

Reactions of Aldehydes with Carbon Dioxide at Nickel(0) Centers. A Detailed Kinetic Analysis

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The reactions of the nickel(0) complex [Ni(bipy)(COD)] (COD = cyclooctadiene, bipy = 2,2'-bipyridine) with benzaldehyde, propionaldehyde, and carbon dioxide/propionaldehyde were investigated. A detailed kinetic analysis revealed that [Ni(bipy)(COD)] reacts reversibly with aldehydes and activation parameters for the forward and back reactions were calculated from a temperature dependence study: forward reaction (benzaldehyde) $\Delta H^\ddagger = 47.8 \pm 0.4$ kJ/mol, $\Delta S^\ddagger = -47 \pm 1$ J/(mol K); back reaction (COD) $\Delta H^\ddagger = 45 \pm 6$ kJ/mol, $\Delta S^\ddagger = -61 \pm 19$ J/(mol K) and forward reaction (propionaldehyde) $\Delta H^\ddagger = 55 \pm 3$ kJ/mol, $\Delta S^\ddagger = -58 \pm 9.0$ J/(mol K); back reaction (COD) $\Delta H^\ddagger = 39 \pm 0.5$ kJ/mol, $\Delta S^\ddagger = -58 \pm 2$ J/(mol K). It could be shown that carbon dioxide did not react with [Ni(bipy)(COD)] directly but with the nickel propionaldehyde complex to form a five-membered cyclic nickel complex. The reaction proceeded according to an associative mechanism, during which the carbon dioxide was inserted into a Ni–O bond by an oxidative coupling step. The activation parameters for this process were $\Delta H^\ddagger = 43 \pm 6$ kJ/mol and $\Delta S^\ddagger = -129 \pm 19$ J/(mol K).

Introduction

Interest in the use of carbon dioxide as a C₁ building block in industrial organic synthesis has increased primarily due to international efforts at reducing the greenhouse gas carbon dioxide in the atmosphere and the diminishing supply of carbon-based fossil fuel resources.^{1–4} Thus far only a relatively small number of reactions with carbon dioxide have found use in industrial synthetic processes,^{1,2} due mainly to the thermodynamic stability and kinetic inertness of the carbon dioxide molecule.¹ To use this molecule in organic synthesis it is therefore necessary to either activate carbon dioxide itself or a substrate. Promising are stoichiometric and catalytic reactions of carbon dioxide taking place at low-valent transition metal complexes with unsaturated cosubstrates or hydrogen, which have been intensively investigated by different groups.^{1,5–13} Carbonic acids, lactones, and pyrones

could be synthesized from alkenes or alkynes and carbon dioxide mainly at Ni(0) centers, but complexes of other metals such as palladium or rhodium have also been used.^{1,2,9–11,14–21} Furthermore, the catalytic coupling reactions of alkynes with carbon dioxide were studied by generating a nickel(0) complex electrochemically.²²

Stoichiometric reactions of carbon dioxide with aldehydes or imines and nickel(0) complexes lead to five-membered cyclic complexes.^{9,19–21} 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 present here a detailed kinetic investigation of the reaction of carbon dioxide with propionaldehyde at a nickel(0) center according to eq 1.

This reaction leads stoichiometrically to a five-membered cyclic nickel complex, where Ni(0) is oxidized to Ni(II) and CO₂ is connected via a new C–O bond to the aldehyde forming a ligand with a formal charge of

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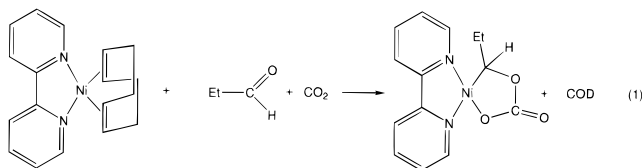
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—II.²¹ Crystal structures of the reactant and the product are known.^{19,23}

Experimental Section

Materials and Methods. All chemicals used were of analytical reagent grade quality. [Ni(bipy)(COD)] was synthesized according to a previously published procedure.²⁴ Benzaldehyde, propionaldehyde, and cyclooctadiene (COD) were distilled and stored under an argon atmosphere in a glovebox. UV–vis spectra were measured on a Hewlett-Packard spectrophotometer 8452 A.

