Journal of Organometallic Chemistry, 482 (1994) 39–44

Hydrogenolysis of carbon–chlorine bonds in carbon tetrachloride and trichlorofluoromethane in the presence of catalytic quantities of tris(triphenylphosphine) ruthenium(II) dichloride

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(Received December 7, 1993; in revised form January 27, 1994)

Abstract

The hydrogenolysis of carbon tetrachloride to chloroform, and of trichlorofluoromethane to hydrodichlorofluoromethane, are catalyzed by the complexes $RuCl_2(PPh_3)_3$ and $RuCl_2(dppe)_2$. The conversion of carbon tetrachloride into chloroform is more complete than the conversion of trichlorofluoromethane into hydrodichlorofluoromethane.

Key words: Ruthenium; Hydrogenolysis; Carbon–chlorine bonds; Homogeneous catalysis

1. Introduction

Aliphatic chlorocarbons and chlorofluorocarbons have found widespread commercial use as refrigerants, industrial solvents, and blow agents for the preparation of rigid polyurethane foams. Recently, however, the environmental problems that are being posed by these compounds are causing their use to be restricted or eliminated. In the case of the chlorofluorocarbons (CFCs), the particular hazard is that they are sufficiently inert that they travel into the stratosphere before they are photodecomposed [1]. This photodecomposition reaction in the stratosphere involves the cleavage of a carbon–chlorine bond in the CFC to give a chlorine atom, which then undergoes a chain reaction with ozone present at this altitude, resulting in a depletion of the ozone layer [2]. Two groups of compounds that are being introduced as replacements for CFCs are hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs). The HCFCs are considered to be less of a potential threat to the ozone layer because the presence of a carbon–hydrogen bond allows them to react with hydroxyl radicals present lower in the atmosphere, resulting in their chemical decomposition before they reach the stratospheric ozone layer [3]. The HFCs cause no significant threat to the ozone layer because they do not contain carbon–chlorine bonds that can undergo photohomolysis.

Because of the reduced environmental hazard of HCFCs and HFCs, chemical reactions that convert carbon–fluorine and carbon–chlorine bonds into carbon–hydrogen bonds are becoming of increasing interest. The high enthalpy of carbon–fluorine bonds means there are relatively few examples of their cleavage under mild reaction conditions [4,5]. Carbon–chlorine bonds, however, have considerably lower bond enthalpies than do carbon–fluorine bonds, and the hydrogenolysis of carbon–chlorine bonds into carbon–hydrogen bonds represents a potentially useful method for obtaining HCFCs from precursors that have a higher chlorine content (eq. 1). Although a number of heterogeneous catalysts have recently been used for reactions such as this involving

$$C\text{–}Cl + H_2 \longrightarrow C\text{–}H + HCl \qquad (1)$$

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0022-328X/94/$7.00
SSDI 0022-328X(94)24615-P

CFCs, little work has yet been published on the use of homogeneous catalysts for such conversions [6]. Nevertheless, a number of systems have been described that can be potentially used for the development of catalytic systems for the cleavage of aromatic C–Cl bonds [7].

The Atherton-Todd reaction of halocarbons with dialkyl phosphonates is one such potentially useful reaction that can be used to carry out such a transformation under homogeneous conditions. With dialkyl phosphonates this reaction leads to the conversion of a carbon–chlorine bond into a carbon–hydrogen bond in a compound such as carbon tetrachloride (eq. 2). This reaction is selective, no products

$$(RO)_2P(O)H + CCl_4 \longrightarrow (RO)_2P(O)Cl + CHCl_3 \quad (2)$$

being formed that have more than one hydrogen atom on a particular carbon. However, since the subsequent hydrogenolysis of the resulting phosphorus–chlorine bond does not occur, a catalytic cycle for such hydrogenolysis reactions cannot be achieved even at high hydrogen pressures [8]. Transition metal complexes, however, offer the possibility of incorporating this hydrogenolysis reaction into a catalytic cycle where the reactive center for the chlorocarbon is a transition metal–hydrogen bond rather than a phosphorus–hydrogen bond.

