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EQUILIBRIA AND KINETICS IN THE CO-INDUCED, REVERSIBLE DISPROPORTIONATION OF $((C_5H_5)_2TiCl)_2$ TO $(C_5H_5)_2TiCl_2$ AND $(C_5H_5)_2Ti(CO)_2$. AN IR STUDY AT ELEVATED CO GAS PRESSURES

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Summary

IR studies of toluene solutions of $((C_5H_5)_2TiCl)_2$ under elevated CO pressures indicate the formation of a carbonyl complex, probably $(C_5H_5)_2Ti(CO)Cl$, with $\nu(CO)$ 2068 cm^{-1}. This species predominates at CO pressures above 100 bar, and is reasonably stable at temperatures around $-30\,^{\circ}C$. At higher temperatures, disproportionation to $(C_5H_5)_2Ti(CO)_2$ and $(C_5H_5)_2TiCl_2$ occurs. This disproportionation is reversible; at $+30\,^{\circ}C$ and 1 bar of CO, roughly equal concentrations of $((C_5H_5)_2TiCl)_2$ and of dicarbonyl and dichloride products are in equilibrium with each other. Practically complete formation of these products occurs at CO pressures above 10 bar. Rate laws and reaction mechanisms have been studied for the disproportionation reaction and for its reverse, the comproportionation of $(C_5H_5)_2Ti(CO)_2$ and $(C_5H_5)_2TiCl_2$ to $((C_5H_5)_2TiCl)_2$, which predominates at lower CO pressures.

Introduction

The comproportionation of the Ti^{IV} and Ti^{II} derivatives Cp_2TiCl_2 and $Cp_2Ti(CO)_2$ ($Cp = \eta^5\text{-}C_5H_5$) has been shown to be a useful method for the preparation of the Ti^{III} derivative $(Cp_2TiCl)_2$ [1]; the CO-induced disproportionation of $(Cp_2TiCl)_2$, on the other hand, has been reported to occur in the reduction of Cp_2TiCl_2 to $Cp_2Ti(CO)_2$ by metals such as Zn or Al [2,3]. We describe here the results of an IR study, conducted at elevated CO pressures by use of an internal-circulation IR cell, of the equilibria and kinetics in the reaction of $(Cp_2TiCl)_2$ with CO, and of intermediates participating in this reaction system.

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Experimental

Dimeric titanocene monochloride, $(Cp_2TiCl)_2$, free of zinc halide contamination, was prepared by a published procedure [4]. All materials were handled with strict exclusion of air. Solids were transferred and weighed in an inert atmosphere glovebox, and solutions were prepared and transferred by standard vacuum-line techniques.

For IR measurements under elevated CO pressures, a pressure-resistant IR cell was constructed in which isobaric and isothermal circulation of gas-saturated solutions between a gas-liquid mixing chamber and the IR window gap is maintained by means of an internal, magnetically driven centrifugal rotor (Fig. 1). The cell block, manufactured from stainless steel (DIN 14571), was thermally insulated by use of foam-rubber linings inside a polyvinyl casing; its temperature was controlled within ± 1° C by a circulation thermostat with isopropanol as heat-transfer liquid. A solution volume of 30–50 ml is required for operation of the cell.

IR absorbance data were collected by means of a double-beam IR spectrophotometer (Perkin–Elmer 398) and transferred to a microcomputer for further processing. Raw absorbance values thus obtained were scaled to constant path length, using the toluene absorption band at 1802 cm^{-1} as a standard, to compensate for increases in optical path lengths at elevated CO pressures. The relationship $l = A_{1802} \cdot 0.0329$ cm, derived from absorbance measurements in calibrated IR cells [6], was used to calculate the cell path length l. The solvent spectrum was then subtracted to give the spectra of the species in solution.

