1970

Acid-Base Catalysis of the Enolization of Acetone

Janet Louise Larson

ACID-BASE CATALYSIS
OF THE
ENOLIZATION OF ACETONE

A Thesis
Submitted in Partial Fulfillment of the
Requirements for the Degree of
Bachelor of Arts and Science with Honors
in Chemistry

By
Janet Louise Larson

Central Washington State College
1970

APPROVED FOR THE HONOR COMMITTEE

____
John E. Meany, COMMITTEE CHAIRMAN

____
Wilfrid W. Newschwander

____
Helmi S. Habib

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

Abstract

Measurements are reported on the rate of iodination of acetone at 25°C in arsenate, phosphate, and diethylmalonic acid buffers at a constant ionic strength of 0.2. Unlike earlier results which indicate that in acetic acid buffer the expression for the reaction velocity contains an appreciable kinetic term involving the product of the concentrations of acid and anion, it has been found from the present work that such a term is experimentally immeasurable for the above mentioned buffers. This finding coupled with the relatively powerful catalysis by the phosphate and arsenate dianions could imply the simultaneous participation of these species in both an acidic and basic capacity.

ACKNOWLEDGMENT

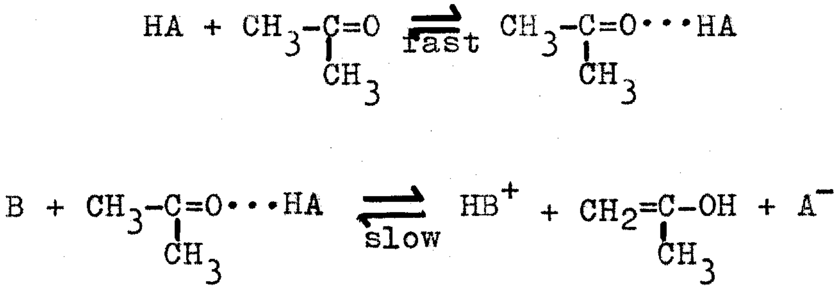
My sincere appreciation is extended to Professor John E. Meany for is advice and patience throughout this research program.

Also, I would like to thank John E. Hughes who did the research on the arsenate buffers.

Introduction

The purpose of this research is to study the kinetics of the acid-base catalysis of the enolization of acetone.

The acid-base catalyzed enolization of acetone may be expressed as follows:[1]



$$HA + CH_3-\underset{\displaystyle CH_3}{C}=O \xrightleftharpoons[fast]{} CH_3-\underset{\displaystyle CH_3}{C}=O\cdots HA$$

$$B + CH_3-\underset{\displaystyle CH_3}{C}=O\cdots HA \xrightleftharpoons[slow]{} HB^+ + CH_2=\underset{\displaystyle CH_3}{C}-OH + A^-$$

It has been noted that for a reaction subject to general acid (or general base) catalysis, the strongest acids (or strongest bases) generally are the best catalysts.

Quantitatively, the logarithm of the catalytic rate coefficients associated with the acid catalysts are unually linear functions of the corresponding values of pK_a of the catalysts. For general base catalysis, similar linear relationships exist between the logarithms of the catalytic constants for a given reaction and the pK_b values of the various basic catalysts.

Mathematically, this relationship may be expressed

$$\log k_{cat} = a \log K_a + b \qquad (1)$$

where the constant a is the slope of the line and the constant b the axial intercept, (actually the value of the catalytic constant, k_{cat}, for a hypothetical acid whose dissociation constant is unity). This constitutes the Brønsted catalysis law.[2]

Bell[3] has postulated the participation of a ternary mechanism in the iodination of acetone with acetate buffers which involves the concerted catalytic action of acetic acid and the acetate ion. In support of this view, Bell claims that the rate of iodination of acetone in acetate buffers contains a small, but detectible term in the form of $k_p[HOAc][OAc^-]$. His results are shown in Table I. The reaction velocities v are all expressed in moles of iodine per liter per minute, referring to the unit concentration of acetone.

Bell plotted $(v-v')/[OAc^-]$ vs. $[HOAc]$ at buffer ratios of $r = 1.00$, $r = 2.00$, and $r = 3.00$ as reproduced in Figure 1.

If $v-v'$ is plotted against $[OAc^-]$, the data for any one buffer ratio gives a line which is markedly convex to the concentration axis. Moreover, the velocities observed at higher concentrations are considerably higher than those calculated from the catalytic constants derived from Bell and Lidwell[4] from measurements at lower concentrations.

Agreement of Bell's data with experiment is good, but no such agreement would be viewed if the product term were omitted: the same point is established by the relatively small probable error in the value k_p. Bell's values of k_A and k_B agree

Table I

Iodination of acetone in acetate buffers.

r = 1.00, 10^8 v' = 9.7.

100 x [OAc^-]	2.54	2.59	4.89	5.74	7.54	8.69	10.19
10^8 v' obs.	60.9	63.0	114	132	169	204	234
10^8 v calc.	60.2	63.0	113	132	173	200	236

