EQUILIBRIUM CONSTANT DETERMINATION FOR BISULFITE ADDITION TO AROMATIC ALDEHYDES

By

Daniel Y. Choi

****

Submitted in partial fulfillment
of the requirements for
Honors in the Department of Chemistry

UNION COLLEGE

June, 1987

ABSTRACT

CHOI, DANIEL   Equilibrium constant determination for bisulfite addition to aromatic aldehydes. Department of Chemistry, June 1987.

Equilibrium constants for bisulfite addition to benzaldehyde and its derivatives were determined by a spectrophotometric method developed by Kokesh and Hall. The concentration of the benzaldehyde derivative was monitored by UV as aliquots of a bisulfite solution are added to a buffered solution of the aldehyde. Additional data on ΔH° and ΔS° for the reactions were derived from the temperature variation of the equilibrium constants.

For benzaldehyde, the reaction had an equilibrium constant at 25°C of 6.2×10^3 M^{-1}, a ΔH° of -54.3 kJ/mol, and a ΔS° of -111 J/Mol·K. o-Tolualdehyde exhibited a lower K_{eq} of 2.4×10^3 M^{-1}, ΔH° of -39.5 kJ/mol and ΔS° of -67.3 J/Mol·K. Similarly, the reaction with o-anisaldehyde had a K_{eq} of 2.6×10^3 M^{-1}, ΔH° of -38.2 kJ/mol and ΔS° of -62.9 J/Mol·K. The reaction involving salicyladehyde exhibited a much lower K_{eq} of 6.9×10^2 M^{-1}, and ΔH° of -38.5 kJ/Mol and ΔS° of -76.1 J/Mol·K.

Upon reflection, I find that this project has been one of the most interesting and enjoyable learning experiences of my life. For this, I must first thank Professor Hull for his guidance throughout the year. His understanding ways have made this project exciting and worth all the time and effort I put into it. I could not have asked for a better research advisor. I also must thank Laurie LeTarte for putting up with me for a whole year. Without her help, less than half of my work would have been accomplished. I am also grateful to the faculty members of this chemistry department for all of their teachings during the four years of my stay here at Union College. I would also like to thank John, Lisa and all my other friends here at Union College for their laughter during this project. My sanity and sense of humor are still intact, separately, thanks to them. Finally, I would like to thank my parents for giving me so many things that I could never repay.

TABLE OF CONTENTS

TABLE OF FIGURES

TABLE OF TABLES

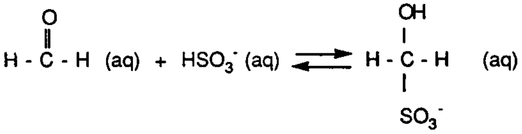
INTRODUCTION

The kinetics involved in the production of acid rain is not perfectly understood. The process involved in the acid rain production is believed[1] to be partly initiated by the oxidation of SO_2 found in the atmosphere, produced mostly by the burning of sulfur containing fuel. This SO_2 reacts with the moisture in the air, mainly rain, fog and cloudwater, to produce HSO_3^-, which in turn is oxidized by hydrogen peroxide to yield the sulfuric acid in the acid rain. This two step reaction can be illustrated by the following equations.

$$SO_2\,(g) + H_2O\,(l) \rightleftharpoons H^+\,(aq) + HSO_3^-\,(aq)$$

$$H_2O_2\,(aq) + HSO_3^-(aq) \longrightarrow H^+\,(aq) + SO_4^{2-}\,(aq) + H_2O\,(l)$$

It has been speculated that formaldehyde and other carbonyl compounds, in a competitive process, react with the bisulfite to create an adduct which will inhibit the production of sulfuric acid[1]. The equation for the aforementioned inhibition process is as follows:



$$H-\overset{\overset{\displaystyle O}{\|}}{C}-H\,(aq) + HSO_3^-\,(aq) \rightleftharpoons H-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle SO_3^-}{|}}{C}}-H\quad(aq)$$

The main drive behind this research is to better understand this inhibition process. Since formaldehyde is difficult to study using a spectroscopic method, due to its low extinction coefficient in the uv-visible range, benzaldehyde was used as a model for this reaction and its equilibrium constant was determined. Also, since formaldehyde constitutes only about a third to a half of atmospheric aldehydes[2], it is important to study other aldehydes and ketones which may participate in a similar inhibition process.

A convenient fact about the reactant and the product involved in the benzaldehyde reaction is the change in extinction coefficients in the ultraviolet region. Toluene, which one may use as a model for the adduct's absorption spectrum since most of absorption in the ultraviolet region is due to the conjugation of the benzene ring, has an extinction coefficient of about 120 at 250nm.[3] Benzaldehyde, on the other hand, has an extinction coefficient of 11200, which is about 100 times greater than toluene's extinction coefficient (figure 1). Therefore, when a spectrum of a solution containing only the adduct and benzaldehyde is taken, one can assume that the absorption due to the adduct is negligible even if it constitutes as much as 90% or the mixture.

In 1932, Stewart and Donnally[4] began the study of the kinetics involved in the above reaction. The study was done in solvents of various pH's and temperature. The equilibrium constant of the reaction was calculated by determinining the amount of unreacted bisulfite ion through titration with iodine. The values obtained for the equilibrium constants for the reaction in acetic acid buffer with pH of 4.77 at 21°C were 1.06×10^4 M^{-1} and 1.07×10^4 M^{-1}.

In 1959, Sousa and Margerum[5] reported values of K_{eq}, $\Delta H°$ and $\Delta S°$ for the same reaction. They obtained these values by monitoring the amount of benzaldehyde present at equilibrium through a uv-spectrophotometric method after placing a specific amount of synthesized benzaldehyde-bisulfite adduct in water. The equilibrium constant obtained by this method at 23°C was 2.11×10^4 M^{-1}. However, this equilibrium constant value for the reaction is strongly dependent on the pH of the solution in which the reaction takes place, but Sousa and Margerum failed to report the pH values for the reactions. Therefore, the values reported are difficult to compare with other reported values.

Olson, Boyce and Hoffmann[6] reported that by using a similar spectrophotometric method, the K_{eq} for the reaction at 25°C and a pH of 3.9 at an ionic strength of 1.0M was determined to be 980 M^{-1}. The equilibrium constant was reported to have increased to 4810 M^{-1} at $\mu = 0.1M$ for the same pH value, suggesting that the K_{eq} is inversely related to the ionic strength of the solution.