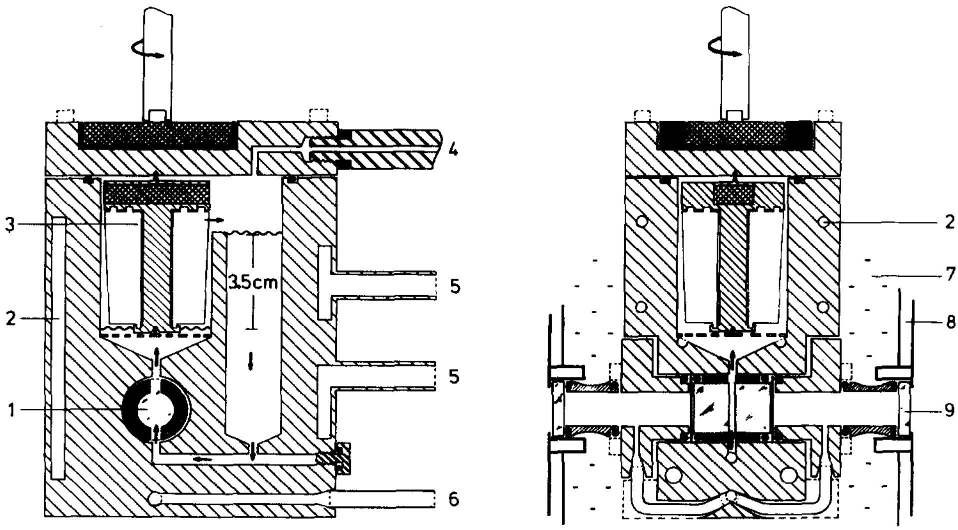

Fig. 1. Pressure-resistant IR cell with internal, isobaric and isothermal circulation. Essential parts: 1, inner, pressure-resistant CaF_2 windows (13 mm thick, 18 mm diam.); 2, channels for thermostatted heat-transfer liquid; 3, internal centrifugal rotor, driven by rotating external magnet bar; 4, inlet/outlet for sample solutions and gases; 5, inlet/outlet for heat transfer liquid; 6, evacuation of space between inner and outer CaF_2 windows; 7, removable foam-rubber insulation; 8, polyvinyl casing; 9, outer CaF_2 windows. Direction of circulation of the sample solution between rotor-agitated gas-liquid mixing chamber, solution reservoir and IR window gap as indicated by small arrows.

TABLE 1

SOLUBILITY DATA FOR CO IN TOLUENE AT ELEVATED CO PRESSURES

Temp. (°C)	Mol fractions of CO ($\times 10^2$) at P_{CO} =				d_{tol} [a]
	20	60	100	138 bar	
20	1.49(7)	4.38(7)	7.14(11)	9.38(3)	0.8614
0	1.43(4)	4.24(4)	6.79(14)	8.64(3)	0.8845
−40	1.37(5)	4.02(3)	5.99(5)	7.73(6)	0.9212

Temp. (°C)	Concentration of CO (mol/l) at P_{CO} =				α ($\times 10^3$)	β ($\times 10^8$)
	20	60	100	138 bar		
20	0.141	0.428	0.719	0.967	7.1	0.3
0	0.139	0.425	0.699	0.908	7.1	2.3
−40	0.139	0.419	0.637	0.837	7.1	5.7

[a] Derived from data given in Internat. Critical Tables, Vol. III, E.W. Washburn (Ed.), New York 1928, p. 29 and in K. Schäfer and G. Beggerow, (Eds.), Landolt-Börnstein, Zahlenwerte und Funktionen, Vol. II., Berlin 1971, part 1, p. 641.

The concentration-proportionality of the absorbance values obtained in this way was checked for solutions of acetonitrile in toluene; absorbances at 2254 cm^{-1} of 1.0 to 6.0 M CH_3CN solutions obeyed the Lambert–Beer law up to absorbances above 1, at both 20 and −40 °C.

The solubility of CO in toluene at elevated CO pressures, for which we could not find useful data in the literature, was determined by gas-volumetric measurements [7]. In a small (40 ml) autoclave, thermally controlled within ±1 °C by means of a circulation thermostat, toluene was saturated with CO by several hours' stirring with a magnetic stirring bar, the CO pressure P_{CO} being read from a pressure transducer with an accuracy of ca. ±1 bar. The CO-saturated toluene solutions were drained, by way of a dip-tube, into a vacuum manifold, where the toluene fractions (about 2 to 10 g) were condensed, at −80 °C, into a cold trap and weighed, while the CO released was transferred, by means of a Töpler pump, into a calibrated reservoir connected to a mercury manometer, and its volume determined.

After discarding of a sufficient forerun, four to six successive samples were measured at each temperature and CO pressure. The CO solubilities determined in this manner are presented in Tab. 1 as mol fractions X_{CO} with estimated mean deviations for the last digit indicated in parentheses. These solubility data were analysed, as recommended [7], with respect to the Krichevsky–Kasarnosky equation [8], $\ln(f_{CO}/X_{CO}) = \ln(K_{CO,\ tol}) + V_{CO} \cdot P_{CO}/(RT)$ using, as a substitute for the unknown fugacities f_{CO} of CO in the equilibrium gas phase, fugacity values of pure, gaseous CO [9]. Plots of $\ln(f_{CO}/X_{CO})$ vs. P_{CO} at constant temperature reveal substantial curvature. Whether these variations in $d(\ln(f_{CO}/X_{CO}))/d(P_{CO})$ do, indeed, indicate changes in the partial volume V_{CO} of CO in these solutions, or are rather due to some systematic error either in our solubility data or in the fugacity data used, is at present an open question.