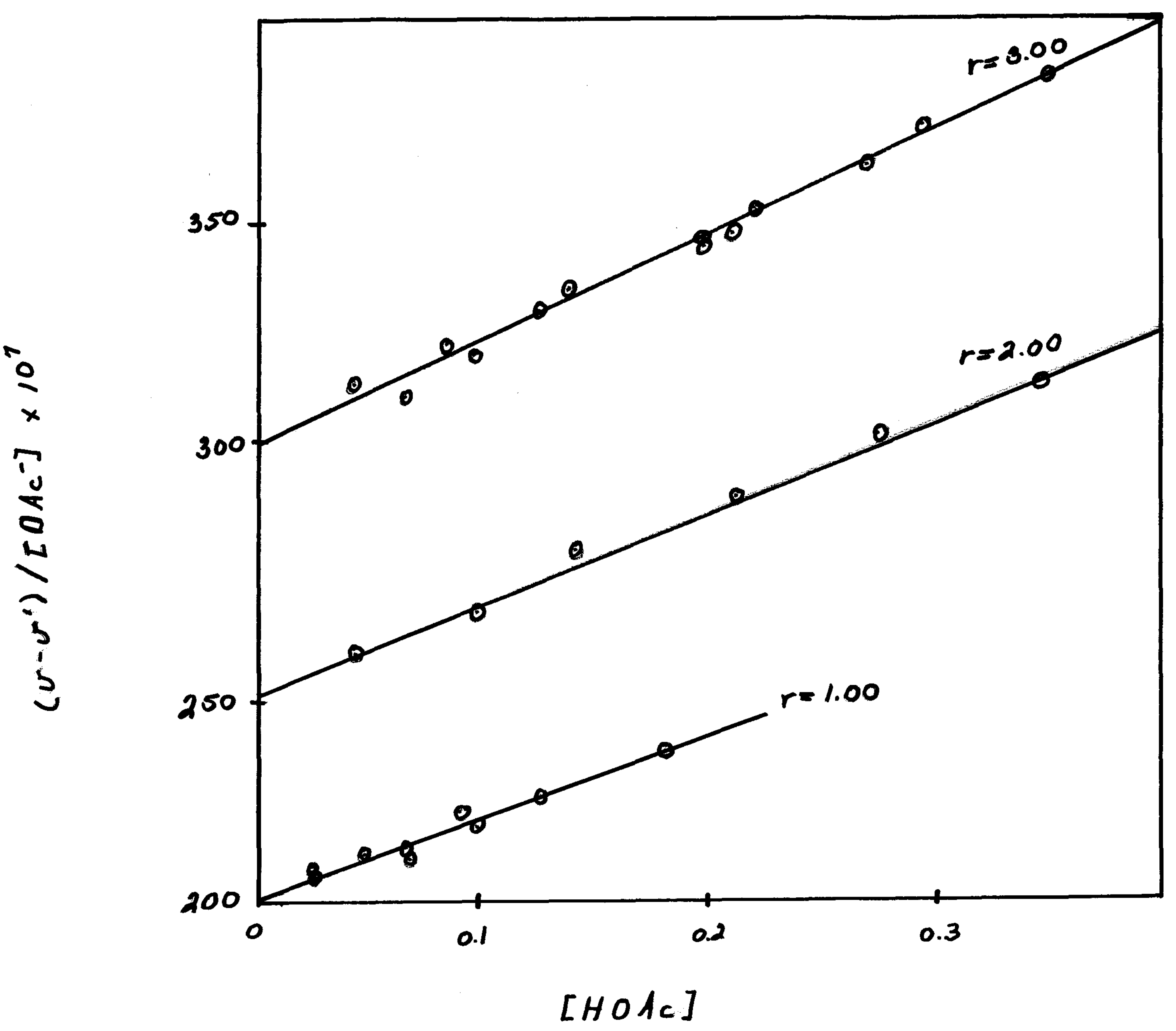
r = 2.00, 10^8 v' = 16.5.

100 x [OAc^-]	2.06	4.98	7.41	10.65	13.64	16.60
10^8 v' obs.	70.5	152	231	373	442	547
10^8 v calc.	70.0	152	225	332	437	546

r = 3.00, 10^8 v' = 23.4.

100 x [OAc^-]	1.59	2.60	3.29	3.95	4.99	5.31
10^8 v' 1bs.	73.7	103	130	150	189	201
10^8 v calc.	72.9	106	129	152	189	201

Figure 1: Bell's plot of velocity vs.[HOAc] at $r = 1.00$, $r = 2.00$, and $r = 3.00$.


r = 3.00
r = 2.00
r = 1.00
350
300
250
200
0
0.1
0.2
0.3
$(\nu-\nu')/[OAc^-] \times 10^7$
[HOAc]

reasonably with those of earlier workers, but the value of k_p is considerably greater than that obtained by Dawson and Spivey.[5] This is presumably because they used high and variable salt concentration (> 0.75 $\underline{N}$) while Bell's experiments refer to a constant ionic strength of $\mu = 0.2$. Bell concludes that the occurrence of a product term is a general phenomenon in this reaction.

Figure 2 indicates the deviation from a linear slope which Bell suggests is due to the $k_p[A][B]$ term from the reaction rate equation

$$k_{obsd} = k' + k_A[A] + k_B[B] + k_p[A][B] \qquad (2)$$

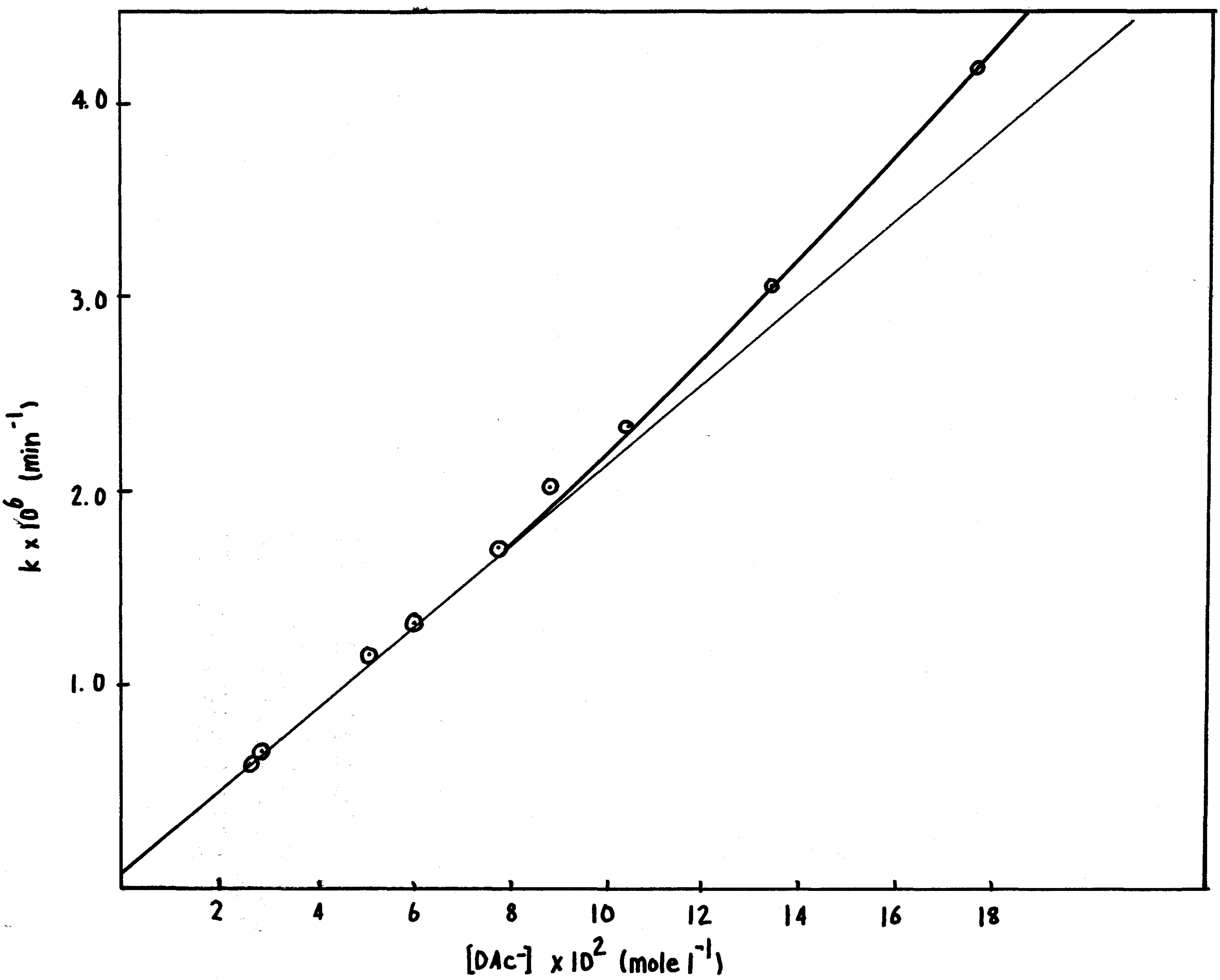
where the reaction rate k' represents the contribution due to catalysis by H_2O, H_3O^+, and OH^-. One of the purposes of our results is to show that the ternary contribution is not general and that the plots of rate constants vs. $[B]$ for certain buffers indicate the absence of a ternary term.