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)] for the kinetic measurements were prepared in the glovebox and transferred in glass syringes to the stopped-flow instrument. Carbon dioxide saturated solutions were prepared by bubbling high-quality carbon dioxide (Linde, Germany, 4.5) through a solution of [Ni(bipy)(COD)] to remove traces of dioxygen and then through the solvent (solubility of carbon dioxide in THF at 25 °C = 205 mmol/L²⁵). 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.17MV instrument (Leatherhead, UK) equipped with a J&M detector connected to a TIDAS 16-416 spectrophotometer (J&M, Aalen, Germany). Slower measurements were performed 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. Data fitting was carried out using the integrated J&M software, the program Specfit (Spectrum Software Associates, Chapel Hill, NC), or the program OLIS (KINFIT routines, On-line Instrument Systems, Bogart, GA).

Results and Discussion

Since it is unlikely that the three reactants in eq 1 are reacting in one step, it was necessary to first study the reaction of [Ni(bipy)(COD)] with either carbon dioxide or the aldehyde. Literature studies have revealed that Ni(0) complexes can react with carbon dioxide,^{26–29} and a structurally characterized carbon dioxide complex was synthesized from a Ni(0) compound.^{26,29} In contrast to these results we found that the UV–vis spectrum of [Ni(bipy)(COD)] in THF did not

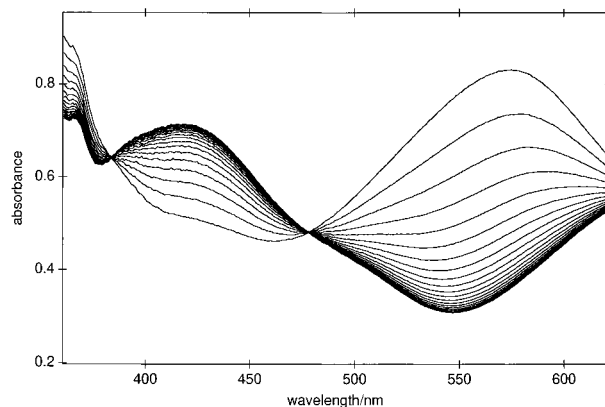


Figure 1. Time-resolved spectra recorded during the reaction of benzaldehyde with [Ni(bipy)(COD)]: benzaldehyde concentration = 20 mM, [Ni(bipy)(COD)] concentration = 0.16 mM, COD concentration = 2.0 mM, solvent = THF, $T = 25\text{ }^{\circ}\text{C}$, $\Delta t = 0.1\text{ s}$.

change upon reaction with carbon dioxide, which indicated that no reaction had occurred. This is consistent with the finding that many transition metal promoted reactions with carbon dioxide go through a process of substrate rather than carbon dioxide activation as discussed in a recent review.⁶

Reactions of carbonyl compounds with Ni(0) complexes according to eq 2 are well-known.^{30,31}



Ketones and aromatic aldehydes form stable complexes with Ni(0) and for compounds with $R = R' = \text{Ph}$, $L = \text{Et}_3\text{P}$; $R = R' = \text{CF}_3$, $L = \text{Ph}_3\text{P}$; and $R = \text{Ph}$, $R' = \text{H}$, $L-L = \text{bipy}$, X-ray structural characterization was possible.^{32–34} Furthermore, the complex Ni(bipy)(benzaldehyde) was not found to react with carbon dioxide according to eq 1. No spectral change was observed when bubbling carbon dioxide through a solution of this complex in THF. This was different for aliphatic aldehydes where it was found that [Ni(bipy)(COD)] catalyzed an aldol reaction in the absence of carbon dioxide.³⁵ However, in the presence of carbon dioxide the reaction proceeded according to eq 1.^{19,21}