It is well known that transition metal hydride complexes react with carbon tetrachloride at ambient temperature to give chloroform and a transition metal chloride in a reaction that involves hydrogen-chlorine interchange (eqn. 3) [9]. If the resulting

$$M\text{–}H + CCl_4 \longrightarrow M\text{–}Cl + CHCl_3 \quad (3)$$

transition metal chloride complex undergoes subsequent hydrogenolysis of the M–Cl bond to give a M–H bond, a two-step reaction sequence leading to a transition metal catalyzed hydrogenolysis of a chlorocarbon into a hydrochlorocarbon can be realized (eqn. 4).

$$M\text{–}Cl + H_2 \longrightarrow M\text{–}H + HCl \quad (4)$$

The hydrogenolysis of a transition metal–chlorine bond is a relatively uncommon reaction because the M–H bond is susceptible to protonolysis, thereby causing the reaction to proceed in the reverse direction [9]. Nevertheless, the complex $RuCl_2(PPh_3)_3$ has been reported to undergo such a reaction under ambient temperature and pressure conditions [10]. In this paper we report the use of $RuCl_2(PPh_3)_3$ for the catalyzed hydrogenolysis of carbon tetrachloride into chloroform, and also of trichlorofluoromethane into dichlorofluoromethane, under relatively mild reaction conditions.

2. Experimental section

The complexes $RuCl_2(PPh_3)_3$, $RuCl_2(dppe)_2$, and $RuHCl(PPh_3)_3$ were synthesized according to literature procedures [11]. Triphenylphosphine was purchased (Aldrich) and used as supplied. Ruthenium trichloride hydrate was supplied by Johnson Matthey Electronics. Carbon tetrachloride, trichlorofluoromethane, dichlorodifluoromethane, chlorodifluoromethane, triethylamine and pyridine were commercial samples which were used as supplied. The compound $CFCl_3$ was purchased in 5 g ampules from Aldrich. Xylene (mixed xylenes), toluene and benzene were dried over sodium, then distilled and stored under a nitrogen atmosphere. Methanol, ethanol, isobutanol and ethylene glycol were distilled under a nitrogen atmosphere prior to use. The ^1H, ^{31}P and ^{19}F NMR spectra were measured either on a Bruker AC 200 or on a GE Omega 400 spectrometer. The ^{19}F and ^{31}P NMR chemical shift data were referenced to CCl_3F and 85% H_3PO_4 respectively. The catalytic reactions were carried out at ambient temperature if possible to minimize the decomposition of the complex to ruthenium metal. Chloroform was quantitatively measured either on a Hewlett-Packard Model 5830 gc/mass spectrometer or on a Sigma gas chromatograph. The instrument sensitivity tests for $CHCl_3$ and CCl_4 were carried out using toluene solutions of the two compounds in different ratios. The yields of $CHCl_3$ in the reactions were obtained by comparison of the peak intensities with those derived from the standard solutions calibrated in these sensitivity tests. The compound $CHFCl_2$ was identified by comparison of its ^1H NMR spectrum ($CDCl_3$): δ 7.46 d (^2J (HF) = 54 Hz), and its ^{19}F NMR spectrum ($CDCl_3$): δ −80.22 d (^2J (HF) = 54 Hz) with the literature values [12]. The complex $RuHCl(PPh_3)_3$ was identified in solution by its ^1H and $^{31}P\{^1H\}$ NMR spectra ($CDCl_3$): $\delta - 17.8$ q (^2J (PH) = 26 Hz) and δ 39.2 respectively; and by its IR spectrum (Nujol mull): ν(Ru–H) 2020 cm^{-1} [10].