However, Kokesh and Hall[7] reported a value of 6400 M^{-1} for the same equilibrium constant value at pH = 3.55 and $\mu = 1.0$ M, which does not show significant deviation from the K_{eq} value of 6250M^{-1} at $\mu = 1.5M$ and pH = 4.0 reported by Geneste, Camaty and Roque[8]. Since Kokesh and Hall also showed that the K_{eq} remains constant for the reaction in the pH range between 3.55 and 5.27, the K_{eq} difference which should have occured due to the difference in ionic strength (according to Hoffmann) between Kokesh and Hall's value and Geneste's value could not have been compensated by the differences in the pH. Therefore, these values seem to be inconsistent with the data presented by Hoffmann, for here the equilibrium constants seem to be independent of the ionic strength. Also, the Keq at pH of 3.9 reported by Hoffmann is much lower than the other reported values at similar pH range.

The experimental method employed by Kokesh and Hall is as follows. After making up benzaldehyde (0.03M - 0.06M) and sulfite (0.05M - 0.10M) stock solutions, the reactions were run in various pH mediums. For the pH of 3.55, 0.63 M acetic acid/sodium acetate buffer was used. The buffer solution along with benzaledhyde was placed in a series of 1.00 cm quartz cuvette, and to each cell various amounts of bisulfite stock solution was added. The difference in the absorption due to benzaldehyde in each cell was used to determine the equilibrium constant.

The mathematics of the method employed stems from the following derivation:

$[A]$ = [Benzaldehyde]
$[B]$ = [Bisulfite]
$[B_0]$ = [Initial Bisulfite]
$[AB]$ = [Benzaldehyde-Bisulfite Adduct]

$[A_{Total}]$ = [Unreacted Benzaldehyde + Reacted Benzaldehyde]
K = Equilibrium Constant
ε_B = Extinction coefficient of benzaldehyde

$$C_6H_5CHO + HSO_3^- \rightleftarrows C_6H_5CH(OH)SO_3^-$$

$$[A] + [B] \overset{K}{\rightleftarrows} [AB]$$

$$K = \frac{[AB]}{[A]\,[B]} = \frac{[AB]}{[A]\,[B_0]} \qquad (1)$$

$$[AB] = K\,[A]\,[B_0]$$

$$A = \varepsilon_B b[A]$$

$$[AB] = K\,[A]\,[B_0]$$

$$[A_{TOTAL}] = [A] + [AB]$$

$$= [A] + K[A][B_0]$$

$$= [A]\,(\,1 + K\,[B_0]\,)$$

$$\Big\downarrow \text{ Solve for } [A]$$

$$[A] = \frac{[A_{TOTAL}]}{1 + K\,[B_0]}$$

$$A = \varepsilon_B \left(\frac{[A_{Total}]}{1 + K\,[B_0]} \right)$$

$$A^{-1} = \left(\frac{\varepsilon_B[A_{Total}]}{1 + K[B_0]}\right)^{-1}$$

$$\frac{1}{A} = \underbrace{\frac{1}{\varepsilon_B[A_{Total}]}}_{\text{(Intercept)}} + \underbrace{\frac{K}{\varepsilon_B[A_{Total}]}}_{\text{(Slope)}}[B_0] \qquad (2)$$

$$\frac{\text{Slope}}{\text{Intercept}} = \frac{\dfrac{K}{\varepsilon_B[A_{Total}]}}{\dfrac{1}{\varepsilon_B[A_{Total}]}} = K \qquad (3)$$

From this derivation, one can see in equation (2), all the quantities except for K and ε_B are known. By plotting 1/A against $[B_0]$ and dividing the slope by the intercept, the extinction coefficient and the benzaldehyde concentration cancels out of the equation leaving only the equilbrium constant, K, as seen in equation (3). This means that the extinction coefficient of benzaldehyde does not have to be known, and the reaction is independent of the benzaldehyde concentration.

In the derivation, two assumptions were made. One of the assumptions was that the bisulfite concentration is unaffected by the amount of the adduct in equation (1), because in the runs, the bisulfite concentration is in large excess of the benzaldehyde concentration. The other assumption was that Beer's Law holds for the reaction. The assumption was tested by constructing a calibration curve of the benzaldehyde in the solvent for the reaction. The reaction was also run under various temperatures to determine the thermodynamic properties of the reaction.

A modified version of Kokesh and Hall's method was employed for this research. In addition to the benzaldehyde, similar reactions involving o-tolualdehyde, anisaldehyde and salicylaldehyde were studied to determined the effect of various substituents in the ortho (to the carbonyl group) position on the reaction rate. The same spectrophotometric method was employed for the determination of the equilibrium constants and the thermodynamic properties for the three compounds.

EXPERIMENTAL

Chemicals:

The reagent grade benzaldehyde and o-tolualdehyde used were purchased from Aldrich Chemical company. The salicylaldehyde used was reagent grade from Matheson, Coleman, and Bell company. All three of these compounds were distilled before their use.

The iodine solution used for the titration of bisulfite solution was made by dissolving 0.1M of I_2 (by weight) to 1.0M KI solution.

Instrumentation:

A Perkin-Elmer Lambda 3 uv-visible spectrophotometer equipped with temperature regulated cell holders connected to an Endocal refrigerated circulating bath was used for the construction of the calibration curves, the equilbrium constant determination and the thermodynamics for all the reactions studied. The temperature was monitiored on Omega 871 digital thermometer with a probe which was placed directly into the cells before the first addition and after the final addition. The average of the two temperature was recorded. Quartz cells (1.00 cm) were used for all the spectrophotometric work.

A 1 in 10 microliter syringe was used to measure out the bisulfite and the aldehydes added to the cuvette.

For all the pH determinations, an Orion Research model 701A digital Ionalyzer was used.

Benzaldehyde stock solution:

The benzaldehyde used for the reactions required a molarity of approximately 0.035 M. The solution was prepared by adding distilled benzaldehyde to a pre-weighed 10 ml volumetric flask with some ethanol in it. After determining the added benzaldehyde's weight, the solution was diluted to the mark with 95% denatured ethanol. The benzaldehyde stock solutions used had molarities of 0 0377 M and 0.0392 M. The stock solution was stored under nitrogen. The purity of the benzaldehyde stock solution was checked by determining the extinction coefficient of the benzaldehyde stock solution in cyclohexane at 240.5 nm and comparing to the literature values. Also, a calibration curve of benzaldehyde in acetic acid buffer solution was constructed for purity checks.

Bisulfite solution:

The sodium bisulfite stock solution was made by weighing out about 5.2 g of sodium bisulfite, which was then diluted to 500 ml using deionized water. The bisulfite stock solution was stored under nitrogen. The molarity of the bisulfite stock solution was determined by periodic titration by KI solution. The bisulfite stock solutions used were 0.0998 M and 0.103 M.

