FREE-RADICAL ADDITION REACTIONS OF OLEFINIC SYSTEMS

By J. I. G. Cadogan and D. H. Hey, Ph.D., D.Sc., F.R.I.C.
(University of London, King's College)

Before 1930 some confusion existed with regard to the reactions of hydrogen halides with ethylenic systems. With the object of reconciling earlier discordant data, an investigation of the addition of hydrogen halides to unsymmetrically substituted alkenes was undertaken by Kharasch and his collaborators in the University of Chicago. It soon became apparent that such anomalies as existed were due in part to the use of ill-defined experimental conditions and in part to the use of impure reactants.

The reaction between hydrogen bromide and allyl bromide may take one of two courses:

$$\mathrm{HBr + CH_2{:}CH{\cdot}CH_2Br} \begin{array}{ll} \nearrow \ \mathrm{CH_3{\cdot}CHBr{\cdot}CH_2Br} & \quad . \quad . \ (A) \\ \\ \searrow \ \mathrm{CH_2Br{\cdot}CH_2{\cdot}CH_2Br} & \quad . \quad . \ (B) \end{array}$$

Kharasch and Mayo [1] established that if the reactants were pure and freshly prepared, and if the reaction was allowed to proceed in the dark and in the absence of oxygen, a quantitative conversion into 1 : 2-dibromopropane (*A*) was obtained after ten days. The reaction thus proceeded according to the Markownikoff rule,[2] which requires that the negative part of the addendum attaches itself to the carbon atom which carries the smaller number of hydrogen atoms. Alternatively, the presence in the reaction mixture of small quantities of oxygen or peroxides, introduced either deliberately or fortuitously by the use of old samples of allyl bromide, caused the rapid formation (30 minutes) of 1 : 3-dibromopropane (*B*). Very many instances of reversal of addition under the influence of added peroxides (the so-called abnormal addition) were reported from Kharasch's laboratory during the period 1933—40, and this work has been reviewed by Mayo and Walling.[3]

It was not until 1937 that a theoretical interpretation of these results was advanced. Hey and Waters,[4] and Kharasch, Engelmann, and Mayo,[5] independently postulated that the fast abnormal addition was a self-propagating chain reaction involving atomic bromine and a free-radical intermediate. Thus, for initiation by benzoyl peroxide:

$$\begin{aligned} \mathrm{(Ph{\cdot}CO{\cdot}O)_2} &\longrightarrow \mathrm{Ph{\cdot}CO{\cdot}O{\cdot} + CO_2 + Ph{\cdot}} \\ \mathrm{Ph{\cdot}\ (or\ Ph{\cdot}CO{\cdot}O{\cdot}) + HBr} &\longrightarrow \mathrm{PhH\ (or\ Ph{\cdot}CO_2H) + Br{\cdot}} \\ \mathrm{Br{\cdot} + CH_2{:}CH{\cdot}CH_2Br} &\longrightarrow \mathrm{CH_2Br{\cdot}\overset{|}{C}H{\cdot}CH_2Br} \\ \mathrm{CH_2Br{\cdot}\overset{|}{C}H{\cdot}CH_2Br + HBr} &\longrightarrow \mathrm{CH_2Br{\cdot}CH_2{\cdot}CH_2Br + Br{\cdot}} \end{aligned}$$

---

[1] Kharasch and Mayo, *J. Amer. Chem. Soc.*, 1933, **55**, 2468.

[2] Markownikoff, *Annalen*, 1870, **153**, 228.

[3] Mayo and Walling, *Chem. Reviews*, 1940, **27**, 351.

[4] Hey and Waters, *ibid.*, 1937, **21**, 169.

[5] Kharasch, Engelmann, and Mayo, *J. Org. Chem.*, 1937, **2**, 288.

The " bromine atom " theory received additional support when it was shown that abnormal addition of hydrogen bromide to olefinic bonds could be effected photochemically, in both the liquid and the vapour phase, without the intervention of oxygen or peroxides.[6] This mechanism has become the prototype for a large number of free-radical addition reactions, many of which are of novel character since they involve a wide variety of addenda which, in the absence of free-radical or photochemical initiation, do not react with olefinic systems at all. These reactions may be represented by the following general scheme :

$$\text{Initiation}\begin{cases} R'\cdot + XY \longrightarrow R'X + Y\cdot & (1)\\ \text{or } XY \xrightarrow{h\nu} X\cdot + Y\cdot & (2)\\ Y\cdot + R\cdot CH{:}CH_2 \longrightarrow R\cdot\overset{|}{C}H\cdot CH_2Y & (3)\end{cases}$$

$$\begin{matrix}\text{Transfer} \\ \text{(to monomer)}\end{matrix}\quad R\cdot\overset{|}{C}H\cdot CH_2Y + XY \longrightarrow R\cdot CHX\cdot CH_2Y + Y\cdot \qquad (4)$$

Addition polymerisation may be regarded as a special case of this process, in which the initial product $R\cdot\overset{|}{C}H\cdot CH_2Y$ reacts with successive molecules of the monomer $R\cdot CH{:}CH_2$ rather than with the molecule XY, to give telomers, *i.e.*, products containing more than one molecule of olefin per molecule of XY. Thus :

$$\text{Propagation :}\quad R\cdot\overset{|}{C}H\cdot CH_2Y + R\cdot CH{:}CH_2 \longrightarrow R\cdot\overset{|}{C}H\cdot CH_2\cdot CHR\cdot CH_2Y \qquad (5)$$

$$R\cdot\overset{|}{C}H\cdot CH_2\cdot CHR\cdot CH_2Y + R\cdot CH{:}CH_2 \longrightarrow R\cdot\overset{|}{C}H\cdot CH_2\cdot CHR\cdot CH_2\cdot CHR\cdot CH_2Y \quad \text{etc.}$$

$$\begin{matrix}\text{Transfer} \\ \text{(to telomer)}\end{matrix}\quad R\cdot\overset{|}{C}H\cdot CH_2\cdot CHR\cdot CH_2Y + XY \longrightarrow R\cdot CHX\cdot CH_2\cdot CHR\cdot CH_2Y + Y\cdot \qquad (6)$$

The chain is assumed to be terminated by dimerisation of radicals or by disproportionation, although in many cases there is no experimental evidence that this is so.

The present Review is directed mainly towards investigations which have led to the isolation and identification of the products of these reactions rather than towards kinetic studies, since reviews on the latter aspect of the subject have recently been published.[7, 8, 8a]

The Addition of Polyhalogenomethanes to Olefins

Jensen, Kharasch, and Urry [9] reported in 1946 that carbon tetrabromide reacts additively with ethylenic compounds under the influence of methyl

[6] Vaughan, Rust, and Evans, *J. Org. Chem.*, 1942, **7**, 477.

[7] Burnett, *Quart. Reviews*, 1950, **4**, 292.

[8] Mayo and Walling, *Chem. Reviews*, 1950, **46**, 191.

[8a] Burnett and Melville, *ibid.*, 1954, **54**, 228.

[9] Jensen, Kharasch, and Urry, *J. Amer. Chem. Soc.*, 1946, **68**, 154.

radicals, generated from acetyl peroxide, or on irradiation by visible light, thus :

$$\mathrm{R{\cdot}CH{:}CH_2 + CBr_4 \xrightarrow[1\text{—}5\%\ (Me{\cdot}CO_2)_2]{} R{\cdot}CHBr{\cdot}CH_2{\cdot}CBr_3}$$

Later,[10] it was shown that carbon tetrachloride, chloroform, and bromoform can be induced to add to olefins containing a terminal double bond (oct-1-ene, styrene, ethyl acrylate, diallyl, propylene, and ethylene) under the influence of added peroxides or light of appropriate wave-length. The reactions are not independent of the mode of initiation, but the differences concern the rate of the reaction rather than the nature of the products. This is not unexpected because, for chain initiation by relatively reactive radicals such as methyl, the energy of activation of the reaction $\cdot\mathrm{CH_3} + \mathrm{CX_4} \rightarrow \mathrm{CH_3X} + \cdot\mathrm{CX_3}$ is probably small, whether X is bromine or chlorine. When, however, the chain initiation reaction is $\mathrm{CX_4} \xrightarrow{h\nu} \cdot\mathrm{CX_3} + \mathrm{X}\cdot$, it will take place more easily with carbon tetrabromide than with carbon tetrachloride, because the energy of activation for homolytic scission of the carbon–bromine bond is less than that for carbon–chlorine scission.* It is therefore apparent that high yields of the one-to-one addition product † will be favoured by the use of either (*a*) a very reactive halide such as $\mathrm{CBr_4}$ and/or (*b*) an olefin $\mathrm{R{\cdot}CH{:}CH_2}$ producing a very reactive intermediate radical $\mathrm{R{\cdot}\overset{|}{C}H{\cdot}CH_2X}$, which will effectively undergo chain transfer with the halide (reaction 4) rather than chain propagation with another molecule of olefin (reaction 5). The reactivity of this radical will be dependent on X. A measure of the relative importance of reactions (4) and (5) can be obtained by calculation of the chain-transfer constants, which express the ratio of the rate of chain transfer (reaction 4) to that of chain growth (reaction 5). Further, a high halide : olefin ratio will favour the formation of the one-to-one adduct. This is true for any addition-polymerisation reaction of this type, but the ease of polymerisation of the olefin, also a major factor, often prevents control of the products merely by change in the ratio of the reactants. In agreement with these postulates Kharasch and his collaborators [9, 10] have shown that, in general, if the halide is $\mathrm{CBr_4}$, a halide : olefin ratio of 2—4 : 1 gives a high yield of $\mathrm{R{\cdot}CHBr{\cdot}CH_2{\cdot}CBr_3}$. To obtain a similar yield using $\mathrm{CCl_4}$ it is necessary to increase the ratio to 5—100 : 1, according to the nature of the olefin. For example, $\mathrm{CCl_4}$ (50 mol.) and styrene (1 mol.) in the presence of benzoyl peroxide (0·01—0·05 mol.) give telomeric products, but $\mathrm{CBr_4}$ (6 mol.) and styrene (1 mol.) give a high yield (96%) of the one-to-one adduct.

