[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

The Stereochemistry of Radical Additions. IV. The Radical Addition of Hydrogen Bromide and Deuterium Bromide to *cis*- and *trans*-2-Bromo-2-butene[1,2]

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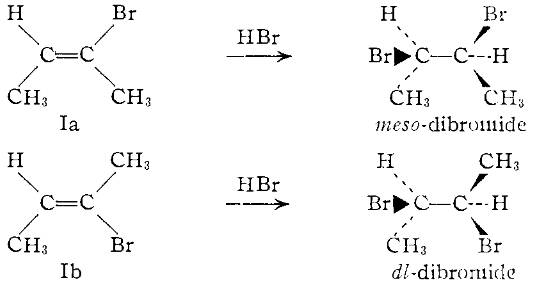
The radical-chain additions of HBr and DBr to the isomeric 2-bromo-2-butenes at −80° in excess liquid HBr or DBr are completely stereospecific. Under these conditions the *trans* addition products are obtained. As the reaction temperature is increased, *i.e.*, as the amount of addendum in the liquid phase decreases, the stereospecificity diminishes to the point where both olefins give essentially the same product at room temperature. Under all conditions the degree of stereospecificity appears to be about the same for HBr and DBr. The intermediate 2,3-dibromobut-2-yl radical reacts about 2.4 times faster with HBr than with DBr. Radical addition gives only 2,3-dibromobutane and ionic addition results in the exclusive formation of 2,2-dibromobutane.

In work described in preceding papers in this series it was found that the radical addition of HBr to 1-bromo-[3,4] and 1-chlorocyclohexene[4] gives the *trans* addition product, *cis*-1-bromo-2-halocyclohexane, almost exclusively. More recently[5] it has been found that the addition of HBr to 1-methyl- and 1-chlorocyclopentene also gives the *trans* addition products, *cis*-1-bromo-2-methylcyclopentane and *cis*-1-bromo-2-chlorocyclopentane. The preponderant or exclusive formation of the least stable of the two possible diastereoisomers in each case shows that the addition is stereospecific in these cyclic systems.

A more rigorous test of stereospecificity of addition reactions than is possible with small cyclic olefins is determining if geometrically isomeric olefins give different products (diastereoisomers or mixtures of diastereoisomers of different composition). In the present work we have extended our studies to an acyclic system, the isomeric 2-bromo-2-butenes (I), in which this criterion of stereospecificity can be applied.

From the earlier work[3-6] it appeared that the most likely case for a stereospecific radical addition reaction in an acyclic system would be the addition of HBr in excess hydrogen bromide as solvent. This was inferred from (a) the observation that HBr adds more stereospecifically than other addenda in cyclic systems[4-6] and (b) evidence that the degree of stereospecificity depends on the life time of the intermediate radical formed in the first (addition) step.[6] That the transfer (second) step is more efficient with HBr than with other addenda (and thus the life time of the intermediate radical is shorter) was apparent from the long chains[7] and the relatively very low tendency for telomer formation.

From earlier work concerning the orientation of radical[3-5,7,8] and ionic[7,9] additions of HBr to vinyl halides it was clear that the radical addition of this addendum to the isomeric 2-bromo-2-butenes would give 2,3-dibromobutane and ionic addition would give 2,2-dibromobutane. As shown below, in this system stereospecific (*trans*) radical addition of HBr to the isomeric 2-bromo-2-butenes results in the formation of different products.



Ia → *meso*-dibromide

Ib → *dl*-dibromide

The paper describes a stereochemical study of the radical additions of HBr and DBr to the isomeric 2-bromo-2-butenes.

Results

The isomeric 2-bromo-2-butenes were prepared by dehydrobromination of pure samples of the isomeric 2,3-dibromobutanes.[10] The *trans*-olefin Ib (derived from the *dl*-dibromide) was purified by careful fractionation with an efficient column. This material was shown to be homogeneous by gas partition chromatography (g.p.c.).[11] The *cis*-olefin Ia (derived from the *meso*-dibromide) was more difficult to purify because of its tendency to isomerize to Ib. Samples containing as little as 0.1% of the *trans* isomer (g.p.c.) were obtained by rapid fractionation at reduced pressure. However, the samples of Ia used in some of the earlier experiments contained as much as 2% of the *trans* isomer.

The radical addition reactions were promoted by irradiation with a quartz-jacketed Hanovia type SC-2537 lamp which fit into the test-tube-shaped reaction vessel. The reaction temperature was varied by immersing the reaction vessel in a cooling bath at the desired temperature.

In the first series of experiments to be described the reactants were mixed and then irradiated for

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[1] This work was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command under contract No. AF18(600)1037.

