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Mechanistic Insight from Activation Parameters for the Reaction of a Ruthenium Hydride Complex with CO_2 in Conventional Solvents and an Ionic Liquid

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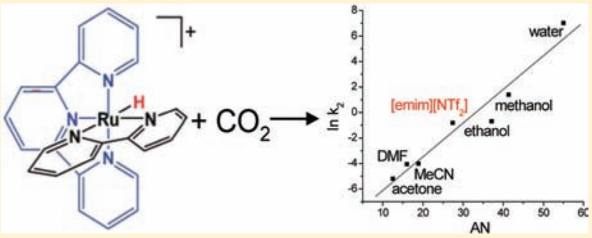
Supporting Information

ABSTRACT: Detailed kinetic studies were performed on the reaction of $[Ru^{II}(terpy)(bpy)H]^+$ (terpy = 2,2′,6′,2″-terpyridine; bpy = 2,2′-bipyridine) with CO_2 in conventional solvents (water, methanol, and ethanol) and in the ionic liquid [emim][NTf_2] ([emim] = 1-ethyl-3-methyl-imidazolium; [NTf_2] = bistrifluoromethylsulfonylamide). Second-order rate constants and activation parameters ($\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta V^{\ddagger}$) were determined for the reaction in all solvents. The second-order rate constants correlate with the acceptor number of the solvent, whereas the activation parameters support the associative nature of the reaction. The results in water, especially the activation entropy (+14 ± 2 J K^{-1} mol^{-1}) and activation volume (−5.9 ± 0.6 cm^3 mol^{-1}), differ significantly from those found for the other solvents.

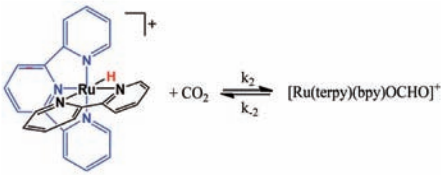


■ INTRODUCTION

Carbon dioxide is one of the most important molecules in human and geological history. Among an abundance of research interests for this molecule, the reduction of CO_2 to a usable resource (fuel or otherwise) is a major goal in current chemical research[1] in an effort to reduce the overall CO_2 output, and at the same time to use the gas generated by several technical and biological processes in a more efficient way.[2−5]

One possible way would be to use a hydride transfer reaction by which CO_2 will first be reduced to formic acid (for use as a C_1 building block in synthesis or a potential way to store hydrogen),[6] followed by reduction to formaldehyde and finally to methanol.[1] The observations by Konno et al.[7] and subsequently by Creutz et al.[8−10] that the activation of hydride in the complex $[Ru^{II}(terpy)(bpy)H]^+$ (**Ru−H**, terpy = 2,2′,6′,2″-terpyridine; bpy = 2,2′-bipyridine) is governed by the acceptor number (AN) of the solvent led us to study the reaction of CO_2 with **Ru−H** in the ionic liquid [emim][NTf_2] ([emim] = 1-ethyl-3-methyl-imidazolium; [NTf_2] = bistrifluoromethylsulfonylamide). In this reaction CO_2 is reduced to form a formate complex (see Scheme 1).

Scheme 1. Reaction of Ru−H with CO_2 Resulting in the Reversible Formation of a Formate Complex



The second-order rate constant, k_2, for this reaction varies by 5 orders of magnitude on changing the solvent (from 5.5×10^{-3} M^{-1} s^{-1} in acetone[7] to up to 850 M^{-1} s^{-1} in water[8] at 25 °C). This is due to the varying stabilization of the hydride ligand in each solvent, which increases or decreases the hydridic character of the complex.[7] Our goal was to investigate whether the reaction when transferred to an ionic liquid such as [emim][NTf_2] occurs at all, and if so to gain more information concerning the influence of the solvent on the hydride transfer process by determining the corresponding activation parameters from the temperature and pressure dependences of the reaction. This ionic liquid was selected on the basis of earlier experience gained in our group on the study of inorganic reaction mechanisms in ionic liquids.[11] We, therefore, redetermined some of the k_2 values reported in the literature for the conventional solvents as a function of temperature and pressure in order to obtain a complete set of activation parameter data ($\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta V^{\ddagger}$) for the solvents methanol, ethanol, water, and [emim][NTf_2], applying stopped-flow techniques.

