Addition Reactions Induced by Ionizing Radiation. I. Bromotrichloromethane to Butadiene

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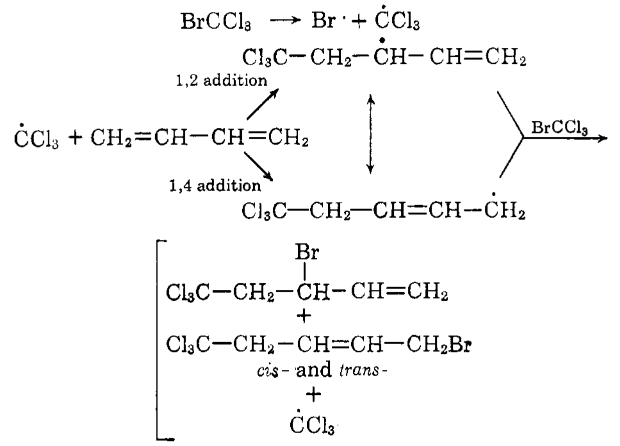
The addition reaction of bromotrichloromethane to butadiene induced by ionizing radiation has been studied. The products were characterized, and their stereoconfigurations were determined by means of infrared and Raman spectroscopy. The kinetics were investigated over the temperature range 25 to 40°; the dose rates ranged from (1.4 to 6.5) $\times 10^3$ rads min.$^{-1}$; and the mole ratio of bromotrichloromethane–butadiene was varied from 1:1 to 46:1. It was observed that the adducts obtained were primarily 1,4-*trans*. The reactions are free radical chain reactions as evidence by the G values (200 to 800 molecules/100 e.v.), by the dose rate dependences (rate $\propto I^{0.5}$; G $\propto I^{-0.5}$), and by a positive activation energy (ΔE_a = 5.5 kcal. mole^{-1}). It also has been found that the reaction is zero order in butadiene.

The addition of bromotrichloromethane to butadiene is believed to be a chain reaction consisting of the following steps.



In peroxide- and in light-initiated reactions at 60–80°, Kharasch and co-workers[1,2] obtained ~75% 1,4-addition product and ~25% 1,2-addition product. However, the stereochemistry of the products (*cis–trans*) has not been investigated. In the polymerization of butadiene and other dienes,[3] the relative amounts of 1,2-, *cis*-1,4, and *trans*-1,4 structure in the polymers have received much study. It has been found that the amount of 1,4-*trans* configuration increases with decreasing reaction temperatures.

Several free radical chain reactions induced by ionizing radiation have been reported in the literature.[4–8] The advantage of studying the previously described addition reaction when initiation is induced by radiation lies in the fact that a much wider range of temperatures, especially lower temperatures, can be employed for the reaction. This provides a convenient way of studying at lower temperatures of the isomer distribution in the products. This paper deals with the addition of bromotrichloromethane to butadiene initiated by X-rays at 25–40° and is concerned with the stereochemistry of the products as well as with the reaction kinetics.

Experimental

Materials.—Research grade butadiene (purity, 99.35%) of Phillips Petroleum Co. was employed. Bromotrichloromethane (Eastman Kodak, practical grade) was fractionated (b.p. 104°); its purity was determined by gas chromatography.

Radiation Source.—X-Rays were obtained from a 250-kv. potential X-ray machine (General Electric Maxitron-250) operated at 6–30 ma., and filtered through 1 mm. each of aluminum and copper. The output of the machine was constant within 3–5%.

Dosimetry.—Dosimetry was conducted by using ferrous sulfate solution in the same reaction vessel as that employed in the radiation of experiments. Since filtration of 1 mm. of aluminum plus1 mm. of copper was used, essentially no energy below about 40 kev. was involved, and the average energy transmitted by the filters was determined previously to be about 150 kev.[9] Thus, it was possible to proceed from ferrous sulfate values in the aqueous system to dose rate values in the various nonaqueous systems by using the mass absorption coefficients at 150 kev. for the aqueous and nonaqueous systems ignoring any contribution from photoelectric effect.[10] Different dose rates were achieved by varying the current with the sample being placed at a fixed distance from the target.

Identification of Products.—The products were identified by means of boiling point, elementary analysis, infrared spectroscopy (a Beckman IR-4 was used), refractive index, and gas chromatography (Podbielniak 9580; column packing, 12 ft. of 15% w./w. Hy-Vac silicone grease on 60/80-mesh Chromosorb-W; column temperature, 166°; gas pressure, 15 p.s.i.g. of helium). The configuration of the main product was determined by means of Raman spectroscopy employing a photoelectric spectrometer described previously[11] as well as by infrared.

Method of Following Kinetics.—The initial reaction rates (first 10–15%) were followed by means of optical absorption in the near infrared employing a Cary ultraviolet spectrometer Model 14. A reaction vessel, as shown in Fig. 1, consisting of a flattop cell for irradiation connected to two Pyrex optical cells of different thicknesses (for different concentrations) and provided with a side tube for sealing off was employed. Thus the contents can be transferred into each cell without having to open the system. Known amounts of reactants were charged into the radiation cell. (At atmospheric pressure and 25°, approximately 1 mole of butadiene can be dissolved in 1 mole of liquid bromotrichloromethane.) The vessel was then attached to a vacuum line and the air removed by alternate freezing and melting three times. It was sealed off at the side tube while the mixture was frozen and under a vacuum of 10^{-2}–10^{-3} mm. The vessel was then positioned underneath the X-ray target. The radiation cell containing the reaction mixture was centered directly under

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[1] M. S. Kharasch and M. Sage, *J. Org. Chem.*, **14**, 537 (1949).

