

w , is the difference in hydration between the initial and transition states and is characteristic of the mechanism involved. Although approximately 100 reactions were examined, some anomalies had been noted.¹³ We have obtained curves, sometimes with a minimum, using the Bunnett plot for the acid-catalyzed hydrolysis of nitrophenyl and dinitrophenyl sulfates (Figure 4 and Results). More significantly, we noted that the catalytic efficiency of the different acids varied. An examination of w values for those few A-1 reactions, where data for all three strong acids (HCl, HClO₄, H₂SO₄) are available,¹³ strikingly reveals the significant differences between the catalytic power of the different acids for a given reaction. Clearly the assumption that the activity coefficient ratio in the Zucker-Hammett equation³³ remains constant is untenable, at least for these reactions, and may well fortuitously cancel for some other reactions.

The difficulty is further compounded by the differential effects of acids on the activity coefficients of the Hammett indicators used.³⁶ We have found that the activity coefficients of *o*-nitroaniline, 4-chloro-2-nitroaniline, and 2,4-dinitroaniline decreased to a different extent as a function of acid concentration.³⁷

Bunnett and Olsen have recently modified their original treatment and showed that plots of $\log k_{\psi} + H_0$ against $H_0 + C_{H^+}$ are linear, and that their slopes, ϕ , are related to the effect of activity coefficients on the reaction rate (*i.e.*, to f_s/f^*). Using this treatment we obtained good linear correlations for all the sulfate esters (Figure 7). The ϕ values (Table VII) correspond to little or no water participation in the transition state,¹⁴ but more significantly it is apparent that perchloric acid has the most pronounced effect on the activity coefficient ratio. This is confirmed by the

(36) E. M. Arnett and G. W. Mach, *J. Amer. Chem. Soc.*, **88**, 1177 (1967).

(37) Unpublished work of C. A. Bunton and J. H. Fendler.

negative salt effect of sodium perchlorate on the spontaneous hydrolysis of 2,4-dinitrophenyl sulfate (Table IV). The acids, therefore, not only affect the reaction rate by their proton-donating power but also by virtue of their electrolyte effects which are specific and are likely to be similar to those of the anions of their sodium salts.

The acid-catalyzed hydrolysis of nitrophenyl³⁸ and dinitrophenyl phosphate¹⁶ showed a high degree of dependence on water activity and exhibited rate maxima in the 4–8 *M* region, but for the dinitrophenyl sulfates plots of $\log k_{\psi} + H_0$ against $H_0 + C_{H^+}$ were linear and gave parallel straight lines for HCl, HClO₄, and H₂SO₄ even at different temperatures. One can conclude that the acid-catalyzed hydrolysis of phosphate and sulfate esters follow different mechanisms.

The linear free-energy relationship for the acid-catalyzed hydrolysis of sulfate esters has a slope of approximately 0.3 (Figure 4). The acid catalysis for sulfate ester hydrolysis is therefore less dependent on the electron-withdrawing power of the leaving group than the neutral hydrolysis, where the corresponding slope is 1.2. For phosphate esters the acid hydrolysis is more sensitive to electron-withdrawing substituents than is the monoanion reaction, but less sensitive than the dianion reaction.¹⁶

Registry No.—*o*-Nitrophenyl sulfate, 17396-91-7; *m*-nitrophenyl sulfate, 3233-64-5; 2,4-dinitrophenyl sulfate, 17396-93-9; 2,5-dinitrophenyl sulfate, 17396-94-0; NaCl, 7647-14-5; NaClO₄, 7601-89-0; Na₂SO₄, 7757-82-6; CuSO₄, 7758-98-7; AgClO₄, 7783-93-9; NaF, 7681-49-4; acetonitrile, 75-05-8; dimethyl sulfoxide, 67-68-5; HCl, 7647-01-0; HClO₄, 7601-90-3; H₂SO₄, 7664-93-9.

(38) P. W. C. Barnard, C. A. Bunton, D. Kellerman, M. M. Mhala, B. A. Silver, C. A. Vernon, and V. A. Welch, *J. Chem. Soc., B*, 227 (1966).

Bromine Telomerization

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Readily polymerizable olefins such as vinyl chloride, ethyl methacrylate, and styrene can be telomerized with bromine by means of the bromine adducts of certain polyhaloethylenes which act as bromine donors. The tri- and tetrachloro- and bromo- and chlorobromoethylenes were especially efficient for this purpose. The vinyl chloride-bromine dimer and trimer have been separated and characterized. A mechanism has been proposed for this reaction which involves the disproportionation of a polyhaloethyl radical to an olefin and a bromine radical. Efficient bromine donors appear to be those materials which contain bulky electronegative substituents that weaken the carbon-bromine bond and which, in the radical form, lack energy delocalization mechanisms such as resonance and rotation about the carbon-carbon bond.