If both acids and bases take part in the rate-determining step of the reaction, certain other mechanistic possibilities appear. For example, the rate-determining step may be a reaction between the conjugate acid of the reactant and the conjugate base of the acid catalysts.

$$S + HA \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} SH^+ + A^- \qquad (3)$$

$$SH^+ + A^- \overset{k_2}{\rightleftharpoons} P + HA \qquad k_{-1} \gg k_2 \qquad (4)$$

Figure 2: Bell's plot of reaction rates vs. $[OAc^-]$ for iodination of acetone in acetate buffers at r = 1.00.


4.0
3.0
2.0
1.0
$k \times 10^6$ (min^{-1})
2
4
6
8
10
12
14
16
18
[DAc$^-$] x 10^2 (mole l^{-1})

Here the rate equation is

$$v = k_2[SH^+][A^-] = \frac{k_1\ k_2}{k_{-1}}[S][HA] \qquad (5)$$

showing that the mechanism may account for the general acid catalysis.

Lowry[6] has suggested that the acid and base interact with the reactant simultaneously rather than in two separate steps as shown in eq. 3 and 4. This does not necessarily require a three-body collision, but can instead be accomplished by having one of the catalysts react with a hydrogen-bonded complex of the other and the reactant, e.g.,

$$S + HA \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} S\cdots HA \qquad (6)$$

$$B + S\cdots HA \overset{k_2}{\rightleftharpoons} P + BH^+ + A^- \qquad k_{-1} \gg k_2 \quad (7)$$

The pseudo first-order rate constants for reactions that are catalyzed by both acids and bases have been found to follow the equation[7]

$$k = \sum^{i} k_i[A_i] + \sum^{i} k_i\ [B_i] \qquad (8)$$

where no terms involve both acid and base. The absence of any termolecular terms in the kinetic equation cannot be given as compelling evidence that the reaction of eq. 7 does not occur. These reactions may have been carried out in the solvent water, which can act as either an acid or a base.

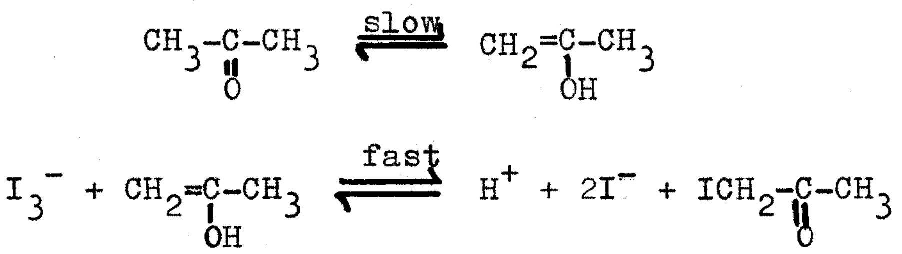
Then, it may be suggested that in general acid (or base) catalysis, water can act as a base (or acid) with its constant concentration being absorbed in the catalytic term.

Dawson and coworkers[5] showed that both the acid and the base catalysis are general, where runs were taken in aqueous acetic acid-sodium acetate. Dawson's last kinetic term, involving both an acid and a base, is of particular interest. His data substantiates Lowry's hypothesis that the reaction involves the simultaneous action of an acid and a base. It has been argued that this term is much smaller than would be expected from the magnitude of the other terms,[8] but Swain very neatly found the fallacy in this argument.[9] He pointed out that the Lowry termolecular mechanism does not require the reaction rate to be proportional to the action of acetic acid as an acid and of the water as a base. It may just as well be due to the action of the hydronium ion as an acid and the anion as a base.

Similarly the anion term might contain that part of the rate due to the acid and the base OH^- as well as that due to the acid H_2O and the anion base. It seems likely that most of the enolization of acetone (and the majority of other acid-base-catalyzed reactions, as well) does not proceed by the termolecular mechanism.

The conversion of ketone to enol or the enolate ion, whatever the mechanism may be, is much slower than the halogenation of the enol. Since it has previously been shown that the rate of iodination of ketones is identical to the rate of enolization the latter process may be monitored by following the disappearance of the tri-iodide ion spectrophotometrically.

This iodination of acetone may be expressed by the following steps:



$$CH_3-\underset{\underset{O}{\|}}{C}-CH_3 \overset{\text{slow}}{\rightleftharpoons} CH_2=\underset{\underset{OH}{|}}{C}-CH_3$$

$$I_3^- + CH_2=\underset{\underset{OH}{|}}{C}-CH_3 \overset{\text{fast}}{\rightleftharpoons} H^+ + 2I^- + ICH_2-\underset{\underset{O}{\|}}{C}-CH_3$$

Kinetic runs were made in the presence of diethylmalonate, phosphate, and arsenate buffers. Conclusions are made in this thesis regarding susceptibility of the above process towards general acid-general base catalysis as well as the catalysis by the hydroxide ion.

The concentration of acetone employed in the kinetic runs were always in great excess of the tri-iodide ion concentration, so that the concentration of the ketone remained essentially constant throughout the runs. Hence, pseudo zero-order kinetics were observed.

Considering that the basicities of diethylmalonate dianion, monohydrogen phosphate and monohydrogen arsenate are almost the same[10], then their capacities to catalyze the enolization of acetone should be similar. However, it will be noted that while both monohydrogen phosphate and monohydrogen arsenate can act bifunctionally in a basic anc acidic capacity, the diethylmalonate dianions, containing no acid protons, can act only in a basic capacity.

Specifically, the present research is designed to test the relative catalytic efficiency of phosphate and arsenate compounds which contain both acidic and basic groups suitably located so they may act simultaneously and compare their catalytic effectiveness to that of the diethylmalonate dianion.

Experimental

Materials. The acetone used in these experiments was obtained from Matheson-Coleman and Bell spectroscopic grade and the concentration used for all kinetic runs was 0.045 M.

The iodine concentration was prepared as a 0.002 M solution in 1 M potassium iodide, and its initial concentration in a reaction mixture was 0.001 M. In general, one concentration of I_3^- was used.

All solutions of the phosphate, arsenate, and diethylmalonate buffers and of the iodide solution were made with distilled H_2O.

