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C13- and H-NMR studies of the bisulfite addition products of simple carbonyl compounds

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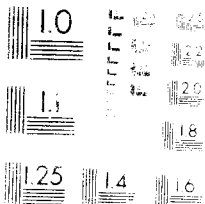
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C13- AND H-NMR STUDIES
OF THE BISULFITE ADDITION PRODUCTS OF
SIMPLE CARBONYL COMPOUNDS

By

Diane A. Piasecki

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Submitted in partial fulfillment

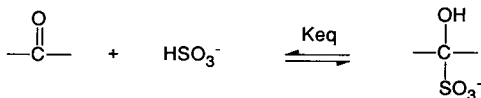of the requirements for

Honors in the Department of Chemistry

UNION COLLEGE

June, 1989

ABSTRACT

PIASECKI, DIANE A. C13 and H-NMR studies of the bisulfite addition products of simple carbonyl compounds. Department of Chemistry, 1989.

   The bisulfite addition products have been characterized for acetone, 2-butanone, propanal, 2-methylpropanal and trimethylacetaldehyde using high field NMR.   The methylene hydrogens of the 2-butanone and the propanal bisulfite addition products, as well as the methyl groups (both C and H) of the 2-methylpropanal bisulfite addition product absorb at slightly different chemical shifts, further substantiating the formation of product.   The diastereotopic nature of the groups causes the observed anisochronism at a field of 200MHz.

$$\underset{\displaystyle -\overset{\textstyle O}{\overset{\|}{C}}-}{} \ + \ HSO_3^- \ \underset{\longrightarrow}{\overset{K_{eq}}{\longleftarrow}} \ -\overset{\textstyle OH}{\underset{\textstyle SO_3^-}{\overset{|}{\underset{|}{C}}}}-$$

   K_{eq} for the formation of the acetone bisulfite addition product is 450. Relative equilibria have been obtained for a series of compounds through experiments involving competition reactions for bisulfite. Pinacolone was unreactive. Results show that the K_{eq} ratios for $(CH_3)_3CCHO$: CH_3COCH_3 = 2.6:1 and $CH_3CH_2COCH_3$: CH_3COCH_3 = 0.3 : 1.

I would like to dedicate this work to my mother, Jean Piasecka, and my sister, Krys, who were always there to listen.

ACKNOWLEDGEMENTS

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INTRODUCTION

The origin of the sulfur species in acid rain is sulfur dioxide emitted from the combustion of fossil fuels. Once present in the atmosphere, oxidation from S(IV) to S(VI), as sulfuric acid, can occur via gas phase reactions, on the surface of solids, through aqueous phase reactions, or some combination of these.* Stockwell and Calvert (1983) have shown that in the gas phase, it is the reaction of SO_2 with a hydroxy radical which leads to formation of the acid.[1]

$$OH + SO_2 \longrightarrow HOSO_2 \qquad (1)$$

$$HOSO_2 + O_2 \longrightarrow HO_2 + SO_3 \qquad (2)$$

$$HO_2 + NO \longrightarrow OH + NO_2 \qquad (3)$$
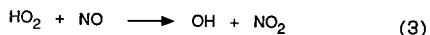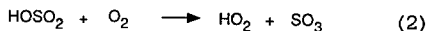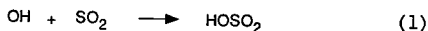
The SO_3 produced in reaction (2) reacts rapidly with water vapor to form the sulfuric acid.

$$SO_3 + H_2O \longrightarrow H_2SO_4 \qquad (4)$$
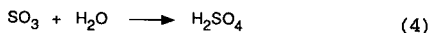
A direct consequence of the above series of reactions is, of course, the sulfuric acid. More important, however, is the regeneration of the hydroxy radical which causes the process to continue. In addition, the coupling of HO_2 with NO leads to the formation of another component of acid rain, nitric acid.

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*Sulfur dioxide exists in water as three species and as such is referred to as total S(IV) concentration. This is represented by the following equation.
$$[S(IV)] = [SO_2H_2O] + [HSO_3^-] + [SO_3^{-2}]$$
The proposed mechanism for aqueous phase oxidation is subsequently discussed. (Reactions 5,6,7)

Another possible means for the conversion of SO_2 to H_2SO_4 is the adsorption and subsequent oxidation of SO_2 on the surface of solids, such as graphite and soot.[2]

These solid surface reactions, however, contribute a small amount to the conversion of SO_2. In addition, the rates for the oxidation of SO_2 in the gas phase reactions are lower than those actually observed.[3,4] As a result, the formation of H_2SO_4 is largely attributed to aqueous phase reactions.

The atmosphere provides an ideal environment in which aqueous reactions can occur - aerosol, clouds, fog, rain are all present in the troposphere. The following mechanism for the oxidation of SO_2 was proposed by Pruppacher and Klett (1978).[5]

$$SO_{2\,(g)} \;+\; H_2O \;\rightleftharpoons\; SO_2H_2O \tag{5}$$

$$SO_2H_2O \;\rightleftharpoons\; HSO_3^- \;+\; H^+ \qquad K_{a1} = 1.32 \times 10^{-2}\,M \tag{6}$$

$$HSO_3^- \;\rightleftharpoons\; SO_3^{-2} \;+\; H^+ \qquad K_{a2} = 6.42 \times 10^{-8}\,M \tag{7}$$

At the pH range of 2-6, which is the range of aqueous atmospheric interest when, the predominant S(IV) species is the bisulfite ion (HSO_3^-), although the hydrated SO_2 and the sulfite ion, SO_3^{2-}, also exist.[6]

The concentrations of these S(IV) species are dependent on the pH of the rain drop. Penkett has shown, however, that with hydrogen peroxide as the dominant oxidizing agent, there is much less dependence on the pH.[7] The complete reaction can be summarized as follows.

$$SO_{2\,(g)} \;+\; H_2O_{(l)} \;\rightleftharpoons\; H^+_{(aq)} \;+\; HSO_3^-{}_{(aq)} \tag{8}$$

$$HSO_3^-{}_{(aq)} \;+\; H_2O_{2\,(aq)} \;\rightleftharpoons\; HSO_4^-{}_{(aq)} \;+\; H_2O_{(l)} \tag{9}$$

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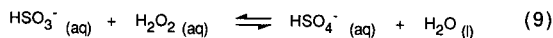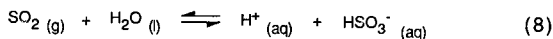
All of the reactions presented above do indeed contribute to the bisulfite concentrations in fog and cloudwater, however, they do not account for all the bisulfite. Richards, et. al., reported that the simultaneously high levels of hydrogen peroxide and bisulfite in Los Angeles cloudwater indicated that a process inhibiting the oxidation reaction between the two species must exist.[8] The inhibition reaction suggested is one which occurs between simple carbonyl compounds, such as aldehydes or ketones, with bisulfite. This reaction then accounts for the higher than expected levels of bisulfite in the cloudwater.

$$HSO_3^-{}_{(aq)} \;+\; R-\overset{O}{\overset{\|}{C}}-H \;_{(aq)} \;\underset{}{\overset{Keq}{\rightleftharpoons}}\; R-\underset{SO_3^-}{\overset{OH}{\underset{|}{\overset{|}{C}}}}-H \;_{(aq)} \qquad (10)$$

$$HSO_3^-{}_{(aq)} \;+\; R-\overset{O}{\overset{\|}{C}}-R' \;_{(aq)} \;\underset{}{\overset{Keq}{\rightleftharpoons}}\; R-\underset{SO_3^-}{\overset{OH}{\underset{|}{\overset{|}{C}}}}-R' \;_{(aq)} \qquad (11)$$
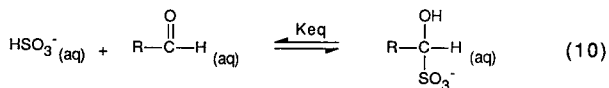
The direct emission of aldehydes from combustion sources, as well as the photochemical oxidation of hydrocarbons, provides a pool of compounds with which HSO_3^- can react. Grosjean (1982), and Schulam (1984), have found that formaldehyde is present in high quantities in the atmosphere.[9,10] Other carbonyl compounds have also been accounted for, including acetaldehyde, propanal, 2-butanone and butanal. Bertman also established the existence of formaldehyde, acetone, and acetaldehyde in cloudwater samples.[11]

In order to understand the extent to which the inhibition reaction occurs, one must closely examine the aldehyde-bisulfite equilibrium. If A represents the aldehyde or ketone and B represents the bisulfite species, then AB is the

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bisulfite-addition product. The equilibrium then is represented as:

$$A + B \xrightleftharpoons{\text{Keq}} AB$$

$$Keq = \frac{[AB]}{[A][B]}$$
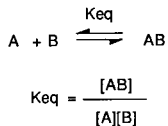
Obviously, the equilibrium constant of the reaction is directly proportional to the concentration of adduct and so the greater the K_{eq}, the more effectively is the bisulfite species tied up.

Munger discusses the formation of the formaldehyde-bisulfite addition product hydroxymethanesulfonic acid (HMSA) based on the equilibrium concentrations of formaldehyde and bisulfite in the atmosphere.[12] It was found that in order for them to be at the experimentally determined levels, the addition to higher carbonyl compounds must also occur. This is consistent with earlier observations made by Grosjean.

Boyce and Hoffman reported that the dissociation of the bisulfite addition product of HMSA is much slower than the formation reaction and so once it is formed, the species is relatively stable.[13] This is consistent with the results reported by Kok, who found that even at very low concentrations of both reactants, the bisulfite and H_2O_2 can coexist for hours, as long as the aldehyde is present.[14]

Equilibrium constants for a number of carbonyl bisulfite addition compounds have been experimentally determined for HMSA, benzaldehyde, acetaldehyde, and acetone, as listed in Table 1. Stewart and Donnelly, using an iodometric titration method, obtained an equilibrium value for the benzaldehyde addition product on the order of 9.43×10^3 and 1.00×10^4 at pH 4.77 and pH 5.21, respectively.[15]

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Dasgupta and Dong (1986), on the other used UV spectrophotometry to measure the absorbance of the unreacted bisulfite species and from this information were thus able to determine K_{eq} for HMSA.[16] Between pH=4.0

TABLE 1: Equilibrium Constants for the Reaction:

$$\underset{R_2}{\overset{R_1}{\diagdown}}C=O \quad + \quad HSO_3^- \quad \overset{Keq}{\underset{\longrightarrow}{\rightleftharpoons}} \quad \underset{R_2}{\overset{R_1}{\diagdown}}C\underset{SO_3^-}{\overset{OH}{\diagup}}$$
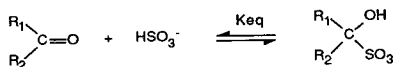
R_1	R_2	pH	K_{eq}	Ref.
H	C_6H_5	4.77	9.43×10^3	12
H	C_6H_5	5.21	1.00×10^4	12
H	H	4.0 - 5.0	8.55×10^6	13
H	H	4.0 - 6.5	3.64×10^6	14
H	H	4.0	1.0×10^7	11
H	H	5 0	6.7×10^6	11
H	CH_3	4.7	1.6×10^4	15
CH_3	CH_3	??	200^^	16

^^All other values for Keq were determined for the reverse of the reaction as written above, that is, for the dissociation of the bisulfite-addition product. The equilibrium constant for the formation of the acetone-bisulfite addition product was determined by Arai as indicated above.

and 5.0 he found that K_{eq} remains constant at the value 8.55×10^6. A recent study by Deister gives a $K_{eq} = 3.64 \times 10^6$ in the pH range of 4.0-6.5.[17] Kok determined the HMSA equilibrium kinetically, but also using the method of Dasgupta. He found $K_{eq} = 1.0 \times 10^7$ and 6.7×10^6 at pH=4.0 and 5.0.[14] All three determinations are relatively consistent.

The equilibrium constant for acetaldehyde was determined by Richard using the method of Dasgupta. The value obtained for pH 4.7 was 1.6×10^4.[18]

Arai has obtained a value for the acetone adduct K_{eq} to be at 200 at a temperature of 0°C. The pH at which the experiment was carried out is not known.[19]

In each of the cases cited, determinations were made on the basis of

unreacted sulfite present in solution without actually observing the carbonyl bisulfite addition product. Through this research, it is hoped that information will be obtained regarding the chemical equilibrium of the system by following the adduct and the carbonyl compound.

Direct observation of the organic compounds involved in the bisulfite-carbonyl system can be accomplished through the use of a high field nuclear magnetic resonance spectrophotometer.

In 1977, Johnson and Jones characterized the bisulfite adducts of α,β-unsaturated aldehydes using NMR spectroscopy.[20] The reaction of citral with excess bisulfite results in the trisodium trisulfonate salts.
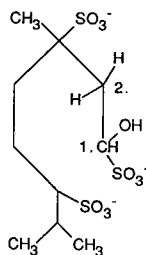
FIGURE 1: Trisodium trisulfonate salt isolated by Johnson from the reaction of citral with excess bisulfite.

