350. *Chlorine Activation by Redox Transfer. Part II.*[1] *The Addition of Carbon Tetrachloride to Olefins.*

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Carbon tetrachloride is added to olefins and vinylic monomers under the catalytic influence of iron(II, III) or copper(I, II) chloride, in a variety of solvents at 70—145°. Copper chloride completely suppresses telomerization. A free-radical chain mechanism is proposed for the addition, in which metal chloride participates in the propagation as a chlorine-atom transfer agent, thereby much enhancing the apparent reactivity of carbon tetrachloride (" redox-transfer "). Experimental support for this mechanism is presented. The reaction with but-2-ene gives a mixture of diastereoisomeric adducts, the composition of which changes with catalyst, and, for copper-catalysis, also with the solvent and with the excess of chloride ion. *cis-* and *trans*-But-2-ene give the same ratio of diastereoisomers.

The initiation mechanism is discussed. At 82°, ferric chloride induces addition of carbon tetrachloride to but-2-ene only in the presence of a reducing agent. This enables one to estimate the kinetic chain-length, which has a much larger value than for a peroxide-induced reaction.

The addition of carbon tetrachloride to olefins has been extensively investigated. Kharasch and his school[2] proposed a free-radical chain mechanism, which is generally accepted, and has the following propagation steps:

$$\mathrm{CCl_3\cdot + CHR{:}CHR' \longrightarrow CCl_3{\cdot}CHR{\cdot}CHR'\cdot} \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (1)$$

$$\mathrm{CCl_3{\cdot}CHR{\cdot}CHR'\cdot + CCl_4 \longrightarrow CCl_3{\cdot}CHR{\cdot}CHR'Cl + \cdot CCl_3} \quad . \ . \ . \ . \ . \ . \quad (2)$$

$$\mathrm{CCl_3{\cdot}CHR{\cdot}CHR'\cdot + CHR{:}CHR' \longrightarrow CCl_3{\cdot}CHR{\cdot}CHR'{\cdot}CHR{\cdot}CHR'\cdot,\ etc.} \quad . \ . \ . \ . \quad (3)$$

Until now the reaction has been described almost exclusively for terminal olefins. Step (3) is of minor importance for non-polymerizable olefins. On the other hand, in reactions of styrene, butadiene, acrylonitrile, and acrylates, this step predominates over (2) to the extent that polymers are obtained, even for carbon tetrachloride–monomer molar ratios as high as 100 : 1.[3] Each polymeric chain incorporates the elements of one molecule of carbon tetrachloride. [Bromotrichloromethane, which is much more reactive than carbon tetrachloride in step (2), gives high yields of 1 : 1 adducts with styrene and butadiene.[4]] The behaviour of ethylene is between that of aliphatic mono-olefins and the

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[1] Part I, Asscher and Vofsi, *J.*, 1961, 2261.
[2] Kharasch, Jensen, and Urry, *J. Amer. Chem. Soc.*, 1947, **69**, 1100.
[3] Mayo, *J. Amer. Chem. Soc.*, 1948, **70**, 3691.
[4] Kharasch, Reinmuth, and Urry, *J. Amer. Chem. Soc.*, 1947, **69**, 1106.

vinyl monomers mentioned. A mixture of telomers * $Cl_3C{\cdot}[CH_2{\cdot}CH_2]_n{\cdot}Cl$ is obtained where n is 1—5 for a 4 : 1 molar ratio of ethylene to carbon tetrachloride.[5]

It has now been found [6] that good yields of 1 : 1 adduct are obtained from carbon tetrachloride and the monomers mentioned, as well as other olefins, in molar ratios of 2 : 1 or less, if the reaction is catalysed by one mole % of copper-(I) or -(II) chloride. With iron-(II) or -(III) chloride, a 1 : 1 adduct, or telomers, or both are obtained, depending on the nature of the olefin and on the reaction conditions (see Table 1). The infrared spectra of the products indicate that butadiene gives the 1 : 4-adduct (1,1,1,5-tetrachloropent-3-ene) under iron- or copper-catalysis. 10 : 1 Ethylene–carbon tetrachloride react under the influence of iron chloride to give chiefly 1,1,1,3-tetrachloropropane. A variety of solvents may be used (methanol, propan-2-ol, chloroform, or acetonitrile).

It is thus clear that the presence of iron or copper chloride strikingly enhances the apparent reactivity of carbon tetrachloride (for a similar chlorine activation see ref. 1).

Our results may be explained by assuming that the radical displacement (" transfer ") reaction (2) is superseded by the reduction–oxidation steps (4) and (5) (" redox-transfer "),

$$CCl_3{\cdot}CHR{\cdot}CHR'{\cdot} + MCl^+ \longrightarrow CCl_3{\cdot}CHR{\cdot}CHR'Cl + M^+ \quad . \; . \; . \; . \; . \; . \quad (4)$$

$$M^+ + CCl_4 \underset{b}{\overset{a}{\rightleftharpoons}} MCl^+ + CCl_3{\cdot} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (5)$$

where M^+ stands for cuprous or ferrous ion and MCl^+ for cupric or ferric ion with at least one chlorine ligand in the co-ordination shell. The metal ion thus functions as a chlorine-atom transfer agent. Step (5*a*) may equally be formulated:

$$M^+ + CCl_4 \rightleftharpoons M^{2+} + CCl_3{\cdot} + Cl^- \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (6)$$

$$M^{2+} + Cl^- \rightleftharpoons MCl^+ \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (7)$$

We cannot, at this stage, distinguish between the two possibilities.