Reaction of Benzaldehyde with [Ni(bipy)(COD)]. To gain a more detailed insight into these reactions we decided to first study the reaction of an aldehyde with [Ni(bipy)(COD)] prior to the reaction with carbon dioxide. To avoid possible problems with the occurrence of an aldol reaction, we chose benzaldehyde (eq 2, $R = \text{Ph}$, $R' = \text{H}$, $L-L = \text{bipy}$) for our investigation. Spectral changes for this reaction are shown in Figure 1. Isosbestic points were observed at 390 and 485 nm. It was found that solutions of [Ni(bipy)(COD)] decompose after

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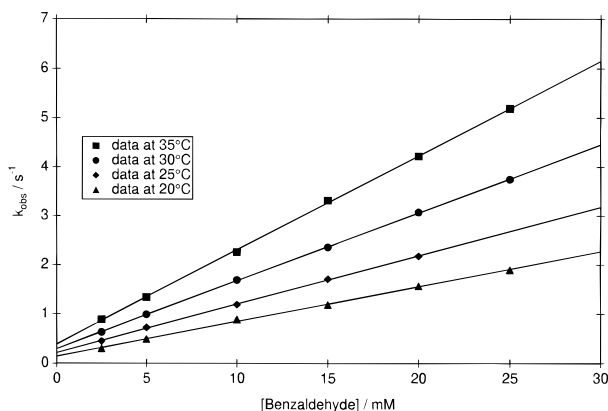


Figure 2. Plot of observed rate constants k_{obs} vs benzaldehyde concentration at different temperatures: [Ni(bipy)(COD)] concentration = 0.25 mM, COD concentration = 2.8 mM.

some time, even under inert conditions. The decomposition which arises from loss of the labile ligand COD could be suppressed by adding an excess of COD to the solution. Absorbance time traces of the reaction of [Ni(bipy)(COD)] with benzaldehyde and COD in excess could be fitted perfectly to a single one-exponential function, and the plot of the observed rate constants k_{obs} vs benzaldehyde concentration is linear at different temperatures as shown in Figure 2 and Table 1. The intercept indicates that the reaction is reversible, and it is possible to measure the back reaction of COD with premixed [Ni(bipy)(COD)] and benzaldehyde. Here again we observe a linear dependence with an intercept. The corresponding rate constants for the forward and backward reaction are consistent with those obtained for the forward reaction (Table 1). Equation 3 for the observed rate constant k_{obs} describes the kinetic findings where k_a and k_b are the second-order rate constants for the forward and back reaction and an equilibrium constant close to 1 was obtained.

$$k_{\text{obs}} = k_a[\text{aldehyde}] + k_b[\text{COD}] \quad (3)$$

The temperature dependence of the second-order rate constants calculated from the slopes of the plots of k_{obs} vs benzaldehyde concentration (Figure 2 and Table 1) or k_{obs} vs COD concentration (Table 1) allowed the determination of the activation parameters for the forward reaction ($\Delta H^\ddagger = 47.8 \pm 0.4$ kJ/mol and $\Delta S^\ddagger = -47 \pm 1$ J/(mol K)) and the back reaction ($\Delta H^\ddagger = 45 \pm 6$ kJ/mol and $\Delta S^\ddagger = -61 \pm 19$ J/(mol K)).

The kinetic findings support an associative mechanism for the reaction of [Ni(bipy)(COD)] with benzaldehyde as well as the back reaction of [Ni(bipy)(benzaldehyde)] with COD; however it is very unlikely that the reaction proceeds in this way. [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.²³ 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.³⁶ Furthermore, it is known that [Ni(bipy)(olefin)] com-

plexes can dissociate in solution, liberating the coordinated olefin.^{37,38} This is consistent with our findings that addition of COD to solutions of [Ni(bipy)(COD)] stabilize the complex as described above. A kinetic study related to this study described the reaction of [Ni(PEt₃)₄] with benzophenone and substituted benzophenones in benzene.³² The authors suggested that here the reactive species is [Ni(PEt₃)₃] which forms in a rapid preequilibrium according to eq 4.^{32,39,40}



The equilibrium constant for this reaction derived from the kinetic measurements was concordant with that obtained earlier from spectrophotometric titrations.⁴¹ [Ni(PEt₃)₃], which formed during the reaction, then reacted further with benzophenone to yield the product complex. Additional support for the proposed mechanism was the finding that an increase in the concentration of PEt₃ led to a decrease in the reaction rate; i.e., an inverse dependence of k_{obs} on PEt₃ concentration.³² However, no temperature dependence studies were performed.

