Alkyl Bromide Photobromination: Catalysis by Hydrogen Bromide and the Elimination–Readdition Pathway

Jean-Ph. Soumillion,* Claude Ronneau, and Pierre Dejaifve
Université Catholique de Louvain, Laboratoire de Chimie Générale et Organique, Place Louis Pasteur 1, B-1348 Louvain-la-Neuve, Belgique

In the photobromination of alkyl bromides, hydrogen bromide is shown to act as a catalyst and a kinetic study implies that two molecules of the acid are involved in catalysis. The catalysis is specific in two ways: only HBr is effective and it operates only with alkyl bromides having a β-hydrogen available for substitution. HBr favours the formation of 1,2-dibromides. This catalytic pathway is superimposed on the classical, uncatalysed mechanism. Isotopic labelling experiments show that an elimination–readdition pathway may also account for part of the reaction (maximum 20%) but cannot explain the migration of bromine which is observed in the formation of β-dibromides.

A qualitative theory predicting substituent effects on the course of radical substitutions is at present widely accepted.[1] Linear free energy relationships quantitatively relating reactivities to polar and resonance effects of substituents were useful in this field.[2] Polar effects were shown to influence greatly reactivity in free radical substitutions. This is the reason why, in hydrocarbons bearing an electron-withdrawing substituent, the β-positions are not the most reactive when a hydrogen atom is abstracted by halogens.

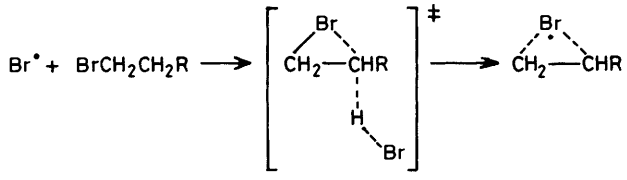
The particular behaviour of bromoalkanes in radical bromination by bromine is also well known.[3] The 1,2-dibromoproduct is largely favoured: the bromine substituent orients substitution towards the vicinal position. Traynham has shown that the bromination of 1-bromomethyl-4-methylcyclohexane proceeds by exclusive attack at the tertiary position vicinal to the bromo-substituent.[4h]

The high yields of 1,2-dibromo-products are associated with stereochemical factors. Radical chain bromination of (+)-1-bromo-2-methylbutane with molecular bromine leads to (−)-1,2-dibromo-2-methylbutane.[4d] This preservation of optical purity as well as other stereochemical results [3a,4] indicate that the reaction proceeds through a bridged radical. Anchimeric assistance was postulated, as shown in Scheme 1. According to Skell [4] the intermediacy of an anchimeric species is well established. However, Tanner took into account the reversibility of the hydrogen abstraction step in bromination by bromine [reaction (1)]. He proposed another explanation

$$\text{R–H} + \text{Br}^\bullet \rightleftharpoons \text{R}^\bullet + \text{H–Br} \qquad (1)$$

for the high yields of β-dibromides: when R$^\bullet$ is a β-bromoalkyl radical, elimination of a bromine atom with formation of an olefin would displace this equilibrium to the right and the addition of molecular bromine to the olefin would be the reason for the observed high β-reactivity.[5] Various other studies were made by the same author [6] showing finally that, in the liquid phase, elimination–readdition may be involved in the mechanistic pathway leading to β-dibromides. On the other hand, gas-phase brominations of bromobutane confirmed that the β-bromoalkyl radical effectively possesses extra stabilisation when compared with other bromoalkyl radicals.[7]

In this paper some new and complementary information is given concerning this problem. We have found that catalysis of the reaction by hydrogen bromide is always present when high vicinal reactivity is observed.



Scheme 1.

Table 1. Evidence for catalysis by HBr in n-butyl bromide photobrominations (*T* 20 °C)

Reaction mixtures [a]				Reaction half-life (min)
C_4H_9Br	CCl_4	CCl_4–HBr [b]	CCl_4–Br_2 [c]	
1.00	2.00	0.00	0.1	16.5
1.00	1.95	0.05	0.1	7.0
1.00	1.90	0.10	0.1	4.5
1.00	1.80	0.20	0.1	2.5
C_4H_9Br	CCl_4	C_6H_5Cl–HBr [b]	C_6H_5Cl–Br_2 [c]	
2.00	1.00	0.00	0.1	58.3
2.00	0.95	0.05	0.1	13.5
2.00	0.90	0.10	0.1	9.3
2.00	0.80	0.20	0.1	7.1

[a] Volumes in cm^3. [b] Carbon tetrachloride or chlorobenzene saturated with gaseous HBr. [c] Carbon tetrachloride or chlorobenzene containing *ca.* 9×10^{-2} mol l^{-1} of bromine.

