

Supplementary Material

Rapid Transfer of Hydride Ion from a Ruthenium Complex to C₁ Species in Water

Carol Creutz and Mei H. Chou

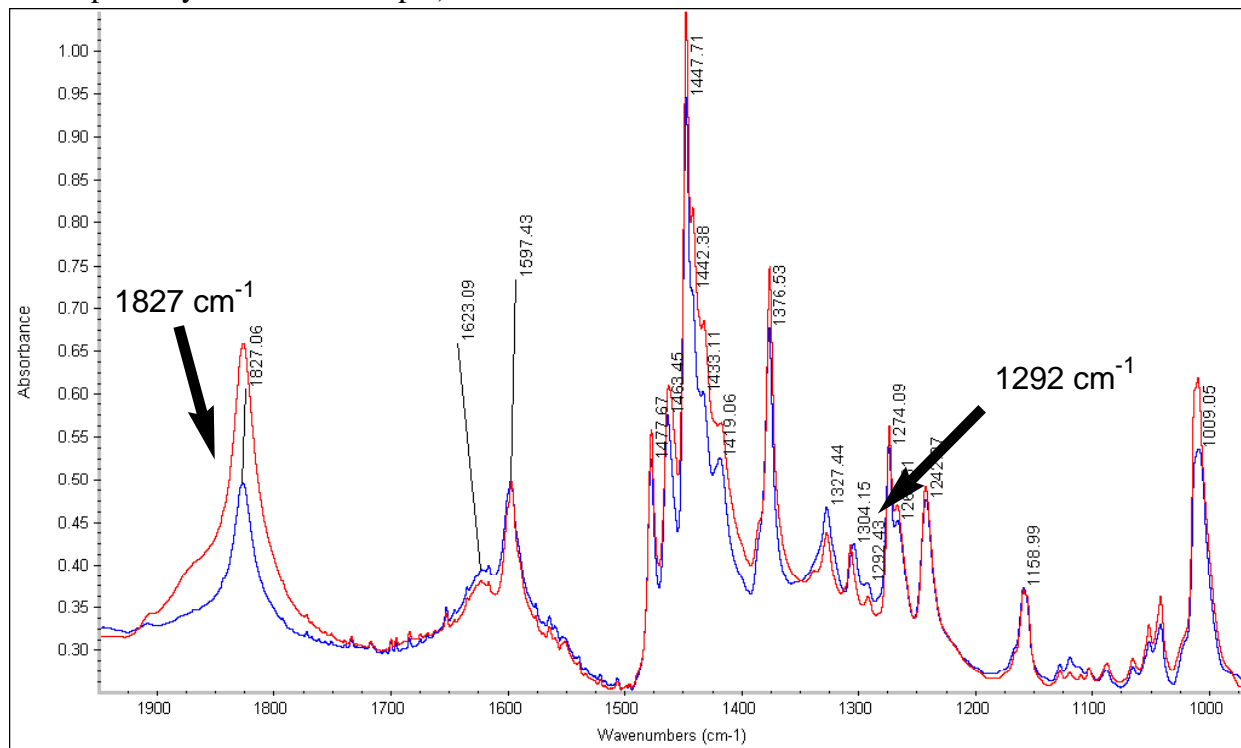
*Chemistry Department, Brookhaven National Laboratory, Upton, New York
11973-5000*

Contents

Experimental Details.....	2
Carbon Dioxide Studies	4
Kinetics	4
Identification of products.....	5
What is the reactant in water? CO ₂ , H ₂ CO ₃ , HCO ₃ ⁻ . ? pH jump experiment	7
CO Studies:	8
Kinetics	8
Product studies	9
Hydrolysis	10
Formaldehyde Studies.....	11
Kinetics of Reaction of RuH ⁺ with formaldehyde:.....	11
Product characterization.....	13
The hydricity of formate.	15

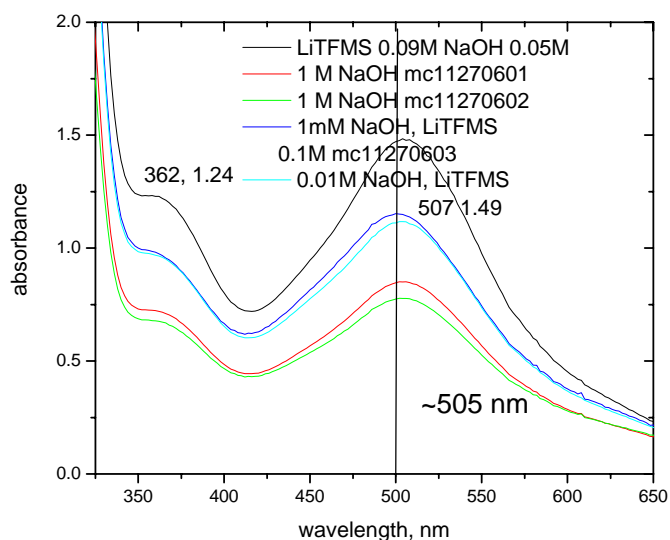
Experimental Details

The hydride complex $[\text{Ru}(\text{terpy})(\text{bpy})\text{H}][\text{PF}_6]$ was prepared as described¹: ^1H NMR ($\text{DMSO}-d_6$ $\delta = -14.7$ in agreement with lit.;¹ IR (KBr pellet) ν_{H} 1827 cm^{-1} , ν_{D} 1292 cm^{-1} (in the spectrum below, the red curve is for all protio $[\text{Ru}(\text{terpy})(\text{bpy})\text{H}][\text{PF}_6]$, while the blue curve was obtained with a partially deuterated sample)

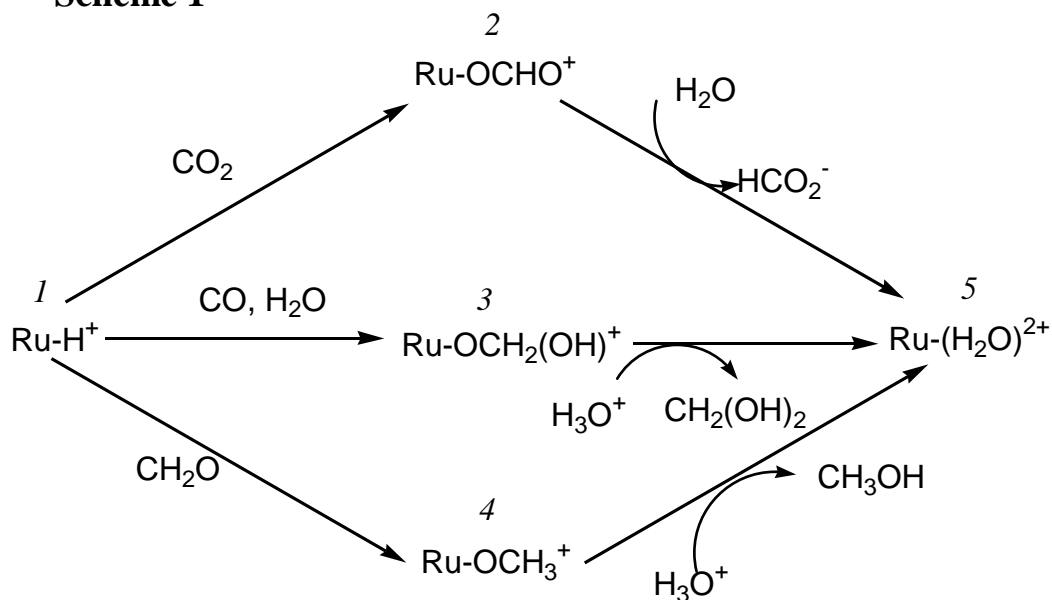


UV-vis 500 nm ($8.5 \times 10^3\text{ M}^{-1}\text{ cm}^{-1}$); mass spec 490 ^{102}Ru .

