

## METAL-OXIDE INDUCED REDOX CHAIN ADDITION OF TETRACHLOROMETHANE TO A CARBON-CARBON DOUBLE BOND\*

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Formation of 1 : 1 adducts in the addition of tetrachloromethane to a terminal carbon-carbon double bond was investigated at 76—200°C. The redox chain addition reaction with 1-octene, electron-deficient alkenes and unconjugated aliphatic dienes induced by catalytic amounts of copper(I) or copper(II) oxides in conjugation with diethylamine or diisopropylamine afforded the corresponding 1 : 1 adducts up to in 85% yields. Aliphatic 1,3-dienes underwent redox chain 1,4-addition giving isomeric 1,1,1,5-tetrachloro-3-alkenes.

Free-radical additions of tetrachloromethane to unsaturated compounds were first described by Kharash and coworkers<sup>1</sup> in 1945. Reactions of this type have then been investigated by a great number of authors and the results were summarised in several monographs<sup>2-4</sup>. The agents introduced by Kharash to initiate these reactions were organic peroxides<sup>2-4</sup>. Later also iron(III) chloride and copper(II) chloride<sup>5-8</sup>, metal carbonyls<sup>9,10</sup>, organocomplexes of metal carbonyls<sup>11</sup> and some ruthenium complexes<sup>12,13</sup> have been recommended as initiators for the addition of tetrachloromethane to 1-alkenes and unconjugated dienes. Moreover, the redox systems based on iron(III) chloride or copper chlorides have been found to catalyse the formation of 1 : 1 adducts with high selectivity also in reactions of tetrachloromethane with electron-deficient alkenes and aliphatic 1,3-dienes, which in the presence of organic peroxides would lead predominantly to telomeric and polymeric products<sup>5-8</sup>. Recently, the addition of tetrachloromethane to styrene<sup>12</sup>, 1,3-butadiene and isoprene (no data given on product stereochemistry)<sup>14</sup> catalysed by dichlorotris(triphenylphosphine)ruthenium(II) has been reported to give the corresponding 1 : 1 adducts in high yields.

In the previous communications of this series we described the activity of metal oxides as initiating agents in addition reactions which proceeded with homolytic cleavage of the carbon-hydrogen bond. In this paper we report on the initiating activity of metal oxides in the homolysis of the carbon-chlorine bond. The addition of tetrachloromethane was chosen as the model reaction; a series of metal oxides were investigated as a potential source of a metal ion in a redox system, which could exhibit optimum effectiveness and versatility also in formation of 1 : 1 adducts

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from electron-deficient alkenes and conjugated or unconjugated aliphatic dienes. The finding reported by Traynham and Couvillon<sup>15</sup> that addition of tetrachloromethane to *cis*-cyclooctene proceeded at 155°C also in the absence of initiators necessitated to follow simultaneously the thermally initiated addition reactions of electron-rich as well as electron-deficient alkenes.

## EXPERIMENTAL

**Chemicals.** Tetrachloromethane, 2-propanol, allyl alcohol, pyridine, diisopropylamine (all from Lachema, Brno), 1,5-hexadiene,  $\alpha$ -methylstyrene, allyl propyl ether, methyl vinyl ketone, methyl acrylate, vinyl acetate (all from Fluka AG., Buchs, Switzerland), 4-vinyl-1-cyclohexene (Koch-Light Ltd, Colnbrook, Great Britain) and diethylamine (Laborchemie, Apolda, GDR) were pure chemicals which were distilled in an atmosphere of nitrogen until chromatographically pure and stored under nitrogen. 1-Octene (Fluka AG.) was freed of peroxides by being passed through a column of activated alumina and then distilled under nitrogen. Acrylonitrile (Fluka AG.) was stirred with a 10% solution of sulphuric acid, then with a 10% solution of sodium hydrogen carbonate saturated with sodium sulphate, dried over magnesium sulphate and distilled under nitrogen. Triphenylphosphine, diethylamine hydrochloride (Lachema), dodecane, hexadecane (internal standards, Fluka AG.) and 1,3-butadiene (Kaučuk, Kralupy/L.) were used without further purification. The metal oxides, *i.e.* Cu<sub>2</sub>O, HgO, ZnO, CdO, NiO, PbO, SnO, SrO, Sb<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>, Bi<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, MnO<sub>2</sub>, TiO<sub>2</sub> (rutil), U<sub>3</sub>O<sub>8</sub>, MoO<sub>3</sub>·x H<sub>2</sub>O (all from Lachema), Tl<sub>2</sub>O<sub>3</sub>, Sc<sub>2</sub>O<sub>3</sub>, In<sub>2</sub>O<sub>3</sub>, Ga<sub>2</sub>O<sub>3</sub>, ThO<sub>2</sub>, RuO<sub>2</sub> (all from Fluka AG.), PbO<sub>2</sub>, GeO<sub>2</sub> and WO<sub>3</sub> (all from British Drug House Ltd, London) were used as obtained; CuO (ref.<sup>16</sup>), Ag<sub>2</sub>O (ref.<sup>17</sup>) and cobalt peroxide<sup>18</sup> were prepared according to known procedures.

**Analytical methods.** Gas chromatographic analysis was carried out on Chrom 31 instrument (Laboratory Instruments, Prague) equipped with a flame-ionisation detector and a stainless-steel column (1.7 m × 3 mm) packed with 7% Silicone OV-17 on Gas-Chrom Q (80—100 mesh). Isolation of some 1 : 1 adducts by preparative gas chromatography was carried out on the same instrument using a stainless-steel column (2.4 m × 8 mm) packed, unless otherwise stated, with 9.1% Apiezon L on Chromatop L. The <sup>1</sup>H-NMR spectra of the isomeric 1 : 1 adducts of tetrachloromethane with isoprene and the <sup>13</sup>C-NMR spectra of the adduct of tetrachloromethane with methyl vinyl ketone in CDCl<sub>3</sub> solutions were recorded on Varian XL 200 spectrometer (50.3 MHz). As to the other 1 : 1 adducts, the <sup>1</sup>H-NMR spectra were recorded on BS 467 Tesla 60 instrument; the chemical shifts ( $\delta$ ) were expressed in ppm relative to tetramethylsilane. The IR spectra were obtained using the Zeiss (Jena) Model UR spectrophotometer.