Kinetics.—When examining l-bromobutane photobromination, it appears immediately that hydrogen bromide catalyses the reaction.[8] This can be shown by comparing the half-life of the reactions with and without initially adding hydrogen bromide: when carbon tetrachloride or chlorobenzene saturated with HBr is introduced into the reaction medium, the half-life drops rapidly (Table 1). This observation was completely unexpected: the hydrogen abstraction step is reversible and thus, HBr is known to inhibit radical bromination.[9,10]

By following the disappearance of bromine in n-butyl bromide saturated with gaseous HBr and illuminated with visible light, a partial order with respect to bromine was determined. A mean value of 1.5 was found leading to the integrated rate expression (2) where *k''* is the apparent rate

$$[Br_2]^{-\frac{1}{2}} = [Br_2]_0^{-\frac{1}{2}}k''t/2 \qquad (2)$$

Table 2. Determination of partial order with respect to bromine in n-butyl bromide photobromination. T 20 °C. n-C_4H_9Br saturated with gaseous HBr (3 cm^3). Br_2 (1 µl)

n [a]	r [a,b]	k'' [c,d]	r [b,c]
1.45	0.996	1.22 ± 0.01	0.999
1.60	0.983	1.28 ± 0.02	0.998
1.40	0.988	1.64 ± 0.03	0.997
1.70	0.994	1.48 ± 0.02	0.998

[a] Obtained from the logarithmic form of the equation $v = k''[Br_2]^n$. [b] Correlation coefficient. [c] From equation (2) with k'' in $l^{\frac{1}{2}}$ $mol^{-\frac{1}{2}}$ min^{-1}. [d] Discrepancies to be attributed to slightly different optical conditions between various runs.

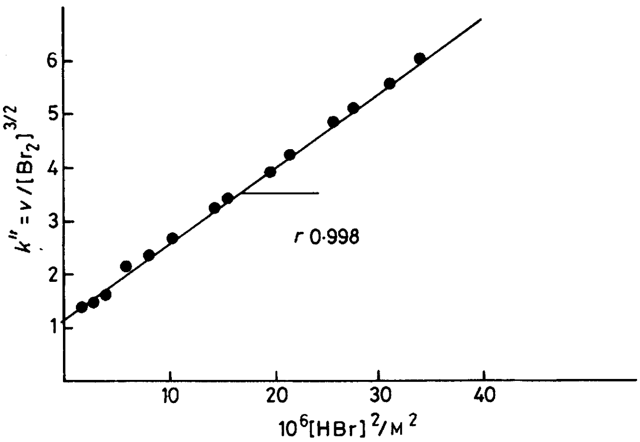


Figure. Determination of partial order with respect to HBr

Table 3. Absorbances recorded during kinetic measurements of n-butyl bromide photobromination and comparison with the calculated values according to equation (4) [a]

Time (min)	$A_{obs.}$ [b]	$A_{calc.}$ [c]
0	1.500	1.500
1.4	1.301	1.301
2.0	1.222	1.219
2.2	1.201	1.191
2.4	1.168	1.164
3.0	1.097	1.079
3.2	1.071	1.051
3.4	1.036	1.022
4.0	0.939	0.934
4.2	0.910	0.904
4.6	0.847	0.845
5.0	0.788	0.786
5.2	0.760	0.756
5.4	0.728	0.727
6.0	0.640	0.642
7.0	0.510	0.511
8.0	0.399	0.400
9.0	0.312	0.311
9.4	0.280	0.282

[a] Initial bromine concentration $[Br_2]_0$ 7.54 10^{-3} mol l^{-1}. The calculated values were obtained with k_o' 1.16 and k_c' 0.1414 × 10^{-6}. [b] Absorbance of bromine measured at 415 nm (ε 198.8). [c] Absorbance of bromine calculated according to equation (4).

constant and $[Br_2]$ and $[Br_2]_0$ are the actual and initial bromine concentrations. The results are presented in Table 2.

It was also possible to estimate the reaction order with respect to HBr by plotting k'' ($= v/[Br_2]^{\frac{3}{2}}$) *versus* the acid concentration. This value was obtained indirectly by calculating the difference between initial and actual bromine concentrations. We checked by titration that the bromine consumption effectively equals HBr production [equation (3)]. A good

$$[HBr]_t = [Br_2]_0 - [Br_2]_t \qquad (3)$$

correlation was obtained only when k'' was related to $[HBr]^2$ (see Figure) and rate equation (4) is thus proposed. Values of

$$v = k_o'[Br_2]^{\frac{3}{2}} + k_c'[Br_2]^{\frac{3}{2}}[HBr]^2 \qquad (4)$$

k_o' and k_c' corresponding respectively to the uncatalysed and catalysed process were found to be: k_o' 1.16 ± 0.04 $l^{\frac{1}{2}}$ $mol^{-\frac{1}{2}}$ min^{-1} and $10^{-6}k_c'$ 0.143 ± 0.002 $l^{\frac{5}{2}}$ $mol^{-\frac{5}{2}}$ min^{-1}.

