# STUDIES ON THE KINETICS OF THE ADDITION OF ACETIC ACID TO ISOBUTENE

Thesis by

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## ABSTRACT

The kinetics of the addition of acetic acid to isobutene with anhydrous and water-containing acetic acid as the solvent were studied. The rate was determined by following the changing unsaturation with bromine. The reaction was found to be sensitive to the presence of water, tertiary butyl alcohol being the principal product, when water was present and no polymerization was observed. Under anhydrous conditions the tertiary butyl acetate was formed and the isobutene was observed to polymerize. The kinetics of the anhydrous reaction were theoretically treated quantitatively and the rate step was shown to be the addition of the proton to the isobutene. The water-containing conditions were studied, but could not be quantitatively interpreted due to the complex equilibrium system set up, the results were however interpreted qualitatively. The concept of the carbonium ion intermediate of Whitmore was shown to be consistent with the esterification and the polymerization reaction.

# INTRODUCTION

The study of the addition of acetic acid to isobutene to give t-butyl acetate

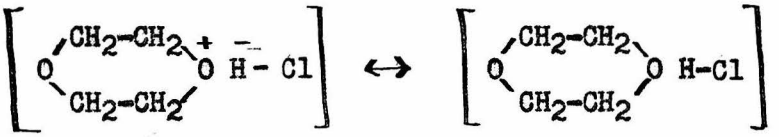
$$CH_3COOH + (CH_3)_2C = CH_2 \rightleftharpoons (CH_3)_3COCOCH_3$$

is analogous to the hydration of isobutene.

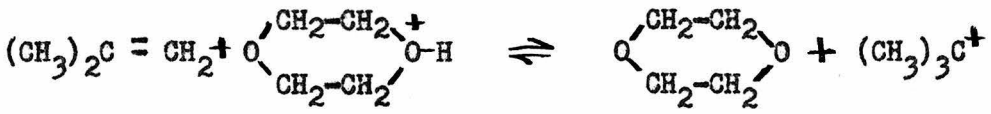
$$(CH_3)_2C = CH_2 + H_2O \rightleftharpoons (CH_3)_3COH$$

whose acid catalyzed reaction was studied by Lucas and Eberz. (1) The acetic acid-isobutene, water-isobutene analogy suggested that the acetic acid molecule would give a "larger handle" for the study of the hydration mechanism as both reactions appear to involve the same type of mechanism. Thus both reactions have been found to be bimolecular (1,2,3,4) and acid catalyzed. (1,4)

Altschul (4) has recently made a study of the addition of benzoic acid, p-nitrobenzoic acid and acetic acid to isobutene using sulfuric acid as catalyst and dioxane as a solvent. This work indicates that the reaction is bimolecular with respect to the acid and the isobutene at constant catalyst concentrations. In the reaction, no polymerization was observed to occur contrasting to the results obtained here when acetic acid was the solvent. This anomaly is explainable on the basis of the recent work of Weith, Hobbs, and Gross (5) who from absorption studies postulated



which would stabilize the dioxane hydrogen ion complex with respect to isobutene



thus eliminating the polymerization reaction

In this work the sulfuric acid catalyzed addition of acetic acid to isobutene using acetic acid as a solvent was studied. The consumption of isobutene by the reaction

$$(CH_3)_2C = CH_2 + CH_3COOH \rightleftharpoons (CH_3)_3COCOCH_3$$

was measured by the method of Lucas and Pressman (6) slightly modified, using the sampling technique of Eberz and Lucas. (7)

## EXPERIMENTAL

### Materials:

Carbon Tetrachloride Technical $CCl_4$ was purified by saturating it with chlorine and exposing to sunlight for two days. The solution was then washed with C.P. dilute NaOH, dried over $CaCl_2$ and distilled to give carbon tetrachloride, b.p. 75.8-76.0° at 748 mm.

t-Butyl Acetate It was prepared by the method of Norris and Rigby, (8) b.p. 97.0-97.1°C at 748 mm, $n_D^{25} = 1,3865$.