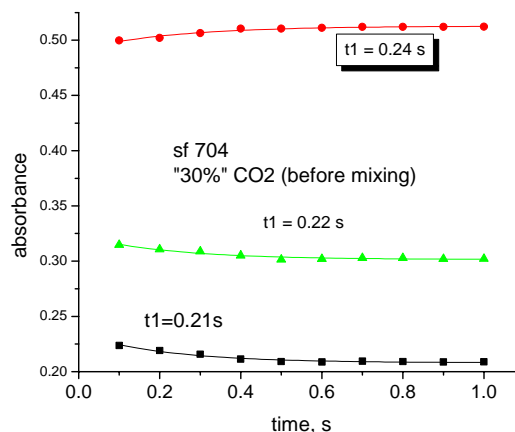
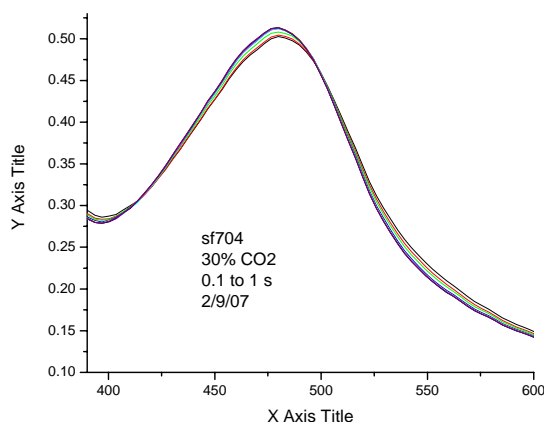
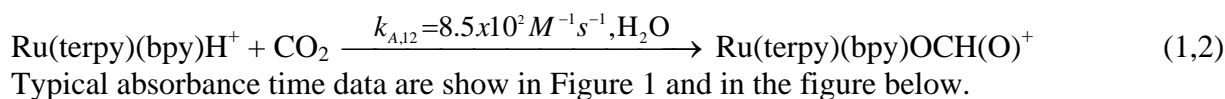
The hydride complex cannot be deprotonated up to pH 14 as indicated by the invariance of the MLCT band between pH 9 (not shown below) and 1 M NaOH.



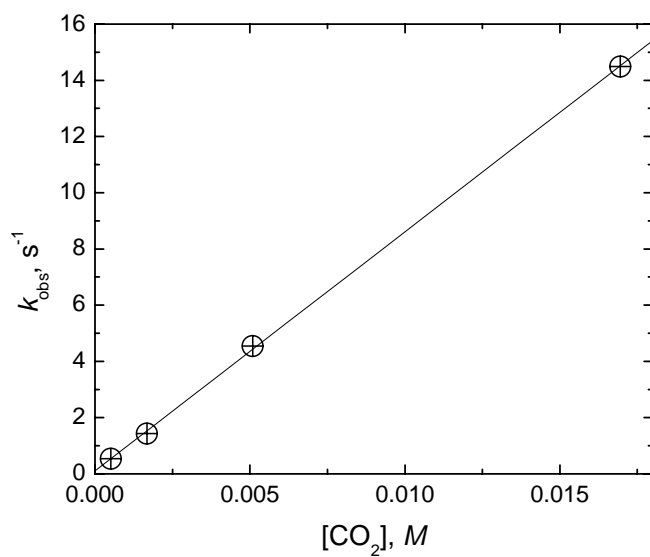
The hydride complex undergoes very rapid exchange with the deuterons of D_2O , CD_3OD , and C_2D_5OD , probably via a dihydrogen complex, and reacts with acid ($k < 10^3 M^{-1}s^{-1}$) to yield dihydrogen (yield $\geq 60\%$); the kinetics and mechanism of these reactions are currently under study. As noted by Konno et al.¹, the hydride complex is not oxygen sensitive, but must be rigorously protected from the carbon dioxide in air. Thus reagents were prepared under argon with freshly drawn millQ water and transferred with use of syringe techniques. Kinetics runs were carried out with 0.03 to 0.1 mM RuH^+ and the C_1 species in at least 10-fold excess. Experiments with CO used 100% and 50% CO/50% Ar-saturated solutions in water (0.94 and 0.47 mM, respectively). Commercial CO_2 /Ar mixtures were used to vary the $[CO_2]$ and the reactions were monitored by diode array on Applied Photophysics stopped-flow spectrometer. Mass spectra were simulated using Isotope Distribution Calculator (<http://www2.sisweb.com/mstools/isotope.htm>) and monitored on a Thermo Finnigan LCQ MS. Samples for comparison with the products of C_1 reactions were synthesized as follows: CO_2 was reacted with RuH^+ in methanol to give the O-bonded formate complex as established by x-ray crystal structure by Konno et al.¹ The formaldehyde adduct was prepared through reaction of $Ru(terpy)(bpy)(H_2O)^{2+}$ with formaldehyde at pH 9 (borate buffer); this reaction is relatively rapid, evidently involving Ru-OH attack on CH_2O (substitution on carbon, not ruthenium). The methanol complex was prepared by dissolving $Ru(terpy)(bpy)(H_2O)[PF_6]_2$ in methanol for an hour. The digitized absorbance-time data from kinetics runs were least-squares-fit to exponential function using OriginTM.

Scheme 1**Carbon Dioxide Studies**

Binding of CO₂ to Ru-H⁺ causes a small blue shift in the MLCT band near 500 nm. Subsequent hydrolysis of the formate complexes yields $\lambda_{\text{max}} = 476$ nm, characteristic of the aquo complex,² as is supported by ESI-MS studies. In support of these conclusions, an “authentic” sample of [Rh(terpy)(bpy)(HCO₂)]⁺, prepared in methanol as reported by Konno et al.¹ exhibited the same behavior.