The addition of bromoform and chloroform follows different courses consequent upon a difference at the initiation stage. Whereas chloroform

---

[10] Jensen, Kharasch, and Urry, *J. Amer. Chem. Soc.*, 1947, **69**, 1100.

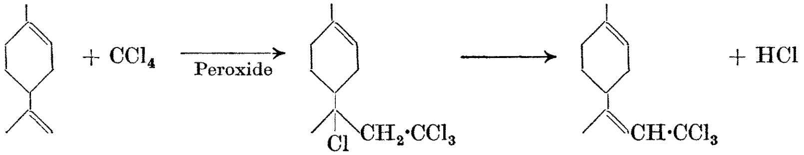
* The absorption continuum of carbon tetrachloride is in the ultra-violet region (2280—2800 Å) (Lowry and Sass, *J.*, 1926, 622), whereas that of carbon tetrabromide approaches the violet of the visible region (~ 3500 Å) (Hennici, *Z. Physik*, 1932, **77**, 35).

† *I.e.*, the simple adduct consisting of 1 molecule XY + 1 molecule $\mathrm{R{\cdot}CH{:}CH_2}$.

yields a trichloromethyl radical, bromoform gives a dibromomethyl radical

$$\begin{aligned} \cdot CH_3 + CHCl_3 &\longrightarrow CH_4 + \cdot CCl_3 \\ \cdot CH_3 + CHBr_3 &\longrightarrow CH_3Br + \cdot CHBr_2 \\ \cdot CCl_3\ (\text{or}\ \cdot CHBr_2) + R\cdot CH{:}CH_2 &\longrightarrow R\cdot \overset{|}{C}H\cdot CH_2\cdot CCl_3\ (\text{or}\ R\cdot \overset{|}{C}H\cdot CH_2\cdot CHBr_2) \end{aligned}$$

The greater lability of the hydrogen atom in chloroform is in agreement with the observation that, in the reaction between benzoyl peroxide and chloroform, the product is benzene and not chlorobenzene.[11] Lower yields of addition products are obtained with these halides owing to the decreased lability of the atoms involved. In agreement with this, Israelashvili and Diamant [12] have shown that carbon tetrachloride, but not bromoform and chloroform, can be induced to add to (+)-limonene. The addition, in this case, is followed by the elimination of hydrogen chloride:



Iodoform behaves like bromoform, as shown by the addition of $\cdot CHI_2$ and I· to limonene.[13] Similar addition reactions have been reported with halogenated acids and their derivatives.[14] In the presence of acetyl peroxide, oct-1-ene reacts with methyl dichloroacetate and with trichloroacetyl chloride as follows:

$$\begin{aligned} C_6H_{13}\cdot CH{:}CH_2 + CHCl_2\cdot CO_2Me &\longrightarrow C_6H_{13}\cdot CH_2\cdot CH_2\cdot CCl_2\cdot CO_2Me \\ C_6H_{13}\cdot CH{:}CH_2 + CCl_3\cdot COCl &\longrightarrow C_6H_{13}\cdot CHCl\cdot CH_2\cdot CCl_2\cdot COCl \end{aligned}$$

These addition reactions involve the free radicals $\cdot CCl_2\cdot CO_2Me$ and $\cdot CCl_2\cdot COCl$. Similar reactions cannot be investigated between (*a*) free radicals such as $\cdot CH_2\cdot CO_2Me$ derived from $CH_3\cdot CO_2Me$ and (*b*) olefins, because the olefin is able to compete with the ester for the methyl radical derived from the peroxide, but, since an α-bromine atom is more susceptible to attack by a free methyl radical than α-hydrogen or any hydrogen in an olefin, it should be possible to use α-bromo-esters to generate non-halogenated ester radicals, which might then undergo addition reactions with olefins. Examples of such addition reactions have now been provided.[15] Thus:

$$C_6H_{13}\cdot CH{:}CH_2 + CH_2Br\cdot CO_2Et \longrightarrow C_6H_{13}\cdot CHBr\cdot CH_2\cdot CH_2\cdot CO_2Et$$

The reactions of bromotrichloromethane resemble those of carbon tetrabromide rather than those of carbon tetrachloride, with regard to both ease of initiation and propagation and the nature of the products formed.[16] The

---

[11] Boeseken and Gelissen, *Rec. Trav. chim.*, 1924, **43**, 869; Hey and Peters, unpublished observation.

[12] Israelashvili and Diamant, *J. Amer. Chem. Soc.*, 1952, **74**, 3185.

[13] Bergmann, Halevy, Israelashvili, and Weizmann, *ibid.*, 1947, **69**, 2569.

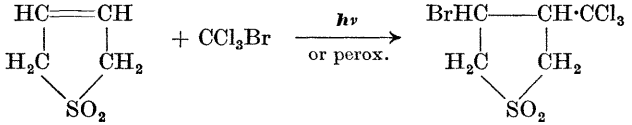
[14] Jensen, Kharasch, and Urry, *ibid.*, 1945, **67**, 1626.

[15] Fisher, Kharasch, and Skell, *ibid.*, 1948, **70**, 1055.

[16] Kharasch, Reinmuth, and Urry, *ibid.*, 1947, **69**, 1105.

initiation process has been represented as $\cdot CH_3 + CCl_3Br \rightarrow CH_3Br + \cdot CCl_3$, or $CCl_3Br \xrightarrow{h\nu} Br\cdot + \cdot CCl_3$. With terminal olefins $R\cdot CH{:}CH_2$, high yields (70—95%) of the one-to-one product ($R\cdot CHBr\cdot CH_2\cdot CCl_3$) are obtained, even when the halide : olefin ratio is as low as 3 : 1. The low energy of activation for the scission of the carbon–bromine bond in bromotrichloromethane is further demonstrated by its addition to styrene to give a high yield of the one-to-one adduct and to olefins such as allyl chloride and oct-2-ene (a non-terminal olefin), to give fair yields of one-to-one adducts, whereas only traces of such products are formed when carbon tetrachloride is used. Bromotrichloromethane will react with "butadiene sulphone" (I) (2 : 5-dihydrothiophen 1 : 1-dioxide), in the presence of a peroxide or when exposed to light, to give the adduct (II).[17] A similar reaction takes place with carbon tetrachloride but, as is to be expected, a higher temperature is required.

(I)



(II)

In peroxide-induced reactions with alk-1-enes (oct-1-ene, propylene, vinyl acetate), bromodichloromethane ($CHCl_2Br$), and dibromodichloromethane (CCl_2Br_2) closely resemble bromoform rather than chloroform,[18] since a bromine atom is abstracted by the initiating radical. It must be emphasised that in none of the reactions reported above has the isolation of any product of the type RX, derived from attack by R· (generated from a peroxide) on CX_4, CX_2Y_2, etc., been reported, although this mechanism for chain initiation has been generally assumed.

The ease of scission of the carbon–bromine bond in bromotrichloromethane has been utilised by Friedlander and Kharasch [19] to initiate and control the heteropolymerisation of sulphur dioxide and olefins to give polysulphones. Light, oxygen, and peroxidic compounds had hitherto been used as initiators, but control of the polymer chain length was impossible. By the use of varying ratios of this halide to sulphur dioxide it is now possible to achieve control. The reactions involved may be represented as follows :

$$CCl_3Br \xrightarrow{h\nu} Br\cdot + \cdot CCl_3$$

$$R\cdot CH{:}CH_2 + \cdot CCl_3 \rightarrow R\cdot \overset{|}{C}H\cdot CH_2\cdot CCl_3 \quad . \quad . \quad . \quad (7)$$

$$R\cdot \overset{|}{C}H\cdot CH_2\cdot CCl_3 + CCl_3Br \rightarrow R\cdot CHBr\cdot CH_2\cdot CCl_3 + \cdot CCl_3 \quad . \quad . \quad (8)$$

$$R\cdot \overset{|}{C}H\cdot CH_2CCl_3 + SO_2 \rightarrow \cdot SO_2\cdot CHR\cdot CH_2\cdot CCl_3 \quad . \quad . \quad (9)$$

$$\cdot SO_2\cdot CHR\cdot CH_2\cdot CCl_3 + R\cdot CH{:}CH_2 \rightarrow R\cdot \overset{|}{C}H\cdot CH_2\cdot SO_2\cdot CHR\cdot CH_2\cdot CCl_3 \quad . \quad . \quad (10)$$

---

[17] Freimann, Kharasch, and Urry, *J. Org. Chem.*, 1948, **13,** 570.

[18] Kharasch, Kuderna, and Urry, *ibid.*, p. 895.

