Polar Radicals. 9. Kinetics and Mechanism of the Vapor-Phase Bromination of 1-Bromobutane[1]

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Abstract: The vapor-phase photobromination of 1-bromobutane with molecular bromine (5:1) yields 11 products resulting from direct substitution or the elimination of a bromine atom from the 1-(bromomethyl)propyl radical. The 1-butene resulting from elimination undergoes addition, and allylic substitution and addition to yield polyhalogenated materials. The major portion of the bromine (65%) produced 1,2,3-tribromobutane and 1,2,3,4-tetrabromobutane. Bromination with bromine-81 produced isotopically enriched products which were consistent with the proposed mechanism and showed that 33% of the 1,2-dibromobutane formed arose from the elimination–readdition process. Vapor phase photobromination carried out to partial completion with high concentrations of bromine and hydrogen bromide resulted in only minimal amounts of β scission of the 1-(bromomethyl)propyl radicals. Under these conditions the bromination of perdeuterio-1-bromobutane allowed the determination of the relative rates of transfer, with bromine and hydrogen bromide, of the radicals formed in the reaction and further allowed the determination of the relative rates of abstraction at each position in the molecule. The relative rates of transfer and abstraction indicate that the radical formed β to the electronegative bromine atom is stabilized (i.e., more easily formed and less reactive with hydrogen bromide) compared to those in the other positions in the molecule.

Introduction

The bromination of 1-bromobutane with molecular bromine has been extensively studied in both the liquid and vapor phase.

The reaction was first investigated by Kharasch in his systematic study of the vapor-phase photobrominations of simple bromo- and chloroalkanes.[3] Four products were detected when the reaction was carried out at 100 °C using a 2.8:1 mol ratio of 1-bromobutane/bromine: 1,2-dibromobutane (30%), 1,3-dibromobutane (13%), an unidentified tribormide (30%), and 1,2,3,4-tetrabromobutane (10%).

Several years later Tedder attempted to study the reaction in the vapor phase using a flow system at 78 and 146 °C; the reaction was reported to be strongly inhibited by a product of the reaction. A large portion of the bromine failed to react and the sides of the vessel became coated with a brown film.[4]

The study of the solution-phase bromination of 1-bromobutane was first reported by Thaler.[5] The products formed from the bromination of a 5:1 mixture of 1-bromobutane and molecular bromine (60 °C) were reported as 1,1-dibromobutane (0.9%), 1,2-dibromobutane (84.6%), and 1,3-dibromobutane (14.6%). The unexpectedly high yield of 1,2-vicinal dibromide formed was rationalized by the proposal that the abstraction of the β hydrogen is anchimerically assisted by the neighboring bromine atom and that this effect enhances the rate of abstraction enough to overcome the normal deactivation of the β hydrogens by an electron-withdrawing substituent.

More recently the solution-phase bromination of 1-bromobutane was reinvestigated.[6] The product composition was reported to be a function of the extent of the reaction. At very low conversion the ratio of 1,2-dibromobutane/1,3-dibromobutane was <1, while at complete reaction the ratio was >5. It was suggested that this change in isomer distribution was due to the differential reversal of the initial radicals formed with the hydrogen bromide produced in the reaction. The β-bromobutyl radical was unique, however, in that it may eliminate a bromine atom to form 1-butene, which would rapidly add bromine and hence produce 1,2-dibromobutane.

Independent support for these results came from a reinvestigation of the vapor-phase bromination of 1-bromobutane with molecular bromine in a static system.[7] Tedder et al. found, in agreement with the above results, a change in the product distribution as the reaction progressed. The ratio of 1,2-/1,3-dibromobutane changed from 0.28 after a reaction time of 10 min to 2.20 after 120 min. Addition of hydrogen bromide was found to dramatically change the product distribution so that, after 10 min reaction time, the ratio of 1,2-/1,3-dibromobutane was 7.7.

The suggestion that the predominant production of 1,2-dibromobutane in the later stages of the reaction was due to an elimination–readdition reaction of the β-bromoalkyl radicals coupled with the extensive reversal of the other radicals in the system was tested for by carrying out the reactions with isotopically enriched bromine-81[8,9] and 1-bromobutane-^{82}Br.[10] The reactions carried out with enriched bromine-81 showed only excess enrichment of bromine-81 in the product 1,2-dibromobutane at higher temperatures, while the reactions carried out with radioactive substrate yielded only a small amount of radioactive hydrogen bromide. It was concluded from these experiments that the elimination–readdition process was not an important reaction during bromination. These observations, although correctly reported, have now been subject to a more critical evaluation and reinvestigation and are not as conclusive as had first been suggested.[11] On the basis of the labeling experiments the originally proposed mechanism was modified.[9] It was proposed that the change in product distribution with percentage conversion could be explained if the reverse reaction with hydrogen bromide was inhibited at the β position by either polar deactivation, as was the forward reaction, or by the formation of a bridge species after abstraction. The initially formed radicals would be differentially scavenged by hydrogen bromide, and since the more reactive radicals (the γ and δ radicals) would reverse the fastest, the products of β abstraction would predominate.

Recently, two communications have appeared questioning the previously reported result that in the bromination of 1-bromobutane with molecular bromine, at less than 20% conversion, the ratio of 1,2-/1,3-dibromobutane was less than unity.[12,13] One group[12] noted a change in the product distribution with percent reaction, although the effect was nowhere near as great as previously reported; in both communications, the ratio of 1,2-/1,3-dibromobutane was greater than one at all stages of the reaction. Likewise, it was reported from this laboratory that the previous observation that this ratio was less than unity at low reaction percents could not be repeated.[14]

Since the original observation that at low conversion the bromination of 1-bromobutane in solution gave a ratio of

Table I. The Products and Yields Obtained from the Photobromination of 1-Bromobutane in the Vapor Phase (22 °C)

	1^a		2^b	
	Mol (10^5)	% yield^c	Mol (10^5)	% yield^c
Starting material				
1-Bromobutane	302.9		131.0	
Bromine	61.00		25.94	
Products				
Hydrogen bromide^d			26.49	102.1
1-Bromobutane (recovered)	264.8		115.69	
1-Bromo-2-butene	0.40	0.7	tr	tr
1,1-Dibromobutane	0.65	1.1	0.29	1.1
1,2-Dibromobutane	12.74	20.9	5.22	20.1
Dibromobutene (unidentified)	0.33	1.1	0.18	1.4
1,3-Dibromobutane	4.80	7.9	2.07	8.0
Dibromobutene (unidentified)	0.52	1.7	0.21	1.6
1,2,2-Tribromobutane	0.47	1.5	0.16	1.2
1,4-Dibromo-2-butene	0.61	2.0	tr	tr
1,2,3-Tribromobutane	10.14	33.2	4.75	36.6
dl-1,2,3,4-Tetrabromobutane	2.21	10.9	1.20	13.9
meso-1,2,3,4-Tetrabromobutane	4.16	20.5	1.39	16.1
Material balance	97.2^e	101.5^f	101.0^e	100.0^f

[a] Reaction carried out in a 12-l. reaction vessel. [b] Reaction carried out in a 5-l. reaction vessel. [c] Percent yield based on bromine consumed. [d] Determined by isolation and titration. [e] Material balance based on 1-bromobutane consumed. [f] Material balance based on bromine consumed, excluding hydrogen bromide formed.

1,2-/1,3-dibromobutane of <1 cannot now be repeated, and since the vapor-phase studies of the photobromination are now in conflict with these later results, a detailed study of the gas-phase photobromination of 1-bromobutane has been carried out. It was anticipated that an understanding of this presumably less complex reaction would lead to an explanation for the conflicting liquid-phase observations.

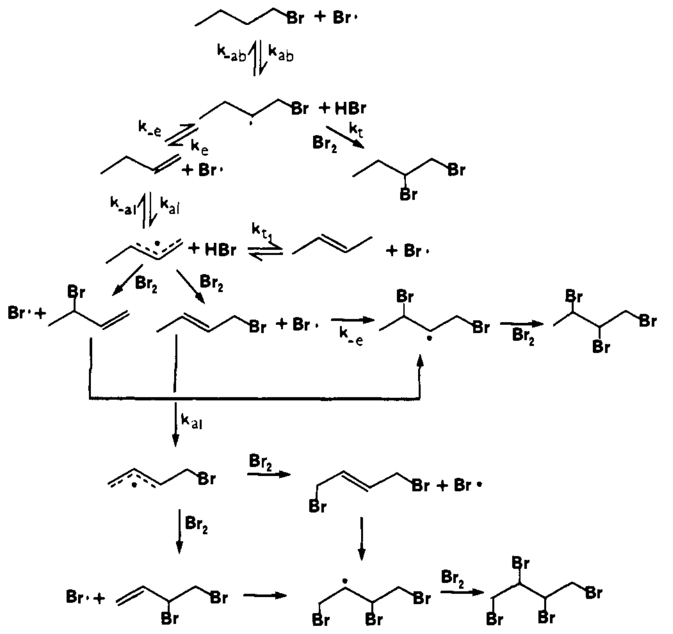
Discussion and Results

Vapor-Phase Bromination of 1-Bromobutane. The photobromination of a 5:1 mixture of 1-bromobutane with molecular bromine at 22 °C yielded 11 products. The major fraction (>65%) of the bromine consumed produced either tri- or tetrabrominated butanes (see Table I).

