# Canadian Journal of Chemistry

Issued by The National Research Council of Canada

VOLUME 39

JULY 1961

NUMBER 7

## THE HYDROGEN ISOTOPE EFFECT IN THE PYROLYSIS OF CYCLOPROPANE<sup>1</sup>

#### ARTHUR T. BLADES

ABSTRACT

The hydrogen isotope effect in the thermal rearrangement of cyclopropane has been determined by the copyrolysis of cyclopropane and cyclopropane- $d_6$ . The isotope effect in the temperature range 407–514° C and at pressures of about 60 cm Hg may be expressed by

#### $k_{\rm H}/k_{\rm D} = 0.82 \exp{(1300/RT)}$ .

The isotope effect is pressure dependent, decreasing from 1.98 at 76 cm Hg to 1.35 at 0.0178 cm Hg at  $482^\circ$  C.

The isotope effect and its temperature and pressure dependence are discussed in relation to the mechanism. The conclusion is reached that though trimethylene may be formed as an intermediate, the isotope effect is consistent only with an activated complex where a hydrogen atom is weakly bonded both to its original and ultimate carbon atoms, a situation which might also lead directly to propylene. A similar argument is presented to account for the previously described isotope effect in the decomposition of cyclobutane.

#### INTRODUCTION

The thermal rearrangement of cyclopropane to propylene is an unusually interesting reaction for a number of reasons. It is a unimolecular reaction wherein chain processes and heterogeneous behavior are readily eliminated, and it is the simplest of a group of cycloalkane reactions which exhibit a quasi-unimolecular behavior at relatively high pressures. Two completely different mechanisms have been proposed (1) for the reaction, one involving the intermediate formation of trimethylene diradical, and the other, formation of a transition state wherein one hydrogen atom is in the act of transferring from one carbon atom to another as the carbon–carbon bond breaks. While both mechanisms have some merit in explaining the accumulated experimental data, the latter is greatly favored on the basis of the theoretical treatment of the reaction by Slater (2).

A study of the hydrogen isotope effect in this reaction provides an important clue to the sequence of events which ultimately leads to reaction. The effect of pressure on the isotope effect may contribute to the understanding of the quasi-unimolecular behavior of unimolecular reactions at low pressures.

The tritium isotope effect in this reaction has been examined by Weston (3) and by Lindquist and Rollefson (4) by comparing the tritium content of a mixture of cyclopropane and cyclopropane  $t_1$  with that of propylenes produced by its isomerization. Lindquist and Rollefson found a relative rate constant expression  $k/k_1 = 0.63$  exp (825/RT) at a pressure of 200 mm Hg in the temperature range  $447-555^{\circ}$  C, the isotope effect being 6-27%. Weston reports  $k/k_1 = 0.86 \exp(385/RT)$  at the same pressure in the temperature range  $406-492^{\circ}$  C with an isotope effect up to only 17% despite the lower temperatures used. Weston also measured the isotope effect down to 0.4 mm Hg where it had decreased to approximately zero. While both of these studies suffer from

<sup>1</sup>Manuscript received February 3, 1961.

Contribution No. 147 from the Research Council of Alberta, Edmonton, Alberta.

Can. J. Chem. Vol. 39 (1961)

#### CANADIAN JOURNAL OF CHEMISTRY, VOL. 39, 1961

the difficulty of tritium analysis, most uncertainty arises in the interpretation of the experimental results, i.e. the conversion of  $k/k_1$  values to true isotope effects. Here the analysis by Weston seems preferable, but the temperature coefficients so obtained  $(5900\pm2000 \text{ and } 8300 \text{ cal/mole})$  are impossibly high, as he states. In his appraisal of the pressure effect, Weston attempted to fit the data to two simple models. Both assumed that the isotope effect had fallen to its low-pressure limit at zero effect and the data fit both equally well. He pointed out that the zero effect at low pressure as found was coincidental since the isotope effect at low pressure is expected to be temperature dependent.

