IR studies at elevated gas pressures

III *. Kinetics of the CO induced disproportionation of (C₅(CH₃)₅)₂TiX (X = Cl, Br, I)

of $(C_5(CH_3)_5)_2TiX$ (X = Cl, Br, I)

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Abstract

The disproportionation of $Cp^*_2TiClCO$ ($Cp^* = \eta^5\text{-}C_5(CH_3)_5$) (formed from Cp^*_2TiCl and CO in toluene solution) into $Cp^*_2TiCl_2$ and $Cp^*_2Ti(CO)_2$ has been studied at CO pressures of between 2 and 90 bar. The rate of reaction was found to be inversely proportional to the CO concentration. The reaction order with respect to $Cp^*_2TiClCO$ changed from 1 to 1.4 with increasing CO pressure. The observations are explained in terms of a kinetic scheme in which Cp^*_2TiCl, which is formed from $Cp^*_2TiClCO$ in a slow reaction, is an essential intermediate.

Introduction

The CO-induced disproportionation of $(Cp_2TiCl)_2$ was recently reported [2] to proceed by a reaction between monomeric Cp_2TiCl and its CO adduct $Cp_2TiClCO$; in the rate-determining step the latter appears to transfer its chlorine ligand to the uncomplexed monomer. The object of the present study was to elucidate the mechanism for the CO-induced disproportionation of the closely related complexes Cp^*_2TiX ($Cp^* = \eta^5\text{-}C_5(CH_3)_5$; X = Cl, Br, I) [3] and to determine in which way differences in electronic and steric properties of the Cp^* and halogen ligands [4] affect disproportionation and comproportionation reactions in reaction systems of this type.

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Experimental

All operations were performed with rigorous exclusion of oxygen and moisture by standard vacuum-line techniques. Solvents were distilled from sodium metal, carefully degassed, and saturated with argon prior to use. Gases (ultrahigh purity) were used as purchased. $Cp^\star_2TiCl$ (1), $Cp^\star_2TiBr$ (4) and $Cp^\star_2TiI$ (5) were prepared by published procedures [5]. NMR experiments were performed in C_6D_6 under CO (ca. 750 torr) in sealed NMR tubes. Kinetic measurements were carried out with 0.05 M solutions in toluene. For IR measurements under elevated pressure, a pressure-resistent IR cell was used as previously described [2]. IR absorbance data were collected and processed as before. Kinetic runs were reproducible within $\pm 10\%$. Concentrations of $Cp^\star_2TiClCO$ (6) and $Cp^\star_2Ti(CO)_2$ (2) were determined as a function of time by use of the absorption maximum at 2014 cm^{-1} for 6 (ϵ 350 ± 30 l/(mol · cm)) and that at 1849 cm^{-1} for 2 (ϵ 1020 ± 50 l/(mol · cm)).

Results

Characterisation of reaction products and intermediates

When 1 is treated with CO, disproportionation to $Cp^\star_2TiCl_2$ (3) and $Cp^\star_2Ti(CO)_2$ (2) (eq. 1) occurs [3]; this reaction is fast at room temperature and CO pressures of or above 1 bar. In contrast to the analogous reaction with $(Cp_2TiCl)_2$ [2], the disproportionation is irreversible: Removal of the CO atmosphere does not lead to the disappearance of the ^1H NMR signals of 2 and 3 by comproportionation to 1. The other halides, 4 and 5, react analogously with CO to give 2 and the respective dihalide complexes $Cp^\star_2TiX_2$ (X = Br, I). Again, NMR studies revealed no comproportionation upon removal of CO.

