

6-1987

# Determination of the kinetic and thermodynamic properties for bisulfite addition to: acetophenone, 2-chloroacetophenone and trans-cinnamaldehyde

Laurie Ann Le Tarte  
*Union College - Schenectady, NY*

Follow this and additional works at: <https://digitalworks.union.edu/theses>

 Part of the [Chemistry Commons](#)

---

## Recommended Citation

Le Tarte, Laurie Ann, "Determination of the kinetic and thermodynamic properties for bisulfite addition to: acetophenone, 2-chloroacetophenone and trans-cinnamaldehyde" (1987). *Honors Theses*. 2012.  
<https://digitalworks.union.edu/theses/2012>

This Open Access is brought to you for free and open access by the Student Work at Union | Digital Works. It has been accepted for inclusion in Honors Theses by an authorized administrator of Union | Digital Works. For more information, please contact [digitalworks@union.edu](mailto:digitalworks@union.edu).

DETERMINATION OF THE KINETIC AND  
THERMODYNAMIC PROPERTIES FOR BISULFITE  
ADDITION TO: ACETOPHENONE,  
2-CHLOROACETOPHENONE AND  
TRANS-CINNAMALDEHYDE

By

Laurie Ann Le Tarte

\*\*\*\*\*

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

Union College

June, 1987

21162  
2645d

## ABSTRACT

LE TARTE, LAURIE Determination of the kinetic and thermodynamic properties for bisulfite addition to: acetophenone, 2-chloroacetophenone and trans-cinnamaldehyde. Department of Chemistry, 1987.

The equilibrium constants for bisulfite addition to acetophenone, 2-chloroacetophenone and trans-cinnamaldehyde were determined using an ultraviolet spectrophotometric method. The absorbance of the carbonyl compound was monitored as aliquots of a bisulfite solution were added to the reaction cell. By plotting  $1/A$  versus  $[\text{HSO}_3^-]$ , and dividing the slope by the intercept, it was possible to determine  $K_{\text{eq}}$ . All determinations were made at pH 4.66 and ionic strength 1.0. By determining  $K_{\text{eq}}$  at various temperatures it was also possible to determine  $\Delta H^\circ$  and  $\Delta S^\circ$ . The equilibrium constants for bisulfite addition to: acetophenone, 2-chloroacetophenone and trans-cinnamaldehyde, were determined to be:  $5.8 \text{ M}^{-1}$ ,  $53 \text{ M}^{-1}$ , and  $1030 \text{ M}^{-1}$  respectively.

The rate constants for bisulfite addition to trans-cinnamaldehyde were also determined using an ultraviolet spectrophotometric method. The change in absorbance, after the addition of bisulfite, was monitored at one second intervals for fifteen minutes. The forward and reverse rate constants for bisulfite addition to trans-cinnamaldehyde were determined to be,  $24.3 \text{ M}^{-1}\text{s}^{-1}$  and  $2.4 \times 10^{-2} \text{ s}^{-1}$  respectively.

I would like to extend my thanks to the Chemistry Department for giving me the opportunity to apply the knowledge that the Professors have faithfully and willingly imparted to me. I would especially like to thank Professor Hull for his patience, and for his ability to steer me in the right direction without necessarily telling me the exact direction to go in. His abundance of knowledge never failed me when I needed it. I would also like to thank my lab partner, Dan Choi. Finding the right answers can be much easier when you have someone to talk the problem out with.

Thank You,

*Laurie A. Feltarte*

## TABLE OF CONTENTS

|                              |    |
|------------------------------|----|
| Abstract .....               | ii |
| Table of Figures .....       | v  |
| Table of Tables .....        | vi |
| Introduction .....           | 1  |
| Experimental .....           | 10 |
| Discussion and Results ..... | 14 |
| References .....             | 29 |
| Appendix .....               | 30 |

## TABLE OF FIGURES

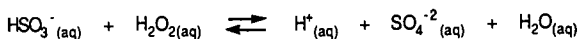
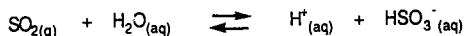
|   |    |
|---|----|
| Abs. at 255 nm versus bisulfite concentration .....             | 15 |
| Abs. at 255 nm versus bisulfite conc. squared .....             | 15 |
| Calibration curve for acetophenone .....                        | 16 |
| $K_{eq}$ at 21.8° C for acetophenone .....                      | 17 |
| $K_{eq}$ for acetophenone at various temperatures .....         | 18 |
| $\ln K_{eq}$ versus $1/T$ for acetophenone .....                | 18 |
| Calibration curve for 2-chloroacetophenone .....                | 19 |
| $K_{eq}$ at 25° C for 2-chloroacetophenone .....                | 20 |
| $K_{eq}$ for 2-chloroacetophenone at various temperatures ..... | 21 |
| $\ln K_{eq}$ versus $1/T$ for 2-chloroacetophenone .....        | 21 |
| Calibration curve for trans-cinnamaldehyde .....                | 22 |
| $K_{eq}$ at 25° C for trans-cinnamaldehyde .....                | 23 |
| $K_{eq}$ for trans-cinnamaldehyde at various temperatures ..... | 24 |
| $\ln K_{eq}$ versus $1/T$ for trans-cinnamaldehyde .....        | 24 |
| $\ln(A-A_{\infty})$ versus time for run 3 .....                 | 25 |
| Determination of $k_1$ for trans-cinnamaldehyde .....           | 26 |

TABLE OF TABLES

|   |    |
|---|----|
| Comparison of extinction coefficients ..... | 9  |
| Summary of results .....                    | 26 |
| Summary of equilibrium constants .....      | 27 |

## INTRODUCTION

Due to an increasing awareness of the need to preserve our environment, much research has gone into developing a better understanding of the production of acid rain. One of the main reactions involved in this process is the oxidation of S(IV) to S(VI):



Sulfur dioxide (S(IV)) is released into the atmosphere upon the combustion of sulfur containing fossil fuels. While S(IV) may be oxidized by other agents in the atmosphere, Penkett found hydrogen peroxide to be the major oxidizing agent (1). Between pH 2 and pH 6, the range of atmospheric interest, the major species of S(IV) in rain or cloudwater is  $\text{HSO}_3^-$ . Above pH 3 the oxidation product,  $\text{HSO}_4^-$ , is completely dissociated. This means that the overall conversion of one molar unit  $\text{SO}_2(\text{g})$  will lead to a two fold that molar unit of free acidity (2).

Richards found that given the concentrations of  $\text{H}_2\text{O}_2$  and S(IV) in the atmosphere, the concentration of S(IV) in acid rain was higher than expected (3). He proposed that an inhibition of the S(IV) oxidation was taking place through the formation of HMSA (hydroxymethane sulfonate). HMSA is the adduct formed when formaldehyde and bisulfite react in aqueous solutions.

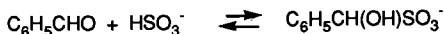


While Richards feels that HMSA inhibits S(IV) oxidation because of its slow dissociation rate, therefore limiting the available S(IV), Hoffman and Jacob feel this is not the case since oxidation proceeds faster than HMSA formation (2).



