various conditions. The early experiments revealed that the shape of the pressure–time curve was similar to that for a first-order decomposition. There was no observable induction period for the conditions employed in the present study. The rate of pressure rise was measured also in the packed bulb with a 34-fold increase in the surface to volume ratio. The average time for 25% reaction for six experiments at 450° with initial pressures of 8–12 mm. in the packed bulb was 7.0 ± 0.1 min. which may be compared with a value of 7.2 min. for seven experiments at about 10 mm. in the unpacked vessel. With such a small difference in rate for the large change in the surface to volume ratio, it appears that at least 99.5% of the reaction in the unpacked bulb takes place in the vapor phase. At higher initial pressures the importance of any surface reaction would be expected to be even less. An experiment[13] in a reaction vessel coated with potassium chloride indicated that this change in the nature of the surface does not affect the quarter-time of the decomposition.

Order of the Reaction.—The time for 25% decomposition was determined at 450° for initial pressures from 400 mm. to about 10 mm. The quarter-times (after small corrections for dead space) are shown in Table II. The constancy of $t_{1/4}$ over a forty-fold variation of the initial pressure, P_0, gives evidence of the first-order character of the decomposition. In addition, the data during an experiment were plotted as log $(2P_0 - P_t)$ *versus* time for various experiments where P_0 is the initial pressure and P_t the total pressure at time t.

TABLE II

QUARTER-TIMES FOR THE DECOMPOSITION OF ETHYLCYCLOBUTANE WITH VARIOUS INITIAL PRESSURES AT 450°

P_0, mm.	$t_{1/4}$, min.	Sample[a]	P_0, mm.	$t_{1/4}$, min.	Sample[a]
416	7.2	B-3(a)	69	7.3	A-2(a)
416	7.2	B-3(a)	68	7.4	N-2
362	7.2	B-3	65	7.0	N-1(a)
195	7.1	B-3(a)	57	7.4	(c)
191	7.1	N-1(a)	45	7.2	N-2
160	7.2	N-2(b)	16.3	7.2	N-2(d,f)
133	7.1	B-4(a)	13.5	7.1	(c)
126	6.9	B-3(a)	11.3	7.0	(c,e,f)
101	6.9	B-3(a)	11.2	7.5	N-2
101	6.8	B-3(a)	11.1	7.3	N-2
75	7.2	A-3(a)	11.0	6.8	N-1(b)
73	7.1	A-3(b)	10.0	7.1	N-2
70	7.2	B-3	9.1	7.3	N-1(b)
70	7.3	A-3(a)	9.0	7.1	N-2(g)
70	7.2	A-4(a)	7.4	7.2	N-2(b)

[a] Letters in parentheses indicate the treatments of ethylcyclobutane prior to decomposition: (a) dried with $CaSO_4$; (b) sodium; (c) pre-pyrolyzed sample; (d) concd. H_2SO_4; (e) activated H_2SO_4; (f) KOH; (g) Ag_2O.

A linear relationship was found to be obeyed very closely until the decomposition was more than 50% complete indicating a first-order reaction. In the later stages of the decomposition there is the possibility that slow secondary reactions affect the pressure measurements slightly.

In order to ascertain whether a trace impurity might be influencing the decomposition a comparison of the results was made for samples treated in various ways and prepared by different methods (see Table II). It was observed that the various treatments did not alter the rate appreciably or change the products formed. Likewise samples from two different sources gave similar rates of decomposition. Some investigators have observed in other decompositions that if impurities are present in the starting material, a prepyrolyzed sample may give a different rate. In three of the experi-

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(13) Performed by Mr. S. Kellner in this Laboratory.

ments listed in Table II pre-pyrolyzed ethylcyclobutane was used. For this sample the material which was condensable at −78° from several experiments was combined and purified. Purification was accomplished (a) by pumping away the volatile impurities and some of the ethylcyclobutane at −40° (or −78°) and (b) in one experiment by a further treatment with activated sulfuric acid followed by potassium hydroxide. In each of the experiments performed with the pre-pyrolyzed samples the quarter-time and the shape of the pressure–time curve agreed with those obtained with unpyrolyzed material.

Effect of Added Substances.—Experiments were carried out in the presence of compounds which often inhibit free radical chain reactions.[14] The compounds used were nitric oxide, propylene and toluene. The results, together with the average values for experiments in the absence of added gases, are given in Table III. It is evident that none of the added materials was effective as an inhibitor. The form of the pressure–time curve was the same as that for the decomposition without an additive.