[19] Friedlander and Kharasch, *ibid.*, p. 882.

$$\mathrm{R{\cdot}\overset{|}{C}H{\cdot}CH_2{\cdot}SO_2{\cdot}CHR{\cdot}CH_2{\cdot}CCl_3 + SO_2 \longrightarrow {\cdot}SO_2{\cdot}CHR{\cdot}CH_2{\cdot}SO_2{\cdot}CHR{\cdot}CH_2{\cdot}CCl_3} \quad (11)$$

$$\mathrm{{\cdot}SO_2{\cdot}CHR{\cdot}CH_2{\cdot}SO_2{\cdot}CHR{\cdot}CH_2{\cdot}CCl_3 + R{\cdot}CH{:}CH_2 \longrightarrow R{\cdot}\overset{|}{C}H{\cdot}[CH_2{\cdot}SO_2{\cdot}CHR]_2{\cdot}CH_2{\cdot}CCl_3} \quad (12)$$

and so on

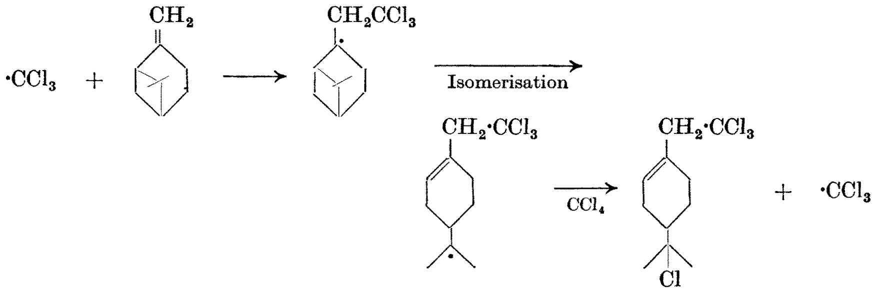
$$\mathrm{R{\cdot}\overset{|}{C}H{\cdot}[CH_2{\cdot}SO_2{\cdot}CHR]_2{\cdot}CH_2{\cdot}CCl_3 + CCl_3Br \longrightarrow R{\cdot}CHBr{\cdot}[CH_2{\cdot}SO_2{\cdot}CHR]_2{\cdot}CH_2{\cdot}CCl_3 + {\cdot}CCl_3} \quad (13)$$

Hence, an increase in the halide : sulphur dioxide ratio for a given amount of olefin will favour reactions (8) and (13) and the product will be of low molecular weight, while a decrease in the ratio favours reactions (9) and (11), etc., to give a higher polymer.

In accordance with this theory, equimolar quantities of bromotrichloromethane, oct-1-ene, and sulphur dioxide give, in addition to the one-to-one adduct of the halide and olefin, 2-bromooctyl 1-(2 : 2 : 2-trichloroethyl)heptyl sulphone :

$$\mathrm{C_6H_{13}{\cdot}CH(CH_2{\cdot}CCl_3){\cdot}SO_2{\cdot}CH_2{\cdot}CHBr{\cdot}C_6H_{13}}$$

It is of interest that the peroxide or light-induced addition of carbon tetrachloride to β-pinene results in the two fragments adding at *non-adjacent* carbon atoms,[20] which may be represented thus :



Haszeldine [21] has shown that the photochemical or thermal decomposition of trifluoroiodomethane produces the trifluoromethyl radical, which is able to bring about the polymerisation of ethylene to give products of the type $\mathrm{CF_3{\cdot}[CH_2{\cdot}CH_2]_n{\cdot}I}$, the mechanism being analogous to the general scheme outlined above. The formation of hexafluoroethane by dimerisation of trifluoromethyl radicals does not occur under his conditions (6 : 1 excess of halide), and the main products have $n = 1$ and 2. The chain-transfer constant therefore appears to be similar to that for bromotrichloromethane. Compounds such as $\mathrm{CHF_3}$, $\mathrm{CF_3{\cdot}CH_2{\cdot}CH_3}$ (which might be formed by hydrogen abstraction), $\mathrm{CF_3{\cdot}CH{:}CH_2}$ (formed by disproportionation), $\mathrm{CF_3{\cdot}[CH_2{\cdot}CH_2]_n{\cdot}CF_3}$ (formed by radical combination), and $\mathrm{I{\cdot}[CH_2{\cdot}CH_2]_n{\cdot}I}$, have not been detected. The addition of trifluoroiodomethane to tetrafluoroethylene, under similar conditions and by a similar mechanism, gives short-chain polymers of the type $\mathrm{CF_3{\cdot}[CF_2{\cdot}CF_2]_n{\cdot}I}$ ($n = 1$—10) [21] having a

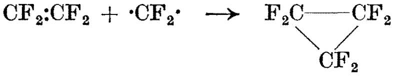
---

[20] Fisher, Goldblatt, and Oldroyd, *J. Amer. Chem. Soc.*, 1950, **72**, 2407.

[21] Haszeldine, *J.*, 1949, 2856.

terminal reactive iodine atom. The lower members of this series, unlike those formed with ethylene, show properties similar to trifluoroiodomethane itself, and readily undergo further reaction with the olefin to yield solid products of higher molecular weight. The main factors which determine the value of n in $CF_3{\cdot}[CF_2{\cdot}CF_2]_n{\cdot}I$ are the relative concentrations of the chain-transfer agent (*i.e.*, CF_3I), the monomer, and the growing telomer radical, and the considerations which apply here are those already mentioned for the addition of bromotrichloromethane and carbon tetrabromide to olefins. Haszeldine [22] has emphasised that chain transfer between the perfluoroalkyl radical, $CF_3{\cdot}CF_2{\cdot}CF_2{\cdot}$, and trifluoroiodomethane is best affected in the liquid phase, where the concentration of trifluoroiodomethane is at a maximum. In the vapour phase, substantially more of the telomer with $n > 2$ is formed, since the relative concentration of trifluoroiodomethane is lower and the possibility that the heptafluoroiodopropane formed can undergo subsequent homolysis to generate a ${\cdot}C_3F_7$ radical, which then reacts with the olefin, is increased. Pentafluoroiodoethane reacts with tetrafluoroethylene [22] under conditions similar to those described for iodotrifluoromethane to give a telomer $CF_3{\cdot}CF_2{\cdot}[CF_2{\cdot}CF_2]_n{\cdot}I$. The compound having $n = 1$ can be prepared in 91% yield, and fluoro-iodides containing up to 16 carbon atoms have been isolated under suitable conditions of concentration. By taking alternate members of the series $CF_3{\cdot}[CF_2{\cdot}CF_2]_n{\cdot}I$ and $CF_3{\cdot}CF_2{\cdot}[CF_2{\cdot}CF_2]_n{\cdot}I$, the complete range of fluoro-iodides $CF_3{\cdot}[CF_2]_m{\cdot}I$ can be obtained. The volatile by-products from these reactions of tetrafluoroethylene are perfluoro*cyclo*butane (1%) and perfluoro*cyclo*propane (3%),[22] the latter product being probably formed by the reaction of a ${\cdot}CF_2{\cdot}$ diradical with tetrafluoroethylene :

$$
\begin{aligned}
{\cdot}CF_3 + CF_2{:}CF_2 &\longrightarrow CF_3{\cdot}CF_2{\cdot} + {\cdot}CF_2{\cdot} \\
\text{or}\quad CF_2{:}CF_2 &\longrightarrow 2\ {\cdot}CF_2{\cdot}
\end{aligned}
$$



Addition polymerisation also occurs when tetrafluorodi-iodoethane is heated with tetrafluoroethylene,[23] the compound $I{\cdot}[CF_2{\cdot}CF_2]_2{\cdot}I$ being isolated in high yield together with small amounts of telomers. Conditions have been devised whereby each member of the series $I{\cdot}[CF_2{\cdot}CF_2]_n{\cdot}I$ can be converted substantially into the next higher member by reaction with tetrafluoroethylene,

$$I{\cdot}CF_2{\cdot}CF_2I \xrightarrow[C_2F_4]{} I{\cdot}[CF_2{\cdot}CF_2]_2{\cdot}I \xrightarrow[C_2F_4]{} I{\cdot}[CF_2{\cdot}CF_2]_3{\cdot}I, \text{ etc.}$$

Thus, compounds having $n = 1$—9 have been prepared. At each stage varying amounts of telomers are formed, the spread in chain length becoming greater as n increases. The mechanism is considered to be of the general radical-chain type, the first few steps being :

$$
\begin{aligned}
I{\cdot}CF_2{\cdot}CF_2I &\xrightarrow{\text{Heat}} I{\cdot}CF_2{\cdot}CF_2{\cdot} + I{\cdot} \\
I{\cdot}CF_2{\cdot}CF_2{\cdot} + CF_2{:}CF_2 &\longrightarrow I{\cdot}CF_2{\cdot}CF_2{\cdot}CF_2{\cdot}CF_2{\cdot}, \text{ etc.}
\end{aligned}
$$

---

[22] Haszeldine, *J.*, 1953, 3761.

[23] *Idem*, *Nature*, 1951, **167**, 139.

Trichloroiodomethane behaves like bromotrichloromethane on irradiation, in that the trichloromethyl radical is formed.[24] The former halide can be induced to add to 3 : 3 : 3-trifluoroprop-1-ene ($CF_3{\cdot}CH{:}CH_2$) to give a high yield of $CF_3{\cdot}CHI{\cdot}CH_2{\cdot}CCl_3$, which readily gives trifluorocrotonic acid under the influence of alcoholic potassium hydroxide followed by concentrated sulphuric acid. This acid has also been obtained by dehydroiodination and hydrolysis of $CF_3{\cdot}CH_2{\cdot}CHI{\cdot}CN$, obtained by the free-radical addition of trifluoroiodomethane to acrylonitrile.[24]

The Relative Reactivity of Olefinic Double Bonds towards Free Radicals.—In the general scheme for free-radical addition reactions outlined above, it is apparent that if the rate of addition of the free radical Y· (reaction 3) is slow, then these radicals accumulate until their concentration becomes so high that the chain is terminated by dimerisation. Alternatively, if reaction (4) is slow, the secondary free radical formed in reaction (3) may

$$Y{\cdot} + R{\cdot}CH{:}CH_2 \longrightarrow R{\cdot}\overset{|}{C}H{\cdot}CH_2Y \quad . \quad . \quad . \quad . \quad (3)$$

$$R{\cdot}\overset{|}{C}H{\cdot}CH_2Y + XY \longrightarrow R{\cdot}CHX{\cdot}CH_2Y + Y{\cdot} \quad . \quad . \quad (4)$$

dimerise, or add to other molecules of olefin to yield telomers. Thus, in order to compare the reactivities of olefins with respect to free-radical addition in reaction (3), reagents which react rapidly in reaction (4) must be selected. From the results of the investigations outlined above, it follows that bromotrichloromethane is such a reagent, and it has been used by Friedlander and Kharasch [25] in the determination of the relative reactivities of several cyclic olefins with respect to the addition of a free trichloromethyl radical (reaction 3). This is achieved by allowing a one-to-one mixture of two olefins to react with a large excess of the halide until about 25% of the mixed olefins present have been consumed. The relative amounts of the one-to-one adducts are taken to be a measure of the relative reactivity of the double bonds in the olefins towards addition of trichloromethyl radicals. It has thus been shown that compounds containing a five-membered unsaturated ring are more reactive than the corresponding six-membered ring compounds. The relative reactivities are therefore correlated with the relative differences in strain between the unsaturated and the corresponding saturated ring compound. Further, the conjugated unsaturated compounds *cyclo*pentadiene, *cyclo*hexadiene, and indene (where the ring strain is greatest) are more reactive than the non-conjugated olefins. This study has been extended by Kharasch and Sage [26] to include many open-chain olefins, the reactivity of oct-1-ene being taken as unity. On this basis, *cyclo*hexene (0·2), allyl chloride (0·5), and allylbenzene (0·7) are less reactive and β-methylstyrene (1·1) is of the same order of reactivity as oct-1-ene. Conjugated olefins such as styrene and butadiene are very much more reactive, so much so that the accuracy of the original experiments in which these olefins were compared directly with the less reactive

---

[24] Haszeldine, *J.*, 1953, 922.