The utilisation of the CO solubility data represented in Tab. 1 for the calculations of equilibrium and rate constants, comparable with those for other, non-volatile ligand species, requires a conversion from mol fractions X_{CO} to concentrations C_{CO} in mol/l. For this purpose, it is necessary to know the volumes of the CO solutions formed from 1 mol of toluene. As an approximation, we have used the

TABLE 2

MOLAR EXTINCTION COEFFICIENTS ϵ(CO) AND HALF-WIDTHS $\Delta\nu$ OF THE IR BAND AT 2134 cm^{-1} OF CO IN TOLUENE SOLUTION

Temp. (°C)	20	0	−20	−40
ϵ(CO) (l mol^{-1} cm^{-1})	37.1(8)	40.0(9)	41.6(6)	45.8(9)
$\Delta\nu$ (cm^{-1})	55	40	32	26

molar volume of the toluene solvent at the relevant temperature and at ambient pressure: At 20°C and P_{CO} 100 bar, for instance, the compressibility of toluene would give rise to a volume decrease by ca. 1%, while the volume of the dissolved CO (as a liquid) would amount to ca. 2% of that of the solvent. Since the partial volume of CO in these solutions is undoubtedly smaller than the liquid volume of CO, these two effects would each be smaller than the estimated data error and would, furthermore, tend to cancel each other out. The CO concentrations C_{CO} in Tab. 1 were, therefore, derived from the corresponding mol fractions X_{CO} by the relationship $C_{CO} = X_{CO} \cdot d_{tol} \cdot 1000/((1 - X_{CO}) \cdot 92.15)$, where 92.15 is the molar mass of toluene and d_{tol} is its density at the temperature indicated, at ambient pressure.

The CO solubility data thus obtained show an evident saturation at higher CO pressures, which is particularly pronounced at lower temperatures. At each temperature, the data are reproduced, within experimental error, by the two-term equation $C_{CO} = P_{CO} \cdot \alpha - (P_{CO})^3 \cdot \beta$, with values of α and β as indicated in Tab. 1. Since α is essentially independent of temperature and since β appears to decrease practically linearly with increasing temperature, the empirical relation $C_{CO} = P_{CO} \cdot 7.1 \cdot 10^{-3} - (P_{CO})^3 \cdot (2.2 - \delta \cdot 9.0 \cdot 10^{-2}) \cdot 10^{-8}$ with δ being the temperature in °C, was used to obtain the CO concentrations in these solutions from known CO pressures P_{CO}.

As a check on these data, IR absorbances of dissolved CO in CO-saturated toluene solutions were measured, at temperatures between −40 and 20°C, over a range of CO saturation pressures between 20 and 130 bar. The CO absorbances at 2134 cm^{-1} thus obtained show, at any given temperature, the same saturation effects as the concentration data in Tab. 1. The rather satisfactory proportionality between these CO absorbances and the CO concentration values calculated for each of these solutions from the dependence of C_{CO} on P_{CO} derived above provides further confirmation of the reliability of this relation, which was used to convert P_{CO} to C_{CO} values for the subsequent calculations of equilibrium and rate constants.

The molar extinction coefficient ϵ_{CO} of these CO solutions decreases noticeably with increasing temperature, together with a significant broadening of its IR band (Tab. 2). The relation $\epsilon_{CO} = 40.0 - 2.9 \cdot \delta$ was used to obtain, at a given temperature δ in °C, the extinction coefficient ϵ_{CO} necessary to check the equilibrium concentration of CO in a reaction mixture by means of its CO absorbance at 2134 cm^{-1}.

Results and discussion

Upon admission of higher CO pressures to $(Cp_2TiCl)_2$ in toluene solution, particularly at temperatures below 0°C, a new IR absorption band appears at 2068

