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Henry L. Friedman, Richard B. Bernstein, and Harry E. Gunning

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C¹³ Isotope Effect in the Thermodecomposition of Ethyl Bromide

HENRY L. FRIEDMAN, RICHARD B. BERNSTEIN,* AND HARRY E. GUNNING Department of Chemistry, Illinois Institute of Technology, Chicago, Illinois (Received June 11, 1954)

The $C^{12}-C^{13}$ fractionation factor in the decomposition of gaseous ethyl bromide has been measured from 350-450°C, using samples of natural isotope abundance. The rate constants are defined as follows:

$$CH_3CH_2Br \rightarrow CH_2 = CH_2 + HBr \qquad k_1,$$

$$CH_3C^*H_2Br \rightarrow CH_2 = C^*H_2 + HBr \qquad k_2,$$

$$C^*H_3CH_2Br \rightarrow C^*H_2 = CH_2 + HBr \qquad k_3.$$

At 400°C, the C12 enrichment of the first fraction of ethylene from decomposition of the ethyl bromide is

$$S_0 \equiv 1 + \epsilon_0 = \frac{2k_1}{k_2 + k_3} = 1.0079 \pm 0.0006,$$

with a temperature coefficient of -2.8×10^{-5} /°C.

The primary and secondary isotope effects are defined, respectively, as $\beta = k_1/k_2 - 1$ and $\gamma = k_1/k_3 - 1$; thus, to a good approximation, $\beta + \gamma = 2\epsilon_0$. According to theory, $\beta > \gamma \ge 0$, so that $\epsilon_0 < \beta \le 2\epsilon_0$ and $\epsilon_0 > \gamma \ge 0$. From the data of 400°C one then obtains as an upper limit $(k_1/k_2)_{\text{max}} \leq 1.0159 \pm 0.0012$. This is significantly lower than the value $k_1/k_2 \ge 1.036$ calculated for the rupture of an isolated C-Br bond. The present results, therefore, favor a mechanism involving the direct intramolecular elimination of HBr.

INTRODUCTION

HE decomposition of ethyl bromide has been the subject of a number of investigations.¹⁻⁶ The free radical mechanism proposed by Daniels and Veltman⁴ involved the primary rupture of the C-Brbond, followed by H atom abstraction from the substrate by Br atoms producing C_2H_4Br and HBr. The $C_2H_4Br \cdot$ was assumed to yield C_2H_4 by dissociation or reaction with C2H5 · radicals. Later, Peri and Daniels⁵ revised this mechanism slightly, on the basis of the results of a series of isotope exchange experiments. They stated that the primary step was wall-catalyzed, i.e., $C_2H_5Br+wall \rightleftharpoons C_2H_5 \cdot wall+Br \cdot$, with essentially the same subsequent steps.

Blades and Murphy,⁶ using the toluene carrier technique, found no evidence for dibenzyl, hydrogen, or ethane, from which they decided that the reaction was not of the free radical but rather of the intramolecular elimination type. They represented the transition state as a four-membered ring,



Similar results were obtained by Leigh and Szwarc.⁷ In view of the above it was thought worthwhile to

make a study of the C13 isotope effect on the rate of decomposition of ethyl bromide, in order to obtain independent mechanistic evidence. Considering first the free radical mechanism, one would expect an appreciable difference in the rate of rupture of the C^{12} -Br and C¹³-Br bonds. On the basis of current theoretical considerations^{8,9} the ratio of the rate of rupture of these bonds should be at least as great as the square root of the appropriate reduced mass ratio, 1.036. This lower limit is based on Slater's¹⁰ treatment for the rupture of an "isolated" bond. In the case of the intramolecular elimination mechanism one would expect the ratio of the rates to be much closer to unity. The lower limit in this case might be estimated to be 1.003, the Slater ratio for the C^{12} –H and C^{13} –H bonds.

The present study was carried out using ethyl bromide of natural isotopic composition, with the three principal isotopic (carbon) modifications: (1) $C^{12}H_3C^{12}H_2Br$, (2) $C^{12}H_3C^{13}H_2Br$, and (3) $C^{13}H_3C^{12}H_2Br$. The primary isotope effect is concerned with the relative rate of decomposition of species (1) versus (2). The secondary isotope effect is associated with the relative rate for (1) versus (3). Because the ethylene-C¹³ produced by the decomposition of (2) is indistinguishable from that of (3) it is not possible to measure separately the primary and secondary isotope effects. However, the observed $C^{12}-C^{13}$ fractionation factor (the quotient of the C^{12}/C^{13} abundance ratio for the first fraction of ethylene, divided by that of the ethylene from total decomposition) is related directly to the sum of these isotope effects. Thus it has been possible to set upper and lower limits for the individual values of the primary and secondary isotope effects. From these

^{*} Present address: Department of Chemistry, University of Michigan, Ann Arbor, Michigan. ¹ E. T. Lessig, J. Phys. Chem. **36**, 2325 (1932).