[25] Friedlander and Kharasch, *J. Org. Chem.*, 1949, **14**, 239.

[26] Kharasch and Sage, *ibid.*, p. 537.

oct-1-ene is questionable, owing to the very small amount of oct-1-ene–CCl_3Br adduct formed. This defect has now been remedied[27] and the reactivities of α-methylstyrene (4·2), butadiene (2·0),* and *p*-chlorostyrene (1·0) have been obtained by direct comparison with styrene (1·0). It is of interest to note the large difference between the reactivities of α- and β-methylstyrene, the double bond being non-terminal in the latter.

The Addition of Alcohols, Aldehydes, and Ketones to Olefins

The peroxide- and the light-induced additions of primary and secondary alcohols to olefins result in replacement of a hydrogen atom attached to the hydroxyl-bearing carbon atom by an alkyl group to give secondary and tertiary alcohols respectively.[28] As with all free-radical addition reactions, small amounts of peroxide or light induce a disproportionately large amount of reaction and, in the addition of alcohols to olefins but not necessarily in the addition of other types of compound, telomers are formed. The reaction of ethanol with ethylene, for example, gives butan-2-ol, hexan-2-ol, octan-2-ol, and decan-2-ol, when initiated by light or *tert.*-butyl peroxide. The general reaction scheme is followed, the first steps being :

$$\begin{aligned} \mathrm{R\cdot + CH_3{\cdot}CH_2{\cdot}OH} &\longrightarrow \mathrm{RH + CH_3{\cdot}\overset{|}{C}H{\cdot}OH} \\ \mathrm{CH_3{\cdot}\overset{|}{C}H{\cdot}OH + CH_2{:}CH_2} &\longrightarrow \mathrm{CH_3{\cdot}CH(OH){\cdot}CH_2{\cdot}CH_2{\cdot}} \\ \mathrm{CH_3{\cdot}CH(OH){\cdot}CH_2{\cdot}CH_2{\cdot} + CH_3{\cdot}CH_2{\cdot}OH} &\longrightarrow \\ &\ \mathrm{CH_3{\cdot}CH(OH){\cdot}CH_2{\cdot}CH_3 + CH_3{\cdot}\overset{|}{C}H{\cdot}OH} \\ &\ \text{or chain transfer} \end{aligned}$$

An interesting aspect of these reactions is the apparent specificity of the inducing agent. The alkyl peroxides are effective, but diacyl peroxides and 2 : 2′-azobis*iso*butyronitrile are not. This is not unexpected because previous work[29] has shown that alkyl peroxides have first-order kinetics with approximately the same rates of decomposition in a wide range of solvents, whereas benzoyl peroxide is rapidly consumed by alcohols in a complex manner[30] and does not, therefore, initiate the free-radical addition to olefins. The chain-transfer constant, and therefore the extent of telomerisation, depends on the nature of the carbon–hydrogen bond broken in the transfer step. Chain transfer takes place more easily with secondary alcohols than with primary alcohols, methanol having the lowest transfer constant (*e.g.*, with a 20 : 1 molar ratio of propan-2-ol and oct-1-ene, a 40—50% conversion into the 1 : 1 adduct is obtained, but with methanol the corresponding conversion is 15%, even when the alcohol : olefin ratio is 50 : 1). The isolation of small quantities of acetaldehyde and *cyclo*hexanone from the reactions with ethanol and *cyclo*hexanol, respectively, suggests that the chain termination step might involve reactions of the type :

---

[27] Kharasch, Nudenberg, and Simon, *J. Org. Chem.*, 1953, **18**, 328.

[28] Huyser, Juveland, Stacey, and Urry, *J. Amer. Chem. Soc.*, 1954, **76**, 450.

[29] Raley, Rust, and Vaughan, *ibid.*, 1948, **70**, 1336.

[30] Bartlett and Nozaki, *ibid.*, 1947, **69**, 2299.

* CCl_3Br + butadiene give 75 ± 10% of 1 : 4-adduct and 25 ± 10% of 1 : 2-adduct (see ref. 26).

$CH_3\cdot\overset{|}{C}H\cdot OH + R\cdot \longrightarrow CH_3\cdot CHO + RH$, where R is a free *tert.*-butoxy, or an intermediate free radical. This type of reaction is apparently dominant in the attempted addition of benzyl alcohol to ethylene in the presence of *tert.*-butyl peroxide since benzaldehyde is obtained instead of the expected addition product.

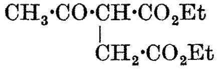
A similar initiation step is involved in the peroxide- or light-induced addition of aldehydes to alk-1-enes.[31] The overall reaction is

$$R\cdot CHO + R'\cdot CH{:}CH_2 \longrightarrow R\cdot CO\cdot CH_2\cdot CH_2R'$$

If a high ratio (6 : 1) of aldehyde to olefin is used the principal products are (*a*) the one-to-one adduct, (*b*) small amounts of telomers (mainly two-to-one adduct), and (*c*) the alkane derived from the alkyl radical of the aldehyde together with an equivalent amount of carbon monoxide. The formation of these products can be explained by assuming that the following initiation reactions take place: $R\cdot CHO + \cdot CH_3 \longrightarrow CH_4 + R\cdot\overset{|}{C}{:}O$ or $R\cdot CHO \xrightarrow{h\nu} R\cdot\overset{|}{C}{:}O + H\cdot$; the $R\cdot\overset{|}{C}{:}O$ radical is then assumed to add to $R\cdot CH{:}CH_2$ to give one-to-one and two-to-one adducts followed by chain transfer with a molecule of ketone. Side reactions such as $R\cdot\overset{|}{C}{:}O \longrightarrow R\cdot + CO$; $R\cdot + R\cdot CHO \longrightarrow RH + R\cdot\overset{|}{C}{:}O$ account for the other products. The formation of diacetyl (30% compared with decan-2-ol formed) in the addition of acetaldehyde to oct-1-ene suggests that chain termination of the type $2R\cdot\overset{|}{C}{:}O \longrightarrow R\cdot CO\cdot CO\cdot R$ is important in this case. Best yields of ketones are obtained when both the aldehyde and the olefin are of long-chain type. Irrespective of the aldehyde used, *cyclo*alkenes give poor yields of ketones. In contrast to the addition of bromotrichloromethane, where the transfer constant is high, the addition of butanol to styrene produces no one-to-one adduct, but mainly telomers of high molecular weight. Kharasch, Kuderna, and Nudenberg[32] have shown that *cyclo*hexanone will undergo this type of addition to oct-1-ene (1 : 8 molar ratio) to give some 2-octyl*cyclo*hexanone.

This work has been extended by Patrick[33] who obtained ethyl acetylsuccinate (III) in 78% yield from ethyl maleate and a three-fold excess of acetaldehyde at 80° in the presence of benzoyl peroxide (0·1%). Similarly, butyraldehyde functions equally well in the synthesis of homologous ethyl succinates. Aldehydes, such as crotonaldehyde and benzaldehyde, do not undergo this addition owing to resonance stabilisation of the intermediate acyl radicals which are then unable to continue the chain reaction.

(III)



$$CH_3\cdot CO\cdot \underset{CH_2\cdot CO_2Et}{\underset{|}{C}H}\cdot CO_2Et$$

Kosher and La Zerte[34] have shown that the free-radical addition of alcohols, aldehydes, and esters to terminally unsaturated perfluoro-olefins

---

[31] Kharasch, Kuderna, and Urry, *J. Org. Chem.*, 1949, **14**, 248.
[32] Kharasch, Kuderna, and Nudenberg, *ibid.*, 1953, **18**, 1225.
[33] Patrick, *ibid.*, 1952, **17**, 1009.
[34] Kosher and La Zerte, Abs. 124th Amer. Chem. Soc. Meeting, 1953, p. 35M.

containing at least three carbon atoms results in high yields (75—95%) of one-to-one adducts. Even with methanol, no telomerisation products were formed, which illustrates the important effect of the olefin on the chain-transfer constant.

The Addition of Phosphorus, Silicon, and Sulphur Compounds to Olefins

The addition of phosphorus trichloride to aliphatic olefins can take place under the influence of peroxides,[35] thus providing a useful method for the preparation of compounds of the type $\mathrm{R{\cdot}CHCl{\cdot}CH_2{\cdot}PCl_2}$, where R is an alkyl group. The reaction with oct-1-ene is initiated by $\mathrm{{\cdot}PCl_2}$ radicals and follows the general reaction scheme to give $\mathrm{C_6H_{13}{\cdot}CHCl{\cdot}CH_2{\cdot}PCl_2}$ as the main product, in addition to smaller amounts of telomers.