**Determination of the initiating activity.** Tetrachloromethane, alkene and metal oxide or amine pyridine or triphenylphosphine (molar ratios are given in Tables I—IV and Figs 1—2) were weighed under nitrogen and introduced into a 10 ml Pyrex glass ampoule; the ampoule was sealed and the vibrationally stirred mixture was heated in an oil bath to 80—200°C. The ampoule content was cooled to room temperature at fixed time intervals and the alkene conversion as well as the yield of the 1 : 1 adduct was determined by gas chromatographic analysis of the reaction mixture. The course of the thermally initiated additions of tetrachloromethane to 1-octene, styrene, acrylonitrile, methyl acrylate and vinyl acetate, which were carried out in the absence of a metal oxide or an amine, was followed in a similar manner. In the addition reactions of styrene performed under normal pressure, the magnetically stirred reaction mixture was heated to reflux (76°C) in an atmosphere of nitrogen.

*Standard procedure for the preparation of 1 : 1 adducts.* Tetrachloromethane, alkene or diene copper(II) oxide and diethylamine were mixed in a molar ratio of 0.2 : 0.01 : 0.0001 : 0.0002 (in the case of 1,3-butadiene the molar ratio was 0.4 : 0.4 : 0.0004 : 0.0008) and transferred under nitrogen into a 40 ml Pyrex glass ampoule (an 80 ml ampoule was used for the addition of tetrachloromethane to 1,3-butadiene); the ampoule was sealed, placed in an oil bath and the vibrationally stirred reaction mixture was heated to 100–140°C under autogeneous pressure. Copper(II) oxide dissolved at the very beginning of the reaction to form a violet solution which gradually turned green and yellow. When the alkene conversion attained 95 to >99% (gas chromatographic analysis), the ampoule was cooled to room temperature. In the case of allyl alcohol, the addition reaction ceased after attaining 86% alcohol conversion. In the addition of tetrachloromethane to 1,5-hexadiene, the reaction was intentionally stopped after a 65% diene conversion. The excess tetrachloromethane and eventually unreacted alkene or diene were removed by evaporation, the oily residue was transferred into a Hickman flask and the 1 : 1 adduct was isolated by distillation under reduced pressure or by preparative gas chromatography of the major fraction. Reaction conditions for the preparation of the 1 : 1 adducts are tabulated.

1,1,1,3-Tetrachlorononane (2.06 g; isolated yield calculated on 1-octene charged: 77.5%), b.p. 89–90°C/226 Pa. For  $C_9H_{16}Cl_4$  (265.9) calculated: 40.63% C, 6.06% H; found: 40.66% C, 6.00% H. The  $^1H$ -NMR spectrum is in accordance with that given in the literature<sup>19</sup>.

1,1,1,3-Tetrachloro-3-phenylpropane (2.01 g; 78%), b.p. 98–100°C/200 Pa (ref.<sup>7</sup> b.p. 84°C: 13.3 Pa). For  $C_9H_8Cl_4$  (248.0) calculated: 41.90% C, 3.13% H; found: 41.93% C, 3.10% H,  $^1H$ -NMR  $\delta$ : 7.38 (s,  $C_6H_5$ ), 5.28 (t, CH,  $J = 6$  Hz), 3.57 (d,  $CH_2$ ,  $J = 6$  Hz); literature<sup>19</sup> gives  $\delta$ : 7.2 (5 H), 5.1 (1 H) and 3.4 (2 H).

$\alpha$ -(2,2-Trichloroethyl)styrene (mentioned in ref.<sup>20</sup> without giving the physical constants) (yield 74%) was isolated by preparative gas chromatography of the crude product (2.04 g, b.p. 94–100°C/227 Pa) which was a mixture of a lower-boiling product (15%) of unknown structure and of the desired product (85%). For  $C_{10}H_9Cl_3$  (235.6) calculated: 50.99% C, 3.85% H; found: 51.46% C, 3.97% H.  $^1H$ -NMR  $\delta$ : 3.88 (s,  $CH_2$ ), 7.0 (m,  $C_6H_5$ ), 5.52 + 5.63 ( $CH_2=$ ,  $J^2 = 1$  Hz).

1,1,1,3-Tetrachloro-6-heptene (1.30 g, 55%), b.p. 102–103°C/1.6 kPa. For  $C_7H_{10}Cl_4$  (236.0) calculated: 35.63% C, 4.27% H; found: 35.63% C, 4.24% H; the  $^1H$ -NMR spectrum was identical with that given in the literature<sup>21</sup>.

4-(1,3,3,3-Tetrachloropropyl)-1-cyclohexene (new compound) (analytical yield 37%), b.p. 105°/213 Pa, was isolated by preparative gas chromatography of the distillation residue (2.65 g) as a lower-boiling fraction containing approx. equal amounts of the desired product (A) and of a mixture of two higher-boiling, unidentified compounds (B, C) (ratio of retention times at 230°C for A : B : C = 1 : 11.3 : 12.3). For  $C_9H_{12}Cl_4$  (A) (262.0) calculated: 41.13% C, 4.62% H; found: 41.37% C, 4.61% H.  $^1H$ -NMR  $\delta$ : 5.72 (CH, olef.), 4.28 (unresolved multiplet, CHCl), 3.17 (q) + 3.25 (q) nonequivalent ( $CH_2$  groups, nonequivalent).