Comparison between the experimental absorbances and the values recalculated with the aid of equation (4) shows that a good agreement is obtained (Table 3). Various runs were performed in different experimental conditions: the initial bromine concentrations and the optical conditions were modified. In each case, the same kinetic treatment was found to fit the results.

The values of k_c'/k_o' were found to vary between 1.2 × 10^5 and 3.9 × 10^5. This is not surprising since the accuracy on the intercept (k_o') cannot be very high considering its small value relative to the slope [see equation (4) and Figure]. Moreover, given the catalytic action of HBr, it is of the utmost necessity to use bromine and n-butyl bromide perfectly free of HBr. If the reactants were contaminated (for instance bromine at the moment of its introduction in the reaction cell) the k_o' value would certainly be overestimated. On the other hand, in these radical processes, the influence of small amounts of impurities cannot be neglected, nor can the role of residual oxygen.[10] In our kinetic experiments, n-butyl bromide was flushed with nitrogen before the experiment was started.

As expected the values of k'' which we derive from k_o' and k_c' are not extrapolable to high HBr concentrations. This was the case of k'' obtained in Table 2 (in HBr-saturated solution). The alkyl bromide saturated with HBr contains *ca.* 5 × 10^{-2} mol l^{-1} of the acid. Using this value and the mean k_o' and k_c' obtained in a series of ten experiments, we found $k'' = 0.9 + 0.17 \times 10^6 (5 \times 10^{-2})^2 = 426$. This is more than two orders of magnitudes greater than the experimental value of k''. This discrepancy can be understood if we remember that HBr will also play the role of an inhibitor: at high acid concentrations k'' is very likely to be given by a more complex expression including an inhibition constant as shown by other authors.[9,10]

At this stage, it is clear that catalysis is operating in this reaction and that two molecules of HBr are involved. Proposing a detailed mechanism seems to be very difficult all the more because the catalysis appears to be very specific.

Catalysis and Selectivity in Alkyl Bromide Photobromination.—The specificity of catalysis can be shown first by conducting kinetic runs with n-butyl bromide saturated with gaseous HCl. In these experiments the partial orders with respect to bromine and HBr were confirmed and the same kinetic treatment was applicable as before. This shows that, unlike HBr, HCl is unable to catalyse the reaction. It may also suggest that HBr catalysis is so specific as to imply some mechanism unique to HBr (HBr_3 involvement?).

On the other hand, by studying the photobromination of alkanes and alkyl bromides we have found that the catalysis is operative only for alkyl bromides with a β-hydrogen available for the substitution (Table 4).

The coincidence between catalysis by HBr and the specific

Table 4. Occurrence of catalysis by HBr in radical bromination

Substrate	Bromine substituent	β-Hydrogen available	Catalysis
Cyclohexane [a]	−		−
Decalin [a]	−		−
1,4-Dimethylcyclohexane [a]	−		−
1-Bromobutane [b]	+	+	+
2-Bromobutane [b]	+	+	+
Bromocyclopentane [b]	+	+	+
1-Bromo-2,2,4-trimethylpentane [a,c]	+	−	−

[a] The kinetic study gave an order of 3/2 with respect to bromine. [b] The kinetic study gave an order of two with respect to HBr. [c] Brominated products were not identified but g.l.c. showed that under the experimental conditions (<1% conversion) tribromo-products were not present.

Table 5. Ratios of hydrogen abstraction at the 2- and 3-positions of n-butyl bromide: $1,2\text{-}Br_2 : 1,3\text{-}Br_2$

Run	$n\text{-}C_4H_9Br$ [a]	Br_2 [a]	Epoxide [a,b]	Initially added HBr	$\frac{1,2\text{-}Br_2}{1,3\text{-}Br_2}$ [c]
1	9.34×10^{-3}	1.5×10^{-4}	8.24×10^{-3}		5.05 ± 0.3
2	9.34×10^{-3}	1.5×10^{-4}	2.06×10^{-3}		5.80 ± 0.3
3	9.34×10^{-3}	1.5×10^{-4}	0.33×10^{-3}		6.30 ± 0.3
4	9.34×10^{-3}	1.5×10^{-4}			8.90 ± 0.3
5	9.34×10^{-3}	1.5×10^{-4}		Saturated	9.80 ± 0.3

[a] In moles; bromine was introduced as a 0.3M solution in α,α,α-trifluorotoluene; butyl bromide and epoxide were pure liquids. [b] Tetramethylethylene oxide. [c] $1,1\text{-}Br_2/1,3\text{-}Br_2 \simeq 0.1$.

effect of a bromine substituent on the selectivity leads to the following conclusion: at least a part of the vicinal dibromide must originate from a catalysed mechanism and catalysis produces only β-dibromide.