The feasibility of telomerizing olefins with bromine using bromine donors has been suggested previously.¹ The mechanism in Scheme I was proposed for the free-radical induced reaction between 1,1,2,2-tetrabromoethane and ethylene. In that reaction 1,2-dibromoethylene, 1,2-dibromoethane, and 1,4-dibromobutane were obtained as well as material believed to be 1,6-dibromohexane.

The above reaction scheme represents a free-radical chain telomerization of ethylene (the taxogen) by

bromine (the telogen) with 1,2-dibromoethylene acting as a bromine carrier. Although proof of this mechanism was not obtained at the time, the material balance was in agreement with the proposed reaction course. The identification of 1,6-dibromohexane, which would have proved telomerization, was only putative, owing to its low concentration in the product.

Further work in these laboratories has now shown that certain olefins can indeed be telomerized with bromine by the use of materials which can act as bromine donors in such systems. High conversions have been obtained with vinyl chloride. Ethyl methacrylate

(1) M. Rogozinski and L. M. Shorr, *J. Org. Chem.*, **29**, 948 (1964).

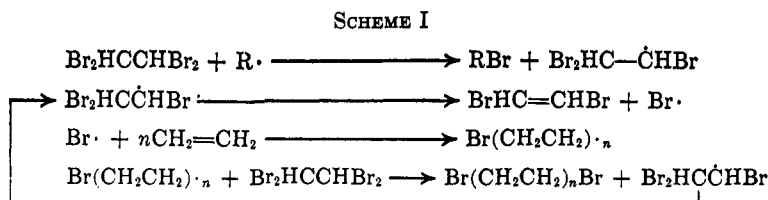


TABLE I
BROMINE TELOMERIZATION OF VINYL CHLORIDE^a

Expt no.	Bromine donor	Bromine carrier	Molar ratio vinyl chloride/donor	Product composition, % ^b					Donor conversion, %	Fraction of donor radicals exhibiting		
				Carrier	Donor	$n = 1$	$n = 2$	$n = 3$		$n = 4^c$	Free rotation	Partial rotation
Type A donors												
1	1,1,2-Tribromotrichloroethane	Bromotrichloroethylene	8	32.5	5.3	2.6	24.7	12.9	4.7	0	0	1
2	1,2-Dibromotetrachloroethane	Tetrachloroethylene	4	37.2	30.1 ^d	11.8		13.7	4.6	0	0	1
3	Pentabromoethane	Tribromoethylene	2 ^e	45.6 ^f				36.5	16.2	1.6	0	1
4	1,2-Dibromotrichloroethane	Trichloroethylene	1	27.9	17.5	17.6	17.6	2.9	0.3	66.6	0	1
5	1,2-Dibromotrichloroethane	Trichloroethylene	2	39.0	13.3	12.6	22.6	10.3	1.0	86.7	0	1
6	1,2-Dibromotrichloroethane	Trichloroethylene	2 ^e	39.7	13.9	7.2	29.1	10.0		86.5	0	1
7	1,2-Dibromotrichloroethane	Trichloroethylene	6	22.2	0.3	4.5	18.5	32.8	11.1	99.6	0	1
Type B donors												
8	Hexabromoethane	Tetrabromoethylene	10 ^g	Traces		Traces	Traces	Traces	Traces	0	0	1
9	1,1,2,2-Tetrabromoethane	1,2-Dibromoethylene	2 ^g	4.3	82.6 ^d	0.6		3.0	2.2	0	0.66	0.33
10	1,2-Dibromo-1,2-dichloroethane	1,2-Dichloroethylene	2	11.9	69.3	2.6	1.4	2.0	1.7	0	0.66	0.33
11	1,1,2-Tribromoethane	Bromoethylene	2	2.3	93.8	1.4	0.2	0.4	Traces	0.33	0.66	0
12	Ethyl α,β -dibromo- α -methylpropionate	Ethyl methacrylate	2	3.4	80.9	0.3	1.4	1.6	1.1	1	0	0
Type C donors												
13	1,2-Dibromochlorotrifluoroethane	Chlorotrifluoroethylene	1			<i>h</i>				0.5	0.5	0
14	1,2-Dibromoethane	Ethylene	2			<i>h</i>				1	0	0
15	α,α' -Dibromosuccinic acid	Maleic acid	8			<i>h, i</i>				1	0	0
16	β -Phenyl- α,β -dibromopropionic acid	Cinnamic acid	8			<i>h, i</i>				1	0	0
17	Dimethyl α,α' -dibromosuccinate	Dimethyl maleate	5			<i>h, i</i>				1	0	0
18	α,β -Dibromopropionitrile	Acrylonitrile	2			<i>h</i>				1	0	0
19	1,2-Dibromo-1,2-diphenylethane	Stilbene	40			<i>h</i>				1	0	0