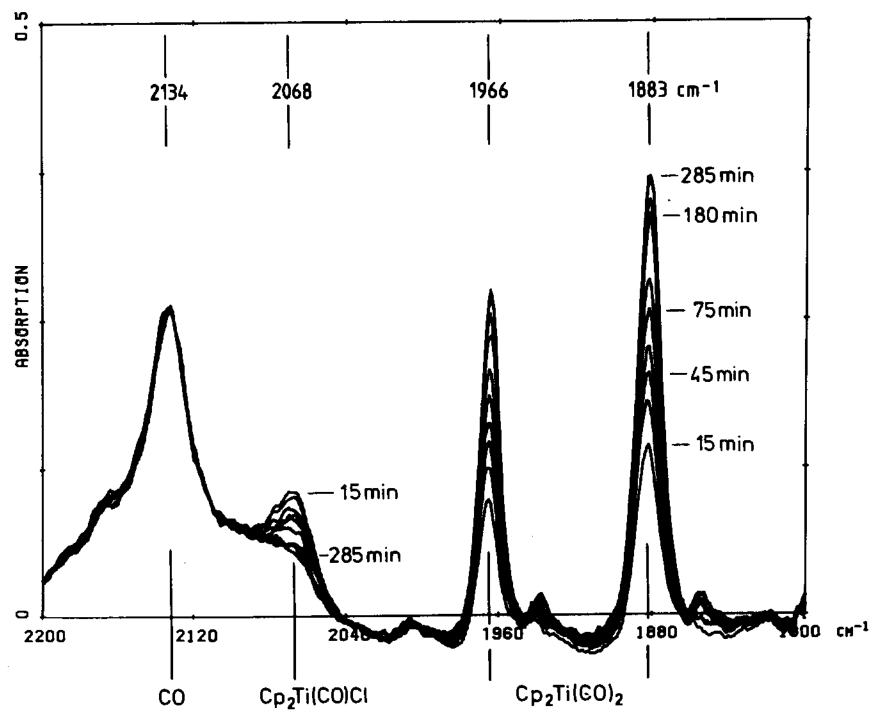

Fig. 2. IR spectra of a 0.025 *M* solution of $(Cp_2TiCl)_2$ in toluene, at −5 °C, 15 to 285 min after admission of 130 bar of CO.

cm^{-1}. This IR band is fully formed within the 4–5 min required for the first measurement; in the course of time it decays again, as a simultaneous increase of IR absorption bands at 1966 and 1883 cm^{-1} indicates the formation of the Ti^{II} complex $(Cp_2Ti(CO)_2$ (Fig. 2).

The reaction of $(Cp_2TiCl)_2$ with CO was first studied at −30 °C, where the secondary reaction is sufficiently slow to allow the new IR band at 2068 cm^{-1} to remain unchanged for several hours. The changes of its intensity with CO pressure – about 25–35 bar of CO are required for half-formation of this species – and with initial concentrations of the dimer $(Cp_2TiCl)_2$ indicate that the carbonyl complex responsible for this IR band is the species $Cp_2Ti(CO)Cl$, formed according to equilibrium (1).

$$(Cp_2TiCl)_2 + 2CO \rightleftharpoons 2Cp_2Ti(CO)Cl \qquad (1)$$

Least-squares fitting of the IR data [*] yields an equilibrium constant $K_1 = 0.65 \pm 0.1$ l/mol for reaction (1) at −30 °C and a molar extinction coefficient $\epsilon(Cp_2Ti(CO)Cl) = 360 \pm 20\ l\ mol^{-1}\ cm^{-1}$.

At −5 °C, where the ensuing disproportionation is still slow enough to allow the determination of initial IR absorbances at 2068 cm^{-1} by extrapolation back to the actual time of CO admission, a value of $K_1 = 0.25 \pm 0.05$ l/mol is found for

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[*] The IR absorbance at 2068 cm^{-1} had to be corrected for a fringe contribution from the IR band of dissolved CO (cf. Fig. 2).

TABLE 3

FIRST-ORDER RATE CONSTANTS k_{app} AND k_{dis} FOR DISPROPORTIONATION OF $(Cp_2TiCl)_2$ IN DEPENDENCE OF CO PRESSURES, AT +30 °C

P_{CO} (bar) C_{CO} (mol/l)	5 0.035	7 0.050	9 0.064	10 0.071	14 0.099
k_{app} (min^{-1})	2.1	2.9	4.3	4.0	7.7×10^{-2}
k_{dis} (l mol^{-1} min^{-1})	5.7	5.6	6.7	5.6	7.7×10^{-1}

reaction (1) if the value of $\epsilon(Cp_2Ti(CO)Cl)$ previously determined at −30 °C is used to analyse the IR absorption data. This temperature dependence of K_1 yields estimates of $\Delta H^0 = -20 \pm 5$ kJ and $\Delta S^0 = -85 \pm 20$ J/K for reaction (1).

The species $Cp_2Ti(CO)Cl$, responsible for the IR band at 2068 cm^{-1}, is closely related to the more stable Ti^{III} carbonyl complexes $Cp_2Ti(CO)C_6F_5$ and $(C_5(CH_3)_5)_2Ti(CO)Cl$, for which Teuben and coworkers have reported IR bands at 2060 and 2000 cm^{-1}, respectively [10].