Kinetics

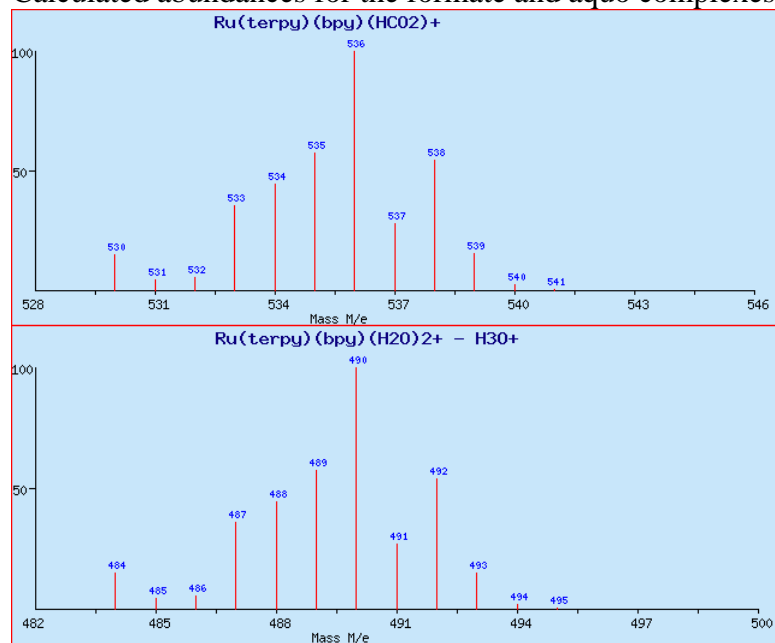
Individual runs are first-order in the ruthenium complex and the dependence on [CO₂] is first order as well as shown in the plot below.



Identification of products.

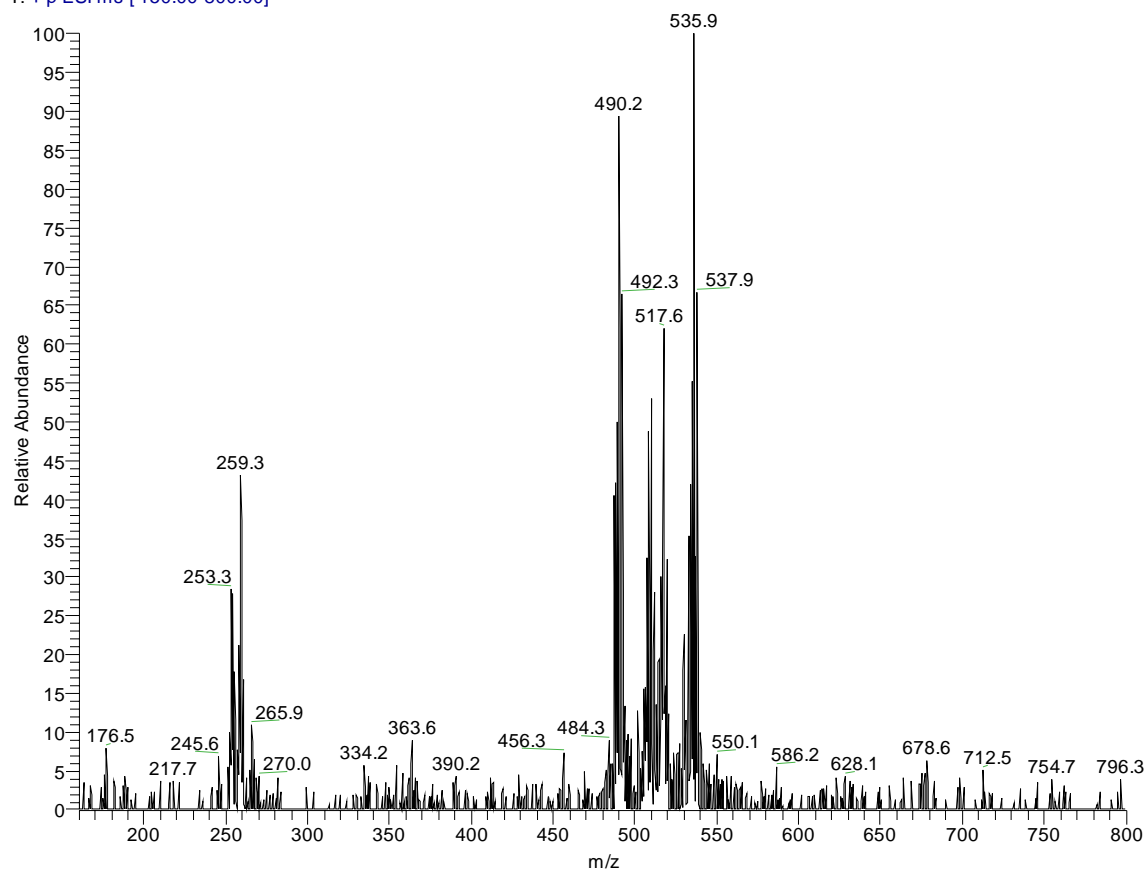
With carbon dioxide. N. B. There are 7 Ru isotopes; ¹⁰²Ru is most abundant.

Calculated abundances for the formate and aquo complexes:

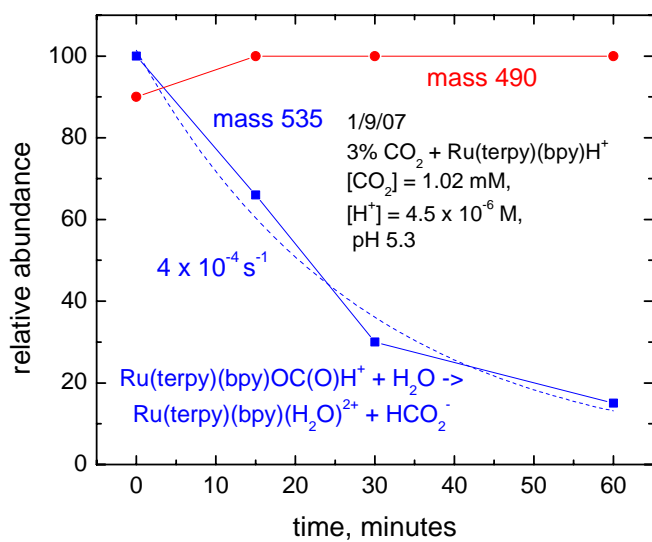


Observed abundance

2007010902 #1 RT: 0.01 AV: 1 NL: 2.87E6
T: + p ESI ms [150.00-800.00]

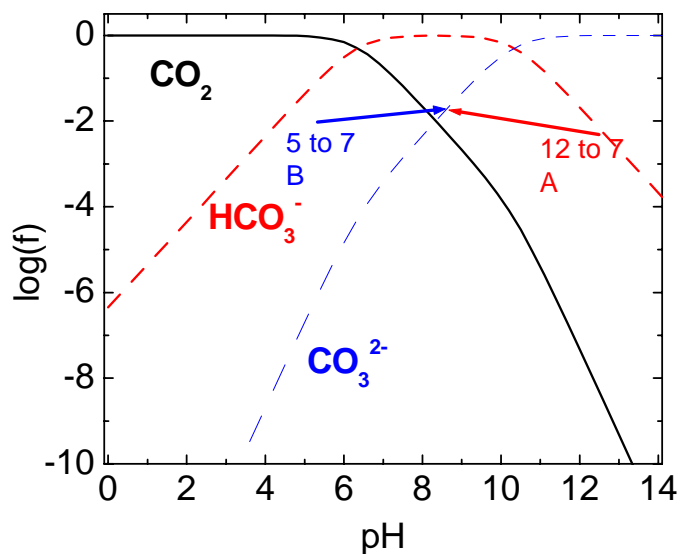


Observed ESI-MS, 1-2 minutes after mixing.
Time profile of the ESI-MS peaks:.

