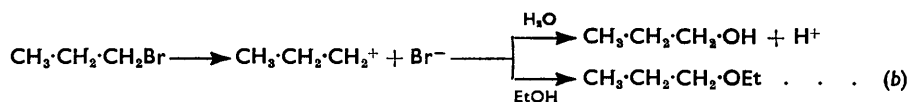
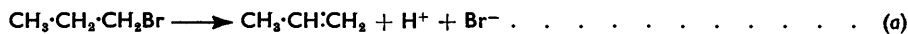


284. The Solvolysis of n-Propyl Bromide in Aqueous Ethanol.

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The solvolysis of *n*-propyl bromide in 44% ethanol, both alone and with added bromide, has been followed. There is no salt effect. From temperature effects the energy of activation has been calculated.

THE reactions of *n*-propyl bromide in aqueous ethanol consist mainly in the replacement of bromine by hydroxyl and ethoxide groups. Two other possible reactions are :



Bateman and Hughes¹ have shown that mechanism (a) is negligible with straight-chain alkyl halides in acidic solutions; the unimolecular mechanism for reaction (b) is also negligible² with these halides. The reaction is therefore uncomplicated, and in the presence of a large excess of solvent is pseudounimolecular; and it is ideal for testing whether or not there are salt effects since the ionic strength gradually increases as the reaction proceeds, hydrobromic acid being highly dissociated in aqueous ethanol.³ By addition of magnesium bromide, which is also completely dissociated (as judged by conductivity data⁴) in the solvent used, namely, 44% (w/w) aqueous ethanol, ionic strengths up to 0.14 were developed. An example is given in Table 1.

TABLE 1. *Solvolysis of 0.05M-n-propyl bromide in 44.05% ethanol at 50°.*

<i>t</i> (min.)	Ml. of 0.1N-AgNO ₃ (x)	log [∞ / (∞ - x)]	<i>I</i>	10% <i>k</i> (sec. ⁻¹)	<i>t</i> (min.)	Ml. of 0.1N-AgNO ₃ (x)	log [∞ / (∞ - x)]	<i>I</i>	10% <i>k</i> (sec. ⁻¹)
3045	2.152	0.1151	0.01211	1.451	9945	5.345	0.3754	0.03007	1.449
4230	2.872	0.1617	0.01616	1.467	11,400	5.823	0.4322	0.03277	1.455
5910	3.731	0.2247	0.02099	1.459	∞	9.230	—	—	—
8485	4.814	0.3198	0.02710	1.447	∞	9.236	—	—	—

TABLE 2. *Average values of the velocity constant (mole l.⁻¹ sec.⁻¹) at 50°.*

[<i>n</i> -Propyl bromide]	0.05M	0.10M	0.10M + 0.025M-MgBr ₂
10% <i>k</i>	1.453, 1.450	1.437, 1.442	1.416, 1.410

The average value of *k* together with the values from other runs is given in Table 2, and within the limits of experimental error the reaction shows no salt effects. The mean value at 50° and other temperatures is :

10% <i>k</i>	1.44	2.37	4.04	9.58
Temp.	50°	55°	60°	70°

From the slope of the plot of log *k* against 1/*T*, which is linear, a mean activation energy of 21.2 ± 0.2 kcal./mole is obtained. From this, the constant *A* in the Arrhenius equation is 1.5 × 10⁹. The same value was obtained by Moelwyn-Hughes⁵ for the hydrolysis of ethyl iodide in water, while Taylor⁶ obtained 1.4 × 10⁹ for the solvolysis of *isopropyl* bromide in 60% ethanol.

EXPERIMENTAL

The reaction was studied in sealed tubes since both solvent and solute are volatile at 50°. Moelwyn-Hughes⁷ has shown that in the hydrolysis of the methyl halides in water there is a rate difference of 10% between reactions carried out in the presence of a small vapour phase

¹ Bateman and Hughes, *J.*, 1940, 903.² Hughes and Ingold, *J.*, 1940, 932.³ Goldschmidt and Dahl, *Z. phys. Chem.*, 1924, 108, 121.⁴ Unpublished results.⁵ Moelwyn-Hughes, *J.*, 1933, 1576.⁶ Taylor, *J.*, 1937, 992.⁷ Moelwyn-Hughes, *Proc. Roy. Soc.*, 1953, A, 220, 386.

and in its absence. For the present work, soft-glass test-tubes were drawn out to give bulbs of about 21 ml. capacity with a neck sufficiently wide before sealing to allow entry of a 20 ml. pipette for introducing the samples. The free space above the liquid after sealing was 3—4% of the total volume. Since *n*-propyl bromide has b. p. 72°, no significant error is likely from the small vapour phase.

A stock solution was made at 15°, 20 ml. being placed in each bulb, which was then sealed and placed in ice. Four of the tubes, which were of Pyrex glass, were placed in boiling water till solvolysis was complete. The reactions of the others were started by placing them in boiling water for a predetermined time requisite to bring them to 50°, then in a thermostat at 50° ± 0.02°. Tubes were withdrawn at intervals, cooled in ice, and opened, and the contents were washed into flasks and titrated for bromide by Volhard's method. 2 ml. of Volhard's indicator were added, followed by excess of 0.1N-silver nitrate from a microburette. Titration with thiocyanate to the red end-point was followed by addition of excess of thiocyanate and titration with silver nitrate. This gave a check on the end-point; the deviation was <0.005 ml. of 0.1N-silver nitrate.

The reverse reaction was proved to be absent by heating a mixture 0.1M in *n*-propyl alcohol and in hydrobromic acid for 6 days at 50° in the same solvent.

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