Acetic acid/sodium acetate buffer solution:

The buffer solution in which the reaction takes place was made up by adding one mole (82.03 g) of sodium acetate to one mole of acetic acid (60.05 g) and diluting to one liter with deionized water. The pH of this solution was determined to be 4.66.

Titration of Bisulfite solution:

The molarity of the bisulfite solution was determined by titrating the solution with KI solution. Approximately 20 ml of sodium bisulfite solution was titrated. This solution was acidified to a pH of approximately 2.0 using less than five drops of concentrated sulfuric acid. After adding two drops of starch indicator, the solution was titrated with 0.10 M $KI/I_2/I_3^-$ solution. This procedure was repeated three times, and the average molarity of the three runs was used as the molarity of the bisulfite solution.

Methods:

For the initial absorbance, 3.0 µl of benzaldehyde in 3.0 ml of 1.0 M acetic acid buffer solution was run against the same buffer solution, and its absorbance at 248.7 nm was measured. In a typical run, 1.0 µl of sodium bisulfite solution was added directly to both the reaction cell and the reference cell. For each subsequent addition, the amount of bisulfite added to each cell was doubled, until a total of 64 µl had been added to the cell For each addition the solutions were left equilibrating in the spectrophotometer until there was no change in the absorbance measurement (approximately 5 to 10 minutes). Absorbance at 248.7 nm was measured for each addition.

For some of the runs, the amount of benzaldehyde added was varied (2.0 µl, 3.0 µl, and 4.0 µl). The temperature in which the reacton takes place was varied from 4°C to 37°C to determine ΔH° and ΔS° of the reaction.

The same expermental procedure used in the determination of K_{eq} and the thermodynamic properties of benzaldehyde was used for the addition reaction of bisulfite to o-tolualdehyde, o-anisaldehyde and salicylaldehyde.

RESULTS AND DISCUSSION

Before any reaction was run, the extinction coefficients were determined for each of the carbonyl compounds involved in the reaction to be studied. First, the extinction coefficient (ε) of benzaldehyde was determined in cyclohexane and in buffer. The ε of benzaldehyde in cyclohexane was compared to the literature value for the ε in heptane. The two values were 1.36×10^4 (literature value)[3] and 1.44×10^4 in cyclohexane (Figure 3). Since the literature value and the experimental values are in good agreement, the benzaldehyde stock solution was considered to be pure. When absorbance was plotted against concentration of benzaldehyde in buffer (Figure 4), the plot yielded a straight line. Thus Beer's law holds for this compound in the acetic acid buffer, which confirms one of the assumptions made for the equilibrium constant calculations as mentioned in the introduction.

The bisulfite addition reaction was run in a quartz cell. By adding bisulfite to both the reference cell and the reaction cell (both cells containing acetic acid buffer), any absorption due to bisulfite and the buffer is cancelled out. This leaves only the absorption due to the benzaldehyde and the adduct. Since the absorption due to the adduct is negligible (about 100 times less) when compared to the absorption due to benzaldehyde as mentioned in the introduction, one can assume that nearly all the absorption is due to the unreacted benzaldehyde. Thus by monitoring the absorption change at ~250nm, one can detect the change in benzaldehyde concentration with respect to bisulfite concentration, and use this data to calculate the equilibrium constant for the reaction. A spectrum of a typical series of run can be seen in Figure 1. By plotting inverse absorbance against the bisulfite concentration (Figure 8), one can determine the K_{eq} by dividing the slope by the intercept as derived in the introduction.

To verify the validity of the equation derived in the introduction, the reactions were run using three different benzaldehyde concentrations. If the derivation is valid, the equilibrium constant be equal. The three equilibrium constants using the three different benzaldehyde concentrations (Figure 8) remained relatively constant (the difference between the 4 µl run and the 3 µl run may be due to the temperature fluctuation). The equilibrium constant (taking the average of the three values) at 25°C was determined to be $6.2 \times 10^3\ M^{-1}$. This value is in close agreement with the value of $6.25 \times 10^3\ M^{-1}$ obtained by Geneste, Camaty and Rogue[8]. It is also in good agreement with Kokesh and Hall's $6.4 \times 10^3\ M^{-1}$ for the equilibrium constant for the same reaction. These agreements in the K_{eq} values further supports the validity of the method employed. The K_{eq} value, however, varies significantly from the value of 980 M^{-1} reported by Olson, Boyce and Hoffmann at a slightly different pH.

To determine the thermodynamic properties of this reaction, the reaction was run at various temperatures. The $\Delta H°$ was determined by plotting ln K of all the runs against inverse temperature (Kelvin) of the runs (Figure 14). The slope times R (8.314 J/K·mol) gives the $-\Delta H°$, while the intercept times R gives the $\Delta S°$. The $\Delta H°$ was determined to be -54.3kJ/mol, while $\Delta S°$ was -111 J/mol·K.

The next reaction studied was the addition of bisulftie to o-tolualdehyde to study the effect of a substituant on the ortho position on the benzene ring. The reaction was studied using the same methods used for the benzaldehyde's addtion reaction. The results for this reaction are summarized in Table 3. The equilibrium constant at 25°C was determined to be $2.4 \times 10^3\ M^{-1}$ (Figure 10). As suspected, the methyl group in the ortho position hinders the addition reaction sterically to decrease the formation of the adduct and consequently lower the equilibrium constant. The ΔH and the ΔS of the reaction was determined to be -39.5 kJ/mol and -67.3 J/mol·K respectively (figure 15).

Salicyladehyde's addition to bisulfite was the next reaction studied. The hydroxy substituant in the ortho position was used to determine the effect of an electron donating group on the equilibrium constant. The equilibrium constant was determined to be 690 M^{-1} (Table 4). This equilibrium constant is much lower than the equilibrium constant for the o-toluadelhyde's addition to bisulfite.

This may be due to the electronic effect of the hydroxy group is much greater than the steric effect due to the methyl group on the reaction. The -OH substituant somehow stabilizes the reactant or destabilizes the product significantly to lower the equilibrium constant approximately ten times from the benzaldehyde's equilibrium constant. The $\Delta H°$ for the reaction was -39 kJ/mol while $\Delta S°$ was -76 J/mol·K (figure 16).

To verify the explanation provided for the relatively low equilibrium constant of sallicylaldehyde's addition reaction, the addition reaction of o-anisaldehyde and bisulfite was studied using the same spectrophotometric method. The equilibrium value was higher than expected. Since the steric effect of the methoxy group should be larger than the hydroxy group, but the electronic effect similar, one would expect the equilibrium constant for the o-anisaldehyde's addition reaction to be lower than the equilibrium constant for the o-tolualdehyde. The equilibrium constant should be similar to the o-tolualdehyde if the electronic effect is less important than the steric effect,since the size of CH_3 and OCH_3 are similar.

