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Contribution from the Departments of Chemistry, Nankai University,
Tianjin, People's Republic of China, and University of Missouri, Columbia, Missouri 65211

Kinetics and Mechanism of the Reaction of a Quasi-Aromatic Nickel(II) Complex, $[Ni((PnAO)\text{-}6H)]^0$, with Formaldehyde

Bin Song,† Qi-Yan Zhang,† Yun-Ti Chen,† and R. Kent Murmann*,‡

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The reaction of $[Ni((PnAO)\text{-}6H)]^0$ (2,2,3,9,10,10-hexamethyl-5,7-dioxa-6-hydra-1,4,8,11-tetraazacyclotetradeca-3,8,11,13-tetraene)nickel(II) (abbreviated to AH), a quasi-aromatic metal ion complex, with formaldehyde has been studied spectrophotometrically. The Ni, 2N, 3C quasi-aromatic heterocyclic ring in AH is highly reactive at the central-aromatic-carbon atom, C12, to most aldehydes. Under neutral conditions in 1/3 (v/v) MeOH–H_2O, the reaction scheme is as follows:

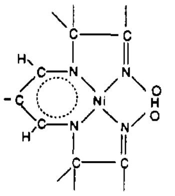
$$\mathrm{AH + CH_2O \xrightarrow{k_1} A{-}CH_2{-}OH \xrightarrow[+AH]{k_2} A{-}CH_2{-}A}$$

$$\mathrm{CH_2O + A{-}CH_2{-}A \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} 2A{-}CH_2{-}OH}$$

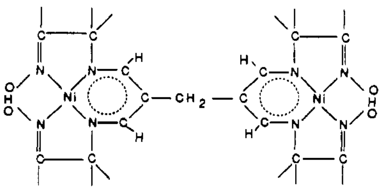
The substances AH, A–CH_2OH, and A–CH_2–A have been isolated and identified by IR, ^1H NMR, mass spectroscopy, and liquid chromatography. The kinetic data support the above reaction sequence. All reactions were second-order overall. The rate constants determined at 29.5 °C were $k_1 = 0.0553$ dm^3 mol^{-1} s^{-1}, $k_2 = 8.52$ dm^3 mol^{-1} s^{-1}, $k_3 = 0.0254$ dm^3 mol^{-1} s^{-1}, $k_{-3} = 0.0264$ dm^3 mol^{-1} s^{-1}. The activation parameters found for each step are as follows: k_1, $\Delta H^{\ddagger} = 55.2 \pm 2.0$ kJ mol^{-1}, $\Delta S^{\ddagger} = -86.6 \pm 6$ J K^{-1} mol^{-1}; k_2, $\Delta H^{\ddagger} = 15.4 \pm 1.5$ kJ mol^{-1}, $\Delta S^{\ddagger} = 176 \pm 4.7$ J K^{-1} mol^{-1}; k_3, $\Delta H^{\ddagger} = 60.4 \pm 0.8$ kJ mol^{-1}, $\Delta S^{\ddagger} = -76.0 \pm 2.8$ J K^{-1} mol^{-1}; k_{-3}, $\Delta H^{\ddagger} = 72.6 \pm 1.3$ kJ mol^{-1}, $\Delta S^{\ddagger} = -35.3 \pm 4.1$ J K^{-1} mol^{-1}. The consequences of these reaction rate constants and their activation parameters are discussed.

Introduction

The high reactivity at the C12 position of AH (A) to electrophilic reagents was apparent by the ease of reaction with halogens and nitrous and nitric acids to give A-X, A-NO, and A-NO_2, respectively.[1] Subsequent studies[2] showed nearly quantitative reaction of AH with $CHOCH_2CHO$ generated by the partial hydrolysis of AH to give a dimer with conjugation between the pseudoaromatic rings through the –CH–CH=CH– grouping. Reaction with simple aldehydes such as formaldehyde and benzaldehyde has been shown to produce A–CH_2–A (B) and A–CHPh–A, respectively, rapidly and in high yields. Crystal structures of the aforementioned compounds[3] have shown the basic nickel(II) complexes to be intact and highly planar with a strong intramolecular hydrogen bond and to have little bond angle or distance differences between the molecules. It was of interest to know the kinetic nature of these reactions, the extent of side reactions, and what intermediates are involved. This work began with a spectrophotometric study of the AH–formaldehyde reaction in essentially neutral methanol–water 1/3 (v/v) solution. Because of the relatively simple nature of the system and the lack of significant side reactions, we were successful in obtaining activation parameters for each step in the reaction.



