

[CONTRIBUTION FROM THE MOORE LABORATORY OF CHEMISTRY, AMHERST COLLEGE, AMHERST, MASS.]

The  $\beta$ -Deuterium Isotope Effect in E1 Eliminations<sup>1</sup>

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Isotope effects of  $\alpha$ -deuteriomethyl groups have been determined for E1-type elimination in the solvolysis of *t*-pentyl chloride in 75% aqueous acetic acid in the presence of potassium acetate or silver nitrate and in the deamination of *t*-pentylamine in acetic acid, at 57°. The  $k_H/k_D$  ratios are approximately 2.5, 3.1 and 1.5, respectively. The results are discussed briefly.

Although the effects of the substitution of deuterium for hydrogen in organic molecules have been widely studied,<sup>2-4</sup> surprisingly limited data are available on the  $\beta$ -deuterium isotope effect in E1 eliminations.<sup>5,6</sup> A direct measurement of this effect has now been made, in connection with a study<sup>7</sup> of *t*-pentyl carbonium ions formed in halide solvolyses and deamination reactions. The compounds examined were  $(\text{CH}_3)_2\text{CXC}_2\text{H}_5$  and  $(\text{CD}_3)_2\text{CXC}_2\text{H}_5$ , X = Cl, NH<sub>2</sub>, where over 95% of the theoretical amount of deuterium was present in the deuterio compounds.<sup>8</sup> The compositions of the olefins from the solvolysis of the chlorides in 75% aqueous acetic acid at 57°, in the presence of a slight excess of either potassium acetate or silver nitrate, and from the deamination of the amines in glacial acetic acid were determined by vapor phase chromatography (v.p.c.). The results of these experiments are summarized in Table I,

TABLE I

ISOTOPE EFFECTS IN THE E1 REACTION<sup>a</sup> OF  $(\text{CH}_3)_2\text{CXC}_2\text{H}_5$  (I) AND  $(\text{CD}_3)_2\text{CXC}_2\text{H}_5$  (II) AT 57°

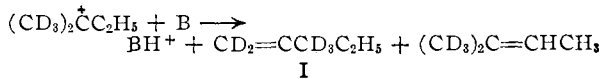
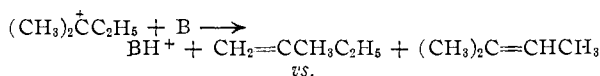
| Compound          | X                           | AgNO <sub>3</sub> | $(\text{CH}_3)_2\overset{\circ}{\text{C}}=\text{CHCH}_3$ <sup>b</sup> % | $k_H/k_D$ <sup>i</sup> |
|-------------------|-----------------------------|-------------------|---|------------------------|
| I <sup>b</sup>    | Cl                          | +                 | 83.4 ± 0.9  |                        |
| II <sup>c</sup>   | Cl                          | +                 | 94.0  | 3.1-3.5                |
| I <sup>d</sup>    | Cl                          | -                 | 79.8 ± 0.6  |                        |
| II <sup>b</sup>   | Cl                          | -                 | 90.0 ± 0.0  | 2.5-2.8                |
| I <sup>e,f</sup>  | N <sub>2</sub> <sup>+</sup> | -                 | 37 <sup>h</sup> ± 0.5   |                        |
| II <sup>e,f</sup> | N <sub>2</sub> <sup>+</sup> | -                 | 47 <sup>i</sup>   | 1.5-1.6                |

<sup>a</sup> Chlorides in 75% HOAc; amines in HOAc. <sup>b</sup> Average of two runs. <sup>c</sup> One run. <sup>d</sup> Average of three runs. <sup>e</sup> Average of four runs. <sup>f</sup> The composition has been corrected for the selective destruction of trimethylethylene. <sup>g</sup> The % of olefin that was trimethylethylene; the rest was 2-methyl-1-butene. <sup>h</sup> Observed, 30%. <sup>i</sup> Observed, 40%. <sup>j</sup> The first value is that obtained with no correction for undeuterated  $\alpha$ -methyls while the second value is calculated assuming 95% deuteration; the true value is presumably between the values given.

controls having been run (see Experimental) to estimate the preferential destruction of trimethylethylene in the deaminations.<sup>7</sup> The value of

$k_H/k_D$  for the deamination is not significantly different whether based on corrected or uncorrected olefin compositions. All  $k_H/k_D$  ratios were calculated assuming zero deuterium isotope effect upon the rate of formation of trimethylethylene for the compounds employed.<sup>5</sup>

The nature of the reactions studied is such<sup>7,9,10</sup> that the isotope effects tabulated presumably represent the  $\beta$ -deuterium isotope effect upon E1-type eliminations from a species of *t*-pentyl carbonium ion (I).



