Kinetic Analysis of the Reaction of Isoprene with Carbon Dioxide and a Nickel(0) Complex

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The reactions of the nickel(0) complex [Ni(bipy)(COD)] (COD = cyclooctadiene, bipy = 2,2′-bipyridine) with isoprene (ip) in the absence and presence of carbon dioxide were investigated. A detailed kinetic analysis revealed that [Ni(bipy)(COD)] reacts reversible with ip and activation parameters for the forward and back reactions were calculated from a temperature dependence study to be the following: $\Delta H^\ddagger = 35 \pm 5$ kJ/mol, $\Delta S^\ddagger = -79 \pm 16$ J/(mol K) forward reaction (ip dependence); $\Delta H^\ddagger = 58 \pm 2$ kJ/mol, $\Delta S^\ddagger = 58 \pm 10$ J/(mol K) back-reaction (COD dependence at low temperatures). It could be shown that CO_2 did not react with [Ni(bipy)(COD)] directly but with the nickel ip complex to form the product complex ((3−5-η^3)-3-methyl-3-pentenylato)nickel bipyridine. The reaction proceeded in an associative way, during which CO_2 was inserted into a Ni−C bond in an oxidative coupling step. The activation parameters were calculated to be $\Delta H^\ddagger = 25 \pm 7$ kJ/mol and $\Delta S^\ddagger = -184 \pm 24$ J/(mol K).

Introduction

Despite the growing interest to use CO_2 as a C_1 building block in organic synthesis, so far there is little knowledge on the mechanisms of reactions of CO_2 with unsaturated compounds at transition metal sites.[1-4] To gain better understanding of such reactions we recently performed a kinetic investigation of reactions of aldehydes with [Ni(bipy)(COD)] in the absence and presence of CO_2.[5] CO_2 can react stoichiometrically with aldehydes or imines and nickel(0) complexes under oxidative coupling to form five-membered nickel(II) complexes with new C−O or C−N bonds.[6-10] Mechanistic studies of such reactions are difficult, mainly because of the extreme sensitivity of dilute solutions of nickel(0) complexes toward traces of dioxygen. We have overcome these difficulties and have now extended our investigations to the reaction of CO_2 with dienes and [Ni(bipy)(COD)]. We present here a detailed kinetic analysis of the reaction shown in eq 1, using the diene isoprene (ip).

It is known that various Ni(0) complexes oligomerize alkenes, dienes and alkynes, both stoichiometrically or catalytically.[11,12] For example the dimerization or trimerization of dienes with nickel−phosphane or −phos-

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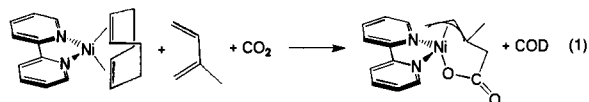
phite complexes was investigated.[13,14] The same complexes also can be used for the cooligomerization of dienes with CO_2 as cosubstrate leading to unsaturated carboxylic acids.[8,15] Usually these products are only formed stoichiometrically,[16-21] but in one case it was found that the reaction can proceed catalytically under appropriate reaction conditions.[22]

[Ni(bipy)(COD)] does not oligomerize dienes in contrast to the Ni(0)−phosphane complexes discussed above. Obviously labile phosphane ligands are necessary for the oligomerization of dienes. However, with [Ni(bipy)(COD)] a stoichiometric reaction with CO_2 and ip occurs.[19,23] During this metalla ring closure reaction a new C−C bond is formed between the diene and CO_2. The crystal structures of the reactant and of closely related product complexes (with the ligands tmed, PPh_3, and PCy_3 instead of bipy) are known.[21,24] A character-

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istic feature of the product is an allylic coordination of three carbon atoms of ip (eq 1). Obviously this η^3 structure is thermodynamically more stable compared to the possible η^1 compounds, which is also observed for the oligomerization of dienes.[25] Only two of the possible isomers are formed during the reaction of ip with CO_2 at [Ni(bipy)(COD)] (main product ((3−5-η^3)-3-methyl-3-pentenylato)nickel bipyridine, side product ((3−5-η^3)-4-methyl-3-pentenylato)nickel bipyridine, ratio 5:1; CO_2 is always connected to the terminal carbon atom of the diene).[19] Overall this means that ip and CO_2 together form a new η^3-allylic carboxylate ligand with a 2-fold negative charge, while nickel(0) is oxidized to the +2 state.