In addition to formaldehyde, bisulfite is known to readily form substituted hydroxymethane sulfonates with higher aldehydes as well as ketones (4). Aldehydes and ketones are produced directly in the combustion of hydrocarbon fuels and indirectly by the atmospheric photooxidation of hydrocarbons. The presence of other carbonyl-bisulfite adducts in the atmosphere would account for S(IV) concentrations in excess of that predicted knowing the formaldehyde-bisulfite equilibrium (5). Grosjean and Wright found formaldehyde to represent only 50 percent of the carbonyl compounds in cloud water (6). Therefore, to better understand the role sulfur plays in acid rain, it is important to determine the equilibrium and rate constants of the reactions between bisulfite and higher carbonyl compounds.

Stewart and Donnally studied the effect of varying pH and temperature on the equilibrium of the benzaldehyde-bisulfite reaction (7).

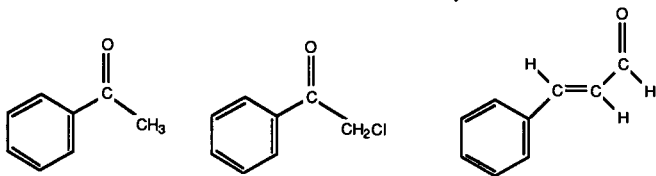


They used an iodometric method in which they measured the extent of reaction by titrating unreacted bisulfite with iodine. They reported that at 21°C and pH 4.77,  $K_{\text{eq}}$  was  $9.4 \times 10^3 \text{ M}^{-1}$ .

Sousa and Margerum also studied the benzaldehyde-bisulfite reaction, but they used a U.V. spectrophotometric method (8). They measured the increase in benzaldehyde absorbance (at 250nm) during adduct dissociation to benzaldehyde and bisulfite. It is not possible to compare their reported equilibrium to others, because they failed to indicate at what pH the data was taken. It is important to note however, that since their use of the U.V. spectrophotometric method many others have used this method, or similar ones, to study the bisulfite addition to aldehydes and ketones. It must be pointed out that simple carbonyls with little or no conjugation (usually the most abundant carbonyls in the atmosphere) will not absorb in the accessible U.V. spectrum, but it is generally felt that the U.V. spectrophotometric methods are more

accurate than the iodometric methods, especially at high pH values (9). While substantial studies have been made on the addition of bisulfite to formaldehyde and benzaldehyde, little work has gone into the study of other carbonyls.

It is the intent of this research project to study the kinetics and thermodynamics of the bisulfite addition to acetophenone, 2-chloroacetophenone and trans-cinnamaldehyde.



Acetophenone

2-chloroacetophenone

trans-cinnamaldehyde

By studying these carbonyls, it will be possible to observe steric and inductive effects on the equilibrium and kinetics of the bisulfite addition reactions.

Young and Jencks have previously determined the equilibrium constants for the addition of bisulfite to acetophenone ( $K_{eq} = 5.5 \text{ M}^{-1}$ ) and p-chloroacetophenone ( $K_{eq} = 8 \text{ M}^{-1}$ ) at 25°C and pH 6.2 (10).

The method used to determine the equilibrium constants will be similar to that used by Kokesh and Hall when they studied the benzaldehyde-bisulfite addition (9). They found that at 25°C and pH 4.0,  $K_{eq}$  was  $6.4 \times 10^3 \text{ M}^{-1}$ .

The derivation used to calculate  $K_{eq}$  is as follows:

If C is the concentration of carbonyl, S is the concentration of bisulfite, and CS is the concentration of adduct, then:



and

$$K_{\text{eq}} = \frac{[\text{CS}]}{[\text{C}][\text{S}]} = \frac{[\text{CS}]}{[\text{C}][\text{S}_0]} \quad (2)$$

where  $[\text{S}]_0$  is the initial concentration of bisulfite. By using initial bisulfite concentrations in excess of initial carbonyl concentrations, it can be assumed that the bisulfite concentration remains constant. Solving eq. 2 for  $[\text{CS}]$  gives:

$$[\text{CS}] = K_{\text{eq}} [\text{C}] [\text{S}]_0 \quad (3)$$

The total concentration of carbonyl,  $[\text{C}]_T$ , in the reaction cell is:

$$[\text{C}]_T = [\text{C}] + [\text{CS}] \quad (4)$$

where  $[\text{C}]$  is the concentration of unreacted carbonyl. Substituting eq. 3 into eq. 4 gives:

$$[\text{C}]_T = [\text{C}] + K_{\text{eq}} [\text{C}] [\text{S}]_0 = [\text{C}] (1 + K_{\text{eq}} [\text{S}]_0) \quad (5)$$

Solving for  $[\text{C}]$  gives:

$$[\text{C}] = \frac{[\text{C}]_T}{1 + K_{\text{eq}} [\text{S}]_0} \quad (6)$$

Substituting eq. 6 into Beer's Law,  $A = \epsilon b[\text{C}]$ , gives:

$$A = \frac{\epsilon [\text{C}]_T}{1 + K_{\text{eq}} [\text{S}]_0} \quad (7)$$

where  $b = 1$  cm. By taking the inverse of both sides of eq. 7 and rearranging, a straight line equation is obtained:

$$\frac{1}{A} = \frac{K_{eq}}{\epsilon [C]_T} [S]_0 + \frac{1}{\epsilon [C]_T} \quad (8)$$

A plot of  $1/A$  versus  $[S]_0$  will give:

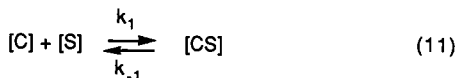
$$\text{slope} = \frac{K_{eq}}{\epsilon [C]_T} \quad \text{and} \quad \text{intercept} = \frac{1}{\epsilon [C]_T} \quad (9)$$

Divide the slope by the intercept to obtain  $K_{eq}$ :

$$K_{eq} = \left[ \frac{K_{eq}}{\epsilon [C]_T} \right] \left[ \frac{\epsilon [C]_T}{1} \right] \quad (10)$$

It is important to note that  $K_{eq}$  is independent of the carbonyl concentration as well as its extinction coefficient. To prove this independence,  $K_{eq}$  was determined using varying concentrations of carbonyl.  $K_{eq}$  was also determined at various temperatures to allow for the calculation of  $\Delta H^\circ$  and  $\Delta S^\circ$ .

The kinetics of a reaction approaching equilibrium can also be used to calculate the forward and reverse rate constants (11):



and

$$\frac{d[CS]}{dt} = k_1 [C] [S] - k_{-1} [CS] \quad (12)$$

The concentration of carbonyl,  $[C]$ , is:

$$[C] = [C]_0 - [CS] \quad (13)$$

where  $[C]_0$  is the initial concentration of carbonyl. Since  $k_1$  and  $[S]$  are constants, they can be combined to form a new constant  $k_1'$ :

$$k_1' = k_1 [S] \quad (14)$$

Substituting eq. 13 and eq. 14 into eq. 12 gives:

$$\frac{d[CS]}{dt} = k_1' ([C]_0 - [CS]) - k_{-1} [CS] \quad (15)$$

At equilibrium, or  $t = \infty$ , the change in adduct concentration is zero. Eq. 15 then becomes:

$$k_1' ([C]_0 - [CS]_{\infty}) = k_{-1} [CS]_{\infty} \quad (16)$$

where  $[CS]_{\infty}$  is the concentration of adduct at equilibrium. Solving eq. 16 for  $k_{-1}$  gives:

$$k_{-1} = \frac{k_1' ([C]_0 - [CS]_{\infty})}{[CS]_{\infty}} \quad (17)$$

Substituting eq. 17 into eq. 15 and rearranging gives:

$$\frac{d[CS]}{dt} = \frac{k_1' [C]_0}{[CS]_{\infty}} ([CS]_{\infty} - [CS]) \quad (18)$$