A similar reaction between oct-1-ene and trichlorosilane has been reported.[36] The reaction is similar to that with chloroform in that both trichlorosilane and chloroform lose a hydrogen atom to give respectively $\mathrm{{\cdot}SiCl_3}$ and $\mathrm{{\cdot}CCl_3}$ radicals. The product is therefore $\mathrm{C_6H_{13}{\cdot}CH_2{\cdot}CH_2{\cdot}SiCl_3}$.

By initiation by ultra-violet light or by *tert.*-butyl peroxide, phosphine can be made to add to a variety of olefins [37] to give mixtures of telomeric organo-phosphines, the relative amounts of each depending on the ratio of phosphine to olefin used. Thus:

$$
\begin{aligned}
\mathrm{PH_3} &\xrightarrow{h\nu} \mathrm{{\cdot}PH_2 + H{\cdot}} \\
\mathrm{{\cdot}PH_2 + R{\cdot}CH{:}CH_2} &\longrightarrow \mathrm{R{\cdot}\overset{|}{C}H{\cdot}CH_2{\cdot}PH_2} \\
\mathrm{R{\cdot}\overset{|}{C}H{\cdot}CH_2{\cdot}PH_2 + R{\cdot}CH{:}CH_2} &\longrightarrow \mathrm{R{\cdot}\overset{|}{C}H{\cdot}CH_2{\cdot}CHR{\cdot}CH_2{\cdot}PH_2} \\
\mathrm{R{\cdot}\overset{|}{C}H{\cdot}CH_2{\cdot}CHR{\cdot}CH_2{\cdot}PH_2 + PH_3} &\longrightarrow \mathrm{R{\cdot}CH_2{\cdot}CH_2{\cdot}CHR{\cdot}CH_2{\cdot}PH_2 + {\cdot}PH_2}
\end{aligned}
$$

The reaction appears to parallel the photochemically induced addition of hydrogen sulphide to unsaturated compounds.[38]

In the addition reactions cited above, the evidence for a free-radical chain mechanism is placed beyond doubt by the fact that either the products formed are different from those resulting from the " normal " ionic addition, or the reactions do not proceed at all unless initiated by a free radical generated either thermally or photolytically. It is, however, possible that under certain conditions addition reactions may take place by both homolytic and heterolytic mechanisms and give the same product. An example of this has been provided by Fuchs and Kharasch,[39] who showed that the addition of thiols to methyl acrylate proceeds in the presence of either a strong base or a peroxide (or ultra-violet light), and in both instances the same product is formed. The former reaction must clearly

---

[35] Jensen, Kharasch, and Urry, *J. Amer. Chem. Soc.*, 1945, **67**, 1864.

[36] Pietruza, Sommer, and Whitmore, *ibid.*, 1947, **69**, 188.

[37] Rust, Stiles, and Vaughan, *ibid.*, 1952, **74**, 3282.

[38] Rust and Vaughan, *J. Org. Chem.*, 1942, **7**, 472.

[39] Fuchs and Kharasch, *ibid.*, 1948, **13**, 97.

be heterolytic and the latter homolytic. These reactions may be represented as follows:

$$\left\{\begin{array}{rcl}[\mathrm{RS}]^- + \mathrm{CH_2{:}CH{\cdot}CO_2Me} & \longrightarrow & [\mathrm{RS{\cdot}CH_2{\cdot}CH{\cdot}CO_2Me}]^- \\ [\mathrm{RS{\cdot}CH_2{\cdot}CH{\cdot}CO_2Me}]^- + \mathrm{RSH} & \longrightarrow & \mathrm{RS{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2Me} + [\mathrm{RS}]^-\end{array}\right.$$

$$\left\{\begin{array}{rcl}\mathrm{RS{\cdot}} + \mathrm{CH_2{:}CH{\cdot}CO_2Me} & \longrightarrow & \mathrm{RS{\cdot}CH_2{\cdot}\overset{|}{C}H{\cdot}CO_2Me} \\ \mathrm{RS{\cdot}CH_2{\cdot}\overset{|}{C}H{\cdot}CO_2Me} + \mathrm{RSH} & \longrightarrow & \mathrm{RS{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2Me} + \mathrm{RS{\cdot}}\end{array}\right.$$

The formation of telomeric products in the latter reaction is in accord with its homolytic nature. No such telomers are found in the base-catalysed reaction. The homolytic addition of a thiol $\mathrm{R'SH}$ to an olefin $\mathrm{R{\cdot}CH{:}CH_2}$, to give the one-to-one adduct, is inhibited by oxygen and the product consists of a mixture of the racemic forms of the hydroxylated sulphoxide $\mathrm{R{\cdot}CH(OH){\cdot}CH_2{\cdot}\underset{\underset{O}{\downarrow}}{S}R'}$.[40] The following mechanism has been suggested for this reaction:

$$\begin{array}{rcl}\mathrm{R'SH} + \mathrm{O_2} & \longrightarrow & \mathrm{R'S{\cdot}} + \mathrm{HO_2{\cdot}} \\ \mathrm{HO_2{\cdot}} + \mathrm{R'SH} & \longrightarrow & \mathrm{R'S{\cdot}} + \mathrm{H_2O_2} \\ \mathrm{R'S{\cdot}} + \mathrm{R{\cdot}CH{:}CH_2} & \longrightarrow & \mathrm{R{\cdot}\overset{|}{C}H{\cdot}CH_2{\cdot}SR'} \\ \mathrm{R{\cdot}\overset{|}{C}H{\cdot}CH_2{\cdot}SR'} + \mathrm{O_2} & \longrightarrow & \mathrm{{\cdot}O_2{\cdot}CHR{\cdot}CH_2{\cdot}SR'} \\ \mathrm{{\cdot}O_2{\cdot}CHR{\cdot}CH_2{\cdot}SR'} + \mathrm{R'SH} & \longrightarrow & \mathrm{HO_2{\cdot}CHR{\cdot}CH_2{\cdot}SR'} + \mathrm{R'S{\cdot}}\end{array}$$

$$\mathrm{HO_2{\cdot}CHR{\cdot}CH_2{\cdot}SR'} \xrightarrow[\text{Isomerisation}]{\qquad\qquad} \mathrm{R{\cdot}CH(OH){\cdot}CH_2{\cdot}\underset{\underset{O}{\downarrow}}{S}R'}$$

This speculative scheme may be relevant to the problem of the nature of the role of oxygen as an inhibitor of thiol-induced polymerisation and copolymerisation.

That addition of sulphuryl chloride to olefins $\mathrm{R{\cdot}CH{:}CH_2}$ induced by benzoyl peroxide can lead to homolytic addition of chlorine to the double bond has been indicated by Brown and Kharasch,[41] the initiation process being:

$$\begin{array}{rcl}\mathrm{R'{\cdot}} + \mathrm{SO_2Cl_2} & \longrightarrow & \mathrm{{\cdot}SO_2Cl} + \mathrm{R'Cl} \\ \mathrm{{\cdot}SO_2Cl} & \longrightarrow & \mathrm{SO_2} + \mathrm{Cl{\cdot}}\end{array}$$

The dissociation of the $\mathrm{{\cdot}SO_2Cl}$ radical can be suppressed if the experiment is conducted with sulphuryl chloride in high dilution in the presence of sulphur dioxide,[42] which results in the formation of a dichlorinated sulphone $\mathrm{(R{\cdot}CHCl{\cdot}CH_2)_2SO_2}$ in addition to the corresponding 1 : 2-dichloroalkane. Evidence is thus provided for the transient existence of the free $\mathrm{{\cdot}SO_2Cl}$ radical, which is considered to add to the olefin in the normal way, the

---

[40] Kharasch, Mantell, and Nudenberg, *J. Org. Chem.*, 1951, **16**, 524.

[41] Brown and Kharasch, *J. Amer. Chem. Soc.*, 1939, **61**, 3432.

[42] Kharasch and Zavist, *ibid.*, 1951, **73**, 964.

intermediate radical so formed then isomerising to a more stable form, as follows :

$$\cdot\mathrm{SO_2Cl} + \mathrm{R{\cdot}CH{:}CH_2} \longrightarrow \mathrm{R{\cdot}\overset{|}{C}H{\cdot}CH_2{\cdot}SO_2Cl} \xrightarrow{\text{Isomerisation}} \mathrm{R{\cdot}CHCl{\cdot}CH_2{\cdot}SO_2}\cdot$$

$$\mathrm{R{\cdot}CHCl{\cdot}CH_2{\cdot}SO_2}\cdot + \mathrm{R{\cdot}CH{:}CH_2} \longrightarrow \mathrm{R{\cdot}\overset{|}{C}H{\cdot}CH_2{\cdot}SO_2{\cdot}CH_2{\cdot}CHRCl}$$

$$\downarrow \mathrm{SO_2Cl_2}$$

$$\mathrm{(R{\cdot}CHCl{\cdot}CH_2)_2SO_2} + \cdot\mathrm{SO_2Cl}$$

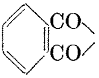
The existence of the free $\cdot SO_2Cl$ radical is confirmed by the results of similar experiments with vinyl chloride [43] in which 1 : 1 : 2-trichloroethane (65%) and 2 : 2-dichloroethanesulphonyl chloride (8%) were formed, but no radical isomerisation takes place in this case :

$$\mathrm{Cl{\cdot}CH{:}CH_2} + \cdot\mathrm{SO_2Cl} \longrightarrow \mathrm{Cl{\cdot}\overset{|}{C}H{\cdot}CH_2{\cdot}SO_2Cl}$$

$$\mathrm{Cl{\cdot}\overset{|}{C}H{\cdot}CH_2{\cdot}SO_2Cl} + \mathrm{SO_2Cl_2} \longrightarrow \mathrm{Cl_2CH{\cdot}CH_2{\cdot}SO_2Cl} + \cdot\mathrm{SO_2Cl}$$

Further evidence that radicals of the $\sim\overset{|}{\mathrm{S}}\mathrm{O_2}$ type react with olefins to form carbon–sulphur rather than carbon–oxygen bonds is supplied by the peroxide-induced reaction of phthaloylsulphamoyl chloride with oct-1-ene,[44] which proceeds as follows :

$$\mathrm{RN{\cdot}SO_2Cl} + \mathrm{R''} \longrightarrow \mathrm{RN{\cdot}\overset{|}{S}O_2} + \mathrm{R''Cl} \quad \text{where R} =$$



$$\mathrm{RN{\cdot}\overset{|}{S}O_2} + \mathrm{R'{\cdot}CH{:}CH_2} \longrightarrow \mathrm{R'{\cdot}\overset{|}{C}H{\cdot}CH_2{\cdot}SO_2{\cdot}NR}$$

$$\mathrm{R'{\cdot}\overset{|}{C}H{\cdot}CH_2{\cdot}SO_2{\cdot}NR} + \mathrm{RN{\cdot}SO_2Cl} \longrightarrow \mathrm{R'{\cdot}CHCl{\cdot}CH_2{\cdot}SO_2{\cdot}NR} + \mathrm{RN{\cdot}\overset{|}{S}O_2}$$

Small amounts (8%) of telomers are also formed.