1,1,1,5-Tetrachloro-3-pentene (mixture of 20% *cis* and 80% *trans* isomers) (3.24 g, 78%), b.p. 80°C/1.6 kPa (ref.<sup>7</sup> b.p. 110°C/3.33 kPa). For  $C_5H_6Cl_4$  (207.9) calculated: 28.89% C, 2.91% H, found: 29.01% C, 2.91% H.  $^1H$ -NMR  $\delta$ : 4.10 (d, *cis* + *trans*  $CH_2Cl$ ,  $J = 5$  Hz), 3.5 (d, *cis*- $CH_2CCl_3$ ,  $J = 6$  Hz), 3.4 (d, *trans*- $CH_2CCl_3$ ,  $J = 5$  Hz), 5.95 (s, *cis*-CH=), 5.8 + 5.9 (m, *trans*-CH=)

*Products of addition of tetrachloromethane to isoprene.* The crude mixture of isomeric 1 : 1 adducts (1.62 g, 73%), b.p. 92–93°C/1.6 kPa (ref.<sup>22</sup> b.p. 64.0–64.5°C/133 Pa), which was obtained by removing excess tetrachloromethane and distilling the oily residue, was analysed by gas chromatography; the analysis showed, in addition to a minor amount (4.4%) of two lower-boiling compounds, three peaks indicating the presence of isomers in an amount of 10.3%

(A), 37.1% (B) and 48.2% (C) (ratio of retention times at 165°C for A : B : C = 1 : 1.2 : 1.4). The isomers, each 88% pure, were isolated by preparative gas chromatography at 165°C using a column (2.4 m × 8 m) packed with Reoplex 400 on Chromaton N-AW and identified by means of <sup>1</sup>H-NMR spectra and elemental analyses. Product A: *cis*-1,1,1,5-Tetrachloro-4-methyl-3-pentene (IV). For C<sub>6</sub>H<sub>8</sub>Cl<sub>4</sub> (221.9) calculated: 32.47% C, 3.63% H; found: 33.00% C, 3.66% H. <sup>1</sup>H-NMR δ: 1.93 (s, CH<sub>3</sub>), 3.39 (d, CH<sub>2</sub>CCl<sub>3</sub>, *J* = 7.5 Hz), 4.00 (s, CH<sub>2</sub>Cl), 5.60 (t, CH=, *J* = 7.5 Hz). Product B: For C<sub>6</sub>H<sub>8</sub>Cl<sub>4</sub> (221.9) calculated: 32.47% C, 3.63% H; found: 32.99% C, 3.65% H. The <sup>1</sup>H-NMR spectrum showed 2 isomers (B-1 and B-2) present in a 1 : 1 ratio. Product B-1: *cis*-1,1,1,5-Tetrachloro-3-methyl-3-pentene (II): δ: 2.07 (s, CH<sub>3</sub>), 3.54 (s, CH<sub>2</sub>CCl<sub>3</sub>), 4.16 (d, CH<sub>2</sub>Cl, *J* = 7.8 Hz), 5.83 (t, CH=, *J* = 7.8 Hz). Product B-2: *trans*-1,1,1,5-Tetrachloro-4-methyl-3-pentene (III): δ: 1.85 (s, CH<sub>3</sub>), 3.44 (d, CH<sub>2</sub>CCl<sub>3</sub>, *J* = 6.8 Hz), 4.08 (s, CH<sub>2</sub>Cl), 5.78 (t, CH=, *J* = 6.8 Hz). Product C: *trans*-1,1,1,5-Tetrachloro-3-methyl-3-pentene (I). For C<sub>6</sub>H<sub>8</sub>Cl<sub>4</sub> (221.9) calculated: 32.47% C, 3.63% H; found: 32.89% C, 3.67% H. <sup>1</sup>H-NMR δ: 1.98 (d, CH<sub>3</sub>, *J* = 1.3 Hz), 3.42 (s, CH<sub>2</sub>CCl<sub>3</sub>), 4.13 (d, CH<sub>2</sub>Cl, *J* = 7.8 Hz), 5.80 (triplet of a doublet, CH=, *J* = 7.8 Hz, *J* = 1.3 Hz) (ref.<sup>22</sup> gives δ: 2.01, 3.43, 4.09, 5.85).

2,4,4,4-Tetrachlorobutanol (1.46 g, 69%), b.p. 96°C/1.6 kPa (ref.<sup>7</sup> b.p. 66°C/133 Pa). For C<sub>4</sub>H<sub>6</sub>Cl<sub>4</sub>O (211.9) calculated: 22.67% C, 2.85% H; found: 22.69% C, 2.77% H. <sup>1</sup>H-NMR δ: ~2.17 (OH), 4.4 (multiplet with a long-range couplings, CHCl), 3.88 (d, CH<sub>2</sub>O—, *J* = 5 Hz), 3.25 (d, CH<sub>2</sub>, *J* = 5 Hz), 3.27 (d, CH<sub>2</sub>, *J* = 5 Hz). IR spectrum (neat): ν(OH)<sub>assoc</sub> 3390, (C—O) 1052 cm<sup>-1</sup>.

2,4,4,4-Tetrachlorobutyl propyl ether (new compound) (1.68 g, 66%), b.p. 97°C/1.6 kPa. For C<sub>7</sub>H<sub>12</sub>Cl<sub>4</sub>O (254.0) calculated: 33.10% C, 4.76% H; found: 32.80% C, 4.67% H. <sup>1</sup>H-NMR δ: 0.95 (t, CH<sub>3</sub>, *J* = 7 Hz), 1.63 (m, —CCH<sub>2</sub>C—, *J* = 7 Hz), 4.31 (m, CHCl); —CH<sub>2</sub>O— and —CH<sub>2</sub>CCl<sub>3</sub> groups exhibit only overlapping multiplets. IR spectrum (neat): ν(O—O) 1127 cm<sup>-1</sup>.