Rearrangement of eq. 18 for integration gives:

$$\int_0^{[CS]_t} \frac{d[CS]}{([CS]_{\infty} - [CS])} = \frac{k_1' [C]_0}{[CS]_{\infty}} \int_0^t dt \quad (19)$$

Integration gives:

$$-\ln \frac{[CS]_{\infty}}{[CS]_{\infty} - [CS]} = \frac{k_1 [C]_0}{[CS]_{\infty}} t \quad (20)$$

Since

$$[CS]_{\infty} = [C]_0 - [C]_{\infty} \quad (21)$$

and

$$[CS] = [C]_0 - [C] \quad (22)$$

substituting eq. 21 and eq. 22 into eq. 20 gives:

$$\ln \frac{[C]_0 - [C]_{\infty}}{[C] - [C]_{\infty}} = \frac{-k_1 [C]_0}{[C]_0 - [C]_{\infty}} t \quad (23)$$

Using Beer's Law to solve for  $[C]_0$ ,  $[C]_{\infty}$ , and  $[C]$  gives:

$$\frac{A_0}{\epsilon} = [C]_0 \quad (24), \quad \frac{A_{\infty}}{\epsilon} = [C]_{\infty} \quad (25), \quad \frac{A}{\epsilon} = [C] \quad (26)$$

Substituting eq.s 24, 25 and 26 into eq. 23 gives:

$$\ln \frac{A_0 - A_{\infty}}{A - A_{\infty}} = \frac{-k_1 A_0}{A_0 - A_{\infty}} t \quad (27)$$

Rearrangement of eq. 27 gives a straight line equation:

$$\ln (A - A_{\infty}) = \frac{-k_1' A_0}{A_0 - A_{\infty}} t + \ln (A_0 - A_{\infty}) \quad (28)$$

A plot of  $\ln (A - A_{\infty})$  versus  $t$  gives:

$$\text{slope} = \frac{-k_1' A_0}{A_0 - A_{\infty}} \quad (29)$$

and

$$\text{Intercept} = \ln (A_0 - A_{\infty}) \quad (30)$$

Therefore,

$$k_1' = \frac{-\text{slope} (A_0 - A_{\infty})}{A_0} \quad (31)$$

and

$$k_1 = \frac{k_1'}{[S]} \quad (32)$$

Since

$$K_{\text{eq}} = \frac{k_1}{k_{-1}} \quad (33)$$

it will be possible to calculate  $k_{-1}$  from the experimental determination of  $K_{\text{eq}}$  and  $k_1$ .

$$k_{-1} = \frac{k_1}{K_{\text{eq}}} \quad (34)$$

An assumption made in the derivations of  $K_{\text{eq}}$  and  $k_1$  is that only the carbonyl compound is absorbing at the wavelength of

interest and not the carbonyl-bisulfite adduct. This can be justified by comparing the extinction coefficients of both species, as, according to Beer's Law absorbance is proportional to the extinction coefficient of a molecule. But, due to the equilibrium being studied, the carbonyl-bisulfite adduct cannot be isolated in solution for extinction coefficient determination. It is the extent of conjugation within a molecule which determines the size of its extinction coefficient, therefore, the extinction coefficients of molecules with identical conjugation as the carbonyl-bisulfite adducts were used for comparison. Toluene was used as a model for the acetophenone and 2-chloroacetophenone bisulfite adducts, while styrene was used as a model for the trans-cinnamaldehyde bisulfite adduct.

Table I. Comparison of extinction coefficients

| <u>Compound</u>      | <u><math>\lambda</math>(nm)</u> | <u><math>\epsilon</math></u> |
|----------------------|---------------------------------|------------------------------|
| Acetophenone         | 245                             | 12,600                       |
| 2-Chloroacetophenone | 245                             | 12,000                       |
| Toluene              | 245                             | 120                          |
| trans-Cinnamaldehyde | 290                             | 25,000                       |
| Styrene              | 290                             | 570                          |

As can be seen from Table I, the extinction coefficients for acetophenone and 2-chloroacetophenone are, at least, one hundred times larger than their bisulfite adducts, and the extinction coefficient for trans-cinnamaldehyde is fifty times larger. For this reason, any absorbance due to the adducts is negligible and can be ignored.



## EXPERIMENTAL

### CHEMICALS

Reagent grade chemicals were used throughout the experiment. Inorganic salts, and organic solids were used without further purification. Organic liquids were redistilled under nitrogen, and refrigerated at  $-4^{\circ}\text{C}$  in brown glass bottles.

### INSTRUMENTATION

All ultraviolet absorbances and spectra were taken on a Perkin-Elmer Lambda 3B spectrophotometer interfaced to a Perkin-Elmer 3600 microcomputer. One cm absorption cells were used throughout the experiment. The temperature within the cell was controlled by a Neslab Endcol RT-9 refrigerated circulating bath which circulated water through the cell compartment. The actual temperature of the solutions within the cell were taken using an Omega 871 digital thermometer. All pH measurements were taken using an Orion 701A digital ionalyzer. All weight measurements were made on analytical top loading balances.

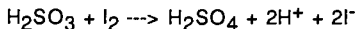
### SOLUTION PREPARATIONS

#### Buffer:

A 1.0 M, 1:1 acetic acid/sodium acetate buffer was used to maintain a pH of 4.66, as well as a constant ionic strength of 1.0, within the reaction cells. The pH was determined for each new buffer solution, and corrected to pH 4.66. The acetate buffer was chosen not only for its pH value, but also because it does not absorb strongly at the wavelengths of interest to this project.

#### Sodium Bisulfite:

A stock solution of approximately 0.8 M was made by weighing 41.624 g sodium bisulfite directly into a 500 mL volumetric flask, and then diluting with distilled water. The exact concentration of the stock solution was the determined by an Iodine titration:



Initially, as S(IV) is easily oxidized to S(VI), the bisulfite solution was titrated before each use. It was found that when nitrogen gas was used to displace free oxygen from within the bisulfite solution and container, as well as keeping the container tightly sealed, the bisulfite concentration changed very little. Therefore, titrations were carried out at time intervals of approximately two weeks.

#### Preparation of a standard Iodine solution:

Since iodine is only slightly soluble in water, but quite soluble in solutions containing iodide ion, the iodine solution is made up in a 10:1 ( $\text{I}^-$  to  $\text{I}_2$ ) potassium iodide solution. To make a 0.1 M iodine standard solution, 183 g potassium iodide was weighed directly into a 1 L volumetric flask and then dissolved in approximately 50 mL distilled water. 25.38 g iodine was then weighed directly into the potassium iodide solution. The entire solution was diluted to 1 L with distilled water.

#### Titration:

Approximately 5 mL of the sodium bisulfite stock was delivered, by buret, into a 50 mL volumetric flask where it was then acidified to pH 2 with concentrated sulfuric acid. 3 drops of fresh starch solution was added as an endpoint indicator. To prevent the possible loss of  $\text{SO}_2(\text{g})$  the flask was covered with paraffin film. A small hole was punctured in the film for the tip of the iodine buret. Throughout the titration vigorous stirring was applied by a magnetic stirrer. When the above steps were not followed, inconsistent, as well as low, results were obtained.