[2] First reported as a Communication, H. L. Goering and D. W. Larsen, THIS JOURNAL, **79**, 2653 (1957).

[3] H. L. Goering, P. I. Abell and B. F. Aycock, *ibid.*, **74**, 3588 (1952).

[4] H. L. Goering and L. L. Sims, *ibid.*, **77**, 3465 (1955).

[5] K. L. Howe and D. W. Larsen, unpublished results.

[6] H. L. Goering, D. I. Relyea and D. W. Larsen, THIS JOURNAL, **78**, 348 (1956).

[7] F. R. Mayo and C. Walling, *Chem. Revs.*, **27**, 351 (1940).

[8] C. Walling, M. S. Kharasch and F. R. Mayo, THIS JOURNAL, **61**, 1711 (1939).

[9] H. L. Goering and L. L. Sims, *ibid.*, **79**, 6270 (1957).

[10] F. G. Bordwell and P. S. Landis, *ibid.*, **79**, 1593 (1957).

[11] Excellent separation of the isomeric 2-bromo-2-butenes, 2,2-dibromobutane and the isomeric 2,3-dibromobutanes was obtained with a 10-ft. column packed with the commercial detergent, Tide. An operating temperature of 70° and flow rate of 40 ml. of helium per minute were used to measure the intercontamination of the isomeric 2-bromo-2-butenes. An operating temperature of 120° was used to analyze mixtures of the dibromobutanes.

five minutes. Air was not excluded in these experiments. At temperatures below the boiling point of HBr (−67°) or DBr (prepared from D_2O and pure PBr_3)[12] the reactions were carried out in excess liquid addendum as solvent. At higher temperatures the olefin was saturated with addendum prior to irradiation and excess addendum was passed through the liquid reaction mixture during the irradiation. After irradiation the excess HBr or DBr was removed by evaporation and the composition of the residual addition product was determined by g.p.c.[11] In all cases components were identified by comparison of infrared spectra with those of authentic samples as well as by comparison of retention times. The results of these experiments are summarized in Table I.

TABLE I

THE RADICAL ADDITION OF HYDROGEN BROMIDE AND DEUTERIUM BROMIDE TO THE ISOMERIC 2-BROMO-2-BUTENES

Temp., °C.	Addendum	No. of runs	Composition of radical addition product[a] *dl*-Dibromide,[b] %
	A. *trans*-2-Bromo-2-butene		
−78	HBr	4	100
	DBr	2	100
−63.5	HBr	4	94 to 100
	DBr	2	94 to 100
−51.6	HBr	2	94 to 96
	DBr	2	92 to 94
−41	HBr	2	92 to 94
−30.6	HBr	4	82 to 86
	DBr	3	83 to 85
−22.8	HBr	1	82
	DBr	1	81
0	HBr	1	83
	DBr	1	79
25	HBr	1	78
	DBr	1	77
	B. *cis*-2-Bromo-2-butene		
			meso-Dibromide,[b] %
−78	HBr	4	90 to 98[c]
	DBr	2	92 to 97
−63.5	DBr	1	91
−51.6	HBr	7	46 to 85
	DBr	2	53 to 65
−41	HBr	2	74 to 81
	DBr	2	27 to 42
−30.6	HBr	2	36 to 43
	DBr	4	39 to 49
−22.8	HBr	1	36
	DBr	1	33
0	HBr	4	25 to 29
	DBr	3	31 to 34

[a] Composition of 2,3-dibromobutane fraction. [b] These adducts are the ones which result from *trans* addition. [c] The *cis*-2-bromo-2-butene used in these experiments contained *ca.* 2% of the *trans* isomer. Thus the formation of 98% *meso*-dibromide corresponds to 100% *trans* addition.

In many of these experiments the only dibromide formed was 2,3-dibromobutane. Since ionic addition gives only 2,2-dibromobutane (see below) it is clear that the 2,3-dibromide results from a radical chain process. In some of the experiments the products contained small amounts of 2,2-dibromobutane which was evidently formed by competing ionic addition. The amount of ionic addition product was generally greater at low temperatures than at high temperatures as would be expected.[3,7] This is probably partly due to the fact that the rate is of a higher order in HBr for the ionic addition[13] than for the radical addition and the concentration increases as the temperature decreases. The amount of competing ionic addition also was found to depend on the time interval between mixing and irradiation. When this interval was <2 minutes only small amounts (*e.g.*, *ca.* 1–3%) of 2,2-dibromobutane were formed at −78°. The last column in Table I shows the composition of the 2,3-dibromide fraction, *i.e.*, the composition of the radical addition product.

