Addition of tetrachloromethane to alkenes catalyzed by cobalt(II)–amine complex

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The cobalt(II)–2-methylpropylamine complex is an efficient catalyst for addition of tetrachloromethane to alkenes under mild reaction conditions (80°C) providing 1 : 1 adducts up to 99.5% yield. Reactions with vinyl monomers provided low yield of 1 : 1 addition products (5–48%) presumably due to radical chain processes favoring telomerization and polymerization.

Keywords: Addition reactions; cobalt(II) catalyst; free radicals

1. Introduction

A number of transition metal salts and complexes (e.g. Cu [1], Fe [2], Pd [3], Al [4], Ru [5,6], Re [6], Mo [7], V [8], W [9], Cr [10,11], Mn [12], Ni [13]) have been reported to catalyze the addition reactions of halocompounds with alkenes providing 1 : 1 adducts in moderate to high yields. Cobaltous chloride was found to be unable to induce addition reactions [14], whilst a cobalt complex (dicobalt octacarbonyl) was reported as a catalyst for the additions of tetrachloromethane [15] and methyl trichloroacetate [16] to alkenes. However, severe reaction conditions (160–180°C, 15–17 h) were required and the yields of 1 : 1 adducts were rather modest (12–40%).

In previous papers we have described copper(I) complexes with nitrogen ligands as efficient catalysts for the addition reactions of halocompounds with alkenes [17–19]. Although, cobalt(II)–amine complexes [20] formed from cobalt(II) salts and various amines as ligands have been known for many years, their catalytic properties in addition reactions have not been examined. The aim of this work was to examine the catalytic activity and selectivity of a selected cobalt(II)–amine complex and to compare its properties with other already known catalysts.

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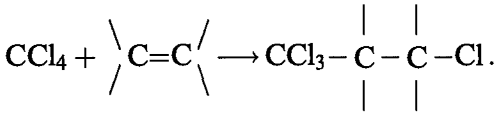
2. Results and discussion

We have observed an activating effect of 2-methylpropylamine on cobalt(II) chloride resulting in an enhanced yield at much lower temperature for the catalytic process previously effected with a dicobalt octacarbonyl complex. It has been assumed that the cobalt(II) salt–amine catalytic system acts by means of a catalytic active cobalt(II)–amine complex similarly as in catalysis by copper(I)–amine complexes. However, significant differences were observed in the course of addition reactions. The molar ratio of cobalt(II) to 2-methylpropylamine had to be at least 8 : 1, in spite of theoretical requirements [20] ((2–4): 1). At lower molar ratios the reaction did not proceed. Moreover, an induction period (50–90 min) has been recorded in every case. Both observations indicate that a catalytically active species of the cobalt(II) complex is formed from cobalt(II) chloride and 2-methylpropylamine in situ in the course of the reaction. However, its low concentration and low stability in solid state prevented the characterization of the catalyst form. In order to get more information on activity and selectivity of the cobalt catalyst it has been tested in the addition reactions of tetrachloromethane with a number of alkenes of different structures. In general, the reaction proceeds as below providing the 1 : 1 adduct as a main product,



$$\mathrm{CCl_4} + {>}\mathrm{C{=}C}{<} \longrightarrow \mathrm{CCl_3}-\overset{|}{\underset{|}{\mathrm{C}}}-\overset{|}{\underset{|}{\mathrm{C}}}-\mathrm{Cl}.$$

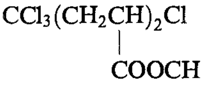
1 **2**

The addition reactions were carried out under mild conditions at 80°C and the results obtained are summarized in table 1.

The highest yields of 1 : 1 adducts were obtained in additions with terminal aliphatic alkenes (80–99.5%). The addition of tetrachloromethane to 1,5-hexadiene resulted in a mixture of monoaddition (27%) and diaddition (48%) products. The formation of both products has been recently explained [21]. The addition to internal alkenes and cycloalkenes resulted in lower yields of 1 : 1 adducts (15–43%), due to their lower reactivity known. Owing to its stereoselectivity cyclopentene gave only one isomer of the 1 : 1 adduct with trans configuration in agreement with the literature [10]. Cyclohexene gave two isomers of the 1 : 1 adduct with the trans : cis ratio 59 : 41, which differs from ruthenium catalyzed additions (96 : 4) [5] but is very close to that obtained with dibenzoyl peroxide (53 : 47) [5] and rhenium complex (55 : 45) [6]. In the case of trans- and cis-2-butenes both diastereoisomers of the 1 : 1 adduct were formed in the ratio 78 : 22, which is almost identical (75 : 25) to that obtained with dibenzoyl peroxide [22] and palladium complex [3].