$$2\ Cp^\star_2TiX\ + 2\ CO \rightarrow\ Cp^\star_2TiX_2 + Cp^\star_2Ti(CO)_2 \tag{1}$$
$$(1, X = Cl; \qquad\qquad (3, X = Cl) \qquad (2)$$
$$4, X = Br;$$
$$5, X = I)$$
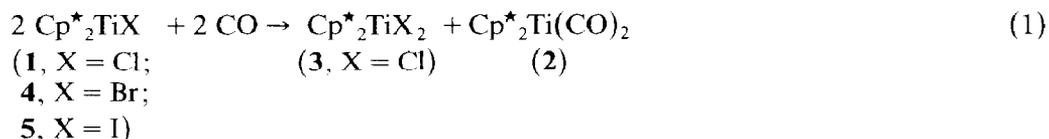
IR spectroscopic studies of the carbonylation of the monohalides 1, 4 and 5 were performed as described by Van Raaij et al. for the related $(Cp_2TiCl)_2$ [2]. Reaction of 1 with CO at lower temperature (e.g. $-30\,^\circ C$) and pressures higher than 2 bar gives exclusively the monocarbonyl adduct $Cp^\star_2TiClCO$ (6). Its formation is quantitative within the time needed to saturate the solution (ca. 3 min), its concentration being independent of CO pressure between 2 and 90 bar. This means that equilibrium 2 lies fully over to the right hand side, in contrast to that for $(Cp_2TiCl)_2$, with which formation of the $Cp_2TiClCO$ adduct is quantitative only at pressures well over 100 bar. Probably both the higher electron density at the metal centre [4] and the monomeric nature of $Cp^\star_2TiCl$ contribute to the enhanced stability of $Cp^\star_2TiClCO$ compared with that of $Cp_2TiClCO$.

$$Cp^\star_2TiCl + CO \rightleftarrows Cp^\star_2TiClCO \tag{2}$$
$$(1) \qquad\qquad (6)$$

Compound 6 is stable at $-30\,^\circ C$ and shows no tendency to disproportionate to 2 and 3 (eq. 1) or to lose CO and form 1. Even when the CO pressure is released and residual CO is swept from the solution with dinitrogen no decrease of [6] is
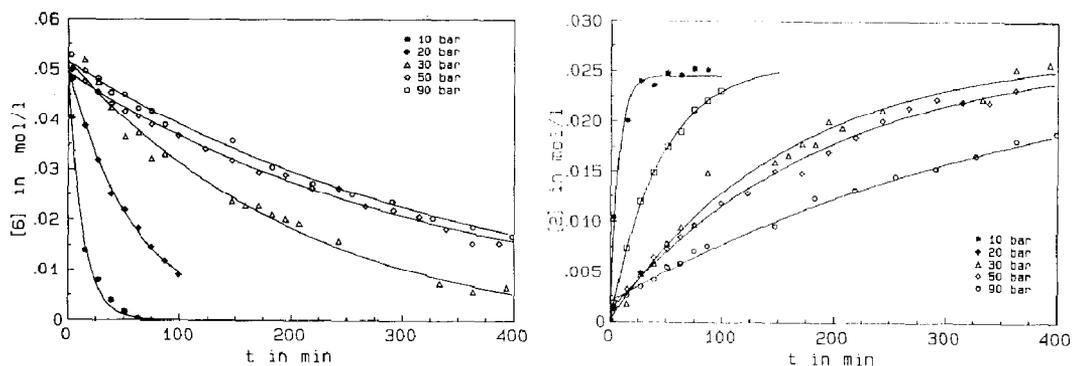
Fig. 1. Disproportionation of $Cp^*_2TiClCO$ (6) to $Cp^*_2Ti(CO)_2$ (2) and $Cp^*_2TiCl_2$ (3) at 5°C under CO pressure from 10 to 90 bar. A: 6 monitored, B: 2 monitored.

observed. At −10°C, 6 is formed quantitatively, and appears to be stable under CO. However, when the CO atmosphere is replaced by dinitrogen, a slow decrease in the amount of [6] (half-life time ca. 14 h) is observed. After ca. 30% of the original amount of 6 has disappeared, characteristic ν(CO) absorptions of 2 appear and indicate the beginning of a disproportionation of 6 into 2 and 3. At higher temperatures (> 0°C) the changes in concentration of 6 and 2 can be measured conveniently, and kinetic studies are possible.