Experimental Section

Materials and Methods. All chemicals used were of analytical reagent grade quality. [Ni(bipy)(COD)] was synthesized according to a published procedure.[26] ip and cyclooctadiene (COD) were distilled and stored under an argon atmosphere in a glovebox.

Kinetic Measurements. Analytical reagent grade quality THF was distilled and stored in a glovebox (Braun, Garching, Germany; dioxygen and water content was less than 1 ppm). Solutions of [Ni(bipy)(COD)] in THF for the kinetic measurements were prepared in the glovebox and transferred in glass syringes to the stopped-flow instrument. CO_2-saturated solutions were prepared by bubbling high-quality CO_2 (Linde, Wiesbaden, Germany, 4.5) through a solution of [Ni(bipy)-(COD)] to remove traces of dioxygen and then through the solvent (solubility of CO_2 in THF at 25 °C = 205 mmol/L [27]). Dilution was accomplished by mixing this solution with an argon-saturated solvent. The reaction was studied under pseudo-first-order conditions, and time-resolved spectra were recorded on an Applied Photophysics stopped-flow SX.18MV instrument (Leatherhead, U.K.) equipped with a J&M detector connected to a TIDAS 16-500 diode array spectrophotometer (J&M, Aalen, Germany). Slower reactions were followed using the rapid kinetics spectrometer accessory Applied Photophysics RX-1000 (Leatherhead, U.K.) on a Hewlett-Packard spectrophotometer 8452 A. In all kinetic experiments the thermostating fluid contained sodium dithionite and was constantly bubbled with nitrogen to avoid contamination by dioxygen. Low-temperature measurements were performed with a modified HI-TECH SF-3L stopped-flow system (HI-TECH, Salisbury, U.K.). The modifications performed by J&M included use of glass tubing instead of Teflon and a modified connection of this tubing to the photometric observation cell (quartz). Light fibers are connected to the cell using an improved optical system. Here again spectra were recorded with the J&M TIDAS 16-500 diode array spectrophotometer. This system allows kinetic measurements of reactions of dioxygen sensitive compounds in organic solvents at temperatures down to −100 °C. Data fitting was carried out using either the integrated J&M software, the program Specfit (Spectrum Software Associates, Chapel Hill, NC), the program OLIS (KINFIT routines, On-line Instrument Systems, Bogart, GA), or Igor Pro (WaveMetrics, Lake Oswego, OR).

Results and Discussion

Reaction of ip with [Ni(bipy)(COD)]. As discussed in our previous paper on the reaction of propion-
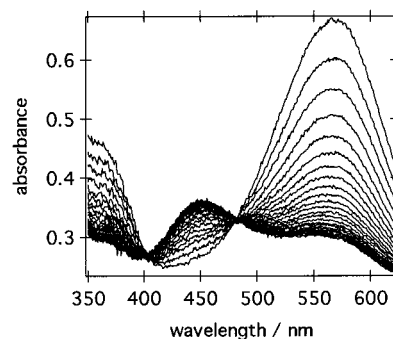

Figure 1. Time-resolved spectra recorded during the reaction of ip with [Ni(bipy)(COD)]: [Ni(bipy)(COD)] concentration = 0.25 mM, ip concentration = 50 mM; solvent = THF; T = 25 °C; Δt = 9 ms.

aldehyde (pa) with CO_2 and [Ni(bipy)(COD)], it is very unlikely that the three reactants in eq 1 react in one step.[5] In the absence of an unsaturated substrate no reaction between CO_2 and [Ni(bipy)(COD)] was observed,[5] even though it is known that Ni(0) complexes are able to form CO_2 complexes.[28] On the other hand reactions of dienes with Ni(0) complexes are well-known and in eq 2 the reaction of ip with [Ni(bipy)(COD)] is shown.[19]

$$[\text{Ni(bipy)(COD)}] + \text{ip} \underset{-\text{COD}}{\rightleftharpoons} [\text{Ni(bipy)(ip)}] \underset{+\text{ip}}{\rightleftharpoons} [\text{Ni(bipy)(ip)}_2] \quad (2)$$

Unfortunately it is not possible to isolate a product from this reaction because the equilibrium is on the left side of eq 2. In an earlier study, however, the crystal structure of the complex with butadiene [(Ni(bipy))₂-(butadiene)₃], prepared via a different pathway, could be solved.[29] NMR studies showed that this complex dissociates in solution to two species, [Ni(bipy)butadiene] and [Ni(bipy)(butadiene)₂], existing in equilibrium with each other.[29] At higher temperatures coordination of only one butadiene is favored, whereas at low temperatures two butadiene molecules are coordinated.