^a Reactions run for 4 hr at 85° with 1 mol % benzoyl peroxide (based on donor) unless stated otherwise. ^b Analysis by gas chromatography. ^c Putative. ^d Not separated from dimer. ^e Photoinitiation, sunlight, 8 hr at ambient temperature. ^f Not separated from monomer. ^g At 110°. ^h No bromine telomer detected. ⁱ Analysis by tlc.

and styrene were also shown to telomerize in this way. Of the materials examined for bromine carrying properties, ethylenes with three or more chlorine or bromine atoms, such as trichloro-, tribromo-, and tetrachloroethylene, were found to be the most efficient.

Attempts to produce chlorine telomerization with chlorinated ethanes proved unsuccessful.

Results

Of all the olefins examined as taxogens only vinyl chloride, ethyl methacrylate, and styrene exhibited high telomerization efficiencies. As the lower vinyl chloride telomers were readily analyzable by gas chromatography, vinyl chloride was the taxogen used for screening most of the bromine donor candidates.

Bromine Donor Candidates.—The results of the reaction of vinyl chloride with various bromine donor candidates are summarized in Table I. The bromine telomer distribution listed refers only to the lower telomers, as materials above the tetramer were not eluted under the gas chromatographic conditions employed. Conversions are given only for 1,2-dibromotrichloroethane for which the ratios of the concentrations of the regenerated carrier and unconverted donor were readily determined by gas chromatography.

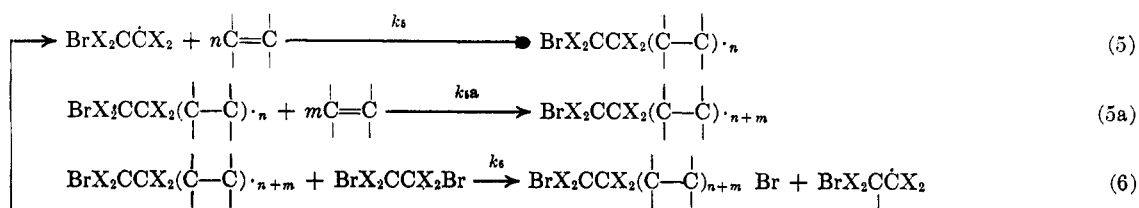
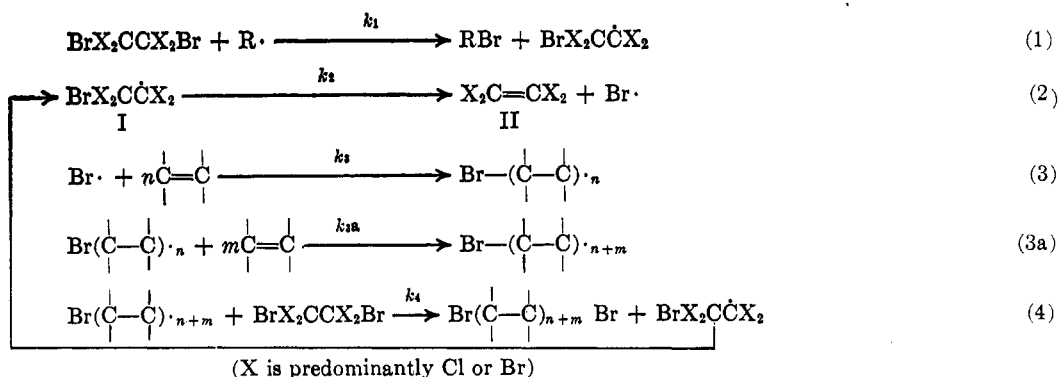
The materials examined can be divided into three groups: (A) efficient bromine donors, (B) poor bro-

mine donors, and (C) materials which did not act as bromine donors.

Group A contains all of the bromine adducts of the tri- and tetrachloro- and bromoethylenes examined except that of tetrabromoethylene. Conversions were not determined for all of the bromine donors, but a comparison of their telomer distributions with those of 1,2-dibromotrichloroethane shows that all the materials in this group gave high conversions which increased with the taxogen-donor ratio. Vinyl chloride conversions were not determined as it was difficult to completely degas the products. However, judging by the amount of vinyl chloride recovered by short degassing periods, the conversions of the latter were also high, and, as would be expected, increased with decreasing taxogen-donor ratio. Experiments 3 and 6 indicate that photoinitiation can be as efficient as peroxide initiation.

Group B consists of material with poor bromine donor properties. All of these, except hexabromoethane, gave rise to viscous products, which were shown by gas chromatography to contain a large number of materials besides low concentrations of bromine telomers.