The Mechanism of the Addition Reaction

The evidence so far presented is overwhelmingly in favour of the free-radical chain mechanism previously postulated.[4, 5] It is convenient to consider the three main stages of the reaction individually. It has already been pointed out that data concerning the initiation step are sparse and no direct evidence in support of the assumption (although reasonable) that chain initiation takes place by reactions of the type $R\cdot + CX_4 \rightarrow \cdot CX_3 + RX$ has been presented in the work so far considered. The general reaction scheme for chain propagation, however, has received ample support as a result of the isolation and identification of the various one-to-one adducts and telomers, and this part of the reaction need not be further discussed. As with the initiation step, only a few attempts have been made to isolate products which would give conclusive proof of the nature of the termination step. The work described in this section is concerned mainly with questions arising from chain initiation and termination.

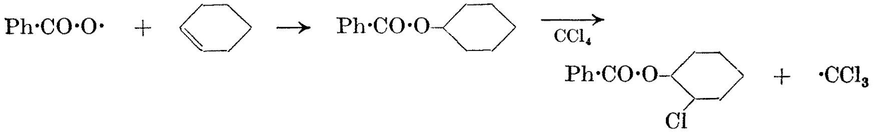
Chain Initiation.—In most free-radical chain reactions the average kinetic chain lengths are very large, and consequently the proportions of groupings

---

[43] Yakubovich and Zinov'ev, *J. Gen. Chem., U.S.S.R.*, 1947, **17**, 2028.

[44] Kharasch and Mosher, *J. Org. Chem.*, 1952, **17**, 453.

or products derived from the initiators are very small. In the addition of carbon tetrachloride to normal olefins, however, 20—40 moles of addition product are formed per mole of peroxide.[10, 16] This led Kooyman and Farenhorst [45] to search for the products of the decomposition of the initiator. Contrary to Kharasch's statement that olefins having non-terminal double bonds fail to add carbon tetrachloride Kooyman and Farenhorst have shown that *cyclo*hexene gives a small amount (~ 10%) of the one-to-one adduct. Further, they have been able to account for 91% of the phenyl radicals derived from the benzoyl peroxide initiator, 55% of them appearing as 2-chloro*cyclo*hexyl benzoate, thus indicating that the main initiation mechanism is one of addition as follows:

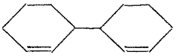


The trichloromethyl radical then adds to *cyclo*hexene according to the general scheme. That chain initiation by the abstraction mechanism, $Ph\cdot + CCl_4 \longrightarrow PhCl + \cdot CCl_3$, is relatively unimportant is shown by the appearance of only 10% of the phenyl radicals as chlorobenzene and 12% as benzoic acid.

Chain Termination.—No hexachloroethane is formed in the addition reactions of carbon tetrachloride with *cyclo*hexene, propene, or hept-1-ene with the proportions 3 moles of halide, 1 mole of olefin, and 0·02—0·04 mole of peroxide.[45] Hence, under these conditions chain termination by dimerisation of trichloromethyl radicals does not take place. A similar situation exists in the free-radical addition of trifluoromethyl radicals to ethylene and tetrafluoroethylene.[21, 22] In order to account for the large amount of peroxide required to give a good yield of addition products the chain-breaking step is considered to consist of the formation of radicals of low reactivity, such as the resonance-stabilised allylic radical, which are incapable of continuing the chain. Thus, the chain might be terminated by *abstraction* of a hydrogen atom from $C_{(3)}$, *i.e.*, from the α-methylenic group, thus:

$$\cdot CCl_3 + \overset{1}{C}H_2{:}\overset{2}{C}H\cdot\overset{3}{C}H_2R \longrightarrow \overset{\bullet}{\overbrace{CH_2\cdot CH\cdot CHR}} + CHCl_3$$

A similar termination mechanism has been postulated by Patrick [33] to explain the failure of the addition of αβ-unsaturated aldehydes to olefins and constitutes an example of "degradative chain-transfer".[46] This mechanism is supported by the isolation of chloroform in all cases. The fate of the allyl radicals in the experiments with propene and hept-1-ene is unknown, but evidence for their dimerisation appears in the reaction with *cyclo*hexene when di*cyclo*hex-2-enyl (IV) is isolated.


(IV)

---

[45] Kooyman and Farenhorst, *Rec. Trav. chim.*, 1951, **70**, 867.
[46] Altschul and Bartlett, *J. Amer. Chem. Soc.*, 1945, **67**, 816.

The formation of a very small amount of 3-chloro*cyclo*hexene indicates that the *cyclo*hexenyl radical is more reactive than open-chain allyl-type radicals towards carbon tetrachloride :

Further support for this type of chain termination has been provided by consideration of the addition of carbon tetrachloride to 3 : 3-dimethylbut-1-ene and allylbenzene.[45] 3 : 3-Dimethylbut-1-ene requires much less peroxide (one-tenth to one-twentieth) to give the same yield of addition products, when compared with hexadec-1-ene and dec-1-ene, on the basis of peroxide decomposed. The absence of allylic hydrogen atoms excludes termination by degradative chain transfer, and it must take place by the slower method of radical–radical interaction. This is supported by the isolation of hexachloroethane even though a very small amount of peroxide (0·15%) is used. Allylbenzene, which gives an allyl-type radical of great stability, on the other hand, exhibits little or no addition (2%), owing to its faster rate of chain breaking. Further, in small amounts it *inhibits* the addition of carbon tetrachloride to 3 : 3-dimethylbut-1-ene.

The overall picture of chain termination is, therefore, consistent with a reaction of the type : $R\cdot + CH_2{:}CH{\cdot}CH_2R' \rightarrow RH + CH_2{:}CH{\cdot}\overset{|}{C}HR'$. Thus a decrease in yield of addition products, on the basis of the same amount of peroxide decomposed, should be caused by the presence of a foreign compound containing an α-methylenic group. Using the addition of carbon tetrachloride to hexadec-1-ene (3 : 1 molar ratio) as a basis for comparison, Kooyman [47] has shown that marked decreases in yield do occur with compounds such as ethylbenzene, cumene, and hept-3-ene. Consistently with this, compounds such as benzene, *tert.*-butylbenzene, and 2 : 2 : 5 : 5-tetramethylhex-3-ene, which do not contain α-methylenic hydrogen atoms, do not retard the addition. Altschul and Bartlett,[46] who found that molecular weights of polymers from allyl chloride and acetate are as low as 500, had previously noted the possibility of chain termination involving the formation of stable allyl radicals. These conclusions have been recently confirmed [48] by studies on the rates of the peroxide-initiated polymerisation of allyl acetate and of allyl acetate containing α-methylenic deuterium atoms. The rates of polymerisation of deuterated allyl acetate are 1·93—2·9 times faster than those observed in identical experiments with allyl acetate, and the average molecular weight of the polymers so produced is 2·38 times greater for the deuterated than for the undeuterated compound. If the reasonable assumption is made that the tendency for atomic abstraction of deuterium is less than that for protium, these observations confirm that the chain-termination step in the polymerisation of allyl acetate involves transfer of an α-methylenic hydrogen atom to a chain-carrying free radical.

Work by Melville and his co-workers is also relevant to the problem of

[47] Kooyman, *Discuss. Faraday Soc.*, 1951, **10**, 163.

[48] Bartlett and Tate, *J. Amer. Chem. Soc.*, 1953, **75**, 91.

chain termination in these reactions. From a study of the kinetics of the photochemically initiated addition of bromotrichloromethane to *cyclo*hexene,[49] carried out under conditions in which the rate-determining stage involves only trichloromethyl radicals (*i.e.* halide : olefin ratio of 10 : 1), it has been shown that chain termination is due exclusively to dimerisation to give hexachloroethane and that attack by the trichloromethyl radical on an α-methylenic hydrogen atom is precluded. These results, at first sight, are apparently at variance with Kooyman's observations, but in fact they are an indication that under different conditions different mechanisms are operative. An experiment on the photochemically initiated addition of carbon tetrachloride to *cyclo*hexene in the presence of benzoyl peroxide [50] has shown that, under Kooyman's conditions, termination is indeed of first order with respect to radical concentration, thus indicating that, when the halide is sufficiently reactive, apparently all the substituted allyl radicals are able to continue reaction chains. Further, if the olefin is present in excess (olefin : halide 10 : 1),[51] the rate-determining stage of the reaction becomes the debromination of bromotrichloromethane by the trichloromethyl*cyclo*hexyl radical, and dimerisation of these radicals constitutes the chain termination reaction. Unfortunately this has not been corroborated by the isolation of 2 : 2′-di(trichloromethyl)di*cyclo*hexyl. This work is of great importance, because it constitutes the first measurement of absolute reactions rates of small free radicals in solution, and it provides a powerful tool for the elucidation of polymerisation mechanisms. It must be stressed, however, that different chain mechanisms may be operative in different systems (see references 28 and 31), and the picture cannot be completed until more experimental results are available.