In the early experiments small amounts of 1,2-dibromobutane were found in the product.[2] This was apparently due to contamination of the isomeric 2-bromo-2-butenes with 1-bromo-1-butene. The 2-bromo-2-butenes used in those experiments were prepared from commercial 2,3-dibromobutane which contained small amounts of 1,2-dibromobutane. In a separate experiment it was found that dehydrobromination of 1,2-dibromobutane gives 2-bromo-1-butene (39%), *cis*-1-bromo-1-butene (24%) and *trans*-1-bromo-1-butene (37%). With the column used for g.p.c. analysis the latter compound has the same retention time as Ia, and *cis*-1-bromo-1-butene has the same retention time as Ib. Thus this contamination was not detected. In the present work it was found that the only dibromides resulting from the addition of HBr to pure I (prepared from pure 2,3-dibromobutane) are 2,3-dibromobutane (radical addition) and 2,2-dibromobutane (ionic addition).

The data in Table I show that the radical addition reactions of HBr and DBr are essentially completely stereospecific (*trans*) at low temperatures, *i.e.*, in liquid addendum as solvent. The *cis*-2-bromo-2-butene used in these experiments contained 2% of the *trans* isomer and thus a 2,3-dibromide fraction consisting of 98% of the *meso* isomer corresponds to a completely stereospecific *trans* addition.

As the temperature is increased (as the concentration of addendum in the reaction mixture decreases) stereospecificity diminishes and the addition is essentially non-stereospecific at 25°. Under these conditions (*i.e.*, at temperatures above −78°) the recovered olefin was partly isomerized. Since the non-stereospecific addition gives about 25% *meso*-2,3-dibromobutane and 75% *dl*-2,3-dibromobutane (or the deuterated analogs if DBr is the addendum) the *cis*-olefin Ia provides a more sensitive measure of stereospecificity than the *trans* isomer Ib. With the *cis*-olefin the product composition can vary from 100% *meso*-dibromide (stereospecific *trans* addition) to 25% *meso*-dibromide (non-stereospecific addition) whereas with the *trans*-olefin Ib the product can vary only from 100% *dl*-dibromide (*trans* addition) to 75% *dl*-dibromide (non-stereospecific addition). It appears from the

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[12] L. C. Leitch and A. T. Morse, *Can. J. Chem.*, **30**, 914 (1952).

[13] F. R. Mayo and M. G. Savoy, THIS JOURNAL, **69**, 1348 (1947); F. R. Mayo and J. J. Katz, *ibid.*, **69**, 1339 (1947).

data in Table I that there is little, if any, difference in the stereospecificities of the additions of hydrogen bromide and deuterium bromide. Under conditions where the radical additions are stereospecific, the addition of DBr to dimethylacetylene gives pure *dl*-2,3-dibromobutane-2,3-d_2 by two successive *trans* addition reactions.

When the reactions were not irradiated, varying amounts of radical and ionic addition products were obtained together with unreacted olefin. Evidently under these conditions the radical addition is promoted by oxygen or adventitious peroxides. In some cases at −78° the ionic addition product, 2,2-dibromobutane, was formed exclusively. At temperatures of over −30° only the radical addition product, 2,3-dibromobutane, was isolated. The radical addition product was examined for a series of dark reactions at different temperatures. The compositions of the 2,3-dibromobutane fractions (*i.e.*, the stereospecificities) at various temperatures corresponded well to those observed for the light-promoted additions (Table I). As in the case of the light-promoted additions, the stereospecificities for HBr and DBr were about the same.

In another series of experiments mixtures of HBr and DBr of known composition were added to the isomeric 2-bromo-2-butenes at −78°. These experiments were designed primarily to measure the relative reactivities of the two addenda in radical addition reactions. However, information concerning (a) the stereochemistry of the radical addition reaction and (b) competition between ionic and radical addition reactions was also obtained and is presented in Table II.

TABLE II

RADICAL ADDITION OF HYDROGEN BROMIDE–DEUTERIUM BROMIDE MIXTURES TO THE ISOMERIC 2-BROMO-2-BUTENES AT −78°[a]

Addendum–olefin ratio[b]	Dibromobutane composition, % 2,2-	2,3-	Composition of radical addition product *dl*-2,3-Dibromobutane, %
	A. *trans*-2-Bromo-2-butene		
31	10	90	100
29	30	70	100
23	5	95	100
9.4	7	93	100
3.8	2	98	100
2.4	1	99	94
1.0[c]	0	100	95
	B. *cis*-2-Bromo-2-butene		
			meso-2,3-Dibromobutane, %
40	29	71	100[d]
21	36	64	97
10	13	87	97
8.0	15	85	96
5.0	3	97	99
2.0	1	99	67
0.7[c]	0	100	78

[a] In these reactions the addendum and olefin were degassed and transferred to the reaction flask on a vacuum line. After the mixture had warmed up from the liquid air temperature, at which the components were frozen out, to Dry Ice temperature it was irradiated. [b] Molar ratio. [c] In this reaction approximately 10% of the unreacted olefin was recovered. [d] Corrected for intracontamination of the *cis*-olefin with trace amounts of the *trans*-olefin.

