THE SECONDARY HYDROGEN ISOTOPE EFFECTS IN THE PYROLYSIS OF ETHYL- d_5 ACETATE AND ETHYL ACETATE- d_3^1

ARTHUR T. BLADES AND P. W. GILDERSON

ABSTRACT

Rate constant expressions have been obtained for ethyl acetate and ethyl- d_b acetate in the temperature ranges 500-603° C and 501-614° C.

 $k_{(\text{ethyl acctate})} = 3.86 \times 10^{12} \exp - (48,000 \pm 400/RT) \sec^{-1}$

$k_{\text{(ethyl-d_5 acetate)}} = 4.84 \times 10^{12} \exp -(49,500 \pm 300/RT) \sec^{-1}$

By measuring the relative rate of production of C_2H_4 and C_2D_4 from identical mixtures of the two esters at the temperatures 387 and 490° C, it has been possible to determine the temperature coefficient of the relative rate constant more accurately. This, coupled with the relative rate constants at 500° C derived from the above equations, gives the relative rate constant expression

$k_{\rm H}/k_{\rm D} = 0.8 \ e^{1515 \pm 35/RT}.$

These data are compared with the intramolecular isotope effect in the decomposition of ethyl-1,1,2,2- d_4 acetate, and the differences attributed to secondary isotope effects. The rate of decomposition of ethyl acetate- d_3 was found to be identical within experimental error with that of the normal acetate.

INTRODUCTION

In the preceding paper (1) it was shown that it was necessary to include bending vibrations and residual and (or) incipient bonding in the activated complex to explain the kinetic isotope effect data on the pyrolysis of ethyl-1,1,2,2- d_4 acetate. In that compound there is relatively little chance for contributions from secondary isotope effects. The comparison of the relative rates of pyrolysis of ethyl and ethyl- d_5 acetates provides an opportunity of evaluating the importance of these effects.

Since this is an intermolecular isotope effect rather than intramolecular as in ethyl-1,1,2,2- d_4 acetate, this pyrolysis serves as a better comparison with the previous isotope effect study on 1-methyl cyclohexyl acetate by De Puy *et al.* (2). This is especially desirable due to their finding of smaller isotope effects than in the d_4 acetate, since in the latter, the occurrence of an isotope effect does not establish that there is an isotope effect in the rate-controlling step.

It has been reported (3) that the pyrolysis of esters of different fatty acids proceed at roughly equivalent rates. It has been found, however, that although ethyl formate and acetate decompose at roughly the same rate, the acetate requires about 4 kcal/mole greater activation energy (4). Believing this to be significant information on the mechanism, an attempt has been made to study the effect of deuteration on the rate of pyrolysis of ethyl acetate- d_3 .

EXPERIMENTAL

All pyrolyses were carried out using the toluene carrier gas technique as has been described previously (5). Since in both rate studies the data had relevance only when compared with normal ethyl acetate, a parallel study was carried out on this compound also. In the ethyl-ethyl- d_5 comparison, alternate runs were carried out under essentially identical conditions with each compound at various temperatures between 500-614° C.

Manuscript received April 22, 1960.

Contribution No. 115 from the Research Council of Alberta, Edmonton, Alberta.

Can. J. Chem. Vol. 38 (1960)

CANADIAN JOURNAL OF CHEMISTRY. VOL. 38, 1960

Experiments were carried out on the ethyl acetate- d_3 at the two extremes of temperature, 502 and 592° C. The percentage decomposition in each case was determined by titration of the acetic acid produced.

Since the isotope effect studies on the ethyl- d_5 acetate gave an unsatisfactorily large error in the activation energy difference, a procedure was developed whereby this could be measured directly, although isotope effects were not measured. The procedure adopted was to mix the ethyl acetate and the ethyl- d_5 acetate as liquids, and then introduce the mixture into the toluene stream for pyrolysis. This provides a mixture of acetates whose composition over a number of experiments, if not constant, is at least changing slowly. This mixture is then decomposed by a small but known amount.