#### Ketone and Aldehyde solutions:

0.02 - 0.06 M stock solutions were made by weighing directly into a 10 mL volumetric flask and then diluting to 10 mL with 95% or 100% ethanol. The stock solutions were stored in brown glass bottles and refrigerated at  $-4^\circ\text{C}$ . Nitrogen gas was used to displace free oxygen from within the solutions and storage bottles between

uses. To check for adherence to Beer's Law, calibration curves were made for each carbonyl compound. This also allowed for the determination of their extinction coefficients in buffer solution.

#### METHOD

For  $K_{eq}$  determinations:

A 3 mL bulb pipet was used to deliver the stock buffer into the reference and sample cells. Typically, 3  $\mu\text{L}$  of the stock ketone or aldehyde was then delivered into the sample cell using a 1-10  $\mu\text{L}$  syringe (resulting in solution concentrations of  $2 \times 10^{-5}$  -  $6 \times 10^{-5}$  M). A spectrum was taken, from 350 nm to 190 nm, before the addition of any bisulfite. A 10-50  $\mu\text{L}$  syringe was used to deliver equal amounts of bisulfite stock into the reference and sample cells. The sample cell was allowed to reach equilibrium after each 10-20  $\mu\text{L}$  addition of bisulfite, and the absorption was then read directly off the U.V. instrument. The total addition of bisulfite ranged from 60-80  $\mu\text{L}$ , resulting in cell concentrations of approximately  $2 \times 10^{-2}$  M. After the final addition of bisulfite, another spectrum was taken. Buffer and bisulfite were added to the reference cell to cancel their absorbance in the sample cell.

Direct absorbance readings were taken at 244 nm for acetophenone, 248 nm for 2-chloroacetophenone, and 291 nm for trans-cinnamaldehyde. The door of the cell compartment was left open between absorbance readings to minimize photolysis.

For  $k_1$  determinations:

For the determination of  $k_1$ , a time drive program was used on the Perkin-Elmer 3600 data station to take absorption readings at one second time intervals after the addition of bisulfite. 3 mL of buffer was delivered into the sample and reference cells. The initial absorbance ( $A_0$ ) was taken after the injection of 3  $\mu\text{L}$  carbonyl stock into the sample cell (resulting in cell concentrations of  $2.54 \times 10^{-5}$  M carbonyl). After the time drive program had been started, 50  $\mu\text{L}$  of bisulfite stock was injected into the sample cell (resulting in cell concentrations of  $1.36 \times 10^{-3}$  M bisulfite), the solution was mixed by inversion, and the cell was

placed back into the compartment. It was important to get the cell back into the compartment as quickly as possible, as the initial absorbance changes are the greatest. The length of time, from bisulfite injection until the appearance of the highest absorbance on the time drive screen, was determined, to give a true time value for each absorbance reading. The time given by the program does not include solution mixing time. The reaction absorption was taken every second for 15 minutes, and stored in time drive. As the reaction had reached equilibrium prior to 15 minutes, the absorbance at 15 minutes was set equal to  $A_{\infty}$ .

## DISCUSSION AND RESULTS

### Acetophenone:

The initial determination of the equilibrium constant, for the bisulfite addition to acetophenone, was made following the method of Kokesh and Hall (9). This method involved making separate buffer solutions containing identical concentrations of the carbonyl compound, but varying concentrations of bisulfite. The absorbance of each solution was taken immediately, and then again at different time intervals to determine the time required to reach equilibrium. Equilibrium was reached quite rapidly for the bisulfite addition to acetophenone, as the absorbances did not change with time. This method was not only time consuming, but introduced more error than was necessary. The difference in absorbance, between solutions, was not only due to different bisulfite concentrations, but also to different acetophenone concentrations. Since a 1-10  $\mu\text{L}$  syringe was used to deliver 3  $\mu\text{L}$  of acetophenone stock into each reaction solution, just a small difference in injection size would contradict the assumption that each solution contained identical acetophenone concentrations. By using the one cell method described earlier, only one measurement of acetophenone was necessary, and therefore involved less error than the Kokesh and Hall method.

Another problem initially encountered, was that plots of  $1/A$  versus  $[\text{HSO}_3^-]$ , for low temperature runs, lost their linearity at high bisulfite concentrations. This can be explained by Golding's proposal that in aqueous solutions bisulfite is in equilibrium with a dimer (12). Golding's proposal was tested by making a calibration curve for bisulfite at 255 nm. A plot of absorbance versus bisulfite concentration does not follow Beer's Law (Figure I). When absorbance was plotted against the square of the bisulfite concentration linearity was obtained (Figure II). While this does not prove Golding's proposal, it does indicate that there is a species present which is related to the square of bisulfite.

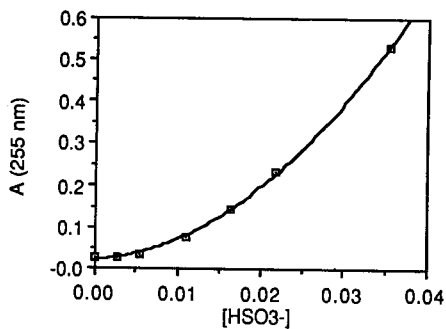


Figure I. Absorbance at 255nm versus bisulfite concentration

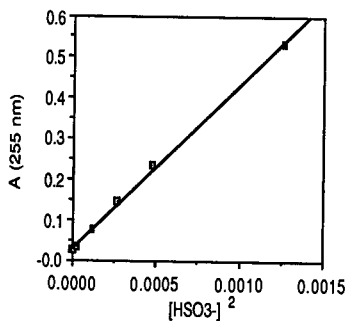


Figure II. Absorbance at 255nm versus the square of the bisulfite concentration

The fact that this species causes a deviation from linearity in the  $K_{eq}$  determination at low temperatures and high bisulfite concentrations can easily be explained. The equilibrium constant

between bisulfite and the dimer is small, so that until high bisulfite concentrations are reached there is not enough dimer present to change the assumed concentration of bisulfite. Nonlinearity did not become a problem until bisulfite concentrations greater than  $2 \times 10^{-2}$  M were reached, and then only for the lowest temperature run ( $0.8^\circ$  C).

The calibration curve for acetophenone, in buffer, revealed that at  $\lambda_{\max}$  (244 nm) the extinction coefficient was 11,800 (Figure III). The literature value for the acetophenone extinction coefficient, in ethanol, is 12,600.