The product of the reaction with tribromoethane produced a thin layer chromatogram (two-dimensional development) consisting of a curve which changed slope twice. The spots could therefore be divided into three groups. The spots nearest the solvent front con-



tained the vinyl chloride-bromine telomers. The largest group of spots was nearest the origin. Several of these were removed and, on analysis, found to contain bromine. This group of spots lay along a curve of slope different from that characteristic of the vinyl chloride-bromine telomers; they may have been tribromoethane-vinyl chloride telomers.

Bromine telomerization therefore appears to be only a side reaction with the group B materials, the major reaction probably being normal telomerization.

Group C includes those materials which gave products in which neither bromine telomers nor regenerated carrier could be detected. Reaction products of 1,2-dibromoethane, dibromosuccinic acid, and dimethyl dibromosuccinate were all solid and were probably either polymers or high molecular weight normal telomers. The separation of the products by tlc and subsequent analysis of several of the spots for bromine indicated that in the first case the product was a polymer and in the third case it was a normal telomer. 1,2-Dibromochlorotrifluoroethane gave a product containing a large number of components, also probably either normal telomers or polymers. Dibromodiphenylethane and dibromophenylpropionic acid apparently acted as inhibitors as all the vinyl chloride was recovered. This also seems to be the case for dibromopropionitrile as there were only minor changes in reactant composition.

Taxogen Candidates.—Several olefins were examined with a number of bromine donors. The results are summarized in Table II. These olefins can be divided into four types. Type I consists of styrene, ethyl methacrylate, and vinyl chloride which readily undergo bromine telomerization. Both styrene and ethyl methacrylate gave products which were much more viscous than the vinyl chloride telomers. Type II includes ethylene and propylene which produced only the monomeric bromine telomers. In two cases there were indications that propylene underwent allylic bromination, as a material with the expected retention time of allyl bromide was detected. Acrylonitrile and chlorotrifluoroethylene can be classed as type III, high-

activity olefins. Acrylonitrile apparently gave rise to normal telomers and chlorotrifluoroethylene polymerized in the presence of the bromine donor. Type IV includes allyl alcohol and vinyl acetate neither of which appeared to undergo any reaction with the bromine donors examined.

Chlorine Telomerization Attempts.—The following olefins were examined with penta- and hexachloroethane under conditions similar to those used for bromine telomerization: vinyl chloride, ethylene, propylene, styrene, ethyl methacrylate, and acrylonitrile. In no case could any regenerated carrier (trichloro- or tetrachloroethylene) be detected.

Discussion

The bromine telomerization reaction involves an olefin, or taxogen,² and a material capable of acting as a bromine donor. The latter is defined as a compound containing at least two vicinal bromine atoms which, upon having one bromine atom removed (by a free radical, thermally or by irradiation), releases the second bromine atom as a free radical (see eq 1 and 2). The resulting olefin (II in eq 2) will be called the bromine carrier (or carrier) and the intermediate radical (I in eq 2) will be called the donor radical.

The above mechanism can be presented in the generalized form given in eq 1-4. Normal telomerization proceeds as in eq 5 and 6.

Whether the reaction will follow the path of normal telomerization (eq 5 and 6) or that of bromine telomerization (eq 2-4) depends both on the stability of the donor radical (I) and the type of taxogen involved.

The Taxogen.—Relatively stable olefins give rise to very reactive radicals.^{3a} In their presence a donor

(2) The two participants of a telomerization reaction $n\text{C}=\text{C} + \text{XY} \rightarrow \text{X}(\text{C}-\text{C})_n\text{Y}$ are the taxogen (the olefin) and the telogen, the chain-transfer agent X-Y, which gives rise to the two terminal groups of the telomer $\text{X}(\text{C}-\text{C})_n\text{Y}$.

(3) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, New York, N. Y., 1953: (a) p 158; (b) p 233.

TABLE II^a

Taxogen	Donor				
	1,2-Dibromotrichloroethane	Pentabromoethane	1,1,2,2-Tetrabromoethane	1,2-Dibromotetrachloroethane	Hexabromoethane
Type I					
Vinyl chloride	B	B		B	B ^b
Styrene	B	B			
Ethyl methacrylate	B	B			
Type II					
Ethylene	M		B ^b		B
Propylene	M, A	M, A	M	M	M ^b
Type III					
Acrylonitrile	T, M ^c	T			
Chlorotrifluoroethylene	P, M ^c				
Type IV					
Allyl alcohol	N				
Vinyl acetate	N	N		N	

^a Abbreviations are as follows: B = bromine telomerization, M = only monomeric telomer formed, P = polymerization, T = normal telomerization, N = no reaction, A = indications of allylic bromination. ^b Poor yields. ^c Traces.

radical which readily disproportionates will produce a very short reaction chain resulting in the formation of the adduct. On the other hand, if the olefin is too reactive, the reaction chain will be very long and the products, although bromine telomers, will be of such high molecular weight that for all practical purposes they can be considered polymers. Other possibilities with very reactive olefins are (1) that the olefin will react with the donor radical before the latter can disproportionate giving rise to normal telomerization and (2) that the bromine donor may not be involved at all and polymerization will result.

