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The Radiation Induced *cis–trans* Isomerization of Polybutadiene. I[1]

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The *cis* double bonds in a high *cis*-polybutadiene in solution are readily converted into *trans* double bonds on exposure to γ-rays in the presence of a suitable sensitizer such as an organic bromide. The isomerization proceeds in the direction of attaining an equilibrium *cis/trans* ratio of approximately 5/95. This reaction is analogous to the recently reported photosensitized *cis–trans* isomerization of polybutadiene. In addition, a very much slower "unsensitized" radiation induced isomerization of the double bonds was also observed in solution. However, no change in *cis/trans* ratio could be obtained on γ-irradiation of the solid polymer. The kinetics of the isomerization of polybutadiene in benzene were studied using allyl bromide, ethyl bromide and ethylene bromide as sensitizers, and found to be first order with respect to the *cis* content in the polymer and somewhat less than half-order in organic bromide. The mechanism is considered to involve π complexing between the double bonds and free bromine atoms formed in the radiolysis of the bromide. An interesting application of this isomerization is its possible use as a dosimeter in radiation chemistry.

Introduction

The *cis–trans* isomerization of compounds containing carbon–carbon double bonds has been known for a very long time, and the role of halogens in catalyzing this isomerization has likewise been studied in fair detail. In the past these investigations were confined to low molecular weight olefins and their derivatives. Until recently, such an isomerization was not known for an unsaturated high polymer. Following the discovery of the photosensitized *cis–trans* isomerization of polybutadiene,[2] it was definitely of interest to see if a similar result could be obtained using high energy radiation. This has indeed been found to be the case, the radiation chemical process being quite comparable to the photochemical one. Both processes are carried out in solution and involve the use of a sensitizer which may be any one of a wide variety of organic bromides, disulfides or mercaptans, as well as elemental bromine itself. These sensitizers vary considerably in their efficiencies, with the bromides as a class being the most efficient so far as γ-radiation is concerned, whereas in the photochemical case the disulfides and the bromides are about equally efficient. Organic sulfides can also be employed to sensitize the photoisomerization but they invariably lead to cross-linking of the polymer when exposed to γ-rays. Although halogen atoms generally are often effective as isomerization catalysts for simple olefinic compounds, the bromides were the only halides which were found to promote the isomerization of polybutadiene. The mobility of the active fragments appears to be essential to the reaction since the polymer could only be isomerized in solution. The isomerization is best carried out in an aromatic solvent inasmuch as aliphatic solvents, such as hexane, cause the polymer to gel on γ-irradiation, making it difficult or impossible to characterize the product.

This paper is concerned with reporting some kinetic data on the radiation induced *cis–trans* isomerization of polybutadiene in benzene solution sensitized by allyl bromide, ethyl bromide and ethylene bromide. At the same time, data are presented for an unsensitized isomerization, *i.e.*, where none of the above-mentioned types of sensitizers was added to the polymer system prior to irradiation.

Experimental

The high *cis*-polybutadienes used in this work were made by stereospecific catalysis and had viscosity average molecular weights in the range 300,000–500,000. They contained approximately 91% *cis*-1,4 and 5% *trans*-1,4 addition units, the rest of the unsaturation consisting of vinyl side groups resulting from 1,2-addition monomer. The latter type of double bonds was not involved in the isomerization, and only the per cent. *cis* double bonds, or *cis/trans* ratio, in the polymer before and after irradiation was significant in this study. The *cis/trans* ratio of the original polymer was thus taken to be 95/5.

Stock solutions of polybutadiene in benzene were made up for γ-irradiation to a concentration of about 10 g./l., to which were added various amounts of allyl, ethyl or ethylene bromide as sensitizers. C.P. materials were used throughout. Portions of the sensitized solutions were placed in ordinary screwcap glass bottles and irradiated at room temperature for various periods of time in a 360-curie Co^{60} γ-ray source which had a radiation intensity of about 1.4×10^5 r./hr. Aliquots of the irradiated solutions were withdrawn after receiving the desired doses and analyzed for residual *cis* content.