The tri- or tetrabromides could have been formed from the bromination of either 1,2- or 1,3-dibromobutane: this was unlikely, however, since the dibromide would have to brominate at a much faster rate than 1-bromobutane itself. Also, if this were the case, one would expect, contrary to what was found,[5,6,9] comparable amounts of tri- and tetrabromides in the liquid-phase reactions. The relative rates of bromination in the vapor phase of 1-bromobutane, 1,2-dibromobutane, and 1,3-dibromobutane vs. cyclohexane were determined in order to substantiate the assumption that the rates of bromination of the product dibromides would not be very much greater than the rates of bromination of the substrate. In accordance with this assumption, the relative rates of disappearance of 1-bromobutane/1,2-dibromobutane, ($k_1/k_{1,2}$ = 4.3) and 1-bromobutane/1,3-dibromobutane ($k_1/k_{1,3}$ = >10) were both found to be >1, and thus the possibility could be eliminated that the polyhalogenated 1-bromobutanes were derived from the product dibromides. It was further noted that an analysis of the tribromides derived from the bromination of each of these dibromides did not give as the major product tribromide, 1,2,3-tribromobutane. The bromination of 1,2-dibromobutane yielded two tribromides, 1,2,2-tribromobutane and 1,2,3-tribromobutane in a ratio of 16:1, while the bromination of 1,3-dibromobutane yielded three tribromides in a ratio of 3.8:18:1. 1,2,3-Tribromobutane comprised only 4% on this mixture. It was noted, however, that a material balance on these products was not obtained.

A plausible mechanism for the formation of the polyhalogenated 1-bromobutanes is given in Scheme I. In this scheme the 1-(bromomethyl)propyl radicals are either trapped by bromine or hydrogen bromide or eliminate bromine atoms to give 1-butene. The alkene may then add bromine to form 1,2-dibromobutane or be allylically brominated to give a mixture of 1-bromo-2-butene and 3-bromo-1-butene, which on addition of bromine, would give 1,2,3-tribromobutane. The allylic bromides may also be allylically brominated to yield either *cis*- and *trans*-1,4-dibromobutene and 3,4-dibromo-1-butene, or 3,3-dibromo-1-butene and 1,3-dibromo-2-butene. Addition of bromine to the first pair will yield mixtures of *dl*- and *meso*-1,2,3,4-tetrabromobutane. No 3-bromo-1-butene nor its products of allylic bromination nor the tetrabromides resulting from their addition were detected, although the small amounts of unidentified dibromobutenes that were isolated may be the allylic bromination products of this unsaturated monobromide.

Scheme I



If the following kinetic requisites were obeyed after the β scission of the 1-(bromomethyl)propyl radical, then the reactions listed in Scheme I would explain the products formed in the bromination: allylic abstraction from 1-butene or 1-bromo-2-butene and 3-bromo-1-butene must be faster (or of comparable rate) than addition to form vicinal dibromide, and addition and allylic bromination of 1-butene or 1-bromo-2-butene and 3-bromo-1-butene must be faster than abstraction from 1-bromobutane.

The vapor-phase reactions of 1-butene with bromine and of 1-bromo-2-butene and 3-bromo-1-butene with bromide were investigated to establish if the mechanism proposed in Scheme I was consistent with the products formed. To determine the importance of elimination in the vapor-phase bromination of 1-bromobutane, the reaction with bromine highly enriched in bromine-81 was also studied.

Vapor-Phase Bromination of 1-Butene. The free-radical chain bromination of 1-butene yields both addition and allylic

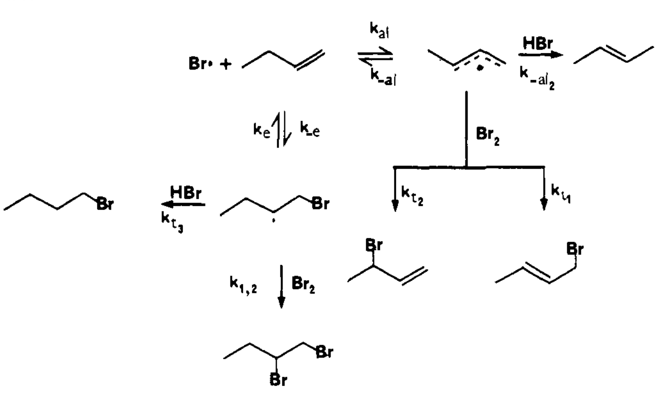
Table II. Vapor-Phase Photobromination of 1-Butene (22 °C)

Reaction	$[C_4H_8]^a$	$[Br_2]^a$	Vol, l. (surface area, cm^2)	Equil. time, min^c	% products^d 1	2	3
1^b	2.25	0.46	5 (1414)	0	28.4	67.4	4.2
2^b	1.65	0.31	5	12	23.6	56.8	19.7
3^b	1.61	0.34	5	20	17.1	43.2	39.6
4^b	0.67	0.13	12 (2535)	20	27.2	65.1	7.7
5	2.87	0.50	12	20	16.5	42.1	41.4
6	1.02 (1.56)^f	0.50	12	21	21.6	55.0	23.4
7	2.72	0.51	22 (3798)	0	26.2	69.2	4.2
8	2.86	0.51	22	22	21.6	55.5	22.9
9^e	0.49	0.07	22	0	25.3	71.7	3.0
10	1.27 (1.26)^f	0.51	22	21	23.8	60.7	15.5

[a] Concentration, M × 10^4. [b] Reaction run at 27 °C. [c] Time (min) reactants were left to equilibrate in the absence of light prior to irradiation. [d] Only four products were detected, 3-bromo-1-butene (**1**), 1-bromo-2-butene (**2**), 1,2-dibromobutane (**3**), and 1-bromobutane. The latter always made up less than 0.4% of the products and is not reported in the results in this table. [e] Reaction run with 7 × 10^{-6} M added hydrogen bromide. [f] Concentration of added 1-bromobutane, M × 10^4.

bromination products (Scheme II). The relative rate of formation of the substitution products to the addition products is given by[15]

Scheme II



$$\frac{d(\text{substitution})/dt}{d(\text{addition})/dt} = \frac{k_{al}}{k_{-e}}\left[1 + \frac{1}{(k_{12}/k_e)[Br_2]}\right] \qquad (1)$$

The assumptions made in the derivation that k_{-al}[HBr] and k_{t_3}[HBr] are small seem to be valid, since only traces of 1-bromobutane are found at the completion of the reaction, and when the bromination was carried out under conditions where k_{-al}[HBr] would be favored, with added hydrogen bromide (reaction 9, Table II), no 2-butene could be detected. The absence of 2-butene substantiated that k_{-al_2} is small, and by implication, k_{-al_1} must also be small. The amount of addition was not found to be independent of olefin concentration, but seemed to be dependent upon its concentration and the surface area of the reaction vessel (see Table II). The dependence of the ratio of addition to substitution indicates that a portion of the addition takes place as an ionic reaction on the surface of the reaction vessel. When the bromination was carried out under conditions more similar to those existent during the bromination of 1-bromobutane, with a mixture of 1-butene and 1-bromobutane (Table II, reactions 6 and 10), it was observed that 1-bromobutane did not react (both allylic substitution and addition were faster than abstraction from 1-bromobutane) and that under the reaction conditions the ratio of addition to substitution was 0.2:1 (allylic bromination was faster than addition). The ratio obtained must be taken as a maximum for the free-radical reaction conditions, since a component of the addition must be proceeding by an ionic pathway. The possibility that a fraction of the 1-bromo-2-butene was formed by an ionic reaction cannot be ruled out. However, the relatively constant ratio of 1-bromo-2-butene/3-bromo-1-butene (2.53 ± 0.09, reactions 1–10, Table II) is an indication that this was not an important reaction, since the ratio would vary considerably between the ionic and radical processes.

