Polar Radicals. III. A Case against Anchimeric Assistance in the Bromination of 1-Bromobutane[1,2]

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Abstract: The photoinitiated bromination of 1-bromobutane with molecular bromine has been reinvestigated. The product distribution obtained at the completion of the reaction was found to be the result of the equilibration of the alkyl radicals which were initially produced by hydrogen abstraction. The alkyl radicals were shown to equilibrate with the hydrogen bromide produced in the reaction, changing the product distribution from that predicted by "normal" polar effects to one which showed an abnormally high yield of 1,2-dibromobutane. The experimental observations clearly rule out participation by a neighboring bromine atom in the rate-determining abstraction step in the halogenation of bromoalkanes. These results are discussed in light of the general problem of bridged bromine intermediates.

Neighboring group participation has been extensively invoked to explain the unusual product distributions obtained in the photoinitiated bromination of bromoalkanes.[5–8] The brominations of *cis*-4-bromo-*t*-butylcyclohexane,[6] 1-bromobutane,[7,9] and *trans*-1-(bromomethyl)-4-methylcyclohexane,[8] among others all give remarkably high yields of the corresponding 1,2-dibrominated alkanes. The chlorination[7,10–13] and bromination[7,12,13] of a series of substituted butanes (see Table I) having electronegative substituents on the terminal carbon have yielded halogenation products whose isomer distributions are strongly influenced by polar deactivation of the hydrogen on the α and β carbons. The results of these substitution reactions suggest that the products of kinetically controlled halogenation reactions of similarly substituted alkanes would show product distributions with low yields of 1,1- and 1,2-disubstituted alkanes. Contrary to these predictions the bromination of a variety of bromoalkanes[6–9] gives anomalous results in that the major product (>80%) is found to be the 1,2-dibrominated hydrocarbon.

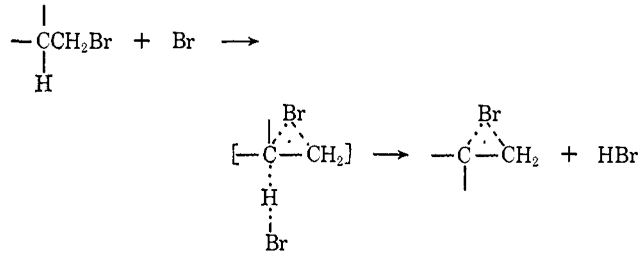

Table I. Product Distributions[a] in the Chlorination or Bromination of Some Substituted Butanes

No.	X	Chlorinations CH_3—	—CH_2—	—CH_2—	—CH_2X	Ref	Brominations CH_3—	—CH_2—	—CH_2—	—CH_2X	Ref
1	Cl	0.40	1	0.48	0.16	10		1	0.49	0.44	7
2	COF	0.24	1	0.37	0.02	11	—	1	0.33	0.42	13
3	COCl	0.44	1	0.40	0.06	11	0.01	1	0.46	0.53	13
4	$OCOCH_3$	0.25	1	0.62	0.03	12	0.01	1	0.40	0.26	12
5	CO_2CH_3	0.29	1	0.70	0.12	13	0.01	1	0.46	0.53	13
6	Br	0.46	1	0.43	0.09	7	—	1	5.78	0.09	7

[a] Relative to the 1,3 isomer.

Recently we have reported that anomalously high selectivities were obtained in the abstraction reactions of chlorine atoms generated from cyanogen chloride.[14] The observed selectivities were shown to be due not to kinetic control, but to the thermodynamic equilibration of the radicals primarily formed. This equilibration of the radicals was demonstrated to be due to the reversibility of reactions between atomic chlorine and the hydrocarbon substrate.

$$RH + Cl\cdot \rightleftharpoons R\cdot_{prim} + HCl$$

$$RH + Cl\cdot \rightleftharpoons R\cdot_{sec} + HCl$$

The well-documented facile reversibility of the reactions of atomic bromine with alkanes[15–17] affords an

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[2] (a) Part I: D. D. Tanner, *J. Am. Chem. Soc.*, **86**, 4674 (1964); (b) Part II: D. D. Tanner and P. B. Van Bostelen, *J. Org. Chem.*, **32**, 1517 (1967).

[3] University of Alberta Postdoctoral Fellow, 1967–1969.

[4] Killam Memorial Postdoctoral Fellow, 1967–1969.

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[15] K. B. Wiberg and L. H. Slaugh, *ibid.*, **80**, 3033 (1958).

