



Effect of Pressure on the Isotope Effect in a Unimolecular Gaseous Reaction : Tritium and Carbon13 Effects in the Isomerization of Cyclopropane

Ralph E. Weston Jr.

Citation: The Journal of Chemical Physics **26**, 975 (1957); doi: 10.1063/1.1743542 View online: http://dx.doi.org/10.1063/1.1743542 View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/26/5?ver=pdfcov Published by the AIP Publishing

Articles you may be interested in

Reaction path Hamiltonian: Tunneling effects in the unimolecular isomerization HNC→HCN J. Chem. Phys. **73**, 2733 (1980); 10.1063/1.440494

Reaction of Cyclopropane with Iodine and Some Observations on the Isomerization of Cyclopropane J. Chem. Phys. **34**, 521 (1961); 10.1063/1.1700977

Reactions Initiated by the β Decay of Tritium. III. The TritiumCyclopropane System J. Chem. Phys. **32**, 1757 (1960); 10.1063/1.1731016

Intermolecular Isotope Effect in Recoil Tritium Reactions with Hydrogen J. Chem. Phys. **32**, 1266 (1960); 10.1063/1.1730893

Tritium Isotope Effect in the Isomerization of Cyclopropane J. Chem. Phys. **23**, 988 (1955); 10.1063/1.1742179



This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 129.120.242.61 On: Sat, 29 Nov 2014 19:07:07

THE JOURNAL OF CHEMICAL PHYSICS

Volume 26, Number 5

May, 1957

Effect of Pressure on the Isotope Effect in a Unimolecular Gaseous Reaction: Tritium and Carbon-13 Effects in the Isomerization of Cyclopropane*

RALPH E. WESTON, JR.

Chemistry Department, Brookhaven National Laboratory, Upton, Long Island, New York (Received May 28, 1956)

As a new means of studying the effect of pressure on unimolecular gaseous reaction kinetics, the tritium isotope effect in the isomerization of cyclopropane to propylene has been measured. At a pressure of 200 mm, the ratio of rate constants for unlabeled and singly-labeled species is given by $k/k' = (0.86\pm0.06) \exp(385\pm95/RT)$. The temperature range was $406-492^{\circ}$ C. As the pressure decreases, the isotope effect is lowered and, within experimental error, disappears at 1 mm. Upon the addition of inert gas to cyclopropane at this pressure, the isotope effect is increased to a value corresponding to a higher pressure of reactant. The relation between these results and the calculations of N. B. Slater on the kinetics of this reaction is discussed.

The carbon-13 isotope effect was measured at 1 atmos and 492°, and was found to be $k/k' = 1.0072 \pm 0.0006$. This may be explained on the basis of a change in either a carbon-carbon or a carbon-hydrogen bond in the transition state.

THE generally accepted mechanism for homogeneous unimolecular gaseous reactions is some form of that originally proposed by Lindemann.¹ According to this, a reactant molecule obtains the necessary activation energy by collision with a second molecule (reactant or added inert gas). At sufficiently high pressure, the activated molecules have a Maxwell-Boltzmann energy distribution, and the rate-determining step is the decomposition of an activated molecule. At very low pressure, this energy distribution is not maintained, and the slow step becomes the transfer of energy by collision. While many of the reactions once used as experimental support for this mechanism have since proven to be complex, recent work²⁻⁴ has given

⁴ Reaction of nitrogen pentoxide with nitric oxide: R. L. Mills and H. S. Johnston, J. Am. Chem. Soc. 73, 938 (1951); H. S. Johnston and R. L. Perrine, *ibid.* 73, 4782 (1951). new proof of its validity. The usual method for investigating the mechanism of energy transfer in such reactions is to study the pressure dependence of the reaction rate. It has been suggested⁵ that the kinetic isotope effect in such a reaction should be a function of the pressure, and this technique has been used here to study the isomerization of cyclopropane.

The Lindemann mechanism may be written⁶

$$A + M \xrightarrow{a_i} A_i^{*} + M,$$
$$A_i^{*} + M \xrightarrow{b_i} A + M,$$
$$A_i^{*} \xrightarrow{c_i} \text{products.}$$

The general expression for the first-order rate constant is

$$k = \sum_{i} \frac{a_i c_i(M)}{b_i(M) + c_i},$$

where the sum is over the energy levels of the activated molecule A_i^* . Hence the ratio of the first-order rate

Copyright @ 1957 by the American Institute of Physics

^{*} Research carried out under the auspices of the U. S. Atomic Energy Commission.

¹ For discussion, cf. L. S. Kassel, *The Kinetics of Homogeneous Gas Reactions* (The Chemical Catalog Company, Inc., New York, 1932), Chap. V.

 ¹ South Control (1932), Chap. V.
 ² Cyclopropane isomerization: T. S. Chambers and G. B. Kistiakowsky, J. Am. Chem. Soc. 56, 399 (1934); E. S. Corner and R. N. Pease, J. Am. Chem. Soc. 67, 2067 (1945); Pritchard, Sowden and Trotman-Dickenson, Proc. Roy. Soc. (London) A217, 563 (1953).

³ Cyclobutane decomposition: Genaux, Kern, and Walters, J. Am. Chem. Soc. **75**, 6196 (1953) and earlier papers; Pritchard, Sowden, and Trotman-Dickenson, Proc. Roy. Soc. (London) **A218**, 416 (1953).

⁶ R. B. Bernstein, J. Phys. Chem. 56, 893 (1952). Since the submission of this paper, the effect of pressure on the decomposition rates of cyclobutane and cyclobutane-d₈ has been reported [B. F. Gray and H. O. Pritchard, J. Chem. Soc. (London) 1956, 1002]. ⁶ H. S. Johnston, J. Chem. Phys. 20, 1103 (1952).

constants for two isotopic species is

$$\frac{k'}{k} = \sum_{j} \frac{a_{j}'c_{j}'(M)}{b_{j}'(M) + c_{j}'} / \sum_{i} \frac{a_{i}c_{i}(M)}{b_{i}(M) + c_{i}}.$$
 (1)

This expression may be simplified at either very high or very low pressures. If (M) is large enough so that $b_i'(M) \gg c_i'$ and $b_i(M) \gg c_i$ for all i and j, then

$$(k'/k)_{\infty} = \sum_{j} a_{j}' c_{j}'/b_{j}'/\sum_{i} a_{i} c_{i}/b_{i}.$$
 (2)

This condition, which implies a Maxwell-Boltzmann energy distribution in the activated molecules, gives a rate constant ratio of the type usually considered in isotope effect experiments.⁷ On the other hand, if (M)is sufficiently small so that $c_j \gg b_j'(M)$ and $c_i \gg b_i(M)$ for all i and j, then

$$(k'/k)_0 = \sum a_j'(M) / \sum a_i(M) = a'/a.$$
(3)

At this low pressure limit, the rate constant ratio is given by the ratio of rate constants for the process of activation by collision. The isotope effect for this process may well be different from that for a bond-breaking process.