From the kinetic results the mechanism shown in Scheme 1 for the reaction of [Ni(bipy)(COD)] (A) with benzaldehyde may be postulated. 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 benzaldehyde is bound (presumably in a $\eta^1(\text{O})$ manner) to [Ni(bipy)(COD')] (B) before, in another reversible reaction, the final product is formed. During this reaction benzaldehyde undergoes a coordination change to $\eta^2(\text{C}, \text{O})$ and the remaining bond to COD is broken. The rate for the formation of [Ni(bipy)(benzaldehyde)] (D) is given by eq 5 (abbreviations for nickel complexes according to Scheme 1; R = C₆H₅).

$$\frac{d[\text{D}]}{dt} = k_2[\text{C}] - k_{-2}[\text{D}][\text{COD}] \quad (5)$$

Because [Ni(bipy)(COD')(benzaldehyde)] (C) is an intermediate, the equation needs to be modified by including the fast preequilibrium between [Ni(bipy)(COD)] (A) and [Ni(bipy)(COD')] (B) and furthermore using the steady state approximation for [Ni(bipy)(COD')(benzaldehyde)] (C). This leads to eq 6 for k_{obs} (description of the derivation of such equations is given in the literature⁴²).

$$k_{\text{obs}} = \frac{\left(\frac{K}{1+K}\right)k_1k_2[\text{benzaldehyde}] + k_{-1}k_{-2}[\text{COD}]}{k_2 + k_{-1}} \quad (6)$$

$K/(1+K)$ represents the fraction of [Ni(bipy)(COD')] (B) species where one Ni–COD bond is broken. From

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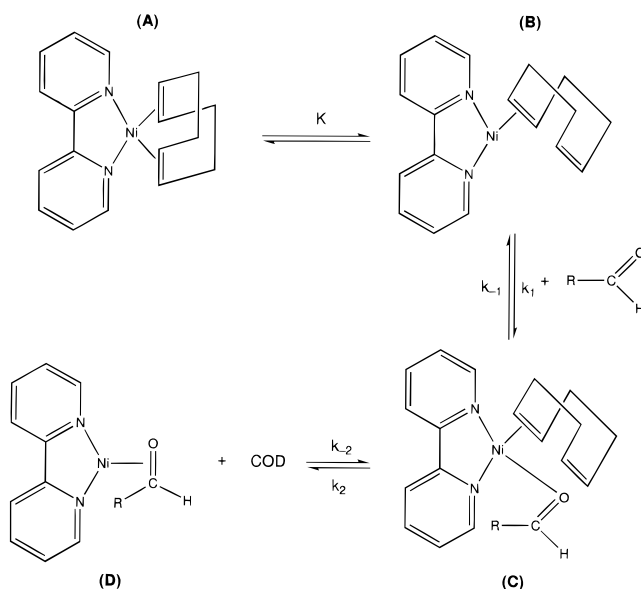
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Table 1. Second-Order Rate Constants for the Reaction of [Ni(bipy)(COD)] with Benzaldehyde and [Ni(bipy)(benzaldehyde)] with COD As Obtained from Eq 3 ([Ni(bipy)(COD)] Concentration = 0.25 mM)

<i>T</i> /°C	[benzaldehyde] dependence			[COD] dependence		
	slope, <i>k_a</i> /M ⁻¹ s ⁻¹	intercept, <i>k_b</i> /M ⁻¹ s ⁻¹	<i>K</i> (= <i>k_a</i> / <i>k_b</i>)	intercept, <i>k_a</i> /M ⁻¹ s ⁻¹	slope, <i>k_b</i> /M ⁻¹ s ⁻¹	<i>K</i> (= <i>k_a</i> / <i>k_b</i>)
15.0				62 ± 5	32.6 ± 0.7	1.9
20.0	71 ± 1	51 ± 7	1.4			
25.0	99 ± 1	74 ± 5	1.3	121 ± 2	55.2 ± 0.4	2.2
30.0	139 ± 1	105 ± 4	1.3			
35.0	192 ± 2	140 ± 10	1.4	209 ± 21	117 ± 3	1.8
Δ <i>H</i> [‡] (kJ/mol)	47.8 ± 0.4	48.3 ± 1.5		42 ± 2	45 ± 6	
Δ <i>S</i> [‡] (J/(mol K))	-47 ± 1	-47 ± 5		-63 ± 6	-61 ± 19	