[16] H. R. Anderson, H. A. Scheraga, and E. R. Van Artsdalen, *J. Chem. Phys.*, **21**, 1258 (1953).

[17] C. Walling, A. L. Rieger, and D. D. Tanner, *J. Am. Chem. Soc.*, **85**, 3129 (1963), and references cited therein.

analogous explanation for the unusual product distribution found in the bromination of bromoalkanes.

In this paper we report the preliminary results of a study of the mechanism of the bromination of bromoalkanes. We feel that our results are relevant both to the question of kinetic acceleration of hydrogen atom abstraction from bromoalkanes, and to the general problem of the intermediacy of bridged bromine species in free-radical reactions.

Results and Discussion

The bromination of 1-bromobutane in the neat liquid and in acetonitrile was investigated using molecular bromine and N-bromosuccinimide as the brominating agents. Using essentially the same reaction conditions as were used by Thaler in his study of the bromination of 1-bromobutane[7] and similar to those used by Skell,[6] and Traynham[8] in their investigation of the bromination of the other aforementioned bromoalkanes, a mixture of molecular bromine (1.325 *M*) and 1-bromobutane (8.1 *M*) in sealed degassed Pyrex ampoules was irradiated with an incandescent lamp until the reaction mixture was colorless (approximately 50 hr). The reaction products were analyzed by glpc, using the reported procedure,[7] and the isomer distribution of dibrominated butanes was found to be in agreement with that reported by Thaler[7] (compare Table II, reaction 9 and Table I, reaction 6). However, when a series of these reactions was carried out and the photolysis stopped before the bromination was complete, analysis of the reaction mixtures showed a variation of the isomer distribution with the percentage reaction (see Table II, reactions 1–9). The distribution of dibrominated butanes found in the reactions run to low conversion (reactions 1–4) was similar to those found for the "normal" polar deactivation of a negatively substituted butane (see Table I), while at high conversions the product distribution was found to change gradually to approximate that previously reported.[7] The variation of the product distribution with the percentage reaction clearly demonstrates that the ratio of products which are finally formed is not the result of a kinetically controlled substitution reaction.

Table II. Variation of the Isomer Distribution with the Percentage Reaction for the Bromination of 1-Bromobutane with Molecular Bromine[a]

Reaction	Isomer distribution[b] 1,4 C	1,3 C	1,2 C	1,1 CBr	Reaction, %
1	...	1.00	0.53	0.52	2
2	...	1.00	0.56	0.40	4
3	...	1.00	0.52	0.35	9
4	...	1.00	0.67	0.43	18
5	...	1.00	1.10	0.26	29
6	...	1.00	1.54	0.08	38
7	...	1.00	2.05	0.08	59
8	...	1.00	4.20	0.09	84
9	...	1.00	7.30	Tr	95[c]

[a] Values are averages of triplicate analyses of each mixture. [b] Fractional ratios relative to the amount of 1,3-dibromobutane. [c] The value reported represents a material balance for the products determined.

The most reasonable explanation for the dependence of the product distribution upon the percentage conversion involves the equilibration of the primarily produced radicals with hydrogen bromide (eq 1). In the

$$C_4H_9Br + Br\cdot \rightleftharpoons C_4H_8Br\cdot + HBr \quad (1)$$

$$C_4H_8Br\cdot + Br_2 \longrightarrow C_4H_8Br_2 + Br\cdot \quad (2)$$

initial stages of the bromination the reversal of reaction 1 would be unimportant and the transfer reaction of the bromoalkyl radicals with molecular bromine (eq 2) would reflect the kinetically determined distribution of isomeric radicals. As the reaction proceeds to completion (higher concentration of hydrogen bromide, lower concentration of molecular bromine) equilibration of the radicals with hydrogen bromide could lead to the anomalous isomer distributions found in the dibrominated butanes. The effect of increased concentration of hydrogen bromide was demonstrated when series of duplicate brominations were carried out with and without added hydrogens bromide, Table III.