Cyclohexene Reagent cyclohexene was redistilled through a 40 cm Vigreux column, b.p. 82.0-82.2°C at 749mm.

Acetic Acid C.P. Baker's glacial acetic acid was made anhydrous by refluxing it for two hours with acetic anhydride, the amount of acetic anhydride being calculated from the freezing point depression of the glacial acetic acid.

100% Sulfuric Acid Smal amounts of C.P. oleum of unknown strength were mixed with varying quantities of C.P. concentrated sulfuric acid in order to adjust the composition by means of melting point determination to give a product m.p. 10.3°C.

Isobutene The isobutene was prepared using C.P. t-butyl alcohol, m.p. 24.5°C and oxalic acid dihydrate as the dehydrating agent. (9) The isobutene, as it was generated, was scrubbed in water, dried by passing through anhydrite, condensed and sealed in large ampoules. The isobutene was dispensed as needed into the stock isobutene-acetic acid solution.

Sodium Thiosulfate Standard Solutions In 1 liter of freshly boiled, cooled water 25 gm of $Na_2S_2O_3 \cdot 5H_2O$ and 0.1 gm $Na_2CO_3$ were dissolved. The solution was then allowed to set for a day and standardized with $K_3Fe(CN)_6$, following the procedure of Kolthoff and Sandell. (10) The solution was frequently restandardized, no change in concentration being observed.

Potassium Bromate-Bromide Standard Solution To 1 liter of distilled water were added 2.5 gm C.P. $KBrO_3$ and 25 gm C.P. KBr. This was standardized against newly standardized $Na_2S_2O_3$ solution, following the procedure of Kolthoff and Sandell. (10) The solution was restandardized frequently, complete stability being observed.

## Equipment

The reaction was carried out on a thermostatt, set at 25.00 ±0.05°C and checked with a Bureau of Standards thermometer, constant stirring being provided by a 1/4 horsepower stirring motor. Special reaction bulbs (Fig. 1) were designed with a pressure sampling head to prevent the loss of isobutene from the system, and absorption of

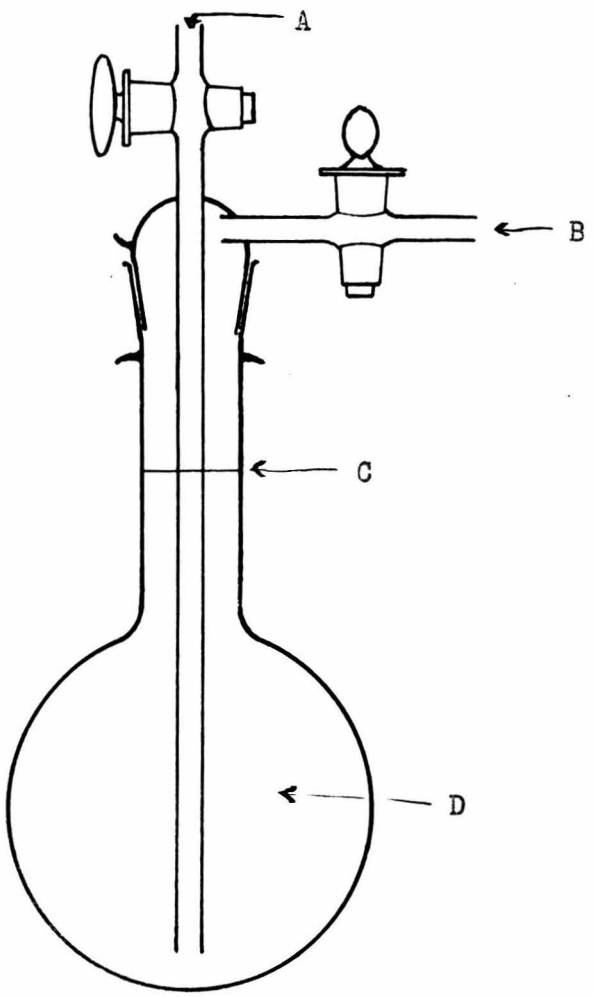



Figure 1

Reaction Bulb

A. Sampling head outlet

B. Nitrogen inlet

C. Volume calibration mark

D. 300 ml. bulb

oxygen from the atmosphere. The reaction bulb was provided with a long neck, so that the reaction mixture would be completely submerged in the thermostat and to keep to a minimum the free volume in the system, thus making the isobutene volatilization negligible and the amount of oxygen present initially minimal. The calibration mark was made on each reaction bulb, so that a known volume of isobutene solution could be added.