[2] M. S. Kharasch, E. Simon, and W. Nudenberg, *ibid.*, **18**, 328 (1953).

[3] C. Walling, "Free Radical Reactions in Solutions," John Wiley and Sons, Inc., New York, N. Y., 1957, pp. 228–232.

[4] L. C. Anderson, B. G. Bray, and J. J. Martin, International Conference on the Peaceful Uses of Atomic Energy, Vol. 15, United Nations, New York, N. Y., 1956, p. 235.

[5] A. M. Lovelace and D. A. Rausch, Wright Air Development Command Technical Report S-5-461, April, 1956.

[6] T. S. Nikitina and Kh. S. Bagdasaryan, *J. Phys. Chem., USSR*, **31**, 704 (1957).

[7] E. Heiba and L. C. Anderson, *J. Am. Chem. Soc.*, **79**, 4940 (1957).

[8] A. Fontijn and J. W. T. Spinks, *Can. J. Chem.*, **35**, 1384–1413 (1957).

[9] Private communication from Dr. L. A. Siegel of these laboratories.

[10] G. J. Hine and G. L. Brownell, Ed., "Radiation Dosimetry," Academic Press, Inc., New York, N. Y., 1956.

[11] R. F. Stamm and C. F. Salzman, Jr., *J. Opt. Soc. Am.*, **43**, 126 (1953).

the target with the flat side up; the optical cells were shielded from radiation by lead sheets so as to prevent them from discoloring. The distance from the target to the surface of the reaction mixture was 10 cm. A constant temperature bath (precision, ±0.2°) was then raised so that the liquid level of the bath was above that of the reaction mixture.

Butadiene gives several peaks in the near infrared of which the strongest and sharpest is the peak at 1.63 μ (6134 cm.$^{-1}$). Bromotrichloromethane is transparent in the near-infrared region, and the reaction product was also found not to interfere at 1.63 μ. The reactions were followed by the decrease of absorbance ($A_{1.63}$) at 1.63 μ after appropriate intervals of irradiation. The disappearance of butadiene was calculated from an analytical working curve based on standards whose spectra were taken while employing the same cell thickness and the same parameters of the spectrometer.

Formation of 1:1 Adduct and 1:2 Adduct.—Two products have been isolated from reactions covering a wide range of conditions such as different mole ratios of bromotrichloromethane to butadiene (in this paper, unless stated to the contrary, the term mole ratio refers to moles of bromotrichloromethane to moles of butadiene), different dose rates, different total irradiation time (total dose), and different temperatures (25–40°).

The 1:1 adduct was a colorless material with a sharp odor, b.p. 44° (0.05 mm.); $n^{25}D$ 1.5318. A gas chromatogram of the product obtained from a 3:1 starting mole ratio showed a big peak representing 96.3% of the total area with a small peak (2.3% area) immediately before it and another small peak (1.4% area) immediately after it. These are attributed to isomers and will be discussed in the next section.

Anal. Calcd. for $C_5H_6BrCl_3$: C, 23.83; H, 2.40; mol. wt., 253.39. Found: C, 24.05; H, 2.55; mol. wt., 254.6.

The 1:2 adduct was a colorless material with a sharp odor, b.p. 95.5° (0.1 mm.).

Anal. Calcd. for $C_9H_{12}BrCl_3$: C, 35.53; H, 3.95; mol. wt., 306.49. Found: C, 35.12; H, 3.82; mol. wt., 304.5.

It was found that the relative amounts of 1:1 adduct and 1:2 adduct in the products varied with the mole ratio and the total reaction time. An increase in irradiation time increased the total conversion; it also increased the relative amount of the 1:2 adduct in the product mixture. Likewise, a lower mole ratio favored the formation of the 1:2 adduct. When the mole ratio of the reactants was 1:1, it was found that at a conversion below 15% there was no 1:2 adduct formed in the product mixture. For higher mole ratios, *e.g.* 6:1, essentially no 1:2 adduct was formed even at a high conversion (60%). It should be mentioned that the conditions which favored the formation of the 1:2 adduct also favored that of nondistillable polymeric substances. Thus, in experiments where a high total dose and a low mole ratio were employed, a considerable amount (10–20%) of polymeric residue was formed. In all experiments where the products were used for determination of configuration, material balance was maintained so that no fraction was lost, and the true ratio of the isomers was obtained. In kinetic studies, all the reactions were carried out so as not to exceed 15% conversion, and, in all these runs, the 1:1 adduct was the only product.

Results

Determination of Configuration by Infrared and Raman Spectroscopy.—From chemical analysis it was demonstrated that the best fraction of what was thought to be the 1:1 adduct of bromotrichloromethane to 1,3-butadiene probably had the empirical formula $C_5H_6BrCl_3$. If the addition proceeded in a straightforward fashion, the 1-1 adduct is expected to be 1-bromo-5,5,5-trichloro-*trans*-2-pentene, or 4-bromo-5,5,5-trichloropentene-1, or 1-bromo-5,5,5-trichloro-*cis*-2-pentene. At room temperature the *cis* isomer should be the least probable product.