TABLE III

DECOMPOSITION OF ETHYLCYCLOBUTANE IN THE PRESENCE OF ADDED SUBSTANCES AT 450°

$P°_{C_6H_{12}}$, mm.	Added subst.	$P°_{A.S.}$, mm.	$t_{1/4}$, min.	Sample[a]
10–200	...	0.0	7.2[b]	
9.9	NO	0.3	6.9	N-1(b)
169	NO	0.9	7.0	B-3(a)
9.9	C_3H_6[c]	4.2	6.8	N-2
165	C_3H_6	79	6.9	B-3(a)
165	C_3H_6	78	6.9	B-3(a)
11.9	C_7H_8[d]	4.3	7.4	N-2
97	C_7H_8	17	7.1	B-3(a)

[a] For sample designations see the Experimental section and Table II. [b] Average of twelve experiments over the range 10–200 mm. [c] C_3H_6 means propylene. [d] C_7H_8 means toluene.

Temperature Dependence.—The effect of a change in the temperature upon the rate of the decomposition was studied over the temperature range 420–460°. Rates were measured for experiments with initial pressures of approximately 10, 70 and 200 mm. The experimental results are summarized in Fig. 1 in the form of a log k *vs.* $1/T$ plot. The rate constants in sec.$^{-1}$ shown in Fig. 1 were calculated from the quarter-times (with dead space correction) by the use of the integrated first-order rate equation. For some of the experiments the rate constant was calculated also from the slope of the plot of log $(2P_0 - P_t)$ against time. The rate constants found by the latter method ordinarily agreed within a few per cent. with those found from the quarter-times.

For the 190–200 mm. experiments the temperature dependence of the rate indicated an activation energy of 62.5 ± 0.5 kcal./mole. However, on the basis of all of the experiments at 10, 70 and 200 mm. an activation energy of 62 ± 1 kcal./mole is obtained from the line shown in Fig. 1. With this activation energy the frequency factor can be calculated from the values of the rate constants, and the Arrhenius equation for the decomposition may be expressed as

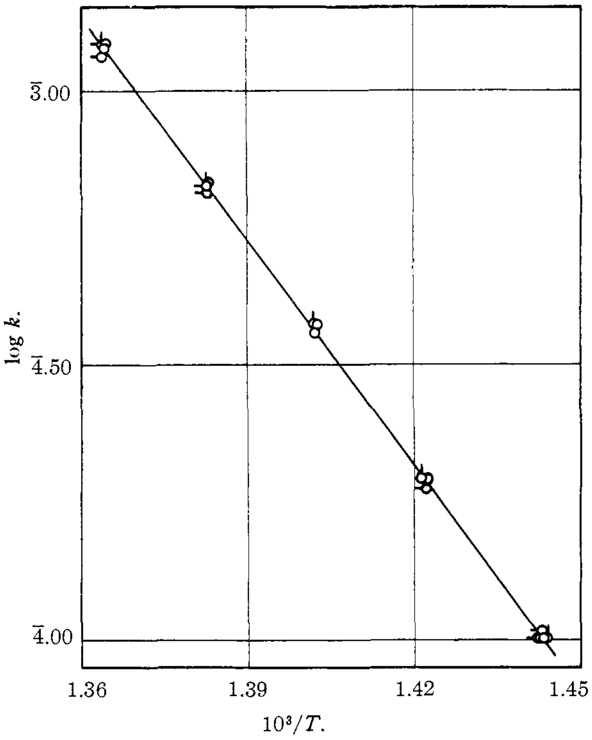

Fig. 1.—Change in rate with temperature: experiments at ∼200 mm., ○; ∼70 mm., -○; ∼10 mm., ȯ. The 10 and 70 mm. points at 450° are averages of two or more experiments.

$$k = 3.6 \times 10^{15}\, e^{-62000/RT} \text{ sec.}^{-1}$$

Discussion.—The experimental results have shown that the thermal decomposition of ethylcyclobutane is a homogeneous, first-order reaction which forms ethylene and 1-butene without appreciable quantities of side-products. Thus this decomposition is quite similar to the decomposition of cyclobutane[2] and other four-membered ring compounds, *e.g.*, cyclobutanone,[15] with respect to the type of ring cleavage and the kinetics of the reaction. Since there is no observable inhibition in the presence of added propylene, toluene or nitric oxide, no evidence has been obtained for a free radical chain mechanism. It appears that the thermal decomposition of ethylcyclobutane may be a unimolecular reaction.

The activation energy found for the decomposition of ethylcyclobutane is close to the value obtained with cyclobutane for which the observed activation energy for 120 mm. experiments was 62.5 kcal./mole and for 15 mm. experiments, 62 kcal./mole.[2b] Since the rate expression reported for cyclobutane was $4.0 \times 10^{15}\, e^{-62500/RT}$ sec.$^{-1}$, the frequency factors in the two decompositions are similar.

For a temperature of 450° the rate constant for the decomposition of ethylcyclobutane appears to

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(14) L. A. K. Staveley and C. N. Hinshelwood, *Proc. Roy. Soc.* (*London*), **154A**, 335 (1936); F. O. Rice and O. L. Polly, *J. Chem. Phys.*, **6**, 273 (1938); M. Szwarc, *ibid.*, **17**, 431 (1949).