2.1. Reactions with CCl_4

2.1.1. With $RuCl_2(PPh_3)_3$ in a mixture of alcohol and xylene

$RuCl_2(PPh_3)_3$ (100 mg, 104 μmol) was dissolved in a deoxygenated solvent consisting of ethanol and xylene in a 1:1 mixture (10 ml). The solution was stirred vigorously for 15 min under a hydrogen pressure of *ca.* 810 torr. The color of the solution changed from brown to violet-brown during this time. Deoxygenated CCl_4 (5 ml) was transferred into this solution by syringe, and the resulting mixture was stirred at room temperature for five days after which a sample was analyzed by ^1H

NMR spectroscopy. No high field resonance attributable to the hydride complex $RuHCl(PPh_3)_3$ was found. The liquid was distilled from the mixture, and the presence of chloroform was identified from a combination of GC/mass and ^1H NMR spectroscopy.

Methanol, isobutanol and ethylene glycol were used instead of ethanol in a 1 : 1 mixture with xylene in the reaction. An analogous reaction using pure xylene as solvent in the absence of any added alcohol was also carried out. In each case, the other experimental procedures were unchanged.

2.1.2. With $RuCl_2(PPh_3)_3$ in toluene or xylene in the presence of base

Triethylamine (0.05 ml, *ca.* 200 μmol) was added to a solution containing $RuCl_2(PPh_3)_3$ (100 mg, 104 μmol) and toluene (10 ml). The solution was then boiled under reflux for 2 h under an atmosphere of hydrogen. The color of the solution changed from brown to purple during this time. A sample of the mixture was analyzed by ^1H NMR spectroscopy, which showed the presence of $RuHCl(PPh_3)_3$. Deoxygenated CCl_4 (5 ml) was added to the solution, and the mixture stirred for 24 h under a hydrogen pressure of 810 torr. A sample of this mixture was analyzed by ^1H NMR spectroscopy, and a resonance at δ 7.58 (CD_3CN solvent) due to chloroform was observed. The upfield resonance in the ^1H NMR spectrum characteristic of $RuHCl(PPh_3)_3$ was absent in this solution. The reaction mixture was distilled and analyzed by GC/mass spectroscopy, but chloroform was present in only trace amounts, and no quantitative data for its formation were obtained. When pyridine (0.1 ml) was used in this reaction in place of triethylamine, no chloroform was detected in the solution at the end of the 24 h reaction time.

The reaction was repeated with a larger quantity of triethylamine under strictly dry and oxygen-free conditions. For this reaction the triethylamine was dried over 4A molecular sieves and the CCl_4 was dried over a mixture of P_2O_5 and K_2CO_3. These liquids were then distilled prior to use under nitrogen and carefully deoxygenated using freeze-thaw techniques. In this reaction a mixture of $RuCl_2(PPh_3)_3$ (100 mg, 104 μmol), xylene (10 ml) and Et_3N (4 ml) was stirred at ambient temperature for 18 h while hydrogen was slowly bubbled through the mixture. Carbon tetrachloride (5 ml) was added, and the mixture stirred for an additional 24 h under hydrogen bubbling. The liquid was distilled from the mixture and analyzed. Yields were determined from the quantity of triethylamine hydrochloride produced during the reaction. This value was determined from the weight of the total solid residue by subtracting that of $RuCl_2(PPh_3)_3$, plus the one equivalent of triethylamine hydrochloride obtained in the formation of $RuHCl(PPh_3)_3$. Yield of triethylamine hydrochloride was 1.3582 g. The formation of chloroform was qualitatively verified by ^1H NMR spectroscopy. The triethylamine hydrochloride formed was purified by washing the total solid residue with toluene, and recrystallizing it from a mixture of chloroform and toluene. The identity of this compound was confirmed by ^1H NMR spectroscopy. The ^1H NMR spectrum of the toluene extract of the solid residue shows no characteristic upfield resonance for $RuHCl(PPh_3)_3$.