The value of the acceptor number (AN) is a measure of the electrophilicity of a solvent introduced by Gutmann in 1976,[12] and describes the capability of a solvent to accept electron density. This forms part of a larger concept of solvent polarity that, combined with the donor number (DN), offers one way of classifying solvents by their electronic properties. Other popular methods include the polarity scale of Reichardt and Dimroth,[13] or the Kamlet Taft parameters α, β, and π^*.[14] Marcus et al.[15] found that these polarity models overlap with each other when

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similar electronic properties are concerned; e.g., DN and AN for organic solvents can be correlated with β and α from the Kamlet Taft parameters, respectively. This is not the case though for ionic liquids, where DN still correlates with the β parameter, although in a much more complex way. The correlation of AN with the α parameter is, however, largely nonexistent.[16] By investigating the reaction in an ionic liquid, we wanted to verify the applicability of the AN or α parameter as a guideline for hydride transfer reactions in nonconventional solvents.

■ RESULTS AND DISCUSSION

Preliminary Observations. In general we studied the reaction of the **Ru−H** complex with CO_2 under pseudo-first-order conditions as a function of CO_2 concentration, temperature, and pressure in different solvents, in order to determine the second-order rate constant, k_2, and the corresponding activation parameters $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta V^{\ddagger}$. The solvents used were methanol, ethanol, water, and [emim][NTf_2]. In all solvents the reaction proceeds too fast for the conventional tandem cuvette technique, and stopped-flow methods had to be applied. To find a suitable wavelength for the stopped-flow studies, tandem cuvette experiments were used to record the UV−vis spectra before, during (where possible), and after the reaction. Typical spectral changes that accompany the reaction are shown in Figures 1 and S1 (Supporting Information). The selected wavelengths for the kinetic measurements were 560 (methanol and ethanol), 550 ([emim][NTf_2]), and 530 nm (water).

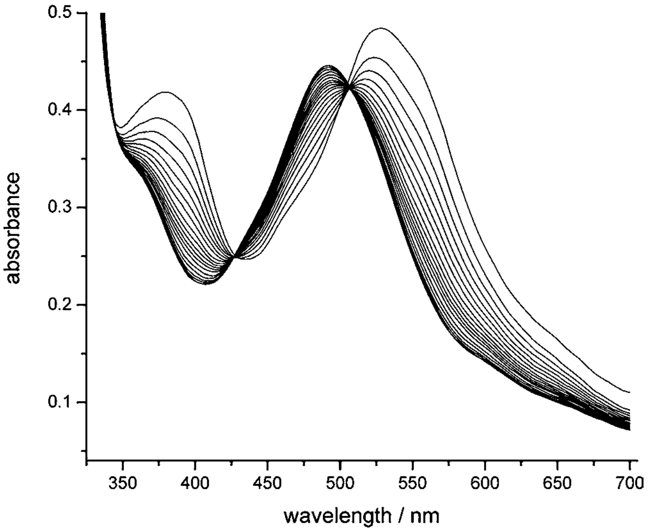

Figure 1. Typical UV−vis spectral changes recorded for the reaction of **Ru−H** with CO_2 in [emim][NTf_2]. Experimental conditions: [**Ru−H**] = 0.08 mM, [CO_2] = 1 mM, T = 25 °C, reaction time 1 h.

Earlier experience obtained in our group showed that stopped-flow kinetic measurements with ionic liquids (ILs) are often hindered by the physical properties of the IL.[17] The higher viscosity of ILs compared to conventional solvents can lead to delays with the mixing of the reactant solutions in the stopped-flow apparatus, especially at elevated pressure. In the case of [emim][NTf_2] employed in this study, the kinetic traces measured at ambient pressure were not influenced by the viscosity of the IL and showed single-exponential curves. The larger dead time associated with the IL was negligible because the reaction in IL was slow enough so that the first 50−100 ms of the kinetic traces could be deleted without affecting the resulting fit. Measurements at higher pressure showed a subsequent drift in the absorbance that increased with increasing pressure. These kinetic traces had to be fitted with a two-exponential function to correct for this drift (for a typical example see Figure S2 in Supporting Information). Figure 2 shows a typical kinetic trace including its one-exponential fit recorded for the reaction in methanol under ambient conditions. The large absorbance change observed for the reaction at the selected wavelength is rather similar for all the studied solvents.