More recently, Schlag and Rabinovitch (5) have reported an isotope effect of 1.22 from a comparison of the rates of isomerization of cyclopropane and cyclopropane- $d_2$  at 718° K. Using Weston's conversion technique, this gives  $(k_{\rm H}/k_{\rm D} = 2.18)$  but this value did not decrease appreciably with pressure.

The present paper reports a study of the isotope effect in cyclopropane- $d_6$  as a function of temperature and pressure.

#### EXPERIMENTAL

The cyclopropane was Ohio Chemical Anesthetic grade and the cyclopropane- $d_6$  was supplied by Merck & Co. Both contained small amounts of impurities, especially propylene, which were removed by vapor phase chromatography. The deuterated compound was 93%  $d_6$ , the remainder being mainly  $d_5$  and  $d_4$ .

The two cylindrical aluminum (2S) pyrolysis furnaces, accommodating 18- and 875-cc Pyrex reaction cells, were heated by directly applied asbestos-insulated Chromel "A" resistance wire and were lagged with 1.5-in. Marinite asbestos board with additional thicknesses at the ends. In each furnace, the reaction cell was surrounded on the sides by 1 in. of aluminum and on the ends by 1.5 in. The temperature of the small reactor was taken from the surrounding aluminum and of the large reactor from an axial thermocouple well extending to the center of the reactor. Temperatures were measured on a calibrated Pt: Pt - 10% Rh thermocouple.

The vacuum system utilized silicone-greased stopcocks throughout. No correction was attempted for reactor dead space as this was an insignificant percentage of the reactor volumes.

If two molecular species are copyrolyzed so that both have the same time and temperature history and if both exhibit first-order kinetics, then

$$k_1/k_2 = f_1/f_2 \cdot \frac{1 + 1/2f_1 + 1/3f_1^2 \dots}{1 + 1/2f_2 + 1/3f_2^2 \dots}$$

where  $f_1$  and  $f_2$  are the fractional conversions, i.e. the ratio of rate constants is the ratio of the fractional conversions modified by a correction term. If the conversions are kept below 0.1, the correction term remains small and great precision is not required in the individual conversions; the ratio of the two may be accurately determined from the ratios of the reactants and of the products. For present purposes a stock mixture of the normal and deuterated cyclopropanes was prepared and used in all subsequent experiments.

Separations of the two propylene products from reactants were carried out on a 15-ft dodecyl phthalate vapor phase chromatographic column at room temperature with hydrogen as carrier gas. The propylenes were collected in liquid-air traps, measured, and examined on a mass spectrometer. Isotope analysis of the first part of a vapor phase

1402

Can. J. Chem. Downloaded from www.nrcresearchpress.com by UNIVERSITY OF MICHIGAN on 11/09/14 For personal use only.

#### BLADES: HYDROGEN ISOTOPE EFFECT

chromatographic peak of a propylene sample indicated some fractionation; care was subsequently taken to collect the total chromatographic "peak".

In the mass spectrometric analysis of the propylene, the parent ions at mass 48 ( $C_3D_6^+$ ) and 42 ( $C_3H_6^+$ ) were taken as indicative of the relative proportions of the two isotopic species. Since the ion  $C_3D_3^+$  makes a significant contribution at mass 42 at 50 v, a correction factor was determined from a sample of propylene- $d_6$  produced by the rearrangement of 10% of a sample of the deuterated cyclopropane. This procedure was also carried out at an ionization potential of 12 v where these corrections are considerably reduced but no significant or systematic difference was noted between the two analyses.

A similar procedure was followed in the analysis of the stock mixture of cyclopropane and cyclopropane- $d_{\theta}$ .

In the study of the temperature coefficient, the small reactor was used throughout, conventional techniques being employed for introducing and retrieving the reactants. In the study of the pressure effect, the small reactor was used down to 50 mm Hg and the large reactor for lower pressures. In the very low pressure range, the pressure was calculated from the quantity of reactants introduced to the reactor. In experiments below 1 mm Hg, several successive runs were combined to provide sufficient sample for isotope-ratio analysis of the products.