The reaction used to investigate these effects was the isomerization of cyclopropane to propylene; the rate of this isomerization has been determined as a function of pressure, and all present evidence indicates that it is a homogeneous, unimolecular reaction.

There is a second reason for interest in this isotope effect; the isomerization has been used by Slater as a test of his theory of unimolecular reactions.8 His calculated rate constant agrees with experiment, if he assumes as a "critical coordinate" the distance from a hydrogen atom to an adjacent carbon atom (to which it is not bonded). On this basis, one would expect to find a hydrogen isotope effect.

The preliminary results of this work have been published.⁹ Since then, the results of similar experiments at a single pressure have also been reported.¹⁰

EXPERIMENTAL

Cyclopropane

The cyclopropane used for comparison experiments and for C¹³ isotope effect experiments was commercial material (Matheson Company) stated to be 99.5% pure. It was passed through a trap at -78° (to remove traces of water), and in some cases bulb-to-bulb distillation was used for purification.

cal Society Meeting, Minneapolis, Minnesota, September, 1955; J. Chem. Phys. 24, 725 (1956). (The latter reference will be designated hereafter as LR.)

Cyclopropane-t

Isotope effect experiments with radioactive isotopes may be invalidated if the reactants contain trace impurities of significantly different specific activity. For this reason, the method of synthesis and the tests for purity will be described in some detail.

An estimated 16 mC (2.6×10^{-7} mole) of carrier-free tritium (Oak Ridge National Laboratory) was sealed off in a capillary attached to the original container. Approximately 3.8×10^{-4} mole of bromine was distilled in vacuo into a similar capillary. The two capillaries were placed in a larger bulb equipped with a break-seal and a seal-off constriction. After evacuation, the capillaries were broken by shaking the bulb; 7.5×10^{-4} mole of hydrogen was added, and the bulb was sealed off. The bulb was then placed in a furnace at 400° for 30 min, at which time the completion of the reaction to form tritium-labeled HBr was evident from the disappearance of color. The excess hydrogen was pumped off while the hydrogen bromide was frozen out at -196° .

From the labeled hydrogen bromide and allyl bromide, 1,3-dibromopropane was synthesized according to the procedure of Kharasch and Mayo.¹¹ A bomb tube containing 0.083 mole of freshly distilled and aerated allyl bromide was evacuated, and the labeled HBr together with 0.136 mole of tank hydrogen bromide was condensed into the tube. Air at a pressure of $\frac{1}{2}$ atmos was added, the tube was sealed off and placed in a steel cylinder, and it was allowed to stand at room temperature for one week. After the tube was opened and excess hydrogen bromide allowed to escape, the reaction mixture was treated with dimethylaniline and ethanol to remove any unreacted allyl bromide. The reaction mixture was washed with 6 N sulfuric acid, a saturated solution of sodium bicarbonate, and water; it was then dried over Anhydrone. The yield before drying was 0.067 mole (81% based on allyl bromide). According to Kharasch and Mayo, this synthesis gives 80-90% of the 1,3 isomer of dibromopropane. In a preliminary experiment with unlabeled material, an 81% yield of dibromopropane was obtained; 80% of this was the 1,3 isomer. The dibromopropane was distilled through a small, vacuum-jacketed column, and the fraction (about 0.048 mole) distilling in the range 162-168° was retained (B.P. 1,3-dibromopropane, 167°). To this was added one mole of Eastman Kodak White Label 1,3dibromopropane.

Cyclopropane-t was prepared from this dibromopropane mixture according to the method of Ashdown, Harris, and Armstrong.¹² One mole of dibromopropane in 400 ml of thoroughly dried ethanol was refluxed with 100 g of zinc dust in a 1-l 3-neck flask. A slow stream of dry nitrogen carried the evolved cyclopropane through a trap at -10° to remove alcohol, and then to a trap at

⁷ J. Bigeleisen, J. Chem. Phys. 17, 675 (1949); J. Phys. Chem. 56, 823 (1952).
⁸ N. B. Slater, Proc. Roy. Soc. (London) A218, 224 (1953).
⁹ R. E. Weston, Jr., J. Chem. Phys. 23, 988 (1955).
¹⁰ R. H. Lindquist and G. K. Rollefson, 128th American Chemical Society Mathematican Chemican Chemican

¹¹ M. S. Kharasch and F. R. Mayo, J. Am. Chem. Soc. 55, 2468 (1933).

¹² Ashdown, Harris, and Armstrong, J. Am. Chem. Soc. 58, 850 (1936).

 -78° where the cyclopropane was condensed as a liquid. The entire apparatus was gas-tight, and was dried before use by flaming it while a current of nitrogen passed through. Careful drying is reported to prevent the formation of propane.¹² The product was distilled into a small gas cylinder, where it was stored as a liquid at room temperature; a few ml of nonvolatile liquid (apparently dibromopropane) remained after this distillation. The cyclopropane was freed from propylene by bubbling through two gas washing bottles containing aqueous iodine and bromine, followed by one containing 30% potassium hydroxide.13 The yield at this point was 0.77 mole (77% based on 1,3-dibromopropane). Again distillation into the storage cylinder left a slight nonvolatile residue (probably dibromopropane produced by reaction of cyclopropane or propylene with iodine bromide).

The specific activity of cyclopropane-t was 0.45 mC/mole. This was considerably lower than the activity (3.0 mC/mole) estimated on the basis of the dilutions during the synthesis; the difference could be produced by an isotope effect of about 10 favoring the reaction of hydrogen with bromine over that of tritium with bromine. This effect is reasonable in light of the factor of about five in favor of hydrogen over deuterium at the temperature used here.¹⁴ The molar ratio of cyclopropane-t to cyclopropane was 1.6×10^{-8} .