Irradiations were ordinarily carried out in air since it was found that gelation of the polymer set in after a dose of about 4×10^5 r. when irradiated in nitrogen, making it impossible to obtain spectra at the higher doses. On the other hand, irradiations in air, while avoiding the difficulty of gel formation, led to very rapid degradation to quite low molecular weights. It was seen, however, that the rate of isomerization was independent of the initial molecular weight and unaffected by the accompanying chain scission in air-irradiation, or by increase in molecular weight to the point of gelation in nitrogen-irradiation. Moreover, although the molecular weight of the polymer irradiated in air rapidly became very small, the spectrum was still acceptable and, except for differences in *cis/trans* ratio, resembled the spectrum for a regular high molecular weight polymer.

The polymer structures were determined by infrared absorption measurements on thin polymer films cast on rock salt plates from benzene solution, using a Perkin-Elmer Model 21 spectrophotometer. Analysis was based on the characteristic absorption bands for the *cis* and *trans* double bonds at 13.6 and 10.35 μ, respectively. The *cis/trans* ratios were calculated from the optical densities of these bands, making use of the fact that the extinction coefficient of the *trans* band is 1.63 times that of the *cis* band.

Typical infrared spectra of the high *cis*-polybutadiene before and after γ-irradiation with allyl bromide as sensitizer are shown in Fig. 1. The observed decrease in the *cis* band corresponds quantitatively to the observed increase in the *trans* band, if the absorbance of the methylene band at 6.9 μ is taken as an internal standard. From the initial *cis/trans* ratio of 95/5, the polymer was isomerized to a structure having a *cis/trans* ratio of about 10/90 in the example given in the figure. At room temperature the isomerization can proceed further until an equilibrium ratio of about 5/95 is

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[1] Presented at the 132nd Meeting of the American Chemical Society in New York, September, 1957. Work was accomplished under Air Force contract, the sponsoring agency being the Materials Laboratory of Wright Air Development Center.

[2] M. A. Golub, *J. Polymer Sci.*, **25**, 373 (1957).

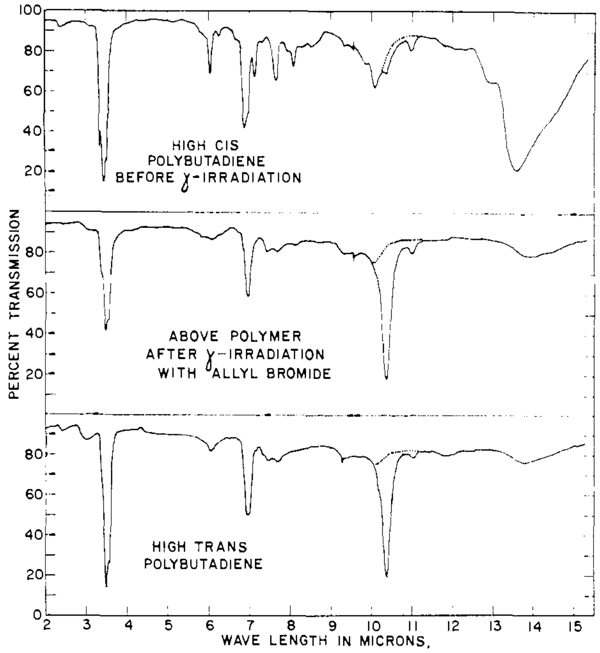

Fig. 1.—The infrared spectra of a high *cis*-polybutadiene before and after γ-irradiation with allyl bromide as sensitizer, compared with the spectrum of a high *trans*-polybutadiene polymerized directly.

attained. In determining the optical density of the *trans* band the background in each spectrum was corrected for the overlapping bands at 10.1 and 11.0 μ (due to the *cis* structure and the vinyl double bonds, respectively), as shown by the dotted lines in Fig. 1. Comparing the spectrum of the irradiated polymer with that of a high *trans*-polybutadiene polymerized directly by stereospecific catalysis, it is evident that, apart from any change in molecular weight accompanying the irradiation, the chief alteration in polymer structure was that of a true *cis* to *trans* isomerization.