If we use our values of k_o' and k_c' to simulate the reaction we are able to estimate the amount of products arising from the uncatalysed and catalysed processes. According to these calculations, bromination of pure n-butyl bromide with conversions of between 5 and 20% should lead to >99% of products originating from catalysis. This does not agree with experiment: the β-dibromide represents a maximum of 90% of the products. The discrepancy we have found here is probably the same as mentioned earlier: we cannot extrapolate our rate constants to high concentrations of HBr.

Experiments were performed under conditions where HBr is scavenged and a series of runs was made in the presence of a suspension of solid potassium carbonate. Under such conditions, the relative reactivities were found to be a function of the carbonate : bromine ratio and of the reaction yield. When large amounts of carbonate were introduced (molar ratio $K_2CO_3 : Br_2 > 70$) the selectivity no longer favoured 1,2-dibromobutane, at least in the early stages of the reaction. Some 1,4-dibromobutane was detected among the products. This is incompatible with atomic bromine as the active species since it is known that bromine is unable to abstract primary hydrogens. A change of selectivity was also observed when using bromine maintained in contact with potassium carbonate before the reaction while, during the reaction itself, no carbonate was present in the medium.

We conclude that a new brominating agent must be produced: potassium carbonate usually contains 3% water which may react with bromine to form hypobromous acid and hydrogen bromide. These acids will be neutralized, and if the anhydride (Br_2O) is formed, a species more active than bromine atom is likely to interfere in the abstraction of hydrogens. This will perturb the selectivity. It seems very difficult to get rid of this problem since even with carefully dried carbonate (<0.1% of water) the same results were obtained. A similar result was observed by Bunce who brominated substituted alkanes with mixtures of bromine and basic mercury(II) oxide.[11a] The intermediacy of Br_2O was recently confirmed by Skell [11b] who found normal bromine atom behaviour if the carbonate : bromine ratio does not exceed 10 and an increasing deviation toward a more reactive hydrogen abstractor with an increasing molar ratio.

In another series of experiments an epoxide was used to scavenge the acid. The results are given in Table 5. It can be seen from Table 5 that the presence of HBr plays a role in the selectivity (compare runs 1 and 5). However it was impossible to reach values lower than 5 for the ratio of 1,2- to 1,3-dibromides even with higher concentrations of epoxide. Therefore, we may conclude that the selectivity favouring 1,2-dibromobutane cannot be related only to the presence of HBr: the catalysis favours β-bromination together with another uncatalysed process. As a matter of fact there are results where the anchimeric effects by bromine cannot be related to the presence of HBr.[12]

If we compare the relative reactivities obtained in runs 1 and 5 we are able to calculate that the β-dibromide forms 90% of the dibromides in run 5 and 82% in run 1. However it is not possible to estimate which part of the mechanism is catalysed since the difference corresponds to a double change in the mechanism: in run 1 with practically no HBr there is no reversibility effect nor catalytic action.