Using a 60 MHz NMR, a doublet of doublets was reported for the C1 proton at 3.64 ppm. Since the protons on C2 are chemically non-equivalent, each acts as if it were a separate proton, splitting the adjacent H into two doublets. The multiplet at 5.13 ppm observed for the C2 protons substantiates the diastereotopic nature of the C2 protons.

As mentioned above, the experiment conducted by Johnson and Jones was performed using a 60MHz spectrometer. Data was reported in terms of

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absolute values for chemical shift but no information was given on the magnitude of the chemical shift differences for the diastereotopic nuclei. The anisochrony was observed but, since the chemical shift differences between diastereotopic nuclei in ^{1}H NMR are quite small, the splitting patterns for the nonequivalent nuclei were often, at best, expressed as a multiplet, as did Johnson for the C2 protons mentioned above. The low field NMR often does not provide sufficient resolution. It must be stressed, then, that the nonequivalence of nuclei is a necessary condition for anisochrony, but it is not a sufficient condition.[21,22] Rather, the observed anisochrony is a spectral phenomenon, more easily seen with high field NMR.

Parker and Taylor, using a 400MHz NMR, together with x-ray structural studies and molecular mechanics calculations, found that the observed non-equivalence of diastereotopic methylene protons in a series of alkyl camphanamides is due to the anisotropy of the camphanamide carbonyl group.[23]   (See Figure 3.)
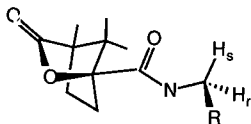
FIGURE 2: Alkyl camphanamide with R = CH_2CH_3.

The chemical shift difference between H_s and H_r where R = CH_2CH_3 was 0.21ppm with J_{HsHr} = 14.3.

While many studies have been done on the anisochronous behavior of diastereotopic nuclei using ^{1}H NMR, relatively few experiments have been conducted using ^{13}C NMR, where the anisochrony may be as readily observed.

Using a 100 MHz NMR, Andrist and Kovelan were able to observe the anisochronous behavior for the diastereotopic geminal methoxyl carbons in the spectrum of 3 - phenyl - endo, endo, cis-6,8-bis(dimethoxymethyl)-3-azabi-cyclo [3.3.0] octan-2,4-dione.[25] (See Figure 4.) The chiral perturber is two atoms removed from the diastereotopic sensors yet an appreciable change in the chemical shift can be seen with $\Delta\delta$ = 1.2 ppm. ([1]H $\Delta\delta$ = 0.09 ppm). One can say, however, that since this is a rigid system, the diastereotopy of the nonequivalent nuclei is enhanced. In addition, it was also found that the further from the chiral perturber (eg. 4 bonds vs. 3) the smaller the observable anisochrony.
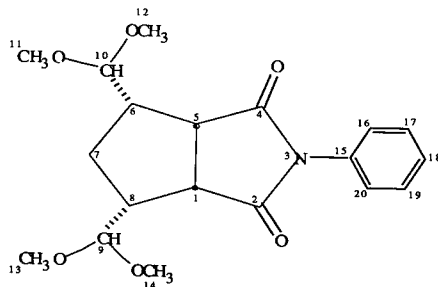
FIGURE 3: 3 - phenyl - endo, endo, cis-6,8-bis(dimethoxymethyl)-3-azabi- cyclo [3.3.0] octan-2,4-dione.

Nuclear magnetic resonance, then, is particularly useful in the study of the bisulfite-carbonyl systems. Not only does the absorption spectrum characterize the addition product but, at suitable concentrations of reactants, the ^{1}H spectrum can also provide useful information regarding the equilibrium constant for the reaction. Recall that the peak areas are in the same ratio as the number of protons giving rise to the signal and so, on the basis of the peak

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areas for the reacted and unreacted species, an equilibrium constant can be obtained. By determining the K_{eq} in this manner, one is able to follow the formation of product directly, in contrast to the UV method where the unreacted bisulfite is observed.

Hooper, in 1967, obtained some equilibrium constants in this manner, using a 60 MHz NMR.[28] The reactions of interest were the addition of water, sodium bisulfite and substituted alcohols to aldehydes and ketones at 35°C. No pH is given. He reported K_{eq} for the bisulfite addition to acetone and 2-butanone as % unreacted species. The values obtained at 35°C were 24.6 and 71.8% respectively. This corresponds to a K_{eq} of 11.5 and 0.64 respectively. There have been no other determinations for the equilibrium of 2-butanone, although the value for acetone, as compared to the one obtained by Arai, is off by more than a factor of 10. It is difficult to assign the cause of these differences to any particular factor since the conditions of either experiment are not explicitly stated.

Studies conducted thus far indicate that nuclear magnetic resonance spectroscopy is very useful in the study of chemical equilibria. However, this method for determining K_{eq} has not been used to its full potential. The main purpose of this research, then, is to study the bisulfite-carbonyl system using high field NMR. It is hoped that relative and absolute equilibrium constants for those compounds which have been identified as present in the atmosphere might be obtained, resulting in some contribution toward the challenge against acid rain. In addition, it is hoped that while studying such carbonyl compounds as acetone, 2-butanone, propanal, 2-methylpropanal, trimethyl-acetaldehyde, 3,3-dimethyl-2-butanone and other compounds in this series, more information might be obtained regarding the phenomenon of diastereotopism.

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EXPERIMENTAL

CHEMICALS:

Reagent grade organic compounds were distilled prior to preparing the bisulfite-addition products and conducting the equilibria experiments. Due to their susceptibility to oxidation, propanal, trimethylacetaldehyde and 2-methylpropanal were distilled under nitrogen gas and stored at 0°C under N_2.

The sodium bisulfite was composed of a mixture of $NaHSO_3$ and $Na_2S_2O_5$ and contained a minimum SO_2 content of 58.5%.

Deuterium oxide and deuterated chloroform, used as solvents for the NMR experiments, contained 99.8 atom % D.

All chemicals were purchased from the Aldrich Chemical Company.

INSTRUMENTATION:

A Varian Gemini 200 MHz spectrophotometer was used for obtaining the ^1H and ^{13}C spectra in the characterization of the aldehyde or ketone and its bisulfite addition product. Proton spectra were used to quantitatively determine the equilibrium constants for the formation of the bisulfite addition product.

Samples were prepared on a weight basis except for the trimethyl-acetaldehyde, which is readily oxidized in air. In this case, the appropriate amount of TMA was measured using a 100 microliter pipette in order to speed sample preparation.

In all other cases, a 10μl syringe was used to introduce the sample and then weighed to get a quantiative value.

SODIUM BISULFITE:

Three saturated solutions of sodium bisulfite were prepared. An aqueous solution was prepared by adding 85g of $NaHSO_3$ to 250 ml deionized water. Also, a 10% ethanol/water solution was prepared by adding 35g of $NaHSO_3$ to 110 ml of 10 H_2O:EtOH solution. Finally, 80g of $NaHSO_3$ were added to 500 ml of a 50% ethanol/water solution. In each case, the solution was heated to ensure saturation and then cooled to 0°C and filtered to remove any excess bisulfite.

BISULFITE ADDITION PRODUCTS:

The bisulfite addition products were isolated for acetone, 2-butanone, propanal and 2-methylpropanal. (Per cent yields were not determined.) The bisulfite addition product was formed, although not isolated, for trimethylacetaldehyde.

To prepare the acetone bisulfite addition product, 300 ml of a saturated bisulfite solution (in 50% ethanol/water), corresponding to ~0.4 moles was cooled to 0°C. About 0.6 moles of acetone was also cooled in an ice water bath and then slowly added, with stirring, to the bisulfite solution. Approximately 200 ml of ethanol was added to precipitate as much of the product as possible. The product was then washed with 10 ml of a cold 15% acetone/water solution and subsequently filtered using a Buchner funnel. The isolated product was left to dry in the air.

The 2-methylpropanal bisulfite addition product was prepared using 50 ml of the 10% ethanol/water solution saturated in $NaHSO_3$. To this, ~0.09 mole of the cold aldehyde was added, with stirring. Precipitation of the product was immediate. It was then washed with ~5 ml of water, to remove

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any remaining bisulfite, and subsequently filtered and dried as stated above.

The bisulfite addition products for 2-butanone and propanal were isolated using an aqueous solution of the bisulfite. In the case of 2-butanone, ~0.06 mole of the cold ketone was added, with vigorous stirring, to approximately 40 ml of the saturated aqueous bisulfite solution. About 10 ml of ethanol, at 0°C, was subsequently added to precipitate the bisulfite addition product. Again, the product was washed with a small amount of H_2O and filtered and dried as previously mentioned.

To isolate the propanal bisulfite addition product, an excess of the aldehyde was added to the reaction mixture. Approximately 0.06 moles of propanal, cooled to 0°C, was added to 100 ml of a saturated aqueous solution of bisulfite. Again, the mixture was vigorously stirred and cooled to 0°C. To 5 ml of this mixture, an additional 0.012 mole of the aldehyde and 0.015 mole of HSO_3^- were added. The addition of 10 ml of dioxane resulted in the precipitation of the product.

The trimethylacetaldehyde bisulfite addition product was formed by reacting 0.038g TMA in 1.072g of 0.20$\underline{M}$ aqueous sodium bisulfite. D_2O was used as the solvent and the product was characterized as subsequently discussed.

CHARACTERIZATION OF THE BISULFITE-ADDITION PRODUCTS:

Nuclear Magnetic Resonance Spectroscopy was used to confirm the formation of the bisulfite addition compound. Aqueous solutions (in D_2O) of acetone, 2-butanone, propanal, 2-methylpropanal, trimethylacetaldehyde and pinacolone wre prepared. The solutions were introduced into an NMR tube using a disposable glass pipette. Nitrogen gas was bubbled directly into the NMR tubes containing the propanal, trimethylacetaldehyde and

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2-methylpropanal to suppress oxidation. ^{13}C and ^1H-spectra were obtained for all samples except for that of trimethylacetaldehyde. In this case, since only a small amount of the TMA dissolved in D_2O, a ^{13}C spectrum could not be obtained.

The bisulfite addition products were also analyzed using NMR. Saturated solutions of the bisulfite adducts which were isolated, including acetone, propanal and 2-methylpropanal, were prepared in D_2O and then filtered by passing the solution through a disposable glass pipette which contained cotton. This was done to assure that no solid particles remained in the NMR tube. The spectra that were obtained were then compared to those obtained for the respective aldehyde or ketone, as stated above.

In the case of 2-butanone, the ^1H spectrum was obtained on a solution which contained $0.10\underline{M}$ 2-butanone and $0.10\underline{M}$ sodium bisulfite in D_2O. This procedure was carried out so that a cleaner and less noisy spectrum could be obtained. The ^{13}C spectrum was obtained for a solution which was prepared by reacting 0.05 g of the 2-butanone in 1ml of a D_2O solution which was saturated in bisulfite.

In the case of trimethylacetaldehyde, since no product was isolated, the ^1H spectrum was obtained for a solution prepared by reacting $0.10\underline{M}$ TMA and $0.10\underline{M}$ HSO_3^- in D_2O. No ^{13}C spectrum could be obtained.

For pinacolone, three experiments were conducted to determine if the bisulfite addition product was formed. First, 50 mg pinacolone was reacted with ~2 g of a saturated aqueous solution (D_2O) of sodium bisulfite. Second, a solution was prepared which was $0.10\underline{M}$ in pinacolone and $0.020\underline{M}$ HSO_3^-. Finally, a reaction mixture which was $0.010\underline{M}$ in both the ketone and the bisulfite was prepared.

In characterizing the bisulfite adducts of the various aldehydes and

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ketones, quantitative procedures were not necessarily followed. In some cases, specific amounts are given. While in others, an appropriate amount of either the aldehyde or ketone, or the bisulfite adduct, was dissolved in D_2O, such that a clean spectrum could be obtained.

DETERMINATION OF THE EQUILIBRIUM CONSTANTS:

FORMATION OF THE ACETONE BISULFITE ADDITION PRODUCT:

The equilibrium constant for the formation of the acetone bisulfite addition product was obtained by reacting equimolar amounts of acetone and bisulfite, at 0.010$\underline{M}$, in D_2O. A 1.00$\underline{M}$ solution of acetone was first prepared by adding 0.058 g of acetone to 1.105 g D_2O. Then, 0.011g of this 1.00$\underline{M}$ acetone solution was reacted with 0.001g of bisulfite in 1.096 g D_2O to bring the concentration of both reactants to 0.010$\underline{M}$. In this case, all reactants were weighed on a Mettler balance. Initially assuming that the equilibrium constant was somewhere on the order of 200, (Arai, 1961), the ratio of the acetone to product will be sufficient to observe the peak absorbances, due to both the reactant and the product, in the proton spectrum.

