minimum mean life-time of an activated azoethane molecule, depending on the efficiency of deactivation by collision and the validity of the values chosen for the collision diameter of the molecule. τ may serve as a useful criterion in estimating the

order of magnitude of the life-time of excited molecules in other unimolecular reactions.

We would like to thank Professor R. A. Marcus for several helpful suggestions.

CHAPEL HILL, N. C.

The Kinetics of the Decompositions of Ethyl, Isopropyl and n-Propyl Bromides

BY ARTHUR T. BLADES AND GEORGE W. MURPHY

The decompositions of ethyl, isopropyl and n-propyl bromides have been studied in a flow system with toluene as a carrier gas. First-order kinetics are obeyed, and the conclusion is reached that the reaction is intramolecular in each case. The rate expressions are: k(ethyl bromide) $= 7.3 \times 10^{12} \exp -(52,300/RT)$; k(isopropyl bromide) $= 4.0 \times 10^{13} \exp -(47,700/RT)$ and k(n-propyl bromide) $= 1.0 \times 10^{13} \exp -(50,700/RT)$ sec.$^{-1}$. The nature of the transition state is discussed.

The decomposition of ethyl bromide has been the subject of extensive research.[1-5]

It was suggested by Goldberg and Daniels that additional evidence on which to base a mechanism for this decomposition might be provided by the toluene carrier gas technique which has been employed in this Laboratory for studying vinyl alkyl ether decompositions.[6] With an excess of toluene it should be possible to suppress chain reactions and focus attention on the intramolecular decomposition.[7]

Recent reports on the decompositions of isopropyl and n-propyl bromides have suggested that the same technique could assist in establishing these mechanisms also. Maccoll and Thomas[8] proposed an intramolecular mechanism for the pure isopropyl bromide decomposition but the reaction is complicated by a falling off of the rate constant in the latter stages. They attribute this to the reverse reaction. Agius and Maccoll[9] found that the decomposition of n-propyl bromide conformed best to a 3/2-order rate expression. They proposed a free radical type mechanism involving the initial break of the C–Br bond.

The present technique does not in itself enable us to analyze the sometimes complex kinetics in the decomposition of the pure bromides, but it does provide a means for isolating the intramolecular reaction. We shall show that the kinetics of all three decompositions under these conditions are similar.

Experimental

The apparatus is essentially the same as that described previously.[6] The aluminum block of the furnace has been replaced by an aluminum bronze block and the Pyrex reaction tube by a quartz tube of approximately the same dimensions. These changes were made in order to allow higher temperature studies.

(1) E. T. Lessig, J. Phys. Chem., **36**, 2335 (1932).

(2) E. L. Vernon and F. Daniels, THIS JOURNAL, **55**, 922 (1933).

(3) P. Fugassi and F. Daniels, ibid., **60**, 771 (1938).

(4) F. Daniels and P. L. Veltman, J. Chem. Phys., **7**, 756 (1939).

(5) A. Goldberg and F. Daniels, forthcoming publication.

(6) A. T. Blades and G. W. Murphy, THIS JOURNAL, **74**, 1039 (1952).

(7) During the course of this research Prof. Daniels received a communication from Prof. M. Szwarc reporting results on ethyl bromide from his laboratory which agree substantially with ours.

(8) A. Maccoll and P. T. Thomas, J. Chem. Phys., **19**, 977 (1951).

(9) P. Agius and A. Maccoll, ibid., **19**, 155 (1950).

The products of the pyrolyses were condensed in a liquid air trap and the course of the reaction followed by the amperometric titration of HBr. In the case of ethyl bromide, quantitative correspondence between the two products HBr and ethylene was checked by volumetric determination. In the other decompositions, identity of the propylene was established by infrared analysis but its total quantity was not determined.

The ethyl bromide was supplied by Dr. A. Goldberg from the same batch used in his own researches.[5] The isopropyl and n-propyl bromides were prepared by the method in reference 10 and were purified by fractionation in a 13-plate metal packed column. The isopropyl bromide boiled at 58.2° (745 mm.) and the n-propyl bromide at 70.0° (745 mm.).