*Addition of tetrachloromethane to methyl vinyl ketone.* The product (1.42 g, b.p. 81—82°C/1.6 kPa) which was obtained by removing excess tetrachloromethane and distilling the oily residue contained, according to gas chromatographic analysis, a lower-boiling (A) and a higher-boiling compound (B) in a 20 : 80 ratio and a minor amount of a long retention time impurity (compound C) (ratio of the retention times at 125°C for A : B : C = 1 : 1.3 : 2.2). Preparative gas chromatography gave analytical samples of 2 products. 5,5,5-Trichloro-2-pentanone (A) (VI). For C<sub>5</sub>H<sub>7</sub>Cl<sub>3</sub>O (189.5) calculated: 32.17% C, 3.72% H; found: 32.07% C, 3.72% H. <sup>13</sup>C-NMR δ: 204.97 (C=O), 99.10 (CCl<sub>3</sub>), 30.08 (CH<sub>3</sub>), 48.82 (CH<sub>2</sub>), 40.45 (CH<sub>2</sub>). 3,5,5,5-Tetrachloro-2-pentanone (B) (V). For C<sub>5</sub>H<sub>6</sub>Cl<sub>4</sub>O (223.9) calculated: 26.82% C, 2.7% H; found: 27.21% C, 2.74% H. <sup>1</sup>H-NMR δ: 2.43 (s, CH<sub>3</sub>); —H<sub>X</sub>CCl—H<sub>A</sub>CH<sub>B</sub>— system: ABX multiplet 4.59 (H<sub>X</sub>), 3.12 (H<sub>A</sub>), 3.89 (H<sub>B</sub>), *J*<sub>AB</sub> = 15.56 Hz, *J*<sub>AX</sub> = 4.32 Hz, *J*<sub>BX</sub> = 6.10 Hz [ref.<sup>19</sup> gives δ: 6.5, 6.2 (2 d, 1 H, *J* = 10 Hz), 5.4, 4.8, 3.7, 3.1 (4 d, 2 H, *J* = 10 Hz) and 2.0 (s, 3 H)]. <sup>13</sup>C-NMR δ: 27.00 (CH<sub>3</sub>), 56.39 (CH<sub>2</sub>), 56.92 (CHCl), 96.11 (CCl<sub>3</sub>), 199.10 (C=O). IR spectrum (neat): ν(C=O) 1730 cm<sup>-1</sup>.

α,γ,γ,γ-Tetrachlorobutyronitrile (1.76 g, 85%), b.p. 79—80°C/1.6 kPa (ref.<sup>7</sup> b.p. 111°C/3.33 kPa). For C<sub>4</sub>H<sub>3</sub>Cl<sub>4</sub>N (206.9) calculated: 23.22% C, 1.46% H; found: 23.40% C, 1.47% H. <sup>1</sup>H-NMR δ: NCCH<sub>X</sub>Cl—H<sub>A</sub>CH<sub>B</sub>Cl<sub>3</sub> — system: 4.88 (H<sub>X</sub>), 3.3 (H<sub>A</sub>), 3.7 (H<sub>B</sub>), *J*<sub>AX</sub> = 5 Hz, *J*<sub>BX</sub> = 8 Hz. IR spectrum (neat): ν(C≡N) 2260 cm<sup>-1</sup>.

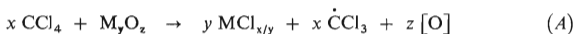
*Methyl α,γ,γ,γ-tetrachlorobutyrate* (1.22 g, 61%), b.p. 77—78°C/1.6 kPa (ref.<sup>7</sup> b.p. 111°C/2.67 kPa). For C<sub>5</sub>H<sub>6</sub>Cl<sub>4</sub>O<sub>2</sub> (239.9) calculated: 25.02% C, 2.52% H; found: 24.99, 2.52% H. <sup>1</sup>H-NMR δ: 3.80 (s, CH<sub>3</sub>); Cl<sub>3</sub>C—H<sub>A</sub>CH<sub>B</sub>—H<sub>X</sub>CCl—COOCH<sub>3</sub> — system: 3.78 (H<sub>A</sub>), 3.22 (H<sub>B</sub>), 4.63 (H<sub>X</sub>), *J*<sub>AX</sub> = 4 Hz, *J*<sub>BX</sub> = 7 Hz, *J*<sub>AB</sub> = 15 Hz. IR spectrum (neat): ν(C=O) 1753 cm<sup>-1</sup>.

1,3,3,3-Tetrachloropropyl acetate (1.49 g, 62%), b.p. 84—86°C/1.6 kPa. For C<sub>5</sub>H<sub>6</sub>Cl<sub>4</sub>O<sub>2</sub> (239.9) calculated: 25.03% C, 2.52% H; found: 25.28% C, 2.52% H. <sup>1</sup>H-NMR δ: 2.13 (s, CH<sub>3</sub>);

$\text{CH}_3\text{COO}-\text{H}_X\text{CCl}-\text{H}_B\text{CH}_A-\text{CCl}_3$  — system: 3.5 ( $\text{H}_A$ ), 3.5 ( $\text{H}_B$ ), 6.87 ( $\text{H}_X$ ),  $J_{AX} = 4$  Hz,  $J_{BX} = 6.5$  Hz. IR spectrum (neat):  $\nu(\text{C}=\text{O})$  1770  $\text{cm}^{-1}$ .

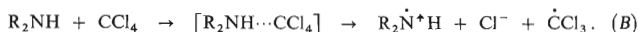
## RESULTS AND DISCUSSION

In the addition of tetrachloromethane to 1-octene carried out in the absence of solvents and organic bases, the copper(I), copper(II), thallium(III) and silver(I) oxides exhibit the highest initiating activity and produce the 1 : 1 adduct, 1,3,3,3-tetrachlorononane, in 57–83% yield. Tungsten(VI) oxide, titanium(IV) oxide and  $\text{U}_3\text{O}_8$  are less active (Table I). In the presence of other 22 metal oxides tested (*cf.* Experimental), the rate of formation of the 1 : 1 adduct does not surpass markedly the rate of the thermally initiated reaction, which starts only at 120°C (Fig. 1, curve 1), proceeds then at a low 1-octene conversion and with low selectivity and gives, under comparable conditions, 1,3,3,3-tetrachlorononane in only 22% yield (Table I). A complete or partial dissolution of metal oxides in the reaction mixture, presumably to form the corresponding metal chlorides, takes place during the addition reaction at temperatures from 120 and 180°C. Chlorination of metal oxides by tetrachloromethane in the gaseous phase has already been reported; contrastingly, temperatures about 500°C were necessary for transforming, for instance, iron(III) oxide into iron(III) chloride<sup>23,24</sup>. The abstraction of a chlorine atom from tetrachloromethane by interaction with a metal oxide in the liquid phase is presumably the initiating step of the addition reaction and the capability of inducing formation of the trichloromethyl radical may then be the major factor determining the initiating activity of a metal oxide (Eq. (A)).



