

**1175.** *Gas Phase Reactions of Sodium. Part II.<sup>1</sup> Rates of Reaction of Cycloalkyl Bromides and Vinyl Bromides*

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The velocity constants for the reactions at 520°K of the cycloalkyl (C<sub>6</sub>-C<sub>3</sub>) bromides and vinyl bromide with sodium have been measured. The gradations in the value of the velocity constants in this series are discussed in terms of bond dissociation energies, strain in the ring and hybridisation changes.

THE velocity constants for the reaction of a considerable number of alkyl, aryl and heterocyclic halides with sodium have been measured, and several correlations of trends of reactivity with structural modification have been reported.<sup>2,3</sup> No published information is available, however, for the corresponding reaction of cycloalkyl halides. Trotman-Dickenson<sup>4</sup> and Gordon<sup>5</sup> have correlated reaction rates and activation energies for (1),



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<sup>1</sup> Part I, B. G. Gowenlock and K. E. Thomas, *J.*, 1965, 5068.

<sup>2</sup> E. Warhurst, *Quart. Rev.*, 1951, **5**, 44.

<sup>3</sup> F. Riding, J. Scanlan, and E. Warhurst, *Trans. Faraday Soc.*, 1956, **52**, 1354.

<sup>4</sup> A. F. Trotman-Dickenson, "Free Radicals," Methuen, London, 1959, p. 84-85.

<sup>5</sup> A. S. Gordon and S. R. Smith, *J. Phys. Chem.*, 1962, **66**, 521. A. S. Gordon in "Pure and Applied Chemistry, Special Lectures presented at the XVIIth International Congress of Pure and Applied Chemistry, Montreal, Canada, August 1961," Butterworths, London, 1962, p. 441.

where R is a cycloalkyl radical, with strain in the ring, and it appeared that the analogous reaction (2)



could afford interesting parallels. In addition to the cycloalkyl compounds it is of interest to consider the corresponding vinyl compound for both reactions (1) and (2), and thus to see whether there is any significance in considering ethylene as a "two membered ring" compound. Evans and Walker<sup>6</sup> have reported a value for the rate constant of the vinyl bromide-sodium reaction at 542°K.

#### EXPERIMENTAL

*Apparatus.*—This is as described in Part I.<sup>1</sup>

*Materials.*—(a) Cyclohexyl bromide. The commercially available material contained *ca.* 0.5% of a low boiling impurity. Fractional distillation, b. p. 163—164°, gave a product shown to be pure by gas chromatography. (b) Cyclopentyl bromide. The commercially available material contained *ca.* 3% of a more volatile impurity. Fractional distillation under reduced pressure gave a product shown to be pure by gas chromatography. (c) Cyclobutyl bromide was synthesised from cyclobutane carboxylic acid by the method of Cason and Way.<sup>7</sup> Most of the chloroform having been removed by distillation, the crude product was purified by large scale preparative gas-liquid chromatography using a dinonylphthalate column. (d) Cyclopropyl bromide was prepared from cyclopropane carboxylic acid by the method of Meek and Osuga.<sup>8</sup> Three repeated fractional distillations under reduced pressure gave a product shown to be pure by gas chromatography. (e) Vinyl bromide was available stabilised with 1% ethanol. The vinyl bromide was distilled in vacuo from -78° and bulb-to-bulb distilled. (f) n-Pentyl bromide was available commercially, and was shown to contain *ca.* 10% of two less-volatile impurities. Repeated fractional distillation yielded a sample with a total impurity content of less than 1%.