[Ni(bipy)(COD)] decomposes over time, even in the glovebox under inert conditions. The decomposition which arises from loss of the labile COD ligand could be suppressed by adding an excess of COD to the solution.[5] Unfortunately even an equimolar addition of COD suppresses the reaction with ip. In contrary to many other Ni(0) complexes, [Ni(bipy)(COD)] does not catalyze the dimerization of dienes and therefore the substitution of COD by ip can be followed spectophotometrically. Spectral changes for this reaction are shown in Figure 1. These spectra are quite similar to those obtained for the reaction of [Ni(bipy)(COD)] with pa, and the reaction behavior is also similar in both cases;[5] a large excess of unsaturated substrate is necessary for the reaction to proceed to completion. Isosbestic points are observed at 403 and 484 nm compared to 390 and 485 nm for pa coordination.

Determination of rate constants for a second-order equilibrium reaction in both directions requires pseudo-first-order conditions for both the forward and backreactions, i.e., use of an at least 10-fold excess of ip and

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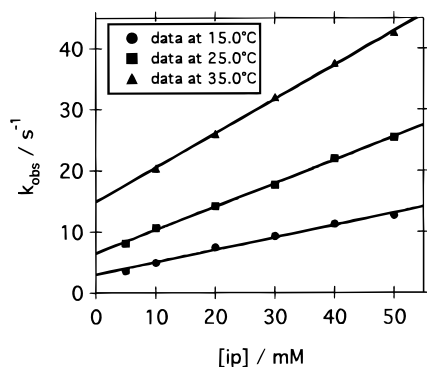
Figure 2. Plot of observed rate constants k_{obs} vs ip concentration at different temperatures: [Ni(bipy)(COD)] concentration = 0.25 mM.

Table 1. Second-Order Rate Constants for the Reaction of [Ni(bipy)(COD)] with Ip and [Ni(bipy)(ip)] with COD As Obtained from Eq 3 (Figures 2 and 4)

T/°C	[ip] dependence: slope k_a/M^{-1} s^{-1}	[COD] dependence: slope k_b/M^{-1} s^{-1}
15.0	203 ± 10	
25.0	382 ± 7	
35.0	560 ± 10	
−60.0		23.2 ± 1.5
−70.0		5.6 ± 0.1
−80.0		0.82 ± 0.04
−90.0		0.097 ± 0.007
ΔH‡ (kJ/mol)	35 ± 5	58 ± 2
ΔS‡ (J/mol K))	−79 ± 16	58 ± 10

COD in our case. Since this is not possible here as mentioned above, the rate constants for the forward reaction (k_a) and back-reaction (k_b) had to be determined in separate measurements. Absorbance time traces of the reaction of [Ni(bipy)(COD)] with ip without additional COD obtained by stopped-flow measurements could be fitted perfectly to a single one exponential function. The plot of the observed rate constants k_{obs1} vs ip concentration is linear at different temperatures (Figure 2, data in Table 1). For an equilibrium reaction the second-order rate constants for the forward and back-reactions, k_a and k_b are related to the observed rate constant k_{obs1} by eq 3.

$$k_{obs1} = k_a[\text{ip}] + k_b[\text{COD}] \qquad (3)$$

For the forward reaction (no COD added) the term k_b[COD] (intercept) was discarded (no pseudo-first-order conditions) and only k_a was calculated from the slopes in Figure 2.