The equilibrium constant was found to be $2.6 \times 10^3\ M^{-1}$ (Table 5), while the $\Delta H°$ was -38.23 kJ/Mol and $\Delta S°$ is -62.93 J/Mol·K (figure 17). The K_{eq} of anisaldehyde reaction was similar to o-tolualdehyde while being much larger than the salicylaldehyde's reaction. This data seem to indicate that the electronic effect is minimal as compared to the steric effect, since o-tolualdehdye and o-anisaldehyde exhibit similar steric effect on the reaction have similar equilibrium constants, while salicylaldehyde and o-anisaldehyde with similar electronic properties have a large difference in their equilibrium constants. The large difference between salicyladehyde and o-anisaldehyde may be due to the stabilization of the starting aldehydes by hydrogen bonding in salicylaldehyde, thereby slowing the formation of the adduct.

All of the experimentally determined equilibrium constants, as well as the related equilibrium constants listed in the literature, are presented in Table 1. As seen in the table, acetaldehyde's equilibrium constant is about five times less than the formaldehyde's equilibrium constant. The $-CH_3$ stabilizes the reactant so that the reaction's drive toward the formation of the product is decreased as compared to the reaction of formaldehyde. A similar trend is seen in the case of benzaldehyde. The formaldehyde's equilibrium constant is about ten times greater than the benzaldehyde's equilibrium, showing the electronic stabilizing effect of the benzene ring. Other compounds such as cinnamaldehyde and salicylaldehyde show similar stabilizing effect.

A drastic change in the equilibrium constant can be seen in the case of acetophenone, in which both of the hydrogens in formaldehyde are replaced by a benzene ring and a methyl group. This compound is much more stable than benzaldehyde, as seen by the much lower equilibrium constant of 5.3 M^{-1}. Also, the steric inhibition of the reaction by the additional substituants in the ketone may add to the significantly lower K_{eq} value as compared to the K_{eq} of similar aldehydes. Again the electronic effect can be seen in a series of acetophenone derivatives. The p-methylacetophenone lowers the equilibrium constant by about a factor of two. When a chlorine, an electron withdrawing group, is added to the methyl group in the acetophenone, the equilibrium constant is significantly increased by the destabilization of the compound due to the electron withdrawing chlorine.

Finally, the affect of ionic strength on the equilibrium constant was measured. To do this, the benzaldehyde reaction was run in a 0.1M acetic acid buffer and was compared to the benzaldehyde reactions run in a 1.0M acetic acid buffer. The results showed no significant deviation. This result is in disagreement with the results presented by Olson, Boyce and Hoffmann. Their values were 980 M^{-1} for the reaction in 1.0 M buffer and 4810 M^{-1} in 0.1 M buffer at a pH of 3.9. However the equilibrium constants determined through our methods were 6200 M^{-1} in 1.0M buffer and 6500 M^{-1} in 0.1M buffer at a pH of 4.66 (Table 6). These values are in agreement with the values presented by Kokesh and Hall, and Geneste, Rogue and Camaty, where their values were quite similar, although the ionic strength and the presented in Table 1. As seen in the table, acetaldehyde's equilibrium constant is about five times less than the formaldehyde's equilibrium constant. The $-CH_3$ stabilizes the reactant so that the reaction's drive toward the formation of the product is decreased as compared to the reaction of formaldehyde. A similar trend is seen in the case of benzaldehyde. The formaldehyde's equilibrium constant is about ten times greater than the benzaldehyde's equilibrium, showing the electronic stabilizing effect of the benzene ring. Other compounds such as cinnamaldehyde and salicylaldehyde show similar stabilizing effect.

A drastic change in the equilibrium constant can be seen in the case of acetophenone, in which both of the hydrogens in formaldehyde are replaced by a benzene ring and a methyl group. This compound is much more stable than benzaldehyde, as seen by the much lower equilibrium constant of 5.3 M^{-1}. Also, the steric inhibition of the reaction by the additional substituants in the ketone may add to the significantly lower K_{eq} value as compared to the K_{eq} of similar aldehydes. Again the electronic effect can be seen in a series of acetophenone derivatives. The p-methylacetophenone lowers the equilibrium constant by about a factor of two. When a chlorine, an electron withdrawing group, is added to the methyl group in the acetophenone, the equilibrium constant is significantly increased by the destabilization of the compound due to the electron withdrawing chlorine.

Finally, the affect of ionic strength on the equilibrium constant was measured. To do this, the benzaldehyde reaction was run in a 0.1M acetic acid buffer and was compared to the benzaldehyde reactions run in a 1.0M acetic acid buffer. The results showed no significant deviation. This result is in disagreement with the results presented by Olson, Boyce and Hoffmann. Their values were 980 M^{-1} for the reaction in 1.0 M buffer and 4810 M^{-1} in 0.1 M buffer at a pH of 3.9. However the equilibrium constants determined through our methods were 6200 M^{-1} in 1.0M buffer and 6500 M^{-1} in 0.1M buffer at a pH of 4.66 (Table 6). These values are in agreement with the values presented by Kokesh and Hall, and Geneste, Rogue and Camaty, although the ionic strength and the pH's were different. The difference in the pH values between Hoffmann's work and our work should not affect the equilibrium constant, for in Kokesh and Hall's work, the equilibrium constant for the reaction remained constant for this (3.55 ~ 5.27) pH region. Therefore, the equilibrium constant was determined not to be affected by the ionic strength of the solvent. It is not clear what could have caused the change in equilibrium constant observed for different ionic strengths by Olson, Boyce and Hoffmann, nor the difference in the equilibrium constant value they observed with respect to others (980 M^{-1} vs. 6200 ~ 6500 M^{-1}).

In sum, we have established that ionic strength does not have a large affect upon the equilibrium constant of the reaction. Also, a substituent in the ortho position sterically hinders the productiion of the adduct, while there seem to be no large electronic effects of an electron donating group in the ortho position on the equilibrium constant. However, substituants which may exhibit hydrogen bonding such as an -OH group may significantly decrease the equilibrium constant. To determine for certain the effect of an electron donor on the reaction, additional studies using a para-subsitituted benzaldehyde derivatives such as p-anisaldehdye should be made. Furthermore, forward and reverse rate constants should be determined to further understand the addition reactions involving the aldehydes studied in this thesis.