By studying the infrared and Raman spectra of a sample of 1:1 adduct obtained from a reaction mixture having a mole ratio of 1:1, it was possible to show that the major component was the 1,4-*trans* isomer and that the main impurity probably was a monosubstituted ethylene. The details follow.

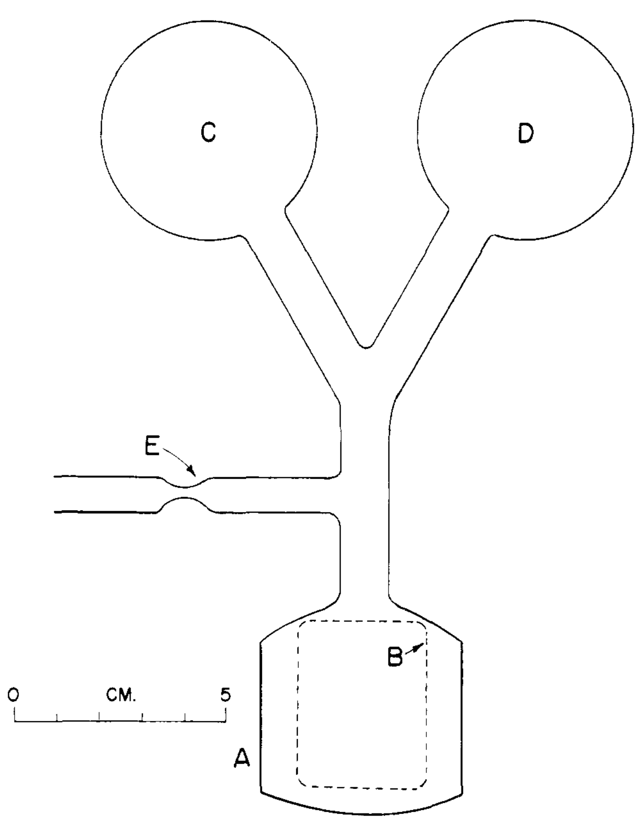


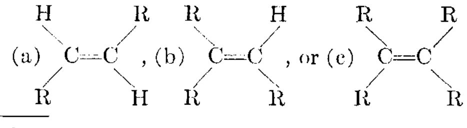
Fig. 1.—Irradiation vessel with attached optical cells. A is irradiation cell with flattened window (B). C and D are Pyrex absorption cells with optically flat windows and path lengths of 10 mm. and 2 mm., respectively. E is constriction for sealing off after degassing.

Infrared.—1. A strong band at 970 cm.$^{-1}$ was assigned to an out-of-plane H-bending mode of a *trans*-disubstituted double bond. (The region from 675–730 cm.$^{-1}$ normally contained in out-of-plane H-bending mode attributable to a *cis*-disubstituted double bond was confused by intense asymmetrical C—Cl stretching frequencies.)

2. Two strong bands normally employed to show the presence of a monosubstituted ethylene should appear at 990 cm.$^{-1}$ (C=C twist) and 925 cm.$^{-1}$ $\left[\begin{matrix}H\\ \\ R\end{matrix}C{=}CH_2 \text{ wag}\right]$. These bands were missing. However, the region near 925 cm.$^{-1}$ was partly obscured by the side of a strong band centered at 944 cm.$^{-1}$. From this it was possible to state only that the content of $RCH{=}CH_2$ was less than 15%.

3. The C=C stretch region contained only very weak bands which were of little value in a positive sense.

Raman.—1. There is a very strong C=C stretch at 1670 cm.$^{-1}$ and a much weaker (though well resolved) C=C at 1640 cm.$^{-1}$. From data presented in a review article[12] on the Raman spectra of olefins, it is seen that the line at 1670 cm.$^{-1}$ could arise from the following configurations.



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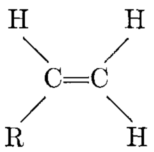
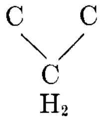
[12] J. Goubeau, *et al.*, *Angew. Chem.*, (A) **59**, 87 (1947), Beiheft Nr. 56 (Table 20).

2. The weak Raman lines at 1640 and 1405 point strongly to a monosubstituted ethylene as the minor component. Admittedly, the frequency of 1405 cm.$^{-1}$ is low for the $=CH_2$ deformation and should be about 1415. However, the band is quite weak and is really not clearly resolved from the low λ side of 1426; thus the measurement of the peak is rendered uncertain. Also there are a few compounds possessing the structure

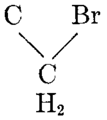


whose Raman spectra have the line in question near 1405 cm.$^{-1}$, *e.g.* allyl alcohol (1407 cm.$^{-1}$). (If this 1405 band showed up in the infrared spectrum, it would be evidence for a *cis* structure. However, there is nothing definite at this position in the infrared spectrum on 25- or 60-min. runs.) As another possibility, if the Raman line at 1405 cm.$^{-1}$ were assigned to the deformation of the $=CH_2$ group of a conjugated system, there would be further complications in the C=C region which are not present. (The C=C stretch of the *cis* isomer would lie at 1647–1650 cm.$^{-1}$ but does not appear in the Raman spectrum.)