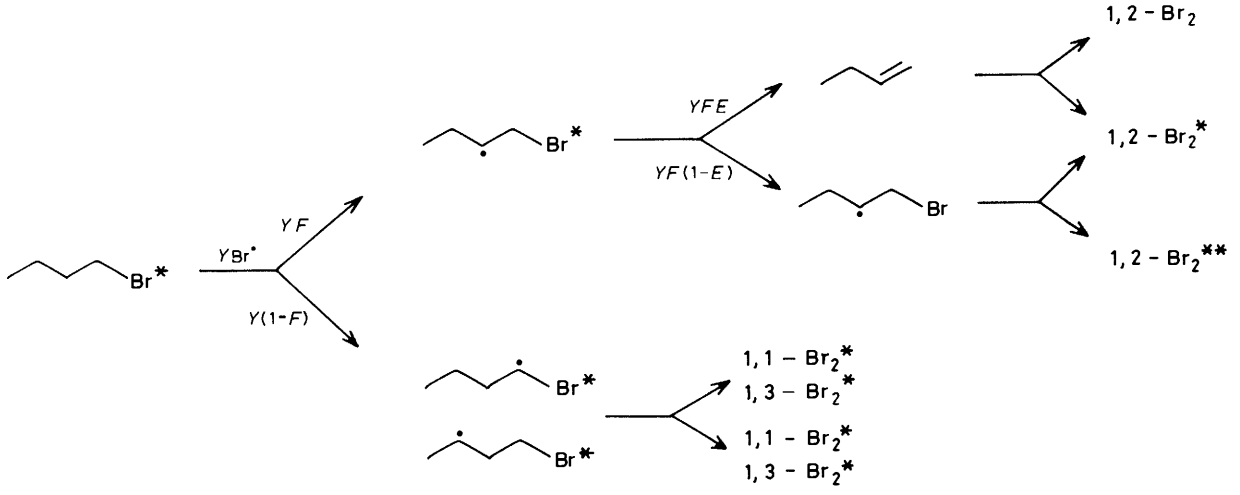
Isotopic Labelling Experiments.—In the course of our mechanistic investigations photobrominations of ^{82}Br-labelled n-butyl bromide were performed in order to measure the extent of elimination occurring in these brominations.[13] The results of typical experiments are reported in Table 6. They show that the radioactive content of the inorganic material (HBr and Br_2) reaches a maximum value of 5%. A blank experiment reveals a very weak loss of radioactivity from the n-butyl bromide under the conditions used for these reactions.

In our previous publication [13] we concluded that the substituent effect of bromine in this reaction cannot be accounted for by an elimination–readdition mechanism.

Table 6. Activities [a] recorded after photobrominations of n-$C_4H_9{}^{82}Br$ by bromine: *T* 20 °C. Reaction mixture n-$C_4H_9{}^{82}Br$–CCl_4–Br_2 [b]

			Dibromides				
Entry	Inorganics [c]	n-C_4H_9Br	1,1-	1,2-	1,3-	Tribromides	Others [d]
1	4 154	144 336	393	20 964	4 193	2 607	2 263
%	2.3	81	0.2	11.7	2.3	1.5	1.3
2	13 563	269 064	4 295	108 164	21 736	20 169	4 491
%	3.1	60	1	25.1	5	4.7	1
3	11 332	235 813	2 350	112 691	22 539	17 454	13 370
%	2.7	57	0.6	27.1	5.4	4.2	3.2
4	5 431	47 910	815	33 195	6 036	4 707	1 336
%	5.5	48	0.8	33.4	6.1	4.7	1.3
5	1 613	221 361					1 902
%	0.7	98.5					0.8

[a] Radioactivity in counts min^{-1}. [b] A typical mixture was (in μl); 20 : 20 : 5 in entry 2. [c] HBr trapped at the head of the chromatographic column. [d] Residual activity in injection port after analysis and activity recorded between peaks. [e] Blank experiment: no bromine engaged.



Scheme 2.

Tanner reconsidered our results and treated our data statistically,[14] taking into account that elimination–readdition may take place on the β-bromoalkyl radical, releasing radiobromine into the HBr–Br_2 pool. According to this hypothesis, radiobromine is available for reincorporation into dibromide. We adopted this hypothesis and made our own calculations, based on Scheme 2, which is very similar to that proposed by Tanner.

Along the lines followed by Tanner we simulated the reaction in a stepwise manner. In each step of the calculation *Y* moles of bromine were involved: a fraction *F* attacks the molecule in the β-position; a fraction *E* of the β-bromobutyl radical gives butene which will readd bromine. Therefore, we should expect dibromides containing two, one, or no radiobromine atoms, this last situation being possible only for β-dibromobutane.

Our calculations were made by using in each case the following features. (1) We added all the recorded counts (441 500 in run 2 of Table 7), the total giving the number of molecules of labelled 1-bromobutane to be used when starting calculations. (2) Looking to the counts recorded for unchanged butyl bromide (269 000 in run 2) the simulation was made so as to reach this residual amount of reactant. This means for instance a conversion of 39% of the butyl bromide in run 2. We have to point out here that Tanner used 87% as a basis for his calculations in this case.[14] (3) The experimental counts recorded on tribromides were redistributed in order to make the calculations possible with dibromides only. Tribromides (20 169 in run 2) were considered as dibromides, being distributed in a ratio of 1 : 60 : 10 between 1,1-, 1,2-, and 1,3-dibromides. This distribution corresponds to a classical ratio between the dibromides. This does not affect the conclusions significantly because the tribromides amount to 13% of the products as a maximum. (4) In each of our calculations the parameters *F* and *E* were chosen and progressively optimized by a simplex algorithm so as to reach the best agreement with our experimental results. Results are shown in Table 7.