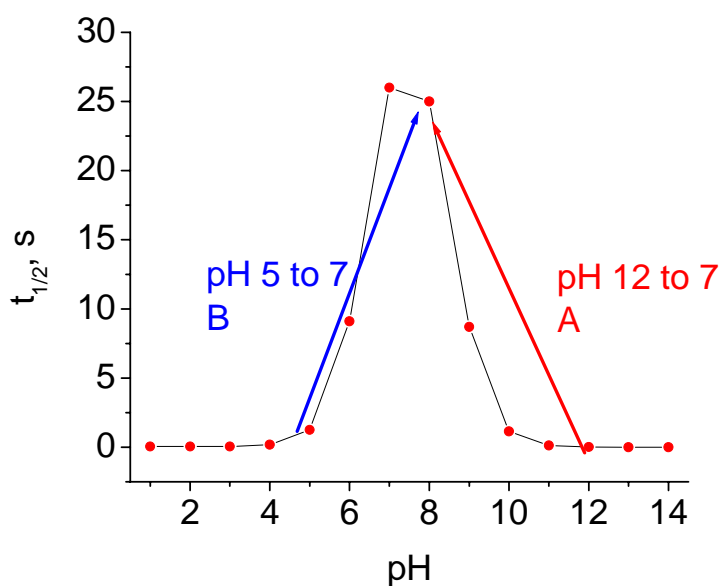


What is the reactant in water? CO_2 , H_2CO_3 , HCO_3^- . ? pH jump experiment

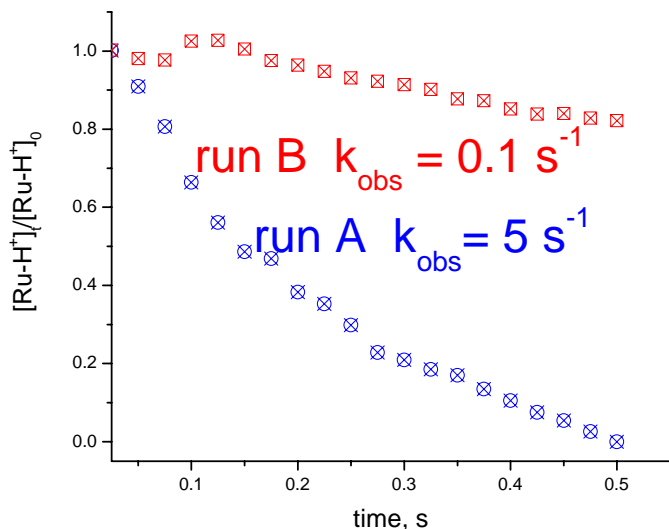
The equilibrium composition of aqueous carbon dioxide solutions depends upon pH as shown at the right, where $\log(f)$ is the logarithm of the fraction of each of the sum of all species present.. We will compare runs A and B, where solution A is held at pH 5 before mixing with the hydride complex at pH 7 and carbonate solution B is held at pH 12 prior to mixing with the hydride complex at pH 7.



The equilibration time for carbon dioxide solutions depends upon pH, being fairly slow near neutral pH as shown below.^{3,4}

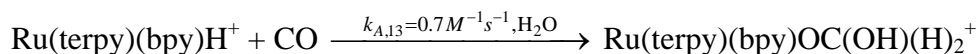


At pH 7 we measure the rate of reaction of $\text{Ru}(\text{bpy})(\text{terpy})\text{H}^+$ with “carbonate” solutions stored at pH 5 (A) and pH 12 (B) and observe the following.



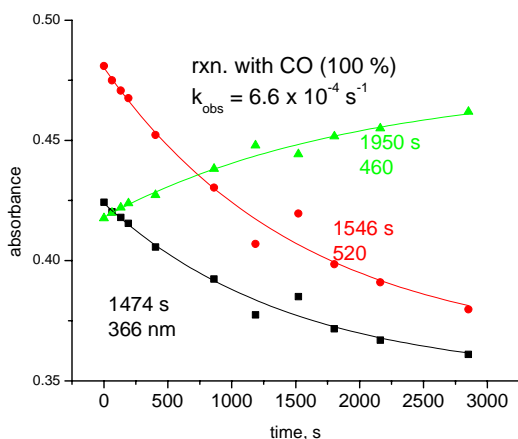
Thus $k_{\text{CO}_2} \gg k_{\text{HCO}_3^-}$

CO Studies:



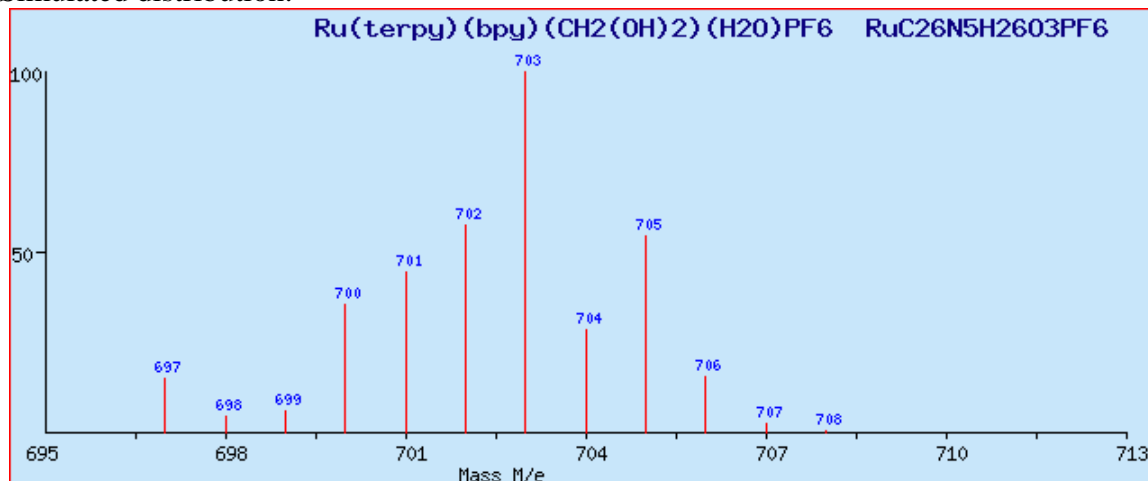
Kinetics

The kinetics of CO addition to $\text{Ru}(\text{terpy})(\text{bpy})\text{H}^+$ were followed by UV-vis and ESI-MS; $k_{\text{obs}} = 6.6 \times 10^{-4} \text{ s}^{-1}$ and $3.1 \times 10^{-4} \text{ s}^{-1}$ with 100% and 50% CO saturated solutions. It was not practical to go to lower CO concentration because the hydrolysis occurs with $1.4 \times 10^{-4} \text{ s}^{-1}$ so that the two steps are not well separated at low $[\text{CO}]$. The second-order rate constant for the first stage was obtained using $0.94 \times 10^{-4} \text{ M/atm.}$ as Henry's constant.