Oxygen was excluded in these experiments. The carefully purified reactants were degassed and transferred to the reaction vessel by distillation in a high vacuum system and the reactions were promoted by light. Under these conditions when the reaction mixture was not irradiated, 2,2-dibromobutane was the only addition product.

The composition of the addendum was not the same for all of the experiments listed in Table II. However, as shown in Table I the stereospecificities for HBr and DBr are similar and thus it would appear that the stereochemical results would be the same regardless of the composition of the hydrogen bromide–deuterium bromide mixture.

It is noteworthy that the radical addition is 100% stereospecific under these conditions providing that the addendum–olefin ratio is high. As this ratio decreases (*i.e.*, as the concentration of addendum in the liquid phase decreases) stereospecificity decreases.

The ratio of ionic to radical addition (*i.e.*, 2,2-dibromide/2,3-dibromide) also varies in a predictable manner as the addendum–olefin ratio varies. As mentioned above the rate of the ionic addition is probably more dependent on addendum concentration than is the rate of the radical process. If the reaction mixture is not irradiated and if the addendum–olefin ratio is high (>10) the olefin is completely consumed by ionic addition in less than an hour at −78°.

A few experiments were carried out at temperatures above the boiling point of HBr. In these cases the liquid phase (olefin saturated with HBr) was stirred with a magnetic stirrer and the progress of the reaction was followed by the change in the HBr pressure above the liquid phase. Under these conditions the stereospecificity was higher than the experiments included in Table I. For example, at 25° the 2,3-dibromobutane fractions from Ia and Ib consisted of 50% and 93% *dl*-dibromide, respectively.

The relative reactivities of HBr and DBr with the isomeric 2-bromo-2-butenes at −78° were determined as follows. A large excess (at least 10-fold) of a mixture of HBr and DBr of known composition (determined from volumes and pressures of gaseous components prior to mixing) and a pure sample of Ia or Ib were irradiated. These reactions were carried out under the same conditions as those described in Table II. Under these conditions the radical additions are essentially or completely stereospecific (see Table II). The radical addition product was separated from the ionic addition product by g.p.c. and the ratio of DBr to HBr adduct was determined by infrared analysis.[14] Control experiments showed that the compositions of mixtures of *meso*-2,3-dibromobutane and *erythro*-2,3-dibromobutane-2-*d* or *dl*-2,3-dibromobutane and *threo*-2,3-dibromobutane-2-*d* could be determined to within about 1%.

If it is assumed that the radical addition involves addition of a bromine atom (reaction 1) followed by transfer (reaction 2), the nature of the product depends only on the second step. In other words, the relative rates of radical addition of HBr and

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(14) H. E. Zimmerman, THIS JOURNAL, **79**, 6554 (1957).

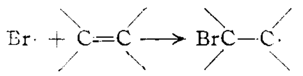
TABLE III

ADDITION OF HYDROGEN BROMIDE–DEUTERIUM BROMIDE MIXTURES TO THE ISOMERIC 2-BROMO-2-BUTENES[a]

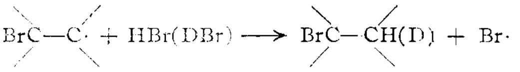
Compn. of addendum % DBr	Compn. of product % DBr adduct[b]	k_H/k_D
	A. *trans*-2-Bromo-2-butene	
82	65	2.5
78	60	2.4
75	53	2.7
53	34	2.2
41	22	2.5
34	18	2.5
21	10	2.4
	B. *cis*-2-Bromo-2-butene	
83	69	2.2
83	67	2.4
76	56	2.5
75	54	2.6
74	55	2.3
51	29	2.6
26	13	2.4

[a] These reactions were run at −78° with oxygen-free mixtures of addendum and olefin. [b] The radical addition product (2,3-dibromobutane) was separated from the ionic addition product by g.p.c. These compositions are for the pure 2,3-dibromobutane fraction.