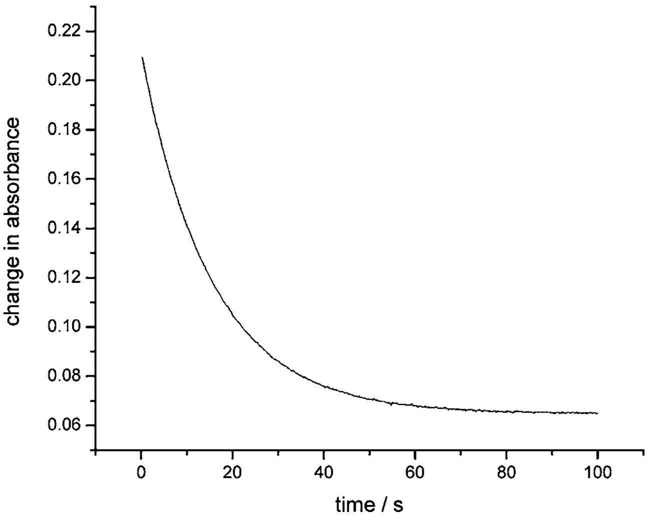

Figure 2. Representative kinetic trace recorded at 560 nm for the reaction of **Ru−H** with CO_2 in methanol including the fitted curve. Experimental conditions: [**Ru−H**] = 0.03 mM, [CO_2] = 14 mM, T = 25 °C.

Concentration and Solvent Dependence. From a plot of the observed rate constant k_{obs} versus the concentration of CO_2, the slope of the linear fit represents the second-order rate constant k_2. Figure 3 shows the concentration dependence of k_{obs} for the reaction in [emim][NTf_2] under ambient

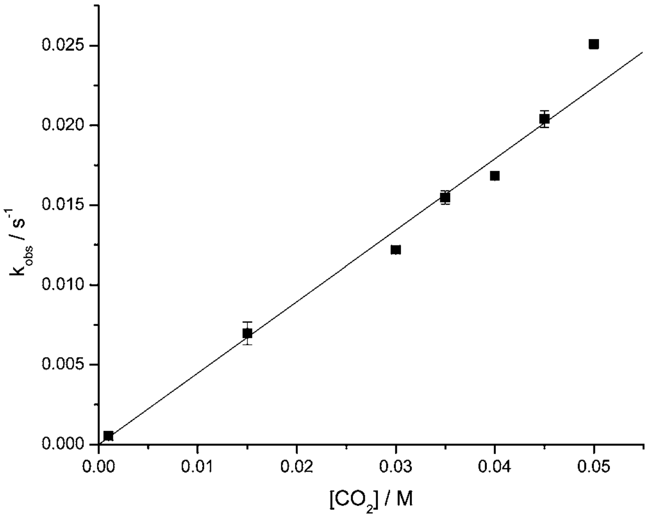

Figure 3. Concentration dependence of k_{obs} for the reaction of Ru−H with CO_2 in [emim[NTf_2] at 25 °C.

conditions. The linear fit shows no significant intercept, and similar results were found for all other solvents studied (see Figure S3 in Supporting Information). Therefore, possible parallel or reverse reactions can be excluded.

The measurements of the CO_2 concentration dependence in methanol, ethanol, and [emim][NTf_2] were all straightforward, and the results are summarized in Table 1. The literature values for k_2 in methanol and ethanol are consistent with our data, and the k_2 value for the reaction in [emim][NTf_2] is close to that found for ethanol. Studying the reaction in pure water proved to be more challenging. Dissolving the **Ru−H** complex in water resulted in an unstable and only slightly violet solution (see Experimental Section), different compared to the intensive violet color when the complex was dissolved in the other solvents. On comparing this finding with the results obtained for the other solvents, we realized that the complex is not stable enough in pure water to extensively study the reaction with CO_2 since it reacts with the protons present in water (even at a low proton concentration of 10^{-7} M at neutral pH) to produce dihydrogen.[10] Because of the high reaction rate of the complex with CO_2 in water, it was still possible to measure the concentration dependence, but longer measurements were inhibited. By dissolving the complex in basic solution at pH 9.5, the solution was then also violet with λ_{max} at 505 nm, and turned out to be stable for several hours. Large spectral and absorbance changes were now observed for the reaction with CO_2 as found for the other solvents studied (see Figure S4 in Supporting Information). Concentration dependence measurements with both complex solutions in water (at pH 7 and pH 9.5) gave the same results.