#### RESULTS

Can. J. Chem. Downloaded from www.nrcresearchpress.com by UNIVERSITY OF MICHIGAN on 11/09/14 For personal use only.

The effect of pressure on the isotope effect is shown in Fig. 1 where  $k_{\rm H}/k_{\rm D}$  at 482° C



FIG. 1. The effect of pressure on the isotope effect at 482° C.

is plotted against the logarithm of pressure for comparison with the similar plot by Weston (3). To determine the isotope effect at infinite pressure, the best plot was that suggested by Schlag and Rabinovitch (5),  $k_{\rm D}/k_{\rm H}$  vs.  $p^{-1/2}$ ; the value so obtained at 482° C is 1.96.

CANADIAN JOURNAL OF CHEMISTRY. VOL. 39, 1961



FIG. 2. The temperature dependence of the isotope effect.

The effect of temperature on the isotope effect is illustrated in Fig. 2 and the pertinent data are presented in Table I. A least-squares treatment of these data gives an isotope effect expression.

$$k_{\rm H}/k_{\rm D} = 0.82 \exp{(1300 \pm 150/RT)}$$

 TABLE I

 Data for the relative rate constants at high pressure

·				
Expt. No.	Pressure, cm Hg	Temperature, °K	Conversion correction	$k_{\rm H}/k_{\rm D}$
$     \begin{array}{r}       16 \\       17 \\       18 \\       25 \\       27 \\       28 \\       30 \\       31 \\       32 \\       33 \\       34 \\       35 \\       26 \\       \end{array} $	$\begin{array}{c} 67.6\\ 66.8\\ 64.4\\ 63.6\\ 62.2\\ 62.1\\ 59.6\\ 58.7\\ 58.1\\ 58.3\\ 57.5\\ 56.6\\ 56.6\\ 56.6\end{array}$	$\begin{array}{c} 720.0\\ 700.4\\ 783.3\\ 758.6\\ 725.7\\ 726.1\\ 678.6\\ 785.1\\ 785.4\\ 769.4\\ 769.6\\ 685.8\\ 685.8\\ 685.2\end{array}$	$\begin{array}{c} 1.026\\ 1.017\\ 1.032\\ 1.027\\ 1.034\\ 1.037\\ 1.036\\ 1.034\\ 1.034\\ 1.034\\ 1.034\\ 1.034\\ 1.037\\ 1.037\\ 1.037\\ 1.009\\ 1.000\\ \end{array}$	$\begin{array}{c} 2.03\\ 2.08\\ 1.89\\ 1.92\\ 2.00\\ 2.01\\ 2.18\\ 1.91\\ 1.91\\ 1.92\\ 1.92\\ 2.12\\ 2.12\\ 2.12\end{array}$
	00.1	00010	1.000	M. 1M

Since these data were obtained in the pressure range 56–68 cm Hg, it would be expected that the pre-exponential term for the isotope effect at infinite pressure would be slightly higher.

#### DISCUSSION

The high-pressure hydrogen isotope effect reported here (2.04 at 445° C) compares favorably with effects observed in other gas phase reactions at the same temperature, for example the ethyl-ethyl- $d_5$  acetate decomposition (2.23) (6) and the abstraction

1404

Can. J. Chem. Downloaded from www.nrcresearchpress.com by UNIVERSITY OF MICHIGAN on 11/09/14 For personal use only.

reaction of  $CD_3$  with acetone and acetone- $d_6$  (2.5) (7). The activation energy difference of 1300 cal/mole is slightly less than the values of 1515 cal/mole and 1670 cal/mole respectively for these two reactions but is still substantially above the maximum value of about 1150 cal/mole derivable from a single C—H stretching frequency being converted to a very weak vibration in the activated complex. It is therefore obvious that the hydrogen isotope effect in this reaction is a primary effect and that considerable carbonhydrogen bond relaxation occurs during activation.