A



B

Experimental Section

1. Materials. $[Ni((PnAO)\text{-}6H)]^0$ was prepared by oxidizing $[Ni((PnAO)\text{-}H)]ClO_4$ with KIO_3 by the method of Vassian.[1] $[Ni((PnAO)\text{-}H)]ClO_4$ was prepared in water solution by Vassian's method[4] from $NiCl_2$ and PnAO followed by crystallization with $NaClO_4$. The formaldehyde solution used was a 35% water solution (AR) and its concentration was analyzed by $NaHSO_3$ potentiometric titration[5] and found to be 13.83 M. Formaldehyde exists in water solution primarily in the hydrated form, $CH_2(OH)_2$. CH_3OH was of AR grade and further purified by the Hartley–Baike method.[6] Deionized and redistilled water was used throughout.

2. Instruments. The UV–vis spectra were recorded on a Shimadzu UV-240 spectrophotometer with a temperature controlled, ±0.2 °C, thermostated cell. Matched quartz cells (1.00 cm) were used. The liquid chromatograms were recorded on Varian 500 liquid chromatograph. The ^1H NMR spectra were obtained using a JEOL FX-90Q spectrometer. Computations of the kinetic data were carried out with an Apple-2 microcomputer using a nonweighted linear least-squares program. These rate constants were reproducible to ±2%.

3. Experimental Conditions. All four of the reactions studied were shown to proceed through second-order kinetics. Some steps could be treated as pseudo first order, with an excess of one reagent. The first-order equation,[7] $\pm\ln\,[(A_\infty - A_t)/(A_\infty - A_0)] = g_i k' t$, was used where A_0, A_∞, and A_t are absorbance at time 0, ∞, and t. g_i is the stoichiometric coefficient of reactant i or product i and k' is a pseudo-first-order rate constant. $k' = k[\mathrm{m}]_0$ where k is the second-order rate constant and $[\mathrm{m}]_0$ is the concentration of the large excess reactant, often aldehyde. Changing $[\mathrm{m}]_0$, in a series of experiments and plotting k' against $[\mathrm{m}]_0$, allowed the calculation of the second-order rate constant k. Second-order rate constants were reproducible to about ±2%.

In some cases, it was impossible to use a large excess of one reactant in the system, so the second-order conditions were used. When the initial concentrations are not equal, the equation is

$$\ln\,[(A_\infty - A_0)/(A_\infty - A_t) - (g_i/g_j)((A_t - A_0)/(A_\infty - A_t))] = (g_j C_{i0} - g_i C_{j0})kt$$

where g_j, g_i and C_{j0}, C_{i0} are the stoichiometric coefficients and initial concentrations of reactant j, i. Conditions were set so $g_j C_{i0} \gg g_i C_{j0}$.

k_{-3} was calculated from the equilibrium constant, K, and k_3 using the expression $K = k_3/k_{-3}$. The equilibrium constant was experimentally determined using the equation

$$C_{ie} = C_{i0} + g_i(A_e - A_0)/Sg_ie_jl \quad K = \Pi_i C_{je} g_j$$

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† Nankai University.
‡ University of Missouri.

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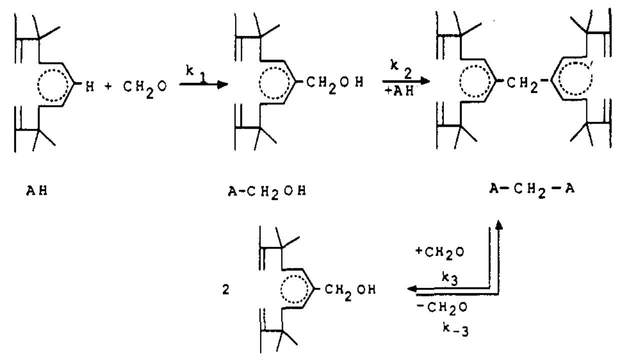
Scheme I