The back-reaction (k_b) was measured by reacting the premixed complex [Ni(bipy)(ip)] with an excess of COD. This reaction was too fast at ambient temperatures for our normal stopped-flow equipment, and hence, a low-temperature kinetic investigation (−60 to −90 °C) was necessary. UV−vis spectral changes in this temperature region are slightly different from those of the spectra near room temperature, and only one isosbestic point at 488 nm can be observed (Figure 3). The time traces could again be fitted to a single-exponential function. A plot of the observed rate constants k_{obs} vs COD concentration shows a linear dependence without a significant intercept (Figure 4, Table 1), and k_b was calculated from the slopes.
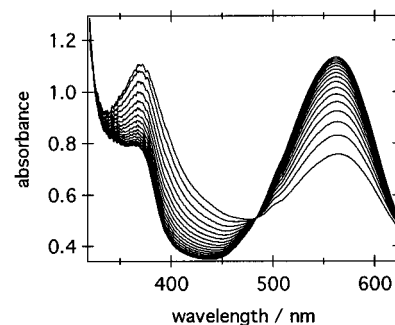

Figure 3. Spectra recorded during the reaction of pre-mixed nickel−ip complex with COD: T = −90 °C; solvent = THF; [Ni(bipy)(COD)] concentration = 0.25 mM; ip concentration = 50 mM; COD concentration = 40 mM; Δt = 4 s.
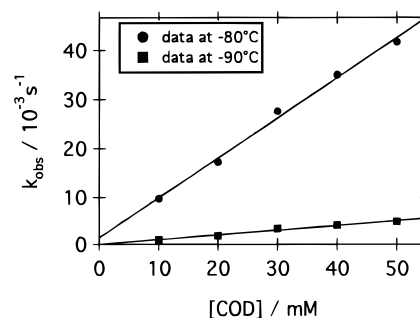

Figure 4. Plot of observed rate constants k_{obs} vs COD concentration at different temperatures: [Ni(bipy)(COD)] concentration = 0.25 mM; ip concentration = 50 mM.

The temperature dependence of the second-order rate constants calculated from the slopes of the plots of k_{obs} vs ip concentration (Figure 3 and Table 1) or k_{obs} vs COD concentration (Figure 4 and Table 1) allowed us to determine the activation parameters for the forward reaction (ΔH‡ = 35 ± 5 kJ/mol and ΔS‡ = −79 ± 16 J/(mol K)) and the back-reaction (low-temperature values; ΔH‡ = 58 ± 2 kJ/mol and ΔS‡ = 58 ± 10 J/(mol K)). The negative activation entropy calculated for the forward reaction measured at ambient temperatures is in accordance with our earlier findings for the [Ni(bipy)-(COD)]/pa system, where we also obtained a similar negative value for ΔS‡ (−58 ± 9 J/(mol K)). These results would support an associative mechanism for the reaction of [Ni(bipy)(COD)] with ip or propionaldehyde. Following the same arguments discussed earlier, we think that an associative mechanism is rather unlikely: [30] [Ni(bipy)(COD)] is a diamagnetic tetrahedral complex where the Ni(0) center is bound to the planar bipyridine ligand and symmetrically coordinated to the two π-bonds of COD.[30] It is well-known that tetrahedral Ni(0) complexes undergo dissociative substitution reactions (with positive activation entropies) and therefore it would be difficult to explain why [Ni(bipy)(COD)] would be an exception.[31] Therefore we propose a mechanism where in a fast preequilibrium step one of the bonds between Ni and COD is cleaved and in a following step ip coordinates to the free coordination site (see Scheme 1).[32] A similar mechanism was proposed for the reaction

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Scheme 1
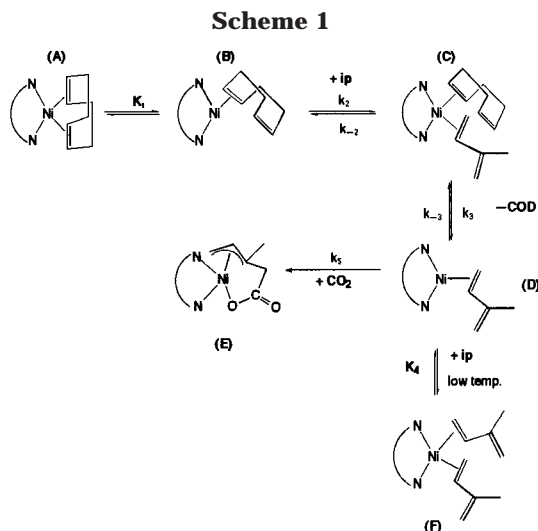
of [Ni(bipy)(COD)] with aldehydes.[30] Even though the reactions of [Ni(bipy)(COD)] with pa and ip are quite similar the rates are very different; at 25 °C ip reacts with [Ni(bipy)(COD)] by a factor of 200 faster than pa.