Table III. Comparison of the Isomer Distribution[a] for the Bromination of 1-Bromobutane with Molecular Bromine with and without Added Hydrogen Bromide

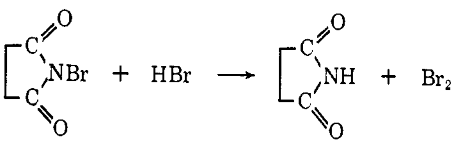
Isomer distribution[b] 1,4 C	1,3 C	1,2 C	1,1 CBr	Time, min	Added hydrogen bromide isomer distribution[b] 1,4 C	1,3 C	1,2 C	1,1 CBr
...	1.00	0.40	0.34	30	...	1.00	2.54	0.30
...	1.00	0.40	0.33	60	...	1.00	4.55	0.20
...	1.00	0.62	0.15	120				
				160	...	1.00	6.34	0.28
...	1.00	1.58	1.40	180				

[a] Relative to 1,3-dibromobutane. [b] Values are averages of triplicate analyses of each reaction.

The brominations carried out in the presence of added hydrogen bromide (0.34 *M*) rapidly (160 min) attained the isomer distribution found at the completion of the reactions without added hydrogen bromide. After equivalent times, similar reactions without added hydrogen bromide showed product distribution typical of those found at the initial stages of the bromination.

An attempt was made to eliminate the effect of hydrogen bromide on product distribution by carrying out the bromination with N-bromosuccinimide (NBS). The well-established mechanism for aliphatic bromination by NBS[17–19] has been shown to proceed by a bromine atom chain.

$$RH + Br\cdot \longrightarrow R\cdot + HBr \quad (3)$$



(4)

$$R\cdot + Br_2 \longrightarrow RBr + Br\cdot \quad (5)$$

Heterogeneous mixtures of NBS and 1-bromobutane showed little time dependence in the isomer distribution of dibrominated products. At all of the investigated reaction times the isomer distributions were close to those reported for bromination with molecular bromine at complete reaction. Under these conditions the reac-

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tion of hydrogen bromide with solid NBS (eq 4) is apparently not fast enough to compete with the reversal of bromoalkyl radical with the hydrogen bromide. It was noted that NBS brominations on this substrate, unlike those for allylic substitution, showed, during the course of the reaction, the color of molecular bromine.

It was found that quantitative yields of the isomeric dibrominated butanes could be obtained in solvent acetonitrile. The use of this solvent allowed the reactions to be carried out in homogeneous solution. It was anticipated that the reverse of eq 3 would be slower than the reaction of NBS with hydrogen bromide (eq 4), if the reactions were carried out in homogeneous solution. At the initial stages of the reaction (high concentration of NBS), the reaction of hydrogen bromide with NBS does predominate over the reversal reaction and the "normal" distribution of dibrominated butanes is observed (see Table IV). At higher conversion (low concentrations of NBS) the reaction of hydrogen bromide with an alkyl radical competes favorably with its reaction with NBS, and the product distribution changes in a manner similar to that obtained upon complete bromination with molecular bromine. Furthermore, as in the NBS brominations carried out as heterogeneous mixtures, the color of molecular bromine was present during photolysis.

Table IV. Variation of the Isomer Distribution with Time[a,b] in the Bromination of 1-Bromobutane with *N*-Bromosuccinimide in Acetonitrile

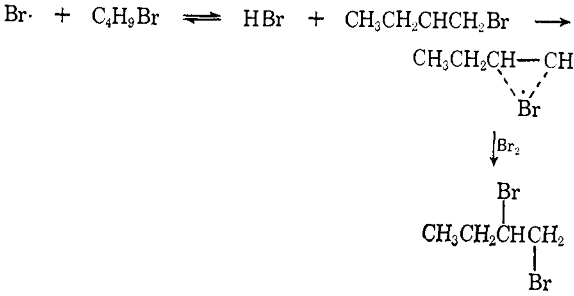
Isomer distribution 1,4 C	 1,3 C	 1,2 C	 1,1 CBr	Time, hr	Total yields of dibromides, %
...	1.00	0.29	0.19	0.5	5.5
...	1.00	0.28	0.23	1	8.0
...	1.00	0.30	0.23	2	8.2
...	1.00	0.38	0.25	3	11.7
...	1.00	0.95	0.24	5	22.6
...	1.00	1.15	0.21	8	23.4
...	1.00	1.23	0.20	12	28.2
...	1.00	2.09	0.15	14	64.7
...	1.00	2.37	0.13	24	75.4
...	1.00	4.61	Trace	26	82.0
...	1.00	5.15	0.12	32	82.3
...	1.00	5.16	0.10	48	
...	1.00	5.09	Trace	72	95.5
...	1.00	5.51	Trace	111	105.0

[a] Values are averages of triplicate analyses of each reaction mixture. [b] Relative to the 1,3 isomer.