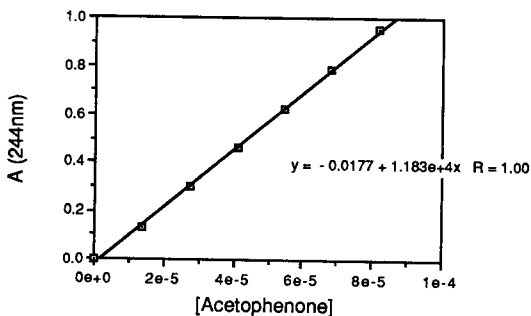


Figure III. Calibration curve for acetophenone

The equilibrium constant for the bisulfite addition to acetophenone was determined at  $21.8^\circ$  C. As mentioned earlier, the equilibrium constant for the bisulfite addition to carbonyl compounds, should be independent of carbonyl concentration. To check this,  $K_{eq}$  was determined for three different bisulfite additions, each containing different initial concentrations of acetophenone:  $3.42 \times 10^{-5}$  M ( $2 \mu$ L stock),  $5.13 \times 10^{-5}$  M ( $3 \mu$ L) and  $6.84 \times 10^{-5}$  M ( $4 \mu$ L) acetophenone. The absorbance was taken before the addition of bisulfite and after the addition of  $10 \mu$ L,  $20 \mu$ L,  $40$

$\mu\text{L}$ , 60  $\mu\text{L}$  and 80  $\mu\text{L}$  bisulfite stock (giving a total bisulfite concentration of  $2.14 \times 10^{-2}$  M). Plots of  $1/A$  versus  $[\text{HSO}_3^-]$  were made for each run and the equilibrium constants were obtained by dividing the slopes by the intercepts (Figure IV).

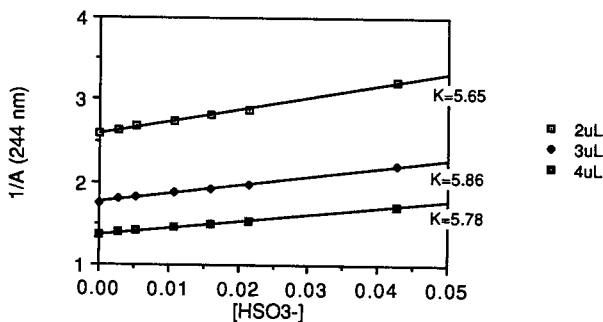


Figure IV.  $K_{\text{eq}}$  at  $21.8^\circ\text{C}$  for varying initial acetophenone concentrations

Figure IV shows that while the slopes and intercepts differ for each solution, the equilibrium constants are essentially the same. The equilibrium constant for the addition of bisulfite to acetophenone is indeed independent of acetophenone concentration. The average equilibrium constant for the three runs was  $5.8\text{ M}^{-1}$ . This value is similar to the value reported by Young and Jencks,  $5.5\text{ M}^{-1}$  at pH 6.2 and  $25^\circ\text{C}$  (9).

The acetophenone-bisulfite equilibrium constant was also determined at various temperatures to allow for the calculation of enthalpy ( $\Delta H^\circ$ ) and entropy ( $\Delta S^\circ$ ) (Figure V). The initial acetophenone concentration for each temperature run was  $5.13 \times 10^{-5}$  M. Figure V shows that as the temperature decreased, the equilibrium constant increased. This trend would be predicted, as the bisulfite addition involves a decrease in entropy (two



molecules --> one), and decreasing entropy is favored by decreasing temperatures.

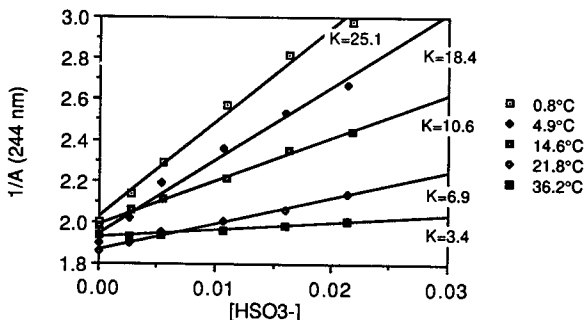


Figure V.  $K_{eq}$  for acetophenone at various temperatures

A plot of  $\ln K_{eq}$  versus  $1/T$  (Figure VI), where temperature is in kelvin, yields  $\Delta H^\circ$  and  $\Delta S^\circ$ .  $\Delta H^\circ = -\text{slope} \times R$  and  $\Delta S^\circ = \text{intercept} \times R$ , where  $R$  is the gas constant ( $8.31441\text{J/mol}\cdot^\circ\text{K}$ ).

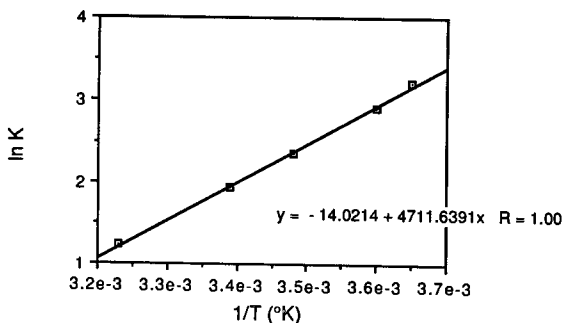


Figure VI.  $\ln K_{eq}$  versus  $1/T$  for acetophenone thermodynamics

For the bisulfite addition to acetophenone,  $\Delta H^\circ = -39 \text{ kJ/mol}$  and  $\Delta S^\circ = -116 \text{ J/mol}\cdot^\circ\text{K}$ .

#### 2-Chloroacetophenone:

The calibration curve for 2-chloroacetophenone, in buffer, revealed that at  $\lambda_{\text{max}}$  (248 nm) the extinction coefficient was 11,700 (figure VII). This was not surprising as acetophenone and 2-chloroacetophenone have identical conjugation, and would therefore have similar extinction coefficients.

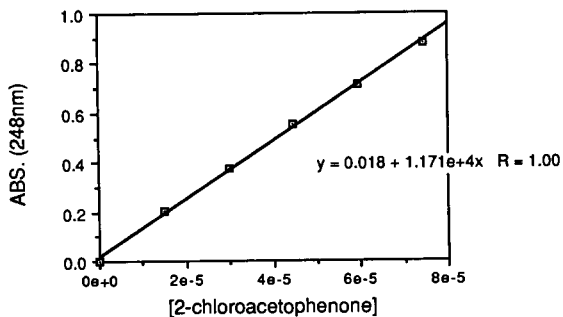


Figure VII. Calibration curve for 2-Chloroacetophenone

After the addition of bisulfite, the cell was allowed to sit until there was no change in absorption. This assured that equilibrium had been reached before a data point was taken. The door to the cell compartment was left open during this time to prevent photolysis. It was found that equilibrium was reached quite rapidly (within seconds) for the bisulfite addition to 2-chloroacetophenone. Therefore, the absorbance was read immediately after bisulfite addition to the cell. The equilibrium constant for the bisulfite addition to 2-chloroacetophenone was determined at 25° C. As with acetophenone, the equilibrium constant for the bisulfite addition to 2-chloroacetophenone was

determined using three different initial concentrations of 2-chloroacetophenone:  $2.98 \times 10^{-5}$  M (2  $\mu$ L stock),  $4.47 \times 10^{-5}$  M (3  $\mu$ L), and  $5.96 \times 10^{-5}$  M (4  $\mu$ L) 2-chloroacetophenone. Figure VIII shows that the equilibrium constant for the bisulfite addition to 2-chloroacetophenone is also independent of carbonyl concentration.

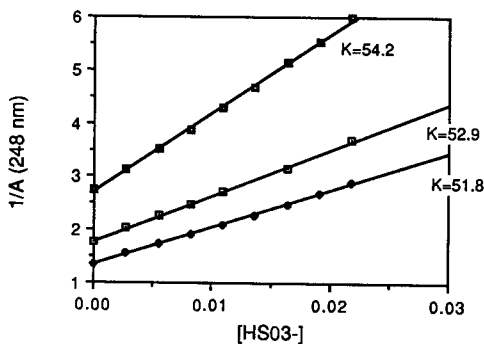


Figure VIII.  $K_{eq}$  at 25° C for varying 2-chloroacetophenone concentrations

The average equilibrium constant for the three 2-chloroacetophenone runs was  $53 \text{ M}^{-1}$ .