Tests of Purity

Several tests were made for impurities of significantly different specific activity than the cyclopropane-t. Concentrated (96%) sulfuric acid absorbs cyclopropane and propylene; this procedure left unabsorbed 0.5%of the gas sample. This gas, perhaps propane, had a specific activity about 2% lower than the cyclopropane-t. Upon absorption in mercuric sulfate or acetate solutions (compare analytical procedure) which remove olefins, 98-100% of the sample was left, and the specific activity was unchanged. Upon scrubbing with unlabeled propylene, followed by this procedure, the specific activity was also unchanged. To test for possible bromide impurities, some cyclopropane was shaken for two days with 40% aqueous potassium hydroxide at room temperature. The aqueous phase gave no test for bromide ion with silver nitrate; the gas phase analyzed 99% cyclopropane of normal specific activity.

Rate constants for isomerization at various pressures and temperatures agree with those for normal cyclopropane, within experimental error. The activation energy for the labeled compound agrees within 0.5 kcal with that reported for normal cyclopropane.² In all experiments, the pressure of the reaction mixture was compared with that of the initial cyclopropane; the ratio of final to initial pressures was 0.98-1.00. This is a sensitive test for polymerization or cracking. The specific activity of reaction mixtures (even after about 35 half-times) was identical with that of the initial cyclopropane, as it should be in the absence of side reactions.

The infrared spectrum of cyclopropane-t had no bands which were not found in a similar spectrum of normal cyclopropane.

Analytical and Radio-Assay Procedures

Some of the early analyses were made using an aqueous solution of mercuric acetate and nitrate as the absorbant for propylene.15 With small samples, some difficulty in reproducing results was encountered. Finally a procedure was adopted in which a saturated solution of mercuric sulfate in 22% sulfuric acid was used as the absorbant.¹⁶ With this, the precision was about 2% (mean error) for 10 μ mole samples of 50% cyclopropane-propylene mixtures. The method was tested with known mixtures of the two gases, and the accuracy was found to be slightly less than the precision. The accuracy decreased when the ratio of gases differed much from unity; hence, most of the kinetic runs were for a period of one half-time. The analytical apparatus consisted of a gas buret with stopcocks arranged so that the measured gas sample could be pumped through a small U-tube containing the absorbant by raising and lowering the mercury in the buret. After this was done several times, the gas was pumped into a small tube containing Anhydrone to remove water vapor. When all water was removed, the remaining cyclopropane was measured and condensed into a counting tube.

The counting tubes were glass tubes of standard design,17 used in this laboratory for tritium and C14 counting. P-10 gas (90% argon-10% methane) at 1 atmos was used as the counting gas for proportional counting in the region of 1900-2100 v. A correction was made for the effective volume of the tube; other work in this laboratory has indicated a counting efficiency for tritium which is 97-98% of the geometric efficiency. The number of counts per sample was always over 10 000, so that the statistical error was less than 1%. The precision in the counting was about 1% (mean error).

Carbon-13 Analyses

The procedure for obtaining and analyzing reaction mixtures was the same as that used in the tritium experiments. Duplicate samples of cyclopropane separated in the analytical procedure were then combined for combustion. The combined samples (50-100 µmoles) were burned for 2-4 hours at 700° over copper oxide, in the presence of excess oxygen. The carbon dioxide from this initial combustion contained traces of im-

¹³ S. Z. Roginski and F. H. Rathmann, J. Am. Chem. Soc. 55,

 <sup>2800 (1933).
 &</sup>lt;sup>14</sup> Bach, Bonhoeffer, and Moelwyn-Hughes, Z. physik. Chem.
 B27, 71 (1934).

 ¹⁶ Pyke, Kahn, and Leroy, Anal. Chem. 19, 65 (1947).
 ¹⁶ Brooks, Murdock, and Zahn, Anal. Chem. 20, 62 (1948).
 ¹⁷ W. Bernstein and R. Ballentine, Rev. Sci. Instr. 21, 158 (1950).



FIG. 1. Rate constant for isomerization of cyclopropane: solid lines, data from reference 2; \bigcirc , labeled cyclopropane; \triangle , labeled cyclopropane with nitrogen; \square , unlabeled cyclopropane. Rate constant at 440° is multiplied by 10.

purities, as shown by the mass spectrum. A second combustion removed these impurities. A Consolidated-Nier model 21–201 mass spectrometer was used to obtain ratios of $C^{13}O_2/C^{12}O_2$. The combustion samples were compared with a sample of tank carbon dioxide, which served as the reference standard. Corrections were made for incomplete resolution, difference in amplifier sensitivity, and natural abundance of O^{17} .

Apparatus for Kinetic Experiments

Some preliminary experiments were made using a 100-ml quartz tube and a small furnace. Later experiments were made with a 1900-ml cylindrical bulb as the reaction vessel. The furnace consisted of a cylindrical steel form (6 in. o.d., $4\frac{1}{4}$ in. i.d., 15 in. long, weight about 50 lbs); this was wound with Nichrome wire in three sections, so that the power in the central and two end windings could be separately controlled. The steel cylinder was contained in a section of 16-in. clay pipe, and the space between filled with infusorial earth. As will be seen below, the isotope effect is relatively insensitive to temperature. However, to facilitate comparison of rate constants with those of other workers, the temperature was controlled rather accurately. A chromel-alumel thermocouple (previously calibrated with standards from the National Bureau of Standards) was inserted in a well along the axis of the reaction vessel. The potential of the thermocouple was measured with a Rubicon potentiometer and an external mirror galvanometer. Light reflected from the galvanometer mirror actuated photocells connected to a thyratron circuit which controlled the power input to the furnace. The temperature variation at 500° was about 0.2° with the vessel evacuated; at 1 atmos it was less than 0.1°. The temperature variation from top to bottom along the axis of the vessel was about 1°. The fraction of the reaction vessel volume outside the furnace amounted to about 1%; no correction was made for this.

The vessel was connected to a vacuum line through a large trap for condensing out reaction products, and to a gas buret for introducing the reactant. The pressure in the reaction vessel was determined by the measured amount of gas introduced. In some experiments the reaction was stopped by rapidly condensing out the entire reaction mixture, which was subsequently analyzed. In others, small samples were taken from the reaction vessel during the course of reaction.

In the one experiment at a pressure greater than atmospheric, cyclopropane was sealed off in a tube small enough to fit into the thermocouple well. After reaction the products were removed by means of a break-seal on the tube.