Then, if $X_{\rm H}^0$, $X_{\rm D}^0$ are the original number of moles of the normal and deuterated compounds, and $k_{\rm H}$ and $k_{\rm D}$ are the corresponding rate constants,

$$\frac{C_2H_4}{C_2D_4} = \frac{X_{\rm H}^0(1-e^{-k_{\rm H}t})}{X_{\rm D}^0(1-e^{-k_{\rm D}t})} \approx \frac{k_{\rm H}tX_{\rm H}^0(1-k_{\rm H}t/2)}{k_{\rm D}tX_{\rm D}^0(1-k_{\rm D}t/2)} + \frac{k_{\rm H}tX_{\rm H}^0(1-k_{\rm H}t/2)}{k_{\rm D}tX_{\rm D}^0(1-k_{\rm D}t/2)} + \frac{k_{\rm H}t}{k_{\rm H}t} \frac{k_{\rm H}t}{k_{\rm H}t} = \frac{k_{\rm H}t}{k_{\rm H}t} \frac{k_{\rm H}t}{k_{\rm H}t} + \frac{k_$$

The approximation is adequate up to about 10% conversion, which must be known to $\pm .5\%$; this accuracy is readily achieved.

Since it was unknown how constant the ratio $X_{\rm H}^0/X_{\rm D}^0$ would remain over a series of runs, the system was further complicated by dividing the reactant stream such that one portion was pyrolyzed at high temperature in a small reactor to about 6% conversion, and the other at lower temperature in a 10 times larger reactor to about 1% conversion. Separate product handling systems were provided such that each experiment provided two mixtures of ethylenes.

$$\frac{\frac{C_{2}H_{4}}{C_{2}D_{4}}\Big|_{T_{1}}}{\frac{C_{2}H_{4}}{C_{2}D_{4}}\Big|_{T_{2}}} \approx \frac{\frac{k_{\mathrm{H}}}{k_{\mathrm{D}}}\Big|_{T_{1}} \frac{(1-k_{\mathrm{H}}t/2)_{T_{1}}}{(1-k_{\mathrm{D}}t/2)_{T_{1}}},$$

$$\frac{\frac{k_{\mathrm{H}}}{k_{\mathrm{D}}}\Big|_{T_{2}} \frac{\frac{k_{\mathrm{H}}}{k_{\mathrm{D}}}\Big|_{T_{2}}}{(1-k_{\mathrm{H}}t/2)_{T_{2}}},$$

which to a sufficient approximation may be written

$$\frac{\frac{C_{2}H_{4}}{C_{2}D_{4}}\Big|_{T_{1}}}{\frac{C_{2}H_{4}}{C_{2}D_{4}}\Big|_{T_{2}}} \approx \frac{\frac{k_{\mathrm{H}}}{k_{\mathrm{D}}}\Big|_{T_{1}}}{\frac{k_{\mathrm{H}}}{k_{\mathrm{D}}}\Big|_{T_{2}}} \qquad \left[1 - \frac{(\alpha_{\mathrm{H}} - \alpha_{\mathrm{D}})_{T_{1}} - (\alpha_{\mathrm{H}} - \alpha_{\mathrm{D}})_{T_{2}}}{2}\right]$$

where $\alpha_{\rm H}$, etc. are the fractional conversions at T_1 , T_2 for the H and D compounds. The temperature coefficient of the isotope effect can then be obtained by an analysis of the two ethylene mixtures and measurements of temperature and approximate conversions in the two furnaces, since

$$\frac{k_{\rm H}/k_{\rm D}|_{T_1}}{k_{\rm H}/k_{\rm D}|_{T_2}} = e^{\frac{-(E_{\rm H}-E_{\rm D})}{R}(\frac{1}{T_1}-\frac{1}{T_2})}$$

where $E_{\rm H}$ and $E_{\rm D}$ are the activation energies for the H and D compounds.