A 0.2 N NaCl solution was prepared of Baker Analyzed reagent-grade sodium chloride. Varying amounts of this solution was added to the buffer mixtures to maintain a constant ionic strength (μ = 0.2 M). Dilutions of $[H_2PO_4^-]/[HPO_4^{2-}]$, $[H_2AsO_4^-]/[HAsO_4^{2-}]$, and $[DEM]/[DEM^-]$ are shown by Table II.

In a buffer solution containing general acid A and its conjugate base B, the buffer ratio, $r = [A]/[B]$ is taken as that obtained by mixing

Table II

Concentrations of arsenate, phosphate and diethylmalonate buffers with NaCl to maintain a constant ionic strength (μ = 0.2 M). Dilutions are made to 100 ml.

Buffers	Acid^a	Conjugate Base^a	NaCl^a	r	pK$_a$
$\frac{H_2AsO_4^-}{HAsO_4^{2-}}$	25.0	25.0	25.0	1.00	6.80
	10.0	25.0	20.0	0.40	
	5.0	25.0	10.0	0.20	
$\frac{H_2PO_4^-}{HPO_4^{2-}}$	25.0	25.0	25.0	1.00	7.12
	10.0	25.0	20.0	0.40	
	5.0	25.0	10.0	0.20	
$\frac{DEM}{DEM^-}$	25.0	25.0	25.0	1.00	7.20

a indicates ml. of 0.2 N solutions

weighed amounts of the components. Phosphate buffer solutions were made from Baker Analyzed reagent-grade potassium dihydrogen phosphate and sodium mono-hydrogen phosphate. Arsenate buffer solutions were made from Baker Analyzed reagent-grade potassium dihydrogen arsenate and sodium monohydrogen arsenate. Diethylmalonate buffer solutions were prepared from the compound synthesized according to Pocker and Meany[11].

The buffer ratios for phosphate and arsenate buffers were used with r = 1.00, r = 0.40, and r = 0.20 of the acid to its conjugate base, while the buffer ratio of the diethylmalonate ion was r = 1.00.

Analytical Instruments. Reaction rates were monitored on a Beckman Kintrac high speed recording spectrophotometer thermostated to 25 ± 0.1° by means of a Beckman Kintrac Thermocircular accessory. Absorbency data was collected also from a Beckman DB Spectrophotometer and a Hitachi Perkin-Elmer 139 UV-Vis Spectrophotometer. The values of pH reported were determined before and after each run by means of a Beckman Century SS expanded scale pH meter, the relative accuracy of which is 0.001 pH unit. A Beckman glass electrode having a low electrical resistance and temperature limits from -5 to 100° was used along with a Beckman Calomel Internal 39301 frit junction reference electrode.

Method. The tri-iodide ion, I_3^-, absorbs at a maximum at 353 $m\mu$ (ϵ = 24,500 mol per liter per cm)[11], and the pseudo zero-order kinetics were observed by determining the rate of diminuation of the tri-iodide absorption band. The reaction velocities were calculated from the slopes of the linear traces obtained, v =slope x 24,500 mole per liter. Since rate constants were determined, the following conversion was made from velocities

$$v = k_{obsd} [CH_3COCH_3] \qquad (9)$$

$$k_{obsd} = v/ [CH_3COCH_3] \qquad (10)$$

The specific rate obtained in this was was reproducable to about 1%.

The kinetic runs were initiated by injection 0.040 ml of a solution formally 2×10^{-3} M in iodine and 1.00 M in potassium iodide[13] into 3.00 ml of the reaction solution using a calibrated Hamilton microliter syringe.

The tri-iodide solution was made by adding 0.005 grams of I_2 to 1.66 grams of KI and diluting to 10.0 ml of distilled H_2O.

Results and Discussion

The enolization of acetone is a general acid, general base-catalyzed reaction in which the acidic and basic components in the reaction medium independently contribute to the over-all reaction rate.[14] The over-all pseudo zero-order rate constant, k_{obsd}, can be represented by

$$k_{obsd} = k' + k_A[A] + k_B[B] + k_p[A][B] \qquad (2)$$

where the reaction rate k' represents the contribution due to catalysis by H_2O, H_3O^+, and OH^-. The reaction rate k isexpressed in liters of iodine per mole per minute, referring to the unit concentration of acetone.

Initially, a series of runs was carried out varying the over-all buffer concentration while maintaining the same buffer ratio and pH. The buffer ratio, r, is defined throughout as the ratio of the concentration of the acid to that of the conjugate base, i.e., $r = [A]/[B]$. The buffer ratios for phosphate, arsenate, and diethylmalonate solutions used in the present work are given by Table II. The range of pK_a values for arsenate, phosphate, and diethylmalonate were in physiological range and typically, the pH values for the arsenate buffers are given in Table III.

Here, certain aliquots of the buffer solution (in this case arsenate) were added with corresponding amounts of 0.2 N NaCl to maintain a constant ionic strength. PH values were taken before and after the kinetic runs and were found to be the same. The table below shows the mls. of arsenate buffer at different buffer ratios added to mls. of 0.2 N NaCl.

Table III

pH values for arsenate buffer ratios at $\mu = 0.2$.