TABLE 1. Hydrogenolysis of Carbon Tetrachloride to Chloroform and of Trichlorofluoromethane to Dichlorofluoromethane Catalyzed by $RuCl_2(PPh_3)_3$ or $RuCl_2(dppe)_2$ at 25°C in Xylene or Toluene Solvent

Catalyst	Reactant	Solvent/Adduct [a]	Reaction time (days)	turnover number [b]
$RuCl_2(PPh_3)_3$	CCl_4	Xylene/MeOH	1.5	19
$RuCl_2(PPh_3)_3$	CCl_4	Xylene/EtOH	5	64
			13	114
$RuCl_2(PPh_3)_3$	CCl_4	Xylene/i-BuOH	3	trace
$RuCl_2(PPh_3)_3$	CCl_4	Xylene/i-BuOH	14	63
$RuCl_2(PPh_3)_3$	CCl_4	Xylene/$(CH_2OH)_2$	1	81
			2	29
			5	15
$RuCl_2(PPh_3)_3$	CCl_4	Xylene	10	2.3
$RuCl_2(PPh_3)_3$	CCl_4	Xylene/Et_3N	1	trace
$RuCl_2(PPh_3)_3$	CCl_4	Xylene/Et_3N (excess)	1	69
$RuCl_2(PPh_3)_3$	$CFCl_3$	Toluene/EtOH	0.5	17
$RuCl_2(PPh_3)_3$	$CFCl_3$	Xylene/Et_3N (excess)	0.5	13
$RuCl_2(dppe)_2$ [c]	$CFCl_3$	Toluene/EtOH	1	trace
$RuCl_2(dppe)_2$	CCl_4	Xylene/EtOH	30	104
$RuCl_2(dppe)_2$	CCl_4	Xylene/$(CH_2OH)_2$	20	1
$RuHCl(PPh_3)_3$	CCl_4	Toluene	1	trace
			9	21

[a] When an alcohol is used, the solvent : alcohol ratio is 1 : 1.

[b] Defined as moles of chloroform obtained per mol of $RuCl_2(PPh_3)_3$ used.

[c] Reaction temperature is 110°C.

2.1.3. With $RuHCl(PPh_3)_3$ in toluene in the absence of alcohol or base

$RuHCl(PPh_3)_3$ (50 mg, 52 μmol) was added to a deoxygenated solvent containing a mixture of toluene (10 ml) and carbon tetrachloride (1 ml), and the mixture stirred vigorously under a hydrogen pressure of 810 torr for 24 h. After this time, the ^1H NMR spectrum showed the presence of chloroform, but the absence of $RuHCl(PPh_3)_3$. The liquid was distilled from the reaction, and analyzed by GC/mass spectroscopy, but chloroform was present in only trace amounts, and no quantitative data for its formation was obtained.

The data obtained in reactions A–C are collected in Table 1.

2.2. Reactions with $CFCl_3$

2.2.1. With $RuCl_2(PPh_3)_3$ in a mixture of alcohol and xylene

A solution of $RuCl_2(PPh_3)_3$ (100 mg, 104 μmol) in a mixed solvent consisting of ethanol and xylene in a 1 : 1 mixture (10 ml) was stirred for 2 h under a hydrogen pressure of 810 torr. $CFCl_3$ (5 ml at 0°C) was added, and the mixture stirred at room temperature for a further ten days. The inlet of the flask was connected to a mercury bubbler in order to prevent significant quantities of the volatile $CHFCl_2$ (bp 8°C) from escaping during the period of the reaction. A sample of this reaction mixture was analyzed by ^{19}F NMR spectroscopy. The reaction mixture was distilled at low pressure, and the $CHFCl_2$ formed was collected in $CDCl_3$ (2 ml) cooled to 77 K. This sample was analyzed by a combination of ^{19}F and ^{1}H NMR spectroscopy. The ^{1}H NMR spectrum showed no upfield resonance characteristic of $RuHCl(PPh_3)_3$. The reaction was repeated under the same experimental conditions except that $RuCl_2(dppe)_2$ was used instead of $RuCl_2(PPh_3)_3$, or that methanol or triethylamine (2 ml) was used in place of ethanol.