Analytical Results and the Reaction Mechanism

Ethyl Bromide.—The products of this decomposition in the presence of toluene proved to be ethylene and HBr. If the reaction proceeded through a free radical mechanism, other products would be
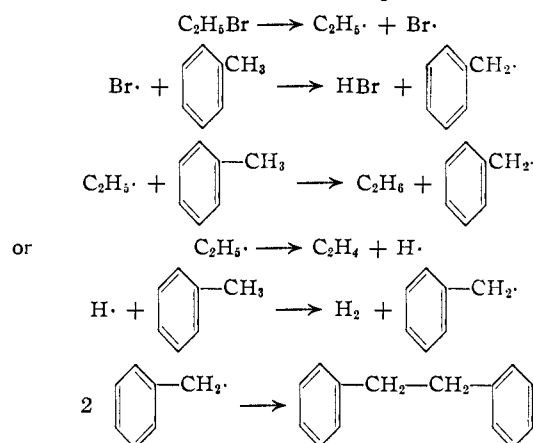
expected. No hydrogen, ethane or dibenzyl nor any other products than ethylene and HBr were found. It must be concluded therefore that the reaction is intramolecular.

Isopropyl and n-Propyl Bromides.—If these decompositions proceeded through a radical mechanism in the presence of toluene, the products should include dibenzyl and one or more from the group hydrogen, methane, ethylene and propane, as may be shown by a reaction series similar to that of the

(10) Blatt, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 25.

preceding paragraph. Since only propylene and HBr could be detected. these decompositions must also be intramolecular.

Results of Rate Studies

For a first-order reaction in a flow system without longitudinal mixing, and involving no volume change, the rate expression is

$$\log (n_0/n) = kt_c$$

where n_0/n is the ratio of the reactant moles initially and after passage through the reaction tube, and t_c is the contact time. The requisite conditions are closely approximated in the present apparatus. Constancy of volume is assured by the large mole ratio of toluene to reactant.

The rate of production of HBr obeyed a first-order rate expression to at least 70–80% completion in each case as may be seen from Fig. 1. This is
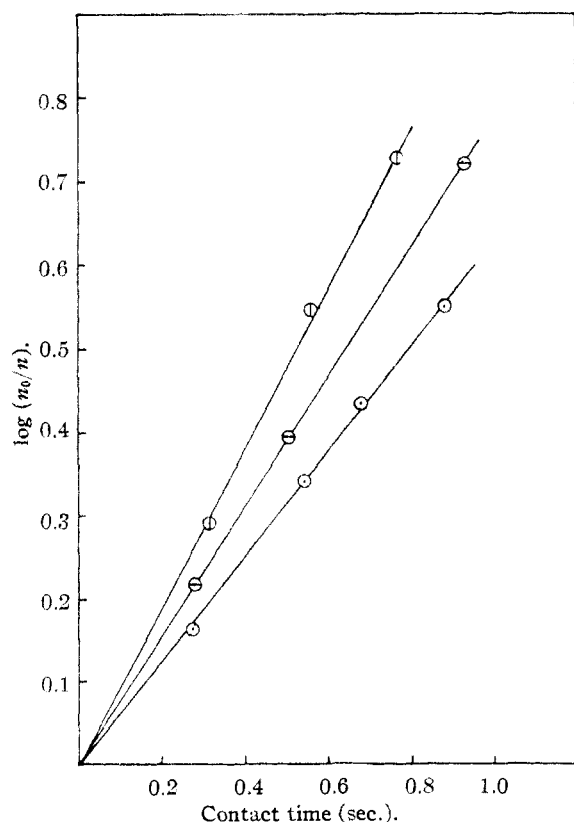

Fig. 1.—Order study: ⊙, ethyl bromide; ⊕, isopropyl bromide; ⊖, n-propyl bromide.

also consistent with an intramolecular mechanism and is to be contrasted with the substantial deviations from unit order in the decompositions of pure isopropyl[8] and n-propyl[9] bromides. The rate constants for the three reactions are plotted in the usual fashion as a function of temperature in Fig. 2. The results may be represented by the equations

$k(\text{ethyl bromide}) = 7.3 \times 10^{12} \exp (-52,300/RT) \text{ sec.}^{-1}$
(800–899°K.)

$k(\text{isopropyl bromide}) = 4.0 \times 10^{13} \exp (-47,700/RT) \text{ sec.}^{-1}$
(688–796°K.)