Step (4) has already been postulated by Minisci and Pallini [7] for the formation of the 1 : 1 adduct of carbon tetrachloride to acrylonitrile, which they and their co-workers [8] obtained in low yield on heating the components in a steel autoclave at 160°:

$$CCl_4 \xrightarrow{Fe} CCl_3{\cdot}$$
$$CCl_3{\cdot} + CH_2{:}CH{\cdot}CN \longrightarrow CCl_3{\cdot}CH_2{\cdot}CH(CN){\cdot}$$
$$CCl_3{\cdot}CH_2{\cdot}CH(CN){\cdot} + FeCl^{2+} \longrightarrow CCl_3{\cdot}CH_2{\cdot}CHCl{\cdot}CN + Fe^{2+}$$

According to their view, the product is obtained in a non-chain reaction and they do not consider the possibility of equilibrium (5).

Reaction (4) is a known chain-breaking reaction,[9] but in a redox-transfer system is followed by the radical-producing equilibrium (5). The existence of step (5*a*) was proved by the isolation of hexachloroethane in a reaction between ferrous chloride and carbon tetrachloride. It is known [10] that, in the presence of ammonia, cuprous ion is instantaneously oxidized by carbon tetrachloride.

Incidentally, a somewhat similar mechanism has been proposed by Nonhebel and

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* " Telomer " denotes an oligomer with a residue from the chain-transfer agent attached at each end (see Hanford and Joyce, U.S.P. 2,440,800/1948).

[5] Nesmeyanov, Freidlina, *et al.*, *Quart. Rev.*, 1956, **10**, 333.

[6] Asscher and Vofsi, *Chem. and Ind.*, 1962, 209.

[7] Minisci and Pallini, *Gazzetta*, 1961, **91**, 1030.

[8] de Malde, Minisci, Pallini, Volterra, and Quilico, *Chimica e Industria*, 1956, 371.

[9] (*a*) Dickerman, Weiss, and Ingberman, *J. Org. Chem.*, 1956, **21**, 380; *J. Amer. Chem. Soc.*, 1958, **80**, 1908; Kumamoto, de la Mare, and Rust, *ibid.*, 1960, **82**, 1935; Kochi, *ibid.*, 1956, **78**, 4815; (*b*) Nonhebel and Waters, *Proc. Roy. Soc.*, 1957, *A*, **242**, 26; (*c*) Kochi, *J. Amer. Chem. Soc.*, 1962, **84**, 774; *Tetrahedron*, 1962, **18**, 483.

[10] Doughty, *J. Amer. Chem. Soc.*, 1919, **41**, 1131.

TABLE 1.

Reaction of olefins (0·1 mole) with carbon tetrachloride (0·2 mole) in solvent (0·2 mole) with catalyst (1 mmole).

Run no.	Solvent	Catalyst	NH_2Et_2Cl (mmole)	Temp.	Hr.	Product	Yield (%) *	Residue (g.)	Note
						Styrene			
1	Pr^iOH	$CuCl_2,2H_2O$	—	120°	9	$CHPhCl{\cdot}CH_2{\cdot}CCl_3$	78	1·2	
2	,,	,,	5	,,	,,	,,	89	1·2	
3	MeCN	,,	1·5	110	7	,,	92	0·8	
4	MeOH	,,	5	100	9	,, (74%) + $MeO{\cdot}CHPh{\cdot}CH_2{\cdot}CCl_3$	77	2·0	1
5	,,	$FeCl_3,6H_2O$	—	115	10	As run 4	45	2·9	2, 3
6	MeCN	,,	1·5	101	10	$CHPhCl{\cdot}CH_2{\cdot}CCl_3$	67	6·0	6
						Butadiene			
7	Pr^iOH	$CuCl_2,2H_2O$	12	100	6	$CCl_3{\cdot}CH_2{\cdot}CH{:}CH{\cdot}CH_2Cl$ (90%) + $CCl_3{\cdot}CH_2{\cdot}CH{:}CH{\cdot}CH_2{\cdot}OPr^i$	80	0·5	
8	,,	,,	6	100	6	As run 7	82	0·5	
9	,,	,,	6	78	12·5	,,	42	0·5	2
10	$CHCl_3$	,,	6	100	12·5	$CCl_3{\cdot}CH_2{\cdot}CH{:}CH{\cdot}CH_2Cl$	80	1·0	
11	,,	,,	6	100	12·5	,,	67	1·8	2, 4
12	MeCN	,,	6	100	6	,,	90	1·2	
13	,,	,,	—	100	10	,,	66	4·2	5
14	,,	$FeCl_3,6H_2O$	6	100	10	,,	32	7·5	6
15	MeOH	,,	—	100	10	,, (70%) + $CCl_3{\cdot}CH_2{\cdot}CH{:}CH{\cdot}CH_2{\cdot}OMe$	30	6·6	1, 6
						Acrylonitrile			
16	MeCN	$CuCl_2,2H_2O$	1·5	110	12	$CCl_3{\cdot}CH_2{\cdot}CHCl{\cdot}CN$	85	0·8	7
17	,,	,,	6	67	64	,,	23	0·8	2
18	Pr^iOH	$FeCl_3,6H_2O$	1·5	101	7	,,	Trace	2·9	6
						Et acrylate			
19	Pr^iOH	$CuCl_2,2H_2O$	6	120	15	$CCl_3{\cdot}CH_2{\cdot}CHCl{\cdot}CO_2Et$	46	2·0	2
						Me acrylate			
20	MeCN	$CuCl_2,2H_2O$	2	109	15	$CCl_2{\cdot}CH_2{\cdot}CHCl{\cdot}CO_2Me$	71	1·2	2, 6
						Allyl alcohol			
21	Pr^iOH	$FeCl_3,6H_2O$	1·5	110	7	$CCl_3{\cdot}CH_2{\cdot}CHCl{\cdot}CH_2{\cdot}OH$	55	1·6	2, 6
						Ethylene			
22	Pr^iOH	$FeCl_3,6H_2O$	1·5	100	3·5	$CCl_3{\cdot}CH_2{\cdot}CH_2Cl$ (73%) + $CCl_3{\cdot}[CH_2{\cdot}CH_2]_2{\cdot}Cl$	—	—	2, 6, 8
						*But-*1*-ene*			
23	MeOH	$CuCl_2,2H_2O$	6	107	15	$CCl_3{\cdot}CH_2{\cdot}CHEtCl$	54	0	2
24	Pr^iOH	$FeCl_3,6H_2O$	1·5	101	16·5	,,	14	0·1	2
25	,,	,,	1·5	82	5	,,	92	0·7	6, 9
						*But-*2*-ene*			
26	See Table 2								
						*Oct-*1*-ene*			
27	Pr^iOH	$CuCl_2,2H_2O$	6	101	12·5	$CCl_3{\cdot}CH_2{\cdot}CHCl{\cdot}C_6H_{13}$	42	0·8	2
28	MeCN	$FeCl_3,6H_2O$	1·5	101	6	,,	96	0·6	6
						*Oct-*2*-ene*			
29	Pr^iOH	$CuCl_2,2H_2O$	6	101	12·5	$CCl_3{\cdot}CHMe{\cdot}CHCl{\cdot}C_5H_{11}$	60	1·2	2, 10