2.2.2. With $RuCl_2(PPh_3)_3$ in xylene in the presence of base

The reaction was repeated with a larger quantity of triethylamine under strictly dry and oxygen-free conditions. For this reaction the triethylamine was dried over 4A molecular sieves, and then both the ampuled $CFCl_3$ and the dry triethylamine were deoxygenated using freeze-pump-thaw techniques. A mixture of $RuCl_2(PPh_3)_3$ (100 mg, 104 μmol), xylene (10 ml) and Et_3N (7 ml) was stirred at ambient temperature for 18 h in a flask equipped with a dry ice condenser while hydrogen was slowly bubbled through the mixture. The $CFCl_3$ (5 ml) was then added, and the mixture stirred for an additional 12 h while hydrogen was continuously bubbled through the mixture. The dry ice condenser was kept filled with dry ice during this period. The mixture was allowed to warm slowly to 40°C and the evolving gas bubbled through ice-cooled $CDCl_3$. The evolution of $CHFCl_2$ was confirmed by ^{19}F NMR spectroscopy. The quantity of triethylamine hydrochloride formed was determined by the method described in the reaction with CCl_4. Yield 0.2621 g of $Et_3N.HCl$. The compound was purified and identified as previously described.

The data obtained in A and B are collected in Table 1.

3. Results

We have found that the complex $RuCl_2(PPh_3)_3$ acts as a catalyst for the hydrogenolysis of carbon tetrachloride and trichlorofluoromethane into chloroform and dichlorofluoromethane respectively under mild reaction conditions. The latter transformation is of some significance because we believe that this is one of the few examples of a discrete transition metal complex being used to catalyze the hydrogenolysis of a carbon–chlorine bond in a CFC to give a HCFC. The reaction with CCl_4 and $CFCl_3$ proceeds at 25°C and at a hydrogen pressure of 810 torr in a mixed solvent containing toluene and an alcohol such as ethanol or methanol. Reduced reactivity is observed when the chelate complex $RuCl_2(dppe)_2$ is used in place of $RuCl_2(PPh_3)_3$. When, however, the hydride complex $RuHCl(PPh_3)_3$ is used in the reaction in place of $RuCl_2(PPh_3)_3$, the conversion of carbon tetrachloride into chloroform is again observed. In the absence of an added alcohol, only small quantities of chloroform are obtained from carbon tetrachloride. The addition of small quantities of triethylamine instead of an alcohol also results in the formation of only small quantities of chloroform. The addition of large quantities of triethylamine, however, leads to the formation of catalytic quantities of both chloroform and dichlorofluoromethane. These data for the catalyzed formation of chloroform and dichlorofluoromethane are collected in Table 1.

The data in Table 1 for the hydrogenolysis of CCl_4 to $CHCl_3$ show that catalytic turnovers of up to approximately 100 can be obtained. From these data it is apparent that the conversion of CCl_4 into $CHCl_3$ is most complete when an alcohol or a large quantity of triethylamine is mixed with the xylene solvent, and that solutions containing i-BuOH have a lower reactivity than do solutions containing MeOH, EtOH or $(CH_2OH)_2$. If oxygen is allowed to enter the catalytic reaction the yield of chloroform is reduced, but not if elemental mercury is added to the reaction.

When $CFCl_3$ is used instead of CCl_4 in the reaction with $RuCl_2(PPh_3)_3$ and hydrogen in a mixed solvent containing xylene and ethanol, dichlorofluoromethane ($CHFCl_2$) is formed with a catalytic turnover number of 17 after 24 h reaction time at 25°C (eqn. 5). The compound $CHFCl_2$ has been identified by its ^{1}H and ^{19}F NMR

$$CFCl_3 + H_2 \longrightarrow CHFCl_2 + HCl \qquad (5)$$

spectrum. No formation of chlorofluoromethane was detected. When $RuCl_2(dppe)_2$ is used in place of $RuCl_2(PPh_3)_3$, even at the elevated temperature of 110°C, only traces of $CHFCl_2$ are formed.