For E1 elimination occurring in the solvolysis<sup>5</sup> of *t*-pentyl chloride in 80% ethanol at 25° and in the decomposition<sup>6</sup> of 2-pentyl chlorosulfite in dioxane,  $k_H/k_D$  was estimated as 1.8 and 1.0, respectively.

E2 eliminations generally manifest  $\beta$ -deuterium isotope effects that are larger than those for E1 reactions. The elimination reaction of  $(\text{CD}_3)_2\text{CHBr}$  with sodium ethoxide<sup>11</sup> has  $k_H/k_D = 6.7$ , and that of  $\text{C}_6\text{H}_5\text{CD}_2\text{CH}_2\text{X}$ , X = Br, OTs,  $\text{SMe}_2\text{Br}$ ,  $\text{NMe}_3\text{Br}$ , with various bases has<sup>12</sup>  $k_H/k_D$  from 3 to 8.

Discussion of the origin of isotope effects upon E1 eliminations must be highly speculative at present, in view of our ignorance of (a) the nature of the carbon-hydrogen bonds in the *t*-pentyl cation<sup>3,13</sup>; (b) the change in hybridization of the various carbon-hydrogen bonds on going from carbonium ion to transition state for elimination (cf. the discussion of ref. 6); (c) the nature of the amine-nitrous acid reaction.<sup>7,10</sup> The results with *t*-pentyl chloride are qualitatively what one would expect for a reaction in which a carbon-hydrogen bond is being broken, although it is perhaps surprising that the effect is so large for a reaction which must have a small activation energy and be fairly exothermic.<sup>14</sup> E1 elimination in the amine-nitrous acid reaction probably is more exothermic than in halide solvolysis.<sup>10</sup> Our expectation (for a reaction in which one bond is being broken<sup>12</sup>) is that

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(10) A. Streitwieser, Jr., *J. Org. Chem.*, **22**, 861 (1957), and references therein.

(11) V. J. Shiner, Jr., *J. Am. Chem. Soc.*, **74**, 5285 (1952).

(12) W. H. Saunders, Jr., and D. H. Edison, *ibid.*, **82**, 138 (1960).

(13) L. S. Bartell, *Tetrahedron Letters*, No. 6, 13 (1960), and Abstracts of the Papers Presented at 138th American Chemical Society Meeting, New York, N. Y., Sept., 1960, p. 35-P.

(14) G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955).

(1) Supported by The Petroleum Research Fund, administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund.

(2) K. B. Wiberg, *Chem. Revs.*, **55**, 713 (1955).

(3) V. J. Shiner and E. Campaigne, Eds., "Conference on Hyperconjugation," Pergamon Press, New York, N. Y., 1959.

(4) K. T. Lefkowitz, J. A. Llewellyn and R. E. Robertson, *Can. J. Chem.*, **38**, 2171 (1960).

(5) V. J. Shiner, Jr., *J. Am. Chem. Soc.*, **75**, 2925 (1953).

(6) C. E. Boozer and E. S. Lewis, *ibid.*, **76**, 794 (1954).

(7) M. S. Silver, *ibid.*, **83**, 3482 (1961).

(8) Dr. Marjorie C. Caserio very kindly determined the n.m.r. spectra of these samples. It was difficult to estimate accurately, visually, the small amount of residual H<sup>1</sup> in the deuterio materials. For the chloride this appeared to be no more than 3%; the amine seemed to have a bit more H<sup>1</sup> than the chloride.

the isotope effect in the former will be smaller,<sup>14</sup> and this is borne out by experiment. Hammond<sup>14</sup> has similarly suggested that the E1 elimination studied by Boozer and Lewis<sup>8</sup> showed a smaller isotope effect than that of Shiner<sup>5</sup> because it was more exothermic.

Both in our E1 reactions and in E2 eliminations,<sup>12</sup> charged substrates show smaller  $\beta$ -deuterium effects than do neutral ones. The resemblance can only be superficial. In the E2 reaction, two bonds are broken in a reasonably concerted fashion. The charged substrates have a higher activation energy than the neutral ones.<sup>12</sup> In the classical E1 reaction, only one bond is broken, since the leaving group has long departed. Elimination from the cation derived from the charged alkyldiazonium ion is believed to have a lower activation energy than the corresponding process for a neutral alkyl halide.