* Calc. on olefin and the content (determined by gas chromatography) of pure product in the crude distillate; for chromatography see asterisked footnote of Table 2; column temp. 180°, except for runs 23—26 (120°).

Notes: (1) Products separated by chromatography on acid-washed alumina; only the tetrachloro-compound is eluted by pentane. (2) Unused olefin remains after reaction. (3) $CHPhMe{\cdot}OMe$ also formed. (4) 1 : 1 Olefin–CCl_6. (5) HCl also formed. (6) 1 Mmole of benzoin added. (7) 0·5 Mmole of benzoin added. (8) 10 : 1 C_2H_4–CCl_4; for yields see text. (9) 1 Mmole of $SnCl_2,2H_2O$ has the same effect as benzoin. (10) Isomers also formed.

Waters [9b] and by Dickerman, Weiss, and Ingberman,[9a] for the Sandmeyer and the Meerwein reaction, with the following steps (for the Meerwein reaction):

$$C_6H_5N_2^+ + Cu^+ \longrightarrow C_6H_5\cdot + N_2 + Cu^{2+} \qquad \text{. . . . . (8)}$$

$$Cu^{2+} + Cl^- \rightleftharpoons CuCl^+$$

$$C_6H_5\cdot + CHR{:}CHR' \longrightarrow C_6H_5\cdot CHR\cdot CHR'\cdot$$

$$C_6H_5\cdot CHR\cdot CHR'\cdot + CuCl^+ \longrightarrow C_6H_5\cdot CHR\cdot CHR'Cl + Cu^+$$

It seems to us likely that the oxidizing species in step (8) is not, as has been suggested, the arenediazonium ion, but the diazonium chloride in its covalent form, according to reaction (9) (cf. also ref. 11 on the reduction of carbonium ion by chromous ion):

$$C_6H_5\cdot N_2Cl + Cu^+ \longrightarrow CuCl^+ + C_6H_5\cdot + N_2 \qquad \text{. . . . . (9)}$$

This tautomer must be present in appreciable amounts under the usual reaction conditions. The oxidizing properties of *N*-chloro-compounds are well known. By this modification the analogy with redox-transfer reactions of carbon tetrachloride becomes closer. Another redox-transfer reaction, involving ligand (carboxylate)-transfer by a transition-metal ion,[9c] is that between per-esters and olefins. There is no need to ascribe catalytic properties specifically to the cupric or cuprous ion.[12] Both are indispensable in any redox-transfer system.

In additions of carbon tetrachloride not involving redox-transfer, step (2) is nearly always the slowest in the propagation series. This, and abstraction of allylic hydrogen from olefin by a trichloromethyl radical, enhance the importance of termination by radical–radical interaction and only rather short kinetic chains result.[13] In a redox-transfer system the situation is different: step (4) is efficient even when unreactive allyl or benzyl radicals are involved. Moreover, reaction (5*a*), which we believe to be the slowest of the propagation sequence (1), (4), and (5), does not involve free radicals as reactants. Consequently, much longer reaction chains are built up, *e.g.*, 375 for the system *cis*-but-2-ene–carbon tetrachloride at 82° (see Table 2, no. 20; for the estimation of chain length see below).

In step (4), cupric chloride is more reactive than ferric chloride (cf. also ref. 9*b*): it completely suppresses telomerization, where ferric chloride does not (compare, in Table 1, nos. 3, 12, and 16 with 6, 14, and 18).

Ferric chloride allows higher telomers to be formed from acrylonitrile than from butadiene. This is in accord with the findings of Bamford, Jenkins, and Johnston [14] that radicals of the electron-donor type (derived from butadiene) are more reactive towards ferric chloride than those of the acceptor type (from acrylonitrile).

In step (5*a*), ferrous ion appears to be more reactive towards carbon tetrachloride than cuprous ion; when adequate initiation is provided (see below), higher conversions of olefins are achieved in an iron chloride-catalysed system, under otherwise identical conditions (compare, in Table 2, nos. 2 and 7 with 13 and 18). With chloroform instead of carbon tetrachloride, the difference is much more pronounced.[6]

Experiments with labelled chloride are being carried out. They should show whether there is exchange between chloride ion and carbon tetrachloride, due to reaction (5*b*), and whether the reaction chain is propagated by steps (4) and (5*a*) only, or also by step (2).

It was pointed out [9] by Nonhebel and Waters and by Rust and his co-workers that reactions such as (4) involve ligand transfer from metal chloride to radical, and not transfer of one electron (step 10), followed by step (11):

$$R\cdot + M^{2+} \longrightarrow R^+ + M^+ \qquad \text{. . . . . (10)}$$

$$R^+ + Cl^- \longrightarrow RCl \qquad \text{. . . . . (11)}$$

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[11] Castro, *J. Amer. Chem. Soc.*, 1961, **83**, 3262.