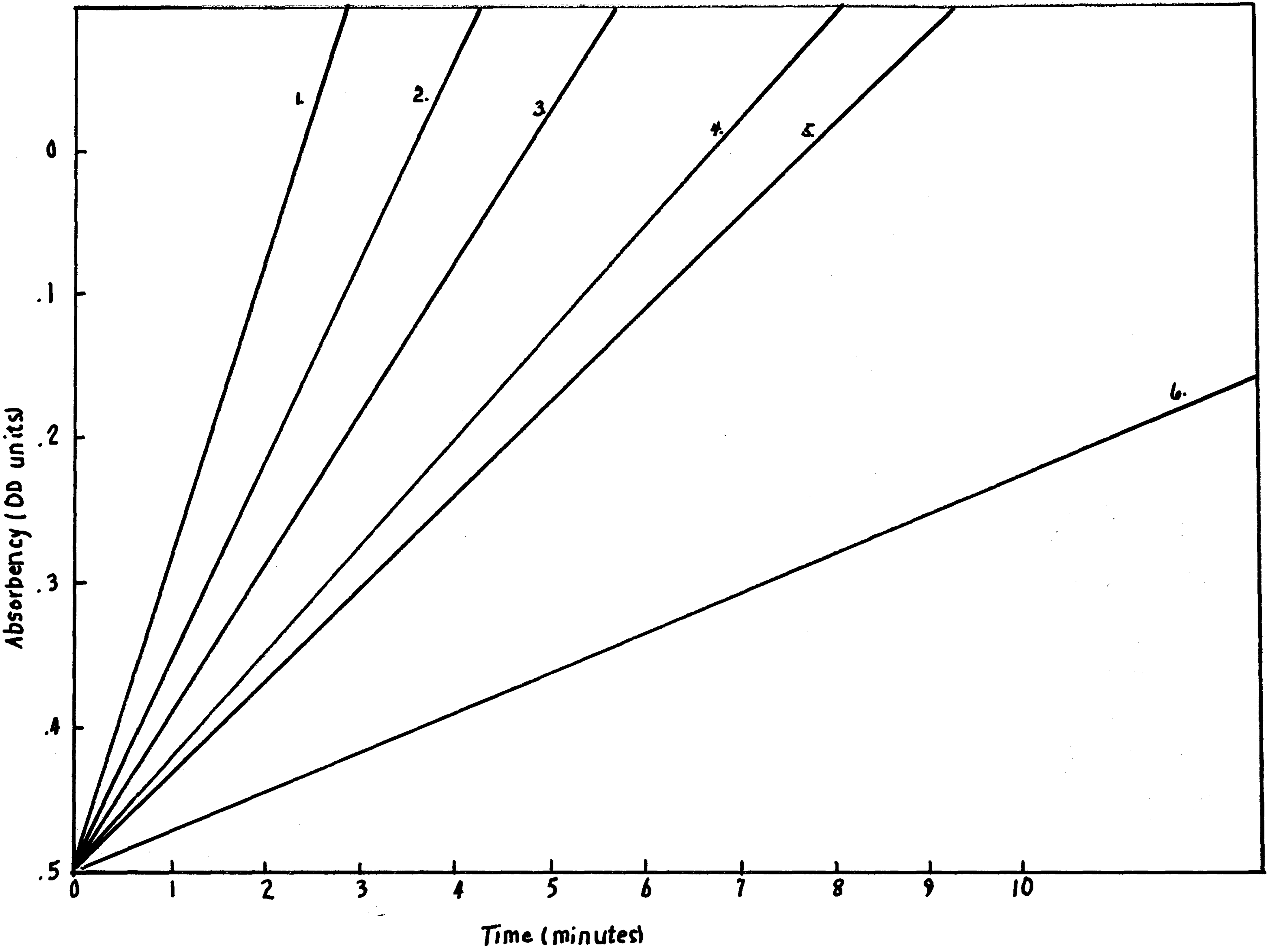
$\frac{[H_2AsO_4^-]}{[HAsO_4^{2-}]}$ [a]	NaCl [a]	$r = \frac{0.05}{0.05}$ M pH	$r = \frac{0.02}{0.05}$ M pH	$r = \frac{0.01}{0.05}$ M pH
6	0	7.24	6.72	7.42
5	1	7.20	6.71	7.38
4	2	7.18	6.69	7.35
3	3	7.20	6.64	7.33
2	4	7.14	6.64	7.32
1	5	6.92	6.61	7.33

a indicates ml of 0.2 N NaCl and Buffer solution

Typical plots of absorbency vs. time were found to be linear for a given buffer ration, as shown by Figure 3. Also, Figure 3 shows the resulting decrease in catalysis as the concentration of $H_2PO_4^-$ and HPO_4^{2-} decrease simultaneously. These series of six runs were at a buffer ratio of 0.40 at pH 6.86 and 25° with $\mu = 0.2$.

Figure 3: Phosphate catalyzed enolization of acetone at buffer ratio r = 0.40 at pH 6.86 and 25° with $\mu = 0.2$:

1., 6 ml of $[H_2PO_4^-]/[HPO_4^{2-}]$;
2., 5 ml of $[H_2PO_4^-]/[HPO_4^{2-}]$ and 1 ml 0.2 N NaCl;
3., 4 ml of $[H_2PO_4^-]/[HPO_4^{2-}]$ and 2 ml 0.2 N NaCl;
4., 3 ml of $[H_2PO_4^-]/[HPO_4^{2-}]$ and 3 ml 0.2 N NaCl;
5., 2 ml of $[H_2PO_4^-]/[HPO_4^{2-}]$ and 4 ml 0.2 N NaCl;
6., 1 ml of $[H_2PO_4^-]/[HPO_4^{2-}]$ and 5 ml 0.2 N NaCl.


1.
2.
3.
4.
5.
6.
0
.1
.2
.3
.4
.5
Absorbency (OD units)
0
1
2
3
4
5
6
7
8
9
10
Time (minutes)

Rearrangement of eq. 2 leads to

$$k_{obsd} = k' + [B](k_B + k_A r) + k_p [A][B] \qquad (11)$$

Values for k_{obsd} were evaluated from the slopes corresponding to the diminishing peaks of absorbence and calculated from

$$k_{obsd} = \frac{\Delta A/\Delta t}{\varepsilon_{I_3^-} [CH_3COCH_3]} \qquad (12)$$

where $\varepsilon_{I_3^-}$ is 24,500 per mole per cm and $[CH_3COCH_3]$ is 0.045 N. Several series of runs at different buffer ratios, r = 1.00, r = 0.40, and r = 0.2 for phossphate and arsenate were made. Table IV shows the rate constants obtained for the monohydrogen phosphate dianion at 0.01 mole per liter, 0.02 mole per liter, 0.03 mole per liter, 0.04 mole per liter, and 0.05 mole per liter for buffer ratios of 0.40 and 1.00.

Table IV

Rate constants for the base-catalysis of phosphate buffer at r = 1.00 and r = 0.40.

r = 1.00		r = 0.40	
$[HPO_4^{2-}]$ mole l^{-1}	$k_{obsd} \times 10^5$ min^{-1}	$[HPO_4^{2-}]$ mole l^{-1}	$k_{obsd} \times 10^5$ min^{-1}
0.01	1.6	0.01	4.9
0.02	3.1	0.02	7.0
0.03	4.5	0.03	10.2
0.04	6.0	0.04	12.6
0.05	7.5	0.05	14.4

Table V shows the values obtained for k_{obsd} for phosphate, aresenate and diethylmalonate dianions at a buffer ratio of 1.00, ionic strength of 0.2 *N*, and a temperature of 25°.