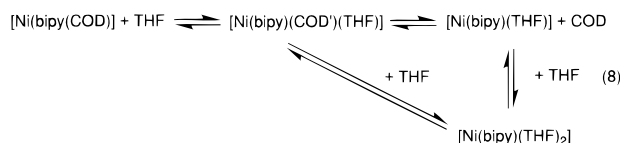
Scheme 1

our kinetic findings we know that the overall equilibrium constant of the reaction is close to 1: $K_{\text{overall}} = Kk_1k_2 \approx 1$. The equilibrium constant K must be small and with $K \ll 1$ we obtain eq 7 for k_{obs} , confirming the kinetic data.

$$k_{\text{obs}} = \left(\frac{Kk_1k_2}{k_2 + k_{-1}} \right) [\text{benzaldehyde}] + \left(\frac{k_{-1}k_{-2}}{k_2 + k_{-1}} \right) [\text{COD}] \quad (7)$$

The back reaction was also studied, and its mechanism is shown in Scheme 1. In this case premixed [Ni(bipy)(benzaldehyde)] (D) is reacted with COD and benzaldehyde is then substituted, forming the [Ni(bipy)(COD)] (A) complex. In both the back and forward reaction the measured rate constants include the rate constants of the different steps as shown in eq 7. This means that the calculated activation parameters are composite values for the mixture of different rate constants and not for a single reaction step. The associative contributions from k_1 and k_{-2} must account for the overall negative activation entropies.

Not included in our mechanism is the possibility of solvent coordination according to eq 8.



We also investigated the reaction in toluene where behavior was similar to that of THF was found. Only small solvent effects were observed for the reaction of [Ni(PET₃)₄] with benzophenone.³² Although a direct comparison of the reaction of [Ni(PET₃)₄] with benzophenone with the reaction of [Ni(bipy)(COD)] is difficult, it is interesting to observe that these reactions proceed at similar rates. Second-order rate constants for the reaction of the different neutral benzophenone ligands range from 22 to 900 M⁻¹ s⁻¹ (depending on the selected substituents) and agree well with our value of 100 M⁻¹ s⁻¹ at 25 °C.

Reaction of Carbon Dioxide with Propionaldehyde and [Ni(bipy)(COD)]. The situation is different when the aliphatic propionaldehyde is reacted with [Ni(bipy)(COD)]. Without carbon dioxide present an aldol condensation to α -methyl- β -ethylacrolein is catalyzed by the nickel complex.³⁵ Under our experimental conditions it is still possible to observe spectrophotometrically the formation of the propionaldehyde nickel complex [Ni(bipy)(propionaldehyde)]. The UV-vis spectrum is very similar to that of [Ni(bipy)(benzaldehyde)], but a much larger excess of propionaldehyde is needed. To exclude the possibility that the green solution obtained during the reaction of propionaldehyde with [Ni(bipy)(COD)] is not [Ni(bipy)(α -methyl- β -ethylacrolein)], formed during the aldol condensation,⁴³ we measured the UV-vis spectrum of this complex by adding α -methyl- β -ethylacrolein to [Ni(bipy)(COD)]. The spectrum is clearly different and shows absorbance maxima at 404 and 628 nm compared to 419 and 662 nm for [Ni(bipy)(propionaldehyde)]. Analogous to the reaction with benzaldehyde, we could study the same reaction with propionaldehyde according to eq 2 ($R = \text{C}_2\text{H}_5$, $R' = \text{H}$, L-L = bipy). Here, addition of COD in a 10-fold excess to the complex solution was not possible because it largely suppressed the reaction. Furthermore, it was necessary to use a higher excess of propionaldehyde in order to follow the reaction to completion. The obtained dependence of the observed rate constant k_{obs} on the concentration of propionaldehyde at different temperatures is again linear with an intercept (Figure 3). Since an excess of COD could not be used, the back reaction is not pseudo-first-order and therefore no rate constants were calculated from the intercept. The second-order rate constants for the reaction of [Ni(bipy)(COD)] with propionaldehyde derived from the slopes are shown in Table 2. The rate constants are approximately a factor of 60 smaller than that for the reaction with benzaldehyde, and the binding