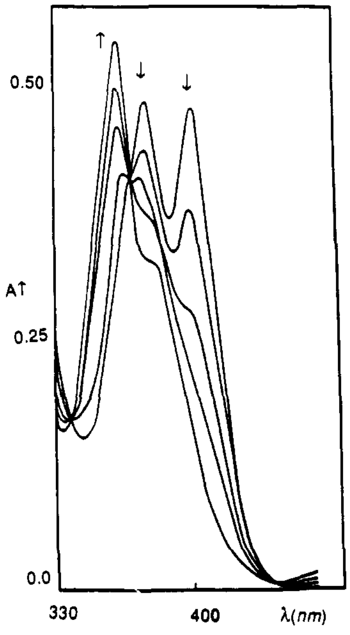


Figure 1. Changes in the visible spectra during the reaction of A–CH$_2$–A with CH$_2$(OH)$_2$: CH$_2$(OH)$_2$ in large molar excess; 5 min between scans (5 × 10^{-5} M, 1.0-cm cells).

where C_{ie} and C_{i0} are the concentrations at equilibrium and initial, respectively, and e_i is the extinction coefficient of substance i. A_0 and A_e are absorbance of the system at initial and equilibrium concentration, respectively.

The experiments were carried out in unbuffered media at nearly neutral conditions (pH = 5–6), because the reactant, AH, decomposes (quite slowly) in acidic solution. This reaction rate is increased in the presence of acid. Because the solubilities of the reactant, the intermediate and the product complexes are low in pure water, a mixture of MeOH and water was used as solvent. Unless otherwise noted the reaction solvent consisted of CH$_3$OH:H$_2$O = 1:3 (v/v).

Results

After a long series of semiquantitative spectral experiments, it was tentatively concluded that the reactions involved when CH$_2$O and AH are reacted are shown in (Scheme I). Some of the experimental facts which support the proposed reaction sequence are as follows:

(a) Identification of the Intermediate and the Product and the Visible Spectra. When equimolar amounts of AH and CH$_2$O are placed in a water solution, an orange crystalline precipitate gradually appears. By isolating the precipitate and analyzing it by mass spectroscopy, IR, and NMR analysis and a single-crystal X-ray structure determination, it was identified as A–CH$_2$–A. When A–CH$_2$–A was placed in CH$_3$OH–H$_2$O and treated with a large excess CH$_2$O and the UV spectral curves were measured, the absorption curves shown in Figure 1 were obtained which have a good isosbestic point consistent with a single absorbing product. After the reaction was complete, the product was removed by extraction with CHCl$_3$. It was washed with NaHSO$_3$ solution and water, to remove CH$_2$O, and the CHCl$_3$ was evaporated. A yellow solid substance was obtained, which by IR and NMR proved to be the ACH$_2$OH. The visible spectra of AH, ACH$_2$OH, and A–CH$_2$–A are shown in Figure 2. The extinction coefficients of AH, ACH$_2$OH, and A–CH$_2$–A at 402.0 nm were 1140, 1230, and 8360, respectively. When solid ACH$_2$OH was added to the CH$_3$OH–H$_2$O solvent, it slowly disproportionated into ACH$_2$A and CH$_2$O. The visible spectrum is similar to that shown in Figure 1 but the change is reversible. This indicates that the third step is a reversible reaction (as are the others). When AH was reacted with a solution of ACH$_2$OH, the reaction proceeded relatively rapidly and ACH$_2$A was the only product. This proved that the second step is the reaction of AH with ACH$_2$OH and it is faster than the initial step.

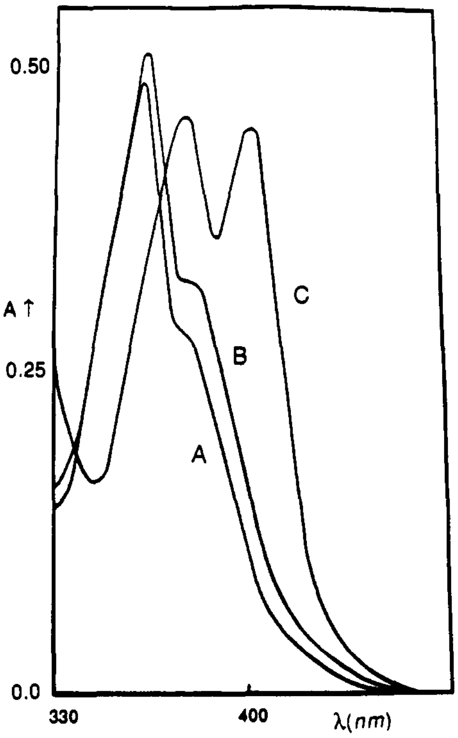


Figure 2. Visible spectra of AH (A), ACH$_2$OH (B), and ACH$_2$A (C) (5 × 10^{-5} M, 1.0-cm cells).