It was thought that the reaction of *t*-pentyl chloride with silver ion might resemble the deamination reaction a little more closely than did the normal halide solvolysis. Judging from both product composition and isotope effect in the silver ion reaction, the opposite appears to be the case. The difference between the olefins from the two *t*-pentyl chloride reactions is small but outside the range of experimental error. The significance of the difference in isotope effects for the two reactions is somewhat questionable, since  $k_H/k_D$  is extremely sensitive to errors in olefin composition analysis when there is a great preponderance of one olefin in the product mixture. This situation is especially encountered in the reaction of the deuteriochloride with silver ion (Table I).

### Experimental

**Materials.**—Starting materials were synthesized by conventional procedures. Reagent grade chemicals were used without further purification. The  $(CD_3)_2CClC_2H_5$  (110 g., b.p. 83.5–84.5°) was prepared essentially by the method of Shiner.<sup>5</sup> Conversion of 83 g. of deuteriochloride to the Grignard reagent and reaction<sup>15</sup> of this Grignard with *O*-methylhydroxylamine gave 21 g. of  $(CD_3)_2CNH_2C_2H_5$ , b.p. 74–76°. The *t*-pentyl chloride, both deuterio and non-deuterio, had less than 1% olefin according to the v.p.c. analysis.

(15) R. Brown and W. E. Jones, *J. Chem. Soc.*, 781 (1946).

**Solvolysis of *t*-Pentyl Chlorides.**—The procedure was as described previously, with no isolation of substitution products.<sup>7</sup> The solvent used contained either 17 g. of silver nitrate or 10 g. of potassium acetate per 10 g. of *t*-pentyl chloride. Table II shows the results of individual runs.

TABLE II

COMPOSITION OF THE OLEFIN FROM THE SOLVOLYSIS OF  $(CH_3)_2CClC_2H_5$  (I) AND  $(CD_3)_2CClC_2H_5$  (II) AT 57° IN 75% ACETIC ACID<sup>a</sup>

| Compound | AgNO <sub>3</sub> | Chloride, g. | Olefin, g. | % $(CH_3)_2C=CHCH_3$ <sup>b</sup> |
|----------|-------------------|--------------|------------|-----------------------------------|
| I        | +                 | 10           | 0.5        | 84.3                              |
| I        | +                 | 10           | 0.4        | 82.5                              |
| I        | —                 | 10           | 1.8        | 80.7                              |
| I        | —                 | 5            | 0.4        | 79.4                              |
| II       | —                 | 10           | 1.3        | 90.9                              |
| I        | —                 | 10           | 1.4        | 79.3                              |
| II       | +                 | 10           | 0.3        | 94.0                              |
| II       | —                 | 5.7          | 0.6        | 90.9                              |

<sup>a</sup> Runs are listed in order of performance. <sup>b</sup> The other product was  $CH_2=CCH_3C_2H_5$ .

**Deamination of *t*-Pentylamine.**—The procedure for the reaction of 30 g. of sodium nitrite and 20 g. of amine in 200 ml. of acetic acid at 57° has been described.<sup>7</sup> Only olefin was isolated. The results are summarized in Table I.

**Controls.**—Most of the controls have been described<sup>7</sup> and the compositions of the olefin fractions in Table I have been corrected for the preferential destruction of trimethylethylene in the deaminations. The experiment to be described demonstrates that there is no appreciable isotope effect upon olefin destruction, so that the controls determined on non-deuterated olefins can be applied to the deuterioamine deamination. Only 1.5 g. of deuterioolefin was available. This was put through the deamination procedure with 70 ml. of acetic acid, 10 g. of sodium nitrite and 6 g. of *t*-butylamine (control 6 of previous<sup>7</sup> work). The control was repeated using 1.5 g. of unlabeled olefin. This was necessary since the change in the composition of the olefin is a function of the amount of olefin taken initially.<sup>7</sup> The deuterioolefin was 62% 2-methyl-1-butene at the start and 81.4% at the finish. For the non-deuterio materials, the percentages were 60.1% and 78.3%, respectively.

**Calculation of Isotope Effect.**—The value of  $k_H/k_D$  is easily calculated by multiplying the ratio 2-methyl-1-butene/2-methyl-2-butene for the undeuterated material times the inverse ratio for the deuterated sample. This calculation assumes 100% deuteration in the  $\alpha$ -methyl groups and no isotope effect on the rate of formation of trimethylethylene.<sup>5</sup> The  $k_H/k_D$  ratio, assuming 95% deuteration, was calculated by essentially the same method. This second calculation also assumes that there is no isotope effect on the <sup>1</sup>H elimination from the  $\alpha$ -methyl groups of the deuterio compounds.