[12] (*a*) Rondestvedt, *Org. Reactions*, 1960, **11**, 196; (*b*) Schrauzer, *Chem. Ber.*, 1961, **94**, 1891.

[13] Walling, "Free Radicals in Solution," Wiley, New York, 1957, p. 261; Kooyman and Farenhorst, *Rec. Trav. chim.*, 1951, **70**, 867.

[14] Bamford, Jenkins, and Johnston, *Trans. Faraday Soc.*, 1959, **55**, 421.

TABLE 2.

Reaction of but-2-ene (0·1 mole) with carbon tetrachloride (0·2 mole) in the presence of solvent (0·2 mole) and catalyst (1 mmole).

Run no.	But-2-ene	Solvent	Catalyst	NH_2Et_2Cl (mmole)	Temp.	Hr.	Amount (%) * of first stereo-isomer	Yield (%) †	Note
1	*cis*	MeOH	$CuCl_2,2H_2O$	—	101°	14	72	23	1
2	,,	,,	,,	—	101	14	71	67	1, 2
3	,,	,,	,,	6	101	14	67	32	1
4	*trans*	,,	,,	—	101	18	73	30	1, 2
5	*cis*	,,	,,	6	145	10	64	95	
6	,,	Pr^iOH	,,	—	101	15	67	38	1, 2
7	,,	,,	,,	6	101	15	67	48	1, 2
8	,,	MeCN	,,	—	101	14	63	26	1
9	*trans*	,,	,,	—	101	15	64	7	1
10	*cis*	,,	,,	6	101	15	67	21	1
11	,,	MeOH	$FeCl_3,6H_2O$	—	101	14	—	0	
12	,,	,,	,,	6	101	14	—	0	3
13	,,	,,	,,	—	101	6	75	95	2
14	,,	,,	,,	6	101	6	75	96	2
15	,,	,,	,,	6	145	10	72	96	
16	,,	,,	$FeCl_2,4H_2O$	—	101	18	76	77	1
17	,,	Pr^iOH	$FeCl_3,6H_2O$	—	101	6	75	96	2
18	,,	,,	,,	6	101	6	75	96	2
19	,,	,,	,,	—	101	5	75	92	1, 4
20	,,	,,	,,	1·5	82	15	78	75	1, 5
21	,,	MeCN	,,	—	101	6	75	95	2
22	,,	,,	,,	6	101	6	76	95	2
23	*trans*	,,	,,	—	101	4	76	26	1, 2
24	*cis*	—	Bz_2O_2	—	101	15	75	47	1, 6
25	,,	—	$Bu^t{}_2O_2$	—	140	19	73	65	1, 7

* Composition of diastereoisomers, as determined by gas chromatography, on a 1·5-m. column, packed with 25% of diethylene glycol polyadipate (LAC 2—R–446, Cambridge Industries Co., Inc., Cambridge, Mass., U.S.A.) on Chromosorb W., at 105°, with flow of helium 80 ml. per min. The retention time of the first diastereoisomer is 13 min., of the second 22 min. The recorded values are obtained by peak-area measurements, and are averages of three determinations. † By-product, including distillation-residues, amounts to 2% or less on total product in all runs.

Notes: (1) Unconverted, unisomerized but-2-ene remains after reaction, as determined by gas chromatography at room temperature, on a 1-m. column, packed with 1 part of a saturated solution of silver nitrate in ethylene glycol on 2 parts of firebrick. (2) 1 Mmole of benzoin added. (3) If reactants are sealed at 0·4 μ, after thorough degassing (freezing in liquid air, thawing, and pumping, three times), a 5% yield is obtained. (4) 0·5 Mmole of benzoin added. (5) 0·1 Mmole of benzoin added; sealed as in (3) (otherwise no reaction takes place). (6) Sealed as in (3); 3 mmoles of Bz_2O_2. (7) 7 Mmoles of $Bu^t{}_2O_2$.

In most of our addition reactions with alcohol as solvent, no product of solvolysis was obtained, which is in accord with this view. Partially solvolysed products have been obtained only when the carbon tetrachloride adducts are reactive allyl or benzyl chlorides (solvolysis of these chlorides is catalysed by cuprous ion; [15] * (see Table 1, nos. 4, 5, 7—9, and 15).

The addition of carbon tetrachloride to but-2-ene is of special interest. Here, *cis*- and *trans*-but-2-ene yield the same mixture of diastereoisomeric adducts, the composition of which can be determined by gas chromatography (see Table 2). In the prevailing conditions *cis*- and *trans*-but-2-ene, and the diastereoisomers, are not interconvertible. The same result (without actual determination of product composition) has been obtained by Skell and Woodworth [16] for the photochemical addition of bromotrichloromethane

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* Most of the reactions listed in Tables 1 and 2 were carried out in the presence of a soluble chloride (diethylammonium chloride). Its effect in a system catalysed by iron chloride is slight, but it prevents precipitation of ferric hydroxide. Cuprous chloride, which is precipitated especially when propan-2-ol is used as solvent, is kept in solution by an excess of chloride ion. Further, side reactions (telomerization and elimination of hydrochloric acid) are prevented, and higher yields of adduct are obtained (compare, in Table 1, nos. 1 and 13 with 2 and 12).

[15] Hatch and Estes, *J. Amer. Chem. Soc.*, **1945**, **67**, 1730.

[16] Skell and Woodworth, *J. Amer. Chem. Soc.*, 1955, **77**, 4638.

to both but-2-enes. Their interpretation, involving the formation of identical or easily interconvertible $CCl_3\cdot CHMe\cdot CHMe\cdot$ radicals evidently applies also to our case, in the presence of metal ions.

Incidentally, the Meerwein reaction (see above) has been postulated [12b] as involving a complex of cupric chloride, olefin, and aryl radical. A similar complex might be formed in reactions of carbon tetrachloride, aryl being replaced by a trichloromethyl radical. Such an arrangement should give some stereospecificity in additions of carbon tetrachloride to *cis*- or *trans*-but-2-ene, but this is not observed (see Table 2, nos. 1, 4, 8, 9, 22, 23).