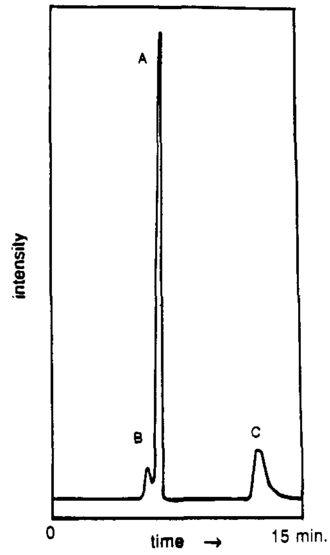


Figure 3. Separation of AH (A), ACH$_2$OH (B), and ACH$_2$A (C) by liquid chromatography (methanol–water (1/1)).

(b) Liquid Chromatography. When a large excess of CH$_2$O was added to a dilute solution of AH and the solution allowed to reach equilibrium, only three peaks were found in the liquid chromatography spectrum (Figure 3). By a comparison of the retention times with those of pure AH, ACH$_2$OH, and A–CH$_2$–A

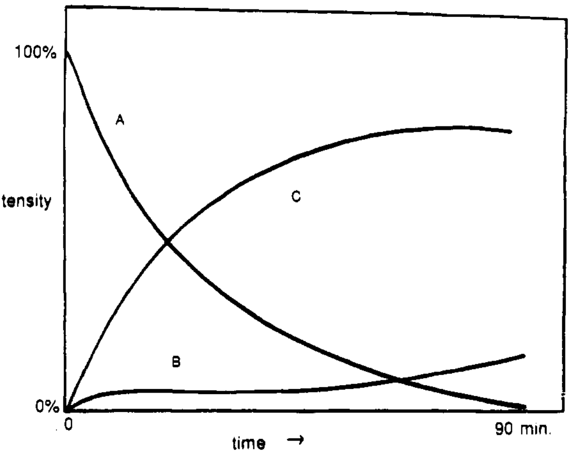


Figure 4. Relative concentrations of AH (A), ACH_2OH (B), and ACH_2A (C) with time as determined by LC (total time shown, 90 min at 29.5 °C).

(when the flow phase was $CH_3OH:H_2O = 7:3$, the retention times were 3.41, 2.70, and 6.55 min, respectively) the peaks were identified and agreed with their visible spectra measured independently. Only these three substances were detected in the reaction system. The changes of the three peaks with time are shown in Figure 4 where it is seen that the amount of AH went down with time and that of ACH_2A went up all the time, but the curve of ACH_2OH went up at the beginning, reached a plateau, and then went up again. This showed that ACH_2OH was an intermediate reacting with AH when the [AH] was high but more slowly when the [AH] decreased.

(c) Reaction of CH_2O with A–CH_2–A, in the absence of added AH, in MeOH–H_2O gave the intermediate A–CH_2OH at a rate comparable to the rate of the other reactions. These facts establish that the reactions involved follow the reaction sequence suggested.

Using the proposed reaction scheme, we have determined the rate constants and the activation parameters of each of the steps.

For all of the reactions of formaldehyde, it should be noted that CH_2O reacts with H_2O and CH_3OH to form $CH_2(OH)_2$, $CH_2(OH)OCH_3$, and $CH_2(OCH_3)_2$,[8] and three main equilibria exist in the solution:[9]

$$CH_2O + H_2O = CH_2(OH)_2 \qquad K = 41.0$$

$$CH_2O + CH_3OH = CH_2(OH)OCH_3 \qquad K = 1310$$

$$CH_2O + 2CH_3OH = CH_2(OCH_3)_2 \qquad K = 183$$

The experimental rate data showed that when the concentration of CH_3OH was increased the rates of the reactions became slower. Therefore we presume that $CH_2(OH)_2$ reacts more rapidly with AH, than does $CH_2(OH)OCH_3$ and or $CH_2(OCH_3)_2$. From the equilibrium constants, under the conditions of the experiment, we calculate that

$$(CH_2(OH)_2) = 0.119(CH_2O)_T$$

where $(CH_2O)_T$ is the total concentration of CH_2O. The concentration of free formaldehyde was very small $(0.00005(CH_2O)_T)$. We have no reliable estimate of the relative reactivities of each of the formaldehyde species, however, it is clear that methylation of CH_2O lowers the rate of reaction. We have calculated the rate constants and equilibrium constants as if only the hydrated form, $CH_2(OH)_2$, were reactive. Its concentration is essentially proportional to that of free formaldehyde.