The two reactor volumes used were about 30 and 300 cc, the relative contact times being about 1:20. The ethylene ratios were determined mass spectrometrically, masses 27 and 32 being used as representative of C_2H_4 and C_2D_4 respectively. In practice, the C_2D_4 made a small contribution at mass 27; this was subtracted from mass 27 for C_2H_4 estimation. Two sets of analyses were made on each ethylene mixture at fixed sample

1408

Then

Can. J. Chem. Downloaded from www.nrcresearchpress.com by 132.174.255.116 on 11/10/14 For personal use only.

BLADES AND GILDERSON: ETHYL-d, ACETATE AND ETHYL ACETATE-d3

pressures as it was found that the ratio of $C_2H_3^+$ to $C_2D_4^+$ varied slightly with sample pressure.

The deuterated ethyl acetates were supplied by Merck & Co., Montreal, and were 99% deuterated as indicated. A correction was applied for 3% of the impurity $CH_3COOCD_2CD_2H$ in the ethyl- d_5 acetate simultaneous pyrolysis experiments. No further purification was attempted on the deuterated compounds.

Rate constant expressions were determined by a least-squares treatment of the rate data, and errors in activation energies were obtained from the average deviation of rate constants from the least-squares line.

RESULTS

The rate data for ethyl and ethyl- d_5 acetates gave the rate constant expressions:

 $k_{\text{(ethyl acetate)}} = 3.86 \times 10^{12} \exp(-48,000 \pm 400/RT) \text{ sec}^{-1}, \qquad T = 500-603^{\circ} \text{ C}$ and

$$k_{\text{(ethyl-d_5 acetate)}} = 4.84 \times 10^{12} \exp(-49,500 \pm 300/RT) \text{ sec}^{-1}, \quad T = 501-614^{\circ} \text{ C}$$

the average error in k being $\pm 1.5\%$ and $\pm 1\%$ respectively. A plot of these data is shown in Fig. 1, along with a single rate determination for ethyl-1,1,2,2-d₄ acetate.



FIG. 1. Arrhenius plot for ethyl, O, ethyl- d_5 , \triangle , and ethyl-1,1,2,2- d_4 , \bigcirc , acetates.

CANADIAN JOURNAL OF CHEMISTRY, VOL. 38, 1960

The results from the direct comparison study are shown in Table I. The average value of " ΔE " is very close to that observed in the separate pyrolysis study, the error being

TABLE I

Data for the copyrolysis of ethyl and ethyl-d ₅ acetates (The duplicate ethylene ratios were determined at different mass spectrometer sample pressures)					
Expt. No.	<i>T</i> 1, °K	<i>T</i> 2, °K	$C_2H_3^+:C_2D_4^+$ at T_1	$C_2H_3^+:C_2D_4^+$ at T_2	ΔE
8	656.8	763.7	2.371	1.971	1590
9	660.5	761.6	2.368	2.010	1480
10	661.8	763.6	2.300 2.377 2.303	2.007 1.950	$1540 \\ 1510$

2.377

2.310

2.449

2.381

2.011

1.961

2.060

 $\bar{2}.006$

1490

1460

1550

1530

Av. 1515 ± 35

reduced from ± 700 to ± 35 cal/mole. The relative rate equation $k_{\rm H}/k_{\rm D} = 0.8 \ e^{1515 \pm 35/RT}$, $T = 387-490^{\circ}$ C, may then be derived, the isotope effect at 500° C being used to fix the pre-exponential factor.

Several rate constant determinations were made on the ethyl acetate- d_3 at 502 and 592° C; no isotope effect in the rate of decomposition could be observed in this temperature range within $\pm 2\%$.

DISCUSSION

In the previous paper on the pyrolysis of ethyl-1,1,2,2- d_4 acetate, the isotope effect was explained on the basis of the reduced mass term and differences in the value of f^{\ddagger} , the value of f being determined solely by symmetry numbers. For the intermolecular isotope effect between ethyl and ethyl- d_5 acetates, the major isotope effect arises in the reduced mass term and f, terms in f^{\ddagger} serving only to reduce the contributions of individual modes of vibration to f. It is therefore convenient to consider only the function f, it being understood that maximum values only are implied.