Table 1. Values of k_2 for the Reaction of Ru−H with CO_2 at 25 °C and Characteristic Solvent Parameters

solvent	k_2/M^{-1} s^{-1} this work	k_2/M^{-1} s^{-1} literature values[7]	AN	α
[emim][NTf_2]	0.447 ± 0.004	not studied	27.4[16]	0.627[18] 0.76[19]
EtOH	0.50 ± 0.01	0.464	37.1[7]	0.86[15]
MeOH	4.08 ± 0.01	4.69	41.3[7]	0.98[15]
water	1320 ± 30	850	55[8]	1.17[15]

The resulting k_2 value for the reaction in water was found to be somewhat different than the value reported in the literature (k_2 = 1320 M^{-1} s^{-1} at 25 °C compared to 850 M^{-1} s^{-1} reported by Creutz et al.[8]). Nevertheless, the data still underline the fact that the reaction is much faster in water than in the other solvents studied.

Konno et al. already noticed the dependence of k_2 on the AN of the solvent.[7] Figures 4 and 5 show plots of ln(k_2) versus the AN and α parameter, respectively, with water being excluded from the fit in Figure 5. Although the second-order rate constant k_2 is essentially the same for ethanol and [emim][NTf_2], the AN of the latter is somewhat lower, and the α parameter of the IL even more so (see Table 1). Although the literature values of α for the IL vary considerably, the overall accuracy of the correlations still remains reasonable.

There are several possible reasons for the high reaction rate found in water as solvent. Water was found to have a decisive impact in several studies that concerned the hydrogenation of carbon dioxide with the help of transition metal complexes, either as ligand itself or as solvent, by forming hydrogen bonds with the reactants and thus changing their reactivity.[20,21] In the case of the **Ru−H** complex, water as a ligand can be excluded since no coordination site on the metal center is accessible for a water molecule. Also, Creutz et al. found no evidence for coordinated water molecules.[10] Theoretical observations on the reaction mechanism by Creutz et al.[10] show that solvent water molecules have a decisive influence on the transition state of the reaction, by forming hydrogen bonds with the oxygen atoms of the inserting carbon dioxide during the transition state. Also, water molecules hydrogen-bonded to the reactant **Ru−H** and the resulting formate complex are certain to play an important role and could account for the drastic increase in reaction rate. The AN of water seems to account for this influence more accurately than the α value.

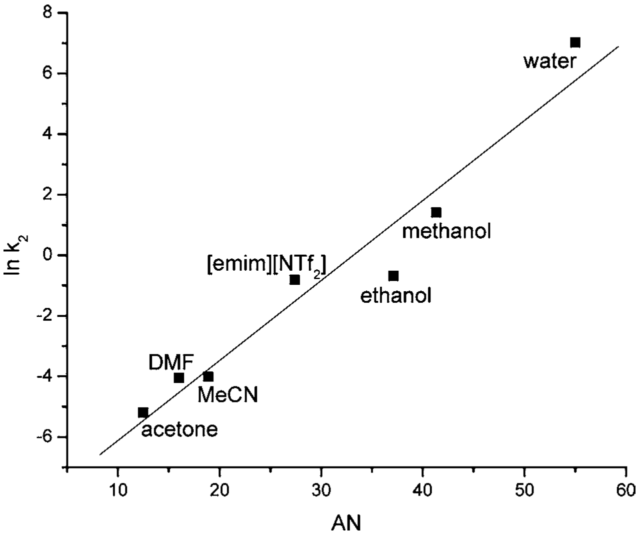

Figure 4. Relationship between ln k_2 and the acceptor number (AN) for various solvents (k_2 values and AN of acetone, DMF, and MeCN taken from Konno et al.[7]).