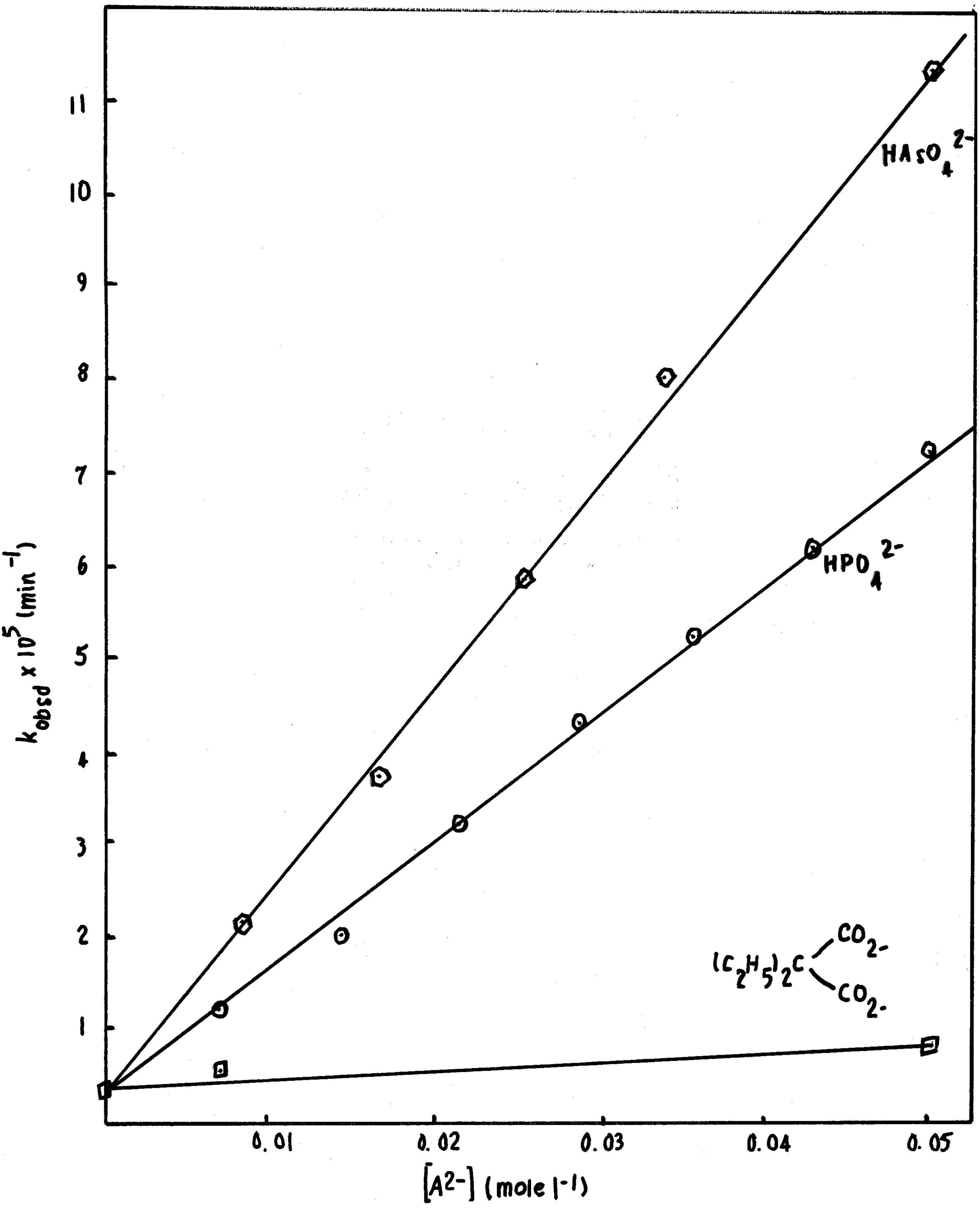
Table V

Rate constants determined for the base catalysis of arsenate, phosphate, and diethylmalonate buffers at a ratio of 1.00 and temperature of 25°.

$[HAsO_4^{2-}]$ mole l^{-1}	$k_{obsd} \times 10^5$ min^{-1}	$[HPO_4^{2-}]$ mole l^{-1}	$k_{obsd} \times 10^5$ min^{-1}	[DEM] mole l^{-1}	$k_{obsd} \times 10^5$ min^{-1}
0.01	2.2	0.01	1.6	0.01	0.25
0.02	4.7	0.02	3.1	0.02	0.50
0.03	7.0	0.03	4.5	0.03	0.60
0.04	9.1	0.04	6.0	0.04	0.70
0.05	11.3	0.05	7.5	0.05	0.90

Figure 4 shows plots of A^{2-} for phosphate, arsenate, and diethylmalonate ions at constant ionic strength of 0.2 *M*. Since these plots are linear, the contribution of the product term in eq. 2, $k_p[A][B]$ appears indetectible. The data from Table VI indicates that catalysis by $HAsO_4^{2-}$ and HPO_4^{2-} is greater than that of diethylmalonate dianion. Also the slope of similar plots at buffer ratios of 0.2 and 0.4 are about the same, implying that catalysis by dihydrogen phosphate and dihydrogen ions is negligible under the experimental conditions employed.

Figure 4: Plots of (k_{obsd} vs. HPO_4^{2-}), (k_{obsd} vs. $HAsO_4^{2-}$), (k_{obsd} vs. DEM) at ionic strength 0.2 <u>M</u> and at r = 1.00.



$k_{obsd} \times 10^5$ (min^{-1})
1
2
3
4
5
6
7
8
9
10
11
0.01
0.02
0.03
0.04
0.05
$[A^{2-}]$ (mole l^{-1})
$HAsO_4^{2-}$
HPO_4^{2-}
$(C_2H_5)_2C(CO_2^-)_2$

Table VI

Slopes, buffer ratios, and pK_a values for arsenate, phosphate, and diethylmalonate dianions.

Anion	$pK_a(25^o)$	r	1/r	slope	$k_A{}^{2-} x\ 10^3$
$HAsO_4{}^{2-}$	6.80	1.00	1.00	2.00×10^3	2.02
		0.40	2.50	2.05×10^3	
		0.20	5.00	1.99×10^3	
$HPO_4{}^{2-}$	7.12	1.00	1.00	1.39×10^3	1.33
		0.40	2.50	1.39×10^3	
		0.20	5.00	1.27×10^3	
DEM	7.20	1.00	1.00	0.02×10^4	0.12