Kinetic analysis

At 5°C and pressures above 10 bar, complete conversion of 1 into 6 is initially observed. At this temperature the disproportionation reaction appears to be substantially slower than the formation of 6, so that 6 builds up to a maximum concentration, which is practically equal to the initial concentration of 1 (cf. Fig. 1). The rate of the subsequent conversion of 6 to 2 and 3 depends on the CO pressure (Table 1). Remarkably, the observed rate constant (eq. 3) is inversely proportional to CO concentration (Fig. 2). This is quite contrary to the observations for the analogous reaction of $(Cp_2TiCl)_2$, which is accelerated by increase in the CO pressure. The decay of 6 and the concomitant increase in the amount of 2 is close to first order with respect to 6. The overall order in [6] depends on the CO concentration; it increases from $n = 1$ to 1.4 as the CO pressure is increased from 10 to 90 bar. This was established by analysing the kinetic data by several methods [6], and independently by using various initial concentrations of 1: At 70 bar CO pressure,

Table 1

Observed dependence of the rate constant k_{obs} on the CO pressure at 5°C (from $\ln([6]_t/[6]_0) = k_{obs}^{decr} \times t$ and $\ln(1-[2]_t/[2]_\infty) = k_{obs}^{incr} \times t$)

P(CO) (bar)	k_{obs}^{decr} (/min)	k_{obs}^{incr} (/min)	Order in [6]
10	0.066	0.068	1.0
20	0.0094	0.012	1.3
30	0.0064	0.0064	1.3
50	0.0043	0.0046	1.3
70	0.0031	0.0032	1.4
90	0.0023	0.0024	1.4
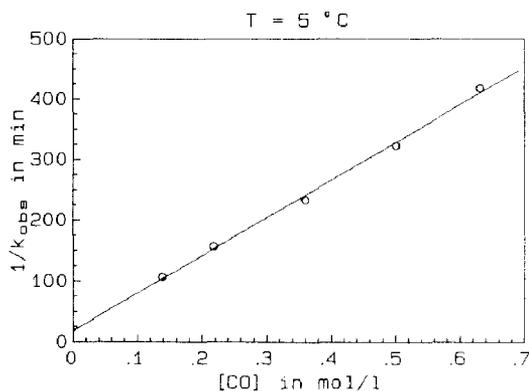
Fig. 2. Inverse of observed rate constant k_{obs} vs. CO concentration at $5\,^{\circ}$C.

for instance, the half-life changed from $\tau_{1/2}$ 170 min for [6] 0.05 mol/l to $\tau_{1/2}$ 220 min for [6] 0.025 mol/l, indicating a reaction order of $n = 1.4$.

At still higher temperatures (12°C) the initial formation of **6** is no longer quantitative, some **2** (up to 40%) even being formed in the time necessary to saturate the solution with CO (Fig. 3). At this temperature the rate of disproportionation is comparable to that of formation of **6**. Higher CO pressures retard the former process to some extent. After the fast initial reaction during the first few minutes, a much slower disproportionation is observed to follow the rate law in eq. 3 (Table 2).

$$v = -\frac{d[6]}{2\,dt} = \frac{d[2]}{dt} = k_{obs}[Ti]^{1-1.4} \tag{3}$$

At 50 bar CO pressure the temperature dependence of k_{obs} gives a linear Eyring plot with $\Delta H^{\ddagger}$ 80 ($\pm$12) kJ/mol and $\Delta S^{\ddagger}$ 105 ($\pm$30) J/mol K (Table 3).