It can be expected that in reaction (12), each species MCl^+ (representing solvated

$$CCl_3\cdot CHMe\cdot CHMe\cdot + MCl^+ \longrightarrow CCl_3\cdot CHMe\cdot CHMeCl + M^+ \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

and/or partially solvolysed cupric or ferric chloride) should give rise to a characteristic ratio of diastereoisomers in the product. Table 2 shows that different ratios are indeed obtained on iron or copper chloride-catalysis. In the latter case, the ratio is also influenced by the solvent. Apparently, cupric chloride is more strongly solvolysed in methanol and in acetonitrile (Table 2, Nos. 1, 2, 4, 8, and 9) than in propan-2-ol (Table 2, No. 6). In the presence of an excess of chloride ion, however, solvolysis is suppressed, and it is likely that then identical species MCl^+ are involved in step (12), giving rise to the same ratio of diastereoisomers (Table 2, Nos. 3, 7, and 10).

The constant ratios obtained in iron chloride-catalysed reactions (Table 2, Nos. 13—23), irrespective of solvent or excess of chloride ion, indicate that only one ferric species reacts in step (12).

For the influence of temperature on product composition, compare Table 2, Nos. 3 and 5 for copper-, and 20, 15, and 18 for iron-catalysis.

The recorded differences in the diastereoisomer ratios, though small, are nevertheless significant, since the results were reproducible within an error of $\pm 1\%$. For comparison, the results are given of reactions which were induced by di-t-butyl peroxide at 145° or dibenzoyl peroxide at 101° (Table 2, Nos. 25 and 24). At 101° a ratio of diastereoisomers is obtained [by step (2)] which is identical with that of an iron chloride-catalysed reaction. Yet, in view of the much longer kinetic chain, one may safely assume that in the latter case the reaction is propagated chiefly, if not exclusively, by redox-transfer.

In addition to propagating the chain, ferrous or cuprous ions can also initiate the reaction (step 5). If only ferric or cupric ions are present from the start, any reaction which reduces them to ferrous or cuprous ion can be regarded as an initiating process, even if no free radicals are formed simultaneously. It was observed that cupric chloride is slowly reduced by methanol or propan-2-ol at 100°. Another mode of initiation, probably of greater importance, is addition of chlorine to the olefin by cupric chloride. Thus, when styrene is refluxed with cupric chloride in acetonitrile, styrene dichloride and cuprous chloride are the sole products. Therefore, in additions of carbon tetrachloride to styrene, half the molar ratio adduct : styrene dichloride gives the chain-length of the reaction if it is assumed that one molecule of styrene reduces two cupric ions. The very small amount of dichloride found does not permit accurate estimation by conventional means, but the chain-length appears to be between 70 and 140 for a reaction carried out at 110°, with 1 mole of catalyst calculated on styrene.

But-2-ene also reduces cupric chloride at 100° in acetonitrile or methanol (unpublished results).

Ferric chloride is not reduced at a sufficient rate to cause reaction between but-2-ene and carbon tetrachloride at 85°. However, in the presence of benzoin or stannous chloride, a fast reaction ensues, and in 6 hours $>90\%$ of the butene reacts (Table 2, nos. 11—14, 17—22; Table 1, no. 25). Ferrous chloride brings about a reaction without a reducing agent (Table 2, no. 16).

At temperatures where ferric chloride alone does not induce a reaction between but-2-ene and carbon tetrachloride, the kinetic chain length in the presence of benzoin can be estimated if it is assumed that benzoin is completely oxidized in the course of the reaction and that one molecule reduces two ferric ions. At 82° a chain-length of 375 is indicated (Table 2, no. 20). For reactions catalysed by cupric chloride, benzoin is not indispensable. Its effect can be seen, however, by comparing yields of nos. 19 and 20 in Table 1 and nos. 1 and 2 in Table 2. The system ferric ion–benzoin has been used by Kern *et al.*[17] in peroxide-induced polymerizations.

The structure of the adducts of carbon tetrachloride to but-2-ene and but-1-ene was not proved. Gas chromatography showed, however, that redox-transfer- and peroxide-induced reactions gave identical products.

1,1,1,5-Tetrachloropent-3-ene * (from the reaction between butadiene and carbon tetrachloride), the structure of which has been proved,[18] gave an isothiouronium chloride whose chloride ion content was a quarter of the total chlorine. The structure of the adduct, 1′,3′,3′,3′-tetrachloropropylbenzene,[19] was proved by hydrolysis to cinnamic acid.[20] $\alpha\gamma\gamma\gamma$-Tetrachlorobutyronitrile (the adduct from acrylonitrile and carbon tetrachloride) was hydrolysed to the amide and carboxylic acid.[8] The same acid, the structure of which has been established,[8,21] was obtained by acid hydrolysis of the corresponding methyl ester (from methyl acrylate and carbon tetrachloride), and, by oxidation with permanganate, from 2,4,4,4-tetrachlorobutan-1-ol (from allyl alcohol and carbon tetrachloride).

EXPERIMENTAL

Materials.—Carbon tetrachloride, methanol, propan-2-ol, acetonitrile, chloroform, ferric chloride hydrate, cupric chloride hydrate, and diethylammonium chloride were B.D.H. products. Styrene, acrylonitrile, and methyl and ethyl acrylate were commercial polymerization-grade products and were used as supplied, without removal of inhibitor. But-1-ene, *cis*- and *trans*-but-2-ene, and butadiene were Matheson, C.P. products, of over 99% purity. Allyl alcohol, oct-1-ene, and oct-2-ene were freshly distilled and free from peroxide.

The physical constants and analyses of the products recorded in Table 3 were obtained after fractionation through a 50-cm. column packed with glass helices. Purity was assessed by gas chromatography.