Table I. Extinction Coefficients of ACH_2A and ACH_2OH at 402 nm (cm^{-1}, M^{-1})

	303 K	308 K	313 K	318 K	323 K
ACH_2OH	1230	1248	1266	1281	1296
ACH_2A	8360	8320	8280	8230	8180

Table II. $10^4k_3'$ as a Function of Temperature and Formaldehyde Concentration

$[CH_2(OH)_2]$, mol/L	302.7 K	306.9 K	311.5 K	316.3 K
0.0137	5.15	7.68	9.43	14.1
0.0275	8.23	12.9	15.6	24.5
0.0411	12.3	18.0	23.7	35.7
0.0548	15.5	22.7	30.3	44.5
k_3, (L/mol) s[a]	0.0254	0.0365	0.0517	0.0748

[a] $k_3' = k3[CH_2(OH)_2]$ + constant. From a graph of k_3' vs $[CH_2(OH)_2]$. *R* (corr coef) was >0.998.

Table III. Rate Constants as a Function of Temperature ((L/mol) s)

	302.7 K	306.9 K	311.5 K	316.3 K
k_1	0.0533	0.0780	0.110	0.148
k_2	8.52	9.66	10.66	11.6
k_3	0.0254	0.0365	0.0517	0.0748
k_{-3}	0.0264	0.0404	0.0604	0.0958

k_1 was determined by having a slight excess of CH_2O in the solution $(([CH_2O]_T/[AH]) = 2)$. At these concentrations the product was almost entirely ACH_2A. Spectrophotometric measurement at 402 nm was employed together with the measured extinction coefficients (Table I) to give the rate parameters. Since $k_2 \gg k_1$, under the experimental conditions employed, the third step of the reaction could be ignored and the steady-state method could be applied:

$$d(ACH_2OH)/dt = k_1(AH)(CH_2(OH)_2) - k_2(AH)(ACH_2OH) = 0$$

$$d(ACH_2A)/dt = k_2(AH)(ACH_2OH) = k_1(AH)(CH_2(OH)_2)$$

$$k_2(AH)(ACH_2OH) = k_1(AH)(CH_2O)$$

Therefore $d(A\text{–}CH_2\text{–}A)/dt = k_1(AH)(CH_2(OH)_2)$.

Because the overall reaction was

$$2AH + CH_2O \Rightarrow A\text{–}CH_2\text{–}A + H_2O$$

g_i has a value of 2 when the second-order equation was utilized.

The value of k_2 was determined by following the reaction of AH with ACH_2OH. Again the wavelength 402 nm was used to follow the reaction. The reaction was begun by injection of a small volume of AH solution into a dilute solution of ACH_2OH. The latter was prepared by reaction of excess CH_2O with AH, extraction with $CHCl_3$, and purification. The kinetic data were treated in accordance with the second-order reaction equation for similar but unequal concentrations of the two reactants.

By observation of the formation of A–CH_2–OH upon injection of a large excess amount of CH_2O into a solution of A–CH_2–A, the rate constant, k_3, was determined. Usually the pseudo-first-order equation was applied to data taken at 402 nm. Although it was a reversible reaction, having CH_2O in very large excess assured that A–CH_2–A changed completely to ACH_2OH. Treatment of the data using a more accurate equation in which the reversible reaction was taken into account gave nearly the same results as shown:

	311.5 K		316.3 K	
	pseudo-first	second	pseudo-first	second
k_3, L/mol·s	0.0517	0.0514	0.0748	0.0721

Four experiments were performed at each temperature when the pseudo-first-order method was used, in which the initial concentration of CH_2O was changed. The results of k_3 versus $[CH_2(OH)_2]$ are shown in Table II.

k_{-3} was calculated from k_3 and the equilibrium constant, *K*. Values for the latter were determined at a series of temperatures.

	302.7 K	306.9 K	311.5 K	316.3 K
K	0.963	0.903	0.856	0.781

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Table IV. Kinetic Activation Parameters for Each Step[a]

	step 1	step 2	step 3	step −3
$\Delta H^{\ddagger}$	54.1 ± 2.0	15.4 ± 1.5	60.4 ± 0.8	72.6 ± 1.3
$\Delta S^{\ddagger}$	−86.6 ± 6.6	−176 ± 4.7	−76.0 ± 2.8	−35.3 ± 4.1
R	0.994	0.992	0.999	0.999

[a] The units for $\Delta H^{\ddagger}$ are kJ/mol and for $\Delta S^{\ddagger}$ are (J/mol) K. *R* is the correlation coefficient of plotting ln (k/T) against $1/T$.