$k(n\text{-propyl bromide}) = 1.0 \times 10^{13} \exp (-50,700/RT) \text{ sec.}^{-1}$
(793–893°K.)

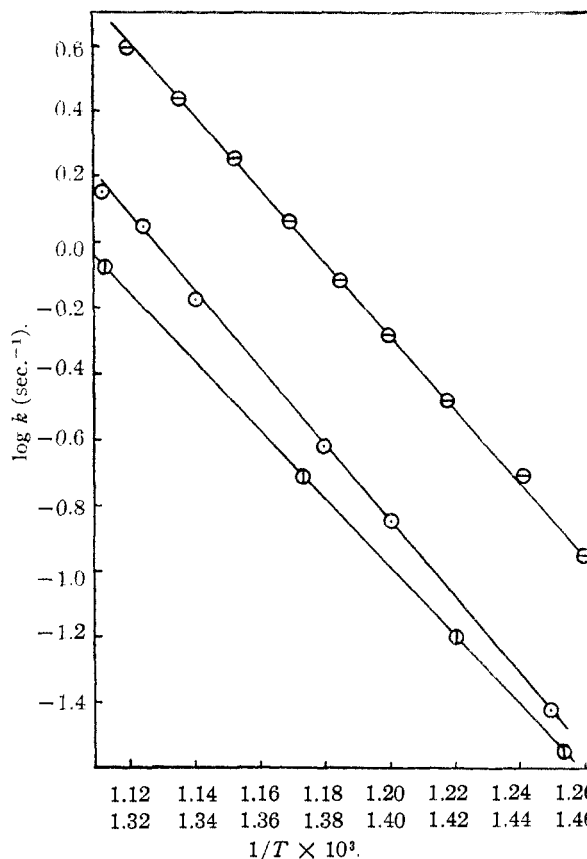The activation energies, expressed in cal./mole, are precise to better than ±100 cal.

Fig. 2.—Temperature dependence of rate constant: symbols same as in Fig. 1. Upper abscissa scale, ethyl and n-propyl bromide. Lower abscissa scale, isopropyl bromide.

Discussion

The dissimilarity in kinetics for the pyrolyses of pure members of a homologous series has been noted in both the bromide[8] and chloride[11] groups. It is therefore particularly satisfying to find similar kinetics for homologs under circumstances such that one mechanism can be clearly specified. The transition state may be represented as

$$
\begin{array}{c}
\text{Br} \text{-----} \text{H} \\
| \quad\quad | \\
-\text{C} \text{------} \text{C}- \\
| \quad\quad |
\end{array}
$$
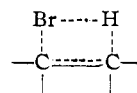
Only in the case of n-propyl bromide is an alternative transition state conceivable
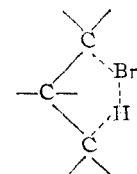
This would require the formation of cyclopropane as an intermediate, followed by its rapid isomerization to propylene. This possibility must be ruled out

(11); D. H. R. Barton, A. J. Head and R. J. Williams, J. Chem. Soc., 2039 (1951); also earlier papers of Barton and co-workers.

however, since the isomerization requires 65 kcal./ mole.[12]

All of the frequency factors are "normal," i.e., around 10^{13} sec.$^{-1}$, implying little, if any, entropy of activation. Although the transition state involves a freezing of a single restricted internal rotation, with a consequent entropy decrease, the fact that there are three equivalent positions leading to reaction on a 360° rotation about the C–C bond of ethyl bromide leads effectively to an entropy increase which must nearly balance the aforementioned decrease. The frequency factor for the isopropyl bromide decomposition is, as expected, higher than for the other two. There are twice as many chances for reaction during internal rotation as there are for ethyl bromide. The numerical value of 5 is somewhat larger than predicted by

(12) T. S. Chambers and G. B. Kistiakowsky, THIS JOURNAL, 56, 399 (1934).

this simple interpolation, but the conclusion is valid within the experimental error.

The lower activation energy observed for isopropyl bromide is in the direction to be expected on the basis of the known electron directing power of the methyl group. Whether the magnitude of this difference in activation energy between this and the other bromides is reasonable, is a question which we are unable to answer.