1,2,3-Tribromobutane was not detected in the brominations of 1-butene with a deficiency of molecular bromine. The alkene was therefore brominated allylically much faster than the allylic bromides added bromine to give tribromide. Since in the bromination of 1-bromobutane allylic bromides were only minor products, the allylic bromides must have added bromine faster than 1-bromobutane brominated.

Competitive Bromination of 1-Bromobutane and 1-Bromo-2-butene and 3-Bromo-1-butene. To substantiate the above proposal, a (3:1) mixture of 1-bromo-2-butene and 3-bromo-1-butene (6.7 × 10^{-5} M) and 1-bromobutane (6.2 × 10^{-5} M) was allowed to react with bromine (5.70 × 10^{-5} M) in the vapor phase. Under these conditions <2% of the 1-bromobutane was brominated, while the reaction of the allylic bromides accounted for a variety of products from their bromination. The rate of bromination of 1-bromobutane relative to that of the allylic bromides can only be approximated (~146:1), since so little of the initial 1-bromobutane had reacted. The multiplicity of products arising from the allylic bromination and addition to the allylic bromides and the lack of appreciable reaction of 1-bromobutane substantiated the proposal that the allylic bromides undergo both substitution and addition faster than 1-bromobutane is brominated.

Bromination of 1-Bromobutane with Bromine-81. The bromination of 1-bromobutane with bromine enriched in bromine-81 was carried out under the conditions previously described for the vapor-phase photobrominations (see Table III). The hydrogen bromide was distilled from the reaction mixture and allowed to react in the dark with cyclohexene. The cyclohexyl bromide from this reaction as well as the products of the bromination of 1-bromobutane were collected by preparative GLC and subjected to mass spectral analysis. Since only 12% of the original 1-bromobutane had been brominated under these conditions (see Table I), it was not surprising that the recovered 1-bromobutane had the same isotopic distribution of bromide as did the starting material (addition of hydrogen bromide to 1-butene was therefore not detectable). The hydrogen bromide produced in the reaction (analyzed as cyclohexyl bromide), however, was highly enriched in bromine-79. Since the only source of bromine-79 was the 1-bromobutane, then enrichment of the hydrogen bromide is con-

Table III. Vapor-Phase Photobromination of 1-Bromobutane with Bromine-81[a]

Compd	Total[b] $^{79}Br:^{81}Br$	Isotopic ratio of bromine: Atom 1	Isotopic ratio of bromine: Atom 2
Starting Material			
1-Bromobutane (294.7×10^{-5} mol)	50.57:49.43		
Bromine (62.10×10^{-5} mol)	2.19:97.81		
Products			
1-Bromobutane	50.56:49.44 ± 0.14		
HBr as $C_6H_{11}Br$	14.16:85.85 ± 0.18		
Bromine (average)	8.17:91.83		
1,1-Dibromobutane	29.01:70.94 ± 0.34	8.14:91.86	49.98:50.02
1,2-Dibromobutane	22.31:77.69 ± 0.16	6.68:93.32	37.94:62.06
1,2,3-Tribromobutane $(P - Br)^+$	11.53:88.47 ± 0.05	11.36:88.64	11.63:88.39
meso-1,2,3,4-Tetrabromobutane $(P - Br)^+$	8.00:92.00 ± 0.02[c]		
dl-,1,2,3,4-Tetrabromobutane $(P - Br)^+$	8.12:91.88 ± 0.02[c]		

[a] Reaction run in a 12-l. reaction vessel to completion (22 °C). [b] Errors are deviations from the mean for five separate mass spectral analyses. [c] Due to the error in measuring the smallest peaks, *m/e* 291 and 293, no individual distribution could be calculated.

sistent with the elimination reaction proposed in Scheme I. If one assumes that a rapid equilibrium exists between the bromine in the hydrogen bromide and the molecular bromine, then the average bromine available for bromination will be the average of the distribution found in the original bromine and the final hydrogen bromide, $^{79}Br:^{81}Br = 8.17:91.83$ (see Table III). This assumption could be substantiated by an analysis of the mass spectral fragmentation intensities obtained from the parent peaks of 1,1-dibromobutane. The formation of 1,1-dibromobutane solely through the intermediacy of the 1-bromo-1-butyl radical (Scheme I) leads to the prediction that one of the bromine atoms in the compound will be the original one ($^{79}Br:^{81}Br = 50.57:49.43$) and the other will have, if the formation of the product is monotonous with time, the average isotopic ratio of bromine ($^{79}Br:^{81}Br = 8.17:91.83$) in the bromine pool. This prediction was found to be correct, since the isotopic ratio of $^{79}Br:^{81}Br$ for each bromine atom in the 1,1-dibromobutane could be determined (atom 1, 49.98:50.02, the original atom; atom 2, 8.14:91.86, the average bromine atom from the pool) from an analysis of the mass spectrum of the geminal dibromide (see Experimental Section).

The formation of 1,2-dibromobutane via two competitive pathways, direct substitution of the 1-(bromomethyl)propyl radical and the elimination–readdition process (both radical and/or ionic) would yield dibromide containing atoms having different isotopic ratios, neither of which having the ratio of the atom originally present in the starting material. The distribution found, $^{79}Br:^{81}Br$, atom 1 (6.68:93.32) and atom 2 (37.94:62.06), is consistent with this mechanism and further allows the estimation of the amount of each of the two processes that are responsible for its formation. The fraction, e, of the 1,2-dibromobutane formed by the addition of bromine to 1-butene contains the average ratio of bromine-79:bromine-81 which makes up the bromine pool (8.17:91.83). The fraction of the 1,2-dibromobutane formed from direct substitution will contain one average bromine (8.17:91.83) and one bromine originally present in the 1-bromobutane (50.57:49.43). If one considers the values of the bromine-79 content of each fraction and the final bromine-79 content of the total 1,2-dibromobutane, then the fraction of the 1,2-dibromobutane formed by the addition process can be calculated.

$$0.294(1 - e) + 0.082e = 0.223$$

$$e = 0.33$$

Unfortunately the mass spectra of the tri- and tetrabromides did not show parent peaks; however, an analysis of the fragment ions m/e $(P - Br)^+$ was quite instructive (see Table III). The tribromide 1,2,3-tribromobutane, contained two isotopically nearly equivalent bromine atoms, neither of which is the original bromine from 1-bromobutane. Although it could not be determined which bromine was lost from the tribromide to form the ion $(P - Br)^+$ or in fact if this mass fragment is a mixture of isomeric ions, the results are consistent with the mechanism proposed from the results of the product and kinetic studies on the bromination of the dibromides, and the combined results show that the tribromide was formed from olefin by bromination followed by addition. The two tetrabromides, likewise, must have been formed via a related mechanistic pathway, since the total isotopic content of its $(P - Br)^+$ fragment cannot contain the original atom of bromine and the average distribution of three of the bromine atoms is remarkably close to that of the average bromine pool.

The fraction of 1-(bromomethyl)propyl radicals that eliminate in the vapor phase may be calculated by combining the ^{81}Br bromination results with those of the normal brominations, if one assumes that the 1,2,2-tribromobutane arises from the bromination of 1,2-dibromobutane and that the unsaturated bromides and the tri- and tetrabromides were derived from the bromination of 1-butene (see Scheme I). Under the reaction conditions, where 33% of the 1,2-dibromobutane, and via inference 33% of the 1,2,2-tribromobutane, arises from addition of bromine to 1-butene, the products formed from 1-butene via substitution and/or addition account for 72% of the β-bromobutyl radicals that proceed to bromination products. Of the radicals that yield bromination products (exclusive of those that reverse with hydrogen bromide), 85% of them are derived from β-hydrogen abstraction.

Brominations with High Concentrations of Molecular Bromine and Hydrogen Bromide. The amounts of elimination relative to substitution of the 1-(bromomethyl)propyl radicals should be dependent upon the lifetime of these radical intermediates. Under conditions where the concentrations of the transfer agents, bromine and hydrogen bromide, are high the shorter lifetime of the radical should limit the amount of elimination. When the bromination was carried out at high concentrations of bromine (reaction 1-3, Table IV) or at high concentrations of bromine and hydrogen bromide (reaction 4, Table IV), only minor amounts of polyhalogenated materials (resulting from elimination) were formed, and no tetrahalogenated materials could be detected.