DBr will be the same as the relative rates at which they undergo the transfer step. Thus relative rates of addition provide a measure of the isotope effect (k_H/k_D) for reaction 2.



$$\mathrm{Br\cdot} + \mathrm{C{=}C} \longrightarrow \mathrm{BrC{-}C\cdot} \qquad (1)$$



$$\mathrm{BrC{-}C\cdot} + \mathrm{HBr(DBr)} \longrightarrow \mathrm{BrC{-}CH(D)} + \mathrm{Br\cdot} \qquad (2)$$

The value of the isotope effect (k_H/k_D) for the reaction of the 2,3-dibromobut-2-yl radical was determined from the relationship of the composition of the addendum and product using the equation.

$$k_H/k_D = [(\mathrm{DBr})/(\mathrm{HBr})][(\text{olefin}\cdot\mathrm{HBr})/(\text{olefin}\cdot\mathrm{DBr})]$$

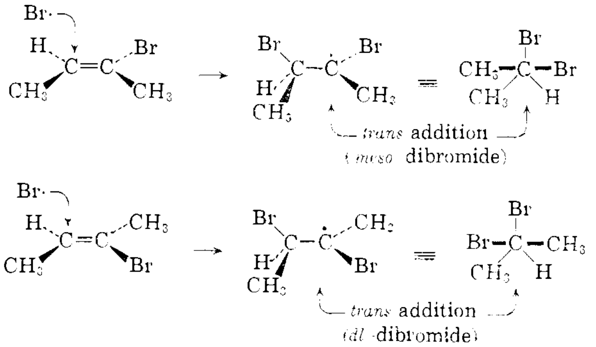
In this equation (olefin·HBr) and (olefin·DBr) represent the hydrogen bromide and deuterium bromide adducts, respectively. The data in Table III show that in the present case the isotope effect for reaction 2 is 2.4 ± 0.1.

Discussion

If the radical chain addition is a two-step process[15] it is clear that isomeric intermediate radicals are formed from the isomeric 2-bromo-2-butenes. As illustrated below, if the process is written in its simplest form (*i.e.*, if the radicals are assumed to have classical structures) the radicals are rotational isomers. In these illustrations it is assumed that the bromine atom approaches from a direction perpendicular to the σ-bonds in the double bond[4] and that the radicals are planar. It should be pointed out that the latter assumption, which is probably correct,[16] is not important in the following discussion. If the radical is non-planar and inverts (oscillates) rapidly, the planar structure represents an average configuration. In any event, the isomeric radicals are interconverted by rotation about the C_2C_3 bond and in no other way without bond rupture.

According to this interpretation the isomeric radicals are intercepted in liquid HBr and DBr more rapidly than they undergo rotation about the C_2C_3 bond. As conditions are made less favorable for a rapid transfer step (by decreasing the addendum concentration) interconversion of the radicals competes with the transfer and stereospecificity diminishes. It is interesting to note that the isomerization of the olefin under conditions where the reaction is not stereospecific is consistent with this picture. It has been shown previously[17] that the barrier for rotation (interconversion) in a radical similar to that involved here is comparable to and probably a little larger than that for reversal of the addition step. In other words, if the radical is not intercepted before it loses its stereochemical identity it would be expected to return in part to isomerized olefin.

The intermediate radicals would be expected to be converted to the *trans* addition products providing the barrier for rotation is higher than that for transfer. The advantages for forming the *trans* adducts are perhaps most apparent from the end-on views of the radicals shown at the right. Bond formation in the direction indicated by the arrows not only avoids interactions with the C_3-bromine, but also permits a smooth transition to product without the eclipsing of bonds.



According to the above picture an apparently second-order transfer step competes successfully with rotation about a σ-bond. Clearly the activation energy for the transfer step—from bond dissociation energies it appears that in the present system this reaction is about thermally neutral—must be very low.[18] Even so it would appear that the energy required for the two reactants to diffuse together would be comparable to that for intercon-

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[15] M. S. Kharasch, H. Engelmann and F. R. Mayo, *J. Org. Chem.*, **2**, 288 (1937); D. H. Hey and W. A. Waters, *Chem. Revs.*, **21**, 169 (1937).

[16] Apparently methyl radicals are planar, T. Cole, H. O. Pritchard, N. R. Davidson and H. M. McConnell, *Molecular Phys.*, **1**, 406 (1958), and it would seem that replacement of hydrogen by larger substituents would make the planar configuration more favorable relative to non-planar configurations. There are other indications that the planar configuration is the most stable one; *e.g.*, see J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, p. 444; and A. Rajbenbach and M. Szwarc, *Proc. Chem. Soc.*, 347 (1958).