COMPETITION EXPERIMENTS:

The equilibrium constants for the formation of the bisulfite addition products of 2-butanone and trimethylacetaldehyde were obtained in a different manner. In each case, the aldehyde or ketone in question was reacted with the sodium bisulfite in the presence of acetone, thus establishing a competition between 2-butanone and acetone, or trimethylacetaldehyde and acetone, for the bisulfite. Proton spectra were obtained and subsequently analyzed.

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2-Butanone/Acetone Competition:

The 2-butanone/acetone competition reaction was prepared as follows. 0.0052 g of NaHSO3 was dissolved in 5.5335 g D2O. Then, 0.0072g 2-butanone and 0.0058 g acetone, in that order, were introduced into the bisulfite solution using a 10µl syringe, although weights were measured using a Mettler balance. The concentration of the reaction mixture was therefore 0.0096$\underline{M}$ in HSO3- and 0.019$\underline{M}$ in both the acetone and the 2-butanone. Approximately 1 ml of this solution was then transferred to an NMR tube and the proton spectrum of the solution obtained. Since 2-butanone and acetone, and their respective bisulfite addition products, have characteristic absorptions in different regions of the spectrum, equilibrium concentrations of both the reactants and products were determined. From the ratio of equilibrium constants, then, the absolute equilibrium constants for the formation of the bisulfite addition products can be determined. To ensure that equilibrium had been reached, another spectrum was acquired twenty four hours later.

Trimethylacetaldehyde/Acetone Competition:

The equilibrium constant for the formation of the trimethylacetaldehdye bisulfite addition product was obtained in the same manner as presented above, except different concentrations of reactants were used. In this case, equimolar amounts of the TMA and the acetone were also used, but at 0.050$\underline{M}$, while the bisulfite concentration was 0.025$\underline{M}$. The solution was prepared in the following manner. To 5.473 g of D_2O was added 0.013g $NaHSO_3$. 0.015g acetone was then added to the vial. Since TMA is readily oxidized, a 100µl pipette was used to introduce 59.9 µl of the aldehyde. The solution was vigorously shaken and then degassed with N_2. Approximately 1

ml of the solution was transferred to the NMR tube. Nitrogen gas was again bubbled through the sample. To ensure that equilibrium had been reached, three spectra were obtained. The first spectrum was obtained immediately after the sample had been prepared. The second and third spectra were acquired 24 and 96 hours later, respectively.

A detailed analysis of all spectra obtained is given in the RESULTS AND DISCUSSION section.

CHARACTERIZATION OF THE BISULFITE ADDITION PRODUCTS:

The bisulfite addition products of acetone, 2-butanone, propanal and 2-methylpropanal have been successfully isolated and characterized, using NMR spectroscopy. The trimethylacetaldehyde bisulfite addition product could not be isolated. However, the adduct does form, as indicated from the proton spectrum.

ACETONE:

The ^1H and ^{13}C spectra were obtained for aqueous solutions of both the acetone and the "acetone bisulfite addition product" to determine if the product had been isolated. The chemical shift data for the two samples is given below.
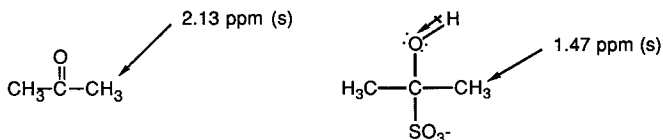
FIGURE 4. ^1H chemical shift data for aqueous solutions of acetone and acetone bisulfite addition product.

The methyl protons of acetone in D_2O characteristically absorb as a singlet at 2.13 ppm. In the spectrum that was obtained for the "bisulfite addition product", the singlet has shifted farther upfield to an absorption of 1.47 ppm. The absorption at 4.7 ppm is characteristic of the HOD exchange. (See Appendix, FIGURE 22.)

This difference in chemical shift is consistent with the structure of the acetone bisulfite addition product. The strongly electronegative oxygen withdraws some of the electron density from the hydroxyl proton. As a result, the hydroxyl proton is much more deshielded and should absorb at higher frequencies. Since the hydroxyl proton exchanges with the deuterium in the solvent, one does not observe this peak. A direct consequence of the deshielding of the hydroxyl proton is the shielding of the methyl protons on the adjacent carbons and, as a result, the absorption shifts upfield.

Since the chemical shift effects are much larger in ^{13}C-NMR, the electron withdrawing group will have a much greater effect on the absorption. The absorption data in Figure 5 shows that the difference between the chemical shifts in the ^{13}C spectra of the aqueous acetone and the "product" is much more dramatic. In the case of acetone, there is a distinct absorption at 218.4 ppm due to the carbonyl carbon. The methyl carbons absorb at 32.3 ppm. The bisulfite addition results in the loss of the carbonyl group and so the peak is shifted to 88.8 ppm. This region is characteristic of the absorption for substituted alcohols and substantiates the formation of the acetone bisulfite addition product. (See Appendix, FIGURE 23.)
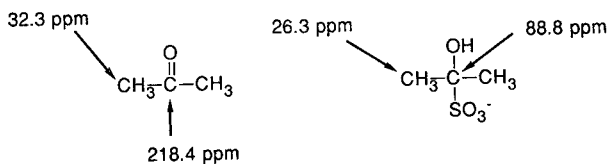
FIGURE 5. ^{13}C chemical shift data for aqueous solutions of acetone and acetone bisulfite addition product.

PROPANAL:

In aqueous solution, the propanal exists in equilibrium with the hydrate, as seen in both the ^{1}H and ^{13}C spectra. Since the solution contained an unknown amount of the aldehyde, the equilibrium constant for the formation of the hydrate was not determined. However, from the proton spectrum, one can say that the aldehyde and the hydrate are present in about a 50% ratio.

In the proton spectrum, the aldehyde proton absorbs at 9.5 ppm and is split by the methylene protons into a triplet. The coupling constant is very small, 1.3 Hz, and so the triplet is not very well resolved in the spectrum. (See Appendix, FIGURE 24.) A quartet is observed for the methylene protons at 2.4 ppm and, at 0.9 ppm, the methyl protons absorb. Once again, the proton due to HOD exchange absorbs at 4.7 ppm.

The remaining peaks in the spectrum are due to the protons on the hydrate, which is essentially the product of the water addition to propanal. As for any carbonyl addition, the carbonyl group is lost and in this case, the hydrate is formed. This results in the increased shielding of the methine proton and so it absorbs farther upfield. Notice that at 4.8 ppm, the methine proton absorbs as a triplet, split by the adjacent methylene protons. FIGURE 6 below summarizes the chemical shift data for the aqueous solution of propanal.
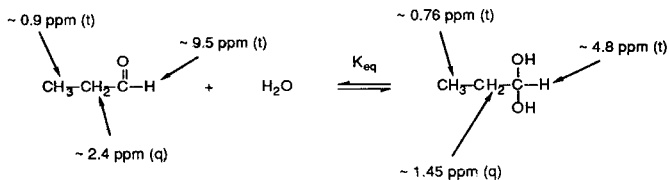
FIGURE 6. ^{1}H chemical shift data for the propanal hydrate equilibrium in D_2O.

The proton spectrum of the "propanal bisulfite addition product" reveals that all of the aldehyde has reacted, since there is no peak downfield due to the aldehyde proton absorption. (See Appendix, FIGURE 25) The presence of the hydrate has been ruled out since none of the chemical shifts correspond to those which are characteristic of the hydrate. The peak at 4.7 ppm is due to the HOD. However, if the bisulfite addition product had been formed, three regions of absorption would be expected; two triplets due to the methyl protons and the methine proton, and a pentet for the methylene protons. Instead, a doublet of doublets appears at 4.25 ppm and a triplet at ~1.0 ppm. In addition, there are two sets of multiplets at 1.9 and 1.6 ppm.
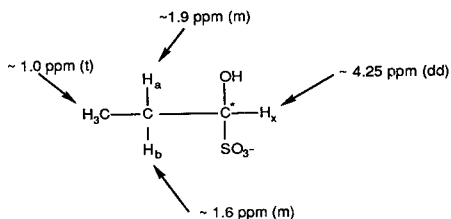
FIGURE 7.   ¹H chemical shift data for the propanal bisulfite addition product in D_2O.

The phenomena occurring here is known as diastereotopism and occurs in the presence of an atom or groups of atoms which, although connectively equivalent, are not chemically equivalent.   When the propanal bisulfite addition product is formed, what was intially the carbonyl carbon becomes a chiral center with four different substituents, as shown above in FIGURE 7.   As a result, the methylene hydrogens exist in different chemical environments and thus are chemically non-equivalent.   As seen from the Newman projections depicted in FIGURE 8, the two protons are obviously in different chemical environments, regardless of the degree of rotation around the C-C

bond. As a result, the chiral perturbing group is able to distinguish between the two nuclei, leading to their diastereotopic nature.
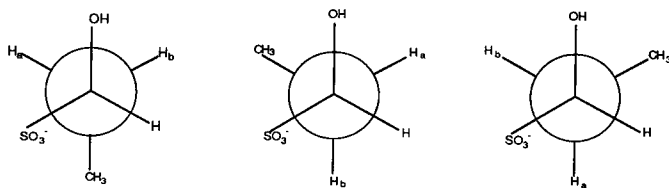
FIGURE 8. Newman projections for the bisulfite addition product of propanal depicting the different chemical environments for H_a and H_b leading to their diastereotopy.

As H_a and H_b, the methylene hydrogens absorb at different regions of the spectrum with a chemical shift difference of 0.30 ppm. The splitting patterns are due to coupling between the different types of hydrogens. The doublet of doublets at 4.3 ppm arises due to the splitting of H_x by each of the diastereotopic hydrogens, H_a and H_b, which have different coupling constants. $J_{ax} = 3.2$ Hz and $J_{bx} = 9.8$ Hz. H_a is also split by H_b, and vice versa, and the coupling between these two hydrogens results in the multiplets observed in the spectrum. The coupling between H_a and H_b has not yet been determined, however, with the acquisition of a spin simulation program, it is hoped that these values can be obtained.

Since the chemical shift difference between the two diastereotopic hydrogens is quite large for a system which is non-rigid, there is some question as to whether the chemical non-equivalence is due to a preferred conformation or rather, if there is an inherent preference by each hydrogen for a particular environment. Additional experiments must be conducted in order to come to a conclusion.

From the proton spectrum of the "propanal bisulfite addition product", then, one can conclude that the bisulfite addition product has indeed been isolated. Not only has the aldehyde proton absorption shifted upfield, but anisochrony is also observed due to the presence of the nonequivalent hydrogens on the bisulfite addition product.

For completeness' sake, however, the ^{13}C spectrum of an aqueous solution of propanal was also obtained. (See Appendix, FIGURE 26.) One can see the chemical shifts due to both the aldehyde and the hydrate. Again, since the hydrate is in equilibrium with the aldehyde, six peaks are observed. The carbonyl carbon absorbs downfield at 212.5 ppm, while the corresponding methine carbon on the hydrate is shifted to 95.1 ppm. The methylene protons for both the aldehyde and the hydrate absorb at 39.3 and 32.7 ppm. It is difficult to distinguish which peak is due to the aldehyde and which is due to the hydrate, although one can say for certain that the more shielded methyl hydrogens will absorb further upfield, at 10.6 and 7.7 ppm. See FIGURE 9 below for a summary of the chemical shift data.

10.6 ppm

7.7 ppm   95.1 ppm

$$CH_3\text{-}CH_2\text{-}\overset{\displaystyle O}{\overset{\|}{C}}\text{-}H \quad + \quad H_2O \quad \overset{K_{eq}}{\rightleftharpoons} \quad CH_3\text{-}CH_2\text{-}\overset{\displaystyle OH}{\underset{\displaystyle OH}{\overset{|}{\underset{|}{C}}}}\text{-}H$$

32.7 ppm   212.5 ppm

39.3 ppm
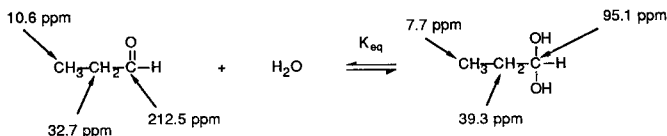
FIGURE 9. ^{13}C chemical shift data for the propanal-hydrate equilibrium in D_2O.

Upon formation of the bisulfite addition product, the carbonyl absorption shifts upfield to 88.3 ppm. (See Appendix, FIGURE 27.) None of the chemical shifts correspond to those obtained in the hydrate spectrum and so one can conclude that no hydrate is present upon formation of the bisulfite addition to propanal. The methylene carbon absorbs at 27.1 ppm and the methyl carbon

absorbs at 12.4 ppm. See FIGURE 10 for a summary of the data obtained.
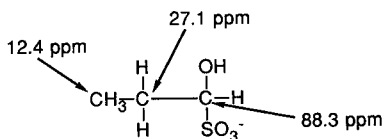
FIGURE 10. ^{13}C chemical shift data for the propanal bisulfite addition product in D_2O.

2-METHYLPROPANAL:

The ^1H spectrum of 2-methyl propanal in D_2O shows that the aldehyde exists in equilibrium with the hydrate. Again, the K_{eq} for the formation of the hydrate was not determined, although there appears to be approximately 10% less hydrate than aldehyde. (See Appendix, Figure 28.)