*Procedure for Measurement of the Velocity Constant.*—This is as described in Part I.<sup>1</sup>

#### RESULTS

The values of the bimolecular velocity constant, *k*, are calculated from the simple diffusion flame equation.<sup>1</sup> The results are given in Table I, all values having been corrected to 520°K as by Warhurst *et al.*<sup>3</sup>

TABLE I

Velocity constants for reaction of organic bromides (RBr) with sodium at 520°K

R	$10^{-11}k$ (ml. mole <sup>-1</sup> sec. <sup>-1</sup> )	No. of runs	R	$10^{-11}k$ (ml. mole <sup>-1</sup> sec. <sup>-1</sup> )	No. of runs
CH <sub>2</sub> =CH .....	1.47 (±0.15)	6	cyclo-C <sub>6</sub> H <sub>9</sub> .....	119 (±9)	8
cyclo-C <sub>3</sub> H <sub>5</sub> .....	10.5 (±1.3)	6	cyclo-C <sub>6</sub> H <sub>11</sub> ...	55.1 (±5.5)	5
cyclo-C <sub>4</sub> H <sub>7</sub> .....	35.9 (±1.3)	4	n-C <sub>5</sub> H <sub>11</sub> .....	61.7 (±11.4)	5

#### DISCUSSION

Our value for cyclohexyl bromide is in good agreement with the unpublished value of Whittle<sup>9</sup> ( $4.68 \times 10^{12}$  ml. mole<sup>-1</sup> sec.<sup>-1</sup>), but there is a large discrepancy between our value for vinyl bromide and that given by Evans and Walker<sup>6</sup> ( $1.8 \times 10^{12}$  ml. mole<sup>-1</sup> sec.<sup>-1</sup> corrected to 520°K). Our value for n-pentyl bromide is, however, in the expected range, being greater than the derived values at 520°K for methyl bromide<sup>10,11</sup> ( $2.1 \times 10^{12}$  ml. mole<sup>-1</sup> sec.<sup>-1</sup> and  $3.6 \times 10^{12}$  ml. mole<sup>-1</sup> sec.<sup>-1</sup>) and ethyl bromide<sup>6</sup> ( $4.6 \times 10^{12}$  ml. mole<sup>-1</sup> sec.<sup>-1</sup>). Relative rates for some of the chlorides have been measured, and give further support to this contention; thus at 548°K the relative rates are<sup>12</sup> 1 : 1.4 : 4.5 for

<sup>6</sup> A. G. Evans and H. Walker, *Trans. Faraday Soc.*, 1944, **40**, 384.

<sup>7</sup> J. Cason and R. L. Way, *J. Org. Chem.*, 1949, **14**, 31.

<sup>8</sup> J. S. Meek and D. T. Osuga, *Org. Synth.*, 1963, **43**, 9.

<sup>9</sup> E. Whittle, M.Sc. Thesis, Manchester, 1950.

<sup>10</sup> L. Frommer and M. Polanyi, *Trans. Faraday Soc.*, 1934, **30**, 519.

<sup>11</sup> J. N. Haresnape, J. M. Stevels, and E. Warhurst, *Trans. Faraday Soc.*, 1940, **36**, 465.

<sup>12</sup> H. v. Hartel, N. Meer, and M. Polanyi, *Z. phys. Chem.*, 1932, **B**, **19**, 139.

$\text{CH}_3\cdot\text{C}_2\text{H}_5\cdot n\text{-C}_5\text{H}_{11}$ , and at  $558^\circ\text{K}$  <sup>13</sup> 1:1.33 for  $\text{CH}_3\cdot\text{C}_2\text{H}_5$ . Since, therefore, our values for cyclohexyl and n-pentyl bromides are in reasonable agreement with those obtained and predicted, we believe that our value for vinyl bromide can be relied upon. In particular, the series of compounds investigated will be internally self-consistent, and the ratios of rates should be substantially correct. Warhurst *et al.*<sup>3</sup> have also noted a similar discrepancy between their results and those of Evans and Walker.<sup>6</sup>

It is interesting to compare our velocity constants for the sodium flame reaction (2) with those obtained for the hydrogen abstraction reaction (1). The appropriate values are given in Table 2. The velocity constants for reaction (1) are calculated from the Arrhenius equation and are quoted as velocity constants per hydrogen atom, *i.e.*, the calculated  $k_1$  value is divided by  $2n$ , the number of equivalent hydrogen atoms in the cycloalkane,  $\text{C}_n\text{H}_{2n}$ . This statistical correction factor makes direct comparison possible.