*Addition of Carbon Tetrachloride to Butadiene, But-*1*-ene, and But-*2*-ene.*—The olefin (0·1 mole) was passed into carbon tetrachloride (0·2 mole), cooled in ice-salt. The resulting solution was introduced into a pre-cooled Carius tube. Catalyst (1 mmole) and the indicated amount of diethylammonium chloride were dissolved in the solvent (0·2 mole) and added to the mixture. After cooling in liquid air, the tube was evacuated to 0·1 mm., sealed, and heated to the indicated temperature. The products were washed with carbon tetrachloride and with 0·1N-aqueous hydrochloric acid (30 ml.). The aqueous layer was extracted with carbon tetrachloride and this extract added to the organic layer. Carbon tetrachloride and unconverted olefin were then distilled off up to 150° (bath)/1 atm. Distillation was continued at 25 mm. up to 180° (bath). The distillate was analysed by gas chromatography (see Table 1, footnote *) and the residue weighed. The amount of residue gives an indication whether or not telomerization has taken place. For analyses and characteristics of products see Table 3.

*Addition of Carbon Tetrachloride to Oct-*1*-ene, Oct-*2*-ene, Styrene, Acrylonitrile, or Methyl or Ethyl Acrylate.*—The olefin (0·1 mole) in carbon tetrachloride (0·2 mole) was added to a solution of catalyst (1 mmole) and (if indicated) diethylammonium hydrochloride in the solvent (0·2 mole). The mixture was introduced into a Carius tube, etc., as described above. After reaction, the products were treated as above, unconverted acrylonitrile or acrylate was distilled

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* This adduct has already been prepared, in low yield, from its components.[18] It is clearly stated that metallic iron or ferric chloride (preferably in the presence of pyrogallol, a reducing agent) is indispensable for the reaction.

[17] Kern and Schulz, *Makromol. Chem.*, 1954, **13**, 210.

[18] Peterson, U.S.P. 2,401,099/1946.

[19] Ladd and Kiley, U.S.P. (*a*) 2,606,213/1952, (*b*) 2,568,859/1951.

[20] Kharasch, Simon, and Nudenberg, *J. Org. Chem.*, 1953, **18**, 332.

[21] Hall and Jacobs, *J.*, 1954, 2034.

TABLE 3.

Adducts and their derivatives.

No.	Compound	B. p./mm.	M. p.	n_D^{25}	Remarks
1	$CCl_3{\cdot}CH_2{\cdot}CHPhCl$	84°/0·1	—	1·5523	Ref. 19*a*: n_D^{20} 1·5557
2	$CCl_3{\cdot}CH_2{\cdot}CHPh{\cdot}OMe$	80°/0·5	—	1·5280	*O*-Me: found, 5·9; calc., 5·9%
3	$CCl_3{\cdot}CH_2{\cdot}CHCl{\cdot}CN$	111°/25	—	1·4931	Ref. 8: n_D^{20} 1·4954
4	$CCl_3{\cdot}CH_2{\cdot}CHCl{\cdot}CO{\cdot}NH_2$	—	86—87° *	—	Ref. 8: m. p. 118°
5	$CCl_3{\cdot}CH_2{\cdot}CHCl{\cdot}CO{\cdot}NHPh$	—	123—124 *	—	Ref. 21: m. p. 124°
6	$CCl_3{\cdot}CH_2{\cdot}CHCl{\cdot}CO_2H$	96°/0·2	—	1·5018	Ref. 8: n_D^{20} 1·4945. Ref. 21: m. p. 27—29°
7	$CH_2Ph{\cdot}S{\cdot}C({:}NH){\cdot}NH_2$ salt of no. 6	—	179—180 †	—	Ref. 8: m. p. 167
8	$CCl_3{\cdot}CH_2{\cdot}CHCl{\cdot}CO_2Me$	111°/20	—	1·4819	Ref. 8: b. p. 102°/17 mm.
9	$CCl_3{\cdot}CH_2{\cdot}CHCl{\cdot}CO_2Et$	122°/25	—	1·4713	
10	$CCl_3{\cdot}CH_2{\cdot}CHEtCl$	87°/25	—	1·4779	
11	$CCl_3{\cdot}CHMe{\cdot}CHMeCl$	93°/25	—	1·4869	Diastereoisomers, 73 : 27
12	,,	93—95°/25	—	1·4872	,, 63 : 37
13	$CCl_3{\cdot}CH_2{\cdot}CH{:}CH{\cdot}CH_2Cl$	110°/25	—	1·5042	Ref. 18: n_D^{25} 1·5068
14	$CCl_3{\cdot}CH_2{\cdot}CH{:}CH{\cdot}CH_2{\cdot}OMe$	103°/20	—	1·4792	*O*-Me: found, 8·3; calc., 7·4%
15	$CCl_3{\cdot}CH_2{\cdot}CH{:}CH{\cdot}CH_2{\cdot}R$ ‡	—	191 §	—	Cl^-: found, 12·55; calc., 12·5%
16	$CCl_3{\cdot}CH_2{\cdot}CHCl{\cdot}CH_2{\cdot}OH$	66°/1	—	1·5066	Ref. 19*b*: n_D^{20} 1·5065

Nos. 2, 9—11, 14, and 15 are new compounds.

* From CCl_4. † From H_2O. ‡ R = $S{\cdot}C(NH_2)_2Cl$. § From Pr^{i}OH.