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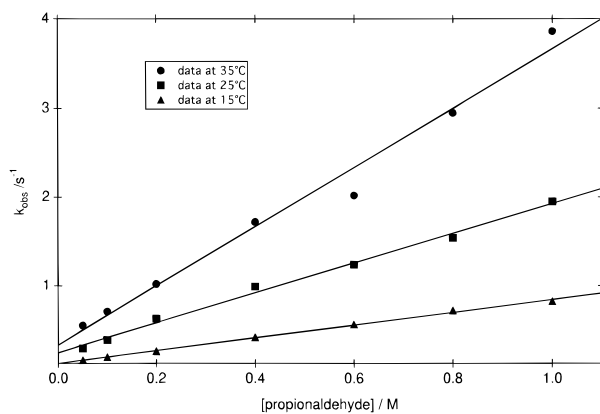


Figure 3. Plot of observed rate constants k_{obs} vs propionaldehyde concentration at different temperatures: $[\text{Ni}(\text{bipy})(\text{COD})]$ concentration = 0.25 mM

Table 2. Second-Order Rate Constants for the Reaction of $[\text{Ni}(\text{bipy})(\text{COD})]$ with Propionaldehyde and $[\text{Ni}(\text{bipy})(\text{propionaldehyde})]$ with COD As Obtained from Eq 3 ($[\text{Ni}(\text{bipy})(\text{COD})]$ Concentration = 0.25 mM)

$T/^\circ\text{C}$	[propionaldehyde] dependence slope, $k_a/\text{M}^{-1}\text{s}^{-1}$	[COD] dependence slope, $k_b/\text{M}^{-1}\text{s}^{-1}$	K ($=k_a/k_b$)
15.0	0.71 ± 0.02	$(0.56 \pm 0.02) \times 10^3$	0.00126
25.0	1.68 ± 0.06	$(0.99 \pm 0.05) \times 10^3$	0.0017
35.0	3.3 ± 0.2	$(1.72 \pm 0.08) \times 10^3$	0.00194
ΔH^\ddagger (kJ/mol)	55 ± 3	39 ± 0.5	
ΔS^\ddagger (J/mol K)	-58 ± 9	-58 ± 2	

of propionaldehyde must therefore be significantly weaker since addition of COD largely suppressed the reaction. The back reaction of COD with the complex $[\text{Ni}(\text{bipy})(\text{propionaldehyde})]$ gave rate constants (Table 2) that are approximately 16 times larger than the ones obtained for the back reaction of the nickel benzaldehyde complex. The overall equilibrium constant K is a factor of 1000 smaller compared to the benzaldehyde reaction with $[\text{Ni}(\text{bipy})(\text{COD})]$. The activation parameters obtained from the temperature dependence of these reactions (Table 2) are similar to those obtained for the reaction of $[\text{Ni}(\text{bipy})(\text{COD})]$ with benzaldehyde, but again it is important to note that these activation parameters do not describe a single-step reaction but are composite values for the combination of several rate constants as discussed above.

Introduction of carbon dioxide into the system allowed us to observe first the formation of $[\text{Ni}(\text{bipy})(\text{propionaldehyde})]$, followed by a slower reaction of this complex with carbon dioxide. Spectral changes occurring during this reaction are shown in Figure 4. The final product is characterized by an absorbance maximum at 475 nm, whereas the absorbance band of $[\text{Ni}(\text{bipy})(\text{COD})]$ at 575 nm disappears during the reaction. The measured rate constant for the first step is the same as that found for the reaction of $[\text{Ni}(\text{bipy})(\text{COD})]$ with propionaldehyde in the absence of carbon dioxide as described above.