In the experiments with nitrogen added as an inert gas, the cyclopropane was swept into the reaction vessel by the nitrogen, and the inert gas pressure was rapidly increased to 700 mm. Since the ratio of nitrogen to cyclopropane was about 1000, it was essential to remove traces of noncondensible gases from the nitrogen. This was done by passing it through Ascarite, Anhydrone, and a trap cooled with liquid nitrogen.

RESULTS

Figure 1 shows the relation between rate constants and pressure for labeled and normal cyclopropane at three temperatures, together with values obtained by



FIG. 2. Specific activity (arbitrary units) of cyclopropane from reaction mixture. T=492-500 °C, P=700 mm.

other workers.² Note that the agreement between the rates for labeled and unlabeled material is within experimental error, while there is a larger deviation from the constants obtained by others. This is probably due to a difference in the absolute temperature: a difference of 1° at 500° changes the rate by about 6%. In addition to this, the spatial temperature variation within the reaction vessel may contribute to the error. Because of the change in thermal conductivity of a gas with pressure, the latter factor may not be constant for all the experiments.

At some pressures, samples were taken at various extents of reaction up to 60%, and the first-order isomerization was demonstrated by a linear relationship between the logarithm of the fraction of cyclopropane unreacted and time.

The isotope effect is expressed here as $\epsilon = 1 - (k'/k)$, where k and k' are rate constants for the isomerization of normal and labeled cyclopropane. If S_0 is the specific activity of the original cyclopropane, and S_f that of

979

the cyclopropane at fraction of reaction f, then

$$\epsilon = -\log(S_f/S_0)/\log(1-f).^{18}$$
(4)

The same formula is applicable to the C^{13} effect, in which case S is $C^{13}O_2/C^{12}O_2$. This predicts a linear relationship between $\log S_f$ and $-\log(1-f)$, which is illustrated in Fig. 2 for the tritium isotope effect, and in Fig. 3 for the C¹³ isotope effect.

The variation of the tritium isotope effect with pressure is given in Fig. 4 and Table I. The mean value of ϵ and the mean deviation are obtained from the mean values of S_f , S_0 , and f for each kinetic run, rather than by averaging values calculated from the individual analyses. The error formula is

$$\frac{\Delta\epsilon}{\epsilon} = 0.4343 \left\{ \frac{1}{\left[\langle \log S_f / S_0 \rangle_{\mathsf{Av}} \right]^2} \left[\left(\frac{\Delta S_f}{\langle S_f \rangle_{\mathsf{Av}}} \right)^2 + \left(\frac{\Delta S_0}{\langle S_0 \rangle_{\mathsf{Av}}} \right)^2 \right] + \frac{1}{\left[\langle \log (1-f) \rangle_{\mathsf{Av}} \right]^2} \left[\frac{\Delta (1-f)}{\langle (1-f) \rangle_{\mathsf{Av}}} \right]^2 \right\}^{\frac{1}{2}}.$$
 (5)



FIG. 3. C¹³ analysis of carbon dioxide from unreacted cyclopropane. $T=492^{\circ}$ C, P=700 mm.

The average mean deviation in S_f is $0.8 \pm 0.3\%$, that in 1-f is $2.0\pm0.8\%$, and that in ϵ is 21%. The isotope effect is very sensitive to errors in S_f/S_0 and relatively insensitive to errors in 1-f; the contribution of the latter is almost negligible in these experiments. This makes possible the use of Eq. (5), which is rigorously correct only when S and f are independent variables. Also, the relative error in ϵ increases as the value decreases. A few points with unusually large deviations in S_f were rejected on the basis of Chauvenet's criterion.¹⁹

The effect of temperature (from 406-492°C) on the tritium isotope effect at 200 mm is shown in Table I and Fig. 5. These experiments were done at a pressure of 200 mm, rather than 1 atmos, in order to facilitate



FIG. 4. Pressure influence on tritium isotope effect: curve 1, theoretical pressure dependence with constant (b/c); curve 2, same with variable (b/c). Experimental points: \bigcirc , 492° and 500°C; \bigcirc , 470°C; \bigcirc , 440°C; \bullet , 406°C; \triangle , 492°C with added nitrogen.

comparison of the results with those of LR. For this purpose an expression of the form k/k' = (A/A') $\times \exp(\Delta \Delta H_{exp}^{\dagger}/RT)$ was assumed; the parameters were evaluated by a least-squares procedure. From the 23 individual values of ϵ , one obtains $A/A' = 0.89 \pm 0.06$ and $\Delta \Delta H_{exp}^{\dagger} = 332 \pm 105$ cal/mole. From the mean values of ϵ at each temperature, $A/A' = 0.86 \pm 0.06$ and $\Delta \Delta H_{exp}^{\ddagger}$ $=385\pm95$ cal/mole. (The mean deviation is that ob-

TABLE I. Tritium isotope effect in the isomerization of cyclopropane.