For additional kinetic information it would have been interesting to obtain activation volumes, too. These measurements were not possible in our case due to the sensitivity of the nickel(0) complexes toward traces of dioxygen. In our high-pressure stopped-flow instrument the complexes decomposed prior to any measurements.

The reaction of [Ni(bipy)(ip)] with COD, the back-reaction in eq 2, is even so much faster compared to [Ni(bipy)(pa)] that it is not possible anymore to follow the reaction at room temperature. At low temperatures we obtained in contrast to the measurements for the forward reaction a positive value of $\Delta S^{\ddagger}$. This is also different for the reaction of COD with [Ni(bipy)(pa)] at ambient temperatures where we obtained a negative $\Delta S^{\ddagger}$ value.[5] The reason for this derives from the equilibrium between two different ip product complexes in which the metal is coordinated to one or two molecules of ip according to eq 2. At low temperatures this equilibrium is shifted toward the 2-fold coordinated complex. Therefore the equilibrium reaction, the dissociation of one ip molecule prior to the reaction with COD, needs to be included and is responsible for the observed positive activation entropy. Binding of a second molecule of ip by [Ni(bipy)(ip)] can be clearly observed in the UV−vis spectrum. Lowering the temperature of a solution of [Ni(bipy)(COD)] with an excess of ip leads to an increase of an absorbance band at 375 nm while the band at 450 nm disappears. The spectrum of the complex at −90 °C can be seen in Figure 3. Lowering the temperature of a solution of [Ni(bipy)-(COD)] with an excess of pa also did lead to similar effects but much less enhanced. Obviously, as postulated earlier, here too a second molecule of pa can coordinate to the nickel complex at low temperature.[33]

From our kinetic findings we therefore postulate the mechanism shown in Scheme 1 for the reaction of

[Ni(bipy)(COD)] with ip. In a fast preequilibrium one of the bonds to COD is broken transforming the four-coordinated [Ni(bipy)(COD)] (**A**) into a reactive three-coordinated species Ni(bipy)(COD′) (**B**). In a reversible reaction ip is binding to **B**, before in another reversible reaction the final product **D** is formed. During that last reaction step the remaining bond to COD is broken. At low temperatures this complex **D** can further react in a consecutive equilibrium with another molecule ip to **F**. This consecutive equilibrium between the mono- and bis-ip complexes is temperature dependent and is not relevant at room temperature. The rate law for the formation of [Ni(bipy)(ip)] (**D**) at ambient temperatures is given by eq 4.

$$\frac{d[\mathbf{D}]}{dt} = k_3[\mathbf{C}] - k_{-3}[\mathbf{D}][COD] \tag{4}$$

Because **C** is an intermediate the equation needs to be modified by including the fast preequilibrium between **A** and **B** and furthermore using the steady-state approximation for **C**. This leads to eq 5 for k_{obs1} (description of the derivation of such equations is given in the literature[34]). $K_1/(1 + K_1)$ represents the fraction of **B** where one Ni−COD bond is broken.

$$k_{obs} = \frac{\left(\dfrac{K_1}{1 + K_1}\right)k_2 k_3[ip] + k_{-2}k_{-3}[COD]}{k_3 + k_{-2}} \tag{5}$$

At low temperatures the equilibrium K_4 leading to the bis-ip complex **F** needs to be included. Therefore in the overall reaction scheme an additional dissociative step is involved in the back reaction of **F** with COD at low temperatures. The modified rate law including the consecutive equilibrium is given in eq 6.

$$\frac{d[N]}{dt} = \frac{d[D]}{dt} + \frac{d[F]}{dt} \tag{6a}$$

$$\frac{d[N]}{dt} = \frac{k_2 k_3[B][ip]}{(k_{-2} + k_3)} - \frac{k_{-2}k_{-3}[D][COD]}{(k_{-2} + k_3)} \tag{6b}$$

$$\frac{d[N]}{dt} = -\frac{k_2 k_3 K_1}{(k_{-2} + k_3)(1 + K_1)}[N][ip] - \frac{k_{-2}k_{-3}}{(k_{-2} + k_3)(1 + K_4[ip])}[N][COD] \tag{6c}$$