When $Cp^{\star}_2TiBr$ (**4**) is treated with 20 bar of CO pressure at 5°C a monohalogenmonocarbonyl $Cp^{\star}_2TiBrCO$ complex (**7**) is formed again, as is indicated by an absorption band at 2014 cm^{-1}, at the same position as for **6**. Compared with **6**, **7** is much more stable towards disproportionation: The half-life for the decay of **7** and for the concomitant increase of **2** ($\tau_{1/2}$ 1800 min) is about 45 times that for **6**. The reaction order is close to 1 as observed for **6**.
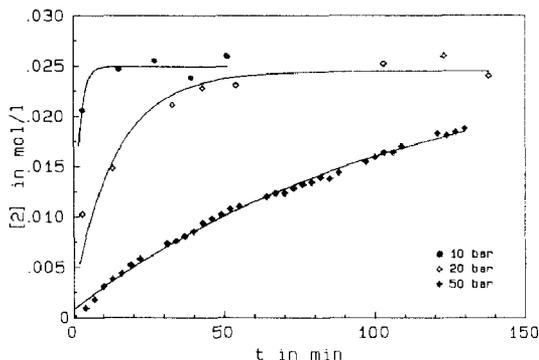
Fig. 3. Disproportionation of $Cp^{\star}_2TiClCO$ (**6**) to $Cp^{\star}_2Ti(CO)_2$ (**2**) and $Cp^{\star}_2TiCl_2$ (**3**) at 12°C under CO pressures of 10, 20 and 50 bar ($Cp^{\star}_2Ti(CO)_2$ monitored).

Table 2

Observed dependence of the rate constant k_{obs} on the CO pressure at 12°C

$P(CO)$ (bar)	k_{obs}^{decr} (/min)	k_{obs}^{incr} (/min)
10	0.1	–
20	0.018	0.019
30	0.013	0.012
50	–	0.007

Table 3

Observed dependence of the rate constant k_{obs} on the temperature at 50 bar CO

T (°C)	k_{obs}^{decr} (/min)	k_{obs}^{incr} (/min)
12	–	0.007
5	0.0043	0.0046
0	0.0013	0.0013
−5	0.00072	0.00082

The disproportionation of $Cp^{\star}_2TiI$ (5) was studied in more detail. Upon admission of CO at 5°C a monocarbonyl adduct $Cp^{\star}_2TiICO$ (8, ν 2014 cm^{-1}) is again formed. At 20 bar of CO pressure the half-life of 8 is comparable to that of 6 ($\tau_{1/2}$ 40 min). For this reaction, however, an increase in CO pressure up to 90 bar does not lead to a retardation such as was found for 6. Instead, there is a very fast disproportionation ($\tau_{1/2}$ 6 min).

The facile disproportionation of 1 with CO prompted us to investigate whether similar reactions could be induced by other substrates, such as ethene, since the stable titanium(II) species $Cp^{\star}_2Ti(\eta^2\text{-}C_2H_4)$ is well characterised [7]. However, the characteristic IR-absorption of this complex at ν 3655 cm^{-1} was not observed at any ethylene pressure up to 40 bar. Equally negative results were obtained with respect to the conceivable reaction of 1 with dihydrogen (90 bar) to 3 and $Cp^{\star}_2TiH_2$ [8] or to $Cp^{\star}_2TiHCl$ [9].

Discussion and conclusions

The observations reported above can be explained in terms of Scheme 1, which is comparable to that relevant to the disproportionation of $(Cp_2TiCl)_2$.

$$Cp^{\star}_2TiClCO \underset{k_f}{\overset{k_d}{\rightleftarrows}} Cp^{\star}_2TiCl + CO \qquad (4)$$
$$\text{(6)} \qquad \qquad \text{(1)}$$

$$Cp^{\star}_2TiClCO + Cp^{\star}_2TiCl \xrightarrow{k_{ir}} Cp^{\star}_2TiCl_2 + Cp^{\star}_2TiCO \qquad (5)$$
$$\text{(6)} \qquad \qquad \text{(1)} \qquad \qquad \text{(3)}$$

$$Cp^{\star}_2TiCO + CO \xrightarrow{fast} Cp^{\star}_2Ti(CO)_2 \qquad (6)$$
$$\text{(2)}$$
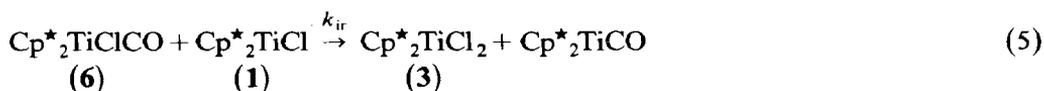
Scheme 1