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results, it appears that the mechanism is primarily of the intramolecular elimination type.

EXPERIMENTAL

Ethyl bromide (Matheson, Practical) was purified by shaking with concentrated sulfuric acid until all color was removed. After neutralization with 10 percent sodium carbonate solution the resulting ethyl bromide was washed with water, dried over anhydrous calcium chloride, and distilled from phosphorus pentoxide in a one-meter column packed with glass helices. The purified sample boiled at 38.37°C at a pressure of 760 mm Hg, in agreement with reported values¹¹⁻¹⁵ which range from 38.34°C at 760 mm Hg to 38.5°C at 765 mm Hg. The refractive index, n_D^{26} was 1.4212. Literature values of the refractive index, ^{11,14,16} interpolated to 25°C gave 1.4208 ± 0.0005 . The vapor pressure at 0°C, determined with a Bodenstein quartz spiral gauge, was 163.5 mm Hg, in agreement with the literature values^{17,18} which ranged between 162.5 and 165.5 mm Hg. The infrared absorption spectrum was determined on a Perkin-Elmer Model 21 double-beam recording infrared spectrophotometer (NaCl optics). The bands corresponded within experimental error to those observed by Cross and Daniels.19

The experiments were carried out in a high-vacuum system provided with a 254-ml fused quartz reaction chamber in an electric furnace whose temperature was controlled to $\pm 1^{\circ}$ C with a Taco-West Model J Thermoregulator. Measurements of the temperature profile of the reaction zone showed a maximum deviation of $\pm 4^{\circ}$ C from the kinetic temperature. The reaction zone was conditioned by prolonged carbonization of ethylene at 400°C.4 Mercury vapor was excluded from the apparatus.

The degassed ethyl bromide was decomposed at initial pressures in the range 90-150 mm Hg, the decomposition being monitored with a Bodenstein gauge. When the desired extent of reaction was attained, the mixture was removed from the reaction zone by freezing with liquid nitrogen. There appeared to be no trend of isotope enrichment with the initial pressure of ethyl bromide.

Ethylene was distilled from the mixture using isopentane slush (-160°C), and oxidized by Toeplerpumping through a copper oxide converter at 720°C. Mass spectrometric analysis of products formed showed 98.7 percent conversion to CO₂ at 600°C and 100 percent conversion at 720°C. Water was removed from the oxidation products by freezing out at -78 °C.

Specific reaction-rate constants based on the firstorder portion of the decomposition were determined from partial decompositions whose initial pressures were greater than 130 mm Hg. The k's were considerably higher than those found by Daniels and Veltman,⁴ but this is probably due to the fact that greater pains were taken to remove O2 in the latter than in the present work. The increase in k with increase in O_2 has been observed previously.4 An activation energy of 50 kcal/mole was approximated from the k's and this agrees with values in the literature^{2,4,6} which range from 52.3 to 54.8 kcal/mole. The rate-determining step should therefore be the same in either case, and there seems to be no reason to belive that the presence of traces of O_2 should favor or retard the decomposition of any of the isotopic species.

The $C^{13}O_2/C^{12}O_2$ ratio (m/e 45/44) of the carbon dioxide was measured on a Consolidated-Nier Isotope Ratio Mass Spectrometer, Model 21-201. The value of the $C^{13}O_2/C^{12}O_2$ ratio of the original ethyl bromide was determined by total decomposition of two samples at 500°C, using the procedure outlined above. Tank CO₂ was used as the reference standard; and in the analyses each unknown sample was run between two standard analyses in the usual way. No correction for resolution or O¹⁷ was employed.