The kinetic studies of the slower reaction, the oxidative coupling of carbon dioxide to the $[\text{Ni}(\text{bipy})(\text{propionaldehyde})]$ complex, proved difficult. The reaction with carbon dioxide is quite slow, and partial decomposition of $[\text{Ni}(\text{bipy})(\text{COD})]$ under these conditions was observed. This slow decomposition could be observed in solution without any other reactants present. Sta-

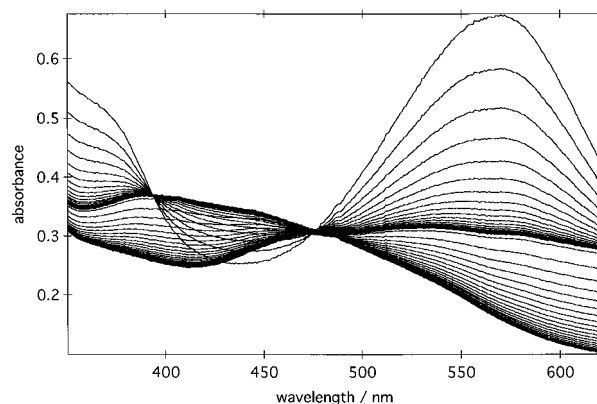


Figure 4. Repetitive scan spectra recorded during the reaction of propionaldehyde and carbon dioxide with $[\text{Ni}(\text{bipy})(\text{COD})]$: propionaldehyde concentration = 0.9 mM, $[\text{Ni}(\text{bipy})(\text{COD})]$ = 1 mM, carbon dioxide concentration = 102.5 mM, solvent = THF, $T = 35^\circ\text{C}$, $\Delta t_1 = 0.06$ s, $\Delta t_2 = 14$ s.

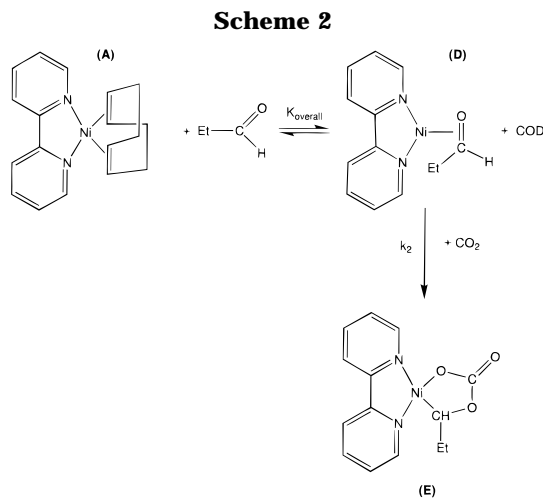
Table 3. Second-Order Rate Constants k_a for the Reaction of Carbon Dioxide with Propionaldehyde and $[\text{Ni}(\text{bipy})(\text{COD})]$ According to Eq 1 ($[\text{Ni}(\text{bipy})(\text{COD})]$ concentration = 1.0 mM)

$T/^\circ\text{C}$	[propionaldehyde] dependence $k_a/10^{-3}\text{M}^{-1}\text{s}^{-1}$ (calculated from slope)	[carbon dioxide] dependence $k_a/10^{-3}\text{M}^{-1}\text{s}^{-1}$ (calculated from slope)
20.0	3.5 ± 0.3	28 ± 4
30.0	5.5 ± 0.2	56 ± 5
35.0		67 ± 5
40.0	11 ± 1.4	
ΔH^\ddagger (kJ/mol)	40 ± 5	43 ± 6
ΔS^\ddagger (J/mol K)	-157 ± 19	-129 ± 19

bilizing the complex by addition of COD was not feasible because this was found to suppress the reaction with carbon dioxide completely. However, it was possible to obtain good kinetic data for the reaction of $[\text{Ni}(\text{bipy})(\text{COD})]$ with propionaldehyde and carbon dioxide according to eq 1. Propionaldehyde and carbon dioxide were always kept in excess over $[\text{Ni}(\text{bipy})(\text{COD})]$ to ensure pseudo-first-order conditions. The dependence of k_{obs} on both (a) carbon dioxide and (b) propionaldehyde concentration at different temperatures showed linear dependence (data are listed in Table 3), and the following formal third-order rate law was obtained (abbreviations for nickel complexes according to Scheme 2):

$$-d[\mathbf{A}]/dt = k[\mathbf{A}][\text{carbon dioxide}][\text{propionaldehyde}] \quad (9)$$