(15) M. N. Das, F. Kern, T. D. Coyle and W. D. Walters, THIS JOURNAL, **76**, 6271 (1954).

be 25 to 30% larger than that for cyclobutane. From the available experimental data it cannot be ascertained whether this slightly faster rate is due mainly to a small decrease in the activation energy or to a change in the frequency factor. It is to be noted that with no change in frequency factor a decrease in the activation energy of 0.38 kcal./mole, which would be within the experimental error of the activation energy measurements, would produce a 30% increase in the rate.

The entropy of activation can be calculated by setting the expression $\kappa e(kT/h)e^{\Delta S^*/R}$ equal to the experimental frequency factor.[16] The calculated value of ΔS^* at 450°, with κ assumed to be unity, is $+ 8.9$ cal./deg. mole. This positive value which might be expected for a reaction of the type shown above involving ring cleavage is quite close to that found for cyclobutane.

Acknowledgment.—The authors wish to thank the Celanese Corporation of America for providing financial assistance, the National Advisory Committee for Aeronautics for supplying a sample of ethylcyclobutane, and Mr. Carl Whiteman for making the infrared measurements.

ROCHESTER, N. Y.

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[16] S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 295.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MICHIGAN]

Electrochemical Fission of the Carbon–Fluorine Bond. *p*H-Dependency of the Process

BY PHILIP J. ELVING AND JOSEPH T. LEONE

RECEIVED DECEMBER 4, 1956

Phenacyl fluoride gives two well-defined, diffusion-controlled cathodic polarographic waves, the first resulting from fission of the carbon–fluorine bond and the second from reduction of the acetophenone formed on fluorine removal. The former represents the first case of carbon–fluorine bond fission at the D.M.E. and the first instance where the carbon–halogen bond fission *per se* has been found to be *p*H-dependent. A mechanism involving induced polarization of the carbon–fluorine bond by the electrode and by hydrogen ion *via* the hydrogen fluoride bond in the transition state or species, has been postulated to explain the *p*H-dependence observed for the first wave below *p*H 6. With decreasing hydrogen ion concentration, the effect decreases and the first wave becomes *p*H-independent.

The electrochemical fission of carbon–halogen bonds has been studied extensively using polarography and electrolysis at constant potential.[1] However, the fission of a carbon–fluorine bond under polarographic conditions has not been previously reported, due apparently to the comparative rarity of fluorine-containing organic compounds and to the greater stability of the C–F bond compared to other carbon–halogen bonds.

The logical approach to the problem of C–F bond fission seemed to be the determination of which structures facilitated carbon–halogen bond fission and then the polarographic study of the fluorine-containing analog. Fluoroacetic acid was considered unsuitable since at about *p*H 1, where carbon–halogen bond fission should be most facile, iodo-, bromo- and chloroacetic acids have $E_{1/2}$ values *vs.* the S.C.E. of -0.16,[2a] -0.55[2a] and -1.64 v. (calculated),[2b] respectively· this would obviously place $E_{1/2}$ of fluoroacetic acid well out of the range of acidic buffers. Ethyl fluoroacetate seemed a more suitable compound for study since carbon–halogen bond fission in esters is *p*H-independent: the ester could be studied in alkaline buffers in which a more negative potential is available before background discharge. However, no wave was obtained at 0°, indicating either that the ester hydrolyzed too rapidly to permit study or that the C–F bond was not reducible in the ammonia and phosphate buffers used.

Since the first waves of tribromoacetic[2a] and trichloroacetic[3] acids occur at less negative potentials (-0.08 v. at *p*H 3.7, and -0.89 v. at *p*H 4.0, respectively), it was thought that trifluoroacetic acid might provide a sufficiently labile bond. The latter compound, however, was not reducible under normal polarographic conditions. In this connection, it is pertinent to note that the C–F bonds in F_2CH_2 and F_3CH are considerably shorter than that in FCH_3[4]; this is reflected in the greater stability of the polyfluoromethanes.[5] If this behavior is generally true of the trifluoromethyl group, the stepwise fission of the carbon–halogen bonds would not be observed as in the case of trichloro- and tribromoacetic acids, but all of the bonds would probably be ruptured in a single step at a potential more negative than that at which the one C–F bond in the monofluoro compound would be reduced.

Study of the polarographic behavior of phenacyl chlorides and bromides[6] showed that there is available an adequate potential span before carbonyl group reduction in which a more difficultly reducible C–F bond might be ruptured. Consequently, phenacyl fluoride was investigated. Fission of the C–F bond was observed: $E_{1/2}$ for the resulting cathodic wave is strongly *p*H-dependent below *p*H 6.

Discussion of Observed Results[7]

Phenacyl fluoride gives two well-defined diffusion-controlled cathodic polarographic waves over the *p*H range of 0.5 to 11.5 (Table I; Figs. 1 to 3).

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[7] Detailed data are available from the authors.