Kinetics of the Bromination of Perdeuterio-1-bromobutane. Since the vapor-phase bromination of 1-bromobutane can be carried out in the presence of excess molecular bromine and hydrogen bromide with a negligible amount of elimination

Table IV. Vapor-Phase Photobromination of 1-Bromobutane with an Excess of Molecular Bromine and Hydrogen Bromide[a]

					% products[c]				
Reaction	$[Br_2]^\circ$	$[C_4H_9Br]$	$[HBr]^\circ$	% conversion[b]	1,1	1,2	1,3	1,2,3	Other
1[e]	0.82	1.46		6	2.1	79.1	16.0	2.9	*d*
2[f]	0.45	47.1		14	1.7	79.6	17.0	1.7	*d*
3[g]	3.14	11.5	48.2	16	1.7	81.9	13.1	3.3	*d*
4[g]	2.3	8.10	35.5	10	1.7	81.8	12.2	1.9	1.6[h]

[a] Concentration, M × 10^4. [b] Percent conversion based on 1-bromobutane. [c] Products were identified by collection using preparative GLC and comparing their ir and mass spectra with those of the authentic material. The percentages listed for reactions 1–3 are relative yield based on the products listed and make up 97.7% of the material having reacted. The yields quoted for reaction 4 are absolute yields. [d] Other tribromide were not analyzed for. [e] Reaction run in a 12-l. reaction bulb, 22 °C. [f] Reaction run in a 5-l. reaction bulb, 24 °C. [g] Reaction run in a 12-l. reaction bulb, 23 °C. [h] A mixture of tribromides were 1.6% 1,2,2-tribromobutane and a trace of 1,3,3-tribromobutane.

Table V. Photobromination of Perdeuterio-1-bromobutane with Excess Bromine and Excess Hydrogen Bromide in the Vapor Phase

	Concentration, M × 10^5			
	1[a]	2[a]	3[b]	4[b]
Reactants[c]				
$[RD(H)]^\circ$	23.36	44.58	16.40	15.56
$[Br_2]^\circ$	83.83	144.13	83.35	83.89
$[HBr]^\circ$	364.8	596.0	865.5	842.6
$[R^\alpha H]^\circ$	1.51	2.88	1.06	1.01
$[R^\beta H]^\circ$	0.26	0.50	0.18	0.18
$[R^\gamma H]^\circ$	0.48	0.92	0.34	0.32
$[R^\delta H]^\circ$	1.88	3.59	1.32	1.25
Products				
$[RD(H)]$	16.03	38.32	14.76	11.33
$[R^\alpha H]$	1.54	2.92	1.07	1.03
$[R^\beta H]$	0.72	0.96	0.28	0.66
$[R^\gamma H]$	1.01	1.58	0.42	0.70
$[R^\delta H]$	1.91	3.61	1.33	1.26
$[R^\alpha Br]$	0.11	0.15	0.02	0.05
$[R^\beta Br]$	5.25	5.98	0.50	2.33
$[R^\gamma Br]$	0.78	0.97	0.05	0.24
$[R^\delta Br]$[d]	0.00	0.00	0.00	0.00
1,2,3-Tribromide[e]	0.14	0.09	0.00	0.06
Others[f]	0.14	0.15	0.00	0.05

Relative rate constants[g]	1[a]	2[a]	3[b]	4[b]	Average
k_{Br_2}/k_{HBr}[h]	26.2	26.6	29.6	30.2	28.2 ± 1.8
k_2/k_{-1}	16.4	15.5	17.0	25.1	18.5 ± 3.3
k_4/k_{-3}[i]	52.3	55.9	51.9	51.1	52.8 ± 1.6
k_6/k_{-5}	6.40	6.08	6.49	6.34	6.33 ± 0.14
k_1/k_5	0.11	0.12	0.20	0.11	0.13 ± 0.03
k_3/k_5	4.57	4.10	4.62	4.71	4.50 ± 0.20
k_7/k_5	0.01	0.01	0.05	0.01	0.02 ± 0.01
Temp, °C	24	26	24	25	

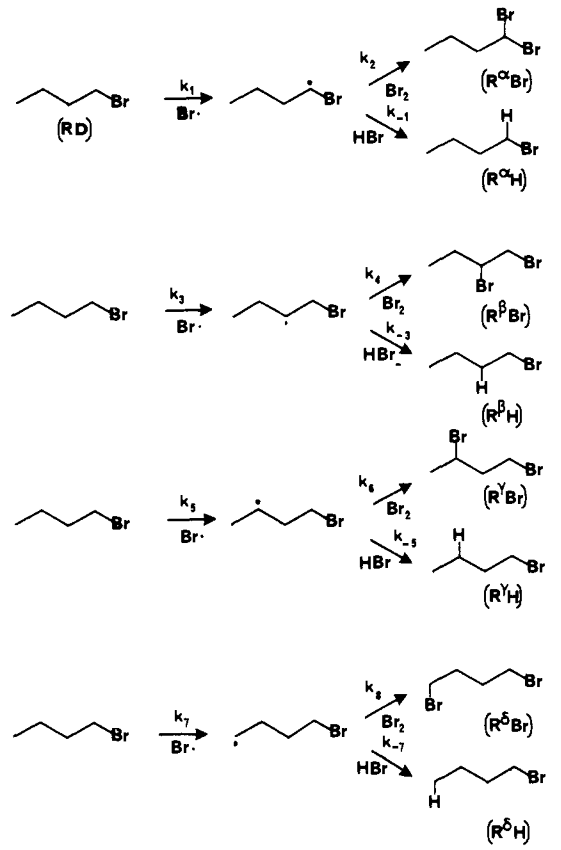
[a] Run in 12-l. reaction vessel, 23 °C. [b] Run in 22-l. reaction vessel, 23 °C. [c] $[RD(H)]$ refers to the concentration of perdeuterio-1-bromobutane and $[R^iH]$ is the average concentration of protium at position *i*. [d] Not detected by GLC. [e] 1,2,3-Tribromobutane. [f] 1,2,2-Tribromobutane (~95%) and 1,3,3-tribromobutane (~5%). [g] See Scheme III. Calculated using eq 2 or 5 or their equivalent equations for the other positions. [h] Relative rate of transfer of all perdeuterio-1-bromobutyl radicals with bromine and hydrogen bromide, using eq 6. [i] The values reported were corrected for the trihalide assuming that $[R^\beta Br] = [R^\beta Br] + [1,2,3\text{-tribromobutane}] + [1,2,2\text{-tribromobutane}]$. The uncorrected values calculated from the data in Table V were within the experimental error reported of the corrected values.

from the 1-(bromomethyl)propyl radicals, the relative rates of abstraction from perdeuterio-1-bromobutane by bromine atoms and the relative rates of transfer of the isomeric perdeuteriobromobutyl radicals with bromine and hydrogen bromide could be determined using the same method as was reported for perdeuterio-1-chlorobutane.[1]

Under these conditions (excess bromine and hydrogen bromide, 12- or 22-l. reaction vessels, see Table V), six products were detected other than unreacted material when the recovered reaction mixture was analyzed by GLC: 1,1-, 1,2-, and 1,3-dibromobutane-d_8, 1,2,2-, 1,3,3-, and 1,2,3-tribromobutane-d_7. These products were identified by comparison of their GLC retention times with those of the authentic, nondeuterated materials on two columns. They were collected by preparative GLC and their mass spectra were found to be identical with those of the protiated compounds when they were corrected for the presence of deuterium instead of protium. Mixtures of known composition of bromine, hydrogen bromide, 1-bromobutane, 1,2-dibromobutane, 1,3-dibromobutane, and 1,2,3-tribromobutane, and added 1,4-dibromobutane which had the same composition as the product mixtures, were subjected to the reaction conditions in the absence of light, reisolated, and reanalyzed. The recovered organic material could be recovered in greater than 98% yield for the mono- and dibrominated material and greater than 97% for the tribrominated material.

The mechanism of the vapor-phase bromination of 1-bromobutane carried out in the presence of high concentrations of bromine and hydrogen bromide is outlined in Scheme III.