The temperature runs for the bisulfite addition to 2-chloroacetophenone showed the same trend as for the addition to acetophenone (Figure IX). As temperature decreased, the equilibrium constant increased.

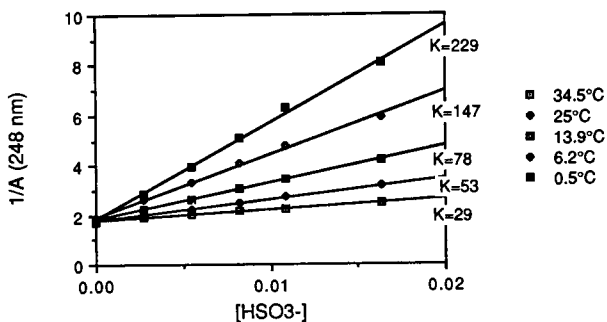


Figure IX.  $K_{eq}$  for 2-chloroacetophenone at various temperatures

A plot of  $\ln K_{eq}$  versus  $1/T$  (kelvin) revealed that  $\Delta H^\circ = -41$  kJ/mol and  $\Delta S^\circ = -106$  J/mol $\cdot$ °K for the addition of bisulfite to 2-chloroacetophenone (Figure X).

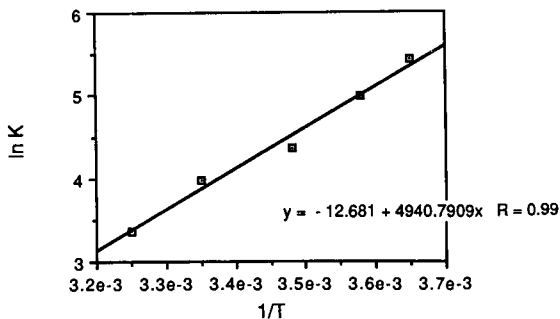


Figure X.  $\ln k_{eq}$  versus  $1/T$  for 2-chloroacetophenone thermodynamics

### trans-Cinnamaldehyde:

As mentioned earlier, an NMR was taken on the distilled trans-cinnamaldehyde to determine whether any cis-cinnamaldehyde was present. By determining the coupling constants for the C=C hydrogens (see Appendix B), and comparing the spectrum to a literature spectrum, it was determined that only trans-cinnamaldehyde was present.

The calibration curve for trans-cinnamaldehyde, in buffer, revealed that at  $\lambda_{\text{max}}$  (291 nm) the extinction coefficient was 25,400 (Figure XI). The literature value for the trans-cinnamaldehyde extinction coefficient, in ethanol, was 25,000.

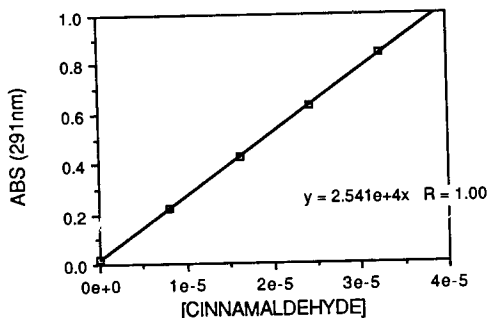


Figure XI. Calibration curve for trans-cinnamaldehyde

The extinction coefficient is larger for trans-cinnamaldehyde because it has more conjugation than the acetophenones. To keep the absorbance below one, it was necessary to use trans-cinnamaldehyde concentrations which were approximately half that of the acetophenone concentrations. Because the equilibrium constant for the bisulfite addition to trans-cinnamaldehyde is larger than the acetophenones, a ten fold decrease in bisulfite concentration was used for the

trans-cinnamaldehyde runs. Without the decrease in bisulfite concentration, most of the trans-cinnamaldehyde had reacted with bisulfite before enough data points had been obtained. Another effect of the larger equilibrium constant was that it took much longer for the cell to reach equilibrium after bisulfite injection. Approximately twelve minutes had to pass before absorbance readings were constant.

The three runs to determine the equilibrium constant, at 25°C, had initial trans-cinnamaldehyde concentrations of:  $1.62 \times 10^{-5}$  M (2  $\mu$ L stock),  $2.45 \times 10^{-5}$  M (3  $\mu$ L),  $3.24 \times 10^{-5}$  M (4  $\mu$ L). The bisulfite additions to the cell were: 10  $\mu$ L, 20  $\mu$ L, 30  $\mu$ L, 40  $\mu$ L, 50  $\mu$ L, and 60  $\mu$ L giving a total bisulfite concentration of  $1.64 \times 10^{-3}$  M. The average equilibrium constant for the three runs was  $1030 \text{ M}^{-1}$  (Figure XII).

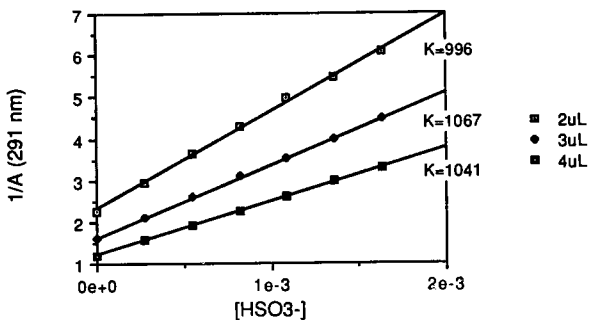


Figure XII.  $K_{eq}$  at 25°C for varying trans-cinnamaldehyde concentrations

The temperature runs to determine  $\Delta H^\circ$  and  $\Delta S^\circ$  showed the same trend as mentioned earlier (Figure XIII), as temperature decreased, the equilibrium constant increased.

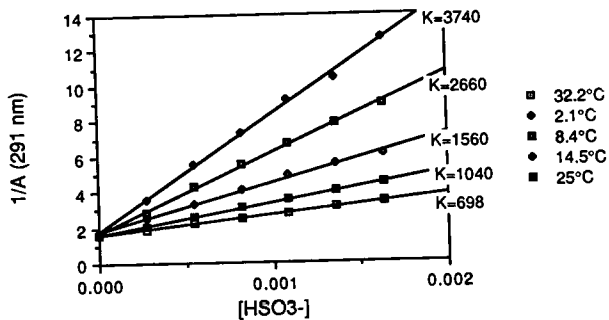


Figure XIII.  $K_{eq}$  for trans-cinnamaldehyde at various temperatures

A plot of  $\ln K_{eq}$  versus  $1/T$  (Figure XIV) revealed that  $\Delta H^\circ = -38$  kJ/mol and  $\Delta S^\circ = -71$  J/mol $\cdot$ K for the bisulfite addition to trans-cinnamaldehyde.