Here it was necessary to derive the equation for d[N]/dt, [N] representing the total concentration of **D** and **F**. The measured k_{obs1} values include the different rate and equilibrium constants, and their relation is given in eq 7.

$$k_{obs1} = \frac{k_2 k_3 K_1}{(k_{-2} + k_3)(1 + K_1)}[ip] + \frac{k_{-2}k_{-3}}{(k_{-2} + k_3)(1 + K_4[ip])}[COD] \tag{7}$$

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(32) A reviewer suggested that an equilibrium might exist between the two possible isomers of [Ni(bipy)(ip)] which could cffect the kinetics of the reaction. This cannot be excluded, but unfortunately it is not possible to distinguish this in our kinetic investigation.

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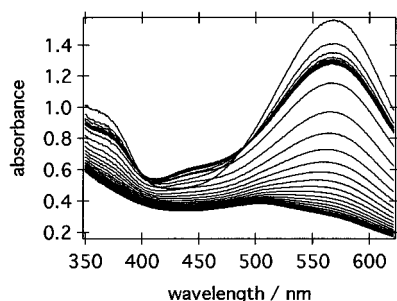
Figure 5. Spectra recorded during the reaction of ip and CO_2 with [Ni(bipy)(COD)]: ip concentration = 10 mM; [Ni(bipy)(COD)] concentration = 1.0 mM; CO_2 concentration = 102.5 mM; solvent = THF; T = 25 °C; Δt_1 = 75 ms; Δt_2 = 40 s.

In the back-reaction at low temperatures, the reaction of **F** with COD, first the dissociation of one ip molecule occurs before in an associative reaction COD coordinates to **D** forming a 4-coordinated complex **C** again. This is followed by the loss of ip leading to **A**. In the back-reaction as well as the forward reaction the measured rate constants include the rate constants of the different steps as shown in eq 6. Furthermore, this means that also the calculated activation parameters are composite values for the mixture of different rate constants and not for a single reaction step.

Reaction of ip with CO_2 and [Ni(bipy)(COD)]. Introducing CO_2 into the system leads to the reaction given in eq 1, where in a first fast reaction step **D** is formed, followed by a slower reaction of this complex with CO_2. Spectral changes occurring during this reaction are shown in Figure 5. The final product **E** is characterized by a weak absorbance maximum at 495 nm, whereas the absorbance band of **A** at 575 nm disappears during the reaction. The absorbance spectrum of the intermediate **D** complex depends highly on the concentration of ip. The measured rate constants for this first step are the same as found for the reaction of **A** with ip in the absence of CO_2 as described above. In the following we report the findings for the slower reaction, the oxidative coupling of CO_2 to **D**.

The spectral changes for the slower reaction with CO_2 could only be fitted to the sum of two exponential functions. For these two reaction steps it was found that the larger rate constant is independent of CO_2 concentration while the lower value is depending on its concentration. Because the reaction with CO_2 is quite slow, partial decomposition of the nickel(0) complexes under these conditions (no COD present) is always observed being responsible for the observed faster reaction step. Similar findings were also made during our investigation of the reaction of [Ni(bipy)(pa)] with CO_2, and furthermore, the decomposition reaction can be observed in the absence of CO_2.

ip and CO_2 were always kept in excess over Ni(bipy)-(COD) to ensure pseudo-first-order conditions. The dependence of the measured rate constant of the product formation (k_{obs2}) on CO_2 concentration is linear for different temperatures as shown in Figure 6 and Table 2, the intercept caused from decomposition of the complex. A formal second-order rate law for that reaction is given in eq 8.
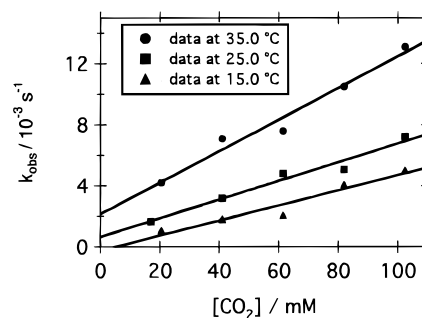
$$-d[\mathbf{D}]/dt = k_5[\mathbf{D}][CO_2] \qquad (8)$$

Figure 6. Plot of observed rate constants k_{obs} vs CO_2 concentration at different temperatures: [Ni(bipy)(COD)] concentration = 1.0 mM; ip concentration = 10 mM.