The aldehyde proton, as expected, absorbs at ~9.5 ppm as a doublet, split by the methine hydrogen. The methine proton is split by the two methyl groups into a septet which is then split by the aldehyde proton at ~2.5 ppm. The coupling between these two types of hydrogens is quite small with J = 1.4 Hz. The methyl hydrogens absorb as a doublet at ~1.0 ppm. Notice also that the methine hydrogen on the alcohol carbon absorbs upfield as a doublet at ~4.64 ppm. See FIGURE 11 below.

FIGURE 11. ^1H chemical shift data for the 2-methylpropanal-hydrate equilibrium in D_2O.

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When the proton spectrum was obtained for the "2-methylpropanal bisulfite addition product", it was found that the product had indeed been isolated. (See Appendix, Figure 29.) However, some interesting splitting patterns were observed due to the diastereotopism of the methyl hydrogens. A doublet arises at 4.14 ppm, as expected, due to the bisulfite addition to the carbonyl group which results in more shielded hydrogens. However, for the methine hydrogen of C2, which absorbs at ~2.1 ppm, one would expect an octet if 1st order splitting were taking place. This is not the case. Apparently, the coupling between the methine hydrogen and those on the methyl groups is different from the coupling with the methine hydrogen on C1. Moreover, it appears that the methyl hydrogens absorb as a triplet at ~0.96 ppm. Actually, each of the diastereotopic methyl hydrogens is split into a doublet by the adjacent methine proton, giving rise to a doublet of doublets. The difference in chemical shifts is 0.03 ppm. This is a fairly large difference when one considers the fact that the diastereotopic methyl hydrogens are one additional bond removed from the chiral perturber.
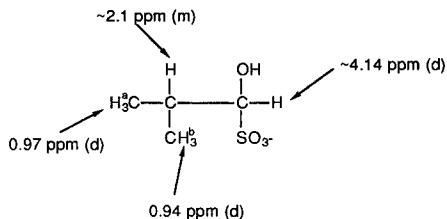
FIGURE 12. ^1H chemical shift data for the 2-methylpropanal bisulfite addition product in D_2O. $\delta H^a - \delta H^b = 0.03$ ppm.

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The ^{13}C spectrum also substantiates the formation of the 2-methyl-propanal bisulfite addition product. (See Appendix, FIGURE 30.) For the 2-methylpropanal, the chemical shift at 215 ppm results from the carbonyl carbon absorption. At 43.3 ppm is the absorption due to the methine carbon. At 17.1 ppm, the methyl carbons absorb. Once again, note the equilibrium with the hydrate and especially the peak at 98 ppm which is due to the absorption of the methine carbon which is doubly substituted by the hydroxyl groups.
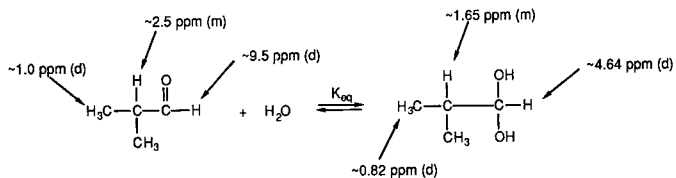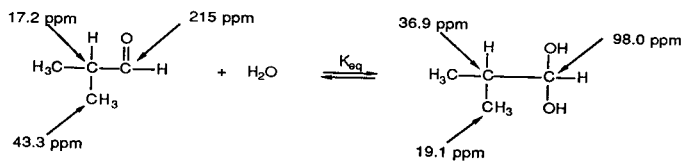

FIGURE 13. ^{13}C chemical shift data for the 2-methylpropanal-hydrate equilibrium in D_2O.

In the spectrum obtained for the "2-methylpropanal bisulfite adduct" note that the carbonyl carbon is no longer present. (See Appendix, FIGURE 31.) Instead, it has been shifted upfield to an absorption of 91 ppm. Notice also that the hydrate carbon, which absorbed at 98 ppm as mentioned above, is no longer present. However, since we have already mentioned the diastereotopism of the methyl hydrogens we would expect to see two peaks due to the absorbances of the two nonequivalent carbons. These are seen at 22.1 ppm and 18.7 ppm.

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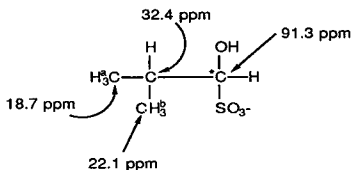
FIGURE 14. [13]C chemical shift data for the 2-methylpropanal bisulfite addition product in D$_2$O. Note that bisulfite addition leads to formation of a chiral center and diastereotopic carbons.

Once again, the formation of the bisulfite addition product has resulted in a chiral center. (See FIGURE 14.) As a result, the geminal methyl carbons absorb at two different regions of the spectrum, with a chemical shift difference of $\delta C_a - \delta C_b = 3.4$ ppm. This is much greater than that observed in the proton spectrum, where the chemical shift difference was on the order of 0.03 ppm. In contrast to the case of the propanal bisulfite addition product, the chiral perturber in the 2-methylpropanal bisulfite adduct also affects the geminal methyl carbons. As a result, the anisochrony is observed in both the proton and ^{13}C spectra.

2-BUTANONE:

An ^{1}H spectrum was obtained for an aqueous solution of 2-butanone. (See Appendix, FIGURE 32.) The methyl protons which are α to the carbonyl carbon, absorb as a singlet at 2.1 ppm. The methylene protons are split by the methyl hydrogens on C4 and thus absorb as a quartet farther downfield at ~2.5 ppm. The methyl protons of C3 absorb as a triplet at 0.9 ppm, split by the methylene hydrogens. FIGURE 15 summarizes the chemical shift data.

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0.9 ppm (t)　　　　　O　　　　2.1 ppm (s)

$$H_3C—CH_2—C—CH_3$$

2.5 ppm (q)

FIGURE 15. ^1H chemical shift data for an aqueous solution of 2-butanone.

The 2-butanone bisulfite addition product was isolated as discussed in the EXPERIMENTAL section. However, it was difficult to obtain a clean spectrum due to the level of noise. To characterize the bisulfite addition product, a solution was prepared which was $0.10\underline{M}$ in 2-butanone and $0.10\underline{M}$ in HSO_3^-. The ^1H spectrum of the "product", compared to that of the ketone, showed that another species was indeed present. (See Appendix, FIGURE 33.) At 2.5, 2.1 and 0.9 ppm are the chemical shifts due to the 2-butanone hydrogens, as described above. A sharp singlet is seen at ~1.37 ppm due to the methyl protons on C1. This is consistent with other observations where absorption of the hydrogens occurs at higher field for the bisulfite adduct. Also, at ~0.9 ppm a triplet is found which is actually due to the chemical shifts of the C4 methyl protons on both the ketone and the bisulfite adduct superimposed upon each other. FIGURE 16 summarizes the chemical shift data.

~1.8 ppm (q)

~0.9 ppm (t)　　　H_a　OH　　1.37 ppm (s)

$$H_3C—C—C—CH_3$$

H_b　SO_3^-

~ 1.8 ppm (q)

FIGURE 16. ^1H chemical shift data for the 2-butanone bisulfite addition product in D_2O.

Further evidence of the formation of the 2-butanone bisulfite addition product is the quartet at 1.8 ppm. Obviously, there has been a shift upfield from that of the 2-butanone absorbance, but more importantly is the anisochrony, although very small, which is observed. The ^1H spectrum clearly shows this anisochrony. The chemical shift difference, $\delta H_a - \delta H_b$ equals 0.015 ppm, much smaller than that for the case of propanal, but still readily observed with the high field NMR. In addition, the chemical shift difference of the diastereotopic hydrogens is so small that the coupling constant difference between H_a or H_b and the C4 methyl hydrogens is not observed.

The ^{13}C spectrum of the 2-butanone depicts the characteristic carbonyl absorption at 221 ppm. (See Appendix, FIGURE 34.) C4 is most shielded and thus absorbs at 9.7 ppm. C1 and the methylene carbon absorb at 39.2 ppm and 31.4 ppm, respectively. See FIGURE 17 for a summary of the chemical shifts.
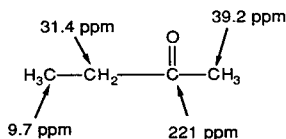
FIGURE 17. ^{13}C chemical shift data for an aqueous solution of 2-butanone.

The ^{13}C spectrum was obtained on a solution which was prepared by reacting 0.05g of 2-butanone in 1ml of a saturated aqueous solution of bisulfite, forcing the reaction to go far to the right. As expected, the C2 absorption has shifted to a higher field at 92 ppm upon formation of the 2-butanone bisulfite addition product. (See Appendix, FIGURE 35.) The remaining three carbons absorb in the order stated above, but shifted upfield. C1 absorbs at 31.3 ppm, the methylene carbon at 32.7 and the C3 methyl

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carbon, which is the most shielded, at 10.1 ppm.

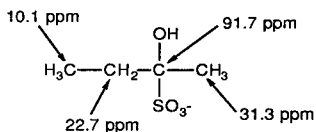
FIGURE 18. ^{13}C chemical shift data for an aqueous solution of the 2-butanone bisulfite addition product.

From both the proton and the ^{13}C spectra, one can then say that the 2-butanone bisulfite addition product has indeed ben formed.

TRIMETHYLACETALDEHYDE:

An aqueous solution of trimethylacetaldehyde was prepared in D_2O. The ^{1}H spectrum indicates that once again, the hydrate is in equilibrium with the aldehyde, although the percent hydrate is much lower than that for either propanal or 2-methylpropanal. (See Appendix, FIGURE 36.)

The aldehyde proton absorbs at 9.4 ppm as a singlet whereas the methine hydrogen on the hydrate absorbs farther upfield, at 4.6 ppm. The shielded methyl protons of both the aldehyde and the hydrate absorb at 0.99 ppm and 0.80 ppm, respectively, as shown in FIGURE 19.
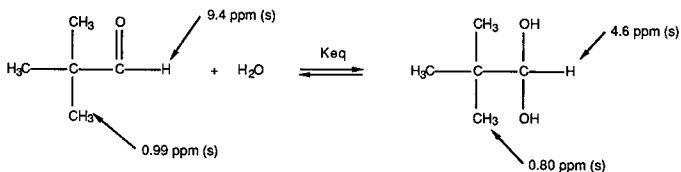

FIGURE 19. ^{1}H chemical shift data for the trimethylacetaldehyde-hydrate equilibrium in D_2O.

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Although the bisulfite addition reaction does occur with trimethyl-acetaldehyde, the product could not be isolated. In order to substantiate that the bisulfite adduct had indeed formed, the reaction was carried out in the NMR tube using 0.10$\underline{M}$ TMA and 0.10$\underline{M}$ HSO_3^- in D_2O. The ^{1}H spectrum indicates that some trimethylacetaldehyde has not reacted and thus remains in equilibrium with the hydrate. (See Appendix, FIGURE 37.) The chemical shifts for these hydrogens correspond to those given in the ^{1}H spectrum of the aqueous trimethylacetaldehyde. In addition, a small amount of the TMA has been oxidized and at 1.1 ppm, the methyl protons of trimethylacetic acid absorb as a singlet. Although there is still a substantial amount of the aldehyde which was unreacted, the remaining peaks prove that the product has indeed formed. At 4.06 ppm, the methine hydrogen of the bisulfite adduct absorbs. This is very distinct from the absorption of the same proton seen for the hydrate, which occurs around 4.6 ppm. In addition, there are two doublets which absorb upfield at 1.0 ppm and at 0.98 ppm. Considering past trends and observations, one can state that the peak at 0.98 ppm is due to the trimethylacetaldehyde bisulfite addition product. (FIGURE 20.)
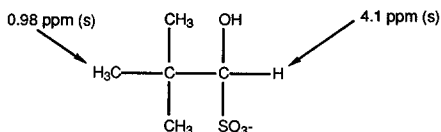
FIGURE 20. [1]H chemical shift data for the trimethylacetaldehyde bisulfite addition product obtained by reacting 0.10$\underline{M}$ TMA and 0.10$\underline{M}$ HSO_3^- in D_2O.

Since trimethylacetaldehyde is non-polar, one can expect that only small amounts will go into aqueous solutions. As a result, the ^{13}C spectra for neither the trimethylacetaldehyde and the TMA bisulfite addition product, could be obtained.

3,3-DIMETHYL-2-BUTANONE:

3,3-dimethyl-2-butanone, also known as pinacolone, has the same structure as trimethylacetaldehyde with an additional methyl group α to the carbonyl group. A proton spectrum was obtained for the compound in aqueous solution. As expected, one sees two peaks, in addition to the HOD peak. (See Appendix, FIGURE 38.)

The methyl protons, adjacent to the α carbon absorb at 2.1 ppm as a singlet whereas the nine equivalent methyl hydrogens absorb, also as a singlet, at 1.06 ppm.