All burets and pipets were calibrated gravimetrically using water at room temperature. The sampling pipets of Eberg and Lucas (7) were calibrated using redistilled mercury. The standard potassium bromate-bromide and thiosulfate solutions were prepared and standardized by the usual analytical procedures, the values being rechecked frequently.

The isobutene solutions were prepared by bubbling isobutene into the acetic acid, using a special head that permitted the system to be sealed from the atmosphere (Fig. 2). The isobutene was bubbled through valve 1 with valve 2 open until the isobutene concentration approximated the desired value. Stopcocks 3 and 4 were then closed. The solution was then dispensed, when desired, into the reaction bulbs, using nitrogen pressure at 2. In this manner it was possible to dispense solutions of the same initial isobutene concentration.

Initially, difficulty was experienced in controlling the sulfuric acid concentration in the reaction mixture. This was overcome by preparing standard sulfuric acid solutions from 100% C.P. $H_2SO_4$ and acetic acid, containing acetic anhydride, in a volu-

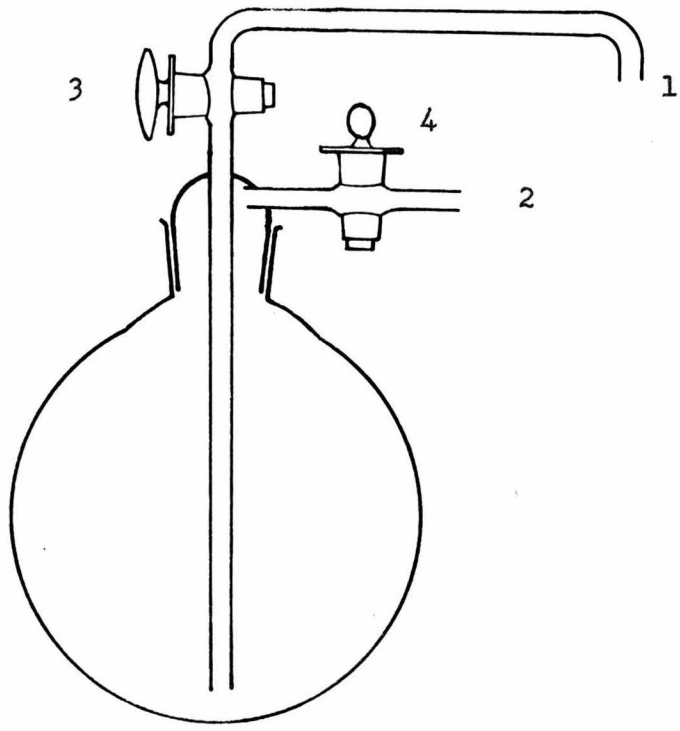



Figure 2

Storage Bulb

metric flask. The sulfuric acid concentration in the reaction mixture was then controlled by the volume pipeted in from a sulfuric-acetic acid standard solution. From the volume of isobutene solution and the volume of sulfuric acid catalyst added, allowing a correction for volume changes, the sulfuric acid and isobutene concentrations in the reaction mixture were calculated. The correction for volume changes due to the non-ideal behavior of sulfuric acid and acetic solutions, was obtained from a series of dilution experiments with sulfuric and acetic acids.

The reaction mixture was sampled by using the sampling pipets of Eberz and Lucas (7) shown in Fig. 3. The reaction solution was forced into the pipette by attaching the pipette to A (Fig. 1) using a rubber tube as a connector to the special reaction bulb head described previously. The $N_2$ used in displacing the solution was dried by passing it through anhydrite. The solution was permitted to rise into 2 (Fig. 3) so as to clean out the pipette and to insure that the solutions came from the main part of the reaction bulb D (Fig. 1). The reaction was then analyzed using the technique of Lucas and Pressman (6), and their special bromination flasks. The sampling pipet was then allowed to drain with liquid in 2 (Fig. 3), being permitted to replace the wash acetic acid on the pipette surface. This minimized the possibility and effect of dilution when the sampling procedure was repeated.