The rate of the addition reaction can, however, be limited by low solubility of the metal oxide or chloride. It is well known that the solubility of some metal chlorides and thereby their catalytic activity in a radical addition reaction may be increased by the presence of polar solvents such as methanol, 2-propanol or acetonitrile or of compounds such as aliphatic amines<sup>7</sup>, ethanolamines<sup>25,26</sup> and dibutylphosphite<sup>25</sup>, called co-catalysts by some authors<sup>27</sup>. The effect of added alcohols, amines, pyridine and triphenylphosphine, which can either solvate the metal chloride or coordinate itself as ligands to a metal ion, was investigated by us first in the addition of tetrachloromethane to 1-octene. A high increase in selectivity of formation of the 1 : 1 adduct was achieved by adding 2-propanol to a reaction mixture containing iron(III) oxide; a combination of the same alcohol with copper(II) oxide was still perceptible, but less effective (Table I). Diethylamine was most active in the series of primary, secondary and tertiary nitrogen bases or ethanolamines, in conjugation with copper(II) oxide. Fig. 1 shows that diisopropylamine and even more diethylamine is more

effective than copper(II) oxide alone. This is consistent with the findings that amines react very easily with tetrachloromethane to form amine hydrochlorides<sup>28</sup>. Interaction of a secondary amine with tetrachloromethane producing the trichloromethyl radical<sup>29</sup> is in this case the initiating step (Eq. (B)),



As follows from Fig. 1, a secondary amine in conjugation with copper(II) oxide exhibits a significant synergic effect (curves 5 and 6). In this context it is of interest

TABLE I

Addition of Tetrachloromethane to 1-Octene Producing 1,1,1,3-Tetrachlorononane in the Presence and Absence of Metal Oxides ( $M_yO_z$ ) as Catalysts

Reactions on a 5 mmol 1-octene scale;  $[CCl_4]_0 : [1\text{-octene}]_0 = 20 : 1$ .

$M_yO_z$	$R^a$	Temperature °C	Time h	Conversion of 1-octene %	Yield <sup>b</sup> %
$Cu_2O$	0.1	175	9	>99	70
$CuO$	0.01	180	5	78	57
$CuO^c$	0.01	160	5	>99	68
$Fe_2O_3$	0.1	140	4	>99	20 <sup>d</sup>
$Fe_2O_3^c$	0.1	140	4	>99	78
$Ag_2O$	0.05	120	15	89	56
$Ag_2O$	0.1	120	5	>99	68
$Ag_2O$	0.3	120	5	>99	83
$Ag_2O$	0.5	120	5	>99	82
$Tl_2O_3$	0.01	175	4	>99	77
$Tl_2O_3$	0.1	140	4	>99	79
$TiO_2$	0.1	160	18	>99	82
$WO_3$	0.1	160	10	>99	75
$U_3O_8$	1	160	9	>99	67
— <sup>e</sup>	—	140	5	8	6
— <sup>e</sup>	—	160	5	16	10
— <sup>e</sup>	—	180	5	25	17
— <sup>e</sup>	—	200	5	34	22

<sup>a</sup> Molar ratio of metal oxide to 1-octene; <sup>b</sup> yield of the 1 : 1 adduct (based on the charged 1-octene) as determined by gas chromatographic analysis using dodecane as the internal standard; <sup>c</sup> mixture containing  $CCl_4$  and 1-octene in 2-propanol as solvent in a molar ratio of 10 : 1 : 10; <sup>d</sup> chromatogram showed the presence of at least 9 lower-boiling compounds as byproducts; hydrogen chloride was detected in the reaction mixture; <sup>e</sup> thermal initiation.

that the above reaction (Eq. (B)) is also catalysed by copper(II) salts<sup>29-31</sup>. Comparison of the data in Tables I and II shows that diethylamine increases significantly the activity of iron(III) oxide as well as copper(II) oxide and, though to a lesser extent, even of titanium(IV) oxide. Replacing diethylamine by its hydrochloride<sup>7</sup> did not cause any marked effect. In the reaction of tetrachloromethane with 1-octene, the redox system based on copper(II) oxide in conjugation with diethylamine (Table II) (Fig. 1) or diisopropylamine (Fig. 1) gave, at an almost complete alkene conversion, 1,1,1,3-tetrachlorononane in a yield (84%) which was three times higher than that obtained with octacarbonyldicobalt as catalyst<sup>10</sup>; only dichlorobis(triphenylphosphine)ruthenium(II) and dichlorotetrakis(triphenylphosphine)ruthenium(II) complexes give higher 1 : 1 adduct yields (97 to 99% based on consumed alkene), but at a substantially lower conversion of 1-octene<sup>12</sup> (60–70%). In the addition of tetrachloromethane to 1-octene, a replacement of a nitrogen base by triphenylphosphine was effective only in conjugation with copper oxides (Table II).

Attention was then turned to addition of tetrachloromethane to styrene, a representative electron-deficient alkene known to undergo easily to telomerisation or polymerisation not only in the presence of organic peroxides<sup>8,32</sup>, but also metal carbonyls<sup>10</sup> and other initiating agents. In contrast to 1-octene, the addition reactions of styrene initiated thermally, by copper(II) oxide in the absence of solvents or by diethylamine alone did not produce any more than a trace of the 1 : 1 adduct (Table III)

TABLE II

Effect of Ligands on the Yield of 1,1,1,3-Tetrachlorononane (A) in the Addition of Tetrachloromethane to 1-Octene Catalysed by Metal Oxide ( $M_yO_z$ )-Ligand Systems

Reactions on a 5 mmol 1-octene scale;  $[CCl_4]_0 : [1\text{-octene}]_0 : [M_yO_z] : [\text{ligand}] = 20 : 1 : 0.01 : 0.02$ ; reaction time 5 h; temperature 140°C.

$M_yO_z$	$(C_2H_5)_2NH.HCl$		Pyridine		$P(C_6H_5)_3$	
	conversion of 1-octene %	yield of A <sup>a</sup> %	conversion of 1-octene %	yield of A <sup>a</sup> %	conversion of 1-octene %	yield of A <sup>a</sup> %
$Fe_2O_3$	>99	76	>99	83	73	—
$Cu_2O$	>99	78	98	69	>99	81
$CuO$	>99	83	>99	73	>99	78
$TiO_2^b$	>99	74	11	—	43	—

<sup>a</sup> Yield of the 1 : 1 adduct (based on charged 1-octene) as determined by gas chromatographic analysis using dodecane as the internal standard; <sup>b</sup>  $[CCl_4]_0 : [1\text{-octene}]_0 : [M_yO_z] : [\text{ligand}] = 20 : 1 : 0.1 : 0.02$  (heterogeneous reaction mixture), temperature 160°C, reaction time 5 h.