The decrease in the reaction rate at higher CO pressures results from the inverse dependence of the steady state concentration of **1** on the CO concentration. The observation that the reaction becomes higher than first order in **6** at higher CO pressures suggests that **1**, which is slowly formed from **6** (eq. 4), reacts with CO and with **6** at comparable rates: If $k_f \cdot [CO]$ is $\ll k_{ir} \cdot [6]$, the overall reaction order, n, would be 1, whereas if $k_f \cdot [CO] \gg k_{ir} \cdot [6]$ then the reaction order would be 2 *. A steady state approximation for the concentration of **1** (a reaction intermediate of low and approximately constant concentration) results in the rate expression given in eq. 7.

$$-\frac{d[6]}{2dt} = \frac{d[2]}{dt} = \frac{k_d k_{ir} [6]^2}{k_f [CO] + k_{ir} [6]} \tag{7}$$

Integration of eq. 7 leads to an expression containing both inverse and logarithmic terms in the concentration of **6**. Accordingly, the overall order, n, for [6] will indeed be somewhere between 1 (logarithmic in [6]) and 2 (inverse in [6]). Instead of numerically evaluating the individual rate constants from the experimental curves, we decided to use the approximation shown in eq. 8, which is valid for at least the first half-life within an error of $\pm 10\%$ (See Appendix) **, and allows the determination of k_{obs} from the slope of a plot of ln [6] against time.

$$[6]_t = [6]_0 \, e^{-k_{obs} \cdot t}, \text{ with} \tag{8}$$

$$1/k_{obs} = \tfrac{1}{2}k_d \left(1 + [CO] \cdot k_f / ([6]_0 \cdot k_{ir})\right) \tag{9}$$

By plotting $1/k_{obs}$ against the CO concentration (eq. 9) we determined k_d and the ratio k_f/k_{ir}. (Neither of these last two rate constants can be measured independently.)

At 5 °C we find $k_d = 0.029 \, (\pm 0.01) \, \text{min}^{-1}$ and $k_f/k_{ir} = 1.8 \, (\pm 0.2)$. The dissociation of CO from **6** can thus be regarded as the rate limiting step for the disproportionation reaction. At low CO pressure the observed rate constant k_{obs} is practically equal to k_d; at higher CO pressures the reverse reaction of **1** with CO becomes increasingly competitive with the irreversible disproportionation, in accord with eq. 5. The ratio $[CO] \cdot k_f/([6] \cdot k_{ir})$, which increases from ca. 2.3 at 10 bar to 23 at 90 bar, indicates that the back reaction to **6** is indeed the fastest reaction, especially at higher CO pressures. Scheme 1 also accounts for the fast initial reaction phase at low CO pressures and higher temperatures (12 °C): During the saturation of the solution with CO, **6** is formed in the presence of comparable amounts of unchanged **1**, so that their mutual reaction (eq. 5) is not held up by the need to dissociate CO from **6**. As the concentration of CO increases and that of **1** decreases, the system approaches the steady-state condition discussed above.

The activation parameters observed for the reaction $2Cp^*_2TiClCO \rightarrow Cp^*_2Ti(CO)_2 + Cp^*_2TiCl_2$, $\Delta H^{\ddagger}$ 80 (± 12) kJ/mol and $\Delta S^{\ddagger}$ 105 (± 30) J/(mol · K), are in accordance with the proposal that dissociation of CO from $Cp^*_2TiClCO$ is rate-limiting: Comparable values of $\Delta H^{\ddagger}$ (100–120 kJ/mol) and $\Delta S^{\ddagger}$ (49–63 J/(mol · K)) have been reported by Basolo and coworkers [10] for ligand exchange reactions of $Cp_2Ti(CO)_2$ and $Cp^*_2Ti(CO)_2$, which have a dissociative mechanism.