CALCULATIONS AND RESULTS

The over-all equations defining the rate constants are:

$$CH_{3}CH_{2}Br \rightarrow CH_{2} = CH_{2} + HBr \quad k_{1}$$

$$CH_{3}C^{*}H_{2}Br \rightarrow CH_{2} = C^{*}H_{2} + HBr \quad k_{2}$$

$$C^{*}H_{4}CH_{9}Br \rightarrow C^{*}H_{9} = CH_{9} + HBr \quad k_{3},$$

The following symbols are employed for concentrations:

$$a_1 = [CH_3CH_2Br], \quad a_2 = [CH_3C^*H_2Br],$$

 $a_3 = [C^*H_3CH_2Br], \quad x_1 = [CH_2 = CH_2],$
 $x_2 = [CH_2 = C^*H_2].$

Superscript 0 refers to initial concentration; the asterisk denotes C13.

Considering the first fraction of ethylene produced by decomposition (assuming infinitesimal extent of reaction), one obtains

$$\frac{dx_1}{dx_2} = \frac{k_1 a_1^0}{k_2 a_2^0 + k_3 a_3^0}.$$
 (1)

For a normal isotope distribution $a_2^0 = a_3^0$, so that one obtains

$$\frac{x_1^0}{x_2^0} = \frac{a_1^0}{a_2^0} \left(\frac{k_1}{k_2 + k_3}\right). \tag{2}$$

We define the separation factor at zero extent of re-

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action, S_0 ,

$$S_{0} = \frac{x_{1}^{0}}{x_{2}^{0}} \left(\frac{a_{2}^{0} + a_{3}^{0}}{a_{1}^{0}}\right) = \frac{x_{1}^{0}}{x_{2}^{0}} \left(\frac{2a_{2}^{0}}{a_{1}^{0}}\right) = \frac{2k_{1}}{k_{2} + k_{3}}.$$
 (3)

One must now relate this separation factor, S_0 , with the measured one, S, based on the assay of CO₂ from the combustion of ethylene samples. This may be done using a procedure similar to that of Bigeleisen,²⁰ which gives the result:

$$S_0 = 2K \frac{\ln(1-f)}{\ln\left[1 - \frac{K(1+r)}{L}\frac{f}{S}\right]},\tag{4}$$

where $f \equiv$ fraction of substrate decomposed $\cong x_1/a_1^0$,

$$S \equiv \text{measured separation factor} = \frac{x_1}{x_2} \left(\frac{a_2^0 + a_3^0}{a_1^0} \right),$$
$$K = \frac{k_2^2 + k_3^2}{(k_2 + k_3)^2}, \quad L = \frac{k_2 + rk_3}{k_2 + k_3}, \quad \text{and} \quad r = \frac{a_3^0}{a_2^0}.$$

Since k_2 and k_3 are believed to differ by less than 2 percent, K is taken to be $\frac{1}{2}$. In addition, it is assumed that r=1. This assumption produces a negligible error in S_0 even if the actual r differs from unity by as much as 10 percent. A greater abnormality in the natural distribution of C^{13} in the ethyl bromide (isotopic inhomogeneity) is very unlikely.

Equation (4) is then simplified to yield the result:

$$S_0 = \frac{2k_1}{k_2 + k_3} = \frac{\ln(1 - f)}{\ln(1 - f/S)}.$$
 (5)

Equation (5) is used to correct to zero extent of reaction.

TABLE I. Summary of experimental results.

Temp. °C (±3°)	f (±0.003)	(±1×10-4)	$S_{0} = \frac{2k_{1}}{k_{2} + k_{3}}$ $(\pm 2 \times 10^{-4})$
351	0.053	1.00885	1.0091
355	0.050	1.0088	1.00905
366	0.056	1.00875	1.0090
366	0.057	1.0080	1.0082_{5}
377	0.062	1.0086	1.0088_{5}
379	0.057	1.0089_{5}	1.00925
387	0.050	1.00755	1.00775
389	0.059	1.0087	1.0090
402	0.061	1.00825	1.0085
403	0.059	1.0072	1.00745
410	0.056	1.00665	1.0068_{5}
410	0.057	1.00735	1.0076
423	0.054	1.0068	1.0070
433	0.063	1.0066	1.0068
442	0.089	1.0054	1.00565
442	0.078	1.0060	1.00625
453	0.123	1.00715	1.00765
453	0.071	1.00635	1.0066

²⁰ J. Bigeleisen, Science 110, 14 (1949).



For experiments carried out to a small extent of reaction (f < 0.1), Eq. (5) may be further simplified to give the following useful approximation formula:

$$\epsilon_0 = \epsilon (1 + f/2), \tag{6}$$

where $\epsilon \equiv S - 1$ and $\epsilon_0 \equiv S_0 - 1$.