To indicate in a qualitative way the change in molecular weight during irradiation, dilute solution viscosity measurements were carried out on some polymer solutions exposed to γ-rays for varying times, with and without sensitizer, in air and nitrogen. Measurements were made at 20 ± 0.1° with standard Ostwald–Fenske viscometers.

The polybutadiene contained the antioxidants N,N′-di-2-naphthyl-*p*-phenylenediamine and di-*t*-butylhydroquinone to the extent originally of about $^1/_2$ and $^1/_4$% by weight, respectively, based on polymer. This polymer displayed a small autocatalytic increase in the rate of isomerization which was completely suppressed by the further addition of about $^1/_2$% by weight of hydroquinone to the polymer. On the other hand, the use of N,N′-diphenyl-*p*-phenylenediamine or some other antioxidant in place of the hydroquinone resulted in a very pronounced autocatalytic effect. Accordingly, the optimum concentration of the hydroquinone, about 1% based on polymer, was used throughout this work.

Results

Typical kinetic plots for the γ-ray induced *cis–trans* isomerization of polybutadiene using allyl bromide as sensitizer are shown in Fig. 2, along with the corresponding plot for the unsensitized isomerization. These plots correspond to the expression for a first-order reversible process[3]

$$k' = \frac{-2.303K}{(1 + K)} \times \frac{d \log (1 - x/x_e)}{dR} \qquad (1)$$

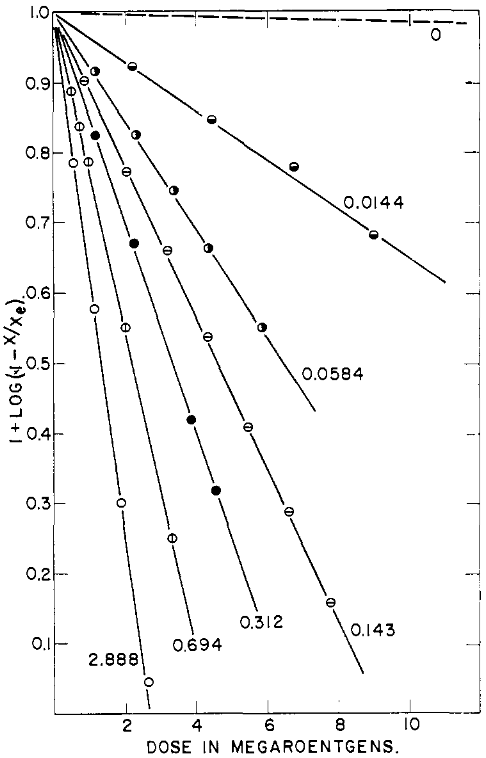

Fig. 2.—Rate of the sensitized isomerization of polybutadiene. Concentrations of allyl bromide are given in moles/l. The dotted line represents the unsensitized isomerization.

where K is the equilibrium constant for the *cis–trans* interconversion, x is the per cent. *cis* changed into *trans* following a radiation dose R, x_e is the per cent. *cis* converted at equilibrium and k' is a quantity which is related to the rate constant k for the sensitized isomerization of the *cis* double bonds through the further expressions

$$k' = k_s + k_u \qquad (2)$$

$$k' = k\,[\text{bromide}]^b + k_u \qquad (3)$$

Here k_u for the unsensitized reaction is just equal to k' in the absence of bromide, and k_s is a convenient quantity representing the rate of the sensitized reaction for a given concentration of bromide. The values of k_s were plotted on log-log paper against the concentrations of allyl bromide used in the various isomerization runs. The value of the slope for the best line through the points of this plot, which determined the exponent b in equation 3, was found to be 0.45, indicating that the rate of isomerization was somewhat less than half-order in organic bromide. A similar 0.45-order in bromide concentration was obtained for the rates of isomerization using ethyl bromide and ethylene bromide. Since the *cis/trans* ratio was initially 95/5 and at equilibrium 5/95, K and x_e had the values 19 and 90%, respectively. ΔF^0 for the equilibrium *cis–trans* interconversion reaction in benzene at 25° was thus approximately −1.74 kcal./mole.