The CO-induced disproportionation of $(Cp_2TiCl)_2$ to $Cp_2Ti(CO)_2$ and Cp_2TiCl_2 was studied at +30 °C, where both this reaction and its reverse occur at conveniently measureable rates. After equilibration, the IR absorptions at 1966 and 1883 cm^{-1} depend on CO pressure in a manner which is in accord with the existence of equilibrium (2).

$$(Cp_2TiCl)_2 + 2CO \rightleftharpoons Cp_2Ti(CO)_2 + Cp_2TiCl_2 \qquad (2)$$

At a CO pressure of 1 bar, about one half of the Ti^{III} dimer is converted to the dicarbonyl and dichloride products at a total Ti concentration of $[Ti]_{tot} = 0.05$ *M*; above 10–15 bar of CO this conversion is essentially complete *. For reaction (2) at 30 °C, an equilibrium constant $K_2 = 207 \pm 30$ l/mol is obtained if the rather low solubility of Cp_2TiCl_2 in toluene, which we found to be 9.8×10^{-3} mol/l at +30 °C, is assumed to keep this species at constant concentration.

The kinetics of the CO-induced disproportionation reaction was studied, at +30 °C, by following the increase in IR absorbances at 1966 and 1883 cm^{-1} caused by an increase in CO pressure from $P_{CO} = 1$ bar to the value indicated in Tab. 3. The pattern of the CO-induced growth of these absorptions of $Cp_2Ti(CO)_2$ with time corresponds with an apparent first-order dependence on $[(Cp_2TiCl)_2]$. The apparent first-order rate constants for the CO-induced disproportionation increase approximately linearly with CO concentration (Tab. 3), so that the empirical rate law would be given by eq. 3.

$$V_{dis} = k_{dis} \cdot [(Cp_2TiCl)_2] \cdot [CO] \qquad (3)$$

In order to satisfy the equilibrium condition (2), the rate of the reverse, comproportionation reaction must be in accord with eq. 4.

$$V_{com} = k_{com} \cdot [Cp_2Ti(CO)_2] \cdot [Cp_2TiCl_2]/[CO] \qquad (4)$$

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* The complete conversion of $(Cp_2TiCl)_2$ in $Cp_2Ti(CO)_2$ and Cp_2TiCl_2 at $P_{CO} > 15$ bar was confirmed by comparison with calibrated solutions of $Cp_2Ti(CO)_2$. Battaglia et al. (ref. 3) had previously observed an incomplete conversion in THF solutioin at $P_{CO} = 1$ bar, and ascribed this to formation of a complex between $(Cp_2TiCl)_2$ and Cp_2TiCl_2.

If the concentration of $[Cp_2TiCl_2]$ is again assumed to be fixed by its solubility limit at 9.8×10^{-3} mol/l, eq. 4 would predict a first-order dependence of the comproportionation rate on $[Cp_2Ti(CO)_2]$. A first-order decrease of $Cp_2Ti(CO)_2$ absorbances at 1966 and 1883 cm^{-1} was indeed observed when the CO pressure was lowered, from ca. 70 bar, where equilibrium (2) lies far to the right, to 1 bar, where $(Cp_2TiCl)_2$, $Cp_2Ti(CO)_2$ and Cp_2TiCl_2 are present in comparable concentrations.

In determining k_{dis} and k_{com} from these data, it is necessary to take into account the fact that both disproportionation and comproportionation were studied under conditions where these reactions approach equilibrium, so that the apparent first-order rate constants k_{app} derived, e.g., from a plot of $\ln(([A]_t - [A]_e)/([A]_0 - [A]_e))$ vs. t * contain additive contributions from forward and backward reaction rates, $k_{app} = k_{frw} + k_{bkw}$, with k_{frw} and k_{bkw} being the overall first-order rate constants for each of these two reactions, for which eqs. 3 and 4 yield $k_{frw} = k_{dis} \cdot [CO]$ and $k_{bkw} = k_{com} \cdot [Cp_2TiCl_2]/[CO]$. With $K_2 = k_{dis}/k_{com}$, we can determine k_{dis} and k_{com} from k_{app} as $k_{dis} = k_{app} \cdot K_2 \cdot [CO]/(K_2 \cdot [CO]^2 + [Cp_2TiCl_2])$ and $k_{com} = k_{app} \cdot [CO]/(K_2 \cdot [CO]^2 + [Cp_2TiCl_2])$. Reasonably constant values of $k_{dis} = 6.3 \pm 0.8 \cdot 10^{-1}$ (l/mol) $\cdot$ min^{-1} are thus obtained from the data in Tab. 3, i.e. in the range of 5 to 14 bar of CO. From $k_{app} = 9.8 \pm 3.4 \cdot 10^{-3}$ min^{-1}, measured for the reverse reaction at $P_{CO} = 1$ bar, one obtains $k_{com} = 3.4 \pm 1.2 \cdot 10^{-3}$ min^{-1}.