(Fig. 2). Another difference resulted from a comparison of the catalytic effectiveness of redox systems such as copper(II) oxide–diisopropylamine and copper(II) oxide–diethylamine (Fig. 2); the addition of tetrachloromethane to styrene catalysed by the latter system proceeded at a faster rate and with higher selectivity giving the 1 : 1 adduct, 1,1,1,3-tetrachloro-3-phenylpropane, in 83% yield (100°C, 1 h) (Fig. 2). The product yield is comparable with that obtained earlier in a slower reaction catalysed by copper(II) chloride–diethylamine hydrochloride in a solution of 2-propanol<sup>7</sup>; higher yield of the 1 : 1 adduct (92%) was achieved only by using copper(II) chloride–diethylamine hydrochloride in acetonitrile solution<sup>7</sup> or dichlorotris(triphenylphosphine)ruthenium(II) (ref.<sup>12</sup>) as catalysts.

It is worthwhile mentioning that in a reaction catalysed by copper(II) oxide–diethylamine the yield of 1,1,1,3-tetrachloro-3-phenylpropane (82–85%) varies only little with the molar ratio of tetrachloromethane to styrene investigated in the range from 2 : 1 to 20 : 1 (Table IV). This result contrasts with the addition of tetrachloro-

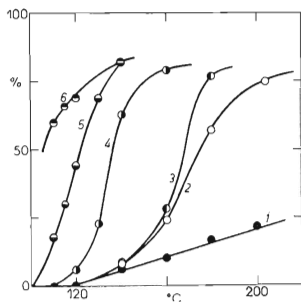


FIG. 1

Temperature Dependence of Formation of 1,1,1,3-Tetrachlorononane in Addition of Tetrachloromethane to 1-Octene Initiated Thermally 1 or by Copper(II) Oxide 2, Diisopropylamine 3, Diethylamine 4, Copper(II) Oxide–Diethylamine 5 and Copper(II) Oxide–Diisopropylamine 6 as Catalysts

$[\text{CCl}_4]_0 : [1\text{-octene}]_0 : [\text{CuO}] : [\text{Base}] =$   
 $= 20 : 1 : 0-0.01 : 0-0.02$ ; reaction time 5 h.

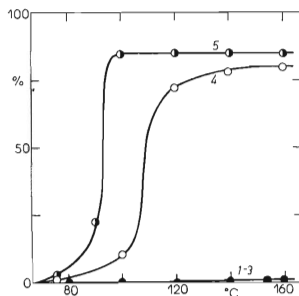


FIG. 2

Temperature Dependence of Formation of 1,1,1,3-Tetrachloro-3-phenylpropane in Addition of Tetrachloromethane to Styrene Initiated Thermally 1 or by Copper(II) Oxide 2, Diethylamine 3, Copper(II) Oxide–Diisopropylamine 4 and Copper(II) Oxide–Diethylamine 5

$[\text{CCl}_4]_0 : [\text{C}_6\text{H}_5\text{CH}=\text{CH}_2]_0 : [\text{CuO}] :$   
 $:\text{[Base} = 20 : 1 : 0-0.01 : 0-0.02$ ; reaction time 1 h.



TABLE III

Formation of 1 : 1 Adducts in the Addition of Tetrachloromethane to Electron-Deficient Alkenes Initiated Thermally or by Copper Oxides ( $\text{Cu}_2\text{O}$ ) at  $170^\circ\text{C}$

Reactions on a 5 mmol alkene scale;  $[\text{CCl}_4]_0 : [\text{alkene}]_0 : [\text{Cu}_2\text{O}] = 20 : 1 : 0$  or  $20 : 1 : 0.01$ .

Alkene	$\text{Cu}_y\text{O}$	Time h	Conversion of alkene <sup>a</sup> %	Yield of 1 : 1 adduct <sup>a</sup> %
Styrene <sup>b</sup>	— <sup>c,d</sup>	5	12	~1
Methyl acrylate	— <sup>c,e</sup>	5	—	~1
Acrylonitrile	$\text{Cu}_2\text{O}^f$	5	—	~1
	— <sup>c</sup>	5	1	0
	$\text{Cu}_2\text{O}^g$	5	27	3
	$\text{CuO}$	5	20	2.5
Vinyl acetate	$\text{CuO}$	12	54	17
	— <sup>c</sup>	5	42	13
	$\text{Cu}_2\text{O}$	5	53	25
	$\text{CuO}$	5	35	20
	$\text{CuO}$	12	80	10

<sup>a</sup> Determined by gas chromatographic analysis using dodecane as the internal standard; <sup>b</sup> reaction at  $160^\circ\text{C}$ ; <sup>c</sup> thermal initiation; <sup>d</sup> traces of the 1 : 1 adduct were formed when  $\text{CuO}$  ( $160^\circ\text{C}$ , 1 h, styrene conversion 38%;  $170^\circ\text{C}$ , 12 h, styrene conversion 83%) or diethylamine (molar ratio of styrene to diethylamine 1 : 0.02,  $160^\circ\text{C}$ , styrene conversion 62%) were used as initiators; <sup>e</sup> reactions initiated by  $\text{CuO}$  ( $170^\circ\text{C}$ , 5 h;  $170^\circ\text{C}$ , 12 h) gave only traces of the 1 : 1 adduct; <sup>f</sup> reactions catalysed by  $\text{Cu}_2\text{O}$  in acetonitrile solution ( $170^\circ\text{C}$ , 16 h) gave the 1 : 1 adduct in 11% yield<sup>33</sup>; <sup>g</sup> reactions catalysed by  $\text{Cu}_2\text{O}$  in acetonitrile solution ( $150^\circ\text{C}$ , 16 h) yielded 33% of the 1 : 1 adduct<sup>33</sup>.