Scheme III



If this scheme is used, the relative rate of production of any pair of dibromides is given by

$$\frac{d[R^{\beta}Br]/dt}{d[R^{\gamma}Br]/dt} = \frac{k_3}{k_5}\frac{k_4}{k_6}\frac{k_{-5}}{k_{-3}}\left[\frac{1 + \dfrac{k_6}{k_{-5}}\dfrac{[Br_2]}{[HBr]}}{1 + \dfrac{k_4}{k_{-3}}\dfrac{[Br_2]}{[HBr]}}\right] \tag{2}$$

$$\frac{d[R^{\alpha}Br]/dt}{d[R^{\gamma}Br]/dt} = \frac{k_1}{k_5}\frac{k_2}{k_6}\frac{k_{-5}}{k_{-1}}\left[\frac{1 + \dfrac{k_6}{k_{-5}}\dfrac{[Br_2]}{[HBr]}}{1 + \dfrac{k_2}{k_{-1}}\dfrac{[Br_2]}{[HBr]}}\right] \tag{3}$$

When these expressions are employed the values for the relative rates of abstraction, k_1/k_5 and k_3/k_5, can be calculated. Equation 4 was derived to calculate the ratio k_7/k_5, since an expression of the form of eq 2 could not be evaluated for the δ position due to the negligible amount of 1,4-dibromobutane formed.

$$\frac{k_7}{k_5} = \frac{[RH] - [RH]^{\circ}}{[RH] - [RH]^{\circ} + [RBr]} \tag{4}$$

The ratio of rate constants for the abstraction of a deuterium atom from perdeuterio-1-bromobutane in the α, β, and γ positions can be equated to the same ratio of rate constants in the undeuterated substrate if the assumption is made that analogous ratios of rate constants for the two substrates are the same,

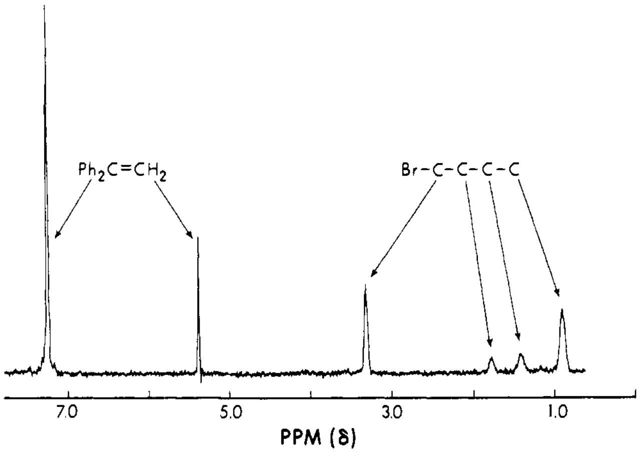


Figure 1. NMR spectrum of a Freon 113 solution of perdeuterio-1-bromobutane (after reaction) and 1,1-diphenylethene (Me_4Si internal standard).

$$k_i^{H}/k_j^{H} = k_i^{D}/k_j^{D} \tag{5}$$

The photobrominations of perdeuterio-1-bromobutane were carried out in 12- and 22-l. reaction vessels at ambient temperature. The concentrations and values obtained from the kinetic analyses are listed in Table V. The reactions were carried out to low conversion where multiple exchange reactions (H for H or D for D) will be negligible. The reaction mixtures were condensed, diluted with Freon 113, and an internal standard (chlorobenzene) was quantitatively added. The mixtures were then freed from hydrogen bromide and molecular bromine by washing with ice-cold aqueous sodium bisulfite. After drying, the mixture was subjected to GLC analysis.

The unbrominated substrate was collected by preparative GLC and the amount of incorporated protium at each position (see Table V) was determined from a comparison of the ^1H 100-MHz spectrum of the residual protium in the starting perdeuterio-1-bromobutane (Merck Sharp and Dohme, 98.3 atom % D) and the spectrum of the recovered unbrominated substrate. The total amount of protium in the starting material and in the recovered unbrominated perdeuterio-1-bromobutane was determined by NMR integration of quantitative mixtures of a standard (1,1-diphenylethene) and the substrate (see Figure 1). Mass spectral analysis of the substrate for total protium content also agreed, within experimental error, with the values obtained by the NMR method.

The relative rates of transfer of the bromobutyl radicals with bromine and hydrogen bromide were determined using

$$\frac{k_{Br_2}}{k_{HBr}} = \frac{[RBr_2][HBr]}{([RH]^{f} - [RH]^{\circ})[Br_2]} \tag{6}$$

They were found to be independent of the ratio of bromine to hydrogen bromide and the volume of the reaction vessel (Table V). The relative rate of transfer for the bromobutyl radicals with bromine and hydrogen bromide was calculated as 28.2 ± 1.4. Thus only 3.4% of the radicals formed reverse with hydrogen bromide when the concentrations of bromine and hydrogen bromide are equal. In the vapor phase 1-bromobutane is more deactivated, under these conditions, toward reversal than 1-chlorobutane (where 7.5% of the radicals reversed with hydrogen bromide)[1] or cyclohexane (where 26% of the radicals reversed with hydrogen bromide).[16]

The relative rates of transfer for the isomeric bromobutyl radicals were 18.5 ± 3.3, 52.8 ± 1.6, and 6.33 ± 0.14 for the

Table VI. Vapor-Phase (22 l.) Photobromination of 1-Bromobutane with Excess Bromine and Excess Hydrogen Bromide[a]

				$R^{\alpha}Br/R^{\gamma}Br$[c]		$R^{\beta}Br/R^{\gamma}Br$[d]	
$[C_4H_9Br]^\circ$	$[Br_2]^\circ$	$[HBr]^\circ$	% reaction[b]	Obsd	Calcd[e]	Obsd	Calcd[e]
3.138[f]	11.47	48.16	16	0.13 ± 0.01	0.18 ± 0.05	6.52 ± 0.21	6.93 ± 0.39
1.497	8.773	39.94	16	0.16 ± 0.01	0.18 ± 0.05	7.20 ± 0.29	7.12 ± 0.41
1.393	3.196	24.31	3	0.15 ± 0.01	0.20 ± 0.06	8.52 ± 0.25	8.66 ± 0.53
1.751[g]	8.754	85.96	15	0.24 ± 0.01	0.22 ± 0.06	9.98 ± 0.41	9.68 ± 0.68
1.657	7.950	99.27	31	0.16 ± 0.01	0.23 ± 0.07	10.89 ± 0.45	10.82 ± 0.71

[a] All concentrations, M × 10^4; reactions run at 23 ± 1 °C. [b] Based on 1-bromobutane. [c] Ratio 1,1-/1,3-dibromobutane. [d] Ratio of products from attack at the 2 position (1,2-dibromobutane, 1,2,2- and 1,2,3-tribromobutane) to 1,3-dibromobutane. 1,2,3-Tribromobutane was always <3% of the total products. [e] Calculated from the integrated forms of eq 2 and 3, using the relative rate data of Table V. [f] Run in a 12-l. reaction bulb. [g] Perdeuterio-1-bromobutane was used in this reaction.

α, β, and γ radicals, respectively. The relative rates of transfer with bromine and hydrogen bromide for the δ position could not be calculated, as no perdeuterio-1,4-dibromobutane was detected. The rate of deuterium abstraction from perdeuterio-1-bromobutane, relative to the rate of abstraction of the γ deuterium were 0.13 ± 0.03, 4.50 ± 0.20, and 0.02 ± 0.01 for the α, β, and δ positions, respectively.

In order to substantiate the values obtained for the relative rates of transfer and abstraction obtained for perdeuterio-1-bromobutane and to reinforce the belief that the kinetics obtained for the deuterated substrate can be applied to the natural protiated substrate (eq 5), the vapor-phase bromination of 1-bromobutane was carried out to low conversions with high concentrations of bromine and hydrogen bromide. The product mixtures were analyzed and the results can be compared with the calculated ratios of products predicted, using the kinetic values obtained from the bromination of perdeuterio-1-bromobutane as the rate constants in the integrated forms of eq 2 and 3. Within experimental error, the observed and calculated ratio of products were the same (see Table VI). The observed and calculated ratios were also determined for the bromination of perdeuterio-1-bromobutane (see Table VI, reaction 4) and were found to be the same.

Kinetic Conclusions. The relative rates of transfer with bromine and hydrogen bromide for the γ radicals are very similar to those for the analogous radicals from perdeuterio-1-chlorobutane ($k_6/k_{-5} = 8.1$).[1]

The α radical in perdeuterio-1-chlorobutane would be anticipated to be more easily formed (more highly resonance stabilized) and less easily destroyed (larger polar effect) by reaction with hydrogen bromide than the analogous intermediate from the bromo analogue. As would be predicted (assuming similar transfer rates with bromine), the relative rates of transfer are higher for 1-chlorobutane ($k_2/k_{-1} = 64.8$)[1] than those for 1-bromobutane ($k_2/k_{-1} = 18.5$; see Table V). The relative rates of abstraction, k_1/k_5, for the α/γ positions reflect the greater ease of formation of this radical from the chloride ($k_1/k_5 = 0.35$)[1] than from the bromide ($k_1/k_5 = 0.13$; see Table V).