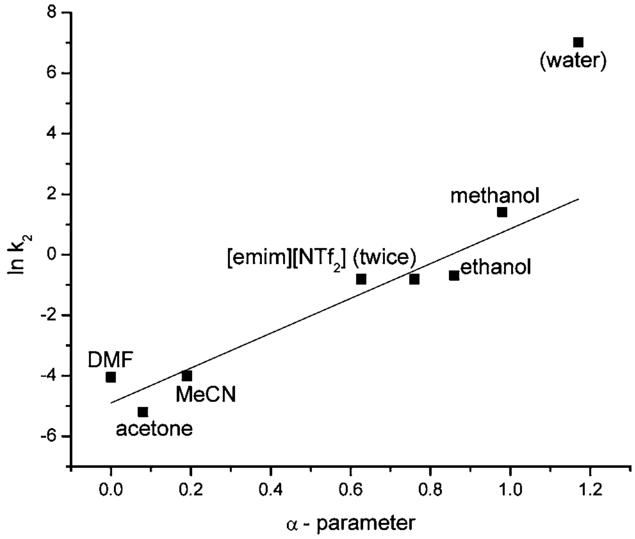

Figure 5. Relationship between ln k_2 and the Kamlet Taft parameter α for various solvents, with water not included into the fit (k_2 values for acetone, DMF, and MeCN taken from Konno et al.,[7] α parameter for these solvents taken from Marcus[15]).

Temperature and Pressure Dependence. Temperature and pressure dependence studies were performed to determine the activation parameters of the reactions. An exemplary Eyring plot is shown in Figure 6, and those for the other solvents are reported in Figure S5 (Supporting Information).

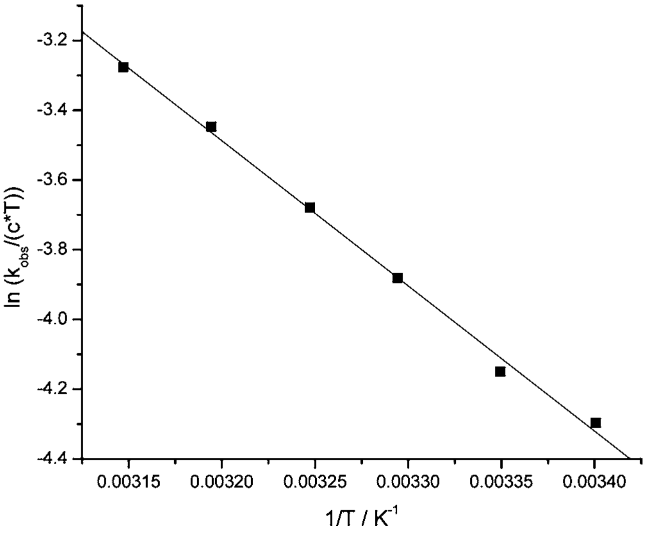

Figure 6. Eyring plot for the temperature dependence of the reaction of **Ru−H** with CO_2 in methanol. Experimental conditions: [**Ru−H**] = 0.05 mM, $[CO_2]$ = 56 mM.

In the case of the pressure dependence of a rate constant, in most cases a linear plot of ln k versus pressure is found in the pressure range up to 150 MPa. Under such conditions the volume of activation is independent of pressure and can be obtained from the slope of the plot, $(\delta \ln k/\delta P)_T = -\Delta V^{\ddagger}/RT$. However, in some cases where the volume of activation depends on pressure, i.e., the transition state is compressible, the plot of ln k versus pressure is curved and other relationships have to be applied.[22] In the case of ethanol, methanol, and [emim][OTf_2], the pressure dependence plots found in this study appeared to be curved and were fitted with an equation given in eq 1[22] instead of using the more common linear fit. In this case the volume of activation is calculated from the initial slope of the plot, where $\Delta V^{\ddagger} = -bRT$ for b = slope, R = 8.314 cm^3 MPa mol^{-1} K^{-1}, and T = 298 K. Figure 7 shows the plot of ln k_{obs} versus pressure for methanol as solvent (for all other solvents see Figure S6 in Supporting Information). For water as solvent, linear fits were used for the interpretation of the pressure dependence since no meaningful curvature was observed.

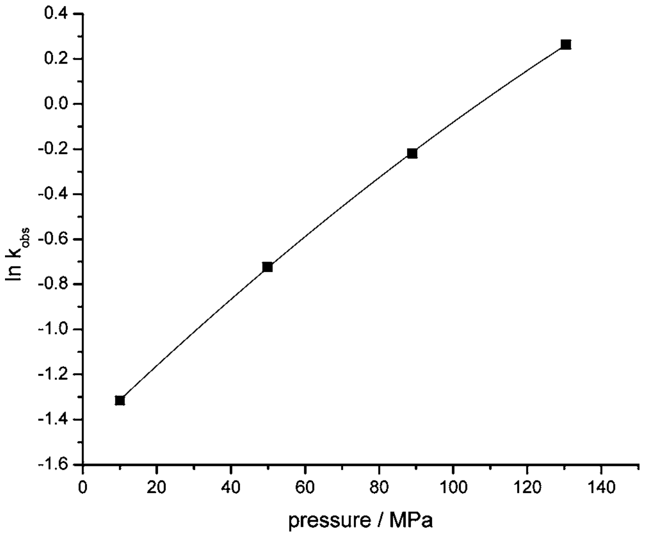

Figure 7. Pressure dependence of the reaction of **Ru−H** with CO_2 in methanol at 25 °C and $[CO_2]$ = 56 mM.