	Found (%)						Required (%)				
No.	C	H	N	Cl	S	Formula	C	H	N	Cl	S
1	42·0	3·0	—	54·0	—	$C_9H_8Cl_4$	41·9	3·1	—	54·95	—
2	47·55	4·15	—	41·8	—	$C_{10}H_{11}Cl_3O$	47·4	4·4	—	41·9	—
3	23·5	1·5	6·8	67·7	—	$C_4H_3Cl_4N$	23·2	1·5	6·8	68·5	—
4	22·3	2·6	6·0	62·9	—	$C_4H_5Cl_4NO$	21·4	2·2	6·2	63·1	—
5	40·1	3·2	4·7	46·6	—	$C_{10}H_9Cl_4NO$	39·9	3·0	4·65	47·1	—
6	22·9	1·8	—	60·5	—	$C_4H_4Cl_4O_2$	21·3	1·8	—	62·8	—
7	—	—	7·1	36·3	8·3	$C_{12}H_{14}Cl_4N_2O_2S$	—	—	7·1	36·2	8·2
8	25·8	2·4	—	57·65	—	$C_5H_6Cl_4O_2$	25·0	2·5	—	59·1	—
9	—	—	—	54·4	—	$C_6H_8Cl_4O_2$	—	—	—	55·8	—
10	28·8	3·9	—	68·1	—	$C_5H_8Cl_4$	28·6	3·8	—	67·6	—
11	29·3	3·7	—	67·1	—						
12	29·0	3·8	—	67·5	—						
13	29·3	2·9	—	67·2	—	$C_5H_6Cl_4$	28·9	2·9	—	68·2	—
14	36·4	4·4	—	51·0	—	$C_6H_9Cl_3O$	35·4	4·45	—	52·3	—
15	—	—	10·2	50·0	11·2	$C_6H_{10}Cl_4N_2S$	—	—	9·9	49·9	11·3
16	23·1	2·7	—	67·2	—	$C_4H_6Cl_4O$	22·7	2·85	—	66·9	—

off at atmospheric pressure, unconverted oct-1-ene, oct-2-ene, and styrene at 20 mm. (bath-temperature up to 150°). For the first three reactants, the distillation was continued at 25 mm. and for the last three at 0·3 mm. (bath-temperature up to 180°).

Reaction of Butadiene and Carbon Tetrachloride, with Ferric Chloride Hydrate as Catalyst (Table 1, no. 14).—Butadiene (135 g., 2·5 moles) was passed into a cooled (ice–salt) solution of benzoin (5·3 g., 25 mmoles) in carbon tetrachloride (770 g., 5 moles). A solution of ferric chloride hexahydrate (6·7 g., 25 mmoles) and diethylammonium chloride (4·1 g., 37·5 mmoles) in acetonitrile (205 g., 5 moles) was added and the homogeneous mixture transferred to a glass sleeve (1·5 l.) which was inserted into an autoclave (2 l.). The autoclave was flushed with butadiene, closed after protection of the thermometer-well with a glass tube, and heated at $\ngtr$100° during 7 hr. (exothermic reaction). The products were washed with 0·1N-hydrochloric acid. Solvent and the excess of carbon tetrachloride were distilled off (bath up to 150°) and distillation continued *in vacuo*. A fraction of b. p. 60—140°/20 mm. (202 g.) was collected. Further distillation at 0·5 mm. gave a fraction of b. p. 90—145°/0·5 mm. (161 g.) (bath up to 185°) (Found: Cl, 54·0. Calc. for $C_9H_{12}Cl_4$: Cl, 54·1%). The mixture has thus an average composition corresponding to the 2 : 1 telomer. The yield, calculated on butadiene, was 61%; 16·2 g. of residue remained (Found: Cl, 51·3%). The fraction of b. p. 60—140°/20 mm. was refractionated through a 60-cm. Vigreux column and a fraction of b. p. 100—120°/20 mm. collected, consisting of pure (gas chromatography) 1,1,1,5-tetrachloropent-3-ene (164 g., 32% calc. on butadiene); 26·4 g. of residue remained (Found: Cl, 57·3. Calc. for $C_5H_6Cl_4$: Cl, 68·2. Calc. for $C_9H_{12}Cl_4$: Cl, 54·1%). The fraction of b. p. 90—145°/0·5 mm. was also refractionated, giving materials of b. p. 55—105°/0·4 mm. (50 g.) (Found: Cl, 56·8%), 105—107°/0·4 mm. (80·9 g.) (Found: Cl, 53·7. Calc. for $C_9H_{12}Cl_4$: Cl, 54·1%), and 107—140°/0·4 mm. (22·6 g.) (Found: Cl, 45·3. Calc. for $C_{13}H_{18}Cl_4$: Cl, 44·9%).

Reaction of Acrylonitrile and Carbon Tetrachloride with Ferric Chloride Hydrate as Catalyst (Table 1, no. 18).—To a solution of benzoin (318 mg., 1·5 mmoles) and acrylonitrile (8 g., 0·15 mole) in carbon tetrachloride (46 g., 0·3 mole) was added one of ferric chloride hexahydrate (405 mg., 1·5 mmoles) and diethylammonium chloride (246 mg., 2·25 mmoles) in propan-2-ol (27 g., 0·45 mole). The mixture was transferred to a Carius tube, cooled in liquid air, evacuated to 0·1 mm., sealed, and heated for 19 hr. at 101° (boiling dioxan). During this period a white precipitate appeared. The products were heated at 100° until ~30 ml. remained. A yellow, sticky material was precipitated. Acetone (30 ml.) was added and the mixture was warmed gently in order to dissolve the resin. The resulting solution was cooled in ice and poured slowly into stirred, ice-cooled propan-2-ol (500 ml.). After 2 hr. at 0° a white precipitate that resulted was removed, washed with propan-2-ol until the filtrate was free from chloride ion, dried in the air for 2 days, ground, and dried again, *in vacuo*, over phosphorus pentoxide for another 2 days. The resulting grey powder (1·2 g.), melted between 98° and 115° (Found: Cl, 20·0%). It is thus a telomeric mixture, with an average of 10·5 acrylonitrile units.