Pressure (mm)	т, °С	nª	(1 − <i>f</i>)	S_f	Sol	100e
1850	492?5	4	0.558 ± 0.008	51.6±0.7	48.1±0.4	11.9 ±2.7
730ª	500?	1	0.815	53.6	52.0 ± 0.2	14.8
		1	0.349	57.7	52.0 ± 0.2	9.9
730ª	500?	4	0.576 ± 0.002	56.4 ± 0.1	52.0 ± 0.2	14.7 ± 1.0
		4	0.396 ± 0.006	56.9 ± 0.7	52.0 ± 0.2	9.7±1.4
700	470	1	0,797	50.3	48.4 ± 0.5	16.9
		1	0.620	51.1 ± 0.6	48.4 + 0.5	11.3
		6	0.474 ± 0.010	52.9 ± 0.6	48.4 ± 0.5	11.9 ± 2.0
212	440	2	0.671 ± 0.003	50.0 ± 0.7	47.4 ± 0.4	13.4 ± 3.9
		3	0.518 ± 0.020	50.9 ± 0.1	47.4 ± 0.4	10.8 ± 1.4
210	406	5	0.496 ± 0.011	51.9 ± 0.4	47.4 ± 0.4	12.9 ± 1.6
200	470	6	0.539 ± 0.010	51.4 ± 0.4	48.5 ± 0.4	9.4 ± 1.9
188	492	6	0.461 ± 0.010	52.5 ± 0.3	48.3 ± 0.4	10.8 ± 1.4
170	440	3	0.541 ± 0.002	50.6 ± 0.6	47.4 ± 0.4	10.6 ± 2.6
80	492	2	0.725 ± 0.006	50.6 ± 0.2	49.1 ± 0.2	9.3 ± 1.8
77	492	4	0.438 ± 0.011	52.4 ± 0.4	49.1 ± 0.2	7.9 ± 1.1
45	470	1	0.502	52.2	49.1 ± 0.2	8.9
43.	492	2	0.497 ± 0.002	50.1 ± 1.1	47.8 ± 0.4	6.7 ± 3.2
43°	492	2	0.494 ± 0.002	50.5 ± 0.1	47.8 ± 0.4	7.8 ± 1.2
43°	492	1	0.495	49.9	47.3 ± 0.4	7.6
28	492	5	0.465 ± 0.016	51.0 ± 0.3	48.3 ± 0.4	7.2 ± 1.4
13.5	492	3	0.491 ± 0.020	50.2 ± 0.5	48.3 ± 0.4	5.4 ± 1.7
6.5	492	4	0.486 ± 0.019	49.9 ± 0.5	48.2 ± 0.4	4.7 ± 1.8
1.7	492	2	0.419 ± 0.009	49.3 ± 0.2	48.1 ± 0.4	2.8 ± 1.1
1.5	492	2	0.483 ± 0.009	49.8 ± 0.4	48.1 ± 0.4	4.8 ± 1.7
0.91	492	1	0.516	49.1	48.1 ± 0.4	3.1
0.430	492	1	0.486	49.0	49.3 ± 0.5	-0.8
0.433	492	1	0.497	48.2	49.3 ± 0.5	-3.2
0.431	492	1	0.485	49.7	49.3 ± 0.5	1.1
0.426	492	1	0.515	49.7	49.3 ± 0.5	1.2
0.411	492	1	0.472	49.4	49.2 ± 0.5	0.6
0.405	492	1	0.510	49.8	49.3 ± 0.5	1.8
0.400	492	1	0.439	49.0	49.0±0.5	0.0

Number of samples analyzed and counted.
Temperature uncertain by a few degrees.
Mean error calculated from mean error in 1 - f and S_I/S₀.
Preliminary experiments in 100 ml quartz vessel, with no temperature control.
Curdenerget and

Cyclopropane pressure, 1 mm; nitrogen pressure, 700 mm, which corresponds in collision efficiency to 43 mm of cyclopropane.
 In arbitrary units.

¹⁸ A. M. Downes and G. M. Harris, J. Chem. Phys. 20, 196

^{(1952).} ¹⁹ A. G. Worthing and J. Geffner, *Treatment of Experimental* ²⁰ New York, 1943), p. 170.



FIG. 5. Temperature dependence of tritium isotope effect at 200 mm.: O, individual analyses;
, mean value (vertical line indi-cates average deviation); solid line, least-squares fit to data.

tained in the least-squares treatment, rather than that from the separate errors in S and f.) This differs from the expression $k/k' = 0.63 \pm 0.02 \exp(825 \pm 60/RT)$ given in LR by an amount outside the estimated experimental errors. There is no apparent explanation for this discrepancy.

The results of the C13 isotope-effect experiments, which were done at 492° and 700 mm, are given in Table II.

DISCUSSION

High Pressure Tritium Isotope Effect

A plot of $1/\epsilon$ against 1/P for the results at 470° and 492° shows that at 700 mm $\epsilon \simeq \epsilon_{\infty}$, the value at infinite pressure. There is roughly a linear relationship at small values of 1/P, but the slope has considerable experimental error. At 200 mm, $\epsilon/\epsilon_{\infty}$ is about 0.9.

A statistical factor in the isotope effect should now be discussed. The possible modes of reaction of labeled and unlabeled species are

$$cyclo-C_{3}H_{6} \longrightarrow CH_{3}-CH=CH_{2} \qquad 12k_{1}$$

$$\text{cyclo-C}_{3}\text{H}_{5}\text{T}\xrightarrow{\text{H shift}}\text{C}\text{H}_{2}\text{T}-\text{C}\text{H}=\text{C}\text{H}_{2} \qquad 4k_{2}$$

T

$$\xrightarrow{\text{shift}} CH_2T - CH = CH_2 \qquad 2k_3$$

$$\xrightarrow{\text{H shift}} \text{CH}_3 - \text{CT} = \text{CH}_2 \qquad 2k_4$$

$$\xrightarrow{\text{H shift}} \text{CH}_3 - \text{CH} = \text{CHT} \qquad 4k_5$$

From this,

$$k/k' = 12k_1/(4k_2+2k_3+2k_4+4k_5).$$
 (6a)

It may be assumed that the individual rate constants are of the Arrhenius form; in general, the expression for k/k' will not be of this form. It is incorrect (at temperatures of 700-800°K) to equate the pre-exponential term on the left side of Eq. (6a) with the expression containing the individual frequency factors: $12A_{1}/(4A_{2}+2A_{3}+2A_{4}+4A_{5})$. The assumption of this equality, as in LR, leads to unreasonable frequency factor ratios. For example, a larger isotope effect is predicted for reaction (4) than for reaction (3) if $A_1 = A_2 = A_5$, and $A_3/A_1 = 0.62$.

A more valid approach is to attempt an estimate of k_2/k_1 , k_4/k_1 , and k_5/k_1 ; it is then possible to obtain k_3/k_1 , the most interesting ratio. There are few data available on relative rates of bond-breaking of the same bond in isotopically different molecules. Results from mass spectra indicate that C-H bond rupture is 20% more probable in CH₃D than in CH₄; the corresponding figure for C₂H₅D versus C₂H₆ is 9%.²⁰ Corresponding effects in more conventional chemical reactions of methane are in line with these figures.²¹ In these same systems, C-H bond rupture is about twice as probable as C-D rupture. On this basis, a reasonable approximation is that $k_2 = k_4 = k_5 = k_1$; let us designate the value of k_1/k_3 obtained from this assumption by $k_{\rm H}/k_{\rm T}$. Then

$$k/k' = 6/[5 + (k_{\rm T}/k_{\rm H})], \quad k_{\rm H}/k_{\rm T} = (1 - 6\epsilon)^{-1}.$$
 (6b)

Thus, at 492°, $\epsilon_{\infty} = 0.122 \pm 0.015$ and $k_{\rm H}/k_{\rm T} = 3.7 \pm 1.9$.