$$\ln k = a + bP + cP^2 \qquad (1)$$

In the case of water as solvent, the temperature and pressure dependence of the CO_2/HCO_3^- equilibrium has to be taken into account since the CO_2 concentration can vary due to the temperature and pressure dependence of reaction 2.

$$CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+ \qquad (2)$$

On using the CO_2/HCO_3^- system itself as buffer, the equilibrium is shifted to the right on increasing both temperature and pressure (ΔH° = 9.15 kJ mol^{-1}, ΔS° = −90.9 J K^{-1} mol^{-1}, ΔV° = −25.6 cm^3 mol^{-1}).[23,24] On the basis of these parameters the pH value of the system decreases from 5.8 to about 5.2 on going from ambient to 130 MPa pressure (for $[CO_2]$ = 1.75 mM and $[HCO_3^-]$ = 0.5 mM at ambient pressure). Although the proton concentration obviously changes in this case, the resulting CO_2 concentration is only marginally influenced, as it is much higher than the proton concentration. Therefore, no correction of the CO_2 concentration had to be made for the determination of $\Delta V^{\ddagger}$. On using MES buffer (2-(N-morpholino)ethanesulfonic acid, pK_a = 6.15 at 20 °C)[25] at a concentration higher than that of the CO_2/HCO_3^- buffer, the proton concentration is now stable since the MES buffer equilibrium is almost independent of the pressure.[26] However, by keeping the proton concentration constant, the shift in the CO_2/HCO_3^- equilibrium has a more pronounced impact on the CO_2 concentration, which now diminishes significantly with increasing pressure and has to be corrected for (a $[CO_2]$ of 1.75 mM at ambient pressure decreases to 1.07 mM at 130 MPa). In both cases, in the presence or absence of MES buffer, the resulting activation volume was found to be the same after the described corrections had been made.

In the case of the temperature dependence of the reaction in water, the results for the thermal activation parameters were found to be the same for both the MES and CO_2/HCO_3^- buffered solutions. This is due to the fact that both buffer equilibria exhibit nearly the same change in their pK_a values as a function of temperature.[26,27] The CO_2 concentration was not affected in both cases and no correction was required. Table 2 summarizes all the activation parameters determined.

Table 2. Summary of All Activation Parameters Determined

solvent	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}	$\Delta V^{\ddagger}$/cm^3 mol^{-1}
[emim][NTf_2]	33.8 ± 0.5	−138 ± 2	−14.4 ± 1.8
EtOH	40.7 ± 0.5	−114 ± 2	−35.9 ± 1.0
MeOH	34.6 ± 1.0	−116 ± 3	−39.3 ± 0.8
water	59.1 ± 0.6	+14 ± 2	−5.9 ± 0.6

The activation volume consists of two components, the intrinsic volume change that is generated by bond breakage or bond formation and the volume change caused by solvation changes. The latter part normally plays a larger role in cases where charge is generated or neutralized on going to the transition state.[28] In the present reaction, where CO_2 is inserted into the Ru(II)−H^- bond, the intrinsic volume change has to be largely negative, as there is no leaving ligand. Also, as there is no overall change in charge on the complex on going to the transition state, the activation volume should mainly reflect the associative nature of the CO_2 insertion reaction.