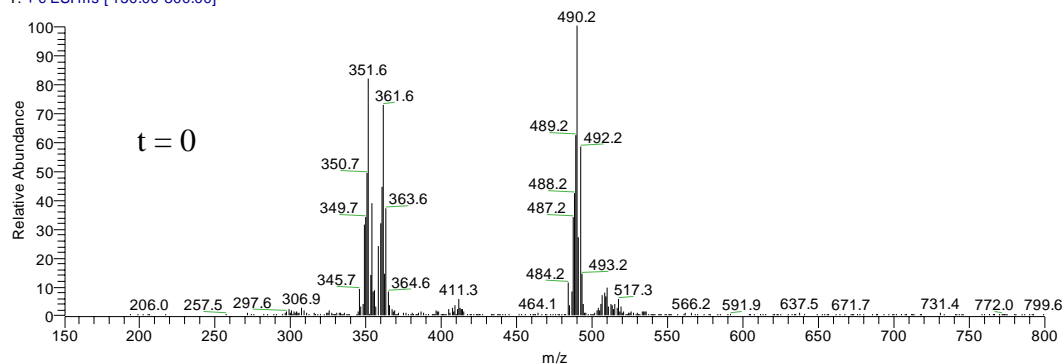
Product studies

Simulated distribution:



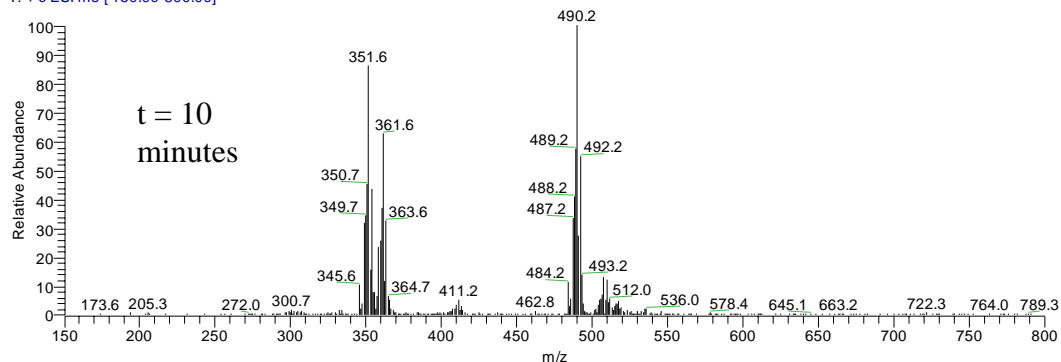
The following are observed ESI MS obtained after mixing an Ar-bubbled RuH^+ solution with 100% CO saturated solution (0.94 mM). The complexed formaldehyde manifests as a peak of m/z 351.6, corresponding to $^{102}\text{Ru(terpy)(bpy)(OCH}_2\text{(OH))PF}_6\text{](H}_3\text{O)}^{2+}$:

mc5100702 #15-38 RT: 0.19-0.49 AV: 24 NL: 1.92E5
T: + c ESI ms [150.00-800.00]

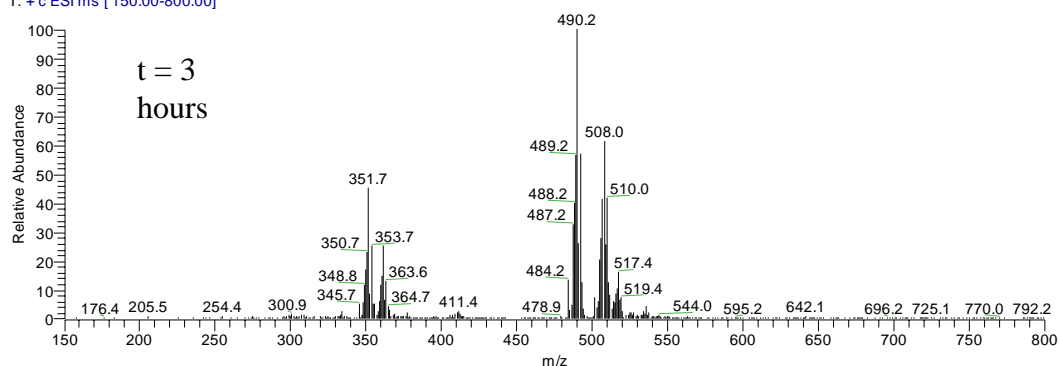


The 351.6 peak rises initially as the hydride-transfer stage is completed, then drops as formaldehyde is released from the Ru coordination sphere.

mc5100703 #24-42 RT: 0.31-0.56 AV: 19 NL: 2.74E5
T: + c ESI ms [150.00-800.00]

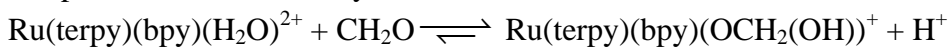


mc51007012 RAW #17-40 RT: 0.22-0.53 AV: 24 NL: 2.72E5
T: + c ESI ms [150.00-800.00]

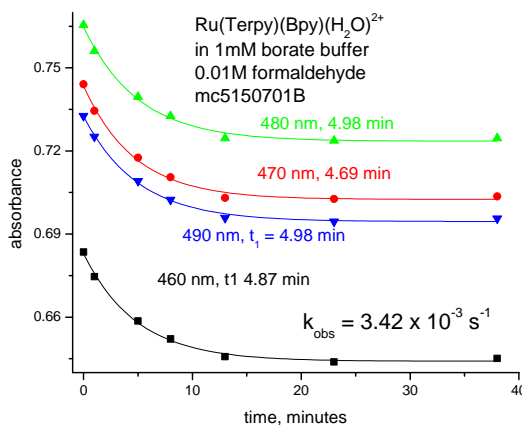
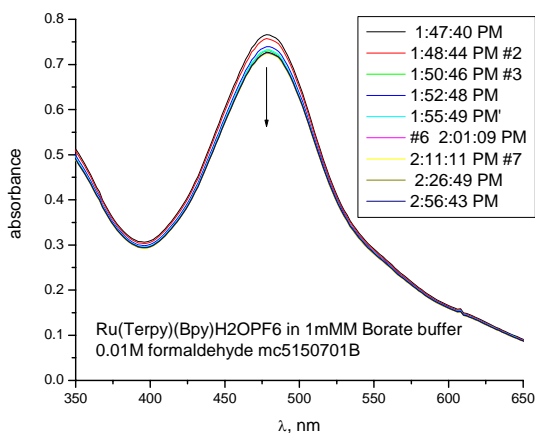


The extent of hydrolysis probably depends on pH (the rate may also), but this has not yet been investigated further.