Carbonyl Compounds	Equilibrium Constant (K_{eq})
Formaldehyde[9]	85000
Acetaldehyde[10]	16000
Benzaldehyde	6200
o-Anisaldehyde	2600
o-Tolualdehyde	2400
Cinnamaldehyde[11]	1035
Salicylaldehyde	690
2-Chloroacetophenone[11]	53
Acetophenone[11]	5.3
p-Methylacetophenone[12]	3

Table 1. Carbonyl Compounds and their Equilibrium Constants For the Bisulfite Addition Reaction

Concentration of Benzaldehyde Stock Solution = 0.0392 M
Concentration of Bisulfite Stock Solution = 0.103 M
Concentration of the Buffer Solution = 1.0 M
pH of the Buffer Solution = 4.66
Wavelength at which Absorbance was measured = 248.7 nm

[Benzaldehyde] (M)	Final [biulfite] (M)	Temperature (°C)	K_{eq} (M^{-1})
3.92×10^{-5}	1.10×10^{-3}	25.0	6.5×10^{3}
2.61×10^{-5}	1.10×10^{-3}	24.6	6.2×10^{3}
5.22×10^{-5}	1.10×10^{-3}	24.6	5.9×10^{3}
3.92×10^{-5}	1.10×10^{-3}	37.4	1.5×10^{3}
3.92×10^{-5}	2.75×10^{-4}	4.6	2.1×10^{4}
3.92×10^{-5}	5.49×10^{-4}	15.3	1.0×10^{4}
3.92×10^{-5}	5.49×10^{-4}	10.5	1.7×10^{4}

ΔH° = -54.3 kJ/mol

ΔS° = -111 J/mol·K

Table 2. Summary of Benzaldehyde Addition Reaction Runs

Concentration of o-Tolualdehyde Stock Solution = 0.0370 M
Concentration of Bisulfite Stock Solution = 0.0772 M
Concentration of the Buffer Solution = 1.0 M
pH of the Buffer Solution = 4.66
Wavelength at which Absorbance was Measured = 252.5 nm

[o-Tolualdehyde] (M)	Final [Bisulfite] (M)	Temperature (°C)	K_{eq} (M^{-1})
3.70×10^{-5}	1.65×10^{-3}	23.8	2.3×10^{3}
4.32×10^{-5}	1.65×10^{-3}	25.1	2.5×10^{3}
3.70×10^{-5}	8.23×10^{-4}	9.9	6.6×10^{3}
3.70×10^{-5}	3.29×10^{-3}	34.7	1.7×10^{3}
3.70×10^{-5}	1.65×10^{-3}	35.0	1.5×10^{3}
3.70×10^{-5}	1.65×10^{-3}	9.0	5.9×10^{3}
3.70×10^{-5}	3.29×10^{-3}	35.0	1.5×10^{3}

$\Delta H° = -39.5$ kJ/Mol

$\Delta S° = -67.3$ J/mol·K

Table 3. Summary of o-Tolualdehyde Addition Reaction Runs

Concentration of Salicylaldehyde Stock Solution	= 0.0311 M
Concentration of Bisulfite Stock Solution	= 0.0816 M
Concentration of the Buffer Solution	= 1.0 M
pH of the Buffer Solution	= 4.66
Wavelength at which Absorbance was Measured	= 254.5 nm

[Salicylaldehyde] (M)	Final [Bisulfite] (M)	Temperature (°C)	K_{eq} (M^{-1})
3.11×10^{-5}	1.74×10^{-3}	24.5	7.3×10^{2}
3.11×10^{-5}	1.74×10^{-3}	24.5	5.4×10^{2}
4.15×10^{-5}	1.74×10^{-3}	24.1	8.0×10^{2}
3.11×10^{-5}	1.74×10^{-3}	8.7	1.2×10^{3}
4.15×10^{-5}	1.74×10^{-3}	9.6	1.5×10^{3}
4.15×10^{-5}	3.48×10^{-3}	33.4	3.9×10^{2}
4.15×10^{-5}	1.74×10^{-3}	33.1	3.2×10^{2}

$\Delta H° = -38.5$ kJ/Mol

$\Delta S° = -76.1$ J/mol·K

Table 4. Summary of Salicylaldehyde Addition Reaction Runs

Concentration of o-Anisaldehyde Stock Solution = 0.0339 M
Concentration of Bisulfite Stock Solution = 0.102 M
Concentration of the Buffer Solution = 1.0 M
pH of the Buffer Solution = 4.66
Wavelength at which Absorbance was Measured = 254.5 nm

[o-Anisaldehyde] (M)	Final [Bisulfite] (M)	Temperature (°C)	K_{eq} (M^{-1})
4.52×10^{-5}	2.18×10^{-3}	25.2	2.5×10^{3}
9.04×10^{-5}	2.18×10^{-3}	25.0	2.2×10^{3}
3.01×10^{-5}	1.09×10^{-3}	25.0	3.0×10^{3}
4.52×10^{-5}	1.09×10^{-3}	34.1	1.6×10^{3}
4.52×10^{-5}	2.18×10^{-3}	34.0	1.7×10^{3}
4.52×10^{-5}	1.09×10^{-3}	10.6	6.6×10^{3}
4.52×10^{-5}	2.18×10^{-3}	10.1	5.0×10^{3}

$\Delta H° = -38.2$ kJ/Mol

$\Delta S° = -62.9$ J/mol·K

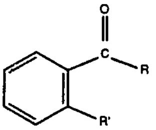
Table 5. Summary of o-Anisaldehyde Addition Reaction Runs

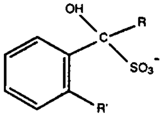
Concentration of Benzaldehyde Stock Solution = 0.0377 M
Concentration of Bisulfite Stock Solution = 0.102 M
Concentration of the Buffer Solution = 0.1 M
pH of the Buffer Solution = 4.66
Wavelength at which Absorbance was Measured = 248.7 nm

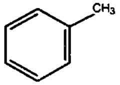
[Benzaldehyde] (M)	Final [Bisulfite] (M)	Temperature (°C)	K_{eq} (M^{-1})
3.77×10^{-5}	1.09×10^{-3}	24.8	7.5×10^{3}
3.77×10^{-5}	1.09×10^{-3}	24.8	5.4×10^{3}
3.77×10^{-5}	1.09×10^{-3}	24.8	6.5×10^{3}
Average			6.5×10^{3}