Even though the temperature dependence was measured, decomposition of $[\text{Ni}(\text{bipy})(\text{COD})]$ only allowed the use of a narrow temperature range and the errors of the individual measurements were larger compared to those of the reactions with aldehydes alone. The calculated activation parameters therefore do not represent the true values but indicate the trend in these parameters. The activation parameters were calculated as $\Delta H^\ddagger = 43 \pm 6$ kJ/mol and $\Delta S^\ddagger = -129 \pm 19$ J/(mol K) (carbon dioxide concentration dependence) and $\Delta H^\ddagger = 41 \pm 6$ kJ/mol and $\Delta S^\ddagger = -154 \pm 20$ J/(mol K) (propionaldehyde concentration dependence). The activation parameters for the two data sets are within the



experimental error of each other and the large negative activation entropy confirms the oxidative coupling step; i. e., bond formation and charge creation in the transition state. Unfortunately, high-pressure measurements for activation volumes were not possible because of the extreme sensitivity of the solutions toward dioxygen.

The kinetic measurements confirmed the assumption that no direct reaction of carbon dioxide with the metal center occurs. Instead, the aldehyde is activated and then a reaction with carbon dioxide can take place. The reaction mechanism shown in Scheme 2 is in accordance with the kinetic findings. The first reaction in Scheme 2 is again a fast preequilibrium which summarizes the overall reaction in Scheme 1 using propionaldehyde instead of benzaldehyde. The reaction with carbon dioxide is irreversible, leading to the final product, the five-membered cyclic nickel complex. Since the equilibrium shown in Scheme 2 lies to the left, the rate equation for this reaction reduces to eq 10 for k_{obs} .

$$k_{\text{obs}} = \frac{k_2 K}{[\text{COD}]} [\text{CO}_2] [\text{propionaldehyde}] \quad (10)$$

Inserting K and the values for the concentrations allows us to calculate the rate constant $k_2 \approx 0.1 \text{ M}^{-1} \text{ s}^{-1}$. This value does not differ significantly for carbon dioxide insertion reactions, and more important, the activation parameters for carbon dioxide insertions into metal-carbon, -hydrogen, or -oxygen bonds are quite similar.^{4,44-46} Presumably these reactions go through a very similar transition state. We assume that here the carbon dioxide molecule approaches the [Ni(bi-

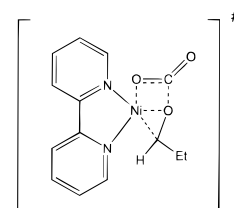


Figure 5. Possible transition state during the reaction of the complex [Ni(bipy)(COD)(propionaldehyde)] with carbon dioxide.

py)(propionaldehyde)] and a four-center transition state is formed as shown by Figure 5. Additional support for the postulated mechanism comes from a theoretical study on formation of the oxanickelacyclopentene complex from nickel(0), carbon dioxide, and alkyne. Here too it has been postulated that alkyne binds to the nickel(0) complex prior to reaction with carbon dioxide.^{47,48}

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 the aldehydes benzaldehyde and propionaldehyde with [Ni(bipy)(COD)] was investigated. It was found that the overall equilibrium constant for the reaction with propionaldehyde is approximately a factor of 1000 smaller compared to benzaldehyde. Our kinetic studies of the reaction of propionaldehyde and carbon dioxide with [Ni(bipy)(COD)] clearly demonstrate that carbon dioxide is not activated by binding with the Ni(0) center but instead reacts with the activated propionaldehyde of the complex [Ni(bipy)(propionaldehyde)].

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