The filtrate was evaporated at 1 atm. up to 165° (bath) and then *in vacuo* (bath to 210°). A resulting yellow oil (0·1 g.), b. p. ~100°/20 mm., consisted of about 80% of $\alpha\gamma\gamma\gamma$-tetrachlorobutyronitrile (identified by gas chromatography). A black hard residue remained (1·7 g.).

Reaction of Ethylene and Carbon Tetrachloride (Table 1, no. 22).—Carbon tetrachloride (15·4 g., 0·1 mole) was added to a solution of benzoin (106 mg., 0·5 mmole), diethylammonium chloride (80 mg., 0·75 mmole), and ferric chloride hexahydrate (135 mg., 0·5 mmole) in propan-2-ol (10 g.). The mixture was cooled in a glass ampoule in liquid air, and ethylene (28 g., 1 mole) was distilled in. The ampoule was transferred to a 200-ml. autoclave, which had been flushed with ethylene; the mixture was left overnight at room temperature, then heated at 100° for 4 hr. and cooled again. The excess of ethylene was released very slowly. The products were washed with water, giving a pale yellow solution (14·6 g.) that, according to gas chromatography, contained carbon tetrachloride (12·4 g.), 1,1,1,3-tetrachloropropane (1·6 g.), 1,1,1,5-tetrachloropentane (0·6 g.), and traces of 1,1,1,7-tetrachloroheptane.

Hexachloroethane from Carbon Tetrachloride and Ferrous Chloride.—A Carius tube was charged with ferrous chloride tetrahydrate (3·96 g., 20 mmoles). A hot solution of diethylammonium chloride (1·1 g., 10 mmoles) in acetonitrile (20 g.) was added, followed by carbon tetrachloride (31 g., 0·2 mole). The tube was cooled in liquid air, evacuated to 0·1 mm., sealed, and heated at 92° for 16 hr. The products were washed thrice with 0·1N-hydrochloric acid. then freed from carbon tetrachloride and acetonitrile by distillation at 1 atm. through a 40-cm. Vigreux column (bath-temperature up to 120°). Distillation at 25 mm. (bath up to 180°) then gave a white sublimate (0·3 g.), identified as hexachloroethane by gas chromatography.

Hydrolysis of $\alpha\gamma\gamma\gamma$-Tetrachlorobutyronitrile.—(*a*) The nitrile (10·3 g., 0·05 mole) was dissolved in concentrated sulphuric acid (20 g.). After a few minutes the solution became very hot and was cooled in water. After 30 min. it was poured on ice (60 g.) and stirred until the precipitated oil had solidified. The white solid was removed, washed with water, and dried in the air (11·1 g.). Recrystallization from carbon tetrachloride (charcoal) gave the amide (9 g.), m. p. 86—87° (Table 3, no. 4).

(*b*) The nitrile (20·7 g., 0·1 mole) and concentrated aqueous hydrochloric acid (50 ml.) were heated in a Carius tube at 115° for 15 hr., cooled in ice–salt, and poured into water (200 ml.). The organic layer was taken up in carbon tetrachloride and separated. The aqueous layer was extracted twice with carbon tetrachloride. After being washed with water, the organic solvent was distilled off at atmospheric pressure (bath temperature up to 150°), and at 25 mm. (bath up to 100°); further heating gave $\alpha\gamma\gamma\gamma$-tetrachlorobutyric acid, b. p. 96°/0·2 mm. (12·0 g.) (Found: Equiv., 223·5. Calc. for $C_4H_4Cl_4O_2$: Equiv., 226). For analysis of the acid, the anilide (prepared by way of the acid chloride), and the *S*-benzylisothiouronium salt, see Table 3, nos. 5, 7, and 6.

Hydrolysis of Methyl $\alpha\gamma\gamma\gamma$-Tetrachlorobutyrate.—Treatment of methyl tetrachlorobutyrate as above gave tetrachlorobutyric acid, which was converted, by way of its chloride, into the amide, m. p. and mixed m. p. 86—87°, and anilide, m. p. and mixed m. p. 123—124°.

Oxidation of 2,4,4,4-*Tetrachlorobutan*-1-*ol to* $\alpha\gamma\gamma\gamma$-*Tetrachlorobutyric Acid.*—A solution of potassium permanganate (2·8 g.) was added to a mixture of tetrachlorobutanol (4 g.), sodium hydrogen carbonate (0·7 g.), and water (3 ml.). After 48 hr. at room temperature and 5 hr. at 70° precipitated manganese peroxide was removed and washed with water. The filtrate was extracted with chloroform three times, and the aqueous layer acidified to pH 2 with concentrated aqueous hydrochloric acid and again extracted three times with chloroform. Solvent was evaporated from the last three extracts, and the residue was dissolved in water (5 ml.) containing sodium hydrogen carbonate (0·1 g.). *S*-Benzylisothiuronium chloride (1 g.) in water (5 ml.) was added. The precipitated salt, when recrystallized from water, had m. p. and mixed m. p. with *S*-benzylsothiouronium $\alpha\gamma\gamma\gamma$-tetrachlorobutyrate, 179—180°.

Hydrolysis of 1′,3′,3′,3′-*Tetrachloropropylbenzene to Cinnamic Acid.*—Treatment with perchloric acid in acetic acid, as described by Kharasch *et al.*[20] for hydrolysis of 1′-bromo-3′,3′,3′-trichloropropylbenzene, gave a 35% yield of cinnamic acid, m. p. and mixed m. p. 132—133°.

Reaction of 1,1,1,5-*Tetrachloropent*-3-*ene with Thiourea.*—1,1,1,5-Tetrachloropent-3-ene (10·4 g., 0·05 mole) was refluxed with thiourea (3·8 g., 0·05 mole) in propan-2-ol (90 ml.) during 1·5 hr. The hot solution was filtered and left overnight at 5°; the isothiouronium chloride (9·3 g.) precipitated was removed, washed with propan-2-ol, dried in the air, and twice recrystallized from propan-2-ol, giving plates, m. p. 191° (Table 3, no. 15).

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