Infrared and Raman.—1. The infrared and Raman bands at 1442 and 1292 cm.$^{-1}$ are the CH_2-deformation and CH_2-wagging frequencies of one or more methylene groups.



2. The infrared and Raman bands at 1426 and 1208 cm.$^{-1}$ are the same modes of the following group.



3. The presence of strong infrared bands in the region 710 to 830 cm.$^{-1}$ indicates that a $—CCl_3$ group *could* be present. The presence of a strongly polarized Raman line at 394 cm.$^{-1}$ also indicates that a CCl_3 group (390–430 cm.$^{-1}$) could be present.[13]

4. The weak infrared band and medium intensity Raman line at 1310 cm.$^{-1}$, (probably originating from an in-plane deformation involving two hydrogens) indicate a *trans* structure.

The spectroscopic data, when considered in conjunction with the empirical formula data and the types of structures to be anticipated lead us to conclude that the major component is the 1,4-*trans* isomer, and the minor component is a monosubstituted ethylene presumably attributable to the 1,2-mode of addition. The assignment of a structure to the minor component practically on the basis of the cm.$^{-1}$ value of one line, the C=C stretch, may appear unjustifiable. However, the frequency of this C=C mode belonging to the type of structure postulated is well founded.

Probable Concentrations.—The intensities of the C=C Raman lines (1670 and 1640 cm.$^{-1}$) were used to obtain concentration ratios of major to minor components. For the product (1:1 adduct) derived from the 1:1 starting mole ratio, the average ratio of C=C peak intensities from three photoelectric spectra was 6.57:1 after correcting for overlapping. The Raman spectrum of the fraction obtained from the distillation of the product formed from a reaction mixture having an initial mole ratio of 3:1 gave a lesser amount of the compound having the C=C at 1640 cm.$^{-1}$ (no longer clearly resolved), and an intensity ratio of 15.6:1 (average from two spectra). When the two compounds are present in equal concentrations, the C=C of the monosubstituted ethylene should be about 10% more intense than that of the *trans* isomer.[12] These assumptions lead to concentration levels of 88 and 12% for the fraction obtained from the 1:1 starting ratio, and 94.5 and 5.5% for the fraction derived from the 3:1 starting ratio. The analytical results on the 1:1 adduct achieved by vapor phase chromatography (three components having per cents of 96.3, 2.3, and 1.4%) are not necessarily at variance with those achieved spectroscopically since identical samples were not examined by both techniques. The spectroscopic results show that the major component is a *trans*-substituted C=C and that a minor component is present which probably is a monosubstituted ethylene and not a *cis* C=C. The concentrations found by Raman effect are only semiquantitative since no working standards were available. However, the changes in concentration levels established by Raman effect in the 1:1 adduct derived from 1:1 and 3:1 starting mole ratios are definite. From the fact that three peaks were measured in the sample of 1:1 adduct studied by v.p.c., we assume that they are attributable to *trans*, 1,2-, and *cis*, respectively. If there were 2–3% of the *cis* isomer present, the C=C line would not have been observed in the Raman spectrum since it would be at 1650 cm.$^{-1}$ and would lie even closer to the intense *trans* C=C stretch. From the degree of fractionation that could be achieved and from the data which were obtained, no more precise statements can be made by the authors regarding the concentrations of these isomers. For the 1:1 adduct from the 3:1 starting mole ratio, the agreement between v.p.c. and Raman effect is as good as could be expected.

Since the compound is probably 94–95% pure, the spectroscopic data are given in Table I. The infrared bands occur at essentially the same positions as the Raman lines with the following exceptions. Above 600 cm.$^{-1}$, the weak Raman lines 1185, 1273, 1405, and 3127 cm.$^{-1}$ do not appear in infrared. Conversely, the infrared bands at 1550, 1685, and 1723 cm.$^{-1}$ (plus some higher overtones and combinations) do not appear in the Raman spectrum. The compound is known to be impure, thus there seems to be no point in attempting to assign all the bands. However, this much should be stated: (1) The total number of Raman lines is 49 of which at least 2 belong to an impurity. Accordingly, there are at least 8 lines present in addition to the 39 ($3N - 6$ where N is equal to 15, the number of atoms) which should appear as fundamentals. (2) In the *trans* configuration, there might be a plane of symmetry present in which case there would be 24 vibrational modes of type A′ symmetrical to the plane (perpendicular-type bands in infrared, polarized in

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[13] H. Gerding and H. G. Haring, *Rec. trav. chim.*, **47**, 1409 (1955).

Table I

Raman Spectrum of 1-Bromo-5,5,5-trichloro-*trans*-2-pentene[a] (Purity, 94–95%)