The decrease in the isotope effect with decreasing pressure confirms the observation of this same effect with cyclopropane  $t_1$  (3). Unlike that effect, which decreased to zero at 0.4 mm Hg, the present effect has not decreased to nearly the same extent at this pressure, nor is there any suggestion of its reaching a limiting value. Since this would happen only when the reaction has become truly second order, the present data must be considered as a more reliable measure of the variation of the effect with pressure.

Two quite distinct mechanisms have been proposed for the rearrangement of cyclopropane: the first, a mechanism wherein a hydrogen atom transfers from one carbon atom to another with the simultaneous breaking of the carbon ring; the second, involving the intermediate formation of a trimethylene diradical by the simple scission of the carbon ring, the propylene being subsequently formed by the transfer of a hydrogen atom from the middle carbon to a terminal one. This latter mechanism has recently been supported by the re-examination of data on the iodination of cyclopropane and on the rearrangement of cyclopropane- $d_2$  by Benson (8). Following the notation of Benson, the mechanism is given as

$$\triangle \underset{b}{\overset{a}{\rightleftharpoons}} \mathbf{T} : \overset{c}{\rightarrow} \mathbf{P}$$

and applying the steady-state treatment, the rate of formation of propylene becomes

$$\frac{d\mathbf{P}}{dt} = \frac{k_a k_c}{k_b} \Delta \left/ \left( 1 + \frac{k_c}{k_b} \right) \right.$$

If the ratio  $k_c/k_b$  is small, then the over-all rate constant for the reaction becomes  $k_a k_c/k_b$ . Hence the hydrogen isotope effect observed must arise in one of these constants, and, since reaction (c) involves the transfer of a hydrogen atom, it must be assumed that  $k_c$  is the source of the primary effect,  $k_a$  and  $k_b$  probably having little, if any, isotope dependence.

The rate constant expressions derived by Benson for  $k_b$  and  $k_c$  indicate that at 444° C the reactions of trimethylene are so rapid that virtually no opportunity exists for collisions even at one atmosphere pressure. If true, this can only mean that the pressure effect in the isomerization occurs in the reaction (a), and, because the isotope effect is postulated to occur in (c) and not (a), then the isotope effect should not be pressure dependent. Since this is contrary to the experimental results, the mechanism must be incorrect unless either the instability of the trimethylene has been exaggerated, or the isotope effect in reaction (a) is of primary importance. Some assurance that the former is not the case may be gained from the results of Flowers and Frey (9), who found that at 100° C, trimethylene from the photolysis of cyclobutanone reacted with ethylene, but no such reaction occurred when cyclopropane was rearranged in the presence of excess ethylene. Both of these results are to be expected on the basis of half lives of the trimethylene radical at the two temperatures as calculated from Benson's rate-constant equations.

#### CANADIAN JOURNAL OF CHEMISTRY. VOL. 39, 1961

Two alternate interpretations may be put on a major isotope effect occurring in the reaction (a). It may be assumed that a transition state exists for the formation of trimethylene which involves a largely broken C—H bond, the hydrogen being in such a position as to considerably influence the carbon-carbon bond break. This would require that reactions (b) and (c) also have isotope effects and that they be of about the same magnitude. Since the geometric isomerization can be explained by the rotation in the trimethylene radical, it is unnecessary that the configuration of the activated complex allow for this alternate reaction. Secondly, it may be assumed that this transition state is such as to allow for geometric isomerism if it reverts to cyclopropane, and that it may go over directly to propylene. This would suggest an activated complex of the structure suggested by Smith (10) in which two hydrogens and the three carbon atoms are coplanar, with one of the hydrogens weakly bonded to its original carbon atom and to its ultimate acceptor. The postulate of a trimethylene intermediate from such a complex is unnecessary in explaining the experimental facts. The hydrogen isotope effect data does not conclusively decide between these two reaction schemes. It seems most reasonable to accept the latter, however, purely on the basis that, if the hydrogen does become bridged from one carbon to the next, as it must if it is to be of any assistance in the rupture of the carbon-carbon bond, then it will be most advantageous for it to continue on its path toward that carbon atom.