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* CO concentrations were calculated from $P(CO)$ by the relationship $[CO] = P(CO) \cdot 7.1 \times 10^{-3} - (P(CO))^3 (2.2 - \delta \cdot 9 \times 10^{-2}) \times 10^{-8}$ (δ = temp in °C) [2].

** In fact the agreement with eq. 8 was found to be quite good for a period of over two half-lifes.

As proposed for the analogous reaction with $(Cp_2TiCl)_2$, the disproportionation of $Cp^*_2TiClCO$ to $Cp^*_2Ti(CO)_2$ and $Cp^*_2TiCl_2$ appears to involve a transfer of a Cl ligand from $Cp^*_2TiClCO$ to Cp^*_2TiCl. The differences between Cp^*_2TiCl and $(Cp_2TiCl)_2$ with respect to their reactions with CO result from the greatly different stabilities of their respective monocarbonyl adducts: At CO pressures below 100 bar, the reaction rate for $(Cp_2TiCl)_2$ increases linearly with the CO pressure and only begins to level off at about 130–140 bar. An inverse dependence of the disproportionation rate on the CO concentrations, such as observed for $Cp^*_2TiClCO$, would be expected for $(Cp_2TiCl)_2$ only at CO pressures far exceeding the experimentally possible range. The kinetics of the reaction of Cp^*_2TiCl with CO can thus be regarded as corresponding to those for reaction of $(Cp_2TiCl)_2$ at the very high pressure limit.

The corresponding disproportionation reaction of Cp^*_2TiBr occurs at a substantially lower rate. If its mechanism is the same as that for Cp^*_2TiCl, the reduced rate might indicate a kinetically more stable monocarbonyl adduct, i.e. a lower rate of dissociation of CO from $Cp^*_2TiBrCO$. For the iodo complex Cp^*_2TiI, on the other hand, the increase of disproportionation rate with CO pressure indicates that the monocarbonyl adduct Cp^*_2TiICO is less stable than the chloro analogue. From our data we cannot however, exclude the possibility that additional factors influence the relative reactivities of these halogen derivatives.

Acknowledgements

Appendix

Scheme 1 can be represented by the following equations (A1,A2): (A: [6], B: [1], D: [2], E: [3])

$$A \underset{k_f}{\overset{k_d}{\rightleftarrows}} B + CO \tag{A1}$$

$$A + B \overset{k_{ir}}{\rightarrow} D + E \tag{A2}$$

$$-\frac{dA}{dt} = k_d A - k_f[CO]B + k_{ir}AB$$

$$-\frac{dB}{dt} = -k_d A + k_f[CO]B + k_{ir}AB$$

$$-\frac{dD}{dt} = -k_{ir}AB$$

Steady-state approximation $\left(\dfrac{dB}{dt} = 0\right)$ yields $B = \dfrac{k_d A}{k_f[CO] + k_{ir}A}$ and

$$-\frac{dA}{2dt} = \frac{k_{ir}k_d A^2}{k_f[CO] + k_{ir}A} = \frac{dD}{dt} \tag{A4}$$

The integrated form $(A_r = A_t/A_0)$,

$$\left(-\frac{k_f[CO]}{2k_{ir}k_d A_0} \frac{1}{A_r} + \frac{1}{2k_d} \ln(A_r A_0) \right)\Bigg|_1^{A_r} = -t \tag{A5}$$

can be approximated for $A_r < 0.5$ within an error limit of 10% by A6:

$$\left(-\frac{k_f[CO]}{2k_{ir}k_d A_0}(1 - \ln A_r) + \frac{1}{2k_d} \ln(A_r A_0) \right)\Bigg|_1^{A_r} = -t \tag{A6}$$

leading to: $\ln(A_t/A_0) = -\dfrac{2k_d k_{ir} A_0}{k_{ir}A_0 + k_f[CO]} t$ \hfill (A7)

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