Chart I

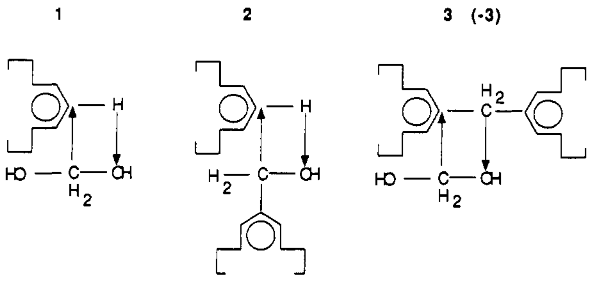

Table III shows the rate constants for each step at different temperatures. The correlation coefficient was >0.995 for all first- or second-order equation fits to the data. The activation parameters calculated for each step are listed in Table IV.

Discussion

The systems were well behaved in a kinetic sense and there was no evidence suggesting significant side reactions. Because of the known sensitivity of the reaction rates to acid, we were concerned that small differences in acidity from sample to sample might decrease the reproducibility. This did not seem to be important however as the reproducibility was excellent. On a broad basis it appears remarkable that all of the reactions studied are so facile at the moderate temperature and concentration conditions used. This must be a reflection of the high reactivity of the C12 position and that probably results from the relatively high partial negative charge on that atom. We suggest that there is a common, similar four-membered ring transition state in each step. The transition states suggested are shown in Chart I. The values of activation enthalpy of steps 1, 3, and −3 are similar and are of the expected magnitude. Step 2 has an appreciably lower value implying either a change in mechanism or an electronic-steric modification.

The fact that the C12 atom in AH is electron rich has been shown by ^1H and ^{13}C NMR: d-^1H, C11 = 7.04, C12 = 5.07; d-^{13}C, C11 = 147.7, C12 = 93.3 ppm) (3,10). A comparison of AH with ACH_2A shows that the chemical shift of C12 changes even more than that of C11 (d-^{13}C: C11 = 148.2, C12 = 104.5 ppm), so we suggest that the electron density of C12 in AH is considerably higher than in ACH_2A. The CH_2 group in ACH_2A has the NMR shift values: d-^1H = 3.36, d-^{13}C = 33.4 ppm. This agrees with our experimental results which give $\Delta H^{\ddagger}$ of the first step smaller than $\Delta H^{\ddagger}$ of the third step. Coupled with this, the steric resistance in ACH_2A is expected to be higher than with AH, so the $\Delta S^{\ddagger}$ of the first step is considerably larger than that of the third step.

The second step is unusually fast with a relatively small $\Delta H^{\ddagger}$ and a very large negative $\Delta S^{\ddagger}$ value. This suggests that there may be an additional binding energy involved in this step. On comparison of ACH_2OH with $CH_2(OH)_2$, the former would be more electrophilic and would be expected to have the lower activation enthalpy of reaction. The negative activation entropy change of step 2 is due to the steric reorganization necessary to bring these two massive molecules into the correct orientation for reaction. As a result of these two factors, step 2 is an order of magnitude faster than the other reactions at room temperature. A comparison of reactions 2 and −3 involving the common reactant ACH_2OH shows a large change in the enthalpy of activation caused presumably by the difference in negative charge on the reacting carbon in AH and ACH_2OH. The reason for the relatively high value for the entropy of activation change is unknown and unexplained. The value for the equilibrium constant for reaction 3 is surprisingly about 1, a relatively low value for the formation of two molecules of ACH_2OH reflecting the high stability of the dimer. The value for the equilibrium constant in step 1 is not known but is considerably greater than that for step 3. This is in keeping with the high nucleophilicity of the C12 in AH.

This work has shown that the reaction of AH with the simplest aldehyde is free from side reactions and proceeds at moderate rates under ordinary conditions. Using the information obtained, one can predict conditions under which either of the products can be obtained in nearly theoretical yields in solution. A concise review of the present state of knowledge in this area has recently become available.[10]

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(10) Murmann, R. K.; Vassian, E. G. *Coord. Chem. Rev.* **1990**, *105*, 1–22.