The radical at the β position of 1-bromobutane, by the same arguments as above, appears to be more readily formed and less readily destroyed by transfer with hydrogen bromide than the 1-(chloromethyl)propyl radical: $k_3/k_5 = 4.5$ and $k_4/k_{-3} = 5.3$ for the bromide (see Table V) vs. $k_3/k_5 = 0.48$ and $k_4/k_{-3} = 15$ for the chloride.[1] Both the relative rates of transfer and the relative rates of abstraction of the β hydrogen suggest that the 1-(bromomethyl)propyl radical is more stable than would be expected for a radical proximate to an electronegative substituent. This extra stabilization appears to be evident only during brominations of this substrate with molecular bromine,[17] and must be due to the sensitivity of this endothermic process to small structural changes. The enhanced rate of abstraction at the β position of 1-bromobutane can only be taken as relative to the reactivity of the other hydrogens in the molecule, since bromoalkanes, as are other electronegatively substituted alkanes, are deactivated relative to their parent hydrocarbons.[14] Enhanced rates of abstraction from bromoalkanes relative to their parent hydrocarbons have recently been reported;[13] however, these "apparent" relative rates have been found to be a function of bromine concentration and have been rationalized as the result of differential reversal with hydrogen bromide.[14]

The stabilization of a radical center β to a bromine atom has been rationalized previously in several ways; by neighboring-group participation (bridged radical formation)[15,18] and halogen hyperconjugative stabilization.[6,19] Although previously rejected,[6] the concept of hyperconjugative stabilization of the β-bromoalkyl radical appears now to be the most attractive explanation for the phenomenon, since this explanation is more consistent with recent spectral observations concerning the geometry of the β-bromoalkyl radical.[20,21]

No new information is available to accommodate the conflicting results reported previously[7] that at short reaction times (unlike our conditions) low ratios of 1,2-/1,3-dibromobutane are produced during the vapor-phase bromination of 1-bromobutane. Since no material balance could be obtained under the reaction conditions reported,[7] it is conceivable that instead of 1,2-dibromobutane more highly halogenated materials (resulting from subsequent reactions of the β-bromoalkyl radicals) were undetected.

In solution the reaction is much more complex, since the bromination of bromoalkanes can not only involve cage phenomena (elimination-readdition and cage reversal of the radicals with hydrogen bromide[16]), but also more extensive reversal with hydrogen tribromide[22] as well as elimination-readdition external to the solvent cage.[11] Catalysis of the elimination processes by hydrogen bromide would also be expected.

One reservation as to the interpretation of these results must still be pointed out, since it has been suggested[7] that mixtures of bromine and hydrogen bromide in the vapor phase catalyze the elimination of hydrogen bromide from 1-bromobutane via a process (presumably a surface-catalyzed reaction) other than a bromine atom induced hydrogen abstraction-β-scission. If this were so, a portion of the increased rate of formation of 1,2-dibromobutane compared to 1,3-dibromobutane could be attributed to this direct process.

Experimental Section

Materials. 1-Bromobutane, commercially available (Aldrich Chemical Co.), was purified by washing several times with concentrated sulfuric acid and then several times with water. It was dried over anhydrous sodium sulfate and then fractionally distilled. GLC showed it to be >99.9% pure.

Perdeuterio-1-bromobutane (Merck Sharp and Dohme Co. of Canada Ltd.) was purified by two preparative GLC collections (6 m × 5 mm 10% Carbowax 20M on Chromosorb P AW, glass column, 50 °C). GLC analysis of the deuterated compound prior to use showed it to be more than 99.5% pure. Mass spectral analysis (AEI MS9, 12 eV) showed it to contain 98.3 (C_4D_9Br) atom % deuterium. ^1H 100-MHz nuclear magnetic resonance spectroscopy (Varian HA100) showed four absorption singlets for perdeuterio-1-bromobutane (δ 0.89, 1.40, 1.76, 3.33, see Figure 1) due to the residual protium in the compound.

1,2-Dibromobutane, 1,3-dibromobutane, 1,4-dibromobutane, 1,4-dibromo-2-butene, and chlorobenzene were commercially available chemicals, and were purified by preparative GLC collection.

1,1-Dibromobutane was prepared by the Hunsdicker reaction on 2-bromopentanoic acid.[23] It gave small parent peaks at *m/e* 214, 216, and 218 (ratio 1:2:1) and its NMR spectrum was consistent with its structure: CCl_4, Me_4Si internal standard, δ 0.99 (t, $J = 6.9$ Hz, 3 H), 1.60 (sextet, $J = 6.9$ Hz, 2 H), 2.39 (quartet, $J = 7$ Hz, 2 H), and 5.72 (t, $J = 6.9$ Hz, 1 H).

1-Butene (Phillips research grade, 99.9%) was degassed in a vacuum line and distilled prior to use.

1,2,3-Tribromobutane was prepared by the addition of a carbon tetrachloride solution of bromine to commercial crotyl bromide. The reaction mixture was washed with 10% aqueous sodium bisulfite and water, dried (Na_2SO_4), and distilled. It was obtained as a colorless liquid, bp 110 °C (16.6 mm), $n^{20}D$ 1.5684 (lit.[24] bp 97 °C (10 mm), $n^{20}D$ 1.5680). The NMR spectrum showed the methyl protons as two doublets (δ 1.85 ($J = 6.3$ Hz) and 1.80 ($J = 6.7$ Hz; 3 H)) and the other protons as a complex pattern at δ 3.6-4.8 (4 H). The ir and NMR spectrum were identical with those of an authentic sample (City Chemical Co.).

1,2,2-Tribromobutane was collected by preparative GLC (2 m × 5 mm 10% DEGS on Diatoport S, 160 °C) from the products of the liquid-phase photobromination of 1,2-dibromobutane. Its mass spectrum showed the parent peaks at *m/e* 292, 294, 296, and 298 (ratio 1:3:3:1) and very intense $(P - Br)^+$ peaks at *m/e* 213, 215, and 217 (ratio 1:2:1). Its NMR spectrum (CCl_4, Me_4Si external standard) showed three sets of absorption peaks, in accordance with its structure: δ 1.20 (t, $J = 6.5$ Hz, 3 H), 2.49 (q, $J = 7$ Hz, 2 H), and δ 4.25 (s, 2 H).

1,3,3-Tribromobutane was presumed to be the major product from the vapor-phase bromination of 1,3-dibromobutane. It was shown that this compound was not 1,2,2- or 1,2,3-tribromobutane by comparing its GLC retention time (2 m × 5 mm 10% DEGS) with that of these compounds. Its mass spectrum showed the parent peaks at *m/e* 292, 294, 296, and 298 in a ratio of 1:3:3:1, as expected for a tribromide.

meso-1,2,3,4-Tetrabromobutane was collected as a solid residue after distillation of the products from the vapor-phase photobromination of 1-bromobutane. Its NMR, ir, and mass spectra were identical with those of an authentic sample (Aldrich Chemical Co.), mp 116-117 °C (lit.[25] mp 118 °C).

dl-1,2,3,4-Tetrabromobutane was collected as a liquid by preparative GLC (6 ft × ¼ in. 10% Carbowax 20M TPA, glass column) from the vapor-phase bromination of 1-bromobutane: MS *m/e* 370, 372, 374, 376, and 378 (1:4:6:4:1); calcd for ($C_4H_6{}^{79}Br_2{}^{81}Br_2$) 373.7160; found 373.7160. It was prepared from commercial crotyl bromide by NBS bromination (carbon tetrachloride, 2 mol % benzoyl peroxide, 80 °C, 3 h), followed by the addition of bromine in carbon tetrachloride until the bromine color was not discharged. The reaction mixture was washed with sodium bisulfite, sodium bicarbonate, and then water. The product was collected by GLC and its ir, NMR, and mass spectra were found to be identical with those of the compound obtained from the bromination of 1-bromobutane. The NMR (CCl_4) showed absorption for four protons at δ 3.82 (d) and 3.89 (s) and for two protons at δ 4.70 (multiplet). Irradiation of the absorption at δ 4.70 changed the absorption at δ 3.82 and 3.89 to a singlet. Irradiation at δ 3.85 changed the absorption at δ 4.70 to a singlet.

1-Bromo-2-butene and 3-bromo-1-butene were obtained by preparative GLC collection (6 m × 5 mm 10% Carbowax) from commercial technical grade "crotyl bromide." Both compounds gave parent peaks in the mass spectrum at *m/e* 134 and 136 (ratio 1:1); the NMR spectrum of 1-bromo-2-butene (CCl_4, Me_4Si internal standard) was consistent with its structure; it showed an apparent doublet at δ 1.74 ($J = 6.5$ Hz, 3 H), and two multiplets at δ 4.15-3.80 and 6.2-5.3, each integrating for two hydrogens. The NMR spectrum of 3-bromo-1-butene was more complex; it showed a doublet at δ 1.77 ($J = 6.4$ Hz, 3 H) and a multiplet at δ 6.5-4.3, integrating for four hydrogens.