The ^{13}C spectrum of the same solution resulted in the following chemical shifts where, once again, the carbonyl carbon absorbs downfield at 226 ppm. The three equivalent methyl carbons absorb at 28.1 ppm, as indicated by the very large peak. The α carbon absorbs at 27.3 ppm and C3 absorbs at 47 ppm.
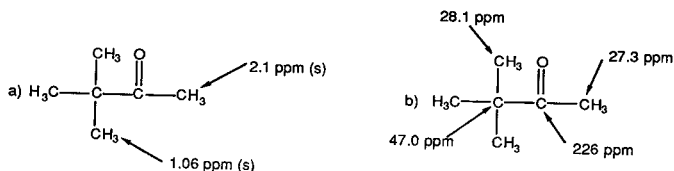
FIGURE 21. a) ^1H and b) ^{13}C chemical shift data for pinacolone in D_2O.

An attempt to isolate the bisulfite addition product of pinacolone was unsuccessful. Moreover, the reaction did not proceed at all. Three attempts were made. First, 50 mg of pinacolone was introduced into approximately 2 grams of a saturated aqeous solution of sodium bisulfite. Second, a solution was prepared which was $0.1\underline{M}$ in pinacolone and $0.02\underline{M}$ HSO_3^-. Finally, a

reaction mixture which was $0.01\underline{M}$ in both the ketone and the bisulfite was prepared. The proton spectra obtained for all three samples indicated that no product had been formed.

SUMMARY OF THE ISOLATION AND CHARACTERIZATION OF THE BISULFITE ADDITION PRODUCTS OF SOME SIMPLE CARBONYL COMPOUNDS:

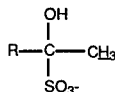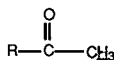The bisulfite addition products of acetone, 2-butanone, propanal and 2-methylpropanal were isolated and characterized. TABLES 2, 3, and 4 depict the chemical shifts that were most important in substantiating the bisulfite addition products. For the aldehydes, the proton spectrum is sufficient to confirm the formation of product due to the large change in chemical shift of the aldehyde proton. For ketones, however, this change is much more subtle and so the ^{13}C spectrum must be obtained for conclusive evidence. Although the bisulfite adduct of trimethylacetaldehyde could not be isolated, the product is indeed formed, as indicated by the proton spectrum. Finally, pinacolone was unreactive toward bisulfite addition, probably due to steric bulk of the t-butyl group which hinders bisulfite attack at the carbonyl carbon.

	$\begin{array}{c} O \\ \parallel \\ R-C-H \end{array}$	$\begin{array}{c} OH \\ \mid \\ R-C-H \\ \mid \\ OH \end{array}$	$\begin{array}{c} OH \\ \mid \\ R-C-H \\ \mid \\ SO_3^- \end{array}$
$R = CH_2CH_3$	9.5 (t)	4.8 (t)	4.25 (dd)
$R = CH(CH_3)_2$	9.5 (d)	4.64 (d)	4.14 (d)
$R = C(CH_3)_3$	9.4 (s)	4.6 (s)	4.1 (s)

TABLE 2. Summary of the characteristic ^1H chemical shifts (in ppm) of some aldehydes and their corresponding hydrates and bisulfite addition products.

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 \qquad R-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle SO_3^-}{|}}{C}}-CH_3$$

	$R-\overset{O}{C}-CH_3$	$R-\overset{OH}{C}(SO_3^-)-CH_3$
R = CH$_3$	2.13 (s)	1.47 (s)
R = CH$_2$CH$_3$	2.1 (s)	1.37 (s)
R = C(CH$_3$)$_3$	2.1 (s)	XX

TABLE 3. Summary of the characteristic ^{1}H chemical shifts (in ppm) of some ketones and their corresponding bisulfite addition products.

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-R' \qquad R-\overset{\overset{\displaystyle OH}{|}}{CR'}-OH \qquad R-\overset{\overset{\displaystyle OH}{|}}{CR'}-SO_3^-$$

	$R-\overset{O}{C}-R'$	$R-\overset{OH}{CR'}-OH$	$R-\overset{OH}{CR'}-SO_3^-$
R = R' = CH$_3$	218.4	XX	88.8
R = CH$_2$CH$_3$ R' = H	212.5	95.1	88.3
R = CH(CH$_3$)$_2$ R' = H	215	98.0	91.3
R = CH$_2$CH$_3$ R' = CH$_3$	221	XX	91.7
R = C(CH$_3$)$_3$ R' = H	XX	XX	XX
R = C(CH$_3$)$_3$ R' = CH$_3$	226	XX	XX

TABLE 4. Summary of the characteristic ^{13}C chemical shifts of some aldehydes and ketones, and their corresponding hydrates and bisulfite addition products. XX designates not applicable.

33

As shown previously, the bisulfite addition products of propanal, 2-methylpropanal and 2-butanone exhibit the phenomenon of diastereotopism. Table 5 is a summary of the chemical shift differences observed for the non-equivalent hydrogens. The magnitude of the chemical shift differences varies although a particular trend can not be cited. In fact, one might expect that the difference in chemical shifts for the methyl hydrogens of 2-methylpropanone would be smaller than the chemical shift difference for the methylene hydrogens of 2-butanone, since the methyl hydrogens are an additional bond removed from the chiral perturber. As mentioned previously, Andrist and Kovelan observed a diminution in the chemical shift difference for those sensors which were 4 bonds removed from the chiral center, compared to three.[24] Their study was concerned with the ^{13}C NMR although one might expect to see the same trend for the ^{1}H NMR. Instead, we observe an increase by a factor of two.

	$\delta H_a - \delta H_b$ (ppm)
H₃C—C(Hₐ)(H_b)—C(OH)(SO₃⁻)—H	0.30
H₃C—C(H)(CH₃_b)—C(OH)(SO₃⁻)—H	0.03
H₃C—C(Hₐ)(H_b)—C(OH)(SO₃⁻)—CH₃	0.015

TABLE 5. Summary of the ^{1}H chemical shift differences for the diastereotopic hydrogens of propanal, 2-methylpropanal, and 2-butanone.

Another interesting observation was the magnitude of the chemical shift difference of the methylene hydrogens of the propanal bisulfite addition product compared to that for the 2-butanone bisulfite addduct. The chemical environments are similar, the only difference being an additional methyl group for the 2-butanone adduct, yet the chemical shift difference for the propanal adduct is greater by a factor of 20! In this case, it is unlikely that the only phenomenon involved is the preference of the hydrogens for a particular conformer. Another possibility that one must consider is the inherent preference of each hydrogen for a particular chemical environment.

Finally, the chemical shift difference of the non-equivalent carbons in the 2-methylpropanal bisulfite addition product was observed in the ^{13}C NMR spectrum. Here, $\delta C_a - \delta C_b = 3.4$ ppm.

DETERMINATION OF K_{eq}.

The equilibrium constants were determined for the formation of the bisulfite addition products of acetone, 2-butanone, and trimethylacetaldehyde using nuclear magnetic resonance spectroscopy.
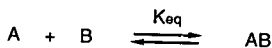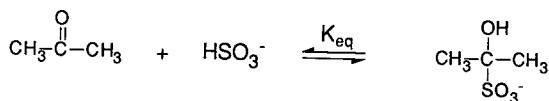
ACETONE:

The equilibrium constant for the formation of the acetone bisulfite addition product was determined by reacting 0.010$\underline{M}$ acetone and 0.010$\underline{M}$ HSO_3^- in D_2O, as discussed in the EXPERIMENTAL section. In this manner, one is able to see the characteristic chemical shifts due to both the acetone and the bisulfite adduct. (See Appendix, FIGURE 39.)

The intensities of the peaks allow one to calculate the final concentrations of the acetone and the bisulfite, as well as the concentration of adduct, at equilibrium. From this information, together with the initial

concentrations of reactant, a K_{eq} of $450\underline{M}^{-1}$ is calculated for the formation of the acetone bisulfite addition product. To assure that equilibrium had been reached, a proton spectrum was obtained for the same sample 24 hours later. The K_{eq} remained the same.

The following figures depict the formation of the acetone bisulfite addition product as well as the data obtained from the ^1H spectrum. Calculations for determining K_{eq} are also shown.

$$CH_3\text{--}\overset{\overset{\displaystyle O}{\|}}{C}\text{--}CH_3 \quad + \quad HSO_3^- \quad \xrightleftharpoons{K_{eq}} \quad CH_3\text{--}\underset{\underset{\displaystyle SO_3^-}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}\text{--}CH_3$$

$$A \quad + \quad B \quad \xrightleftharpoons{K_{eq}} \quad AB$$

	δ (ppm)	INTENSITY
A	2.15	85.3
AB	1.47	143

Let I_A = Intensity of the methyl proton absorption of acetone

I_{AB} = Intensity of the methyl proton absorption for the acetone bisulfite addition product

$[A]_i$ = Initial concentration of acetone

$[B]_i$ = Initial concentration of HSO_3^-

$[A]_f$ = equilibrium concentration of acetone

$[B]_f$ = equilibrium concentration of HSO_3^-

$[AB]$ = equilibrium concentration of the acetone bisulfite addition product

36

$$[A]_i \;=\; 0.010\underline{M}$$

$$[A]_f \;=\; \frac{I_A}{I_A + I_{AB}}\,[A]_i \;=\; \frac{85.3}{85.3 + 143}\;X\;\;0.010\underline{M}\;=\;0.0037\underline{M}$$

$$[AB] \;=\; \frac{I_{AB}}{I_A + I_{AB}}\,[A]_i \;=\; \frac{143}{85.3 + 143}\;X\;\;0.010\underline{M}\;=\;0.0063\underline{M}$$

$$[B]_i \;=\; 0.010\underline{M}$$

$$[B]_f \;=\; [B]_i - [AB] \;=\; 0.010\underline{M} - 0.0063\underline{M} = 0.0037\ \underline{M}$$

$$K_{eq} \;=\; \frac{[AB]}{[A]_f - [B]_f} \;=\; \frac{0.0063\underline{M}}{(0.0037\underline{M})^2} \;=\; 450\ \underline{M}^{-1}$$

2-BUTANONE:

In order to determine K_{eq} for the formation of the 2-butanone bisulfite adduct, competition experiments were conducted. An equimolar amount (0.019$\underline{M}$) of acetone and 2-butanone were reacted with 0.0096$\underline{M}$ HSO_3^-. In the proton spectrum obtained for the aqueous reaction, one sees the chemical shifts due to both the reactants and their adducts. (See Appendix, FIGURE 40.) The C1 methyl protons of the 2-butanone (B) abosrb as a singlet at 2.1 ppm while those of the bisulfite adduct (BB) absorb, also as a singlet, at 1.4 ppm. Again, the methyl protons absorb at 2.1 ppm for the acetone (A) and at 1.4 ppm for the acetone bisulfite addition product (AB).

Again, the peak intensities allow one to calculate the equilibrium concentrations of the reactants and the products. The bisulfite concentration at equilibrium is not known, but this does not enter into the calculation. The ratio of the equilibrium constant of 2-butanone to that of acetone is found to be

0.3. This tells us that acetone is a better competitor for the bisulfite and thus will have a larger K_{eq}. The absolute value for the equilibrium constant for the formation of the 2-butanone bisulfite addition product is $135\underline{M}^{-1}$.
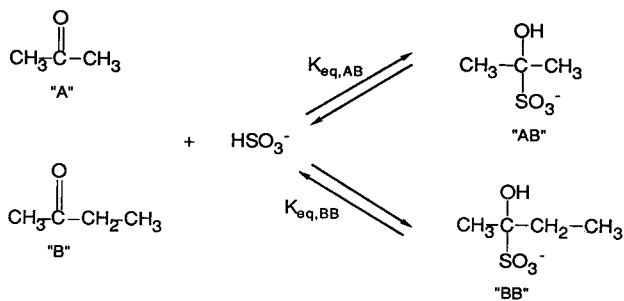
$$K_{eq,AB} = \frac{[AB]}{[A]_f\,[HSO_3^-]_f} \qquad K_{eq,BB} = \frac{[BB]}{[B]_f\,[HSO_3^-]_f}$$

$$\frac{K_{eq,BB}}{K_{eq,AB}} = \frac{[BB]}{[B]_f\,[HSO_3^-]_f} \times \frac{[A]_f\,[HSO_3^-]_f}{[AB]}$$

$$\frac{K_{eq,BB}}{K_{eq,AB}} = \frac{[BB][A]_f}{[B]_f[AB]}$$

		δ (ppm)	INTENSITY
A	ACETONE	2.116	210
AB	ACETONE-BISULFITE ADDITION PRODUCT	1.435	145
B	2-BUTANONE	2.087	57
BB	2-BUTANONE BISULFITE ADDITION PRODUCT	1.357	12

$[A]_i = 0.019\underline{M}$

$[A]_f = 0.0112\underline{M}$
$[AB] = 0.0078\underline{M}$

$[B]_i = 0.019\underline{M}$

$[B]_f = 0.0157\underline{M}$
$[BB] = 0.0033\underline{M}$

$[HSO_3^-]_i = 0.0096\underline{M}$

$[HSO_3^-]_f = ???$

$$K_{eq,AB} = \frac{0.69}{[HSO_3^-]_f} \qquad K_{eq,BB} = \frac{0.21}{[HSO_3^-]_f}$$

$$\frac{K_{eq,BB}}{K_{eq,AB}} = \frac{0.21}{[HSO_3^-]_f} \times \frac{[HSO_3^-]_f}{0.69}$$

$$\frac{K_{eq,BB}}{K_{eq,AB}} = 0.30$$

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TRIMETHYLACETALDEHYDE:

A competition experiment was also carried out betwen trimethyl-acetaldehyde and acetone to determine K_{eq}. In this case, 0.050$\underline{M}$ trimethylacetaldehyde was reacted with 0.050$\underline{M}$ acetone in an aqueous solution of sodium bisulfite which was 0.025$\underline{M}$ in HSO_3^-. (See Appendix, FIGURE 41.)