A central question concerning the course of the CO-induced disproportionation of $(Cp_2TiCl)_2$ involves the role of the monocarbonyl complex $Cp_2Ti(CO)Cl$. The first-order increase of the disproportionation rate with C_{CO} suggests a rate-determining step for this reaction in which the monocarbonyl complex $Cp_2Ti(CO)Cl$ reacts with monomeric Cp_2TiCl (formed by dissociation of $(Cp_2TiCl)_2$) according to eq. 5,

$$Cp_2Ti(CO)Cl + Cp_2TiCl \rightarrow Cp_2Ti(CO) + Cp_2TiCl_2 \qquad (5)$$

with $Cp_2Ti(CO)$ then taking up a second CO in a fast subsequent step. Such a reaction sequence would obey the overall rate law (eq. 6).

$$V_{dis} = k_6 \cdot [Cp_2Ti(CO)Cl] \cdot [Cp_2TiCl] \qquad (6)$$

The concentrations of the two Ti^{III} species in eq. (6) are determined by equilibrium reaction (7); the product of their concentrations would, therefore, be given by $[Cp_2Ti(CO)Cl] \cdot [Cp_2TiCl] = K_7 \cdot [(Cp_2TiCl)_2] \cdot [CO]$. Equation 6 is thus equivalent to the observed rate law (3) as long as the CO pressures are low enough to keep equilibrium (7) essentially on the left hand side, i.e. as long as $(Cp_2TiCl)_2$ is the predominant Ti^{III} species present.

$$(Cp_2TiCl)_2 + CO \rightleftharpoons Cp_2Ti(CO)Cl + Cp_2TiCl \qquad (7)$$

At higher CO pressures, where the formation of $Cp_2Ti(CO)Cl$ approaches completion, the involvement of this species in the rate-determining step should cause the disproportionation rate V_{dis} to level off as C_{CO} is increased further. With $Cp_2Ti(CO)Cl$ becoming the predominant Ti^{III} species, the disproportionation reaction should, furthermore, approach a second-order rate law with respect to the total, residual Ti^{III} concentration $[Ti]_{tot}$. In order to clarify these aspects, the dispro-

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* The expressions $[A]_t$, $[A]_0$ and $[A]_e$ refer to the concentrations of the decaying species ($(Cp_2TiCl)_2$ for disproportionation, and $Cp_2Ti(CO)_2$ for comproportionation reactions) at time t, for zero reaction, and after establishment of equilibrium, respectively.

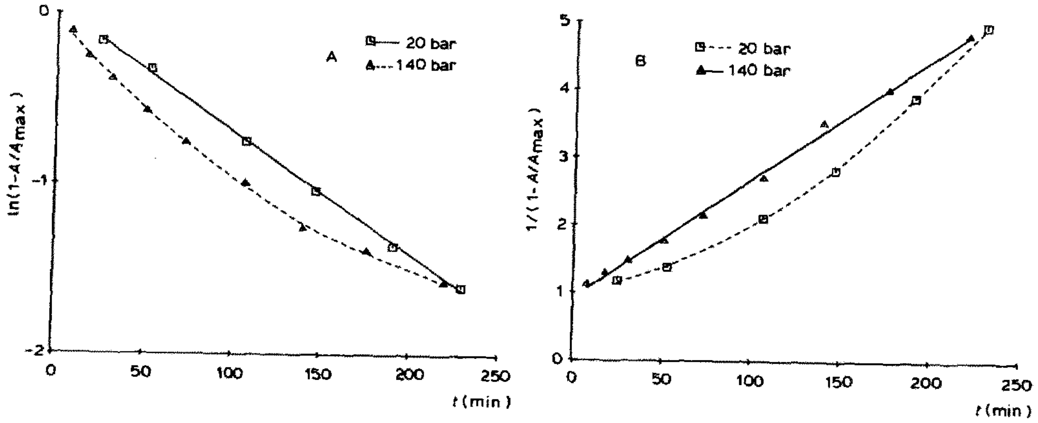

Fig. 3. Disproportionation of $(Cp_2TiCl)_2$ ($[Ti]_{tot} = 0.05$ *M* in toluene) at $-5\,°C$ under CO pressures of 20 and 140 bar as measured by absorbance A at 1883 cm^{-1}; A_{max}: A at time $t > 1000$ min. A: First-order plot ($\ln(1 - A/A_{max})$ vs. t); solid line: first-order reaction with $k = 7.1 \times 10^{-3}$ min^{-1}. B: Second-order plot ($1/(1 - A/A_{max})$ vs. t); solid line: second-order reaction with $k = 1.8 \times 10^{-2}$ min^{-1}.