TABLE II. C¹³ Isotope effect at 492°C and 700 mm.

nª	1 — <i>f</i>	$10^{6}(45/44)^{b}$	100ε
5°	1.000	10 972±3°	* * *
(3	0.795 ± 0.004	10.988 ± 1	0.65
{3	$0.788 {\pm} 0.005$	$10993{\pm}1$	0.80
(3	0.610 ± 0.011	11007 ± 3	0.65
13	0.592 ± 0.012	11014 ± 2	0.72
(3	$0.472 {\pm} 0.006$	11.035 ± 3	0.76
14	0.461 ± 0.015	11.037 ± 3	0.76

^a No. of analyses, combined for combustion and M. S. analysis. ^b Corrected for O¹⁷ abundance, incomplete resolution, and amplifier factor. • Average for original cyclopropane, and unseparated reaction mixtures. Samples connected by braces are duplicates.

This statistical factor also complicates the significance of the observed activation energy difference. Since

$$k_{\rm H}/k_{\rm T} = (A_{\rm H}/A_{\rm T}) \exp(\Delta H_{\rm T}^{\ddagger} - \Delta H_{\rm H}^{\ddagger})/RT, \quad (7)$$

one obtains, upon differentiation with respect to temperature

$$RT^{2}d\ln(k/k')/dT \equiv \Delta\Delta H_{exp}^{\ddagger} = (\Delta H_{T}^{\ddagger} - \Delta H_{H}^{\ddagger})/[1 + (5k_{H}/k_{T})]. \quad (8)$$

Since $k_{\rm H}/k_{\rm T}$ is temperature-dependent, so is $\Delta\Delta H_{\rm exp}^{\ddagger}$; again, this is probably hidden by experimental error.

Another method of treating the temperature dependence is to plot $\log(k_{\rm T}/k_{\rm H}) = \log(1-6\epsilon)$ against $1/{\rm T}$ and from this to obtain the parameters in the Arrhenius expression. The experimental error is enlarged in this procedure, and it is doubtful if the results are significant. A least-squares treatment gives $\log(A_T/A_H) = 1.31$

 ²⁰ Krauss, Wahrhaftig, and Eyring, Ann. Rev. Nuclear Science 5, 241 (1955).
 ²¹ G. M. Harris, J. Phys. Chem. 56, 891 (1952); D. W. Coillet and G. M. Harris, J. Am. Chem. Soc. 75, 1486 (1953).

 ± 0.61 and $\Delta H_T^{\dagger} - \Delta H_H^{\dagger} = 5890 \pm 2000$ cal/mole. These results are not changed, beyond experimental error, if the values of ϵ are corrected to infinite pressure.

The activation energy obtained here is considerably lower than the value 825 cal/mole reported in LR. From this value of $\Delta \Delta H_{exp}^{\dagger}$, at the mid-point of the temperature range, one obtains $\Delta H_T^{\dagger} - \Delta H_H^{\dagger} \simeq 8300$ cal/mole. This value (and indeed the value of 5890 found in the foregoing) is unreasonably high. The largest possible difference in activation energy is the zeropoint energy difference in the reactant molecule caused by isotopic substitution. A rough estimate of the zeropoint energies may be made from the data of Baker and Lord²² on the vibrational spectra of C_3H_6 and C_3D_6 . For these two molecules, the ratio of zero-point energies is roughly equal to $(1+\frac{1}{12})^{\frac{1}{2}}/(\frac{1}{2}+\frac{1}{12})^{\frac{1}{2}}$. (This is probably because the largest contribution is from C-H stretching frequencies.) If a corresponding relationship is extended to C_3H_6 and C_3T_6 , then the zero-point energy difference is 12 800 cm⁻¹. But for C₃H₅T, the difference is one-sixth of this,23 or 2133 cm⁻¹, which is 3060 cal/ mole. This is an upper limit for the activation energy difference.

It is possible to calculate the expected isotope effect *a priori*, if a model for the transition state is chosen. Slater's⁸ treatment of this reaction gives a value for the "critical coordinate," which is the distance between a hydrogen atom and an adjacent nonbonded carbon atom in what corresponds to the transition state. This determines only the distance between the hydrogen and carbon atoms, and not their positions; however, because of the relative masses it is reasonable to assume as an approximation that only the hydrogen atom moves. Hence the positions of all the atoms in the transition state, as well as in the initial state, are known.

The transition state method gives for the rate contant of a unimolecular reaction

$$k = \kappa (\mathbf{k} T/h) Q^{\ddagger}/Q, \qquad (9)$$

where κ is the transmission coefficient, and Q and Q^{\ddagger} are partition functions of the initial state and transition state. If one assumes that $\kappa' = \kappa$, then

$$k_{\rm T}/k_{\rm H} = (Q_{\rm T}^{\ddagger}/Q_{\rm H}^{\ddagger})/(Q_{\rm T}/Q_{\rm H}).$$
 (10)

Since there is no change in mass, all translational terms in the partition function ratio drop out and the rotational and vibrational contributions are left. The former is

$$\frac{Q_{rT}^{\dagger}Q_{rH}}{Q_{rH}^{\dagger}Q_{rT}} = \frac{\sigma_{H}^{\dagger}\sigma_{T}}{\sigma_{T}^{\dagger}\sigma_{H}} \left(\frac{A_{T}^{\dagger}B_{T}^{\dagger}C_{T}^{\dagger}}{A_{H}^{\dagger}B_{H}^{\dagger}C_{H}^{\dagger}}\right)^{\frac{1}{2}} \left(\frac{A_{H}B_{H}C_{H}}{A_{T}B_{T}C_{T}}\right)^{\frac{1}{2}}, \quad (11)$$

where A, B, and C are principal moments of inertia of the species indicated. The term in the σ 's is a statistical factor which has already been considered in going from k'/k to the experimental $k_{\rm T}/k_{\rm H}$. When the atomic positions suggested by Slater's model are used, Eq. (11) is found to have the value 0.876.