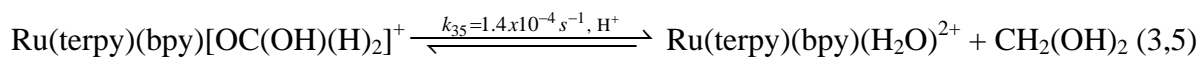
In addition, the formaldehyde complex was generated in solution by mixing the aquo complex at pH 8.8 with formaldehyde:



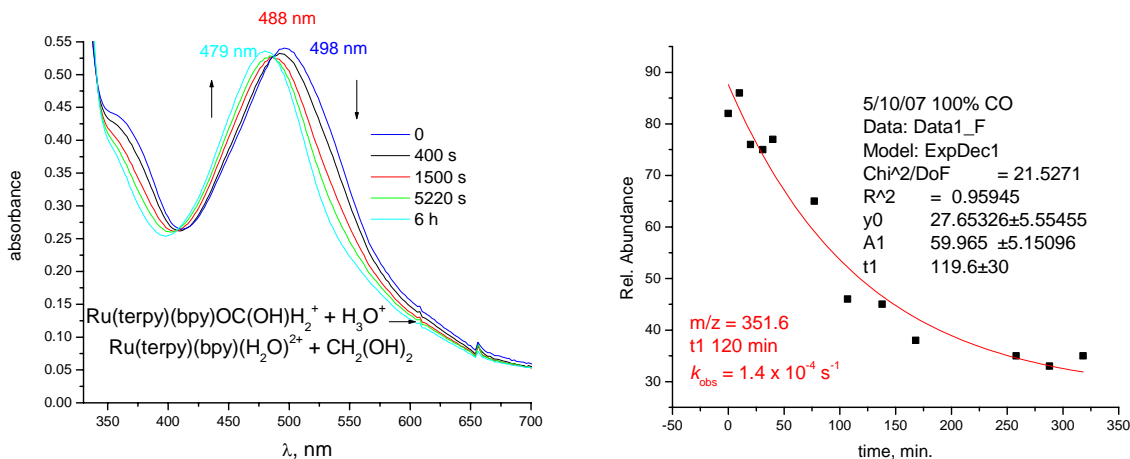
The MLCT band dropped in intensity and red-shifted, consistent with formation of the formaldehyde complex and a peak grew at m/z 351.9 in the ESI-MS.



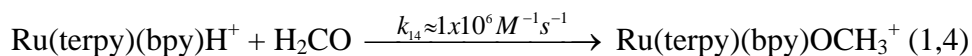
Hydrolysis



Spectral changes are shown at the left and kinetic fit (to ESI MS data) is shown at the right.

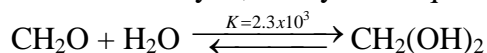


Formaldehyde Studies

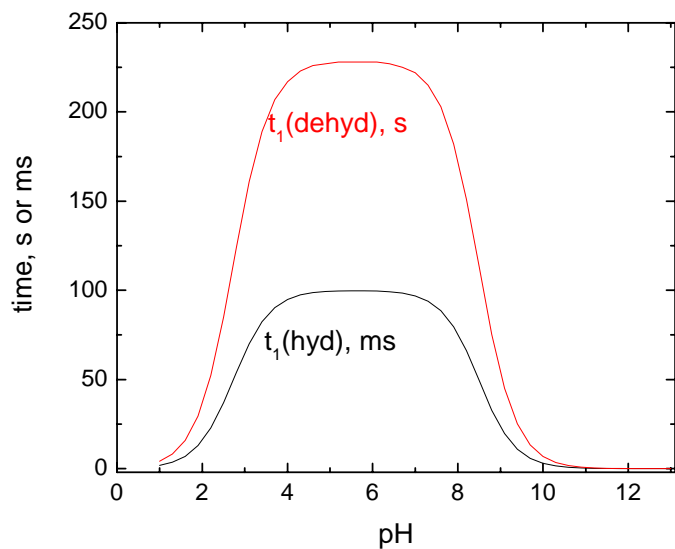


Kinetics of Reaction of RuH^+ with formaldehyde:

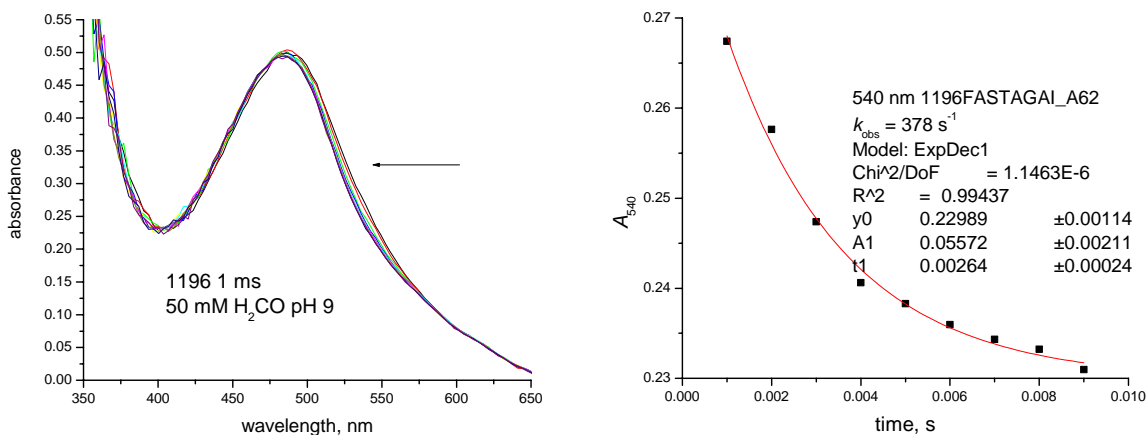
For formaldehyde, the hydrate equilibrium lies very far to the right:



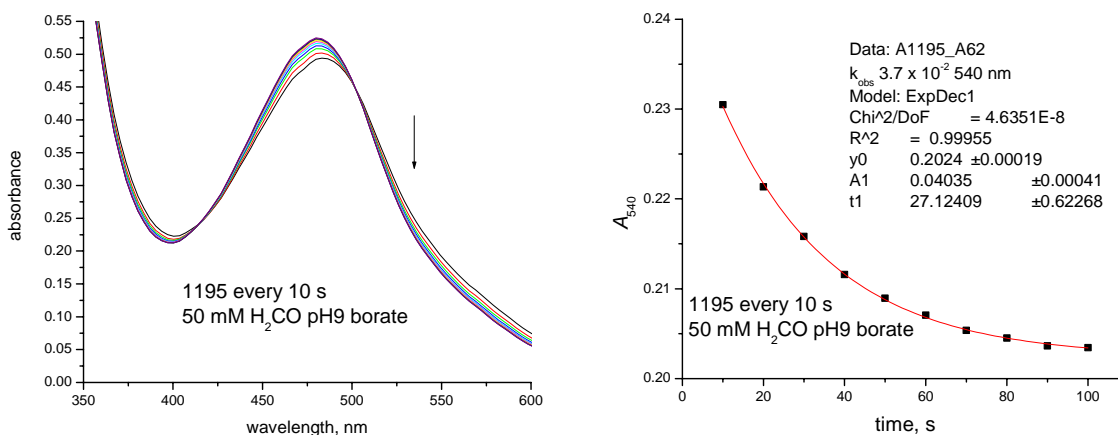
As also found for CO_2 , the hydrate equilibration is slow near neutral pH. Plots of $1/k_{\text{obs}}$ values for formaldehyde dehydration (red curve, seconds) and hydration (black curve, milliseconds), calculated from rate constants reported by Greenzaid et al.⁵ are shown below.