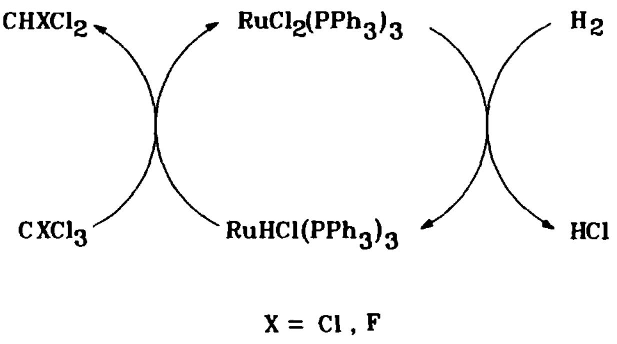
The reaction of CF_2Cl_2 with hydrogen under the same conditions in the presence of catalytic quantities of $RuCl_2(PPh_3)_3$ has also been investigated. No reaction is observed at 25°C, but when the reaction is again carried out at 90°C in the presence of triethylamine in a mixed solvent system containing xylene and an alcohol, small quantities of CHF_2Cl (δ −71.8 d (^2J(HF) = 64 Hz) have been detected by ^{19}F NMR spectroscopy. The quantities of CHF_2Cl are, however, too small to determine conclusively whether the conversion was catalytic in $RuCl_2(PPh_3)_3$. The presence of CHF_2Cl can be ascertained by the presence of a resonance in the ^{19}F NMR spectrum at δ −71.8 (^2J(HF) = 64 Hz), a value that we measured using a commercial sample of the compound.

Although the presence of small quantities of triethylamine (0.05 ml) in place of an alcohol does not lead to an increase in the yield of chloroform from carbon tetrachloride, the addition of larger quantities (4 ml) under anhydrous reaction conditions results in a catalytic turnover number of 69 being observed for the formation of chloroform from carbon tetrachloride. Similarly, under analogous reaction conditions a catalytic turnover number of 13 is observed for the formation of dichlorofluoromethane from trichlorofluoromethane. Under these anhydrous conditions the turnover number has been determined by the yield of triethylamine hydrochloride, with the identity of the product halomethane being determined by a combination of ^1H and ^{19}F NMR spectroscopy.

4. Discussion

From our results it is apparent that the complex $RuCl_2(PPh_3)_3$ can be used as a catalyst for the conversion of a C–Cl bond in CCl_4 and in $CFCl_3$ into a C–H bond, but that the chelate complex $RuCl_2(dppe)_2$ is less active as a catalyst. The presence of a chelate ligand, and hence the lack of a vacant coordination site in the 18-electron complex $RuCl_2(dppe)_2$, causes a lowering of the catalytic activity as compared to $RuCl_2(PPh_3)_3$. The addition of elemental mercury to catalytic solutions containing $RuCl_2(PPh_3)_3$ does not result in decreased activity, which argues against elemental ruthenium being the active catalyst [13]. Further support for a homogeneously catalyzed reaction comes from the finding that no further catalytic activity is observed when the reaction is carried out over long reaction times after the decomposition of $RuCl_2(PPh_3)_3$ to elemental ruthenium is essentially complete.