Table 6. Summary of Benzaldehyde Addition Reaction Runs in 0.1M Buffer

REACTANTS **PRODUCTS** **TOLUENE**







R = H, CH_3, CH_2Cl

R' = H, OH, CH_3, OCH_3

Benzaldehyde

Toluene

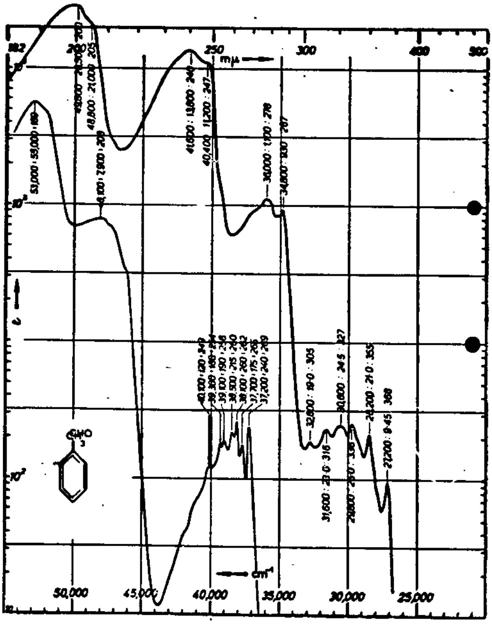


Figure 1. Extinction Coefficient of Reactants and Products

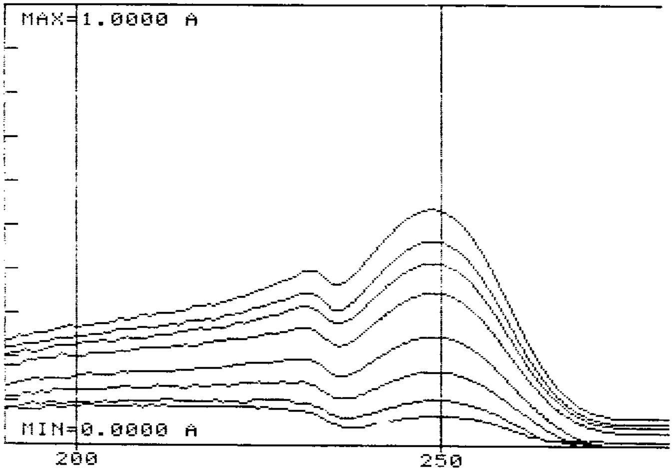


Figure 2. Spectrum of a Series of Benzaldehyde Addition Reaction

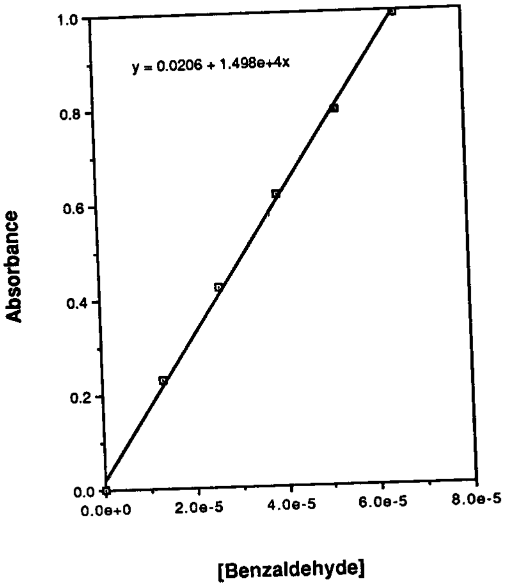


Figure 3. Extinction Coefficient of Benzaldehyde in Cyclohexane

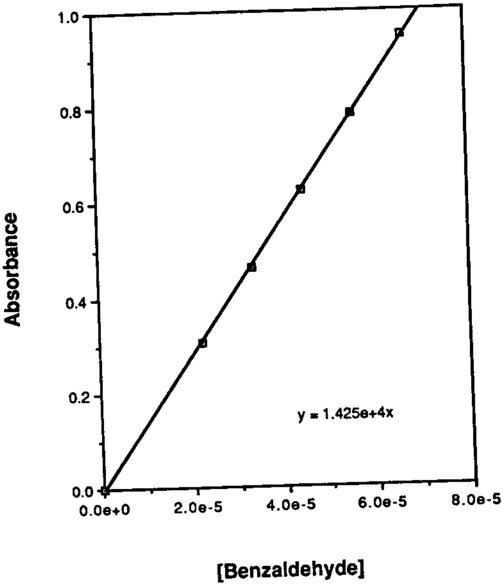


Figure 4. Extinction Coefficient of Benzaldehyde in Buffer

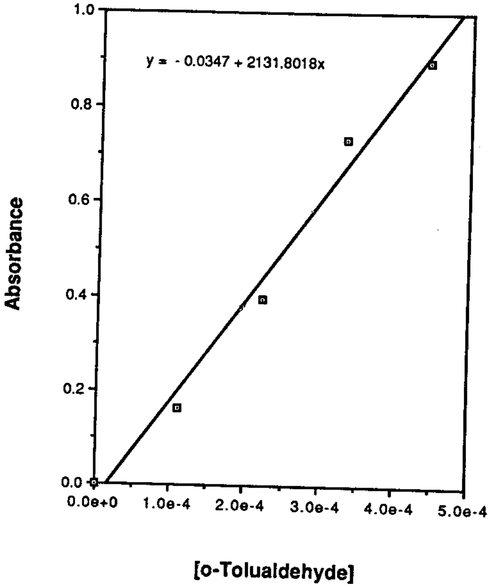


Figure 5. Extinction Coefficient of o-Tolualdehyde in Buffer

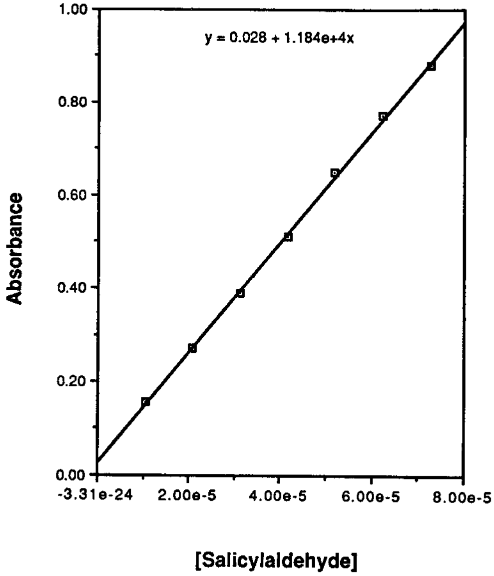


Figure 6. Extinction Coefficient of Salicylaldehyde in Buffer

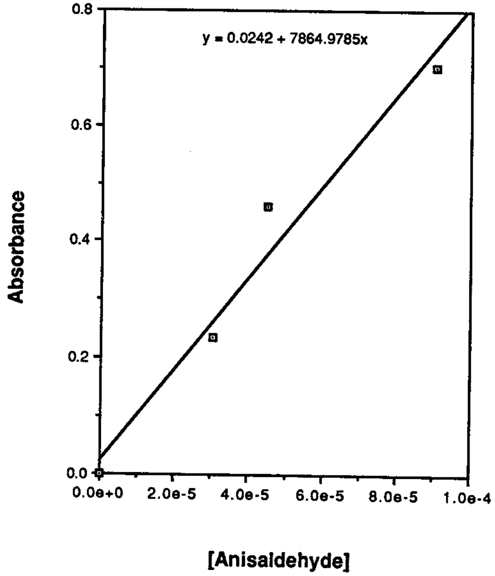


Figure 7. Extinction Coefficient of Anisaldehyde in Buffer

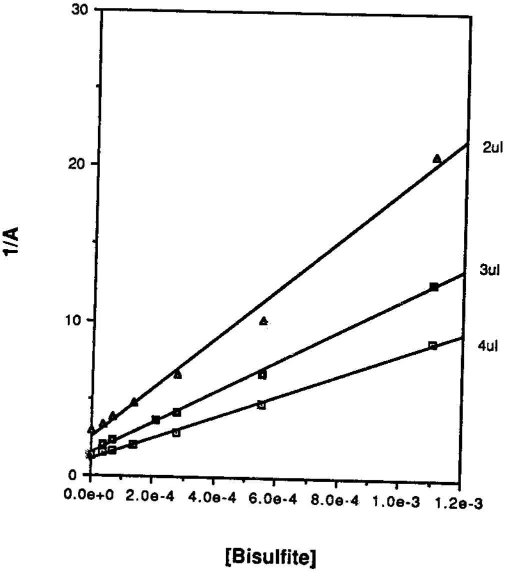


Figure 8. Benzaldehyde Addition Reaction Using Various Benzaldehyde Concentrations

