Tetrahedron Letters No. 28, pp 2413 - 2416, 1976. Pergamon Press. Printed in Great Britain.

POLAR RADICALS X. THE ROLE OF THE ELIMINATION REACTION IN THE MECHANISM OF THE FREE RADICAL BROMINATION OF 1-BROMOBUTANE[1].

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(Received in USA 19 December 1975; received in UK for publication 7 June 1976)

The high selectivity for the formation of vicinal dibromides in the bromination of bromoalkanes with molecular bromine had originally been rationalized by a mechanism involving anchimeric assistance by the neighbouring bromine atom during the abstraction of the β-hydrogen[3].

An alternative explanation to rationalize the high selectivity found during bromination suggested that the reaction was governed by reversal of the radicals formed with the hydrogen bromide produced in the reaction. The β-bromoalkyl radical was unique in that it was capable of elimination to form olefin, which would add bromine to give 1,2-dibromide, and if appreciable reversal of the other radicals occurred a predominance of vicinal product would be produced[4]. A test of this proposal was subsequently reported by Bruylants and Co-workers by carrying out the bromination of 1-bromobutane-^{82}Br with molecular bromine[5]. Their results, as reported, are listed in Table 1.

Table 1

RADIOACTIVITY REGISTERED AFTER PHOTOBROMINATION OF LABELLED n-BUTYL BROMIDE

Temperatures : 20°C - Reaction mixture : 20 µl C_4H_9Br* + 5 µl Br_2 + 20 µl CCl_4

	Inorg. species	C_4H_9Br	1,1-dibromo	1,2-	1,3-	Tribromo	(x)
Activity (‡)	13563	269064	4295	108164	21736	20169	4491
(%)	3	60	1	25	5	5	1

(x) Activity of products retained between peaks. (‡) In counts per minute.

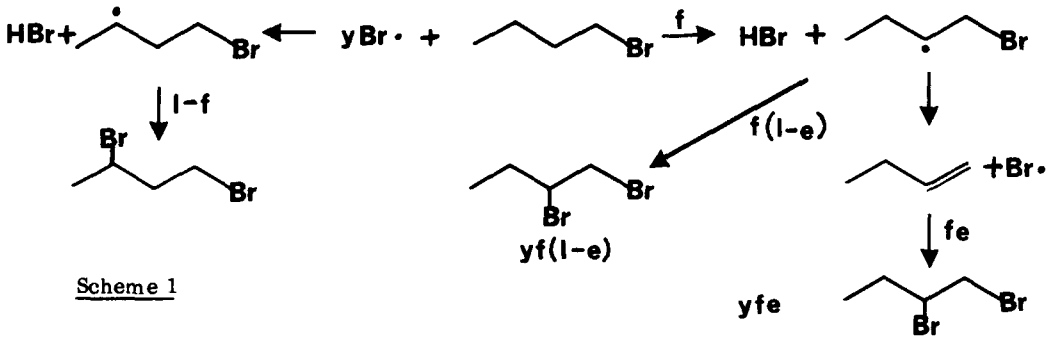
The base catalyzed elimination of hydrogen bromide from the 1,2-dibromobutane formed yielded labelled 1- and 2-bromobutene. The distribution of activity was found to be 10% in the 2-bromo, and 90% in the 1-bromobutene. The authors concluded, from the low amount of activity found in the hydrogen bromide produced, that no appreciable elimination had taken place, and that a small amount of rearrangement (10%) was responsible for the activity found in the 2-position of the 1,2-dibromobutane.

Since the report that some of the original data that the alternative mechanism was based upon is not

reproducible[6,7,8], we have actively been engaged in a detailed investigation of this bromination reaction and we would like to report in this communication some of the results obtained relating to the extent of elimination observed in the bromination of 1-bromobutane.