As expected in the case of methanol and ethanol, the results show that the reaction follows such a mechanism with a negative activation entropy, and negative activation volume that is of the order of the partial molar volume of CO_2. The situation seems to be more complex in the case of water and [emim][NTf_2] as solvent. For the IL the activation entropy is even somewhat more negative than in the case of methanol or ethanol, but the activation volume is more positive than that found for ethanol and methanol, suggesting that less bond formation occurs in the transition state of the insertion process. The partial molar volume of CO_2 in ionic liquids seems to be in the range of that in conventional solvents, viz. 39.4 $cm^3\ mol^{-1}$ in [hmim][Ntf_2], an ionic liquid with the same anion but a longer alkyl chain on the cation.[29] Other partial molar volume measurements of CO_2 or other dissolved gases in ILs are still very rare. A molecular dynamics study by Huang et al. showed that supercritical CO_2 behaves quite differently.[30] The partial molar volume of supercritical CO_2 dissolved in [bmim][PF_6] or other ILs is very low compared to that of bulk supercritical CO_2. The study accounts for this behavior in terms of cavities that are formed by the IL components which can be occupied by CO_2 molecules. Such an effect may also partially account for the significantly more positive activation volume found for the reaction in [emim][NTf_2]. The partial molar volume of gases in ILs is obviously not yet completely understood, which certainly complicates the interpretation of the activation volume measured in [emim][NTf_2].

In the case of water as solvent, the activation entropy and activation volume become even more positive, indicating that the insertion process is presumably controlled by other factors than simply bond formation. As discussed before, hydrogen-bonded water molecules play an important role in the insertion process and account for the rather peculiar activation parameters. The intrinsic volume change is expected to be the same as for the other solvents studied, but the formation and breakage of hydrogen bonds on going to the transition state could affect local charge formation/neutralization and contribute towards the observed volume of activation in terms of solvational changes. Similar effects can also account for the significantly more positive activation entropy found for the reaction in water.

CONCLUSIONS

The system of AN and α parameter offers a picture of ionic liquids that can help to predict the reaction rate of **Ru−H** with CO_2. Further studies on ionic liquids with different cationic or anionic components could offer more insight into the use of such solvent parameters for the application of ionic liquids in hydride transfer reactions.

The activation parameters underline the nature of the insertion reaction, but the values for the reaction in the ionic liquid and water show that the solvational component contributes significantly to the activation volumes and activation entropies found in these solvents. Computational studies on the transition state of this reaction including the solvation shell of water show that hydrogen-bonded water molecules play an important part in the acceleration of the reaction and the activation parameters.

EXPERIMENTAL SECTION

Materials. All chemicals used were of analytical reagent grade and of the highest purity commercially available. The organic solvents used for spectroscopic measurements and synthetic work were purchased from Acros Organics at the highest purity commercially available. The water used for spectroscopic measurements was freshly prepared Milli-Q water bubbled with argon to exclude HCO_3^- contamination. CO_2 was obtained from Air Liquide at 99.95% purity.

Synthesis. The Ru(II)−hydride complex [Ru(terpy)(bpy)H]$^+$ (**Ru−H**) (terpy = 2,2′:6′,2″-terpyridine, bpy = 2,2′-bipyridine) was synthesized using a modification of the synthesis described in the literature.[7] To a deaerated solution of [Ru(terpy)(bpy)Cl]PF_6 (263.0 mg) in a mixture of ethanol (43 mL) and water (20 mL) was added an aqueous solution of $NaBH_4$ (279.0 mg) dropwise, and then the mixture was refluxed for 20 min under Ar atmosphere. After addition of a saturated aqueous solution of KPF_6 (1 mL) to the mixture at room temperature, the solution was evaporated under reduced pressure at room temperature to obtain a dark oily liquid. This liquid was then purified by column chromatography with a solvent mixture of 3:1 MeCN/toluene using basic aluminum oxide (**Ru−H** is very acid sensitive, even neutral aluminum oxide already reacts with the product and drastically lowers the yield). The chromatographic purification should be carried out under Ar atmosphere and reduced light. The first violet band was collected, and the solvent was removed under reduced pressure at room temperature to yield a dark violet solid of **Ru−H**. The product was identified by ^1H NMR spectroscopy, giving the characteristic singlet at −14.7 ppm[8] (see Figure S7, Supporting Information). As noted by Konno et al.,[7] the complex does not react with oxygen, but very rapidly with CO_2 and thus has to be stored under an inert gas atmosphere. The precursor complexes of **Ru−H**, viz. Ru(terpy)Cl_3 and [Ru(terpy)(bpy)Cl]PF_6, were synthesized as described in the literature.[31,32] The **Ru−H** complex is stable for at least several hours in organic solvents and in the ionic liquid [emim][NTf_2]. It immediately reacts with the ionic liquid [emim][OTf] ([OTf] = trifluoromethylsulfonate), which was the first IL used in preliminary experiments with the complex because of its high AN.