Olefins of intermediate reactivity would therefore be expected to be the most promising candidates for bromine telomerization. Although the reactivity of olefins cannot be classified precisely as it is dependent on the radical involved,^{4a} the susceptibility to polymerization can be taken as a rough measure.

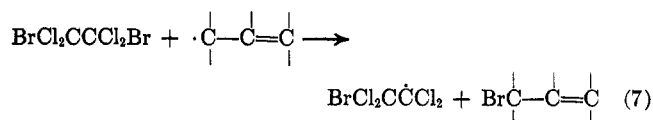
The results reported here support the above conclusions. Neither highly active olefins nor olefins of low activity could be bromine telomerized to any appreciable extent.

Of the three olefins of intermediate reactivity which were readily bromine telomerized (type I), styrene and ethyl methacrylate appeared to be more reactive than vinyl chloride, as they gave rise to more viscous products under the same conditions. This indicates longer reaction chains and is consistent with their greater ease of polymerization and the fact that they are more reactive than vinyl chloride to a variety of radicals.^{4a}

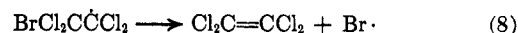
For highly active olefins a bromine donor highly susceptible to bromine abstraction would be required so that it could compete with the olefin for the free radicals. Similarly, with an olefin of low activity a bromine donor of low activity would be required. It has been shown that the second case is indeed feasible and that bromine telomerization can be achieved with olefins of low activity by the use of bromine carriers of low activity.¹ No bromine carrier of sufficiently high activity could be found which would result in bromine telomerization of highly active olefins; the major reaction invariably was normal telomerization or polymerization.

The reported telomerization of acrylonitrile with molecular chlorine⁵ can be considered as an example of the reaction of a highly active olefin with a highly active halogen. A similar reaction could not be induced with molecular bromine⁵ which is less reactive.

Allylic bromination is also a possible side reaction. Huyser and Demott⁶ have found that 1,2-dibromotetrachloroethane can act as an allylic brominating agent. The chain-transfer step proposed by them is given in eq 7. The proposed propagation step in-



involved a β elimination (eq 8) similar to that proposed¹ as the critical step in bromine telomerization.



None of these reactions is mutually exclusive and there were indications in the work reported here that in many cases several of the above-mentioned reactions were indeed occurring simultaneously.

The Bromine Donor.—The conditions necessary for bromine telomerization can therefore be expressed as follows: $k_2 \gg k_5$, $k_{3a} \approx k_4$.

Two properties appear to be essential for a material to serve as an effective bromine donor, *viz.*, (1) susceptibility to bromine abstraction by free radicals (thermally or by irradiation) and (2) disproportionation of the resulting radical into a bromine radical and an olefin.

These two properties could be conferred by substituents which weaken the carbon-bromine bond and/or produce steric strain. Chlorine and bromine answer both these requirements in being both electronegative and bulky. Electronegative substituents, in addition to weakening the carbon-bromine bond, also stabilize the resultant radical. For example, the CCl_3 and CBr_3 radicals are stabilized by 12 kcal of resonance energy.^{4b} This is highly desirable for the first step, as it would favor bromine abstraction, but undesirable for the

(4) C. Walling, "Free Radicals in Solution," John Wiley & Sons, Inc., New York, N. Y., 1957: (a) p 120; (b) p 255.

(5) W. W. Moyer, T. Anyos, and J. L. Dennis, *J. Org. Chem.*, **31**, 1094 (1966).

(6) E. S. Huyser and D. N. DeMott, *Chem. Ind. (London)*, 1954 (1963).

second step, as it would hinder disproportionation. Such stabilization would favor normal telomerization. Other electronegative groups, such as nitrile, carboxyl, phenyl and nitro, would also weaken the carbon-bromine bond but are not so bulky as bromine and would also result in resonance stabilization of the donor radical.