A more quantitative evaluation of the extent of elimination taking place during the bromination of 1-bromobutane-^{82}Br can be obtained from the data listed in Table 1 if one assumes that the rearrangement of the label observed was not due to a rearrangement reaction but was due to the elimination-readdition mechanism that was purportedly being tested for.

A scheme can be constructed which treats the data statistically, and takes into account the fact that if radioactivity is released as hydrogen bromide to the bromine pool, by the formation of 1-butene, and if the hydrogen bromide and molecular bromine are in rapid equilibrium, a portion of the radioactive halogen will readd to the olefin to reform radioactively brominated substrate (see Scheme 1)



Scheme 1

The reaction was simulated stepwise. In each step, **y** moles of Br· attack the molecule, and of these a fraction, **f**, abstracts a β-hydrogen. A fraction of the β-bromobutyl radicals, **e**, eliminates bromine atoms to give 1-butene, which then adds bromine to form, 1,2-dibromobutane. The value of **f** was calculated at 0.8 from the data reported in Table 1. The value for **e** was varied from 0 to 1 until a best fit for the distribution of radioactivity in the 1,2 and 1,3-dibromobutanes was found. The reaction was simulated to 87% conversion, assuming that the data in Table 1 constituted a material balance. The reaction was simulated in 10,000 steps, i.e. **y** was set at 8.7×10^{-5}. After each step the radioactivity in each reactant and product was determined and these new concentrations were used for the next step in the reaction.

This method of treating the data predicted the distribution of radioactivity in the 1,3- and 1,2-dibromobutanes listed in Table 1, when **e**, the amount of elimination from the 1-bromo-2-butyl radicals, was equal to 37%. The radioactivity in the hydrogen bromide was predicted to be 8%. The discrepancy between the calculated and observed values of activity in the hydrogen bromide (3%) could be accommodated by the fact that activity was also found in the product 1,1-dibromobutane and the unidentified tribromide, and by the fact that the method of analysis of the activity in the hydrogen bromide was, presumably, less accurate than that of the other products[5].

The scheme incorporates the approximation that the values of **f** and **e** are constant with percentage reaction. Although these assumptions are only approximate the average values used are remarkably close to the value of **f** (0.85) obtained in a study of the vapor phase bromination of 1-bromobutane[1] and the value for **e** obtained from the study of the bromination of 1-bromobutane with bromine-81 (see below).

The Bromination of 1-Bromobutane with Bromine-81 - Mixtures (5:1 mole ratio) of 1-bromobutane and molecular bromine highly enriched in bromine-81 were placed in degassed pyrex ampoules thermostated at 40° and were photolyzed (incandescent lamp) until the bromine colour was completely discharged. The products, 1,2-dibromobutane and 1,3-dibromobutane were isolated by preparative glpc (2 m x 5 mm, 10% DEGS on Diatoport, glass column) and their high resolution mass spectrum were obtained (AEI MS9, 70 ev), see Table 2.

Table 2

Mass Spectral Analysis of the Products of the Bromination of 1-Bromobutane with Bromine-81 (40°)[a]

Run	Products	Mass Spectral Peaks[b] (relative intensities) P_1/P_1	P_2/P_1	P_3/P_1	Isotopic Content (total molecule) ^{79}Br	^{81}Br	Isotopic Ratio ^{79}Br : ^{81}Br Bromine atom 1	Bromine atom 2
1)	1,2-Dibromobutane	1.0	10.8	12.7	0.26	0.74	0.43:0.57	0.10:0.90
	1,3-Dibromobutane	1.0	5.8	5.1	0.33	0.67	0.48:0.52	0.18:0.82
2)	1,2-Dibromobutane	1.00	10.95	13.05	0.261	0.739	0.424:0.576	0.094:0.907
	1,3-Dibromobutane	1.00	5.76	5.07	0.328	0.672	0.481:0.519	0.176:0.824
3)	1,2-Dibromobutane	1.00	10.57	12.39	0.264	0.736	0.427:0.573	0.098:0.902

a) A mole ratio of 5:1 of 1-bromobutane (^{79}Br: ^{81}Br, 50.46:49.64):Br_2(^{79}Br: ^{81}Br, 3.96:96.04) was photolyzed (2 x 100 W incadescent lamps) to complete reaction.

b) The ratio of the parent ions P_1(m/e 214), P_2(m/e 216) and P_3 (m/e 218).