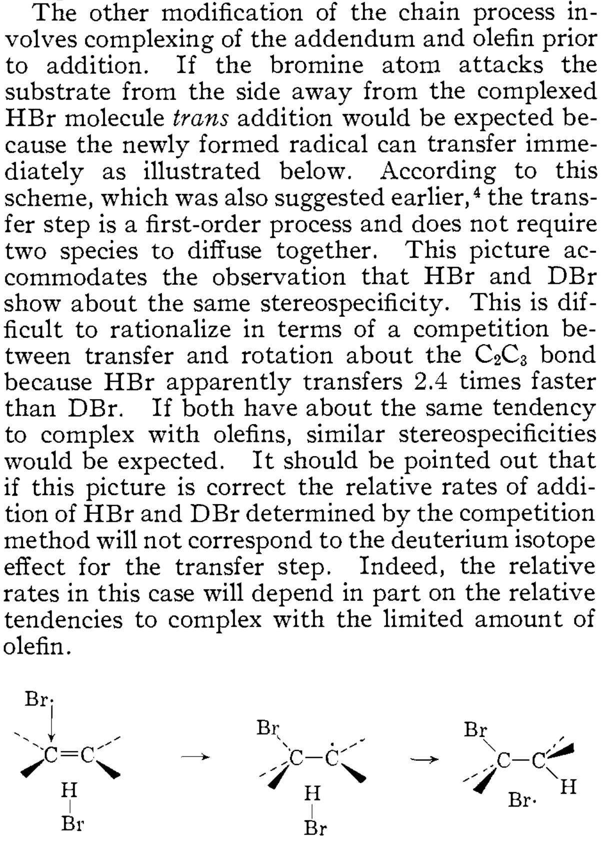
[17] H. Steinmetz and R. M. Noyes, THIS JOURNAL, **74**, 4141 (1952).

[18] The activation energy for $CH_3\cdot$ + HBr (vapor phase) is 1.5 ± 1 kcal.; H. C. Andersen and G. B. Kistiakowsky, *J. Chem. Phys.*, **11**, 6 (1943).

version of the radicals. The scheme can be modified in two ways to accommodate the observation that under favorable conditions the transfer reaction can be isolated from the interconversion of the isomeric radicals. In one of these the barrier for rotation about the C_2C_3 bond in the radical is increased. In the other the transfer step is facilitated and in fact becomes first order.

It seems possible that the barrier for rotation about the C_2C_3 bond may be higher than expected because of interaction between the C_3-bromine and the trivalent carbon, *e.g.*, the radical may have a bridged structure.[3] This was proposed in an earlier paper[3] to account for the preferred *trans* addition in cyclic systems and could well account for the fact that with a reactive transfer agent present in high concentration the radicals are intercepted before being interconverted.

The other modification of the chain process involves complexing of the addendum and olefin prior to addition. If the bromine atom attacks the substrate from the side away from the complexed HBr molecule *trans* addition would be expected because the newly formed radical can transfer immediately as illustrated below. According to this scheme, which was also suggested earlier,[4] the transfer step is a first-order process and does not require two species to diffuse together. This picture accommodates the observation that HBr and DBr show about the same stereospecificity. This is difficult to rationalize in terms of a competition between transfer and rotation about the C_2C_3 bond because HBr apparently transfers 2.4 times faster than DBr. If both have about the same tendency to complex with olefins, similar stereospecificities would be expected. It should be pointed out that if this picture is correct the relative rates of addition of HBr and DBr determined by the competition method will not correspond to the deuterium isotope effect for the transfer step. Indeed, the relative rates in this case will depend in part on the relative tendencies to complex with the limited amount of olefin.



From the present results it seems doubtful that stereospecific radical additions in acyclic systems will be observed with other addenda. Judging from chain length and tendencies to give telomers, HBr and DBr are much more efficient transfer agents than other addenda. With these compounds stereospecificity is observed only under conditions which are the most favorable for a rapid transfer step. It would appear that sulfhydryl compounds would be the next most likely type of addenda to add stereospecifically. In this connection it is noteworthy that preliminary results indicate that the addition of hydrogen sulfide to the isomeric 2-chloro-2-butenes in excess liquid hydrogen sulfide is not stereospecific. The formation of identical copolymers from the copolymerization of vinyl acetate with the isomeric dichloroethylenes[19] indicates that the propagation step in polymerizations probably does not intercept the radical fast enough to preserve stereochemistry. From this it would appear that addenda which transfer so sluggishly that telomers are formed with reactive monomers will not add stereospecifically. In this connection it is interesting to note that the addition of bromotrichloromethane to the isomeric 2-butenes is not stereospecific.[20]