1,1-Diphenylethene (Aldrich) was distilled prior to use, bp 136.5-137.0 °C (9 mm), $n^{20}D$ 1.6088 (lit.[26] bp 139 °C (11 mm), $n^{20}D$ 1.6085); NMR spectroscopy and GLC analysis showed it to have no detectable impurities.

Freon 113 (Matheson) and Freon 112 (PCR) were distilled from phosphorus pentoxide through a 30-cm Vigreux column, bp 45.5 and 88.0 °C (700 mm), respectively.

Molecular bromine (McArthur Chemical Co., reagent grade) was washed with concentrated sulfuric acid and freshly distilled from phosphorus pentoxide, bp 57.3 °C (700 mm). Bromine-81 (Isotope Development Centre, Oak Ridge National Laboratory) was distilled by trap-to-trap distillation prior to use.

Hydrogen bromide (Matheson) was introduced into a vacuum system through molecular sieves 4A or anhydrous calcium chloride, frozen in liquid nitrogen and degassed. The solid hydrogen bromide was sublimed twice at −98 °C (methanol slush bath) and finally distilled.

Gas-Liquid Partition Chromatography. The GLC analyses were carried out on instruments equipped with thermal conductivity detectors. Glass columns were used throughout. All compounds studied were found to be stable (collection and reanalyses) on the columns used. Analyses were carried out in at least triplicate and the integrated area ratios were converted into mole ratios of compounds vs. internal standards using synthesized calibration curves.[27] Retention time comparisons were obtained by the addition of authentic materials to a portion of the sample (spiking) and reanalyses by GLC.

Vapor-Phase Photobromination of 1-Bromobutane. The contents of degassed break seals containing 1-bromobutane and molecular bromine were introduced into an evacuated 5- or 12-l. reaction bulb. The reaction vessel was sealed and the reaction mixture was allowed to equilibrate in the flask for 30 min. The mixture was irradiated with a 40-W incandescent lamp until all of the bromine color was discharged (see Table I). The contents of the reaction bulb were condensed (24 h) into a liquid-nitrogen cooled trap, the mixture was added to an aqueous mixture of potassium iodide, and the solution was titrated iodometrically for hydrogen bromide.[28] An aliquot of a standard chlorobenzene solution of Freon 112 was added to the mixture and the organic phase was separated and dried over $MgSO_4$ and analyzed by GLC (6 ft × ¼ in. 10% Carbowax 20M TPA, glass column, 70-200 °C). The solid material left in the trap after distillation (*meso*-1,2,3,4-tetrabromobutane) was collected, dried, and weighed. A small portion of the *meso*-tetrabromide was detected by GLC and the equivalent amount of the solid was added to the amount determined from isolation. The other reaction products were collected by preparative GLC and their GLC retention times, mass spectra, ir, and NMR (for the products produced in >2% yield) spectra were compared with those of the authentic materials.

A mixture of products made up of authentic materials, similar to that obtained in the bromination of 1-bromobutane carried out in the 12-l. reaction vessel, was subjected to the reaction condition. The material was isolated and reanalyzed as above. The reanalyzed materials were all reisolated in >97% yield.

Competitive Brominations of 1-Bromobutane vs. 1,2-Dibromobutane and 1,3-Dibromobutane. Mixtures of 1-bromobutane and cyclohexane, 1,2-dibromobutane and cyclohexane, and 1,3-dibromobutane and cyclohexane each containing an internal standard, Freon 113, were prepared. The mixtures were analyzed by GLC (2 m × 5 mm 10% DEGS on Diatoport S, 140 °C). To each mixture was added molecular bromine and an aliquot of each was introduced into a degassed 5-l. reaction vessel. The mixture containing approximately 1.1:1.1:1:1 quantities of brominated hydrocarbon/cyclohexane/Freon 113/bromine (5×10^{-4} mol) were in turn allowed to equilibrate in the reaction vessel and then photolyzed until the bromine color was discharged. The contents of the reaction vessels were condensed in a trap cooled by liquid nitrogen. The organic material was analyzed by GLC. From the relative disappearance of starting material $k_1/k_{1,2} = 4.3$ (1-bromobutane/1,2-dibromobutane) and $k_1/k_{1,3} = >10$ (1-bromobutane/1,3-dibromobutane) could be calculated.[14]

Photobromination of 1,2- and 1,3-Dibromobutane. An aliquot sample (~0.05 ml) of a 0.8 M bromine solution in the dibromide was placed in a 5-l. reaction bulb. After degassing, the substrates were allowed to vaporize and they were irradiated until all the bromine color was destroyed. The products were collected and analyzed by GLC (2 m × 5 mm 10% DEGS on Diatoport S, 140 °C). 1,2-Dibromobutane gave two products, 1,2,2-tribromobutane (94%) and 1,2,3-tribromobutane (6%), while 1,3-dibromobutane gave three products in a ratio of 3.8:18.4:1.0 (in order of elution times). The product with the highest retention time, which made up 4% of the three products, was 1,2,3-tribromobutane, identified by spiking with the authentic material.

Bromination of 1-Butene. 1-Butene, measured in a vacuum line, was distilled into a breakseal and sealed. Bromine was weighed into a breakseal, degassed once, and sealed. The breakseals were attached to the reaction vessel (5, 12, or 22 l.), which was evacuated, and the bromine was introduced into the bulb and allowed to equilibrate for at least 10 min. The 1-butene breakseal was then broken: in the reactions where the reactants were not allowed to equilibrate, the irradiation of the bulb was started before the butene breakseal was broken. The bromine color was rapidly discharged (<5 s). The contents of the bulb were collected, an internal standard (chlorobenzene) and some solid sodium bicarbonate were added, and the solution was analyzed by GLC (3 m × 3 mm 5% Carbowax 20M on Chromosorb P AW, glass column). Four products were detected other than unreacted 1-butene; these were identified by spiking with authentic materials as 1-bromobutane, 3-bromo-1-butene, 1-bromo-2-butene, and 1,2-dibromobutane (see Table II). The reaction mixture was also analyzed on a 3 m × 5 mm 20% Silicone Oil 200 on Chromosorb W glass column at 23 °C to check if any 2-butene was formed. The products were collected by preparative GLC (3 m × 5 mm 10% Carbowax 20M TPA on Chromosorb P AW, glass column). 1-Bromobutane was collected as a mixture with 3-bromo-1-butene. The NMR and mass spectra of these products were identical with those of the authentic materials. A control mixture of 1-bromobutane and 3-bromo-1-butene in the same ratios as listed showed that 1-bromobutane could easily be detected by NMR and mass spectroscopy.

Competitive Bromination of the Allylic Bromides and 1-Bromobutane in the Vapor Phase. An aliquot (0.20 ml) of a Freon 113 solution of 1-bromobutane (1.542 M) and a mixture (3.0:1.0) of 1-bromo-2-butene and 3-bromo-1-butene (1.691 M) was introduced into a degassed 5-l. reaction bulb and allowed to equilibrate for 30 min. A degassed breakseal containing 0.0456 g (2.85×10^{-4} mol) of bromine which was attached to the reaction vessel was broken and the bromine was introduced into the bulb as the reaction mixture was being irradiated (60-W incandescent lamp). The bromine color was discharged in less than 5 s. After the contents of the bulb were collected, an aliquot of a chlorobenzene (internal standard) solution in Freon 113 and some sodium bicarbonate were added, and the solution analyzed for starting materials (6 m × 3 mm 5% UCON POLAR on Chromosorb W) and products (6 m × 3 mm 5% DEGS on Chromosorb W). GLC showed that the solution contained $(3.04 \pm 0.05) \times 10^{-4}$ mol of 1-bromobutane, $(5.19 \pm 0.08) \times 10^{-5}$ mol of allylic bromides, $(3.05 \pm 0.01) \times 10^{-6}$ mol of 1,2-dibromobutane, $(1.48 \pm 0.01) \times 10^{-6}$ mol of 1,3-dibromobutane, and $(2.74 \pm 0.003) \times 10^{-4}$ mol of 1,2,3-tribromobutane. The products were identified by comparison of their retention times with those of authentic materials and spiking. The rate of bromination of the allylic bromides (k_a) relative to that of 1-bromobutane (k_b) was then calculated as

$$\frac{\ln \dfrac{(\mathrm{ABr})^{\mathrm{o}}}{(\mathrm{ABr})^{\mathrm{f}}}}{\ln \dfrac{(\mathrm{RBr})^{\mathrm{o}}}{(\mathrm{RBr})^{\mathrm{f}}}} = \frac{k_a}{k_b} = 146 \tag{7}$$