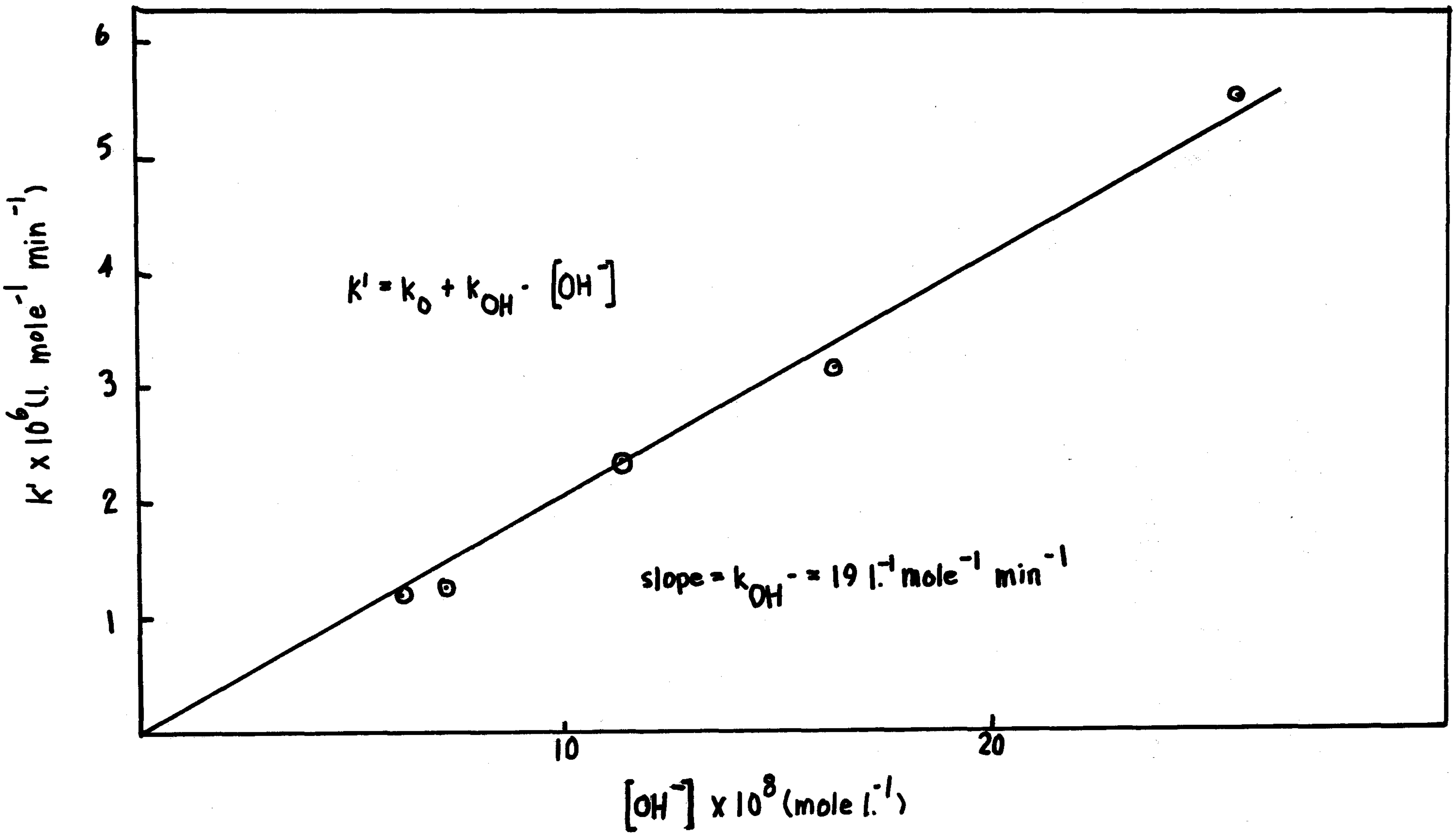
According to eq. 11, the slope of the straight line, S, is

$$S = k_o + k_A/ r \qquad (12)$$

A plot of k' vs. OH^- will give a slope k_{OH^-} and an intercept of k_o. Figure 5 shows that the intercept k_o is indistinguishable from zero, implying that the spontaneous k_o is very small. The value of k_{OH^-} is determined from the slope as 19 liters per mole per minute.

Since the value of S appears to be independent of the buffer ratio, it is assumed that the catalytic coefficient associated with the acidic components

Figure 5: A plot of k' x 10^6 vs. $[OH^-]$ to determine values for k_{OH^-} and k_o.


$k' = k_0 + k_{OH^-} \cdot [OH^-]$
slope = k_{OH^-} = 19 l.$^{-1}$ mole^{-1} min^{-1}
$k' \times 10^6$ (l. mole^{-1} min^{-1})
1
2
3
4
5
6
10
20
$[OH^-] \times 10^8$ (mole l.$^{-1}$)

negligibly small. Consequently the values of k_B for monohydrogen phosphate, monohydrogen arsenate, and diethylmalonate were evaluated by taking the average values of the slopes given in Table VI.

Since $k_a[A]$ does not contribute to the reaction rate, then eq. 11 becomes

$$k_{obsd} = k_B[B] + k_p[A][B] \tag{13}$$

Bell proposed that the rate reaction for the enolization of acetone is given as

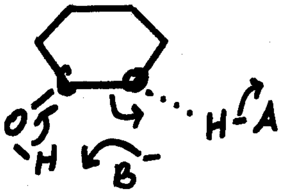
$$k_{obsd} = k_o + k_A[A] + k_B[B] + k_p[A][B] \tag{2}$$

He states that the termolecular term $k_p[A][B]$ is due to the simultaneous action of the general acid and general base and is shown by a definite convex curve (Figure 2). Several series of runs at constant buffer ratios were carried out. The plot of k_{obsd} vs. A^{2-}, where A^{2-} was $HAsO_4^{2-}$, HPO_4^{2-}, and DEM^{2-}, were found to be linear. Since our plots were linear, the termolecular term is indetectible. Thus, under these conditions, the termolecular term did not contribute to the rate equation and hence there exists no detectible concerted action of the acid and the base.

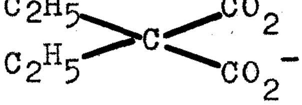
For most of the present work, one concentration of I_2 was used (I_2 = 0.01 M). However, variation of I_2 concentration did not affect the rate of iodination. Hence, our results are consistent with those obtained by other workers[3,4] suggesting that the enolization process is the rate-determining step.

Table VI shows that the slopes (of k_{obsd} vs. A^{2-}) are the same although the buffer ratios vary. As their values increase, the A^- concentration increased and the A^{2-} concentration remained constant. Since the slopes remained constant, the rate is not subject to acid catalysis. If $HAsO_4^{2-}$ or HPO_4^{2-} acts as a base and an acid, then there is no need for the acid $H_2AsO_4^-$ or $H_2PO_4^-$, as the molecule is a self-contained polyfunctional group. Now we have seen that the general equation for the pseudo zero-rate constant for general base catalyzed reactions involves no dependence on acid concentration.

The mutarotation of glucose in aqueous solution is subject to general acid and general base catalysis.[15] The mechanism below shows the bimolecular attack of glucose by an acid and a base.



It was observed that mutarotation of the tetramethyl glucose carried out in benzene solution involved catalysis by both an acid and a base. In this case, the catalyst was 2-hydroxypyridine, in which the acidic and basic centers are held rigidly in position favorable for attack.[2] Spatially, the catalytic requirements are almost identical for glucose and acetone except that in the aliphatic ketone more degrees of freedom exist through the ability of the methyl groups to rotate freely.

The present research showed that $HAsO_4^{2-}$, HPO_4^{2-}, and , and OH^-

catalyzed the enolization process. Indeed, the present work indicates that the catalytic components of phosphate dianion HPO_4^{2-} and of arsenate dianion[16] $HAsO_4^{2-}$ are at least 10 and 20 times more efficient than those involved in diethylmalonate dianions. The diethylmalonate structure indicates its low catalytic affect due to the absence of a removable proton. The catalysis due k_{OH^-} was determined to be 19 liters per mole per minute.