The disproportionation of negatively substituted haloethyl radicals is well known. The reversibility of the addition of halogen radicals has been used to explain the *cis-trans* isomerization of 1,2-dihaloethylenes and other negatively substituted ethylenes in the presence of halogens.⁷ The mechanism proposed involves the reversible addition of a halogen radical to the olefin to produce a trihaloethyl radical which is in a vibrationally excited state and in which rotation about the carbon-carbon bond occurs. It has been suggested that the lifetime of the trichloroethyl radical is substantially longer than its period of internal rotation about the carbon-carbon bond.^{7e,g}

Examination of molecular models of the various donor radicals permitted their classification into three groups. This classification was based on the extent of internal rotation about the carbon-carbon bond and fitted the experimentally found classification as shown in Table I.⁸ The materials whose radicals are completely hindered rotationally are the efficient bromine donors of group A. Those producing partially rotationally hindered radicals are the poor bromine donors of group B. Materials giving rise to radicals possessing free internal rotation have no bromine donor properties and belong to group C. There are three exceptions to this classification. Hexabromoethane should belong to group A but was found to behave as a group B material. This is probably due to its very low solubility. Ethyl dibromomethylpropionate would be expected to belong to group C but behaved as a group B material. Dibromochlorotrifluoroethane exhibited the reverse behavior. These exceptions are not surprising as the donor radical's rotational properties are not the only criterion for disproportionation, the strength of the carbon-bromine bond being involved also. Fluorine substitution has only a minor effect on the carbon-bromine bond strength^{9,10} and it was therefore not surprising to find that dibromochlorotrifluoroethane acted as a group C material whereas the rotational properties of its radical place it in group B.

This suggests that restricted rotation about the carbon-carbon bond confers the bromine donor properties which make materials effective bromine telomerization agents. Even a limited internal rotation in the donor radical would permit realignment resulting in a less strained configuration and, in addition, might also facilitate orbital overlap of the free electron with a

substituent on the adjacent carbon atom, resulting in stabilization of the radical. When such internal rotation is not feasible the radical would be less stable, the steric strain and electrostatic repulsion of the halogens being relieved by disproportionation as the carbon atom adjacent to the radical carbon goes from a tetrahedral to a trigonal configuration.¹¹

As radicals of the group C materials have completely free internal rotation, there is no steric crowding or hindrance to any possibility of orbital overlap and therefore little or no tendency for such radicals to disproportionate. Three of the group C materials, dibromosuccinic acid, dibromodiphenylethane, and dibromophenylpropionic acid, have very low solubilities in vinyl chloride. This could account for their lack of donor activity. However, the fact that two of these materials (dibromodiphenylethane and dibromophenylpropionic acid) acted as inhibitors indicates that their low solubility did not prevent their participation in a radical reaction, as in their absence the vinyl chloride would have been expected to polymerize. In addition, hexabromoethane, which also has a very low solubility in vinyl chloride, did give rise to some reaction.

For the group B materials at least two types of radicals with different rotational limitations are possible. The most likely type of radicals to be formed would be those whose formation involves the greatest relief of strain or produces the more stable radical form. This would account for the fact that with the type B materials bromine telomerization is a minor side reaction.

The failure of attempts to produce chlorine telomerization with penta- and hexachloroethanes, the corresponding radicals of which are also completely hindered rotationally, is probably due to the greater strength of the carbon-chlorine bond. Although a chlorine atom can be readily abstracted from these polychloroethanes, the driving force to relieve steric strain by disproportionation is apparently insufficient to rupture the carbon-chlorine bond.

Experimental Section

Apparatus.—All reactions except those involving ethylene were performed in Pyrex Carius tube reactors fitted with high pressure needle valves.¹² Gaseous olefins were distilled into the reactor which was immersed in a Dry Ice-acetone bath. In the case of liquid olefins the reactor was flushed with nitrogen prior to reaction. For homogeneous systems no mixing was employed, the reactors being immersed in a thermostatically controlled water bath. For heterogeneous systems the reactor was placed in a resistance wire wound metal tube tied to a rocking unit. Reactions involving ethylene were performed in a stainless steel rocking autoclave.

Reaction Conditions.—Reactions were initiated with 1 mol % of benzoyl peroxide, based on the bromine donor, and held 4 hr at 85° except where indicated otherwise. Photoinitiated reactions were performed by placing the reactor in direct sunlight for 8 hr at ambient temperature (25–30°).

Materials. Taxogens.—Liquid olefins were distilled immediately before use. Gaseous olefins were used without additional purification. Nonstabilized vinyl chloride was used throughout.

Bromine Donors.—When not readily available, these were prepared by photobromination of the corresponding olefin. In the case of 1,2-dibromotrifluoroethane a nonstabilized trichloroethylene was used.