The Orientation of Free-radical Addition

In all cases of free-radical addition to olefins of the type $R\cdot CH{:}CH_2$ so far considered the point of initial attack has been exclusively at the terminal CH_2 group. This has been incorporated in a " radical addition " rule due to Farmer,[52] which requires that the radical component initiating the reaction must add exclusively to the more hydrogenated ethylenic carbon atom. This empirical rule, however, does not tell us *why* the additions are so orientated.

Three theories have been considered to account for the orientation in free-radical addition :

(i) Waters [53] has suggested that free halogen atoms are electrophilic in character, and thus attack the point of highest electron density. This statement does not necessarily include all free radicals although this has sometimes been assumed. This theory has been criticised by Barton,[54] who suggests that free radicals attack preferentially points of high *differential*

---

[49] Melville, Robb, and Tutton, *Discuss. Faraday Soc.*, 1951, **10**, 154.

[50] *Idem, ibid.*, p. 224.

[51] *Idem, ibid.*, 1953, **14**, 150.

[52] Farmer, *J. Soc. Chem. Ind.*, 1947, **66**, 86.

[53] Waters, " Chemistry of Free Radicals ", Oxford Univ. Press, 1946, p. 182.

[54] Barton, *Nature*, 1948, **162**, 182.

electron density, *i.e.*, differential in either direction with respect to the unsymmetrical unsubstituted system.

(ii) The point of attack is determined by steric factors.[8 (p. 261)]

(iii) The point of attack depends on the relative stability of the two radicals which may be formed.[3 (p. 373)]

New experimental results relating to the problem of orientation have recently been published by Haszeldine. It having been established that trifluoroiodomethane is a suitable source of trifluoromethyl radicals,[21] its addition to a wide range of unsymmetrical olefins has been studied. Attack by the trifluoromethyl radical on the olefins $R{\cdot}CH{:}CH_2$($R = Me$, Cl, F, or CO_2Me) [55] and $R{\cdot}CH{:}CH_2$ ($R = CF_3$ or CN) [56] is, within the accuracy of the experiments (*ca.* 5%), exclusively at the CH_2 group. The addition takes place by the general reaction scheme previously shown and the conditions were such that formation of the one-to-one adduct was favoured. Since in ionic reactions $R{\cdot}CH{:}CH_2$ has a polarisation $R{\cdot}\overset{\delta+}{CH}{=}\overset{\delta-}{CH_2}$ ($R = Me$, Cl, or F) or $R{\cdot}\overset{\delta-}{CH}{=}\overset{\delta+}{CH_2}$ ($R = CF_3$, CN, or CO_2Me), it is evident that the polar nature of R, and hence the apparent polarisation of the double bond, is of little importance in determining the orientation of free-radical attack (presupposing that the *direction* of the polarisation is the same for ionic and radical additions). Changes in R do, however, affect the rate of the addition, the addition to $CF_3{\cdot}CH{:}CH_2$ being much slower than to propene. In agreement with these observations, Henne and Neger [57] have shown that in the free-radical addition of hydrogen bromide, fluoroiodomethane, and bromotrichloromethane to 3 : 3 : 3-trifluoroprop-1-ene ($R = CF_3$), the bromine atom, the trifluoromethyl radical, and the trichloromethyl radical attack the CH_2 group exclusively, and that the additions are slower than to propene itself. Thus, in these reactions, the observed orientations are not accommodated by theory (i), whether it refers to all free radicals or merely to halogen atoms.

The free-radical addition of trifluoroiodomethane and bromotrichloromethane to chlorotrifluoroethylene, $CF_2{:}CFCl$, has been attended by some controversy. Henne and Kraus [58] claimed that trifluoromethyl and trichloromethyl radicals attacked the CFCl group exclusively to give $ICF_2{\cdot}CFCl{\cdot}CF_3$ and $BrCF_2{\cdot}CFCl{\cdot}CCl_3$ respectively. These results have been criticised on theoretical grounds by Haszeldine and Steele [59] and a repetition of this work [60] has shown that the products of the addition of trifluoroiodomethane to chlorotrifluoroethylene are of general formula $CF_3{\cdot}[C_2ClF_3]_n{\cdot}I$, n being dependent on the ratio of the reactants. The compounds having $n = 1$—5 have been shown to be derived from the exclusive attack of a trifluoromethyl radical on the CF_2 group. Elucidation of the structure of the telomers having $n = 2$—5 invalidated the argument that the trifluoromethyl radical might attack the CFCl group to a small extent to give

---

[55] Haszeldine and Steele, *J.*, 1953, 1199. [56] Haszeldine, *J.*, 1952, 2504, 3490.

[57] Henne and Nager, *J. Amer. Chem. Soc.*, 1951, **73,** 5527.

[58] Henne and Kraus, *ibid.*, p. 1791.

[59] Haszeldine and Steele, *Chem. and Ind.*, 1951, 684. [60] *Idem*, *J.*, 1953, 1592.

$CF_3{\cdot}CFCl{\cdot}CF_2{\cdot}$, which might be more reactive than $CF_3{\cdot}CF_2{\cdot}CFCl{\cdot}$ and would thus combine with a second molecule of $CF_2{\cdot}CFCl$ at a much greater rate. This would mean that the compound with $n = 1$ is $CF_3{\cdot}CF_2{\cdot}CFClI$, but the compounds with $n = 2$—5 could be $CF_3{\cdot}CFCl{\cdot}CF_2{\cdot}[C_2ClF_3]_{n-1}{\cdot}I$, implying that radical attack is not exclusively on the CF_2 group. Haszeldine and Steele's results have been supported by Howald and Miller.[61] More recently Henne and Kraus [62] have re-investigated their products and have accepted and experimentally confirmed the results of Haszeldine and Steele.

The photochemical addition of trifluoroiodomethane and hydrogen bromide to hexafluoropropene, $CF_3{\cdot}CF{:}CF_2$, yields products derived from the exclusive attack of a trifluoromethyl radical or a bromine atom on the CF_2 group.[63] Trifluoroiodomethane reacts only very slowly with hexafluoropropene when exposed to light of wave-length >3000 Å, which only the iodide can absorb, and yields the one-to-one adduct only. The reaction is faster in silica vessels (*i.e.*, with light of wave-length >2200 Å) and yields telomers the structures of which indicate that the direction of the addition is independent of the wave-length of the light used to initiate the reaction. The polarisation of hexafluoropropene, established by the direction of addition of hydrogen bromide under ionic conditions, is $CF_3{\cdot}\overset{\delta-}{C}F{=}\overset{\delta+}{C}F_2$. Thus again, assuming the polarisation of the double bond to be in the same direction for ionic and radical attack, it follows that radical attack takes place at the more positive carbon atom, and not at the less positive, as would be required if the radical is to be regarded as an electrophilic reagent. Similarly, radical attack on $CF_3{\cdot}CR{:}CH_2$ ($R = CF_3$ or CF_2Cl) takes place exclusively at the CH_2 group and is independent of the polarisation of the bond.[64] Tarrant and Lovelace [65] have shown that the peroxide-induced addition of dibromodifluoromethane to propene and 2-methylprop-1-ene proceeds by the initial attack by a bromodifluoromethyl radical ($\cdot CF_2Br$) on the terminal CH_2 group, thus:

$$(CH_3)_2C{:}CH_2 \longrightarrow (CH_3)_2CBr{\cdot}CH_2{\cdot}CF_2Br$$

That this reagent cannot be induced to add to 3 : 3 : 3-trifluoroprop-1-ene is in agreement with previous observations on the slow addition reactions of this olefin.[55, 56, 57]

In all the above reactions the initial attack has been at the terminal CH_2 or CF_2 groups. An explanation of this marked specificity of radical attack is that the carbon atom attacked is that most favoured on steric grounds [theory (ii)]. This is supported by the observed direction of addition of CF_2Br_2 to 2-fluorobut-2-ene,[65] which has a non-terminal double bond, thus:

$$CH_3{\cdot}CF{:}CH{\cdot}CH_3 \longrightarrow CH_3{\cdot}CFBr{\cdot}CH(CH_3){\cdot}CF_2Br$$

It is difficult, however, on steric grounds alone, to account for the specificity

---

[61] Howald and Miller, Abs. 122nd Amer. Chem. Soc. Meeting, 1952, p. 12K.

[62] Henne and Kraus, *J. Amer. Chem. Soc.*, 1954, **76**, 1175.

[63] Haszeldine, *J.*, 1953, 3559.

[64] *Idem, ibid.*, p. 3565.

[65] Tarrant and Lovelace, Abs. 124th Amer. Chem. Soc. Meeting, 1953, p. 35M.

of attack on this olefin, because fluorine is only slightly larger than hydrogen : the same considerations apply to the addition to vinyl fluoride.[55] Indeed, it has been demonstrated by Haszeldine [64] that radical addition can occur in a direction contrary to that predicted on steric grounds alone. He has established that attack by a trifluoromethyl radical, a trichloromethyl radical, or a bromine atom on 1 : 1-difluoroprop-1-ene ($CH_3{\cdot}CH{:}CF_2$) is exclusively at the central carbon atom. It is noteworthy that, as is the case with propene,[55] no, or very slight, abstraction of allylic hydrogen atoms occurs despite the possibility for resonance stabilisation of the resultant radical.

