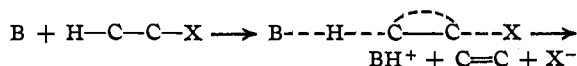


[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF DUKE UNIVERSITY]

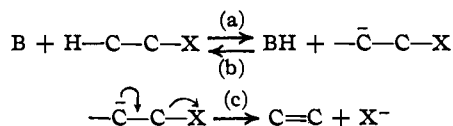
**The Mechanism of  $\beta$ -Elimination with Alkyl Halides<sup>1</sup>**BY PHILIP S. SKELL<sup>2</sup> AND CHARLES R. HAUSER

Ingold, Hughes and co-workers<sup>3</sup> have postulated that, in  $\beta$ -eliminations with alkyl halides and bases to form olefins (E2), the  $\beta$ -proton and halide ion are removed simultaneously. The mechanism is considered to involve an intermediate stabilized by resonance, thus



In the present investigation experimental evidence for this mechanism is presented.

It seems generally agreed that the type of reaction under consideration does not involve the removal of hydrogen and halogen atoms, nor the removal first of halide ion to form a carbonium ion which then loses a proton, although examples of the latter mechanism have been realized.<sup>4</sup> Therefore, only two possibilities remain for consideration. Either the  $\beta$ -proton and halide ion are removed simultaneously as discussed above or the  $\beta$ -proton is removed first to form an anion which then releases halide ion. In this latter two-step reaction, which is represented by the following general equations, step (c) would be rate-controlling.



Which of these two possibilities is correct might be proved by a kinetic analysis since the rate would depend on  $(B) \times (RX)/(BH)$  if (c) were the slow step, and  $(B) \times (RX)$  if (a) were the slow step (simultaneous elimination of H and X). Usually, however, BH is the solvent, so that this term is not apparent as a variable. However, if the solvent were a deuterium containing medium,

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(3) Hughes, Ingold, Masterman and McNulty, *J. Chem. Soc.*, 899 (1942).

(4) See Hughes and Ingold, *Trans. Faraday Soc.*, **37**, 657 (1941).

then if (a) were the slow step, the organic halide would accumulate no deuterium, whereas if (c) were the slow step, then (b) would proceed at a significant rate and the halide would become a mixture of  $H-C-C-X$  and  $D-C-C-X$ . In order to test these two possibilities,  $\beta$ -phenylethyl bromide was treated with sodium ethylate in ethanol containing  $C_2H_5OD$ . When 50-60% of the bromide had been converted to styrene, the reaction was stopped, pure bromide was isolated and analyzed for deuterium content. If the exchange had been complete, the bromide could contain a maximum of 7.9 atom % deuterium; actually, it contained only  $0.02 \pm 0.01$  atom % deuterium, indicating a simultaneous loss of H and Br. Since, in  $\beta$ -phenylethyl bromide, the  $\beta$ -hydrogen is highly activated by the phenyl group and the bromine is held more firmly than it is in most primary aliphatic bromides,<sup>3</sup> it seems probable that most alkyl halides lose the elements of H and X simultaneously in  $\beta$ -elimination.

**Experimental**

To 65.04 g. (1.413 mole) of cold anhydrous ethanol (dried by diethyl phthalate method), 3.22 g. (0.140 mole) of clean sodium was added. When the sodium had dissolved, 6.980 g. (0.695 mole of D) of 99.6% ( $d^{20}$ , 1.1050<sup>2</sup>) deuterium oxide, and 29.33 g. (0.159 mole) of  $\beta$ -phenylethyl bromide were added (the bromide used was a distilled sample of Eastman Kodak product, b. p. 90.5-91.0° (10 mm.),  $n^{20}_D$  1.5549). After reacting for two hours and ten minutes at room temperature, the unchanged bromide was recovered by diluting with water, neutralizing the alkali, and extracting with purified petroleum ether. The petroleum ether extract was washed with concentrated sulfuric acid, and the bromide was recovered by distillation *in vacuo*, b. p. 91.5° (10 mm.). Found: 0.02  $\pm$  0.01 atom % deuterium, 43.07% Br (Carius); calculated for  $C_8H_9Br$ : 43.2% Br. (Parr bomb halogen analyses gave inconsistent high results.)

**Summary**

During the conversion of  $\beta$ -phenylethyl bromide to styrene with sodium ethylate in  $C_2H_5OD$ , the unreacted bromide does not accumulate deuterium. This indicates that H and Br are lost simultaneously as postulated by Hughes, Ingold, *et al.*, for the E2 mechanism.

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