(7) (a) R. E. Wood and R. G. Dickinson, *J. Amer. Chem. Soc.*, **61**, 3259 (1939); (b) R. M. Noyes, R. G. Dickinson, and U. Schomaker, *ibid.*, **67**, 1319 (1945); (c) R. G. Dickinson, R. F. Wallis, and R. E. Wood, *ibid.*, **71**, 1238 (1949); (d) H. Steinmetz and R. M. Noyes, *ibid.*, **74**, 4141 (1952); (e) P. B. Ayscough, A. J. Crocker, and F. S. Dainton, *Trans. Faraday Soc.*, **58**, 284 (1962); (f) R. G. Dickinson and H. Lotzkar, *J. Amer. Chem. Soc.*, **59**, 472 (1937); (g) H. Komazawa, A. D. Stefani, and M. Szwarc, *ibid.*, **85**, 2403 (1963).

(8) All the possible radicals formed by removal of the various bromine atoms from the donor were examined. Of the total number of possible radicals for each material the fractions having completely free rotation, partial rotation, and no rotation are listed in Table I.

(9) $D(\text{CH}_2\text{Br}) = 68 \text{ kcal}$, $D(\text{CCl}_2\text{Br}) = 49.5 \text{ kcal}$, $D(\text{CF}_2\text{Br}) = 64.5 \text{ kcal}$.¹⁰

(10) C. T. Mortimer, "Reaction Heats and Bond Strengths," Pergamon Press, Oxford, 1962, p 134.

(11) The comments of one of the referees regarding this point were helpful and are appreciated.

(12) L. M. Shorr, M. Rogozinski, and U. Hashman, *Chem. Ind. (London)*, 52 (1964).

Solid materials were recrystallized to constant melting point. Bromotrichloroethylene was prepared by dehydrobrominating 1,2-dibromotrichloroethane with alcoholic KOH. After bromination and recrystallization the product, 1,1,2-tribromotrichloroethane, was found to contain 10% 1,1,2,2-tetrabromodichloroethane. It had a sealed tube melting point of 175–177° (lit.¹³ mp 175–180°) and was used without further purification.

Dimethyl α,α' -dibromosuccinate was prepared by dissolving the acid in an excess of methanol and adding an excess of concentrated sulfuric acid. The mixture was then refluxed for 20 min. The product after recrystallization had a melting point of 96–101°, but as only a small quantity was available and gas chromatography indicated the presence of only one impurity in low concentration, the product was used without further purification.

All other bromine donors had purities above 98%.

Analysis.—Gas chromatography involved the use of a 4-ft, 0.25-in.-o.d. column packed with 10% silicone gum SE-30 on 60–80 mesh Chromosorb P. The column was programmed from 100 to 350° at 15°/min.

Thin layer chromatography was performed on 0.25-mm-thick films of silica gel G. The developing solvents used were mixtures of hexane with benzene, carbon tetrachloride, or chloroform. Development was two dimensional and detection, by spraying with a 0.1% aqueous solution of crystal violet. Blue spots on a pale violet background were produced. For halogen determination the relevant spot was transferred to a filter paper and combusted in an oxygen flask, the products being absorbed in 0.1 N NaOH.

The absence of the regenerated bromine carrier in the reaction product was considered as indicating that no bromine telomerization had occurred. This test was often the only one that could be performed on intractable solids, which were solvent extracted for the purpose.

Product Examination. Vinyl Chloride.—Both the regenerated carrier and the monomeric telomer, 1,2-dibromochloroethane, were identified by retention time comparison with authentic samples. The dimer and trimer were separated by fractional vacuum distillation of a vinyl chloride–1,2-dibromotrichloroethane reaction product. The dimer was further purified by preparative gas chromatography. The trimer was difficult to trap out of the carrier gas stream owing to aerosolizing and no further purification was undertaken.

Dimer.—The dimer fraction contained 97.4% dimer, 1.2% trimer, and several unidentified materials.

The principle ir absorption bands were 3.3 (w), 7.0 (s), 7.7 (sh m), 10.0 (s), 10.7 (sh m), 10.8 (s), 13.1 (s b) and 14.2 μ (s b).

Physical properties were as follows: $d^{25.5}_4$ 1.980; $n^{25.5}_D$ 1.5460; specific refraction, 0.1600 (calcd 0.1606); bp (gc estimated) 235°. Elementary analysis¹⁴ was in good agreement with calculated values.

Anal. Calcd for $C_4H_6Cl_2Br_2$: C, 61.87; H, 2.14; Cl, 24.90; Br, 56.11. Found: C, 16.88; H, 2.14; Cl, 25.10; Br, 56.04.

Nmr spectroscopy indicated the following: δ ~6.1 (symmetrical ten line, one proton, $-CHBrCl$), ~4.28 (multiplet, one proton, $>CHCl$), ~3.79 (multiplet, two protons, $-CH_2Br$); ~2.92 ppm (multiplet, two protons, $>CH_2$).