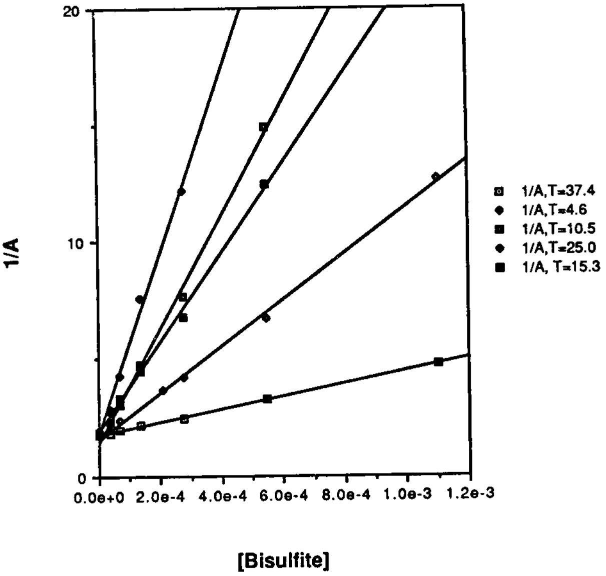


Figure 9. Benzaldehyde Addition Reaction at Various Temperatures

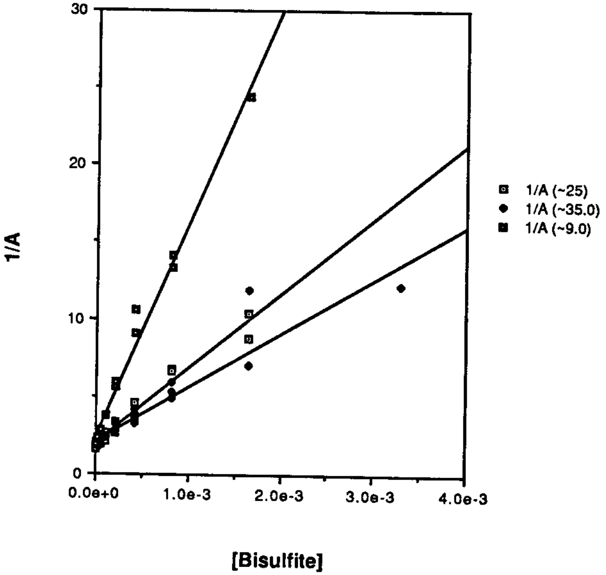


Figure 10. o-Tolualdehyde Addition Reactions

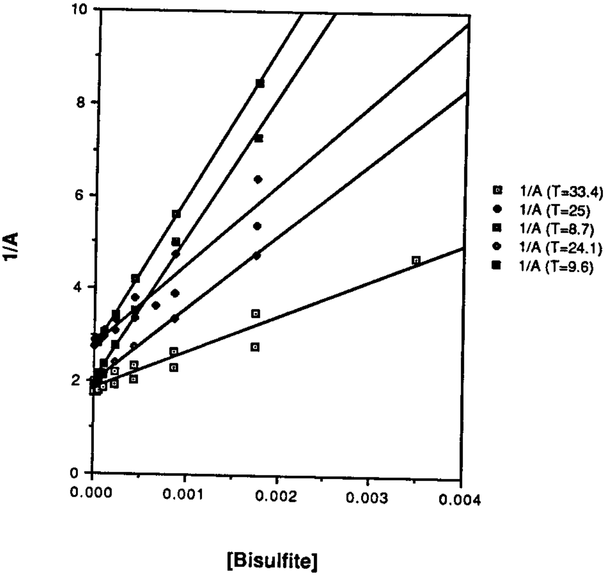


Figure 11. Salicylaldehyde Addition Reactions

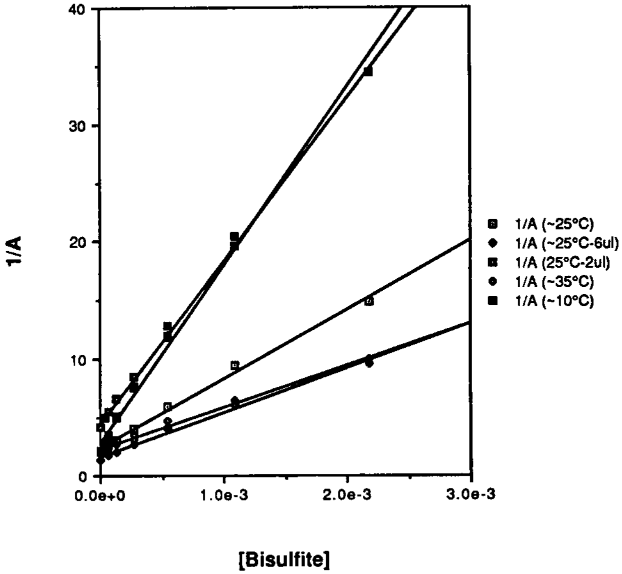


Figure 12. Anisaldehyde Addition Reaction at Various Temperatures

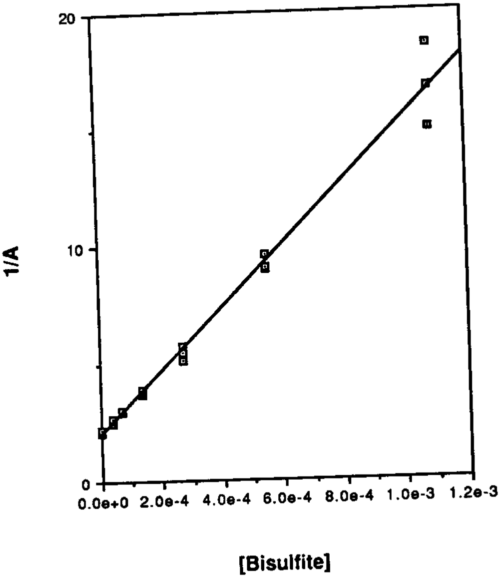


Figure 13. Benzaldehyde Addition Reaction in 0.1M Buffer Solution

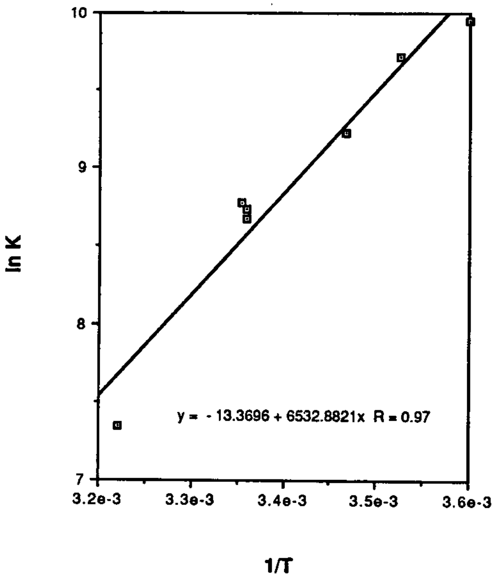


Figure 14. ΔH and ΔS Determination for Benzaldehyde Addition Reaction

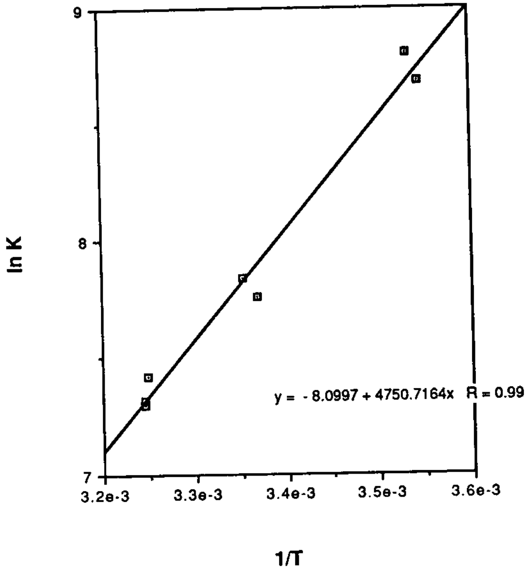


Figure 15. ΔH and ΔS Determination for o-Tolualdehyde Addition Reaction

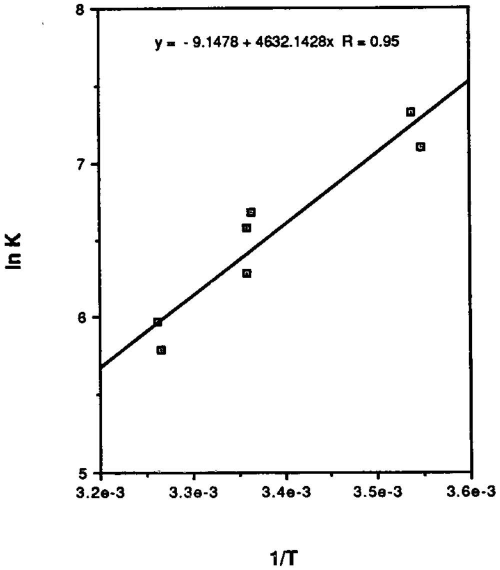


Figure 16. ΔH and ΔS Determination for Salicylaldehyde Addition Reaction

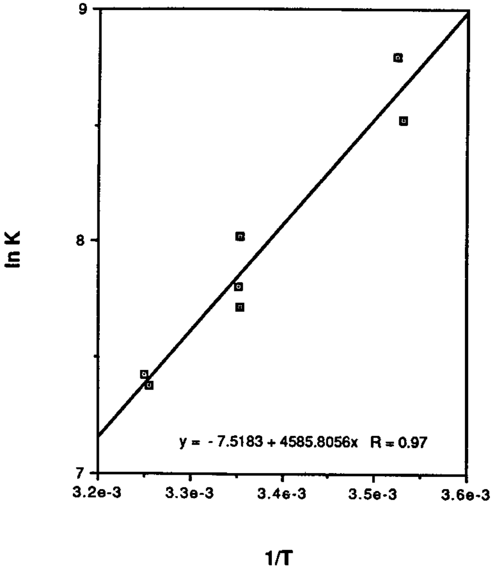


Figure 17. ΔH and ΔS Determination for Anisaldehyde Addition Reaction