		δ (ppm)	INTENSITY
A	ACETONE	2.124	56.0
AB	ACETONE-BISULFITE ADDITION PRODUCT	1.442	34.9
TMA	TRIMETHYLACETALDEHYDE	9.36	4.8
TH	TMA HYDRATE	0.79	24.0
TB	TMA BISULFITE ADDITION PRODUCT	4.05	9.5

Both samples used were freshly distilled and prepared under nitrogen, however, some oxidation occurred forming the trimethylacetic acid. The methyl protons absorb as a singlet at ~1.1 ppm and the peak integrates to ~1.4. This is a small amount of acid but still must be taken into consideration when calculating the equilibrium concentrations.

$$[HSO_3]_i = 0.025\underline{M}$$

$$[HSO_3]_i = ???$$

$$[acid] = \frac{(1/9)(1.4)}{(1/9)(1.4) + 4.8 + 9.5 + (1/9)(24.0)} \times 0.050\underline{M} = 4.54 \times 10^{-4}\,\underline{M}$$

$$[\text{TMA}]_i = 0.050\underline{M} - 4.54 \times 10^{-4}\underline{M} = 0.050\underline{M}$$

$$[\text{TMA}]_f = \frac{4.8}{4.8 + 9.5 + (1/9)(24.0)} \times 0.050\underline{M} = 0.014\underline{M}$$

$$[\text{TB}] = \frac{9.5}{4.8 + 9.5 + (1/9)(24.0)} \times 0.050\underline{M} = 0.028\underline{M}$$

$$K_{eq,TB} = \frac{0.028\underline{M}}{0.014\underline{M}\,[\text{HSO}_3^-]} = \frac{2}{[\text{HSO}_3^-]}$$

$$[\text{A}]_i = 0.050M$$

$$[\text{A}]_f = \frac{56.0}{56.0 + 34.9} \times 0.050\underline{M} = 0.031\underline{M}$$

$$[\text{AB}] = \frac{34.9}{56.0 + 34.9} \times 0.050\underline{M} = 0.019\underline{M}$$

$$K_{eq,AB} = \frac{0.019}{0.031\underline{M}\,[\text{HSO}_3^-]} = \frac{0.613}{[\text{HSO}_3^-]}$$

$$\frac{K_{eq,TB}}{K_{eq,AB}} = 2.7$$

In this particular experiment, the amount of acid present in the initial amount of TMA used is negligible. However, to ensure that equilibrium had been reached, that is to say, that the ratio of equilibrium constants remained constant, a proton spectrum of the same sample was obtained at two different times, 24 hours and 96 hours after the first spectrum had been obtained. During this time period, the NMR tube was placed in a test tube which was flushed with nitrogen and then stopped with a rubber stopper and sealed with parafilm. These measures did not halt the oxidation of the aldehyde and so for subsequent calculations, the amount of acid present in the intital

concentration of TMA was substantial. A summary of the ratios of the two equilibrium constants is given below. The values converge to a ratio of 2.6.

TIME (hours)	K_{TB}/K_{AB}
0	2.7
24	2.3
96	2.7

TABLE 6. Ratio of the Keq's obtained for the formation of the TMA bisulfite addition product and the formation of the acetone bisulfite addition product obtained over a period of time.

In this case, the acetone is not as good a competitor for the bisulfite and so the equilibrium constant for the formation of the trimethylacetaldehyde bisulfite addition product is greater than that for the acetone bisulfite adduct by more than a factor of 2. K_{eq}, then, for the formation of the trimethyl-acetaldehyde bisulfite addition product is 1170$\underline{M}^{-1}$.

SUMMARY OF THE EQUILIBRIUM EXPERIMENTS CONDUCTED FOR THE FORMATION OF THE BISULFITE ADDITION PRODUCTS OF SIMPLE CARBONYL COMPOUNDS

The equilibrium constants were obtained for the formation of the bisulfite addition products of acetone, 2-butanone and trimethylacetaldehyde.

COMPOUND	K_{eq} (M^{-1})
Acetone	450
2-butanone	135
Trimethylacetaldehyde	1170

TABLE 3. Summary of equlibrium constants for the formation of the bisulfite addition products of acetone, 2-butanone, and trimethylacetaldehyde.

Generally, aldehydes are more reactive to bisulfite attack than ketones. This is due to the fact that the ketone has greater electron stabilizing capability and thus stabilizes the electron deficient carbonyl carbon. As a result, the product is not as readily formed and K_{eq} decreases. This trend is apparent in the results obtained although additional compounds need to be studied. Literature also tends to agree with this observation, as seen in the data in TABLE 1 of the INTRODUCTION. Note that K_{eq} for the formation of the bisulfite adduct of formaldehyde is greatest, with acetaldehyde and benzaldehyde following.

In addition, steric hindrance leads to a decrease in reactivity due to the inability of the bisulfite to add to the carbonyl compound. One might guess, then, that the K_{eq} for the formation of the propanal bisulfite adduct would be much greater than that of the trimethylacetaldehyde. It is also not surprising, then, that pinacolone was unreactive to bisulfite attack.

CONCLUSIONS:

High field nuclear magnetic resonance spectroscopy is obviously a powerful tool in characterizing the bisulfite addition products of carbonyl compounds, due to absorptions which are characteristic of both reactants and products. Perhaps, as a result of this research, NMR will be used further in studying these carbonyl-bisulfite systems and determining the equilibrium constants for the formation of the bisulfite adducts which are particularly of atmospheric interest.

Also, it has been shown that for propanal, 2-methylpropanal and trimethylacetaldehyde, the aldehyde exists in equilibrium with the hydrate. Since solutions were not accurately weighed, the equilibrium constants for the formation of the hydrates were not obtained. It is obvious, though, that NMR would be useful in studying these systems as well.

Since the formation of the bisulfite adducts, in some instances, can lead to the formation of a chiral center, the anisochrony resulting from either non-equivalent hydrogens, as in the case of propanal and 2-butanone, or non-equivalent carbons, as seen in 2-methylpropanal, is readily observed with high field NMR. The differences in chemical shifts of such stereochemically nonrigid systems, together with their splitting patterns and coupling constants, should be studied in greater detail to determine the actual cause of the non-equivalence.

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APPENDIX

47
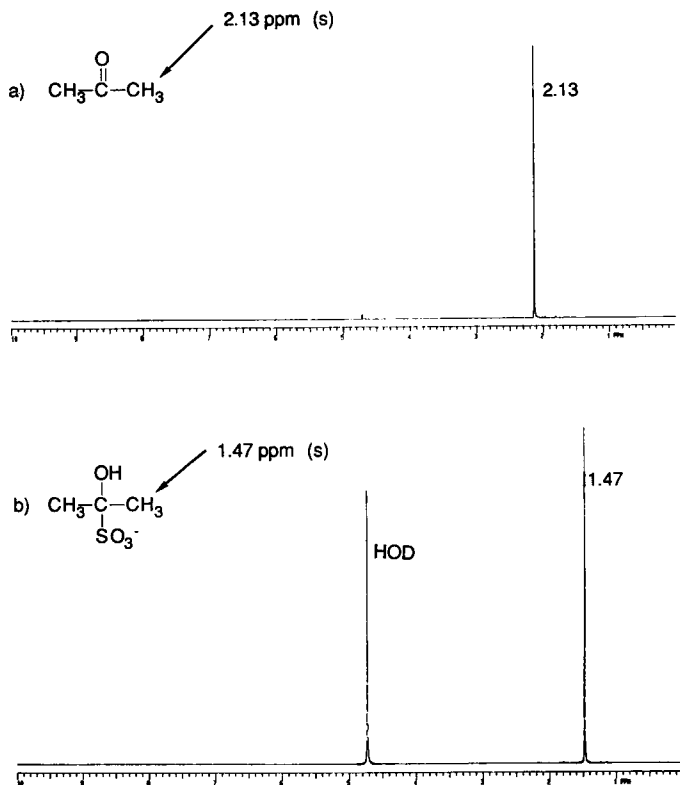
FIGURE 22. ¹H spectra for aqueous solutions of a) acetone and b) acetone bisulfite addition product.

48
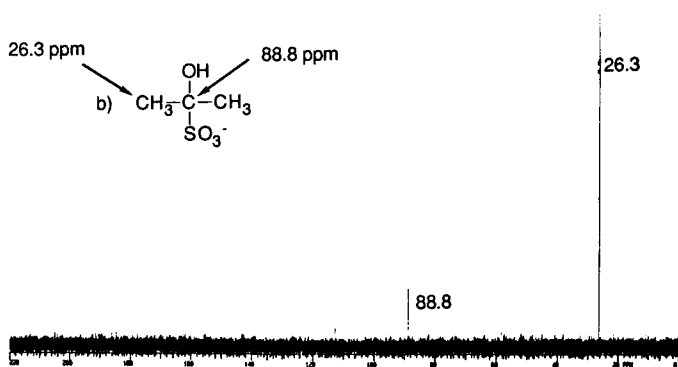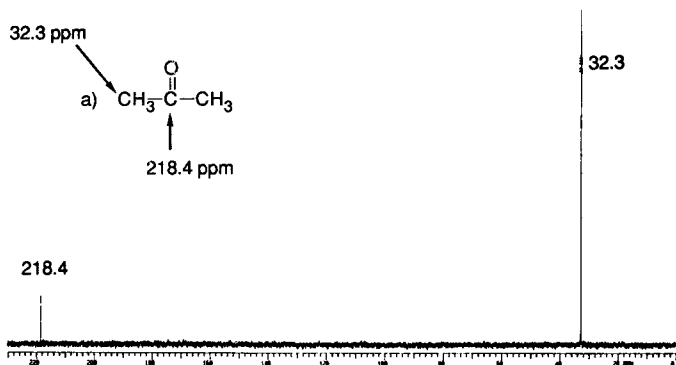
FIGURE 23. ^{13}C spectra for aqueous solutions of a) acetone and b) acetone bisulfite addition product.

49

~ 0.9 ppm (t)

~ 9.5 ppm (t)

$$CH_3-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-H \; + \; H_2O$$

~ 2.4 ppm (q)

K_{eq}

~ 0.76 ppm (t)

~ 4.8 ppm (t)

$$CH_3-CH_2-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-H$$

~ 1.45 ppm (q)

9.5   4.8   2.4   1.45   0.9   0.76
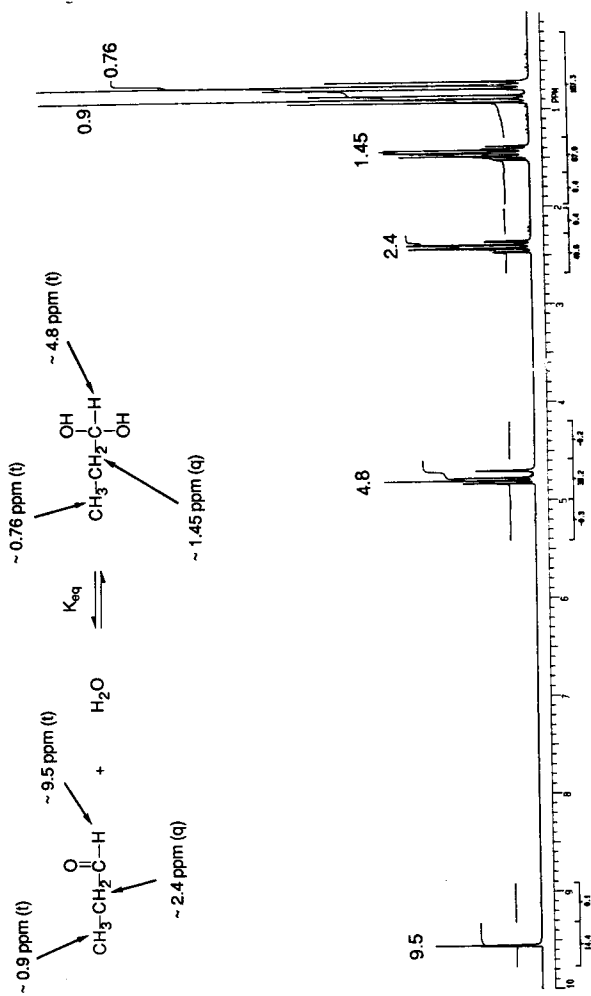
FIGURE 24. ^1H spectrum for the propanal-hydrate equilibrium in D_2O.