The $RuCl_2(PPh_3)_3$ catalyzed reaction can be described by the sequence of reactions shown in Scheme 1. This sequence involves the initial hydrogenolysis of $RuCl_2(PPh_3)_3$ to give $RuHCl(PPh_3)_3$, followed by reaction of $RuHCl(PPh_3)_3$ with CCl_4 to give $RuCl_2(PPh_3)_3$ and $CHCl_3$. The data in Table 1 show that the hydrogenolysis reaction is catalytic in xylene solvent in the absence of an alcohol, but with higher turnover numbers in the presence of an alcohol. Similarly, higher turnover numbers can be achieved by the addition of triethylamine. The role of the alcohol or triethylamine in the solvent mixture is to promote the formation of $RuHCl(PPh_3)_3$ from $RuCl_2(PPh_3)_3$ [14,15]. For alcohols the hydride is obtained by a β-hydride transfer reaction, whereas for triethylamine the hydride is obtained in a slow reaction between $RuCl_2(PPh_3)_3$ and hydrogen in the presence of a large excess of the base [10]. The hydride complex $RuHCl(PPh_3)_3$ is also an active catalyst for the hydrogenolysis of CCl_4 to $CHCl_3$ when it is added to the reaction in place of $RuCl_2(PPh_3)_3$. Furthermore, the detection of small amounts of $RuHCl(PPh_3)_3$ in reactions catalyzed by $RuCl_2(PPh_3)_3$ supports the hypothesis that this hydride complex is formed in these catalytic solutions. The complex $RuHCl(PPh_3)_3$ is observed in the presence of triethylamine, which serves to remove any HCl formed in the reaction before it reacts to give $RuCl_2(PPh_3)_3$ and hydrogen. Our results complement those of Rempel, with the additional contribution from a hydrogenolysis pathway to the overall reaction.



Scheme 1.

Qualitatively, it appears that the conversion of carbon tetrachloride into chloroform in the presence of $RuHCl(PPh_3)_3$ is a radical reaction. This suggestion is borne out by the observation that it is difficult to obtain consistent turnover numbers in consecutive reactions. The data for ethylene glycol in Table 1 exemplify this difficulty where three catalytic runs carried out over increasing times result in progressively reduced turnover numbers for chloroform formation. A radical pathway is supported by evidence from the literature relating to the reaction between $RuCl_2(PPh_3)_3$ and CCl_4 [16].

The reduced reactivity of $CFCl_3$ as compared to CCl_4, and the very low reactivity observed for CF_2Cl_2

toward $RuHCl(PPh_3)_3$, are analogous to the reactivity sequence found for these chlorocarbons with dialkyl phosphonates in the Atherton-Todd reaction [8]. This difference in reactivity is not immediately apparent. If the rate-determining step in the reaction is single electron transfer to form an alkyl anion, the replacement of chlorine substituents by fluorine would be expected to favor the reaction of $CFCl_3$ over that of CCl_4. If the reaction of transition metal hydrides with CCl_4 is indeed a free radical reaction, bond homolysis considerations could be expected to provide an explanation for the relative reactivities. The bond enthalpy of the C–Cl bond in CCl_4 is 73.1 ± 1.8 kcal/mol, whereas the value in $CFCl_3$ is 73 ± 2 kcal/mol [17]. Clearly these values are identical, and simple homolysis of the C–Cl bond does not therefore provide a simple explanation for the difference in reactivity between the three compounds.

A plausible explanation for the observed sequence of reactivity is that the reaction involves electron transfer to give the radical anions $CCl_4^{\overline{\cdot}}$, $CFCl_3^{\overline{\cdot}}$ and $CF_2Cl_2^{\overline{\cdot}}$, and that the lower reactivity of the CFCs is due to the increased stability of the anions $CFCl_3^{\overline{\cdot}}$ and $CF_2Cl_2^{\overline{\cdot}}$ as compared to $CCl_4^{\overline{\cdot}}$. The free radical character of the reaction is supported by the observation that the yield of $CHFCl_2$ is decreased in the presence of oxygen in the reaction, presumably because of side reactions between oxygen and the radical intermediates. This explanation has not, however, been verified, and other reaction pathways and mechanisms for these interchange reactions between hydrogen and halogen in haloalkanes are currently being explored by computational methods [18].

Acknowledgments

We thank the Center for Bioenvironmental Research at Tulane University and the National Science Foundation (INT 9113923) for financial support, and Johnson Matthey Electronics for a loan of ruthenium trichloride.

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