The results of the various rate measurements are summarized in Table I. Since the value of the reaction yield, G, which may be defined here as the number of *cis* double bonds isomerized per 100

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(3) A similar equation was used by H. Steinmetz and R. M. Noyes, This Journal, **74**, 4141 (1952), for the bromine atom-catalyzed isomerization of dibromoethylene.

e.v. of energy absorbed by the entire solution falls off logarithmically with dose, a value G_0 was determined for each isomerization run by extrapolating the G values to zero dose. These G_0 values are given in the table. In calculating the reaction yields, it was assumed that a dose of one megaroentgen represented an energy absorption of 5.6 $\times 10^{19}$ e.v./g. by the polymer solution, 5.0 $\times 10^{19}$ e.v./g. by allyl or ethyl bromide and 4.8 $\times 10^{19}$ e.v./g. by ethylene bromide. The last column in the table indicates values of G_0^s calculated as the number of *cis* double bonds isomerized per 100 e.v. of energy absorbed by the bromide itself through the direct action of the γ-rays, assuming no energy transfer between the solvent or polymer and the sensitizer or *vice versa*. This idealized quantity G_0^s is the analog of the quantum yield in the corresponding photosensitized reaction where the optical energy absorbed by the system is completely taken up by the bromide. Although the yield G_0 increased with increase in the concentration of the sensitizer, the value of G_0^s, which was a measure of the efficiency of bromide sensitization, decreased markedly with concentration. Thus, the value of G_0 increased only about seven-fold for a two hundred-fold increase in concentration of the sensitizer. At the same time, the efficiency of sensitization dropped to about one twenty-fifth of that in the solution having the smallest bromide concentration.

Figure 3 shows the change in the reduced viscosity of the polymer in benzene solution on γ-irradiation in air and nitrogen in the presence and absence of sensitizer. The molecular weight dropped rapidly from about 380,000 to 8,000–10,000 on irradiation in air with allyl bromide. On the other hand, the molecular weight increased to somewhere around 570,000 on similar irradiation in nitrogen, beyond which point extensive gelation occurred. The latter molecular weight was only a rough estimate since part of the change in viscosity was due, no doubt, to branching, and the viscosity–molecular weight relation for the linear polymer could not be used reliably for molecules with a high degree of non-linearity. Polymer degradation also occurred on γ-irradiation in the absence of sensitizer, being somewhat slower in nitrogen than in air.

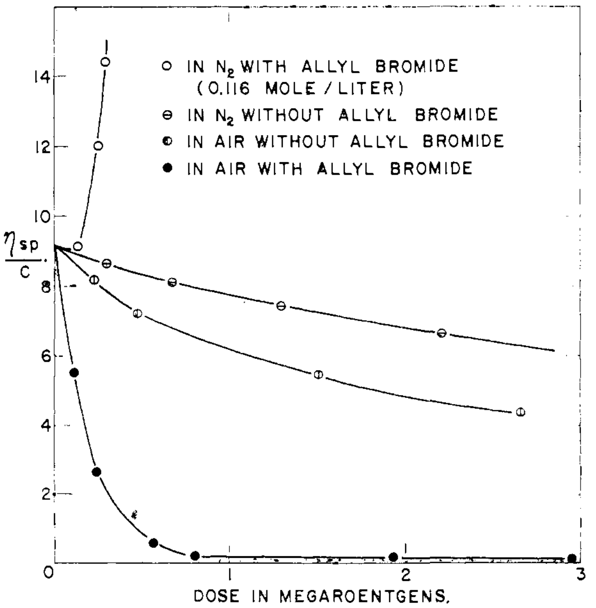

Fig. 3.—Change of the reduced viscosity of a benzene solution of polybutadiene at 20° on γ-irradiation. Concentration of the polymer was 5.30 g./l., and intrinsic viscosity was 3.2.