Kinetics and Mechanism of the Acid-Catalyzed Decomposition of Diazoacetone[1]

BY CHARLES E. MCCAULEY AND CECIL V. KING

In dilute aqueous acids the conversion of diazoacetone to hydroxyacetone is catalyzed by hydronium ion but not by other acids. Neutral salts increase the rate, the effect of each salt being somewhat specific and showing little or no influence of the charge type of the cation. With halides present, considerable amounts of haloacetone are formed; with nitrates, a small amount of nitric acid enters the product. The mechanism of reaction with water and halogen acids is similar to that of diazoacetic ester; the rate-determining steps are subsequent to an equilibrium reaction with hydrogen ion, prior to or simultaneous with nitrogen expulsion.

The convenient synthesis of diazoketones discovered by Arndt and Eistert in 1927 has made these compounds useful intermediates in organic preparative chemistry.[2] Since no kinetic studies have been published, it was decided to examine the decomposition rate of diazoacetone in aqueous acid solutions. It was proposed to determine (a) the general level of rates as compared to other aliphatic diazo compounds, (b) the order of reaction with respect to diazoacetone and acid, (c) whether there is general acid or only specific hydronium ion catalysis, (d) the nature and magnitude of neutral salt effects, (e) whether the reaction can be used to measure unknown hydrogen ion concentrations, (f) whether any acid anions enter the product or act as specific catalysts, and (g) whether the kinetic results might elucidate the reaction mechanism. More or less satisfactory information has been obtained on all these points.

Materials and Method

Diazoacetone was prepared by the reaction of freshly distilled acetyl chloride with a sevenfold excess of diazomethane in dry ether.[3] After removing all ether, it was distilled through a short helix-packed column at 11.5 mm. Starting with 25 ml. (28 g.) of acetyl chloride, about 20 g. of diazoacetone could be collected at 46.0–46.8°. The specific gravity $^{28}/_{28}$ was 1.058, n^{21}D was 1.488. Arndt and Amende

(1) Manuscript prepared from a thesis submitted by Charles E. McCauley in partial fulfillment of the requirements for the Ph.D. degree at New York University, February, 1952.

(2) W. E. Bachman and W. S. Struve, "Organic Reactions," Vol. I, John Wiley and Sons, New York, N. Y., 1942, Chap. 2.

(3) F. Arndt and J. Amende, Ber., 61, 1124 (1928).

report a boiling point of 49° at 13 mm. The compound gave 98% of the theoretical nitrogen from dilute acid, as determined in the rate measuring apparatus by careful comparison with hydrogen evolution from zinc and acid. There was no deterioration over a period of 16 months.

Stock sodium hydroxide solution (carbonate-free) was prepared with especial care and standardized with a precision of two parts in 1500; this was used to standardize the various acids. Monochloroacetic acid was recrystallized from water, then from benzene.

Barium perchlorate stock solutions were made from pure barium carbonate and standard perchloric acid; zinc perchlorate from C.P. metal; lanthanum perchlorate from the commercial nitrate via oxalate ignited to oxide, followed by dissolution in standard perchloric acid. Sodium perchlorate solutions were prepared both from pure sodium carbonate and from the commercial salt after recrystallization and dehydration. Sodium benzenesulfonate was decolorized with charcoal and recrystallized from ethanol. A titration curve showed no weak acid anions present. Other salts were of analytical grade and were dried at 125° for weighing, or the solutions were standardized.

Rates were measured by following nitrogen pressure in an apparatus similar to that described by Brönsted and Duus.[4] The solution volume was 50 ml. and the diazoacetone sample was normally 0.04 ml. Since in some solutions the reaction was quite rapid (half-time 3 to 5 min.) it was necessary to maintain an optimum shaking rate[5] (200 per minute with the apparatus used). Ordinarily first-order rate constants were evaluated by the Guggenheim method in the most rapid experiments by using the final pressure readings. There was always sufficient excess reagent to make the rates essentially first order.

The bath thermometer was compared with one calibrated at the National Bureau of Standards. It is believed that the error in computing each rate constant k is less than 1%. Rates were nearly always reproducible within 3%, usually

(4) J. N. Brönsted and H. Duus, Z. physik. Chem., 117, 229 (1925).

(5) K. J. Pedersen, THIS JOURNAL, 49, 2681 (1927).