TABLE 4

INITIAL RATES V_{dis} FOR THE DISPROPORTIONATION OF $(Cp_2TiCl)_2$, IN DEPENDENCE OF THE CONCENTRATIONS OF CO, AT −5 °C

P_{CO} (bar)	20	40	80	130	140
C_{CO} (mol/l)	0.142	0.283	0.554	0.865	0.918
$[Cp_2Ti(CO)Cl]$	0.0100	0.0179	0.0286	0.0361	0.0370 [a]
$[(Cp_2TiCl)_2]$	0.0200	0.0160	0.0107	0.0070	0.0065 [b]
$[Cp_2TiCl]/K_9^{1/2}$	0.141	0.126	0.103	0.083	0.081 [c]
V_{dis} (calcd.) [d]	1.4	2.3	2.9	3.0	3.0 ($\times 10^{-4}$)
V_{dis} (exptl.) [e]	1.8	2.1	2.7	3.0	3.0 ($\times 10^{-4}$)

[a] $[Cp_2Ti(CO)Cl] = -A/2 + 1/2 \cdot (A^2 + 4 \cdot A \cdot [Ti]_{tot})^{1/2}$ mol/l, with $A = K_1 \cdot [CO]^2/2$, $K_1 = 0.25$ l/mol and $[Ti]_{tot} = 0.05$ mol/l. [b] $[(Cp_2TiCl)_2] = ([Ti]_{tot} - [Cp_2Ti(CO)Cl])/2$. [c] $[Cp_2TiCl]/K_9^{1/2} = ([(Cp_2TiCl)_2])^{1/2}$ $(mol/l)^{1/2}$. [d] According to eq. 8 with $k_6 \cdot K_9^{1/2} = 0.10$; in (mol/l) min^{-1}. [e] Derived from initial slope, k_{ini}, of $\ln(1 - A_t/A_{max})$ vs. t by $V_{dis} = k_{ini} \cdot [(Cp_2TiCl)_2]_0 = k_{ini} \cdot [Ti]_{tot}/2$ (mol/l) min^{-1}.

portionation kinetics were studied in the P_{CO} range of 20 to 140 bar, at a temperature of −5 °C, where reaction rates were conveniently measurable even at higher CO pressures, and where the rate of the comproportionation reaction had been found to be negligable. It is apparent from Fig. 3 that the disproportionation still closely adheres to first-order kinetics at $P_{CO} = 20$ bar, whereas at 140 bar the change to second-order kinetics appears to be practically complete. The initial disproportionation rates, V_{dis}, determined under these conditions (Tab. 4) increase indeed much less than proportionally to C_{CO}, and become practically independent of C_{CO} at higher CO concentrations.

The rate data in Tab. 4 were analysed in terms of their agreement with rate equation (6) by calculating concentrations of $Cp_2Ti(CO)Cl$ from equilibrium (1) using a value of $K_1 = 0.25$ l/mol, as found at −5 °C, and concentrations of Cp_2TiCl from the residual concentrations of $(Cp_2TiCl)_2$ as $[Cp_2TiCl] = (K_9 \cdot [(Cp_2TiCl)_2])^{1/2}$ (cf. eq. 8) *; K_9 is the dissociation constant of $(Cp_2TiCl)_2$ according to eq. 9.

$$V_{dis} = k_6 \cdot [Cp_2Ti(CO)Cl] \cdot (K_9 \cdot [(Cp_2TiCl)_2])^{1/2} \qquad (8)$$

$$(Cp_2TiCl)_2 \rightleftharpoons 2Cp_2TiCl \qquad (9)$$

Since neither K_7 nor K_9 are known under the reaction conditions used **, we can only determine the product $k_6 \cdot K_9^{1/2}$ from the rate data given in Tab. 4. The acceptable agreement of the experimental data for V_{dis} with the values for V_{dis} calculated from eq. 8 with a mean value of $k_6 \cdot K_9^{1/2} = 0.10 \pm 0.02$ $(l/mol)^{1/2} \cdot min^{-1}$, in particular their levelling-off at higher CO concentrations, together with the concomitant change from first-order to second-order kinetics, represent reasonable evidence that a bimolecular reaction between $Cp_2Ti(CO)Cl$ and monomeric Cp_2TiCl according to eq. 6 is, indeed, rate-determining for the CO-induced disproportionation of $(Cp_2TiCl)_2$.