Table 2. Second-Order Rate Constants k for the Reaction of CO_2 with ip and [Ni(bipy)(COD)] According to Eq 1[a]

T/°C	[CO_2] dependence: $k/10^{-2}\,M^{-1}\,s^{-1}$ (slopes of Figure 6)
15.0	4.9 ± 0.8
25.0	6.1 ± 0.7
35.0	10.3 ± 1.1
$\Delta H^{\ddagger}$ (kJ/mol)	25 ± 7
$\Delta S^{\ddagger}$ (J/mol K)	-184 ± 24

[a] [Ni(bipy)(COD)] Concentration = 1.0 mM; CO_2 Concentration = 102.5 mM; calculated from Figure 6.

Using the approximation of a fast preequilibrium for the formation of **D** in Scheme 1, the following equation for k_{obs2} is obtained:

$$k_{obs2} = \frac{k_5[CO_2][ip] + K_1}{[ip]K_1 + [COD]} \qquad (9)$$

The equation is in accordance with the measured results. We do find that the observed rate constants depend on the concentration of CO_2 but also on the concentration of ip. The measured values for k_{obs2} show larger experimental errors compared to the ones obtained from measurements with ip alone, but in a plot of k_{obs2} vs concentration of ip it clearly can be seen that no linear dependence but a curved saturation dependence is obtained.

The temperature dependence was measured, but the instability of [Ni(bipy)(COD)] only allowed the use of a small temperature window. The calculated activation parameters therefore do not represent exact data but indicate the trend in these parameters. Using the values of the slopes from Figure 6 (data in Table 2) the activation parameters were calculated to be $\Delta H^{\ddagger}$ = 25 ± 7 kJ/mol and $\Delta S^{\ddagger}$ = − 184 ± 24 J/(mol K). The large negative activation entropy confirms the associative mechanism of the reaction and the bond formation in the transition state of the two molecules. Also charge creation in the transition state contributes to the large negative value of $\Delta S^{\ddagger}$. The kinetic measurements confirm the assumption that no direct reaction of CO_2 with the metal center occurs. Instead, the diene is activated and then a reaction with CO_2 can take place. This means, that we observe activation of ip rather than CO_2. This behavior is consistent with our results from the investigation of the [Ni(bipy)(COD)]/pa system for which similar activation parameters were obtained ($\Delta H^{\ddagger}$

$= 43 \pm 6$ kJ/mol and $\Delta S^{\ddagger} = -129 \pm 19$ J/(mol K)).[5] The reaction mechanism shown in Scheme 1 is in accordance with the kinetic findings. The reaction with CO_2 is irreversible, leading to the final product, ((3−5-η^3)-3-methyl-3-pentenylato)nickel bipyridine. Additional support for this postulated mechanism comes from a theoretical study on the reaction of a nickel(0) complex, CO_2, and an alkyne.[35,36]

Conclusions

Even though the nickel(0) complexes used in this study were very sensitive toward traces of dioxygen, we were able to successfully perform kinetic measurements. The complex formation of ip with [Ni(bipy)(COD)] was investigated and compared with our earlier investigation on pa. It was found that ip reacts much faster than pa and furthermore the back-reaction with COD was accelerated too. Still, reactions of pa and ip with [Ni(bipy)(COD)] showed some interesting common features: both pa and ip form a complex with the [Ni(bipy)] complex fragment that can only be characterized spec-troscopically if a large excess of ip or pa is used over [Ni(bipy)(COD)]. The use of excess of the substrate demonstrates that the equilibrium for the reversible coordination of pa or ip is mainly on the left side. This also explains why the addition of COD suppresses the coordination of the unsaturated compounds. The situation is different for the aromatic benzaldehyde. Here a stable complex could be isolated and an equimolar amount already leads to the observation of the product in the UV−vis spectrum. In other words, for the reaction with CO_2 it is necessary that ligands are only weakly bound to the nickel complex to ensure their further reaction with CO_2, a reaction pathway that is not possible with strongly coordinated ligands such as benzaldehyde.

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