$\Delta\nu^b$	I^c	$\rho_n{}^d$	$\Delta\nu$	I	ρ_n	$\Delta\nu$	I	ρ_n
150	0.9	0.51	708	16.9	0.74	1273	5.2	0.78
160	11.0	.31	773	20.2	.65	1292	10.8	.45
178	5.9	.73	797	15.8	.61	1310	14.3	.38
204	10.4	.61	837	4.2	..	1340	1.9	..
235	9.9	.61	865	2.1	..	1405^g	1.8	..
287	28.0	.67	887	2.3	..	1426	9.5	.70
322	24.9	.40	943	4.2	.82	1442	7.8	.66
347	16.9	.30	975	2.4	..	1640^g	9.1	P
394	14.4	.15	1027	10.9	.88	1670	119.8	0.33
407	21.5	.27	1065	2.3	..	2787	45.2	.18
428	3.4	.36	1087	7.7	.61	2830	5.5	.26
483	18.5	.21	1149	20.2	.68	2857	2.9	..
516	2.9	..	1185^h	4.6	..	2872	11.6	.14
573	28.0	.14	1208	72.0	.44	2920	28.4	.13
612	67.4	.29	1226	13.1	.77	2967	38.0	.24
651^h	..	..	1252	0.7	..	3023	23.6	.43
						3127	6.2	.17

[a] Toronto type spiral arc, Hg λ 4358.35 Å. excitation, $NaNO_2$ filter, 5 cm.$^{-1}$, spectral slit width, spectrum recorded photoelectrically. [b] $\Delta\nu$, cm.$^{-1}$ (vac.). [c] $I = 100[I(\Delta\nu)/I(CHCl_3, \Delta\nu\ 667\ cm.^{-1}) \times n^2(CHCl_3)/n^2(X)]$; direct photoelectric peak intensities. [d] Depolarization values obtained by method of Edsall and Wilson[e] using modification of Rank and Kagarise.[f] [e] J. T. Edsall and E. B. Wilson, Jr., *J. Chem. Phys.*, **6**, 124 (1938). [f] D. H. Rank and R. E. Kagarise, *J. Opt. Soc. Am.*, **40**, 89 (1950). [g] Believed due to isomer arising from 1,2-addition. [h] Shoulders; poorly defined lines.

Raman effect) and 15 modes of type A″ antisymmetrical to the plane (parallel-type infrared bands, depolarized in Raman effect). Since all the Raman lines (save one weak line) are polarized, there probably is no plane of symmetry.

Kinetics.—The results on the standardizations of butadiene solutions in bromotrichloromethane of low (up to 6%), intermediate (6–10%), and high (10–25%) concentrations with regard to the absorbance [log (I_0/I)] at 1.63 μ are represented in Fig. 2. In all cases Beer's law was obeyed, and it was also verified that appropriate concentrations of bromotrichloromethane and of the 1:1 adduct did not vitiate the calibration plots.

Typical kinetic plots for the X-ray induced reaction between bromotrichloromethane and butadiene are shown in Fig. 3. It is seen that the disappearance of butadiene is linear with time. The kinetic data covering various experimental conditions are recorded in Table II. For the reaction at 25° when employing a mole ratio of 3:1, it was found that the rate was pro-

Table II

Data for Addition of Bromotrichloromethane to Butadiene Initiated by X-Rays (250 kv. Potential)

Mole ratio $BrCCl_3:C_4H_6$	Temperature, °C. ± 0.2	Dose rate[a] rads min.$^{-1}$	Rate × 10^3, moles kg.$^{-1}$ min.$^{-1}$	G value[b]
3.01:1	25	1447	1.22	797
3.08:1	25	3725	2.00	516
3.19:1	25	5977	2.44	394
0.95:1	25	5341	1.11	199
2.67:1	25	5898	2.62	428
4.69:1	25	6081	2.23	354
8.37:1	25	6187	2.54	382
18.4:1	25	6261	2.72	419
46:1	25	6300	2.59	397
2.70:1	32.5	5922	3.08	500
3.14:1	40	5973	3.54	572
2.67:1	40	5898	3.80	621

[a] Dose rate calculated, based on the composition of the starting material, from the dose rate obtained for Fe^{+2}–Fe^{+3} dosimeter under the same conditions. Filtration: 1 mm. of aluminum + 1 mm. of copper. [b] Molecules of butadiene reacted per 100 e.v. absorbed.

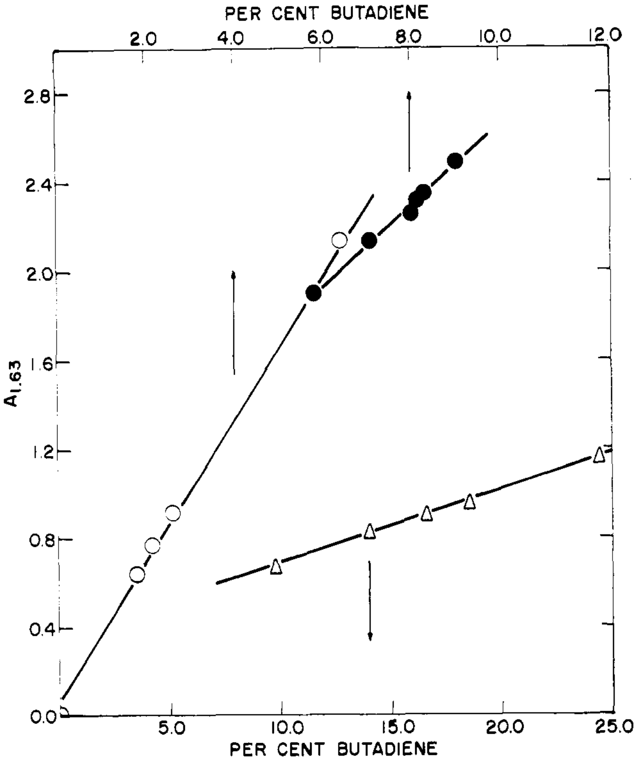


Fig. 2.—Standardization of butadiene solutions in bromotrichloromethane. ○: 10-mm. cell; geometrical slit width = 0.12 mm.; $A_{1.63}$ = 0.3309 (C_4H_6 %) + 0.049. ●: 10-mm. cell; copper screen filter (T = 0.1), slit width = 1.2 mm.; $A_{1.63}$ = 0.224(C_4H_6 %) + 0.381. Δ: 2-mm. cell; slit width = 0.12 mm.; $A_{1.63}$ = 0.03362 (C_4H_6 %) + 0.3464.