An example of the original data and calculations for a typical experiment follows.

$$T = 423 \pm 3^{\circ}$$
C. $f = 0.054 \pm 0.004$.

Mass spectrometer ratios (45/44) for CO₂ from:

- (a) Product fraction C_2H_4 0.014961±0.000006
- (b) Total decomposition C_2H_4 0.015059 \pm 0.000003
- (c) Tank reference standard 0.014938 ± 0.000004

 $S = 1.0068 \pm 0.0001$; $\epsilon_0 = 0.0070 \pm 0.0002$

$$\frac{2k_1}{k_2 + k_3} = 1.0070 \pm 0.0002.$$

The data for eighteen experiments are summarized in Table I. Figure 1 shows a graph of the data of Table I. The least-squares line drawn through the data passes through the point 1.0079 at 400°C, with a slope of -2.8×10^{-5} /°C. The average deviation of the points from the line is ± 0.0006 . The uncertainty in the slope is approximately $\pm 1.0 \times 10^{-5}$ /°C.

DISCUSSION

It is of interest to evaluate the primary and secondary isotope effects from the measured quantity

$${}_{0} \equiv \frac{2k_{1}}{k_{2}+k_{3}} - 1$$

Defining the primary isotope effect as

$$\beta \equiv \frac{k_1}{k_2} - 1,$$



and the secondary isotope effect as

one obtains

$$\frac{2}{1+\epsilon_0} = \frac{1}{1+\beta} + \frac{1}{1+\gamma},$$

 $\gamma \equiv \frac{k_1}{k_2} - 1,$

so that $\beta + \gamma + 2\beta\gamma = \epsilon_0(2+\beta+\gamma)$. Neglecting secondorder products, $\beta + \gamma = 2\epsilon_0$. Thus the sum of the primary and secondary isotope effects is twice the observed overall isotope effect.

According to any reasonable theory, $\beta > \gamma \ge 0$. The upper limit for β may be found by setting $\gamma=0$; the lower limit by assuming $\gamma=\beta$. Thus $\beta_{\max}=2\epsilon_0$, and $\beta_{\min}=\epsilon_0$. Similarly γ is found to lie between the limits 0 and ϵ_0 .

 $\epsilon_0 < \beta \leq 2\epsilon_0$

In summary

and

$$\beta + \gamma = 2\epsilon_0$$

 $\epsilon_0 > \gamma > 0$

Figure 2 shows a graph of $(k_1/k_2)_{\text{max}}$ versus T°C. From the data at 400°C, at which $\epsilon_0 = 0.0079$, $(k_1/k_2)_{\text{max}} = 1.0159 \pm 0.0012$.

This is significantly lower than the value $k_1/k_2 \ge 1.036$ calculated for the case of the rupture of an isolated C-Br bond.

The theoretical treatment of Bigeleisen⁸ based on the transition-state theory is:

$$\frac{k_1}{k_2} = \left(\frac{m^{*\ddagger}}{m\ddagger}\right)^{\ddagger} [1 + \sum_i G(u_i) \Delta u_i - \sum_i G(u_i\ddagger) \Delta u_i\ddagger],$$

where m^{\ddagger} and $m^{*\ddagger}$ represent the reduced masses of the normal and isotopic activated complexes along the decomposition coordinate and the other quantities have their usual significance. For the free radical C-Br rupture mechanism one would expect the reduced mass term to be 1.036. The quantity in brackets, known as the free energy term, is greater than unity, but decreases to unity as $T \rightarrow \infty$. The observed negative temperature dependence is of the proper sign, but its magnitude is in doubt by such a large amount that it offers no critical test of the theory.

For the intramolecular mechanism, the reduced mass ratio would be expected to lie somewhere between 1.003 and 1.036. No explicit theoretical formulation is available to enable a calculation of the appropriate reduced mass ratio for such a "four-center" reaction. However, Bigeleisen and Wolfsberg²¹ have shown that for 3-center isotopic reactions the reduced mass ratio nearly always shows an initial decrease with an increase in the "reaction coordinate parameter" p, which is a measure of the relative amount of bond formation to bond rupture. It might be presumed that for the present case similar qualitative considerations might apply.

It is therefore believed that the results of the present investigation eliminate from consideration the simple free radical mechanism and offer support for the direct intramolecular elimination mechanism.

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