Table I

Radiation Induced Isomerization of Polybutadiene[a]

[Bromide], mole/l.	$10^7\, k_s$,[b] r.$^{-1}$	$10^7 k$, r.$^{-1}$ (mole/l.)$^{-0.45}$	Reaction yield G_0[c]	Reaction yield G_0^s
		Allyl bromide		
2.888	8.07	5.01	117	367
0.694	4.95	5.83	90	1090
.312	3.24	5.47	67	1790
.143	2.33	5.57	50	2870
.0584	1.64	5.90	37	4910
.0144	0.75	5.04	17.3	9660
	Av.	5.47 ± 0.38		
		Ethyl bromide		
0.656	1.91	2.31	39.4	563
.131	0.99	2.47	28.7	2020
.0437	0.59	2.41	14.0	2940
	Av.	2.40 ± 0.08		
		Ethylene bromide		
0.923	10.04	10.41	175	1140
.462	6.90	9.95	145	1806
.115	3.38	8.94	81	3950
.0575	2.67	9.64	61	5920
	Av.	9.74 ± 0.72		

[a] Concentration of polymer in benzene was 11.5 g./l. [b] k_u was 0.038 $\times 10^{-7}$ r.$^{-1}$. k_s values were obtained by equation 2. [c] G_0 for the unsensitized reaction was 0.92. The values given in this column were corrected for the unsensitized reaction.

Irradiations also were carried out at various temperatures over the range 30 to 60° on a set of polybutadiene solutions all with the same concentration of allyl bromide. It was found that the kinetic plots overlapped completely, indicating that the radiation induced isomerization was temperature independent.

Attempts to induce isomerization in the solid polybutadiene by γ-irradiation were unsuccessful. No indications of any *cis–trans* change could be detected in the spectra of thin polymer films exposed to doses up to 15 megaroentgens. Films cast from benzene solution onto rock salt crystals were used here in place of solid pieces of polymer, since the latter were invariably highly cross-linked when irradiated to about 1.5 megaroentgens, making it impossible to prepare samples for infrared analysis.

Discussion

The results of the sensitized *cis–trans* isomerization of polybutadiene can be explained by a mechanism involving the individual steps

$$\text{R—Br} \rightsquigarrow \text{R} + \text{Br} \tag{I}$$

$$\text{Br} + cis\text{-P} \rightleftharpoons cis\text{-PBr} \tag{II}$$

$$\text{Br} + trans\text{-P} \rightleftharpoons trans\text{-PBr} \tag{III}$$

$$cis\text{-PBr} \rightleftharpoons trans\text{-PBr} \qquad \text{(IV)}$$

$$\text{Br} + \text{Br} \longrightarrow \text{Br}_2 \qquad \text{(V)}$$

$$\text{Br}_2 + \text{R} \longrightarrow \text{RBr} + \text{Br} \qquad \text{(VI)}$$

Other processes doubtless take place on γ-irradiation of the bromide–polymer–solvent system, such as those resulting in the formation of hydrogen bromide known to occur in the radiolysis of pure organic bromides, those leading to cross-linking or chain scission in the polymer, as well as those giving rise to the usual radiolytic products from organic materials. However, these various other processes are considered to make a negligible contribution to the isomerization kinetics in the sensitized case, although excited and ionized molecules or radicals from benzene may be very important in the "unsensitized" case.

Steps II to IV are readily reversible and involve π complexing of the bromine atoms with the olefinic double bonds of the polymer, either *cis* or *trans*, to give the corresponding radical transition states which are capable of free rotation and interconversion. When the complexed bromine atoms are subsequently released and the double bonds reestablished, the geometric configuration formed predominantly is that of the more stable isomeric form which, in the case of polybutadiene, is evidently the *trans* form.