TABLE 2

Values for the velocity constants at  $520^\circ\text{K}$  for reactions (1) and (2)

No. of C atoms	$10^{-5}k_1$ (ml. mole <sup>-1</sup> sec. <sup>-1</sup> )		$10^{-11}k_2$ (ml. mole <sup>-1</sup> sec. <sup>-1</sup> )	No. of C atoms	$10^{-5}k_1$ (ml. mole <sup>-1</sup> sec. <sup>-1</sup> )		$10^{-11}k_2$ (ml. mole <sup>-1</sup> sec. <sup>-1</sup> )
	Ref. 4	Ref. 5			Ref. 4	Ref. 5	
2	31.1	—	1.47	5	81.3	129	119
3	7.8	3.2	10.5	6	53.8	120	55.1
4	38.6	61.6	35.9				

It is apparent that for the genuine cycloalkanes ( $n = 3-6$ ) there is a general correlation between the two reaction rates, *i.e.*,  $\text{C}_5 > \text{C}_6 > \text{C}_4 > \text{C}_3$ , and that the relative sequence of values shows an enheartening similarity having regard to the necessary extrapolations of the H-abstraction data. The sequence in reaction rates is apparently independent of the difference in polarities of the bonds broken and formed in the two cases. Trotman-Dickenson<sup>4</sup> has stated that the trend in reaction rate for (1) is in essential agreement with the views of Brown *et al.*<sup>14</sup> on the internal strain accompanying heterolysis of a bond to C in ring compounds where the rate can be predicted to exhibit the order  $\text{C}_5 > \text{C}_6 > \text{C}_4 \gg \text{C}_3$ : these workers suggested that homolytic fission, also, would follow the same relative order of rates. It thus appears that the greater the degree of strain in the ring, the stronger is the C-H bond, and Trotman-Dickenson<sup>15</sup> has suggested recently that the  $D(\text{C-H})$  values in cycloalkanes are reflected in the activation energy values for (1). By direct analogy the same will apply for the bromides: this is equivalent to interpreting the trend in rates for reaction (2) entirely in terms of the  $\Delta E = \alpha D$  correlation and thereby implying the absence of a "negative group" effect.<sup>2</sup>

It is possible that the reaction (1) for the case of ethylene is in need of re-investigation. Gordon<sup>16</sup> reports that abstraction is difficult in this example, and that increase in the temperature to a region where the reaction could presumably be easily followed allows the onset of a propene-producing reaction. Abstraction of hydrogen from the propene is easy, and leads to a different source of  $\text{CD}_3\text{H}$ , hence making the Arrhenius parameters for reaction (1) inaccurate. Consequently, we query the value given for ethylene in Table 2, and suggest that it is probable that  $k_1$  is smaller than the value quoted.

Another correlation of velocity constant with structural change is possible, although this correlation is probably related to the internal strain argument. The hybridisation in cyclopentane is  $sp^3$  and in ethylene  $sp^2$ . Linnett<sup>17</sup> and Walsh<sup>18</sup> both concluded that the C-H bonds in cyclopropane were approaching  $sp^2$  character. On this basis, the smooth

<sup>13</sup> J. A. Kerr, E. A. Lissi, and A. F. Trotman-Dickenson, *J.*, 1964, 1673.

<sup>14</sup> H. C. Brown, R. S. Fletcher, and R. B. Johannsen, *J. Amer. Chem. Soc.*, 1951, **73**, 212.

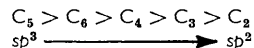
<sup>15</sup> A. F. Trotman-Dickenson, *Chem. and Ind.*, 1965, 379.

<sup>16</sup> A. S. Gordon, personal communication.

<sup>17</sup> J. W. Linnett, *Nature*, 1947, **160**, 162.

<sup>18</sup> A. D. Walsh, *Nature*, 1947, **160**, 902.

trend in reaction rates for both the reaction (1) and (2) could be related to the sequence of hybridisation change



This implies that the ionic contribution is subject only to minor variation in the bromides, and that for the sodium flame reaction the change in rate constant is reflected primarily in activation energy changes, with only minor changes in the pre-exponential factor. Study of these reactions by the recent <sup>13</sup>C competitive technique could check this assumption.

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