TABLE IV

Dependence of the 1 : 1 Adduct Yield upon the Molar Ratio of Tetrachloromethane (A) to Alkene (B) and upon Kind of Initiation

Reactions on a 5 mmol alkene scale and at alkene conversions >99%.

Alkene	Initiator <sup>a</sup>	Temperature $^\circ\text{C}$	Time h	Yield <sup>b</sup> , % at molar ratio A : B			
				2 : 1	5 : 1	10 : 1	20 : 1
1-Octene	DTBP	140	5	65 <sup>c</sup>	77	76	78
1-Octene	$\text{CuO}$ -DEA	140	5	70 <sup>c</sup>	74	76	84
Styrene <sup>d</sup>	$\text{CuO}$ -DEA	100	4	82 <sup>e</sup>	84 <sup>e</sup>	84 <sup>e</sup>	85 <sup>f</sup>

<sup>a</sup> Concentration of di-tert-butyl peroxide (DTBP) or  $\text{CuO}$  was 1% mol. on the alkene charged; the molar ratio of  $\text{CuO}$  to diethylamine (DEA) was 1 : 2; <sup>b</sup> yield calculated on the charged alkene and determined by gas chromatographic analysis; <sup>c</sup> reaction time 10 h; <sup>d</sup> in the presence of DTBP only telomeric or polymeric products were formed; <sup>e</sup> the reaction time was not optimised; <sup>f</sup> reaction time 1 h.

TABLE V

Redox Chain Addition of Tetrachloromethane to Unsaturated Substrates Catalysed by Copper(II) Oxide in Conjugation with Diethylamine (DEA)

Reactions on a 10 mmol scale of the unsaturated substrate; molar ratio of  $\text{CCl}_4$  to this substrate, CuO and DEA was, unless otherwise stated, 20 : 1 : 0.01 : 0.02.

Substrate	Temperature °C	Time h	Conversion of substrate <sup>a</sup> %	Yield <sup>b</sup> %	Product
1-Octene	145	5	>99	77.5 (84) <sup>c</sup>	$\text{Cl}_3\text{CCH}_2\text{CHCl}(\text{CH}_2)_5\text{CH}_3$
Styrene	100	1	>99	78 (85)	$\text{Cl}_3\text{CCH}_2\text{CHClC}_6\text{H}_5$
$\alpha$ -Methylstyrene	120	8	>99	74 (—)	$\text{Cl}_3\text{CCH}_2(\text{CH}_2)_2\text{CC}_6\text{H}_5$
1,5-Hexadiene	140	1	65	55 (61)	$\text{Cl}_3\text{CCH}_2\text{CHCl}(\text{CH}_2)_2\text{CH}=\text{CH}_2$
4-Vinyl-1-cyclohexene	140	10	>99	37 (—)	$\text{Cl}_3\text{CCH}_2\text{CHClCH}(\text{CH}_2)_2\text{CH}=\text{CHCH}_2$
1,3-Butadiene <sup>d</sup>	100	12	98	78 (—)	$\text{Cl}_3\text{CCH}_2\text{CH}=\text{CHCH}_2\text{Cl}^e$
Isoprene	120	8	>99	(48)	<i>I</i>
				(37)	<i>II + III</i>
				(10)	<i>IV</i>
Allyl alcohol	140	6	86	69 (—)	$\text{Cl}_3\text{CCH}_2\text{CHClCH}_2\text{OH}$
Allyl propyl ether	140	8	95	66 (—)	$\text{Cl}_3\text{CCH}_2\text{CHClCH}_2\text{O}(\text{CH}_2)_2\text{CH}_3$
Methyl vinyl ketone	130	6	>99	(51)	<i>V</i>
				(13)	<i>VI</i>
Acrylonitrile	120	11	>99	85 (—)	$\text{Cl}_3\text{CCH}_2\text{CH}(\text{Cl})\text{CN}$
Methyl acrylate <sup>f</sup>	144	4	>99	61 (—)	$\text{Cl}_3\text{CCH}_2\text{CHClCOOCH}_3$
Vinyl acetate	140	6	>99	62 (—)	$\text{Cl}_3\text{CCH}_2\text{CH}(\text{Cl})\text{OCOCH}_3$

<sup>a</sup> Calculated on the substrate charged; <sup>b</sup> isolated yield; number in parentheses refer to yields determined by gas chromatographic analysis; <sup>c</sup> at a molar ratio of  $\text{CCl}_4$  to the substrate, CuO and DEA equal to 5 : 1 : 0.01 : 0.02 and 2 : 1 : 0.01 : 0.02 and under otherwise identical conditions, the analytical yield of product was 72 and 68%, respectively; <sup>d</sup> molar ratio of  $\text{CCl}_4$  to the substrate, CuO and DEA was 10 : 1 : 0.01 : 0.02; <sup>e</sup> a mixture of 80% *trans* and 20% *cis* isomers; <sup>f</sup> molar ratio of  $\text{CCl}_4$  to the substrate, CuO and DEA was 20 : 1 : 0.03 : 0.06, reaction run at a molar ratio of 20 : 1 : 0.01 : 0.02 (120°C, 8 h) gave the 1 : 1 adduct in 51% yield.

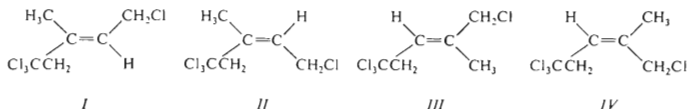
methane to 1-octene, an electron-rich alkene, where the 1 : 1 adduct yield increases significantly with decreasing alkene concentration in the presence of di-tert-butyl peroxide as well as copper(II) oxide in conjugation with diethylamine (Table IV).

As to the other electron-deficient alkenes, thermally initiated reactions of methyl acrylate and acrylonitrile produce, similarly as in the case of styrene, only traces of the 1 : 1 adducts; under the same conditions, vinyl acetate gives only minor amounts of 1,3,3,3-tetrachloropropyl acetate. Reactions of acrylonitrile<sup>33</sup> and vinyl acetate catalysed by copper(I) or copper(II) oxides in the absence of solvents give, even under forced conditions, the 1 : 1 adducts in low yields and the telomeric or polymeric compounds are always the major products (Table III). According to an earlier report, also the addition of tetrachloromethane to methyl acrylate and acrylonitrile in the presence of ruthenium complexes failed to give the 1 : 1 adducts in acceptable yields<sup>12</sup>.