From the data presented in Table II it is apparent that the highest degree of stereospecificity is observed under conditions least favorable for isolating the radical addition from the ionic addition. Even with the present system, which is relatively unreactive toward electrophilic addition, ionic addition competes under conditions where the radical addition is completely stereospecific. Since a halogen atom greatly reduces the reactivity of a double bond for ionic addition[21] and slightly increases it for radical addition,[22] it is clear that competing ionic addition would be more serious with dialkylethylenes than with the present system. The present techniques probably could be modified to reduce ionic addition somewhat, *e.g.*, by shortening the time between contact of the reactants and irradiation. However, it appears that dialkylethylenes may be consumed at least in part and perhaps largely by ionic addition under conditions required for stereospecific radical addition. To be sure, the radical addition can be readily isolated from the ionic addition with dialkylethylenes[7] (but evidently not with trialkylethylenes[3]). However, under these conditions the addition is not stereospecific in acyclic systems.

Experimental

Materials.—Anhydrous hydrogen bromide was obtained from the Matheson Co., and was used without purification except by distillation. Deuterium bromide was prepared from D_2O (Stuart Oxygen Co., >99.5% deuterium) and PBr_3.[12] That quite pure DBr was obtained was shown by the n.m.r. spectrum of *dl*-2,3-dibromobutane-2,3-d_2, the adduct obtained with 2-butyne. This spectrum showed no indication of the presence of the undeuterated adduct.

meso-2,3-Dibromobutane was prepared in about 95% yield by the addition of bromine to *trans*-2-butene (Matheson Co., >99% *trans* isomer).[10] This product which contained <2% of the *dl* isomer (g.p.c.), was used to prepare *cis*-2-bromo-2-butene. Samples containing <0.5% of the *dl* isomer were obtained by careful fractionation with an efficient column.

dl-2,3-Dibromobutane was prepared in a similar manner and in comparable yields from *cis*-2-butene.[10] This product contained <2% of the *meso* isomer and was used to prepare *trans*-2-bromo-2-butene. Pure samples were obtained by fractionation.

cis-2-Bromo-2-butene was prepared by the dehydrobromination of *meso*-2,3-dibromobutane.[10] This product contained about 2% of the *trans* isomer. Because of thermal isomerization to the lower boiling *trans* isomer this material could not be purified by fractionation at atmospheric pressure. The material used in some of the experiments contained about 2% of the *trans* isomer. The purest samples (as little as 0.1% *trans* isomer) were obtained by rapid fractionation at 160 mm.

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[19] F. R. Mayo and K. E. Wilzbach, THIS JOURNAL, **71**, 1124 (1949).

[20] P. S. Skell and R. C. Woodworth, *ibid.*, **77**, 4638 (1955).

[21] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapt. 12.

[22] C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 121.

trans-2-Bromo-2-butene was prepared in a similar manner from *dl*-2,3-dibromobutane.[10] This material contained about 2% of the *cis* isomer and was purified by fractionation. Samples containing <0.1% of the higher boiling *cis* isomer were obtained in this way.

2,2-Dibromobutane was prepared by the ionic addition of hydrogen bromide to 2-bromo-2-butene. This material was identified by its physical properties[8] and by its rapid hydrolysis to methyl ethyl ketone when refluxed with water. The physical properties of the bromobutenes and dibromobutanes prepared in the present work are shown in Table IV.

TABLE IV

PHYSICAL PROPERTIES OF THE 2-BROMO-2-BUTENES AND DIBROMOBUTANES [a]

	B.p. °C.	Mm.	$n^{25}D$	d^{25}_4
trans-2-Bromo-2-butene	84.5–85.0	740	1.4565	1.3174
	41.7–42.0	160		
cis-2-Bromo-2-butene	92.5–93.5	740	1.4620	1.3320
	49.0–49.5	160		
meso-2,3-Dibromobutane	103–104	160	1.5093	1.7665
	73.5–74.0	50		
dl-2,3-Dibromobutane	107–108	160	1.5126	1.7864
	75.5–76.5	50		
2,2-Dibromobutane	93.5–94.0	160	1.4990	

[a] These values agree well with those reported previously, ref. 8 and 10; R. T. Dillon, W. G. Young and H. J. Lucas, THIS JOURNAL, **52**, 1953 (1930); A. S. Dreiding and R. J. Pratt, *ibid.*, **76**, 1902 (1954); M. Lepingle, *Bull. soc. chim. France* [4] **39**, 741 (1926); J. Wislicenus and P. Schmidt, *Ann.*, **313**, 216 (1900).