Brominations of 1-bromobutane with molecular bromine in acetonitrile gave results similar to those obtained in the neat liquid, although quantitative yields of dibrominated butane could not be obtained due to the reactions of molecular bromine with acetonitrile.

Although the establishment of the equilibration of the initially produced radicals with hydrogen bromide clearly rules out a kinetically accelerated abstraction of the β hydrogen, the question remains unanswered as to why the radical leading to 1,2-dibromobutane should apparently give rise to preferential product formation relative to the α or γ radicals which lead to 1,1- or 1,3-dibromobutane.

Several possible explanations for the preference for β bromination can be proposed although at this time no definite conclusion can be reached. One possibility is the formation of a bridged intermediate after abstraction (eq 6), but this seems rather unlikely since no kinetic acceleration was observed.



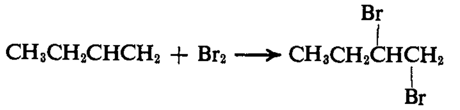
(6)

Resonance stabilization of the β radical by the neighboring bromine atoms (eq 7) is another possible explanation of the enhanced stability of the β radical.

$$\begin{array}{r} Br\cdot + CH_3CH_2CH_2CH_2Br \rightleftharpoons HBr + CH_3CH_2\underset{\cdot}{C}HCH_2Br \\ \updownarrow \quad\quad \\ CH_3CH_2CH{=}CH_2Br\cdot \end{array} \quad (7)$$

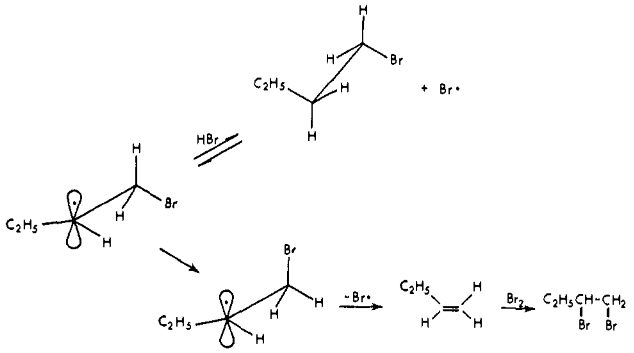
An attractive alternative explanation for the observed product distribution is in terms of the well-documented elimination of a bromine atom by β-scisson to form the olefin[20,21] and the subsequent addition of molecular bromine to form the 1,2-disubstituted dibromide (eq 8 and 9).

$$CH_3CH_2CHH_2\dot{C}Br \longrightarrow CH_3CH_2CH{=}CH_2 + Br\cdot \quad (8)$$



$$CH_3CH_2CHCH_2 + Br_2 \longrightarrow CH_3CH_2\overset{Br}{\overset{|}{C}}H\underset{\underset{Br}{|}}{C}H_2 \quad (9)$$

Our results may well be explained by this last proposal. The initially formed radicals undergo rapid reaction with hydrogen bromide, and reversibility competes with chain transfer with molecular bromine. When the radical formed is β to the bromine substituent, it has the additional possibility of being able to eliminate to give the olefin,[22] if it is in the proper steric orientation.



The olefin so formed rapidly adds bromine,[23] by either an ionic or a free-radical mechanism, giving in either case a predominantly *trans* dibromide. A similar elimination–addition mechanism has previously been put forward in a similar context to explain the re-

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(20) B. P. McGrath and J. M. Tedder, *Proc. Chem. Soc.*, 80, 199 (1961).

(21) C. Walling, "Free Radicals in Solution," John Wiley & Sons, Inc., New York, N. Y., 1957, pp 302–308.

(22) P. S. Fredricks and J. M. Tedder, *J. Chem. Soc.*, 144 (1960).

(23) W. O. Haag and E. I. Heiba, *Tetrahedron Lett.*, 3679 (1965).

arrangement products found in the chlorination of *t*-butyl bromide by *t*-butyl hypochlorite.[24] Similarly, a precedent exists in the chlorination of 1-bromobutane, in which 1,2-dichlorobutane is suggested as arising through an elimination–addition process.[22]

The elimination–addition mechanism could be subject to further modification. As pointed out by a referee the conversion of the alkyl bromide to olefin could be catalyzed by hydrogen bromide by a process involving simultaneous hydrogen abstraction by Br· and loss of Br· which is complexed to HBr.