When a comparison is made with the results obtained by Tanner,[14] the following differences are evident. (1) *F* Values were optimized and not chosen: an average value of 0.86 was reached while the value chosen by Tanner was 0.80. Our result agrees remarkably with the result obtained in vapour-phase bromination of 1-bromobutane (0.85).[7] (2) The value obtained for *E* (0.20) is clearly lower than the one derived by Tanner (0.37). (3) The agreement between the experimental and calculated values is very good, even where the inorganic material is concerned.

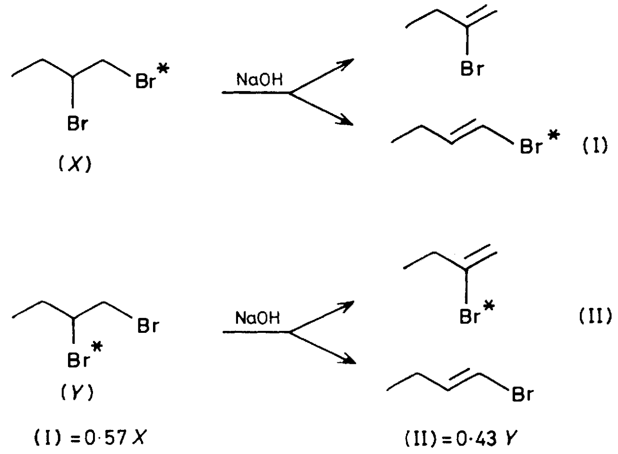
According to these results we now conclude, as did Tanner, that an elimination–readdition pathway may interfere with the normal mechanism in the case of the β-dibromides but we assume that it is not as important as previously announced.

Isotope location experiments were also made in order to detect any rearrangement occurring during the course of the reaction. 1,2-Dibromobutane (non-active) was dehydro-

Table 7. Photobromination of labelled n-butyl bromide: results of statistical simulations

Entry [a]	Activity found in [b]	Experimental counts [c]	Calculated counts [d]	$Br_2{}^0$ [e]	$Br_2{}^*$ [f]	$Br_2{}^{**}$ [g]	β-Addition [h]	β-Substitution [i]	*F*	*E*
1	In	4 154	3 773						0.87	0.24
	α + γ	4 993	4 638		4 202	218				
	β	23 184	24 285	6 401	22 073	1 106	7 099	22 480		
2	In	13 563	13 439						0.84	0.18
	α + γ	29 155	28 188		26 212	988				
	β	125 204	123 219	23 836	114 709	4 255	25 704	117 096		
3	In	5 431	5 078						0.86	0.22
	α + γ	7 577	7 455		6 813	321				
	β	37 155	36 593	8 733	33 513	1 540	9 642	34 184		
4	In	11 332	11 920						0.85	0.15
	α + γ	27 595	27 258		25 662	798				
	β	130 403	132 648	21 135	124 962	3 843	22 491	127 449		
									0.86 [j]	0.20 [j]

[a] Corresponds to Table 6. [b] In = inorganics. α + γ = 1,1- and 1,3-dibromide; β = 1,2-dibromide. [c] According to Table 6 after redistribution of the activities of tribromides (see text). [d] Obtained by the stepwise simulation according to Scheme 2. [e] Dibromides without radiobromine. [f] Dibromides with one radiobromine atom. [g] Dibromides with two radiobromine atoms. [h] 1,2-Dibromides originating from elimination–readdition pathway. [i] 1,2-Dibromides originating from the normal substitution mechanism. [j] Mean values.

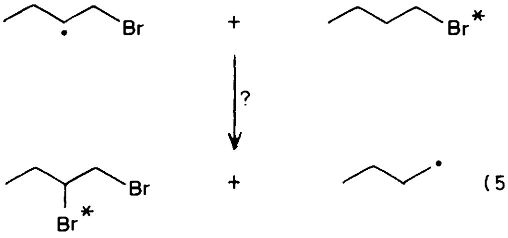


Scheme 3.

Table 8. Results obtained by dehydrobromination of radioactive 1,2-dibromobutanes [a]

Entry	Activities [b] (I) [a]	Activities [b] (II) [a]	*X* [a] (%)	*Y* [a] (%)
1	15 253	1 071	91	9
2	16 432	1 300	91	9
3	6 420	623	89	11
4	1 464	111	91	9
5	6 340	636	88	12

[a] See Scheme 3. [b] In counts min^{-1}.