Addition of Hydrogen Bromide and Deuterium Bromide to 2-Bromo-2-butene. Method A.—The data recorded in Table I were obtained as follows. The apparatus consisted of a test-tube shaped reaction flask into which was fitted a quartz jacketed Hanovia type SC-2537 lamp (85% of the light in the 2537 Å. band). The reaction flask was equipped with a capillary inlet tube (at the bottom) and side arm (for Dry Ice condenser or drying tube). During the addition reactions the flask was placed in a cooling bath at the desired temperature. Various temperatures were obtained by freezing solvents to a slurry, *e.g.*, carbon tetrachloride −23°; bromobenzene −31°; acetonitrile −41°; *n*-hexanol −52°; chloroform −64°. Dry Ice in trichloroethylene (−78°) was also used.

In a typical experiment about 1 ml. of liquid hydrogen bromide was distilled into the reaction flask (cooled −78°) containing 0.5 ml. of *trans*-2-bromo-2-butene. After this transfer was complete (5 minutes) the mixture was irradiated for 5 minutes. The reaction flask was then removed from the bath and the excess HBr allowed to evaporate.

At temperatures above the boiling point of HBr and DBr the olefin was saturated with HBr prior to irradiation. During the 5-minute irradiation period HBr was passed through the solution.

The composition of the product was determined by gas chromatography.[11] The retention times varied for different columns and conditions. However, the relative retention times were quite constant. The following relative retention times were observed at 120°: *trans*-2-bromo-2-butene (0.27 ± 0.01); *cis*-2-bromo-2-butene (0.33 ± 0.01); 2,2-dibromobutane = 1; *meso*-2,3-dibromobutane (1.33 ± 0.02); and *dl*-2,3-dibromobutane (1.49 ± 0.02). The various fractions were collected as they emerged from the column and their infrared spectra were compared with those of authentic samples. In these comparisons the spectra were indistinguishable in every case.

Method B.—The apparatus described above was attached to a vacuum line. In a typical experiment HBr was degassed by repeated evacuation of a solid sample at liquid air temperature. Between evacuations the sample was melted and resolidified. The degassed HBr was then allowed to vaporize into a 1-liter container (equipped with a manometer) and then recondensed in a trap containing P_2O_5 on glass wool. This was repeated until the desired amount of HBr (measured by the volume and pressure of the vapor) was collected. The desired amount of DBr was collected in the same trap. About 1.6 g. of degassed *cis*-olefin was transferred to the reaction flask after which the HBr–DBr mixture was also transferred to the reaction flask. The liquid air bath was replaced by a Dry Ice-in-trichloroethylene-bath. After temperature equilibration (15 minutes was allowed for this) the homogeneous solution was irradiated for 2 minutes. The excess addendum was transferred back to the trap in which it had originally been collected and the reaction product was distilled out of the reaction vessel into a trap. The vacuum system was then opened and the product was analyzed by g.p.c. The results of these experiments are shown in Table II.

Both methods were used to add DBr as well as HBr. Under conditions where HBr additions were stereospecific the addition of DBr to *trans*-2-bromo-2-butene gave a compound which had the same retention time and boiling point as *dl*-2,3-dibromobutane. The DBr adduct had a slightly lower refractive index and considerably different infrared and n.m.r. spectra from the HBr adduct. Elimination of HBr and DBr converted the DBr adduct to an olefin that had the same retention time as *trans*-2-bromo-2-butene. The stereospecific addition of DBr to *cis*-2-bromo-2-butene similarly gave an adduct that had the same retention time, slightly lower refractive index and different infrared and n.m.r. spectra from *meso*-2,3-dibromobutane.

The infrared spectra of *meso*- and *dl*-2,3-dibromobutane (HBr adducts) and the deuterated analogs (DBr adducts) have characteristic bands in the infrared region. All of the spectra have strong bands at 6.9 and 7.2 μ. The spectra of *meso*- and *dl*-2,3-dibromobutane have almost identical strong bands at 11.8 μ (only weak peaks in the spectra of the DBr adducts) and the spectra of *erythro*- and *threo*-2,3-dibromobutane-2-*d* have bands at 11.4 and 12.6 μ (absent in the spectra of the HBr adducts). The bands at 11.4 μ (DBr adduct) and 11.8 μ (HBr adduct) were used for the quantitative analysis of mixtures of DBr and HBr adducts.

The data presented in Table III were obtained using the analytical method described by Zimmerman.[14] Spectra of pure liquids were used and the method was calibrated by using synthetic mixtures. A plot of calculated composition *versus* known composition (data for synthetic mixtures) was used to correct all apparent compositions of unknown samples. Control experiments indicated the analysis of DBr–HBr adduct mixtures to be accurate to about ±1%. This error would cause an error in the calculated deuterium isotope effect (relative rate) of from ±0.1 when the product contains 50% DBr adduct to ±0.3 when the product contains 10% DBr adduct.

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