These results indicate the following structure for the dimer: $Br(CHClCH_2)_2Br$, 1,4-dibromo-1,3-dichlorobutane, which is in agreement with the head to tail coupling normally obtained in vinyl polymerization.^{13b}

Trimer.—The trimer fraction consisted of 93.3% trimer, 3.4% dimer, and three unidentified materials.

The principle ir absorption bands were (μ) 3.3 (w), 7.0 (s), 7.6 (sh m), 7.7 (m), 7.9 (s), 8.0 (s), 8.2 (s), 8.3 (sh s), 9.6 (m), 10.5 (m s), 13.1 (s b), 14.0 (s b).

Physical properties were as follows: d^{25}_4 1.8310; n^{25}_D 1.5474; specific refraction, 0.1733 (calcd 0.1724); bp (gc estimated) 304°. Elementary analysis¹⁴ was in agreement with the calculated values.

Anal. Calcd for $C_6H_8Cl_3Br_3$: C, 20.75; H, 2.61; Cl, 30.62; Br, 46.02. Found: C, 20.71; H, 2.47; Cl, 30.73; Br, 46.28.

Nmr spectroscopy indicated the following: δ ~5.95 [triplet (split), one proton, $-CHBrCl$], ~4.29 (multiplet, two protons,

$2>CHCl$), ~3.56 (multiplet, two protons, $-CH_2Br$), ~2.5 ppm (multiplet, four protons, $2>CH_2$).

These results indicate the following structure for the trimer, $Br(CHClCH_2)_3Br$, 1,6-dibromo-1,3,5-trichlorohexane, which is in agreement with the structure expected from head to tail coupling.

The major gas chromatographic peak emerging after the trimer was assumed to be the tetramer as its separation from the trimer was the approximately constant distance between the lower telomers. This even spacing is characteristic of an homologous series in programmed temperature gas chromatography. As the identity of the monomer, dimer, and trimer had been established for the vinyl chloride–dibromotrichloroethane reaction product, the gas chromatographic spectrum of the latter was used as a reference for examination of other vinyl chloride–bromine donor reaction products. The distilled dimer and trimer were also used as standards in the tlc examination of other vinyl chloride–bromine donor reaction products.

For products of low vinyl chloride–dibromotrichloroethane ratios, tlc gave semiquantitative results in good agreement with those of gas chromatography. For products of higher vinyl chloride–dibromotrichloroethane ratios, tlc showed a large number of spots below the trimer. Several of the spots were removed and found to contain bromine. A plot of the logarithm of the R_F values vs. the degree of telomerization, assuming the spot below the trimer to be the tetramer, the next lower spot the pentamer, etc., was almost linear. As this behavior is characteristic of homologous series,¹⁵ the lower spots appearing on the chromatoplates can be assigned to higher telomers.

Styrene and Ethyl Methacrylate.—Products involving these materials were examined by tlc. With these olefins the evidence of bromine telomerization was indirect and based on the following reasoning. A taxogen which bromine telomerizes with two different bromine donors should give products with identical tlc spectra—except for the two different bromine donors and regenerated carriers. Both these taxogens were treated independently with 1,2-dibromotrichloroethane and pentabromoethane and each gave products producing identical tlc spectra for both bromine donors with the exception of the unreacted bromine donors.¹⁶ In each case several of the spots were removed and found to contain bromine. The presence of the monomer was also established in each product by comparison with the taxogen–molecular bromine addition product. Gas chromatographic analysis showed the regenerated carrier to be present in high concentration in all products. The distribution of spots indicated an homologous series.

Acrylonitrile.—The products obtained from this taxogen were invariably intractable solids and no suitable developing solvent for tlc could be found. They were separated by paper chromatography from the bromine donor by eluting the latter from the static spot. Halogen analysis of the residual spot gave a chlorine–bromine ratio approaching that of the carrier (1.6), indicating the product to be a high molecular weight normal telomer.

Chlorotrifluoroethylene.—This olefin gave a semisolid product which gas chromatography showed to contain a large number of components of extremely wide boiling range, including small quantities of the regenerated carrier (trichloroethylene) and the monomeric telomer (1,2-dibromochlorotrifluoroethane). However, tlc showed that, excluding the bromine donor, none of the large number of spots contained bromine.¹⁷ These spots therefore represented polymers.

Registry No.—1,6-Dibromo-1,3,5-trichlorohexane, 17223-88-0; 1,4-dibromo-1,3-dichlorobutane, 17223-89-1.

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(15) E. Lederer and M. Lederer, "Chromatography," Elsevier Publishing Co., New York, N. Y., 1953, p 76.

(16) The regenerated carriers apparently volatilized off the chromatoplates.

(17) The monomer apparently volatilized off the chromatoplates.