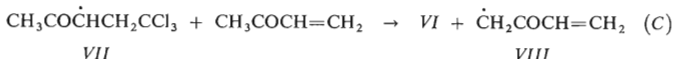
Conditions for the predominant formation of 1 : 1 adducts of tetrachloromethane with electron-deficient alkenes and unconjugated or conjugated aliphatic dienes in the redox chain addition reactions catalysed by copper(II) oxide-diethylamine in the absence of solvents at 100–140°C are listed in Table V.\* Selectivities achieved in these reactions are comparable with those observed by Asscher and Vofsi<sup>7</sup> using copper(II) chloride-diethylamine hydrochloride or iron(III) chloride-diethylamine hydrochloride as catalysts in methanol, 2-propanol or acetonitrile solutions and in the presence of benzoin as the sensitizing agent. In all cases we have obtained the expected 1 : 1 adducts, with but one exception; the unstable 1 : 1 adduct resulting from the addition of tetrachloromethane to  $\alpha$ -methylstyrene underwent easily the dehydrochlorination reaction yielding  $\alpha$ -(2,2,2-trichloroethyl)styrene as the final product. The 1 : 1 adducts prepared from unconjugated dienes were obtained by stopping the reaction at a partial diene conversion preventing the addition of tetrachloromethane to take place across the second carbon-carbon double bond; the yield of 1,1,1,3-tetrachloro-6-heptene from the addition reaction of 1,5-hexadiene is comparable with that achieved in a substantially slower reaction catalysed by naphthalenetetracarboxyl(tetrahydrofuran)chromium<sup>11</sup>. The redox chain 1,4-addition of tetrachloromethane to isoprene yielded regio- and stereoisomeric 1 : 1 adducts; the preparative gas chromatography of the mixture gave *trans*-1,1,1,5-tetrachloro-3-methyl-3-pentene (*I*), an inseparable mixture (1 : 1) of *cis*-1,1,1,5-tetrachloro-3-methyl-3-pentene (*II*) along with *trans*-1,1,1,5-tetrachloro-4-methyl-3-pentene (*III*), and *cis*-1,1,1,5-tetrachloro-4-methyl-3-pentene (*IV*) as major products (*cf.* Experimental)

\* Tetrachloromethane reacts, though at a slow rate, with acrylonitrile or methyl acrylate in the presence of copper(II) oxide and diethylamine (molar ratio 20 : 1 : 0.01 : 0.02) also at 76°C to form the corresponding 1 : 1 adducts in low yield along with byproducts of unknown structure; the reactions stop, however, after amine consumption and start again only after further addition of the amine.

present in a ratio of  $I : II : III : IV = 48 : 19 : 19 : 10$ . Structures of the isomers were assigned on the basis of their  $^1\text{H-NMR}$  spectra.



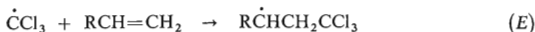
The major product of the redox chain addition of tetrachloromethane to methyl vinyl ketone, 3,5,5-tetrachloro-2-pentanone (*V*), was accompanied by a lower-boiling compound (ratio 80 : 20), which was identified unambiguously by means of elemental analysis and  $^{13}\text{C-NMR}$  spectra as 5,5,5-trichloro-2-pentanone (*VI*). Its formation presumably results from interaction of the intermediate radical *VII* with methyl vinyl ketone (Eq. (C));

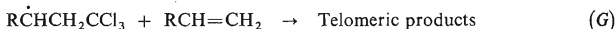


the radical *VIII* generated simultaneously can react further to produce either a dimer or another product.

The reaction of tetrachloromethane with methyl vinyl ketone catalysed by a ruthenium complex has been reported by Sasson and Rempel<sup>19</sup> to form also the tetrachloro ketone *V*. However, the  $^1\text{H-NMR}$  spectrum of the product obtained by these authors differs markedly from that of our tetrachloro ketone *V* (*cf.* Experimental) and a question arises whether the ruthenium complex catalysed reaction does not lead to another product.

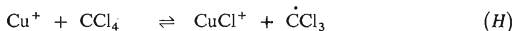
From all the above results it follows that the mechanism of radical additions of tetrachloromethane to a carbon-carbon double bond initiated by a metal oxide alone or by a secondary amine is analogous to that suggested earlier by Kharash<sup>1</sup> for addition reactions initiated by organic peroxides (Eqs (D)–(G)). A metal oxide (Eq. (A)) or an amine base (Eq. (B)) both may act as initiators abstracting a chlorine atom from tetrachloromethane to form trichloromethyl radical. The activation energy for this process is evidently lower than that for the thermal homolysis of the carbon-chlorine bond.





The equation (D) schematically expresses the equations (A) and (B). The step (G) is less important in free-radical addition reactions of electron-rich alkenes. The step (G) predominates, however, over the step (F) in reactions of electron-deficient alkenes initiated thermally or by metal oxides in the absence of amines and telomeric or polymeric compounds are then the major products.

The mechanism followed by addition reactions catalysed by a redox system copper(II) oxide–diethylamine seems to be qualitatively different from that expressed by Eqs (D)–(G). In the presence of an amine, the initiation according to Eq. (D) becomes unimportant. Supposing that the copper oxides are transformed in the reaction mixture into copper chlorides, the reaction mechanism will be analogous to that suggested by Asscher and Vofsi<sup>7</sup> for reactions catalysed by the redox system copper(II) chloride–diethylamine involving activation of the carbon–chlorine bond by copper(I) chloride (Eqs (H)–(K)).



According to this mechanism, the step (F), which applies in the redox chain addition reactions only to a small extent, is replaced by the chain transfer described by Eqs (H) and (K). This mechanism does not take into account the known capability of amines<sup>31,34,35</sup> or alkenes<sup>36</sup> to form complexes with the copper ion. Formation of copper complexes and their transformations during the redox chain addition of tetrachloromethane to unsaturated compounds is the subject of an ensuing communication<sup>37</sup>.

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