Explanations of the direction of addition based solely on steric considerations therefore appear to be unsuitable for general application. It could be argued that the trifluoromethyl radical might attack the olefinic carbon atom with which it will form the strongest bond. Thus, since the carbon–carbon bond in $—CF_2{\cdot}CF_2—$ is very probably stronger than that in $—CH_2{\cdot}CH_2—$ in a hydrocarbon,[66] it would follow that the free radical would attack a CF_2 group in preference to a CH_2 group or to a CFCl or CF group. While this theory predicts the product successfully for $CF_2{:}CFCl$ ($\rightarrow CF_3{\cdot}CF_2{\cdot}CFClI$) or $CF_3{\cdot}CF{:}CF_2$ ($\rightarrow CF_3{\cdot}CFI{\cdot}CF_2CF_3$), it fails for 1 : 1-difluoroethylene $CF_2{:}CH_2$ ($\rightarrow CF_2I{\cdot}CH_2{\cdot}CF_3$).[66]

The main factor influencing the direction of addition of a free radical X· to unsaturated systems $R{\cdot}CH{:}CH_2$ appears to be the relative stabilities of the intermediate radicals $R{\cdot}\overset{|}{C}H{\cdot}CH_2{\cdot}X$ and $R{\cdot}CHX{\cdot}CH_2{\cdot}$. The preferred reaction path will be that involving the transition state of least energy increment which, in general, will be the route from the starting materials to the thermodynamically more stable of the possible products of addition of the radical to the unsaturated compound. If this is so, then, in general, the secondary radicals $R{\cdot}\overset{|}{C}H{\cdot}CH_2{\cdot}X$ are more stable than the primary radicals $R{\cdot}CHX{\cdot}CH_2{\cdot}$,* and it follows from Haszeldine's observations on the addition of trifluoroiodomethane to $(CF_3)_2C{:}CH_2$ and $(CF_3)(CF_2Cl)C{:}CH_2$, that the tertiary radicals $(CF_3)_2\overset{|}{C}{\cdot}CH_2{\cdot}CF_3$ and $(CF_3)(CF_2Cl)\overset{|}{C}{\cdot}CH_2CF_3$ are more stable than the corresponding primary radicals $(CF_3)_3C{\cdot}CH_2{\cdot}$ and $(CF_3)_2(CF_2Cl)C{\cdot}CH_2{\cdot}$. The results of the addition of trifluoroiodomethane, bromotrichloromethane, and hydrogen bromide to 1 : 1-difluoroprop-1-ene ($CH_3{\cdot}CH{:}CF_2$) indicate that the order of radical stability is not always tertiary > secondary > primary, since the primary radicals $CF_3{\cdot}CH(CH_3){\cdot}CF_2{\cdot}$, $CCl_3{\cdot}CH(CH_3){\cdot}CF_2{\cdot}$, and $BrCH(CH_3){\cdot}CF_2{\cdot}$ are more stable than the secondary radicals $CH_3{\cdot}\overset{|}{C}H{\cdot}CF_2{\cdot}CF_3$, $CH_3{\cdot}\overset{|}{C}H{\cdot}CF_2{\cdot}CCl_3$, and $\overset{|}{C}H_3{\cdot}CH{\cdot}CF_2Br$. The relative stabilities of radicals estimated from this chemical evidence is parallelled by the radical stabilities estimated from ultra-violet spectroscopic data.[67]

Haszeldine [44] has postulated that radical stability decreases as the number of hydrogen atoms attached directly to the carbon atom carrying the lone electron is increased. It follows that for decreasing radical stability,

---

[66] Haszeldine and Steele, *J.*, 1954, 923. [67] Haszeldine, *J.*, 1953, 1764.

* The terms primary, secondary, and tertiary refer to the carbon skeleton.

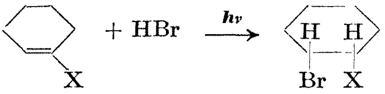
tertiary ($\geqslant$C·) > secondary (>CH·) > primary (—CH_2·) where the terms primary, secondary, and tertiary indicate not the carbon skeleton but the number of atoms or groups *other* than hydrogen which are attached to the carbon atom formally carrying the lone electron. Haszeldine claims that all relevant free radicals so far studied fall into this classification, which however does not include the radicals derived from addition to such compounds as CF_2:CFCl and CF_3·CF:CF_2. There remains the further possibility that by suitable choice of groups R and R′ and a secondary radical RR′CH·, the stability of a secondary radical can be made greater than that for a tertiary radical.

It should be stressed that the approach to the problem of orientation has so far been solely empirical and a satisfactory theoretical interpretation of the experimental observations has yet to be made.

The Stereochemistry of Free-radical Addition

The homolytic addition of hydrogen bromide to simple olefins is not stereospecific because the addition of atomic bromine is reversible,[68] and *cis–trans*-isomerisation of stilbene is much faster than free-radical addition of hydrogen bromide.[69] Similarly, chlorostilbene [70] and 2-bromobutene [71] are rapidly isomerised by bromine atoms. With cyclic systems, however, complications due to *cis–trans*-isomerisation of the double bonds are avoided. Abell, Aycock, and Goering [72] have shown that the free-radical addition of hydrogen bromide to 1-bromo*cyclo*hexene gives exclusively *cis*-1 : 2-dibromo*cyclo*hexane, indicating that *trans*-addition takes place. Since the product is the thermodynamically less stable isomer, the possibility that *cis*-addition to give the *trans*-isomer first takes place, followed by *trans* ⟶ *cis*-isomerisation, is eliminated. 1-Methyl*cyclo*hexene also undergoes *trans*-addition of hydrogen bromide to give *cis*-1-bromo-2-methyl*cyclo*hexane.

Thus,



X = CH_3 or Br.

It is noteworthy that 1-methyl*cyclo*hexene exhibits the rare property of undergoing ionic and radical additions at comparable rates. The relative importance of the two mechanisms varies with conditions : the reaction is exclusively heterolytic at − 80° and exclusively homolytic at + 35°. The results of Friedlander and Kharasch [25] indicate that *trans*-addition also takes place in the radical chain addition of bromotrichloromethane to *cyclo*hexene. Fawcett [73] has suggested that *trans*-addition is due to the preferred

---

[68] Derbyshire and Waters, *Trans. Faraday Soc.*, 1949, **45**, 749.

[69] Kharasch, Mansfield, and Mayo, *J. Amer. Chem. Soc.*, 1937, **59**, 1155.

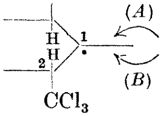
[70] Murray and Taylor, *J.*, 1938, 2078.

[71] Lepingle, *Bull. Soc. chim.*, 1926, **39**, 741.

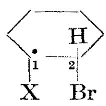
[72] Abell, Aycock, and Goering, *J. Amer. Chem. Soc.*, 1952, **74**, 3588.

[73] Fawcett, *Chem. Reviews*, 1950, **47**, 235.

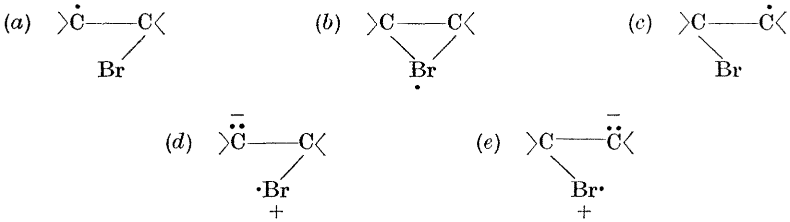
approach (*A*) of the bromotrichloromethane molecule to the intermediate radical (V), because a steric interaction which would be involved in approach (*B*). But, if the trichloromethyl group at $C_{(2)}$ occupies the more thermodynamically stable equatorial position there is obviously no steric difference between approach from either direction, hence the *trans*-isomer, and not the *cis* as observed, would be formed preferentially owing to its greater thermodynamical stability. *trans*-Addition of hydrogen bromide to 1-substituted *cyclo*hexenes to give the *cis*-isomer suggests that the intermediate radical is not adequately described by (VI), which would lead, by the argument presented above, to a mixture of *cis*- and *trans*-isomers with a preponderance of the *trans*-form. It seems likely that the bromine atom is situated centrally between carbon atoms 1 and 2, and Abell *et al.*[72] have invoked resonance between the following forms to suggest why (VI) should react with hydrogen bromide in the direction remote from the bromine atom.



(V)



(VI) $X = Br, CH_3$



This formulation is consistent with the orientation of free-radical addition of hydrogen bromide, because this is governed by the relative importance of (*a*) and (*c*), *i.e.*, the relative stabilities of the two forms. With this modification the general reaction scheme can accommodate all the known facts including *trans*-addition.

Free-radical Addition to Carbon–Carbon Triple Bonds

Although strictly beyond the scope of this Review, brief reference may be made to the photochemical additions of trifluoroiodomethane [74] and heptafluoroiodopropane [75] to acetylene. These reactions proceed readily by a mechanism similar to that for addition to ethylene, to give mainly the one-to-one adduct in each case, 3 : 3 : 3-trifluoro-1-iodoprop-1-ene (CF_3·CH:CHI) and 3 : 3 : 4 : 4 : 5 : 5 : 5-heptafluoro-1-iodopent-1-ene (C_3F_7·CH:CHI) respectively. The addition of two molecules of the halide to acetylene occurs to only a small extent, if at all. Both the photochemical

---

[74] Haszeldine, *J.*, 1950, 3037.

[75] *Idem, ibid.*, p. 2789.

and the ionic addition of hydrogen bromide to 3 : 3 : 3-trifluoropropyne give exclusively 1-bromo-3 : 3 : 3-trifluoropropene : [56]

$$CF_3{\cdot}C{\vdots}CH + HBr \longrightarrow CF_3{\cdot}CH{:}CHBr$$

Bromotrichloromethane and carbon tetrachloride can also be made to undergo photochemical or peroxide-induced additions to alkynes.[76] In both cases only one molecule of halide adds to the alkyne. Bromotrichloromethane yields one-to-one products together with telomers, but very small amounts of one-to-one products are formed in the reaction with carbon tetrachloride. It has been established [76] that in general alk-1-ynes are less reactive than the corresponding alk-1-enes, both in the ability to add a trichloromethyl radical and in the ability of the free radical thus formed to react with the halide.

---

[76] Jerome, Kharasch, and Urry, *J. Org. Chem.*, 1950, **15**, 966.