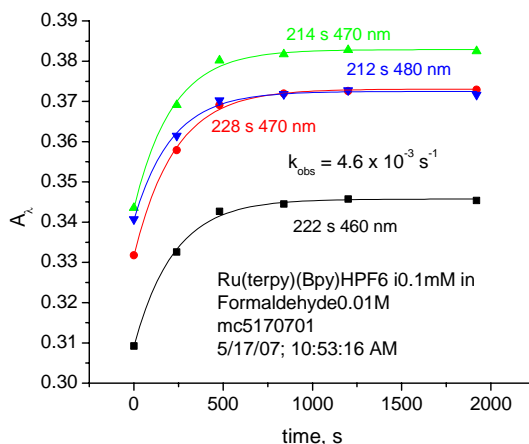
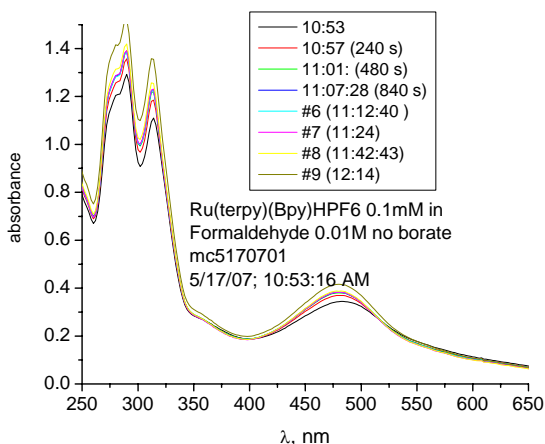
With 50 mM CH_2O , pH 8.8 borate buffer the reaction (1,4) occurs on two timescales. Spectral shifts and kinetics plots for the first stage are illustrated below:



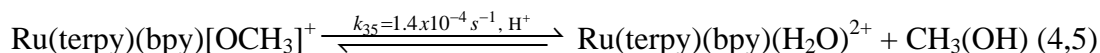
Half of the initially 0.056 mM RuH^+ reacts in a very rapid stage. The very rapid change shown above is due to reaction of the keto form of ca. 30 μM formaldehyde (corresponding to $2.8 \times 10^{-5}/(50 \times 10^{-3} \text{ M})$ formaldehyde, 0.056% vs. 0.0437% calculated for pure water⁵). The rate constant can be roughly estimated (the conditions are not simple pseudo-first-order or equal-concentration second-order) as $378 \text{ s}^{-1}/5.6 \times 10^{-5} = 10^6 \text{ M}^{-1} \text{ s}^{-1}$. The rest of the RuH^+ reacts as more of the dehydrated formaldehyde forms. As shown below, in borate at pH 8.8, this process occurs with about a 30-second time constant controlled by the rate of formaldehyde dehydration.



When no borate is added the stage above is replaced by the slower stage below, consistent with the very slow dehydration near neutral pH.

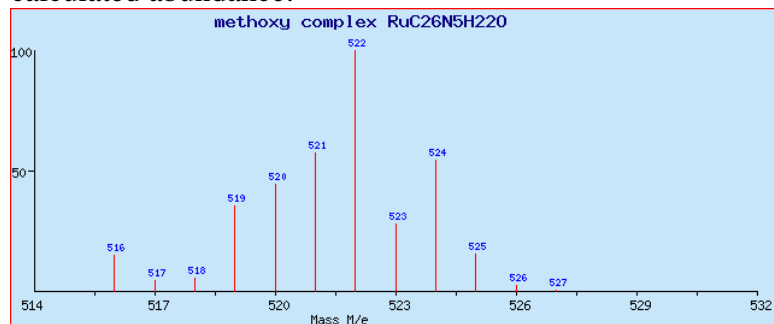


Product characterization.



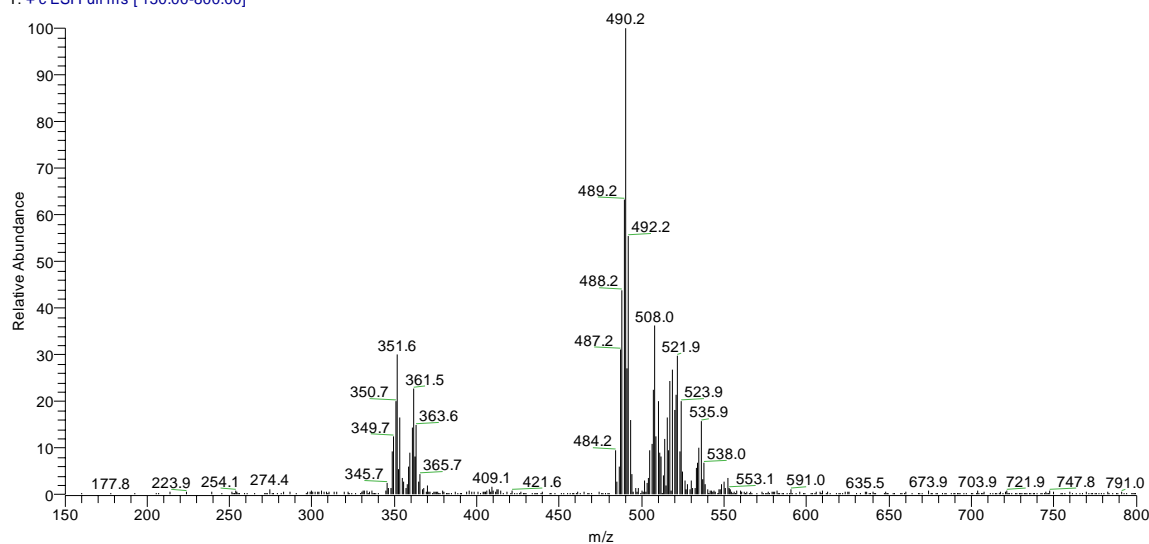
The product the ($^{102}\text{Ru(terpy)(bpy)(CH}_3\text{OH)}^+$) manifested as a peak at $m/z = 523$ in the ESI MS at full intensity only when the collision energy was reduced to 25%: At full collision energy the 522 ($^{102}\text{Ru(terpy)(bpy)(CH}_3\text{O)}^+$) m/z peak (30% max) drops as the 508 $\text{Ru(terpy)(bpy)(H}_2\text{O)}^{2+}$ intensity increases. To an Ar-bubbled solution 0.01 M in formaldehyde in fresh, carbon-dioxide free, water was added Ru(terpy)(bpy)(H)[PF₆] to final concentration of 1×10^{-4} M and the ESI MS and the UV vis were followed with time as illustrated by the data given below.

calculated abundance:



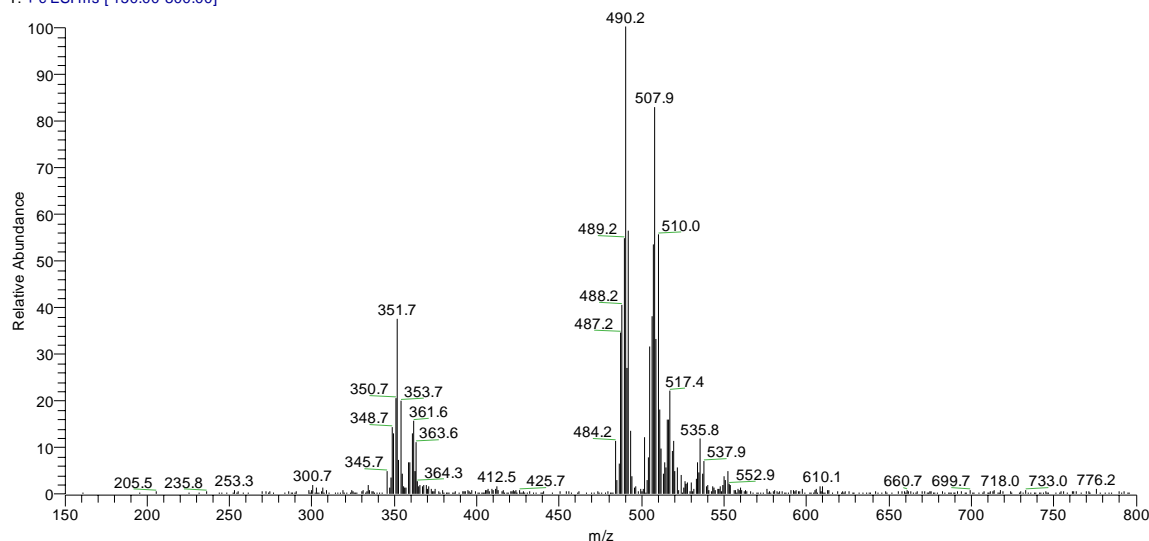
Initial ESI-MS:

mc5170701 #27-52 RT: 0.35-0.69 AV: 26 NL: 1.86E5
T: + c ESI Full ms [150.00-800.00]

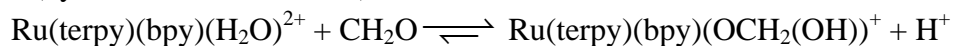


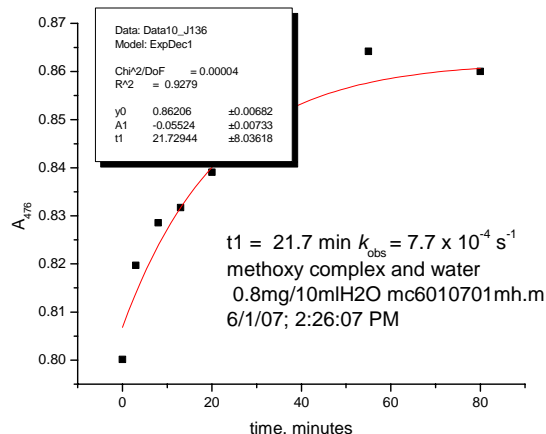
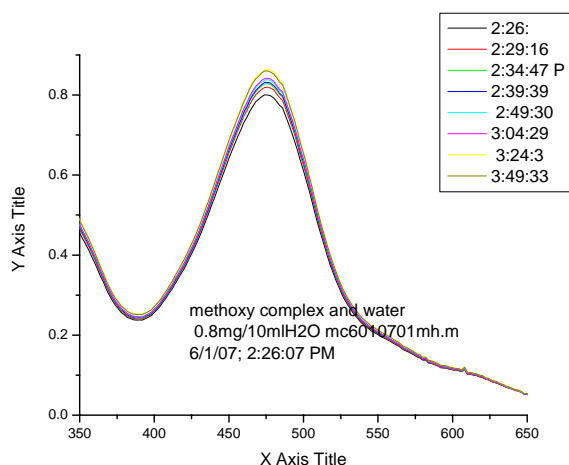
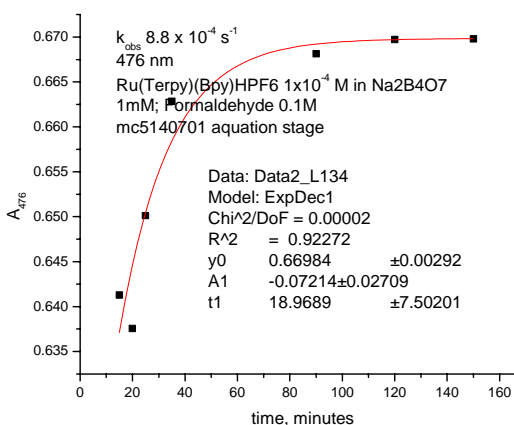
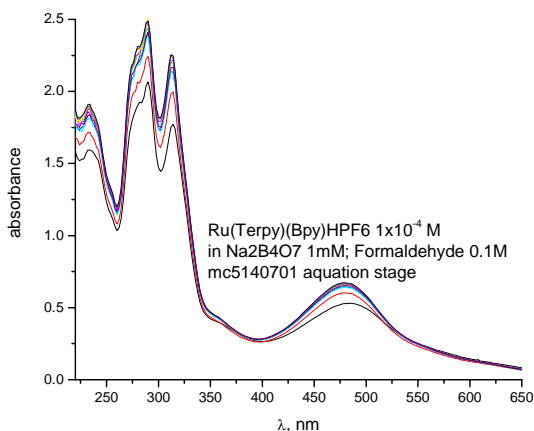
After 30 minutes:

mc5170706RAW #10-21 RT: 0.12-0.27 AV: 12 NL: 3.48E5
T: + c ESI ms [150.00-800.00]



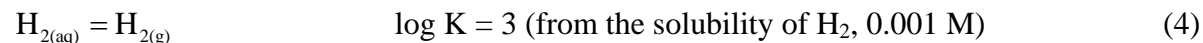
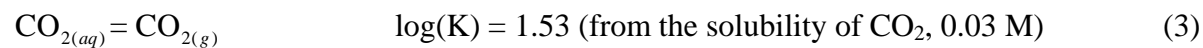
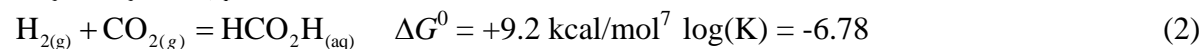
As noted above, the persistent 351.7 peak suggests the formation of $\text{Ru(terpy)(bpy)(OCH}_2\text{(OH))}^+[\text{PF}_6]^-$ by the reaction of excess formaldehyde with the aquo complex (by substitution at carbon).





The hydricity of formate.

We use this cycle:



References

- (1) Konno, H.; Kobayashi, A.; Sakamoto, K.; Fagalde, F.; Katz, N. E.; Saitoh, H.; Ishitani, O. *Inorg. Chim. Acta* **2000**, 299, 155-163.
- (2) Davies, N. R.; Mullins, T. L. *Aust. J. Chem.* **1967**, 20, 657-668.

- (3) Lymar, S. V.; Hurst, J. K. *J. Am. Chem. Soc.* **1995**, *117*, 8867-8868.
- (4) Kern, D. M. *J. Chem. Ed.* **1960**, *37*, 14-23.
- (5) Greenzaid, P.; Luz, Z.; Samuel, D. *Trans. Faraday Soc.* **1968**, *64*, 2780 - 2786.
- (6) Kelly, C. A.; Rosseinsky, D. R. *Phys. Chem. Chem. Phys.* **2001**, *3*, 2086-2090.
- (7) Latimer, W. M. *Oxidation Potentials*; second ed.; Prentice-Hall: Englewood Cliffs, N. J., 1952.