50

~ 1.9 ppm (m)

~ 1.0 ppm (t)

~ 4.25 ppm (dd)

~ 1.6 ppm (m)

$\delta H_a - \delta H_b = 0.30$ ppm

J_{ax} = 3.2 Hz
J_{bx} = 9.8 Hz
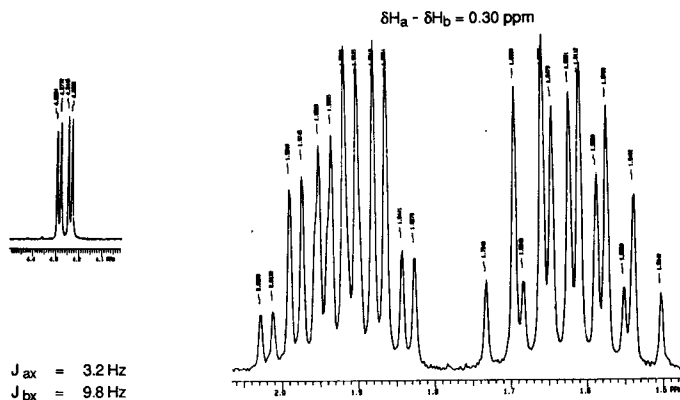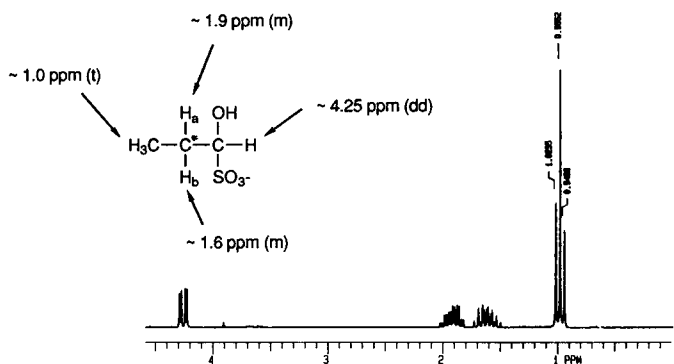
FIGURE 25. a) ^1H spectrum for the propanal bisulfite addition product in D_2O.

b) Expansion of ^1H spectrum for the propanal bisulfite addition product which depicts the splitting due to diastereotopism.

51
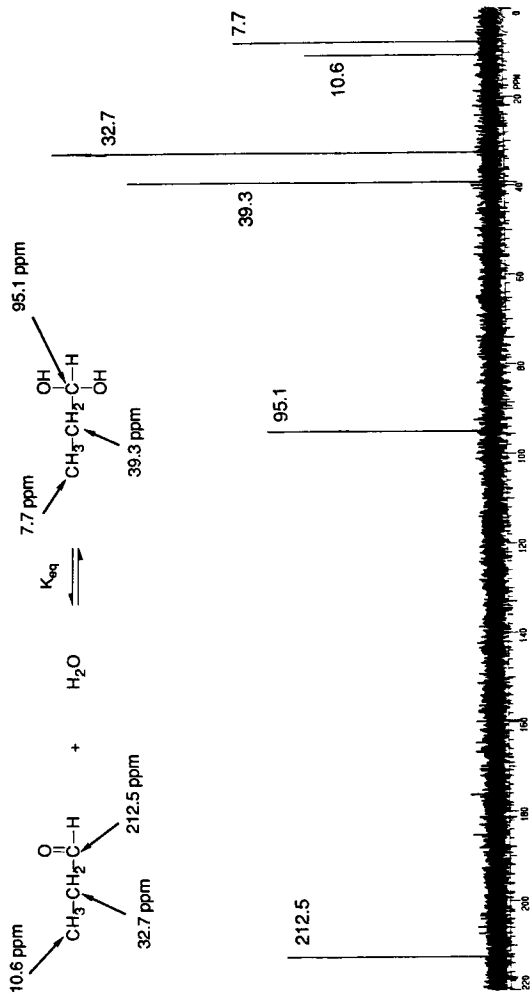
FIGURE 26. ^{13}C spectrum for the propanal-hydrate equilibrium in D_2O.

52
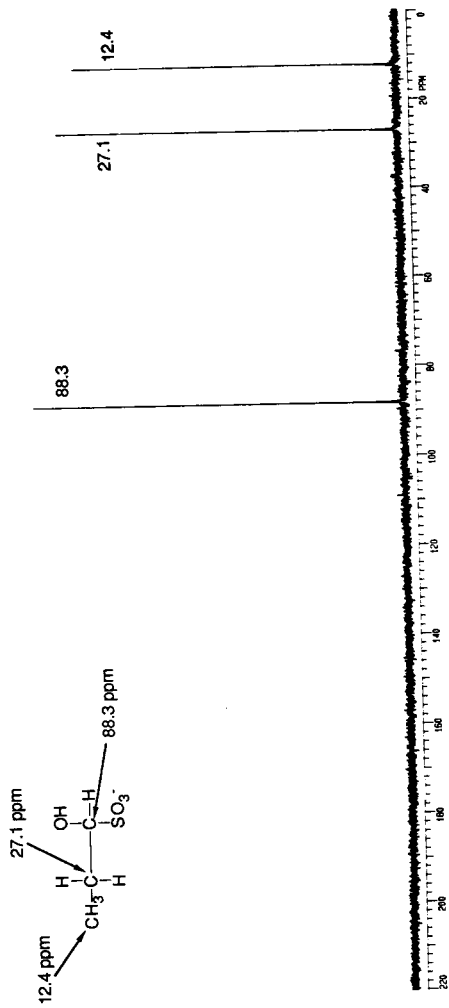
FIGURE 27. ^{13}C spectrum for the propanal bisulfite addition product in D_2O.

53
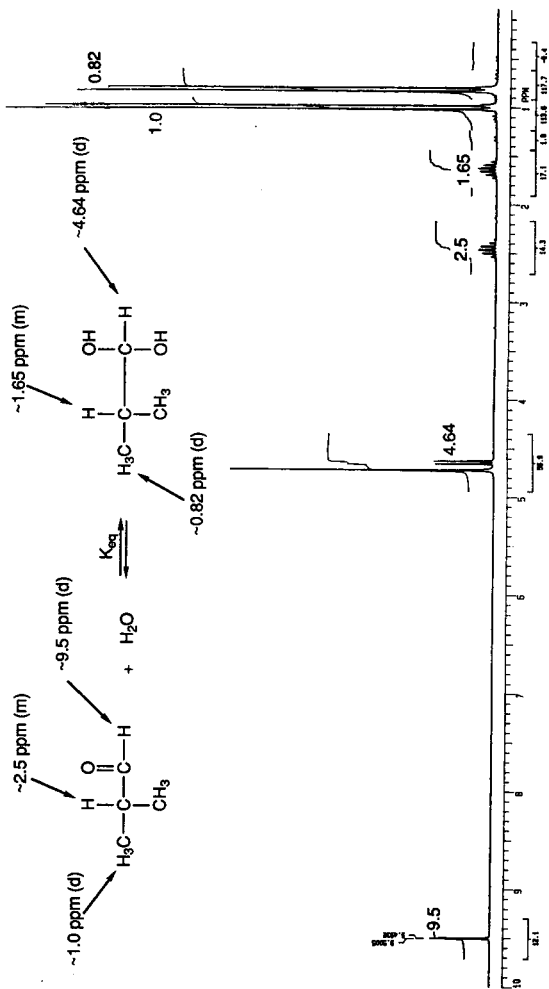
FIGURE 28. ¹H spectrum for the 2-methylpropanal-hydrate equilibrium in D_2O.

54
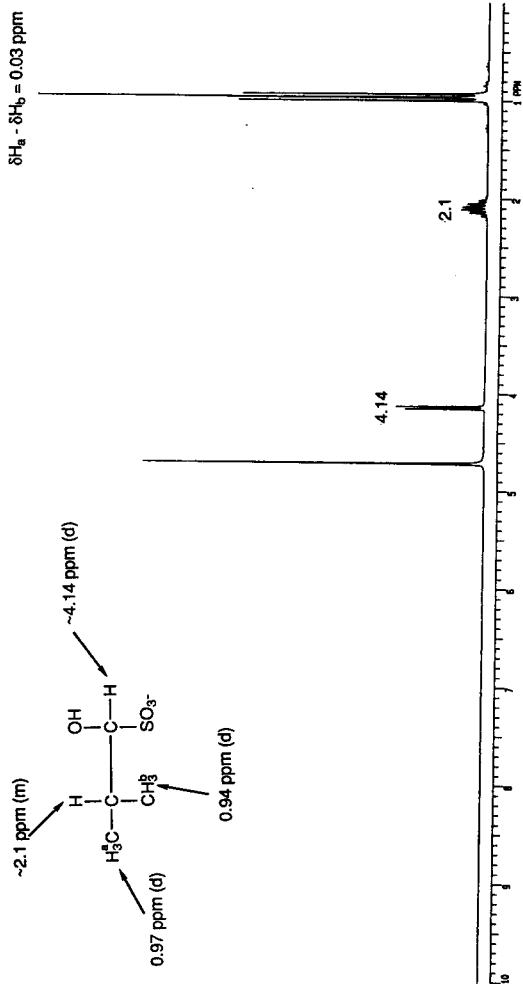
FIGURE 29. 1H spectrum for the 2-methylpropanal bisulfite addition product in D_2O.

55

FIGURE 30. ¹³C spectrum for the 2-methylpropanal-hydrate equilibrium in D_2O.

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FIGURE 31. ^{13}C spectrum for the 2-methylpropanal bisulfite addition product in D_2O. The methyl carbons are chemically non-equivalent and absorb at different regions of the spectrum. $\delta C_a - \delta C_b = 3.4$ ppm.

57
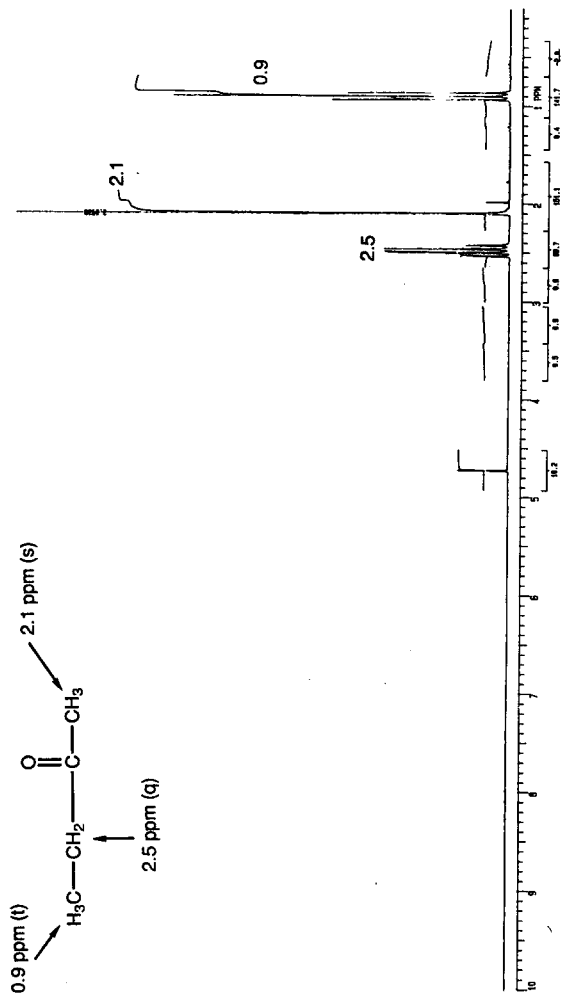
FIGURE 32. ¹H spectrum of 2-butanone in D_2O.