Finally, in the brominations carried out by means of NBS, it might be expected that if elimination to the olefin (eq 8) occurs, then the allylic substitution product should be formed, as usually happens in NBS brominations. However, our reactions with the deactivated substrate 1-bromobutane were characterized by abnormally long reaction times compared with reactions of unsubstituted hydrocarbons. During the reaction molecular bromine attained a sufficiently large concentration to be visible, and since allylic bromination is dependent upon the concentration of molecular bromine being very small,[20] addition of bromine to the olefin is the predominant reaction.

Experimental Section

Materials. All chemicals were commercially available. Purification of 1-bromobutane was accomplished by washing with concentrated sulfuric acid followed by fractional distillation. Acetonitrile was distilled from phosphorus pentoxide and stored over activated molecular sieve No. 3A. Bromine and N-bromosuccinimide were used without further purification.

Bromination of 1-Bromobutane with Molecular Bromine. The reaction mixture consisted of a 1:6 mole ratio of bromine to the neat alkyl halide. The solutions were degassed by the freeze–thaw method and irradiated in sealed Pyrex ampoules with a 100-W incandescent lamp at 30°. The ampoules were removed after various lengths of time, 1,4-dichlorobutane was added as an external standard, and the reactions were analyzed on a 10 ft × 0.25 in. SE-30 glpc column. Molar amounts of the brominated products were calculated from calibration plots of area ratios *vs.* the authentic samples. Three of the brominated products were identified by comparison of their retention times on three different glpc columns with those of commercially available compounds. 1,1-Dibromobutane was identified by its nmr and ir spectra. The results of these brominations are shown in Table II.

Bromination of 1-Bromobutane with N-Bromosuccinimide. The reaction mixtures consisted of a 1:6 mole ratio of N-bromosuccinimide to the neat alkyl halide. The reaction mixtures were degassed by the freeze–thaw method and irradiated in sealed Pyrex ampoules with two 200-W incandescent lamps at 30°. After 4 hr, the ampoules were analyzed as above and the isomer distribution was found to be 1.00:6.19 (1,3:1,2-dibromobutane).

In a alternative method, reaction mixtures consisted of 1:4 mole ratio of N-bromosuccinimide to the alkyl halide in acetonitrile. The reaction mixtures were degassed by the freeze–thaw method and irradiated in sealed Pyrex ampoules with two 200-W incandescent lamps at 30°. The tubes were removed after varying lengths of times and analyzed as above. The results are shown in Table IV.

Bromination of 1-Bromobutane with Molecular Bromine in Acetonitrile. The reaction mixtures consisted of 1:4 mole ratios of molecular bromine to the alkyl halide in acetonitrile. The reaction mixtures were degassed by the freeze–thaw method and irradiated in sealed Pyrex ampoules with two 200-watt incandescent lamps at 30°. The ampoules were removed after varying lengths of time and analyzed as above.

Bromination of 1-Bromobutane with Added Hydrogen Bromide. The reaction mixtures consisted of a 1:6 mole ratio of molecular bromine to the neat alkyl halide had been saturated with hydrogen bromide (0.34 *M*). The reaction mixtures were degassed by the freeze–thaw method and irradiated at 30°, along with identical reaction mixtures without added hydrogen bromide. The ampoules were removed after varying lengths of time and analyzed as above. The results are shown in Table III.

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Activation Parameters for the Electron Transfer between Cyclooctatetraene Dianion and Anion Radical[1]

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Abstract: Rate constants and activation parameters have been determined for electron transfer between cyclooctatetraene (COT) dianion and the anion radical for various COT–solvent–M (where M = Li, Na, K) systems. As determined by electron spin and nuclear magnetic resonance, the rate constant for electron transfer (eq 1) is very dependent upon the solvent and the counterion. Even in ammonia, a relatively protic and ionizing solvent, the rate of electron transfer is dependent upon the counterion. Possible line-broadening mechanisms in this solvent are discussed.

Electron spin resonance (esr) spectral parameters for COT–solvent–M systems are temperature, solvent, and counterion dependent.[2] Of particular interest is the reported rate difference of 10^4 for the electron transfer (eq 1) (where π = COT, and $\pi\cdot^{-}M^{+}$ and $\pi^{2-}M_2^{+}$ represent all forms of the ions from tight ion pairs and/or higher agglomerates[3] to dissociated ions) for the

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[1] Anion Radicals in Liquid Ammonia. III. Part II: F. J. Smentowski and G.R. Stevenson, *J. Phys. Chem.*, 73, 340 (1969).

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