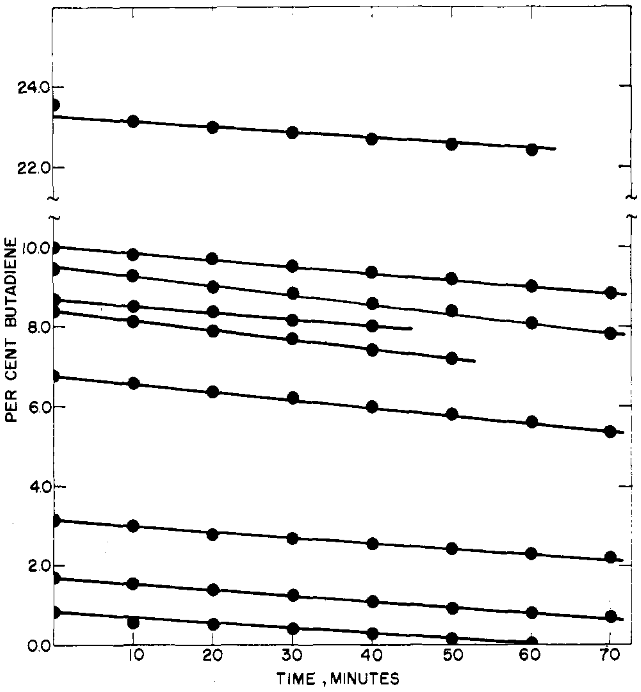


Fig. 3. Some typical plots in reactions between butadiene and bromotrichloromethane as expressed in disappearance of butadiene *vs.* time.

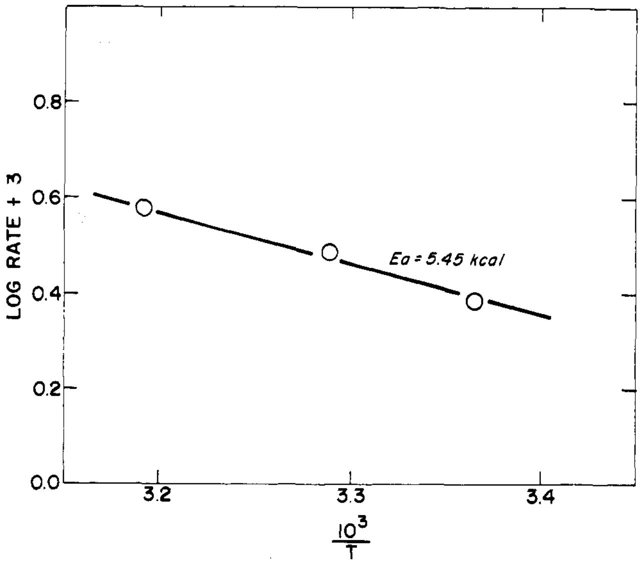


Fig. 4.—Arrhenius plot for addition of bromotrichloromethane to butadiene. Mole ratio, 3:1; dose rate: 6 × 10^3 rads min.$^{-1}$.

portional to the 0.5 power of the dose rate (rate $\propto I^{0.5}$) and that the G value was inversely proportional to the 0.5 power of the dose rate (G $I \propto {}^{-0.5}$). Table III represents the dependence of rates on the mole fraction of bromotrichloromethane at 25°. Figure 4 shows the Arrhenius plot involving temperatures of 25, 32.5, and 40°. An activation energy of 5.45 kcal. mole^{-1} was calculated.

TABLE III

DEPENDENCE OF RATE ON THE CONCENTRATION OF BROMOTRICHLOROMETHANE[a]

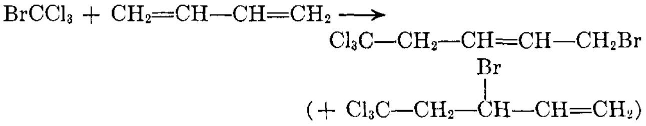
Mole ratio $BrCCl_3$:C_4H_6	[$BrCCl_3$], moles kg.$^{-1}$	Rate × 10^3, moles kg.$^{-1}$ min.$^{-1}$
0.95:1	3.92	1.18
2.69:1	4.58	2.65
3.19:1	4.62	2.46
4.69:1	4.77	2.22
8.37:1	4.88	2.51
18.4:1	4.97	2.67
46:1	5.01	2.53

[a] Dose rate, 6025 rads min.$^{-1}$.