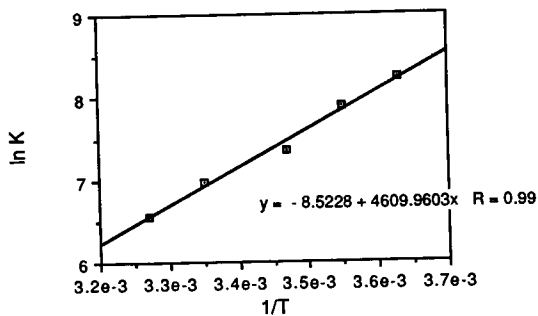


Figure XIV.  $\ln k_{eq}$  versus  $1/T$  for trans-cinnamaldehyde thermodynamics

The forward and reverse rate constants,  $k_1$  and  $k_{-1}$ , for the bisulfite addition to trans-cinnamaldehyde were also determined. Refer to the introduction for the definition of constants, and details of the method used in these determinations.

$k_1'$  was determined at 25° C for three different runs, each having different concentrations of bisulfite. A plot of  $\ln(A-A_\infty)$  versus time (sec), gives:  $k_1' = -(\text{slope} \times (A_0 - A_\infty)) / A_0$ . See Table II for a summary of run conditions and Figure XV for an example plot of  $\ln(A-A_\infty)$  versus time.

Table II. Summary of run conditions used in the determination of  $k_1$  and  $k_{-1}$

|                       | <u>run 1</u>          | <u>run 2</u>          | <u>run 3</u>          |
|-----------------------|-----------------------|-----------------------|-----------------------|
| Cinnamaldehyde (M)    | $2.43 \times 10^{-5}$ | $2.54 \times 10^{-5}$ | $2.54 \times 10^{-5}$ |
| Bisulfite (M)         | $1.36 \times 10^{-3}$ | $7.43 \times 10^{-4}$ | $3.72 \times 10^{-4}$ |
| $k_1'$ (sec $^{-1}$ ) | $3.37 \times 10^{-2}$ | $1.83 \times 10^{-2}$ | $1.07 \times 10^{-2}$ |
| $A_0$                 | 0.627                 | 0.684                 | 0.616                 |
| $A_\infty$            | 0.250                 | 0.378                 | 0.439                 |

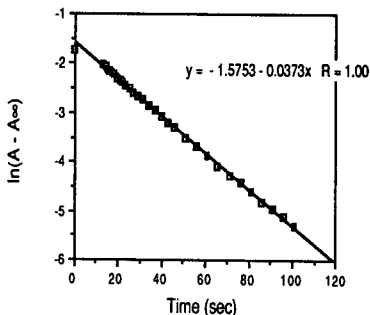


Figure XV.  $\ln(A-A_\infty)$  versus time for run 3



Since  $k_1' = k_1[\text{HSO}_3^-]$ , a plot of  $k_1'$  versus bisulfite concentration will have a slope equal to  $k_1$ , the forward rate constant (Figure XVI).

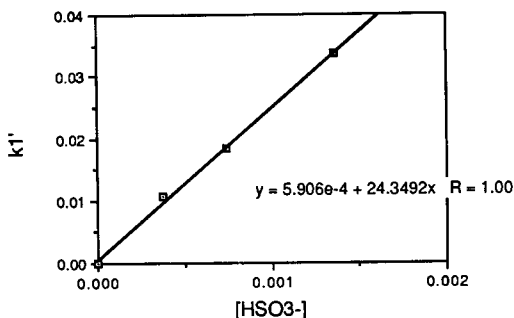


Figure XVI. Determination of  $k_1$  for trans-cinnamaldehyde

Figure XVI revealed that the forward rate constant for the bisulfite addition to trans-cinnamaldehyde was  $24.3 \text{ M}^{-1} \text{ sec}^{-1}$ . The reverse rate constant was determined by dividing the forward rate constant ( $24.3 \text{ M}^{-1} \text{ sec}^{-1}$ ) by the equilibrium constant ( $1030 \text{ M}^{-1}$ ) giving a reverse rate constant equal to  $2.4 \times 10^{-2} \text{ sec}^{-1}$ .

A summary table of the properties determined in this research project follows:

Table II. Summary of results

| Carbonyl Compound    | $K_{\text{eq}}$ ( $\text{M}^{-1}$ ) | $\Delta H^\circ$ (kJ/mol) | $\Delta S^\circ$ (J/mol $^\circ\text{K}$ ) | $k_1$ ( $\text{M}^{-1}\text{s}^{-1}$ ) | $k_{-1}$ ( $\text{s}^{-1}$ ) |
|----------------------|-------------------------------------|---------------------------|--|--|------------------------------|
| Acetophenone         | 5.8                                 | -39                       | -116                                       | ---                                    | ---                          |
| 2-Chloroacetophenone | 53                                  | -41                       | -106                                       | ---                                    | ---                          |
| trans-Cinnamaldehyde | 1030                                | -38                       | -71  | 24.3                                   | $2.4 \times 10^{-2}$         |

All determinations were made at pH 4.66, and an ionic strength of 1.0. The equilibrium constant for acetophenone was determined at 21.8° C, while the equilibrium constants for 2-chloroacetophenone and trans-cinnamaldehyde, as well as the rate constants for trans-cinnamaldehyde, were determined at 25° C. The error involved in all determinations, was estimated to be  $\pm 5\%$ . This estimation was made by drawing high and low lines through the data points, and then comparing these lines to the line obtained by linear regression.

As mentioned earlier, one of the reasons for studying these particular compounds was to observe steric and inductive effects on the kinetics of the bisulfite addition to carbonyl compounds. While there has not yet been enough data collected on the rate constants, it is possible to compare the equilibrium constants for this addition to various carbonyl compounds. See Table III for a summary of equilibrium constants.

Table III. Summary of Equilibrium Constants

| Carbonyl Compound    | pH   | $K_{eq}$ ( $M^{-1}$ ) |
|----------------------|------|-----------------------|
| Formaldehyde(13)     | 5.0  | 85,000                |
| Acetaldehyde(14)     | 4.7  | 16,000                |
| Benzaldehyde(15)     | 4.66 | 6,400                 |
| o-Anisaldehyde(15)   | 4.66 | 2,600                 |
| o-Tolualdehyde(15)   | 4.66 | 2,400                 |
| trans-Cinnamaldehyde | 4.66 | 1,030                 |
| Salicylaldehyde(15)  | 4.66 | 690                   |
| 2-Chloroacetophenone | 4.66 | 53                    |
| Acetophenone         | 4.66 | 5.8                   |

There is a dramatic drop in  $K_{eq}$  between formaldehyde and acetaldehyde. This can be explained by both steric and inductive effects. The methyl group is not only bulky, compared to hydrogen, but is also an electron donor. The addition of a bulky group to the carbonyl compound would make the product less stable than the