The vibrational contribution to (10) is

$$(Q_{\boldsymbol{v}\mathbf{T}}^{\ddagger}/Q_{\boldsymbol{v}\mathbf{H}}^{\ddagger})/(Q_{\boldsymbol{v}\mathbf{T}}/Q_{\boldsymbol{v}\mathbf{H}}), \qquad (12)$$

3n - 6where $Q_v = \prod e^{-u_i/2} (1 - e^{-u_i})^{-1}$ and $u_i = hc\omega_i/kT$. Q_v^{\ddagger} is similar, but with the product over only 3n-7 degrees of freedom, since one of the vibrational modes has been taken out as the mode corresponding to the reaction coordinate. It is not possible to calculate the value of this vibrational contribution, a priori, without more knowledge of the transition state than is available. It is interesting, but not necessarily significant, that the assumption that only a C-H stretching mode is lost in going to the transition state leads to a temperature dependence of fair agreement with experiment if the temperature-independent factor is taken as 0.876 from Eq. (11)]. However, the value of Eq. (11) differs from what one would obtain from the usual assumption⁷ that only one bond is changed in going from the ground state to the transition state. This makes any estimate of Eq. (12) subject to considerable uncertainty. In particular, the possibility that the terms in $1-e^{-u}$ may be important makes it impossible rigorously to equate the experimentally observable activation energy difference with the difference in zero-point vibrational energy. The same consideration applies to the temperature-independent term. In addition to these difficulties, there may be a correction for quantum-mechanical tunneling, which again will have a somewhat complicated temperature dependence. For these reasons it does not appear profitable to attempt a further correlation between the experimental results and theoretical predictions.

In LR it is suggested that a CH_2 deformation mode is the one that becomes the reaction coordinate. This motion is a considerably better approximation to Slater's "critical coordinate" than a C--H stretching mode. The corresponding frequency for CHT can be obtained rather accurately by treating the group as a triatomic molecule, with force constants calculated from CH_2 . The bending frequency is found to be 1230 cm⁻¹, compared to 1475 cm⁻¹ for CH₂. (The value of 910 cm⁻¹ given in LR is approximately that of CT_2 .) Unfortunately, the corresponding zero-point energy difference is an order of magnitude less than the experimental $\Delta H_T^{\dagger} - \Delta H_H^{\dagger}$. This probably indicates a gross oversimplification in the use of the one-bond model.

An estimate of the effect of partial bond formation in the transition state was attempted, by use of the procedure discussed by Bigeleisen and Wolfsberg.²⁴ The effect on the relative rate of passage over the potential barrier is at most about 10%. However, there may be a

 ²² A. W. Baker and R. C. Lord, J. Chem. Phys. 23, 1636 (1955).
 ²³ H. J. Bernstein and A. D. E. Pullin, J. Chem. Phys. 21, 2188 (1953).

²⁴ J. Bigeleisen and M. Wolfsberg, J. Chem. Phys. 21, 1972 (1953); *ibid.* 22, 1264 (1954).

larger (and incalculable) effect on the other vibrational frequencies.

The change in position of a carbon atom in the transition state makes very little difference in Eq. (11). Most of the difference from unity in this equation results from the term for the molecules in the initial state.

To explain their observation that $A_{\rm T}/A_{\rm H}$ is greater than unity, Lindquist and Rollefson have discussed the possibility of a Fermi resonance between two vibrational modes which resemble the reaction coordinate. The two modes involved (CHT deformation and ring deformation) have frequencies of 1230 cm⁻¹ (see above) and 1029 cm^{-1,22} rather than 910 and 865 cm⁻¹ as used in LR. However, there is a ring breathing mode at 1188 cm⁻¹, which should not change much upon substitution of a tritium atom. In the lower symmetry of the labeled molecule, this could mix with the CHT deformation frequency.

In general, Fermi resonance should have little effect on the reaction rate constant. The zero-point energy term will be unaffected, since the perturbed vibrational levels are shifted symmetrically with respect to the hypothetical unperturbed level. The frequency factor in the rate constant depends on the product of 3n-6normal mode frequencies. Since one frequency shifts up and the other down, their product will change little. As a reasonable example, consider two accidentally degenerate vibrations of 1000 cm⁻¹, which are split 200 cm⁻¹ by the perturbation leading to resonance. The frequency products for the perturbed and unperturbed levels will differ by only 1%. There are examples of molecules in which one isotopic species is subject to resonance while the other is not. Nevertheless, the Teller-Redlich product rule (relating the products of all frequencies of the two species) is still valid.

If one needs to consider the amplitude of the resonating frequencies, as in the Slater rate formulation, there should still be no abnormal effect. Quantummechanically the amplitude is related to the frequency, and if one mode is increased the other must decrease. The situation may not be compared with the classical case in which the modes are alternately excited.

An alternative possibility, although it seems unlikely to change the frequency factor ratio significantly from unity, is that some of the terms in $1-e^{-u}$ are not negligible. Low frequencies which contribute little to the zero-point energy difference may contribute to the pre-exponential term provided they are mass-sensitive and changed in the transition state.

There is another explanation of the relative smallness of the observed isotope effect which cannot be ruled out. This may be caused, not by the statistical factor previously discussed, but by its being a secondary effect in which the C-H bond is not broken. In this case there would be no statistical factor. It should be possible to decide this question unambiguously by measuring the isotope effect for cyclopropane- d_6 .

High-Pressure Carbon Isotope Effect

At 492° and one atmos, the isotope effect for C¹³ is $\epsilon = 0.0072 \pm 0.0006$ (Table II), so that k'/k = 0.9928. Since the C¹⁴ effect is twice the C¹³ effect, in general, one should find k'/k = 0.9856 for C¹⁴. This is not significantly different from the value 1.00 ± 0.01 reported by Lindquist and Rollefson.¹⁰ Again, there is a statistical factor to consider; the possible modes of reaction are

cyclo-C¹²H₂C¹²H₂C¹²H₂
$$\xrightarrow{3k_1}$$
C¹²H₃ \rightarrow C¹²H = C¹²H₂
cyclo-C¹³H₂C¹²H₂C¹²H₂ $\xrightarrow{k_2}$ C¹²H₃ \rightarrow C¹²H = C¹³H₂
 $\xrightarrow{k_3}$ C¹³H₃ \rightarrow C¹²H = C¹²H₂
 $\xrightarrow{k_4}$ $\xrightarrow{k_4}$ C¹²H₃ \rightarrow C¹³H = C¹²H₂.