(5)

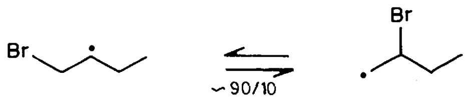
brominated over solid sodium hydroxide. 2- and 1-bromobutenes were found in the relative amounts of 43 and 57%, respectively. Labelled 1,2-dibromobutane isolated from experiments like those reported in Table 6 was submitted to the same treatment and the proportion of the two active butenes was measured. The dehydrobromination of the two possible 1,2-dibromobutanes follows Scheme 3. This allowed us to calculate the relative concentrations *X* and *Y* starting from the measured proportion of (I) and (II) (Table 8).

To reinforce the interpretation of these data is was important to check the possibility of exchange between inactive β-bromoalkyl radicals and active n-butyl bromide [reaction (5)]. Indeed, in certain cases, for instance in the photochlorination of bromoalkanes, intermolecular transfer of bromine has been detected.[15,16] However, under our reaction conditions bromine rearrangement is not induced by an exchange of this type: we performed photobromination of active ethyl bromide mixed with inactive butyl bromide. The activity detected in the brominated butanes was of the same order of magnitude as the isotopic exchange (<1%) already detected in the blank experiment of Table 6.

The results of Table 8 show that 10% of the labelled 1,2-dibromide contains a radiobromine atom located in the 2-position. The origin of this rearrangement may be the migration of bromine in the β-bromobutyl radical or the result of an elimination–readdition process.

By examining the detailed results of Table 7 the distribution of the radiobromine atoms in the dibromides may be predicted. The calculations for experiment 2, for instance, lead to the following conclusions: among the 25 704 dibromide molecules originating from elimination–readdition 23 836 have no radiobromine. If this pathway is the only source of rearrangement we need to find 10% of the total labelled β-dibromide (118 694) having a radiobromine atom in position 2 and originating from addition. This is impossible since the labelled β-dibromide coming from addition amounts to 1 868 as a maximum: this represents 1.5% only. The same type of observation can be made for the other experiments.

We conclude that the amount of rearrangement observed is related to the relative stability of the two radicals involved. An equilibrium between these two species greatly favours the secondary (unrearranged) one (Scheme 4). Rearrangement results found in the literature [4a,b] often show similar trends. Moreover, such a rearrangement would be consistent with the presence of an unsymmetrically bridged β-bromoalkyl radical.



Scheme 4.

Conclusions.—The observations made in this study show that HBr influences the reaction in a very complex manner: it acts as a catalyst whilst it is known that it inhibits the reaction through the reversibility of the hydrogen abstraction step.

The occurrence of the catalysis is restricted to substrates bearing a bromine substituent and available β-hydrogens. Furthermore, HBr cannot be replaced by another hydrogen halide and seems to contribute to the high yields of vicinal bromide. However, the catalytic mechanism is not the main pathway for the formation of β-dibromides. We thus still need a reason for the special stabilisation of the β-bromobutyl radical to explain the distribution of the products.

Isotopic labelling experiments have shown that if elimination–readdition is a plausible complication of the mechanism, its extent is limited. This pathway cannot explain the observed rearrangement of the bromine substituent and it can only account for *ca.* 20% of the β-dibromide.

Since it was shown that HBr catalyses only part of the vicinal dibromide formation (see Table 5) it seems reasonable to explain it by catalysis of the elimination process.

Therefore, we still think that the main reason for the high selectivity of bromination in the β-position is the anchimeric assistance proposed by Skell.

A coherent picture of the reaction may be given from the following distribution of the products: according to anchimeric assistance 86% of β-bromoalkyl radical would be formed. A maximum of 20% will eliminate under the catalytic influence of HBr giving 1,2-dibromide in an irreversible way. Among the total 1,2-dibromide 10% of rearrangement is found which cannot originate from the elimination pathway.

Experimental

Materials.—Bromine (Merck, pro analysi) was used without further purification. n-Butyl bromide (Koch–Light, puriss.) was washed several times with sulphuric acid, then distilled and treated with bromine in the dark. After removal of bromine the product was distilled over phosphorus pentaoxide. The purity was always >99.5% (g.l.c.). Bromoethane (Koch–Light) was treated as above. Chlorobenzene was a UCB chromatographic grade product. Carbon tetrachloride was of pro analysi quality.

Kinetic Studies.—Unicam spectrophotometers (SP600 and SP500) were modified to follow bromine disappearance without interrupting irradiation of the reacting mixture. The original source of the spectrophotometers were replaced by a cell containing n-butyl bromide and bromine. External incandescent lamps were used (150 or 36 W) at *ca.* 50 cm from the cell. The light, without selection of the wavelength, was focused by two lenses and passed through the reacting cell (classical u.v. cell) before entering the apparatus. Bromine (*ca.* 1 μl) was added to n-butyl bromide (3 ml) after flushing with nitrogen. The disappearance of bromine was followed at 415 nm (extinction coefficient of bromine 198.8 mol^{-1} cm^{-1}).