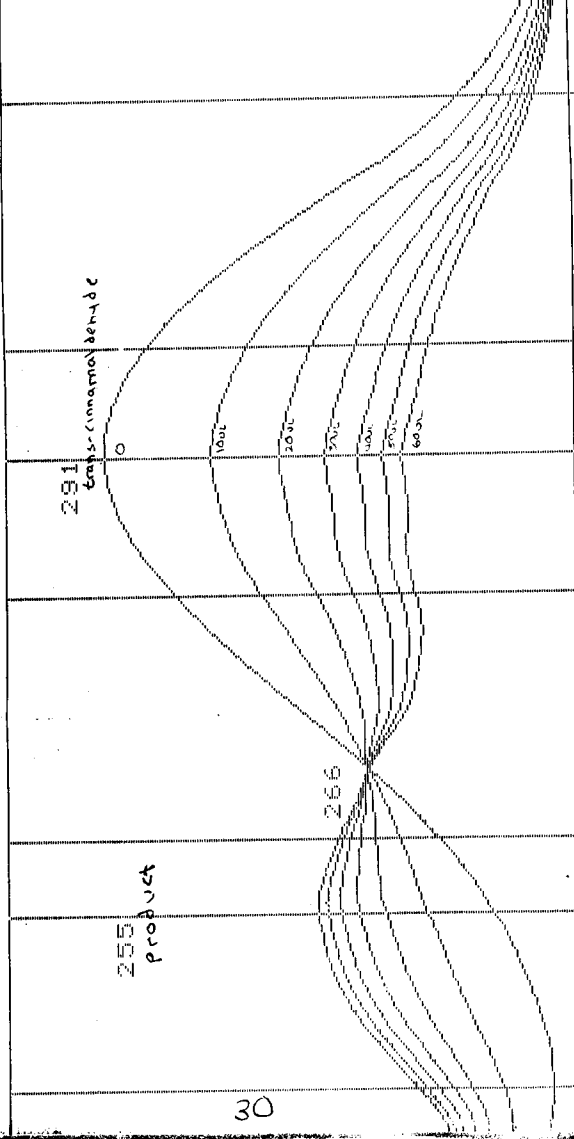
reactant, as the bond angles of the products are less than the reactants, therefore making the product more crowded. There is another drop in  $K_{eq}$  when the methyl group on acetaldehyde is replaced by the aromatic ring in benzaldehyde. This can be explained by the added stability of the reactant due to conjugation between the aromatic ring and the oxygen of the carbonyl group. The similarity of the equilibrium constants for o-anisaldehyde and o-tolualdehyde indicate that this drop in  $K_{eq}$  is due to a steric effect rather than inductive. The drop in  $K_{eq}$  for trans-cinnamaldehyde can be explained by an even greater extent of conjugation than benzaldehyde. Because the drop in  $K_{eq}$  for o-anisaldehyde was primarily due to steric effects, one would expect that  $K_{eq}$  for salicylaldehyde would be larger, as the hydroxy group is less bulky than the methoxy group. It can be seen in Table III, that  $K_{eq}$  for salicylaldehyde is in fact much smaller. The added stability of salicylaldehyde can be explained by hydrogen bonding between the hydrogen of the hydroxy group and the oxygen of the carbonyl group. There is another large drop in  $K_{eq}$  for the ketones. This is due to the replacement of both formaldehyde hydrogens by bulky groups. The drop in  $K_{eq}$  for 2-chloroacetophenone is not as great as for acetophenone, this is due to the electron withdrawing ability of chlorine.

#### REFERENCES

1. S. A. Penkett, B. M. R. Jones, K. A. Bruce, A. E. J. Eggleton, Atmos. Environ., 13, 123 (1979).
2. M. R. Hoffman, D. J. Jacob, J. Geophys. Res., 88, 6611 (1983).
3. L. W. Richards, J. A. Anderson, D. L. Blumenthal, J. A. McDonald, Atmos. Environ., 17, 911 (1983).
4. T. H. Lowry, K. S. Richardson, Mechanism and Theory in Organic Chemistry, 2nd Ed, 612 (1981).
5. W. Munger, D. J. Jacob, M. R. Hoffman, J. Atmos. Chem., 1, 335 (1984).
6. D. Grosjean, B. Wright, Atmos. Environ., 17, 2093 (1983).
7. T. D. Stewart, L. H. Donnally, J. Am. Chem. Soc., 54, 3555 (1932).
8. J. A. Sousa, J. D. Margerum, J. Am. Chem. Soc., 82, 3013 (1960).
9. F. C. Kokesh, R. E. Hall, J. Org. Chem., 40, 1632 (1974).
10. P. R. Young, W. D. Jencks, J. Am. Chem. Soc., 101, 3288 (1979).
11. K. J. Ladler, Chemical Kinetics, 19 (1965).
12. R. M. Golding, J. Am. Chem. Soc., 3711 (1960).
13. P. K. Dasgupta, Atmos. Environ., 15, 1090 (1981).
14. M. B. Richards, Senior Thesis, Union College (1985).
15. D. Y. Choi, Senior Theses, Union College (1987).

MAX=1.

MIN=0

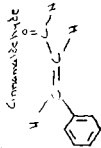


291  
trans-cinnamaldehyde

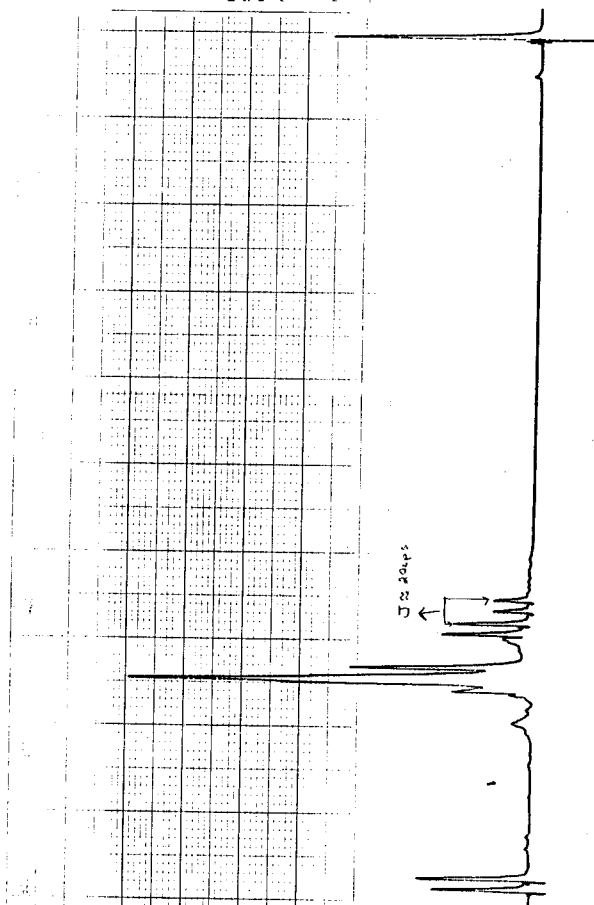
255  
product

30

Appendix 1: Example of run used to determine key for the  
bivariate addition to trans-cinnamaldehyde.



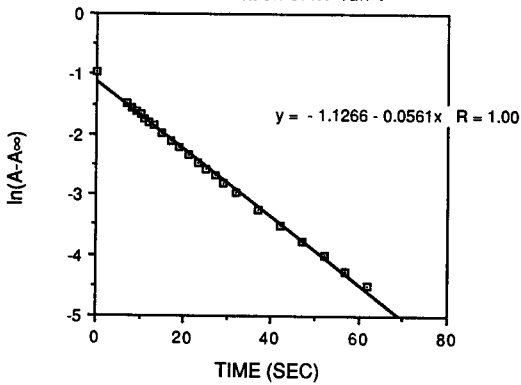
REFERENCE: TMS  
 SOLVENT: Me<sub>2</sub>S  
 CONC: 10%  
 AMPLITUDE: 2  
 SPECTRUM: 2  
 INTEGRAL: 1  
 N-TETEL



WATER

Appendix B

Appendix C  
Determination of  $k_1'$  run 1



Appendix D  
Determination of  $k_1'$  run 2