Since there was no temperature dependence of isomerization rate, little or no energy of activation is associated with step II, or for that matter with step III. This is generally true for simple olefins[3] and it is not surprising that it is also true for double bonds in a high polymer molecule. The energy of activation for the over-all isomerization is involved essentially in the formation of the free bromine atoms, as in step I, and this energy is amply supplied by the γ-rays.

The recombination of the organic radical and free bromine depicted in step VI constitutes the reverse of the radiolysis of the bromide given in step I. The importance of this back reaction was noted by Schuler and Hamill[4] who pointed out that 90% of the bromine atoms originally produced were involved in it. Reactions I, V and VI together determine the steady-state bromine atom concentration, which was found to be proportional to the 0.45-power of the bromide concentration.

While the mechanism for the sensitized isomerization appears fairly well understood, little is known about the details of the unsensitized reaction. A reasonable assumption, however, would be that the latter involves excitation of the π electrons of the double bonds through impact mainly with excited molecules or radicals or ions from the solvent surrounding the polymer, and to some extent perhaps with slow secondary electrons of 20 to 100 e.v. energy. With the double bonds thus raised to a higher energy level where the barrier to free rotation is overcome, interconversion can then take place. On return of the transitory species to the ground state with release of this excitational energy, the double bonds are again formed, but with the more stable isomeric form predominating. The possible sensitization by trace impurities in the otherwise unsensitized polymer system was ruled out since a sample of polymer which was carefully purified by reprecipitation from benzene solution not only continued to show isomerization but also at the same rate as formerly.

In this connection some recent work by Charlesby[5] is of considerable interest. In studying the cross-linking produced in long chain olefins by ionizing radiation, he found incidentally that molten *cis* and *trans* octadecenes isomerized to an equilibrium state with a *cis*/*trans* ratio of 65/35. This result was analogous to the unsensitized radiation induced isomerization of polybutadiene. An estimate of the first-order rate constant for conversion of *cis*-octadecene-2 to the *trans* isomer was made using Charlesby's data and equation 1. The rate constant obtained in this way was 1.3×10^{-9} r.$^{-1}$ whereas a value of 3.8×10^{-9} r.$^{-1}$ had been obtained for the unsensitized isomerization of polybutadiene. The mechanism of the octadecene isomerization may be pictured as involving excitation of the double bonds in these molecules, principally through collisions of the second kind with excited species from other octadecene molecules, in a manner comparable to the assumed excitation of polymer double bonds through impact with energetic species from benzene. Now, the octadecene molecule has one double bond for 18 carbon atoms, while the polymer molecule has one double bond for four carbon atoms. Thus, if the above view of the mechanism is substantially correct, and assuming random absorption of energy from the γ-radiation in the two systems, the likelihood of an energetic mobile entity encountering and transferring excitational energy to the double bond in the polymer should be, as a rough approximation, about 4.5 times the probability in octadecene. Accordingly, the rate of isomerization of the former should be 4.5 times that of the latter. Actually, the rate constant for the polymer was about three times that for the octadecene. Although this may be an over-simplified picture, the very close agreement between the rate constants for two quite different olefinic compounds strongly suggests that the mechanisms involved in the two isomerizations are very similar, whatever the detailed nature of these processes may be.

It might be thought that *cis*-polybutadiene could undergo some isomerization on γ-irradiation not only in the absence of a sensitizer, such as an organic bromide, but even without the possible sensitizing action of the solvent itself. Thus, in the case of the solid polymer, it would seem reasonable, in principle, to expect that slow secondary electrons generated on passage of the γ-rays through the polymer could interact with the electrons of the double bonds and excite these bonds to a higher energy level where they could interconvert. Such an isomerization, if it actually occurred, would be very slow indeed, very much slower, in fact, than that taking place in the benzene solution of polymer (about 3.5% *cis* to *trans* conversion for a dose of 10 megaroentgens). The failure to detect any isomerization in the solid polymer on exposure to a dose of 15 megaroentgens may be due, then, to an

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[4] R. H. Schuler and W. H. Hamill, THIS JOURNAL, **74**, 6171 (1952).