Discussion

Based on the results of infrared and Raman spectroscopy described in a previous section it can be stated that the radiation-induced addition of bromotrichloromethane to butadiene in the vicinity of room temperature (25–40°) produces primarily the 1,4-*trans* 1:1 adduct. One might say that the addition is nearly stereospecific; however, the product obtained is also close to the equilibrium mixture of isomers which is high in *trans*-1,4. It is difficult to distinguish between addition products and isomerization product. It has also been found that higher ratios of bromotrichloromethane to butadiene favor the 1,4-*trans* addition as well as the formation of 1:1 adduct as was indicated by the results in the Raman and infrared analyses for the products obtained from reactions involving 3:1 and 1:1 mole ratios of the reactants. The fact that the ratio of 1:2 adduct to 1:1 adduct increases with reaction time suggests that the 1:2 adduct does not result from straight telomerization but rather from reaction of the 1:1 adduct with butadiene.

Because of the pressure, reactions of high mole ratios of butadiene to bromotrichloromethane (>1:1) have not been studied. Also, by the present analytical method the peak at 1.63 μ would be too intense to be measured by Cary 14 spectrometer even with a 1-mm. cell. It can be visualized that under those conditions other types of reactions, telomerization and polymerization, will be favored. Consequently, the rate of disappearance of butadiene probably will increase. It should be emphasized that in all the kinetic studies reported here the conditions were chosen so that the 1:1 adduct was the only product. Therefore, the rates reported are those pertaining to the following reaction.


$$BrCCl_3 + CH_2{=}CH{-}CH{=}CH_2 \longrightarrow Cl_3C{-}CH_2{-}CH{=}CH{-}CH_2Br$$
$$(+\ Cl_3C{-}CH_2{-}\underset{}{\overset{\displaystyle Br}{\overset{|}{C}H}}{-}CH{=}CH_2)$$

small amount

This reaction and other addition reactions of polyhalomethane–olefin systems initiated by light or peroxides have been demonstrated to be free radical chain reactions.[1-3] The kinetics have been reported for the systems bromotrichloromethane–cyclohexene and bromotrichloromethane–vinyl acetate for reactions initiated by light by Melville and co-workers[14] and Bengough and co-workers.[15] Our results show that the addition reaction of bromotrichloromethane to butadiene induced by X-rays is a free radical chain reaction as indicated by the high G values (number of molecules reacted per 100 e.v.), by the dose rate dependences, rate $\propto I^{0.5}$ and G $\propto I^{-0.5}$, and by the activation energy (5.45 kcal. mole^{-1}). These kinetic results together with the chemical and spectroscopic results discussed above lend credence to the following homogeneous kinetic scheme.

Initiation: $$BrCCl_3 \xrightarrow{\ \ I\ \ } \dot{B}r + CCl_3$$

Propagation: $$\dot{C}Cl_3 + CH_2{=}CH{-}CH{=}CH_2 \xrightarrow{k_2} Cl_3CCH_2{-}CH{=}CH{-}CH_2$$

$$Cl_3CCH_2{-}CH{=}CH{-}\dot{C}H_2 + BrCCl_3 \xrightarrow{k_3} Cl_3CCH_2{-}CH{=}CH{-}CH_2Br + \dot{C}Cl_3$$

Termination: $$2\dot{C}Cl_3 \xrightarrow{k_4} C_2Cl_6$$

$$2Cl_3CCH_2{-}CH{=}CH{-}\dot{C}H_2 \xrightarrow{k_5} (Cl_3CCH_2{-}CH{=}CH{-}CH_2 \not{)}_2$$

$$\dot{C}Cl_3 + Cl_3C{-}CH_2{-}CH{=}CH{-}\dot{C}H_2 \xrightarrow{k_6} Cl_3CCH_2{-}CH{=}CH{-}CH_2{-}CCl_3$$

The linear plots (Fig. 3) obtained for concentrations of butadiene *vs.* time indicate that under the conditions investigated (Table II) the reaction is zero order

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(14) H. W. Melville, J. C. Robb, and R. C. Tutton, *Discussions Faraday Soc.*, **10**, 154. 224 (1951); **14**, 150 (1953).

(15) W. I. Bengough and R. A. M. Thomson, *Trans. Faraday Soc.*, **56**, 407, (1960); **57**, 1928 (1961).

in butadiene and that step 2 is not rate determining. Based on the results shown in Table III, from mole ratios of 1:1 to 3:1 the reaction is dependent on the concentration of bromotrichloromethane. However, it is difficult to draw any conclusion about the dependence on bromotrichloromethane at higher mole ratios. For a great change in mole ratio from 3:1 to 46:1 only results in a 30% change in the absolute concentration of bromotrichloromethane.

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Addition Reactions Induced by Ionizing Radiation. II. Bromotrichloromethane to Isoprene and 2,3-Dimethylbutadiene