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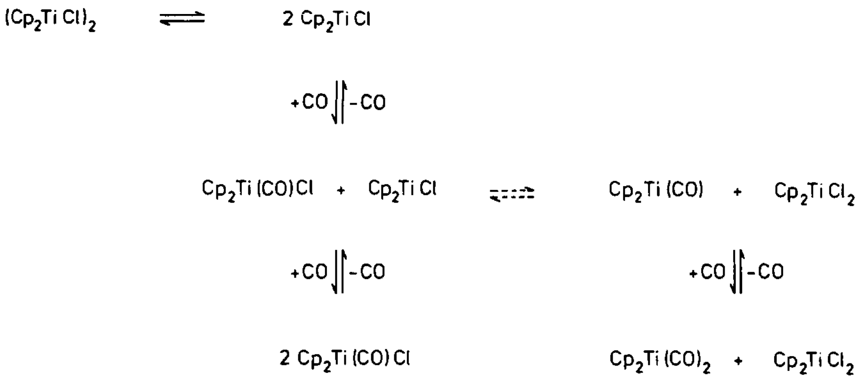
* For this we assume that only a small fraction of $(Cp_2TiCl)_2$ is dissociated into Cp_2TiCl in these solutions, as indicated by a value of $2.6 \cdot 10^{-6}$ mol/l reported for K_9 in toluene at 80 °C (ref. 11).

** K_1, K_7 and K_9 are interconnected by the relation $K_7 = (K_1 \cdot K_9)^{1/2}$.



SCHEME 1. Intermediates in the CO-induced interconversion between $(Cp_2TiCl)_2$, $Cp_2Ti(CO)_2$ and Cp_2TiCl_2. Rate-determining step indicated by broken arrows (⇄).

Such a reaction could occur either via an outer-sphere electron transfer to yield $Cp_2Ti(CO)Cl^-$ and Cp_2TiCl^+, from which the final products could then be formed by rapid ligand exchange, or via an inner-sphere halogen transfer from $Cp_2Ti(CO)Cl$ to Cp_2TiCl. Electrochemical studies on the oxidation of Cp_2TiCl and the reduction of $Cp_2Ti(CO)Cl$ [12,13] indicate that an electron transfer between these species would be endothermic by ca. 100–150 kJ/mol in THF solution (and hence even more so in toluene), which would let an outer-sphere path appear rather unlikely.

An inner-sphere halogen transfer, on the other hand, would require the intermediate formation of a Cl-bridged binuclear species of the type $Cp_2Ti(CO)$–Cl–(Cl)$TiCp_2$. Such a species might conceivably be accessible directly from $(Cp_2TiCl)_2$ and CO without prior formation of $Cp_2Ti(CO)Cl$ and Cp_2TiCl. Our spectral data indicate, however, that the species absorbing at 2068 cm^{-1} has the composition $Cp_2Ti(CO)Cl$ rather than $(Cp_2TiCl)_2(CO)$; a Cl-bridged, binuclear carbonyl species would thus probably be a collision complex arising from $Cp_2Ti(CO)Cl$ and Cp_2TiCl.

In any case, microreversibility requires that in the comproportionation of Cp_2TiCl_2 and $Cp_2Ti(CO)_2$, the reverse of reaction 5, i.e. a bimolecular reaction of $Cp_2Ti(CO)$ with Cp_2TiCl_2 must be rate-determining, with $Cp_2Ti(CO)$ arising from $Cp_2Ti(CO)_2$ by reversible loss of CO. In a recent study of ligand substitution reactions of $Cp_2Ti(CO)_2$, Basolo and coworkers [14] have shown that many of these substitution reactions do, indeed, proceed via a reversible predissociation of CO from $Cp_2Ti(CO)_2$. It is entirely reasonable, therefore, that a coordinatively unsaturated complex $Cp_2Ti(CO)$ is an essential intermediate also in redox reactions of $Cp_2Ti(CO)_2$ such as that with Cp_2TiCl_2 considered here, especially if it proceeds via an inner-sphere halogen-ligand transfer route.

Essential steps of the interconversion between $(Cp_2TiCl)_2$, $Cp_2Ti(CO)_2$ and Cp_2TiCl_2, as derived from our study, are summarised in Scheme 1.

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