From the intensities of the mass spectra of its parent ions the isotopic content of each dibromide could be calculated[9] (see Table 2). Furthermore, since the intensities of the parent ions are equal to the coefficients in a binomial expansion[9] the distribution of isotopic bromine for each position in the molecule could be determined by the solution of an expression, $x^2 - P_2/P_1\, x + P_3/P_1 = 0$, which predicts the ratio of mass spectral fragments containing two bromine atoms each having two isotopes (see Table 2)[1].

A mechanism for the formation of 1,2- and 1,3-dibromobutane proceeding by direct substitution predicts that in each of the dibromides one of the bromine atoms would have the isotopic content of its original bromine (^{79}Br: ^{81}Br, 0.505 : 0.495), and the other bromine atom resulting from substitution, would have the isotopic content of the bromine-81 pool (^{79}Br: ^{81}Br, 0.0396 : 0.9604). The original bromine atom (atom 1) in both the 1,2- and 1,3-dibromobutane were found to be enriched with bromine-81 from the bromine pool. The second bromine atom in both compounds was found to be highly enriched in bromine-79 over that predicted from a direct substitution reaction. Since the only source of bromine-79 in the reaction mixture is from the original 1-bromobutane (^{79}Br: ^{81}Br, 0.505:0.495) the enrichment observed must be due to elimination from the 1-bromo-2-butyl radical.

With two pathways for the formation of 1,2-dibromobutane, direct substitution and elimination-readdition, only a fraction, **e**, of the 1,2-dibromobutane molecules will be formed by addition of bromine to 1-butene. The molecules in this fraction have two identical bromine atoms which both have the average isotopic content of the second bromine atom in 1,3-dibromobutane (^{79}Br: ^{81}Br, 0.18:0.82). The fraction of the 1,2-dibromobutane arising from direct substitution, **1 - e**, contains molecules having the same overall total distribution of bromine as does the 1,3-dibromobutane, a product formed by an analogous mechansim. (A small amount of incorporation is seen in the first atom of bromine in the 1,3-dibromobutane, and presumably is from the addition of hydrogen bromide to 1-butene to reform 1-bromobutane. This process would effect equally the distribution found in both 1,2- and 1,3-dibromides formed by direct substitution). Considering the bromine-79 content of the molecules, and knowing this value for the total 1,2-dibromobutane (^{79}Br, 0.26), the value for **e** can be calculated since the isotopic content of each fraction, **e** and **1-e** is known.

$$0.33(1-e)+0.18e=0.26 \quad ; \quad e=0.47$$

The calculated value for the percentage of the 1-bromo-2-butyl radicals that undergo elimination from the experiments carried out with bromine-81, 47% is in remarkably good agreement with the value obtained by the statistical treatment of the data reported for the bromination of 1-bromobutane-^{82}Br, 37%. The lower temperature used in the later experiments as well as the approximations made in the statistical treatment (i.e. neglect of the tribromide and monotomic formation of products) can easily account for the difference. Since the products formed from **β**-abstraction from 1-bromobutane account for 85%of the **radicals** that proceed to bromination products[3] and 47% of these result in elimination, the complication which arises from the elimination-readdition pathway does not appear to be negligible. The occurrance of extensive elimination during the bromination of 1-bromobutane is not sufficient to rationalize the high yield of 1,2-dibromobutane formed, since this process must be coupled with extensive reversal of the radicals formed, with the hydrogen bromide produced in the reaction. Preliminary results[10] seem to indicate that reversal of the deactivated radicals formed by abstraction from 1-bromobutane is not extensive enough to explain the product distribution found.

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