[emim]Br and Li[NTf_2] were purchased from IoLiTec GmbH; [emim]Br was purified at least two times by recrystallization to reach the desired purity and was obtained as a white solid. [emim][NTf_2] was synthesized according to an anion metathesis procedure described in the literature.[33]The resulting [emim][NTf_2] was washed with water at least eight times to remove halide residues. It was then treated with activated charcoal, dried under vacuum, and obtained as a colorless liquid. The water content of the IL was found to be 70−90 ppm as determined by Karl Fisher titration.

Instrumentation, Measurements, and Analysis of Data. Karl Fisher titrations were done on a 756 KF coulometer. NMR spectroscopy (Bruker Avance DRX 400WB FT spectrometer) was used for chemical analysis and compound characterization. UV−vis spectra and slow kinetic measurements were recorded in gastight tandem cuvettes with an optical path length of 0.88 cm on a Varian Cary 1G spectrophotometer and an AnalyticJena Specord S 600 spectrophotometer, both equipped with a thermostatted cell holder. Stopped-flow kinetic measurements at ambient pressure were performed on a Durrum D110 (Dionex) stopped-flow instrument with 2 cm optical path length in the case of the ionic liquid, and on an Applied Photophysics Spectra Kinetic stopped-flow instrument with a 1 cm optical path length for all other solvents. Rapid-scan measurements were made with the help of a J&M Tidas detector. High pressure stopped-flow experiments were performed at pressures up to 130 MPa on a custom-built instrument with n-heptane as pressure medium as described elsewhere.[34] The temperature of the instruments was controlled with an accuracy of ±0.1 K.

The reactions were studied under pseudo-first-order conditions by using at least a 10-fold excess of CO_2. All listed rate constants represent the average value of at least five kinetic runs under each experimental condition. Kinetic traces were analyzed with the use of OriginPro 7.5 SR0 (Originlab Corporation) software. All kinetic traces were fitted with a single exponential function, except for the pressure dependence measurements in the ionic liquid. These kinetic traces had to be fitted with a double exponential function to compensate for a slow drift in absorbance, which was already encountered in our earlier work on pressure dependences in ionic liquids.[17]

Preparation of Solutions. Solvents were saturated with Ar before use, and the preparation of the complex solutions was performed under Ar atmosphere. The complex concentration was chosen between 0.03 and 0.1 mM **Ru−H**. In all solvents except water, the complex dissolved readily and the violet solution was stable for at least a day. In the case of water as solvent, the solution of the complex was not stable in pure water. The complex dissolved very poorly and had to be stirred for up to 30 min to reach a high enough concentration for the measurements. In this time the complex already started to react with the protons in solution to produce hydrogen. Although this reaction is not very fast at pH 7,[10] only concentration dependence measurements could be performed. The solution was not stable enough for longer measurements like temperature and pressure dependences. Using an ultrasonic bath for faster dissolution led to the destruction of the complex. By dissolving the complex in water at pH 9.5 (adjusted by NaOH), it dissolved much more readily and stayed stable enough for at least 12 h, enabling us to perform measurements in water which required several hours with a single stable complex solution.

CO_2 solutions were prepared by bubbling the gas through the solvent to reach maximum solubility and then diluting this solution via gastight syringes to receive the desired concentration. In the case of water, the solution was buffered at pH 5.8 by bubbling CO_2 through a solution of 10 mM HCO_3^- in water, using the CO_2/HCO_3^- equilibrium itself as buffer (Henry constant $K_h = 0.0339$, $pK_{a1} = 6.35$, $pK_{a2} = 10.33$ at room temperature and low ionic strength[35]). The mixture was then diluted with pure water to obtain the desired CO_2 concentration. The CO_2 buffer assured a pH of 5.8 during mixing and measurement, and the pH jump that occurred during mixing did not interfere. Comparative measurements showed the same results for the concentration dependence for both complex solutions (neutral and alkaline). For measurements at elevated temperature and pressure, the CO_2 solution was diluted with a MES buffer solution at pH 5.8 and low ionic strength (at least 10 times more than the HCO_3^- concentration, though at most $I = 0.05$ M), to overrule the CO_2/HCO_3^- buffer. Both CO_2/HCO_3^- buffered and MES buffered solutions were used for measuring the activation parameters.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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