58
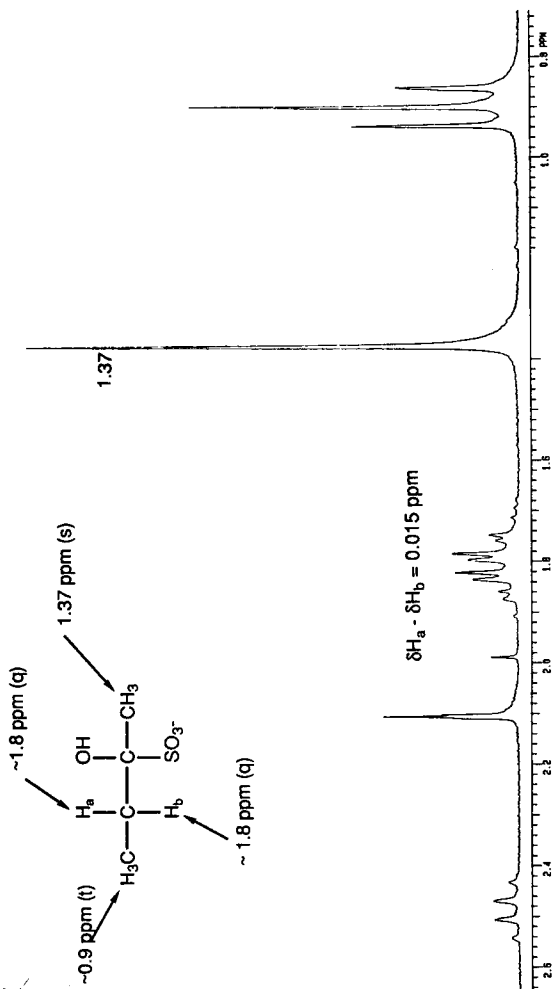
FIGURE 33. ^{1}H spectrum for the 2-butanone bisulfite addition product in equilibrium with 2-butanone in D_2O. The methylene hydrogens are split into a doublet of quartets due to the diastereotopism.

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FIGURE 34. ^{13}C spectrum of 2-butanone in D_2O.
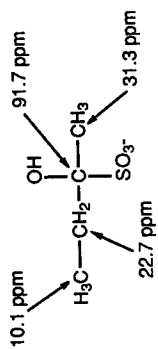
FIGURE 35. ^{13}C spectrum for the 2-butanone bisulfite addition product prepared by reacting 0.05g 2-butanone in ~1ml saturated HSO_3^-.
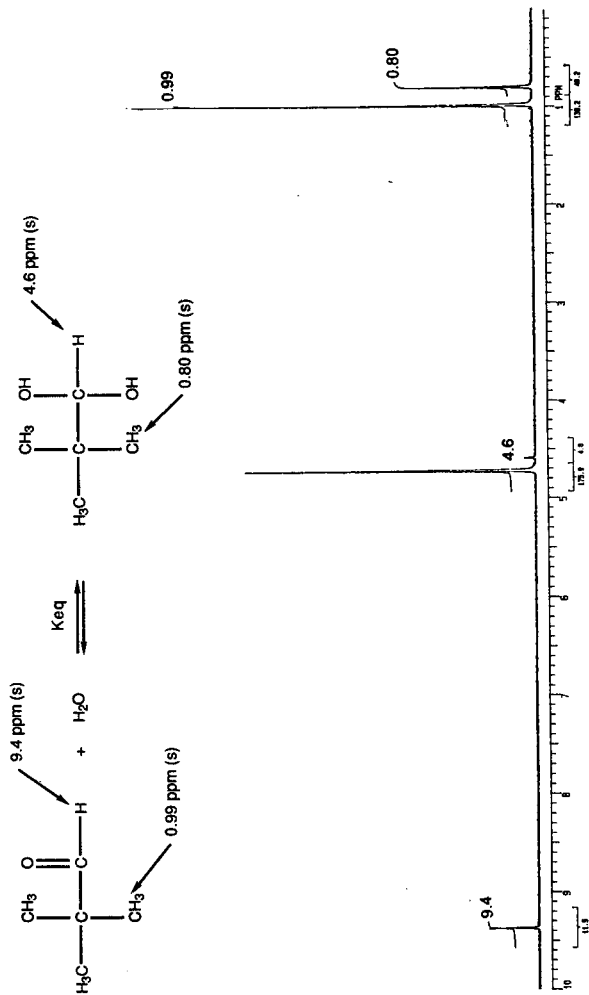
61

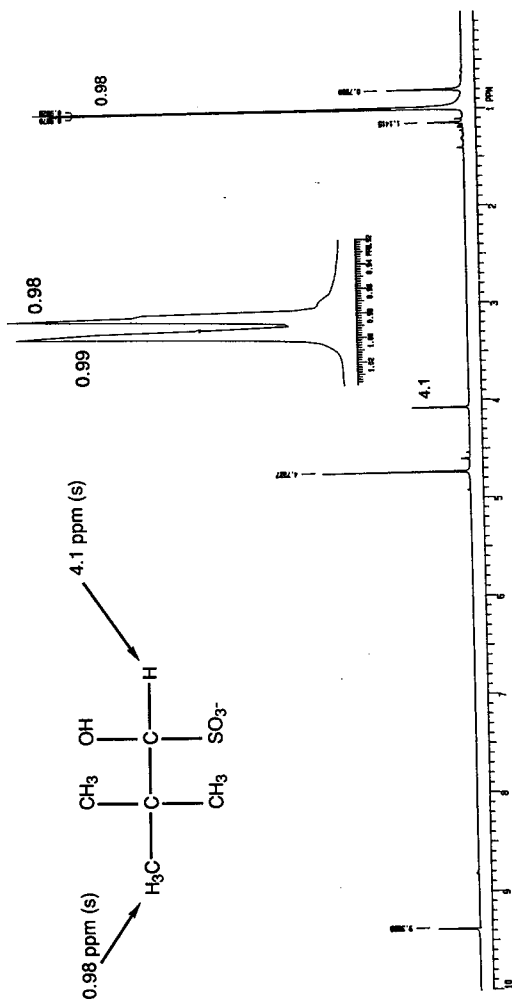**FIGURE 36.** 1H spectrum for the trimethylacetaldehyde-hydrate equilibrium in D_2O.

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FIGURE 37. 1H spectrum for the trimethylacetaldehyde bisulfite addition product in equilibrium with unreacted trimethylacetaldehyde and hydrate. Inset depicts the small difference in chemical shift between the methyl hydrogens of the TMA and those of the bisulfite adduct.
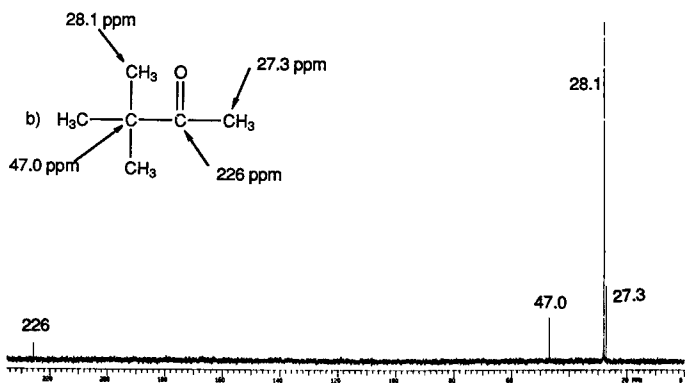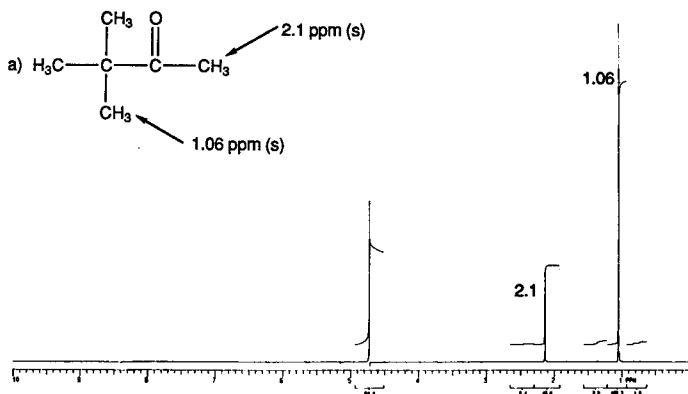
FIGURE 38. a) ^1H spectrum for the aqueous solution of pinacolone.
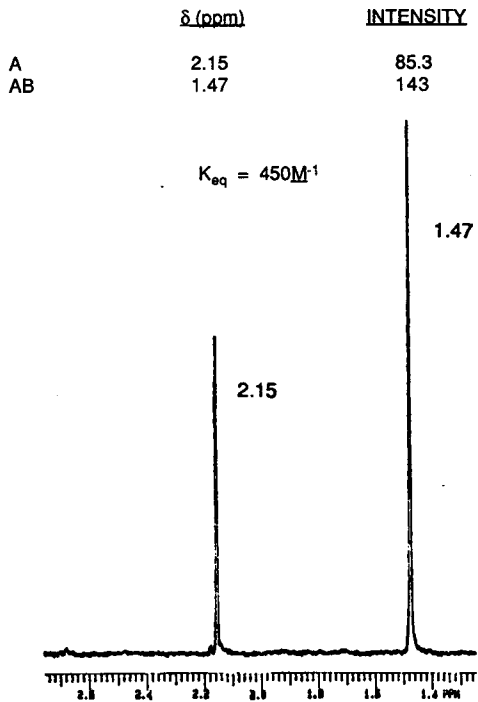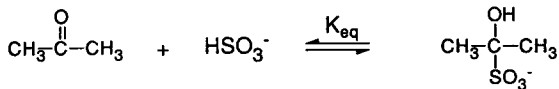b) ^{13}C spectrum for the aqueous solution of pinacolone.

FIGURE 39. ^1H spectrum for 0.010$\underline{M}$ acetone and 0.010$\underline{M}$ HSO$_3^-$ used to determine K_{eq} for the formation of the acetone bisulfite addition product.

65

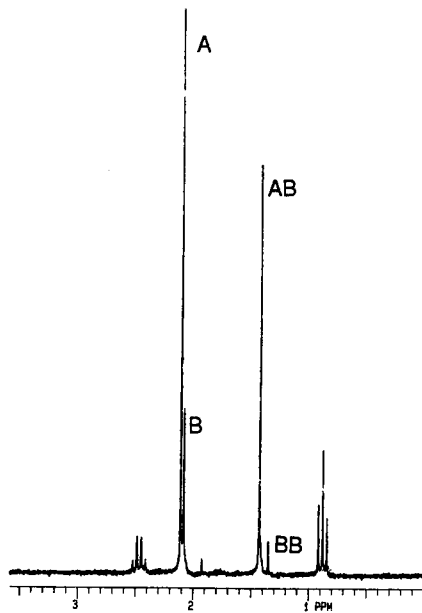|		δ (ppm)	INTENSITY
A	ACETONE	2.116	210
AB	ACETONE-BISULFITE ADDITION PRODUCT	1.435	145
B	2-BUTANONE	2.087	57
BB	2-BUTANONE BISULFITE ADDITION PRODUCT	1.357	12

FIGURE 40. ^1H spectrum obtained from the competition experiment between 0.019$\underline{M}$ acetone, 0.019$\underline{M}$ 2-butanone and 0.0096$\underline{M}$ NaHSO$_3$ in D$_2$O.

66

	δ (ppm)	INTENSITY
A ACETONE	2.124	56.0
AB ACETONE-BISULFITE ADDITION PRODUCT	1.442	34.9
TMA TRIMETHYLACETALDEHYDE	9.36	4.8
TH TMA HYDRATE	0.79	24.0
TB TMA BISULFITE ADDITION PRODUCT	4.05	9.5
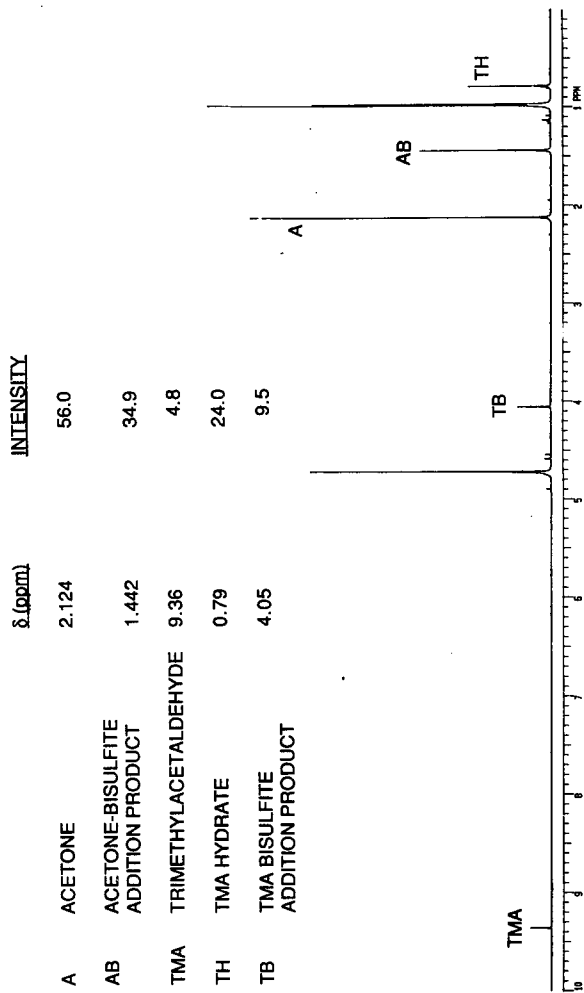
FIGURE 41. ^1H spectrum obtained from the competition experiment between 0.050$\underline{M}$ trimethyl-acetaldehyde and 0.050$\underline{M}$ acetone for 0.025$\underline{M}$ NaHSO$_3$ in D$_2$O.