Photobromination of 1-Bromobutane and Perdeuterio-1-bromobutane with Excess Bromine and Hydrogen Bromide. The brominated substrate, bromine, and hydrogen bromide were separately placed in each of three degassed breakseals and attached to a reaction vessel (5, 12, or 22 l.) which was evacuated and sealed. The breakseals were opened in the absence of light (in the order RBr, hydrogen bromide, and bromine, with 20-min intervals between each breakseal). The mixture of the three reactants was allowed to equilibrate for about 30 min, and then the bulb was irradiated (one 100-W incandescent lamp). The contents of the bulb were condensed in the absence of light into a tube attached to the bulb. The tube was opened, an internal standard added (chlorobenzene), and the excess bromine and hydrogen bromide were destroyed with cold (0 °C) aqueous sodium bisulfite (10%). The organic substrates were extracted with Freon 113 (about 25 ml), the Freon solution washed with cold water and dried ($MgSO_4$). It was analyzed by GLC (2 m × 5 mm 10% UCON 50 LB550X on Chromosorb P AW, glass column) for starting material and products. The solution was concentrated on a 60-cm Teflon spinning-band column to about 4 ml, and the unreacted starting material was collected and recollected by preparative GLC (6 m × 5 mm 10% Carbowax 20M, 50 °C), see Tables IV-VI.

The control experiments that were performed to check the recovery and isolation of the starting material and products were carried out as described above, except that a breakseal containing the products was also attached to the reaction vessel. The products were introduced into the reaction bulb with the other three substrates and the mixture was allowed to stand in the absence of light for at least 1 h. The contents were then collected, isolated, and analyzed as above. The bromination products were each reisolated in from 99.0 to 97.2% yield.

Determination of Residual Protium in the Perdeuterated Substrate. i. Using Mass Spectrometry. The perdeuterated substrate was analyzed on an AEI MS9 spectrometer at 12 eV, using slow magnetic scanning to eliminate peak clipping by the galvanometers. Two samples of RD were scanned five times at the molecular ion region and from the average heights of the peaks, the fraction of protium in the sample was determined by the method of Biemann.[29] This gave the total amount of protium in RD. The amount of protium at each position of the molecule was then determined from the ratio of the signals of the different protons in the 100-MHz ^1H spectrum.

ii. Using Nuclear Magnetic Resonance Spectroscopy. Accurately prepared solutions of RD and 1,1-diphenylethene in Freon 113 were analyzed by NMR spectroscopy using a Varian HR 100 spectrometer. Two spectra were run (normal and deuterium decoupled) with the phenyl protons as lock and reference. A small amount of Me_4Si was added and two more spectra, normal and deuterium decoupled, were run, with Me_4Si as lock and references (see Figure 1). Each spectrum was integrated at least five times and the average values for the integrated areas were again averaged for the four spectra. Both decoupled and undecoupled spectra gave the same integration values within experimental error, showing the absence of any experimentally important Overhauser effects. From the areas of the signal/s from RD and the olefinic protons of 1,1-diphenylethene (δ 5.37), the amount of protium in each position of RD could be determined.

Although the total amounts of protium in the deuterated substrates was always ~0.5% lower when analyzed by the mass spectral method, the differences in protium content between the starting material and the recovered protium-incorporated substrate determined by the NMR and mass spectral methods was always the same, within the experimental limitation given in Table V.

Photobromination of 1-Bromobutane with Isotopically Enriched Bromine-81. Two breakseals containing 1-bromobutane (403.8 mg; 294.7×10^{-5} mol) and molecular bromine (100.6 mg; 62.10×10^{-5} mol, 2.19% bromine-79, 97.81% bromine-81), respectively, were attached to an evacuated 12-l. reaction vessel. The two reactants were introduced into the reaction vessel and allowed to equilibrate in the absence of light for 30 min. The mixture was then irradiated (150-W incandescent lamp) until all of the bromine color was discharged. The contents of the bulb was collected and the hydrogen bromide was distilled and collected in a reaction vessel containing cyclohexene (200 μl). The reaction vessel containing the hydrogen bromide and cyclohexene was shaken at room temperature for 12 h and the cyclohexyl bromide formed was collected by preparative GLC (10 ft × ¼ in. 10% Carbowax 20M TPA, glass column). The trap containing the remaining products from the bromination of 1-bromobutane was frozen (liquid nitrogen) and 4 ml of Freon 113 was added to the frozen mixture. The mixture was thawed and washed with sodium bicarbonate and water and then dried (magnesium sulfate). The reaction products were collected by preparative GLC (10 ft × ¼ in. 10% Carbowax 20M TPA, glass column). The isolated products were analyzed by mass spectrometry (AEI MS9) for their bromine content (see Table III).

Calculation of the Isotopic Distribution of the Individual Atoms in the Dihalides. The relative peak intensities of the parent ions in the mass spectral fragmentation pattern of the dibromide are determined by the expression $(a + b)(a' + b')$, where a and a' are the fractions of bromine-79 in atoms 1 and 2 and b and b' are the fractions of bromine-81 in atoms 1 and 2.[29] Since the products of the expression represent the coefficients of a binomial expansion, the substitution of the intensities of parent ions P_1, P_2, and P_3 (m/e 214, 216, and 218) into a quadratic expression gives the following: $X^2 - (P_2/P_1) + (P_3/P_1) = 0$. The two roots of the quadratic will represent the ratio of $^{79}Br/^{81}Br$ in each atom. Since the sum of fractions $a + b = 1$ and $a' + b' = 1$, a unique isotopic distribution for each atom can be determined.

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Rearrangement of Ethylenebenzenium Ions to α-Phenylethyl (Styryl) Cations. Determination of the Relative Energies of the σ-Bridged Ethylenebenzenium Ion, the Open-Chain 2-Phenylethyl Cation, and the α-Styryl Cation[1]

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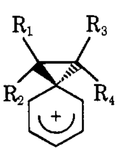
Abstract: 2-Chloroethylbenzene (**3**-H) is initially ring protonated by HF-SbF$_5$ (1:1) in SO$_2$ClF, but upon standing at −78 °C, an irreversible reaction occurs to form the ethylenebenzenium ion (**4**-H). The subsequent quantitative rearrangement of **4**-H to the α-styryl cation (**5**-H) was followed by ^{1}H NMR spectroscopy; for this reaction E_a = 13 kcal/mol, log A = 13.6. **5**-H is stable even at elevated temperatures and does not rearrange to the methyltropylium ion. The analogous rearrangement of **4**-OMe to **5**-OMe was also observed, using *p*-(2-chloroethyl)methoxybenzene as the precursor. The relative energy of the σ-bridged **4**-H and the open-chain 2-phenylethyl cation (**8**-H) are discussed in terms of these results. Carbon-13 chemical shifts are discussed in relation to the structure and charge distribution of these, and related, carbocations.

The solvolytic behavior of β-arylalkyl systems has been one of the most studied and most controversial topics of modern physical organic chemistry.[3] The original proposal by Cram[3a] that the intermediates in these reactions were σ-bridged ethylenebenzenium (phenonium)[4] ions (**1**) was criticized by Brown,[3b,c] who suggested that the experimental data could alternatively be rationalized in terms of weakly π-bridged, rapidly equilibrating ions (**2a**, **2b**). Further solvolytic studies led to the conclusion by Brown that a continuous spectrum of ions exists, from open to completely bridged ions, depending upon solvent and substitution in the ions.[5] It has also been suggested from studies of isotope effects that the initial intermediates in the aryl-assisted pathways are unsymmetrically bridged ions, which may subsequently collapse to ethylenearenium ions (**1**).[3d,6,7] The behavior of 2-arylethyl systems is possibly the most diverse of all the β-arylalkyl systems. Competition between the aryl-assisted and solvent-assisted pathways, which characterize many of the β-arylalkyl solvolyses, is finely balanced.[3d,8]



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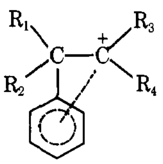
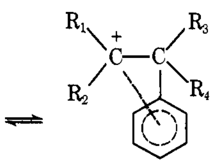


2a



2b

A number of studies aimed at resolving the structure of the intermediate ions from β-arylalkyl precursors by examining these systems under stable ion conditions have been published.