Hence, $k'/k = (k_2+k_3+k_4)/3k_1$, and $\epsilon_{calo} = 1 - (1/3) \times [(k_2/k_1) + (k_3/k_1) + (k_4/k_1)].$

In the case of the C¹³ effect, Eq. (12) may not be approximated by the neglect of the terms in $1-e^{-u_i}$. The effect of C¹³ substitution on skeletal vibrations, which contribute most to such terms, is comparable to the total observed effect. For this reason, it does not seem feasible to make use of Slater's model in evaluating Eqs. (10)-(12). Instead, the formula which is an expansion of these valid for $u_i - u_i' \ll 1$ will be used. This is:

$$k'/k = (m^*/m^{*'})^{\frac{1}{2}} \left[1 + \Sigma G(u_i^{\dagger}) \Delta u_i^{\dagger} - \Sigma G(u_i) \Delta u_i\right]^{7}$$
(13)

For the sake of generality, the reduced mass term can be calculated for a three-center reaction with the formula of Bigeleisen and Wolfsberg.²⁴ In this case, one C-H bond is being broken and a new one formed. It is found that the maximum value for the reduced mass term in ϵ is 0.0010 for either complete bond-breaking or complete bond-formation in the transition state. Intermediate cases lower this value. If the usual assumption (which should be valid at 500°C) is made: that the intramolecular isotope effect is given by the reduced mass term alone, then there is no temperature-dependent term for k_2/k_3 and k_4/k_3 . This is equivalent to making the temperature-dependent terms equal for k_2/k_1 , k_3/k_1 , and k_4/k_1 . Hence, the temperature-dependent contribution to ϵ is the value of $\Sigma G(u_i) \Delta u_i - \Sigma G(u_i^{\ddagger}) \Delta u_i^{\ddagger}$ for k_2/k_1 . To fit the experimental ϵ this must be 0.0062. Since the difference between a C¹²-H and a C¹³-H stretching frequency corresponds to $G(u)\Delta u = 0.0048$, the value of 0.0062 is not impossibly large.

The same procedure may be used to calculate the effect for a C-C bond change in the transition state. Since a double bond is being formed while a single bond is breaking, a three-center formulation is again appropriate. However, it is found that the reduced mass part of ϵ_{eale} is independent of the relative amount of bond-breaking and formation: it is 0.0128. This is considerably higher than the experimental value. If

this mechanism is correct, there must be some tightening of bonds in the transition state to lower the isotope effect. An argument similar to that used in the preceding paragraph leads to $\Sigma G(u_i^{\dagger}) \Delta u_i^{\dagger} - \Sigma G(u_i) \Delta u_i = 0.0055$. This is equivalent to an increase in bonding in the transition state slightly greater than the change of a single bond to a double bond.

In conclusion, it must be said that the carbon isotope effect does not allow an unequivocal choice between a transition state in which (a) a carbon-hydrogen bond is changing, and there is appreciable bond loosening, (b) a carbon-carbon is changing, and there is appreciable bond tightening, or (c) some combination of (a) and (b). Further information might be obtained by a study of the intramolecular isotope effects of reactions (2), (3), and (4).

Pressure Dependence of the Tritium Isotope Effect

Equation (1), relating isotope effect to pressure, is not usable in its exact form because of the summations over energy levels. Two approximate forms will be considered:

(a) It is assumed that the rate constants are independent of energy (Hinshelwood theory). Then the expression becomes

$$k'/k = (a'c'/ac)[b(M)+c]/[b'(M)+c'].$$
 (14)

The data combined to calculate the isotope effect at various pressures (Fig. 4, curve 1) are the value of ϵ at 1 atmos, the zero value at low pressures, and the value b/c obtained by extrapolation to infinite pressure.

(b) A value of b/c which would give the observed rate constant (for the unlabeled compound) is calculated at each pressure. This ratio is combined with the other data used in assumption (a) to give ϵ as a function of pressure (Fig. 4, curve 2).

Both of these approximations are surely oversimplified; the experimental error is so large that they fit the data equally well. Note that although the lowest pressure used is still far above the region where the rate is determined by the activation step,^{2e} the assumption that a'/a is unity at zero pressure leads to the prediction that ϵ is very small at 1 mm.

The effect of inert gas in increasing the low pressure isotope effect is shown by the experiments at 43 mm. Actually in these experiments the cyclopropane pressure was 1 mm, and 700 mm of nitrogen was added. According to the experiments of Pritchard *et al.*, the collision efficiency of nitrogen relative to cyclopropane in maintaining the isomerization rate is 0.060. Hence, the gas mixture corresponds to 43 mm of cyclopropane. The value for ϵ obtained in these experiments is in agreement with the pressure trend observed in the experiments with no inert gas added. This is added confirmation of the mechanism of activation by collision.

Low-Pressure Effect

The rate constant for activation by collision is

$$a = Z^*/(A)(M),$$

where Z^* is the number of collisions per unit volume per unit time in which the total energy involved is greater than the activation energy.²⁵ If this energy may be drawn from the total relative translational energy of A and M, and from *s*-internal vibrations of these molecules, then

$$Z^* = Ze^{-E^*/RT} \sum_{r=0}^{s+1} (1/r!) (E^*/RT)^{r.26}$$
(15)

With this formula one can calculate values of a'/a as a function of ΔE^* and s, by use of the observed $E^*=65$ kcal/mole, and the assumption that the collision diameters of the two isotopic species are the same.²⁷ From the results, it appears that for reasonable values of s (the heat capacity at 500° corresponds to 15 classical oscillators), ΔE^* must be less than 100 cal/mole for a'/a to be unity, within experimental error. This is considerably less than the observed value of $\Delta\Delta H_{exp}^{\dagger} = 332 \pm 105$ cal/mole. It does not seem possible to determine the details of the activation process, although the results are in qualitative agreement with the Lindemann mechanism.

ACKNOWLEDGMENTS

I wish to thank Dr. Jacob Bigeleisen and Dr. Max Wolfsberg for many helpful discussions concerning this work. The problem of isotope effects in unimolecular reactions is discussed by them in "Theoretical and Experimental Aspects of Isotope Effects in Chemical Kinetics," a chapter of *Advances in Chemical Physics* (Interscience Publishers, Inc., New York, to be published).

²⁵ The similar case of energy transfer in bimolecular reactions has been recently discussed by H. O. Pritchard, Rec. trav. chim. 74, 779 (1955).

^{74, 779 (1955).} ²⁶ R. H. Fowler and E. A. Guggenheim, Statistical Thermodynamics (Cambridge University Press, Cambridge, 1939), p. 498.

²⁷ Since the collision diameter for intermolecular energy transfer is expected to depend on vibrational frequencies, this assumption is not rigorously correct. However, the perturbing effect of the single tritium atom should be relatively small.