REFERENCES

1. D.J. Jacob and M.R. Hoffmann, J. Geophys. Res., **88**, 6611, (1983).

2. L.W. Richards, J.A. Anderson, D.L. Blumenthal and J.S. McDonald, Atmos. Environ., **17**, 911, (1983).

3. UV Atlas of Organic Compounds, **5**, D8/13, (1971).

4. T.D. Stewart and L.H. Donnally, J. Am. Chem. Soc, **54**, 3555, (1932).

5. J.A. Sousa and J.D. Margerum, J. Am. Chem. Soc, **82**, 3013, (1960).

6. T.M. Olson, S.D. Boyce and M.R. Hoffmann, Pepr-Am. Chem. Soc., Div. Pet.Chem., **31(2)**, 546, (1986).

7. F.C. Kokesh and R.E. Hall, J. Org. Chem., **40**, 1632, (1975).

8. P. Geneste, G. Lamaty and J. Rogue, Red. Trav. Chim. Pay-Bas, **91**, 188, (1972).

9. P.K. Dasgupta, K.B. DeCesare and J.C. Ullrey, Analyt. Chem., **52**, 1912, (1980).

10. M.B. Richard, Senior Thesis, Union College, (1985).

11. L.A. LeTarte, Senior Thesis, Union College, (1987).

12. P.R. Young and W.P. Jenks, J. Am. Chem. Soc., **100**, 1228, (1978).