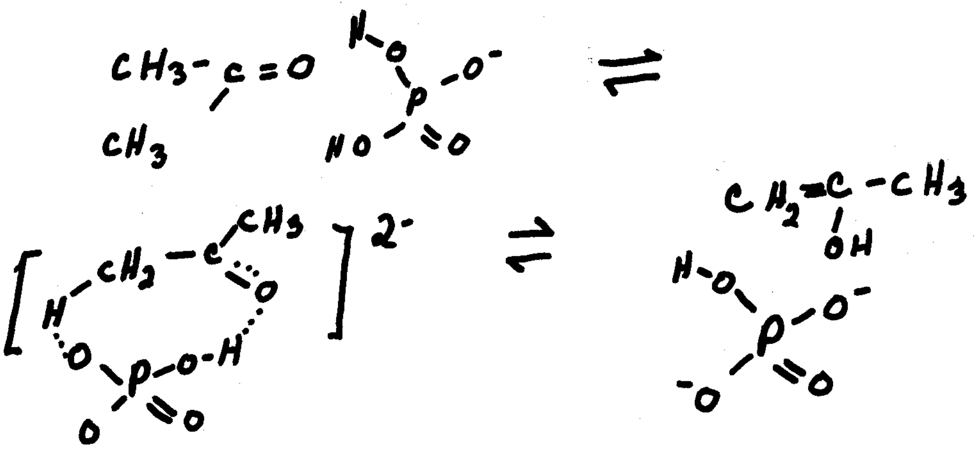
Finally, these phosphate, arsenate, and diethylmalonate buffers appear to be best suited for pH control around physiological pH.

This substantiates the general-base catalyzed nature of the process as stated by the early workers.[3,4] Since we did work at physiological pH, little $H_2PO_4^-$ or $H_2AsO_4^-$ contribution was observed as opposed to Bell[3], who worked at a lower pH.

In determining the rate coefficients for the components of phosphate, diethylmalonate, and arsenate buffers, it was observed that the catalysis of ketone enolization by monohydrogen phosphate is ten times faster than that due to diethylmalonate dianion and the catalysis of ketone enolization by monohydrogen arsenate is twenty times faster than that of diethylmalonate dianion even though the three bases have comparative values of pK_a (Table VI).

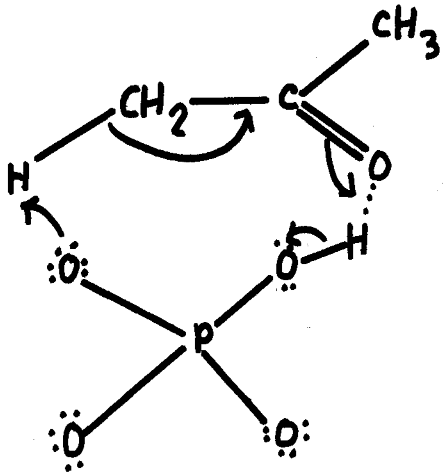
One may suggest that $H_2PO_4^-$ participates in the enolization by a mechanism involving simultaneous general base and general acid catalysis, therefore facilitating the transfer of H to the acetone.[11]

It is interesting to note that Pocker and Meany[11]



have observed strong catalysis by HPO_4^{2-} in the hydration of acetaldehyde. Here too, the acceleration shown by these results may explain the enhanced catalysis of HPO_4^{2-} and $HAsO_4^{2-}$ in the enolization of acetone. This catalytic effect is explained by the facilitation of the transfer of H_2O to the aldehyde by a mechanism involving simultaneous general acid and general base catalysis. Also, Pocker and Meany found no termolecular term with the use of phosphate buffers in the hydration of acetaldehyde.

Due to the exceptionally strong catalysis by phosphate and arsenate and also the absence of a significant ternary term, a possible mechanism is to invoke:



If this is the case, it is not necessary for both the $H_2PO_4^-$ and HPO_4^{2-} species to participate in the catalysis since HPO_4^{2-} may satisfy the acid-base catalytic requirement. Relatively strong catalysis may be interpreted to imply such "polyfunctional" catalysis.

Arsenate dianion may be more catalytic than phosphate dianion due to its larger size or greater electrostatic ability.

Further catalytic information may be obtained by experimentation carried out in methyl substituted phosphate or arsenates. Since methyl substituted phosphates have no removable proton, esperimentally, its rate value should be close to that of DEM. Also, further studies of DEM buffers at values of r = 0.40 and r = 0.20 to determine comparable reaction rates with that of phosphate and arsenate. However, much more research can be done of this aspect of general acid-base catalysis with regard to "fit" of polyfunctional groups to the site of enolization group.

In summary, the following points were obtained from the data:

1. Variation in I_2 concentration did not affect the rate of I_3^- disappearance. Therefore, the enolization step is the rate-determining step.
2. No termolecular term was detectible, unlike that suggested by Bell.
3. The same slope for various buffer ratios indicate the rate is not subject to acid catalysis.
4. $HAsO_4^{2-}$, HPO_4^{2-}, DEM, and OH^- catalyze the system and substantiates the general base catalyzed nature of the process.

5. The catalytic effect of $HAsO_4^{2-}$, and HPO_4^{-2} are 10 and 20 times greater than DEM.

6. Arsenate dianion is the best catalyst of the arsenate, phosphate, and diethylmalonate buffers, probably due to its size and electrostatic ability.

7. Extension of this work is suggested with methyl substituted phosphates and arsenates to propose a definite catalytic mechanism.

BIBLIOGRAPHY

1. Hammett, *Physical Organic Chemistry*, 1st ed., New York, McGraw-Hill, p. 230 (1940).

2. Gould, *Mechanism and Structure in Organic Chemistry*, New York, Holt, Rinehard and Winstron (1962).

3. Bell, R.P., and Jones, P., *J. Chem. Soc.*, *88*, (1953).

4. Bell and Lidwell, *Proc. Roy. Soc.*, *176*, 88 (1940).

5. Dawson and Spivey, *J. Chem Soc.*, 2180 (1930).

6. Lowry, T. M., *J. Chem Soc.*, 2554 (1927).

7. Hine, *Physical Organic Chemistry*, 2nd ed., New York, McGraw-Hill, p. 106-112 (1962).

8. Pederson, K.J., *J. Phys. Chem.*, *38*, 590 (1934).

9. Swain, C.G., *J. Am. Chem. Soc.*, *72*, 4578 (1950).

10. Kortum, G., Vogel, W., and Andresson, K., "Dissociation Constants of Acids in Aqueous Solutions", Butterworths, London, p. 335 (1961).

11. Pocker, Y., and Meany, J.E., *J. Phys. Chem.*, *71*, 3113 (1967).

12. Albery, W.J., Bell., R.P. and Powell, A. L., *Trans Faraday Soc.*, *61*, 1194 (1965).

13. The equilibrium constant for $I^- + I_2 \rightleftharpoons I_3^-$ has the value 714 $\underline{M}^{-1}$.

14. Bell, R.P., Rand, M.H., and Wynne-Hones, K.M.A., *Trans. Faraday Soc.*, *52*, 1093 (1956).

15. Brønsted and Guggenheim, *J. Am. Chem. Soc.*, *49*, 2554 (1929).

16. Hughes, J.E., unpublished work at Central Washington State College.