The extinction coefficient used to measure the bromine concentration is different from the value which must be considered in the photochemical kinetics. This last one must be a mean value to be estimated over the whole spectrum of bromine between 330 nm (below 330 the light intensity is almost zero) and 580 nm (above 580 nm, the light will not break Br–Br bonds [17]). Starting from measured extinction coefficients and calculated light intensities the mean absorbance was estimated to be about ten times lower than the one measured at 415 nm.

In order to verify whether the measurements performed with polychromatic light are correct, a comparison was made between the results obtained with polychromatic and monochromatic light sources. For these experiments, *cis*-decalin was used as the substrate and chlorobenzene as solvent.

A monochromatic light source was first used (λ 415 nm ± 1; monochromator SAFAS) and disappearance of bromine was followed starting with an initial absorbance of 1.48. In this case, the measured absorbance equals the real absorbance in the reacting cell. The complex rate expression (6) was found to

$$v = -\mathrm{d}[\mathrm{Br}_2]/\mathrm{d}t = k'' (1-10^{-\varepsilon[\mathrm{Br}_2]})^{\frac{1}{2}}[\mathrm{Br}_2] \qquad (6)$$

apply. In a second experiment polychromatic light (incandescent lamp) was used as in the other experiments. In this case, the measured absorbance (at 415 nm) is not the effective absorbance of the solution. The disappearance of bromine was followed with an initial measured absorbance of 1.57. A simple kinetic expression corresponding to equation (1) was found to apply. In the two cases rate constants were obtained with correlation coefficients greater than 0.99.

Photobromination of n-Butyl Bromide.—Reaction mixtures were irradiated in Pyrex-stoppered tubes with one or two incandescent lamps of 150 W. The temperature was kept at *ca.* 20 °C and HBr was destoyed by washing with aqueous carbonate. After drying, g.l.c. analysis was performed on a QF-1 column (temperature programmed from 40 to 150 °C). Dibromides were identified by comparison with authentic samples. Peak areas were measured by reference to an internal standard (nitrobenzene). When potassium carbonate was used the solid was introduced as a finely ground powder and the reaction mixture was stirred vigorously during the experiment. When specially dried, the solid was heated in a Abder–Alden apparatus at 140 °C under vacuum for one week. The water content was measured by thermogravimetry.

^{82}Br *Labelled n-Butyl Bromide.*—Commercial n-butyl bromide, purified as above, was irradiated with thermal neutrons. Two days after irradiation labelled n-butyl bromide was isolated from the by-products by preparative g.l.c. The proportion of labelled molecules with respect to unlabelled material is very low (*ca.* 10^{-9}).

1-*Bromo*-2,2,4-*trimethylpentane.*—This was prepared by reaction of the corresponding alcohol with triphenylphosphine and carbon tetrabromide.[18] The product was finally purified by preparative g.l.c. (Carbowax 20M with the temperature programmed between 135 and 230 °C) (Found: Br, 40.6. Calc. for $C_8H_{17}Br$: Br, 41.4%), δ 0.95—1 (12 H, d + s), 1.23—1.3 (3 H, d + m), and 3.2 (2 H, s).

1,1,2,2-*Tetramethylethylene Oxide.*—This was prepared according to the procedure of Sorenson and Campbell,[19] by dropwise addition of peracetic acid (40% in acetic acid) into a suspension of sodium carbonate and tetramethylethylene in dichloromethane.

Labelled n-Butyl Bromide Photobromination.—The reaction mixtures were irradiated in sealed quartz tubes with incandescent lamps. After irradiation, the microtubes were broken into the chromatograph sample inlet. During analysis, inorganics (HBr essentially) were trapped in a short glass tube mounted on the chromatograph and filled with ferrocyanide powder. Organic products were trapped at the end of the column on active charcoal at *ca.* −5 °C. The radioactivity was recorded by means of a Baird Atomic scintillator counter; NaI(Tl). Corrections were made for dead time of the counting chain.

Dehydrobrominations of Radioactive 1,2-*Dibromobutane*.—The active dibromide was collected at the chromatograph exit in a trap filled with sodium hydroxide (finely ground, dried in an oven and adsorbed on silica gel). The trap was then heated for 5—10 min at the head (in the insert tube) of the g.l.c. column (SE 52). The tubes were then inserted into the carrier gas line allowing the products to escape into the chromatograph.

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