[5] A. Charlesby, *Radiation Research*, **2**, 96 (1955).

extremely slow reaction in the polymer film which has thus far escaped detection, and not necessarily to the absence of any such effect. Further study of this aspect is planned.

In determining the efficiency of a radiation induced reaction in a system of several components, particularly in a liquid where the active species have considerable mobility, there is always the problem of ascertaining the contribution to the over-all yield made by energy transfer between the various components. Whereas in a photochemical reaction the energy may be absorbed exclusively by one component, in a radiation chemical reaction the energy is absorbed randomly by the entire system, with the absorption coefficients depending on the average electron densities of the various components. Thus, in the former case the quantum yield can often be determined quite precisely, while in the latter case the value selected for the radiation yield will depend on the extent of energy transfer in the system and whether, accordingly, the G value is calculated on the basis of the energy absorbed by the entire system or that portion of the energy absorbed by a particular component. Since in the present study dealing with a system made up of sensitizer, polymer and solvent, there is no information available concerning the extent of energy transfer between the polymer or solvent molecule and the sensitizer molecule, both types of G values were calculated.

If it is assumed that energy transfer is negligible or that there is an approximate balance between the energy given up by, and that acquired by, the sensitizer molecule in collisions with the surrounding solvent and polymer molecules, the G_0^s values given in Table I can be regarded as a fair measure of the very high efficiency of sensitization of the polybutadiene isomerization. This efficiency evidently increases rapidly on dilution of the sensitizer. This would be expected on the basis of the increased tortuous path that the free bromine atom can follow in its isomerizing action before it is removed by collision with an organic radical or in some other way. Thus, at an allyl bromide concentration of 0.0144 mole/l. the number of *cis* double bonds isomerized per 100 e.v. of energy absorbed directly by the bromide was initially as high as about 10,000.

Schuler and Hamill[4] investigated the X-ray decomposition of pure ethyl bromide and ethylene bromide and reported G values for the formation of hydrogen bromide from these organic bromides as 2.0 and 17.8, respectively. When triphenylmethane was added to the ethyl bromide prior to irradiation, a G value of 5.1 was obtained. The yield of hydrogen bromide from the ethylene bromide was, therefore, about 3 to 9 times the yield from ethyl bromide. In the present work, it was seen that the isomerization yield G_0 for ethylene bromide was about four times that of ethyl bromide at the same molar concentrations of sensitizer. The relative formation of hydrogen bromide in the X-ray decomposition of the two bromides was thus of the same order of magnitude as the relative formation of the free bromine atoms in the isomerization case. It should be noted, however, that hydrogen bromide is not a sensitizer of the isomerization,[6] but rather the bromine atoms which, formed in the radiolysis of the alkyl bromide, eventually end up as hydrogen bromide.

A possible application in radiation chemistry generally of the isomerization described in this paper is its use as a dosimeter. The particular merits of this system would be its convenience and complete stability before and after irradiation. The procedure would make use of a standardized high *cis*-polybutadiene sample in about a 1% solution in benzene. A graph depicting the rate of isomerization of this polymer in the presence of a particular concentration of sensitizer could be constructed similar to Fig. 2. For doses up to 5×10^7 r. the polymer solution could contain about 0.01 mole/l. of allyl bromide, while for doses up to about 5×10^8 r. the polymer solution could be employed without a sensitizer. After exposure of the solution to some unknown radiation dose, the infrared spectrum of the polymer could be obtained, the residual *cis* content calculated and the dose corresponding to this amount of *cis* read off from the appropriate graph.

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[6] M. S. Kharasch, J. V. Mansfield and F. R. Mayo, THIS JOURNAL, **59**, 1155 (1937).