During the additions to easily polymerizable vinyl monomers (styrene, methyl acrylate) telomerization and polymerization was observed. The addition to methyl acrylate yielded the 1 : 1 adduct (48.6%) accompanied by formation of the 2 : 1

Table 1
Addition of tetrachloromethane to alkenes catalyzed by cobalt(II)–2-methylpropylamine complex at 80°C

Alkene[a]	Product[b]	Time (h)	Yield[c] (%)
$CH_2{=}CHCH_2CH_3$	$CCl_3CH_2CHClCH_2CH_3$	7	79.9
$CH_2{=}C(CH_3)_2$	$CCl_3CH_2C(CH_3)_2Cl$	8	92.5
$CH_2{=}CHCH(CH_3)_2$	$CCl_3CH_2CHClCH(CH_3)_2$	10	82.9
$CH_2{=}CH(CH_2)_3CH_3$	$CCl_3CH_2CHCl(CH_2)_3CH_3$	7	99.5
$CH_2{=}CHC(CH_3)_3$	$CCl_3CH_2CHClC(CH_3)_3$	8	93.5
$CH_2{=}CH(CH_2)_5CH_3$	$CCl_3CH_2CHCl(CH_2)_5CH_3$	7	92.2
$CH_2{=}CHCH_2Ph$	$CCl_3CH_2CHClCH_2Ph$	6	69.5
$CH_2{=}CH(CH_2)_2CH{=}CH_2$	$CCl_3CH_2CHCl(CH_2)_2CH{=}CH_2$	7.5	27.0
	$CCl_3CH_2CHCl(CH_2)_2CHClCH_2CCl_3$		48.5
$\underline{CH{=}CH(CH_2)_3}$	$CCl_3\underline{CHCHCl(CH_2)_3}$	10	39.9
$\underline{CH{=}CH(CH_2)_4}$	$CCl_3\underline{CHCHCl(CH_2)_4}$	7	27.4
trans-$CH_3CH{=}CHCH_3$	$CCl_3(CH_3)CHCHCl(CH_3)$	6.5	43.2
cis-$CH_3CH{=}CHCH_3$	$CCl_3(CH_3)CHCHCl(CH_3)$	6.5	34.4
$CH_3CH{=}C(CH_3)_2$	$CCl_3(CH_3)CHCCl(CH_3)_2$	7	26.7
$(CH_3)_2C{=}C(CH_3)_2$	$CCl_3(CH_3)_2CCCl(CH_3)_2$	11	15.8
$PhCH{=}CH_2$	$PhCHClCH_2CCl_3$	7	5.2
$CH_2{=}CHCOOCH_3$	$CCl_3CH_2CHClCOOCH_3$	1.5	48.6
	 $CCl_3(CH_2\underset{\underset{COOCH_3}{\vert}}{C}H)_2Cl$		13.3

[a] Molar ratio of CCl_4 : alkene : $CoCl_2$: amine = 5 : 1 : 0.02 : 0.16; 10 mmol alkene scale, catalyst prepared in situ.
[b] Characterized by MS, ^1H and ^{13}C NMR analysis.
[c] Determined by GC analysis using an internal standard.

adduct (13.3%) and higher molecular weight products (telomers). In the addition of tetrachloromethane to styrene the styrene polymerization proceeded preferentially. Only a low yield of the 1 : 1 adduct (5.2%) was obtained. Polymerization of vinyl monomers was also observed when catalyzed by dicobalt octacarbonyl [15,16], but never observed with copper(I)–amine catalysts [17–19].

Concerning the reaction mechanism, the results obtained in this study indicate that there is a cobalt-catalyzed addition, which is rather complicated to elucidate unambiguously. Because of the high selectivity observed in the reactions of aliphatic alkenes, the cobalt(II)–amine complex could be considered as a true catalyst. This assumption is supported by the observation which proved hydroquinone had no inhibiting effect on the reaction rate. However, the significant side-polymerization of styrene and the telomerization of methyl acrylate, evidently due to chain processes, indicate the presence of free radicals in the cobalt-catalyzed reactions. This contradictory assumption is supported by the stereoselectivity data obtained in the reactions with cyclohexene and 2-butenes, where the trans : cis product isomer ratios are almost identical to that obtained from dibenzoyl peroxide initiated reactions.

These results differ markedly from the ruthenium- [5] and copper-complexes [18,21,23] catalyzed addition reactions where a non-chain mechanism (reaction in the coordination sphere) is thought to prevail. Although we have not carried out a detailed mechanistic study, the results indicate that the cobalt complex may act as a catalyst as well as a free radical initiator via single electron transfer. High yields of the addition reactions with aliphatic alkenes may be also explained by an efficient chain transfer by the cobalt complex, which is not, on the other hand, sufficiently effective to prevent polymerization and telomerization of vinyl monomers due to free radical processes. We propose the mechanism involving both catalytic and free radical chain steps. A similar mechanism has been proposed for the addition reactions catalyzed by palladium [3] and rhenium [6] complexes. A more detailed mechanistic study is in progress.

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