Since the activated complexes have identical structures in the ethyl- d_4 , and the ethyl and the ethyl- d_5 acetate decompositions, it must be assumed that all of the modes contributing to the primary effect in the former must remain operative in the latter. The major interest in the latter centers then on the decreased frequency factor ratio (0.99 to 0.80) and on the increased activation energy difference (1145 to 1515 cal/mole). All primary effects have been accounted for in the d_4 isotope effect, so these changed constants must be a result of secondary effects.

The most obvious source of these secondary effects is in the bending vibrations at the β -carbon atom, some of which have already been considered in the d_4 compound analysis; the justification for their reconsideration is that their contribution has been increased, e.g.

the
$$C < {\searrow D \atop D}$$
 : $C < {\searrow D \atop D}$ comparison has become $C < {\searrow H \atop H}$: $C < {\searrow D \atop D}$.

1410

Can. J. Chem. Downloaded from www.nrcresearchpress.com by 132.174.255.116 on 11/10/14 For personal use only. =

11

14

660.6

659.9

763.2

762.4

BLADES AND GILDERSON: ETHYL-d. ACETATE AND ETHYL ACETATE-d. 1411

An additional, and probably important, source of secondary isotope effects could arise at the α -carbon atom if the C-O bond is breaking in the reaction co-ordinate. Both the

 $C < \sum_{O}^{j}$ bending and further contributions from bending at the β -carbon atom would have

the effect of reducing the frequency factor ratio, and increasing the activation energy difference over the d_4 compound, where these effects could not exist. The coincidence of this model with the observed facts instills considerable confidence not only in the present rationalization, but also in the previous analysis of the ethyl- d_4 acetate data. The suggestion of secondary isotope effects at the α -carbon atom has further interesting implications with respect to the activated complex, suggesting a concerted mechanism, wherein the β -hydrogen transfers to the acyl-oxygen atom simultaneously with the C-O bond break.

A direct comparison can be made between this intermolecular isotope effect and a similar isotope effect in the decomposition of 1-methyl cyclohexyl $2,2,6,6-d_4$ acetate (2). For that molecule, De Puy et al. found an isotope effect of 1.7 at 500° C and 1.9 at 400° C, whereas in this study our isotope effects at the same two temperatures are 2.1 and 2.4 respectively, slightly higher, in fact, than the intramolecular effect shown by ethyl- d_4 acetate as reported in the previous paper. The inconsistency between the two intermolecular effects supports the view that the reaction co-ordinates of cyclohexyl and ethyl esters are appreciably different.

The failure to observe an isotope effect in the decomposition of ethyl acetate- d_3 lends no support to the suggestion that this methyl influences the rate through an inductive effect. Recently, however, it has been shown by Weston (6) that such an isotope effect, being due to the failure of isotopic molecules to have exactly the same potential energy surfaces, would be immeasurably small for organic reactions. The present results will serve as experimental justification of this theory, if independent evidence for this supposed inductive effect can be found.

ACKNOWLEDGMENTS

The authors are indebted to Dr. M. G. H. Wallbridge and to Dr. R. M. Elofson for many fruitful discussions.

REFERENCES

- A. T. BLADES and P. W. GILDERSON. Can. J. Chem. 38, 1401 (1960). C. H. DE PUY, R. W. KING, and D. H. FROEMSDORF. Tetrahedron, 2
- Tetrahedron, 7, 123 (1959).

 - W. J. BAILEY and J. J. HEWITT. J. Org. Chem. 21, 543 (1956).
 A. T. BLADES. Can. J. Chem. 32, 366 (1954).
 A. T. BLADES and G. W. MURPHY. J. Am. Chem. Soc. 74, 6219 J. Am. Chem. Soc. 74, 6219 (1952),
 - R. E. WESTON. Tetrahedron, 6, 31 (1959).

Can. J. Chem. Downloaded from www.nrcresearchpress.com by 132.174.255.116 on 11/10/14 For personal use only.