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For comparison with the previously reported[1] addition of bromotrichloromethane to butadiene induced by ionizing radiation, similar reactions involving isoprene and 2,3-dimethylbutadiene have been investigated. In the isoprene reaction using three moles of bromotrichloromethane to isoprene, the 1:1 adduct was shown to contain products resulting from 72% 1,4-addition, 26% 4,1-addition, and a small amount of 1,2- and 4,3-additions. In the 2,3-dimethylbutadiene reaction, in all mole ratios studied, the product obtained was exclusively the 1:1 adduct resulting from 1,4-addition. The kinetics of the reaction were investigated over the temperature range 25 to 40°; the dose rate ranged from $(1.4 \text{ to } 6.3) \times 10^3$ rads min.$^{-1}$; and the mole ratio of bromotrichloromethane:diene was varied from 1:2 to 19:1. It was observed that 2,3-dimethylbutadiene was the most reactive among the three dienes. The activation energies were 3.96 kcal. mole^{-1} for isoprene and 3.09 kcal. mole^{-1} for 2,3-dimethylbutadiene. The G values (molecules of diene consumed/100 e.v. absorbed) ranged from 450–1000 for isoprene and 1000–3650 for 2,3-dimethylbutadiene. The dose rate dependences were: for isoprene, rate $\propto$ dose rate$^{0.53}$; G $\propto$ dose rate$^{-0.48}$; for 2,3-dimethylbutadiene, rate $\propto$ dose rate$^{0.58}$; G $\propto$ dose rate$^{-0.42}$. In the cases of both isoprene and 2,3-dimethylbutadiene, the reactions are zero order in the diene over the entire range of mole ratios investigated.

The addition reaction of bromotrichloromethane to butadiene induced by ionizing radiation has been found to yield primarily the 1,4-*trans* adduct.[1] This investigation deals with the same type of reaction involving some substituted butadienes—2-methylbutadiene (isoprene) and 2,3-dimethylbutadiene. One of our purposes was to study the modes of addition of bromotrichloromethane to these dienes induced by ionizing radiation in the vicinity of room temperature. In the case of 2,3-dimethylbutadiene 1,2- and 1,4-additions similar to those described for the butadiene reaction[1] are possible, while in the case of isoprene all 1,2-, 1,4-, 4,1-, and 4,3-additions leading to various products are possible. Another purpose was that of comparing the reactions involving the unsubstituted and substituted butadienes from a kinetic point of view. It was hoped that these findings would help us to understand more clearly the mechanisms of the described reactions.

Experimental

Materials.—Research grade isoprene of Phillips Petroleum Co. was employed. Both 2,3-dimethylbutadiene and bromotrichloromethane were supplied by Eastman Kodak Co. and purified by fractionation shortly before use.

The radiation source, dosimetry, and other experimental procedures were similar to those described for the butadiene reaction.[1]

Gas-liquid chromatographic analyses were carried out using a Podbielniak Co. instrument, Model 9580. A 12-ft. column packed with 15% w./w. Hy-Vac silicone grease on 60/80-mesh Chromosorb-W solid support was used. The column temperature was 166°, and the helium gas pressure was 15 p.s.i.g.

N.m.r. spectra were obtained with a Varian V4300B high-resolution spectrometer at 40 Mc. in carbon tetrachloride solution with tetramethylsilane as an internal standard.

Identification of Products. Bromotrichloromethane–Isoprene Reaction.—Similarly to the bromotrichloromethane–butadiene reactions,[1] the bromotrichloromethane–isoprene reactions produced both the 1:1 adduct [$C_6H_8Cl_3Br$, b.p. 49.0–54.3° (0.025 mm.)] and the 1:2 adduct [$C_{11}H_{16}Cl_3Br$, b.p. 90° (0.075 mm.)].

Anal. (1:1 adduct). Calcd. for $C_6H_8Cl_3Br$: C, 27.05; H, 3.03; Cl, 31.81; Br, 23.89. Found: C, 27.58; H, 3.51. (1:2 adduct). Calcd. for $C_{11}H_{16}Cl_3Br$: C, 39.49; H, 4.82; Cl, 31.81; Br, 23.89. Found: C, 39.33; H, 4.70.

However, the 1:2 adduct was obtained only in cases where the initial concentration of isoprene was high (1:1 mole ratio) or when the mixture was exposed to radiation for a long time; it was also formed in smaller amounts in comparison with the corresponding butadiene reactions.[1]

The 1:1 adduct (I) formed in the addition reaction of bromotrichloromethane to isoprene (3:1 mole ratio) induced by X-rays (dose rate: 6×10^3 rads min.$^{-1}$) was shown by infrared and Raman spectroscopy to contain less than 5% terminal double bond resulting from either 1,2-addition or 4,3-addition. The vibrational spectra showed conclusively the presence of —CH_2Br and —CCl_3 groups as major components. In addition, the cleanness of the Raman spectrum indicated that the 1:1 adduct contained either a single compound or else a mixture of compounds whose structures were such as to yield identical spectra for the several components. However, these methods were unable to distinguish between *cis* and *trans* structures with regard to the locations of the H atom and —CH_3 group on the residual double bond. Also, the amounts of 1,4- and 4,1-addition products could not be ascertained. A gas-liquid chromatograph of I showed two minor peaks, 0.5 and 1.5%, before two major peaks, 26.1 and 71.9%. The n.m.r. spectrum of I showed a mixture of the 1,4- and 4,1-adduct with the component possessing a doublet at lower field being present in greater concentration. The compound Br—CH_2—CH=C(CH_3)—CH_2—CCl_3 would be the more abundant component if the H resonances on the methylene adjacent to the Br atom appear at a lower field than those on the methylene adjacent to the —CCl_3 group. A preliminary look at the models Br—CH_3 and Cl_3C—CH_3 showed that the difference was very slight and possibly in the reverse order. Another approach was

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[1] C. S. Hsia Chen and R. F. Stamm, *J. Org. Chem.*, **28**, 1580 (1963).