It is interesting to compare the isotope effect in this reaction with that observed for the decomposition of cyclobutane (11) to ethylene where the effect is 1.37 at 449° C, and the activation energy difference, 1400 cal/mole. The existence of this effect, despite the fact that the hydrogens do not transfer during the reaction, suggests that there is some similarity between the cyclopropane rearrangement and this decomposition. The similarity of the activation energy differences (1400 and 1300 cal/mole) suggests that the critical processes involved in reaching the activated complex are the same for each. If then, for the sake of argument, one proposes a mechanism for cyclobutane involving the tetramethylene diradical as an intermediate in the path to ethylene, and applies

$$\Box \stackrel{a}{\underset{h}{\rightleftharpoons}} T \stackrel{c}{\to} 2E$$

the same steady-state treatment as for cyclopropane, it must be true that reaction (a) is the isotope-dependent step since the effect is again pressure dependent. The reaction (c) in cyclobutane does not involve a hydrogen transfer and would not be expected to involve a hydrogen isotope effect. In reaction (b), however, the activated complex is the same as for the forward reaction, and a roughly equivalent C—H bond weakening must occur as in reaction (a); hence a fairly large activation energy difference would be expected. Since this would tend to cancel the energy difference in (a), a relatively small temperature coefficient would have been expected in the isotope effect. The experimental value does not support this thesis, and it therefore seems reasonable to suggest that the decomposition of cyclobutane involves a transition state in which the carbon-carbon bond split is assisted by the partial bonding of one hydrogen to its neighboring carbon atom.

If this is a reasonable description of the mechanism of the reaction, some correlation must exist between the critical difference between the cyclopropane and cyclobutane mechanisms, i.e. the transfer and non-transfer of hydrogen atoms, and the considerable difference in the isotope effects, i.e. 2.04 vs. 1.37. The fact that the ratio of these two numbers is about 1.5 suggests that this difference arises from that part of the isotope

Can. J. Chem. Downloaded from www.nrcresearchpress.com by UNIVERSITY OF MICHIGAN on 11/09/14 For personal use only.

#### BLADES: HYDROGEN ISOTOPE EFFECT

effect which is due to the relative reduced mass ratio in the reaction co-ordinate in the region of the transition state, which, for hydrogen isotope effects, is about 1.4. This implies that the difference in these isotope effects arises not in the mode of formation of the activated complex nor of its geometry, but rather in the unique way in which the hydrogen atom is concerned in that degree of freedom of the complex which results in reaction.

### ACKNOWLEDGMENTS

The author wishes to thank Dr. B. S. Rabinovitch for his manuscript prior to publication and Dr. M. G. H. Wallbridge and P. W. Gilderson for fruitful discussions. Assistance in the form of a grant for fundamental research from the National Research Council is also gratefully acknowledged.

#### REFERENCES

T. S. CHAMBERS and G. B. KISTIAKOWSKY. J. Am. Chem. Soc. 56, 399 (1934).
 N. B. SLATER. Proc. Roy. Soc. A, 218, 224 (1953).
 P. E. WESTON, JR. J. Chem. Phys. 26, 975 (1957).
 R. H. LINDQUIST and G. K. ROLLEFSON. J. Chem. Phys. 24, 725 (1956).
 E. W. SCHLAG and B. S. RABINOVITCH. J. Am. Chem. Soc. 82, 5996 (1960).
 A. T. BLADES and P. W. GILDERSON. Can. J. Chem. 38, 1407 (1960).
 J. R. MCNESBY, T. W. DAVIS, and A. S. GORDON. J. Am. Chem. Soc. 76, 823 (1954).
 S. W. BENSON. J. Chem. Phys. 34, 521 (1961).
 M. C. FLOWERS and H. M. FREY. J. Chem. Soc. 2758 (1960).
 F. T. SMITH. J. Chem. Phys. 29, 235 (1958).
 I. LANGRISH and H. O. PRITCHARD. I. Phys. Chem. 62, 761 (1958).

11. J. LANGRISH and H. O. PRITCHARD. J. Phys. Chem. 62, 761 (1958).