Analytical Procedure

The analytical procedure of Lucas and Pressman was modified slightly when it was found that the mercuric sulfate and sodium chloride could be eliminated from the reaction mixture. The potassium

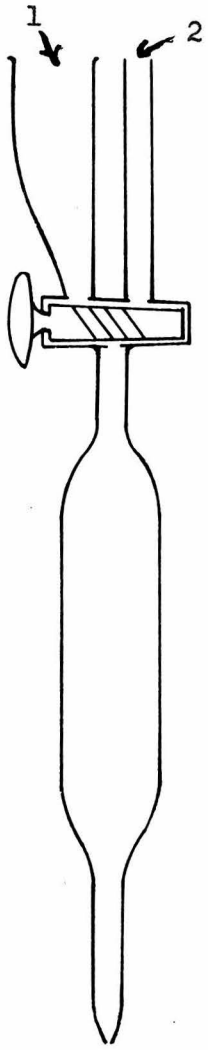



Figure 3

Sampling Pipette

bromate-bromide solution was made up with 15% excess of KBr over that required for generating the bromine. The substitutive bromination of isobutene was found to increase when the bromination time was increased, however, the three minute period used in these experiments gave negligible substitution. To avoid an excess of bromine greater than 10-15%, it was necessary to vary the amounts of standard bromate bromide solution. This was accomplished by using only one sampling pipet and varying the volume of standard bromate bromide solution that was pipeted into the analyzing flasks, this being accomplished by using a series of calibrated pipets (± 0.1%). This permitted the preparation of the brominating solutions prior to the reaction rate experiment and greatly facilitated the analyses. It was found that there was a negligible blank so no correction was made for it in the computations. This procedure was checked against standard cyclohexene solutions and was found to give an accuracy of 0.5%.

Typical Run

Prior to each reaction rate study, the reaction bulb (Fig. 1) containing the acetic acid-isobutene solution was placed in the thermostat and allowed to come to equilibrium at 25.00°C. Then it was taken from the thermostat and the volume reduced to the calibration mark. The catalyst solution was then accurately pipeted into the isobutene solution, the reaction head replaced and the reaction bulb shaken vigorously to insure complete mixing. The bulb was returned to the thermostat. The zero time is chosen as the instant when the catalyst was added, the entire time being about forty-five seconds before the reaction bulb was returned to the thermostat. Sampling was begun immediately

so as to obtain as many initial observations as possible, the frequency being dependent upon the initial concentrations. The time for each reading was taken as the instant of addition to the brominating mixture, the indeterminacy being five seconds. The sampling was continued until the solution was exhausted.

The data obtained experimentally in this manner are tabulated in Table I. The isobutene concentration was calculated from a knowledge of reactions involved in the analysis:

$$(CH_3)_2C = CH_2 + Br_2 \longrightarrow (CH_3)_2CBr\ CH_2Br$$

$$\text{excess}\ \ Br_2 + 3I^- \longrightarrow I_3^- + 2Br^-$$

$$I_3^- + 2S_2O_3^{=} \longrightarrow S_4O_6^{=} + 3I^-$$

Identification of Reaction Mixture Products

In some preliminary experiments, it was observed that water had a marked influence on the course of the reaction. This indicated that water was forming t-butyl alcohol, in addition to the t-butyl acetate.

Using an acetic acid solution, containing 5% water, 2.5 gm of isobutene were bubbled into 300 ml acetic acid and 19 ml of concentrated C. P. Sulfuric acid were added. The solution was shaken for 3 minutes then placed in a separatory funnel and added dropwise, with stirring, to an ice-water solution of 450 gm $Na_2CO_3 \cdot H_2O$. Upon neutralizing the acid solution, the basic solution was steam distilled, no second phase being obtained. A portion of the distillate was poured into an excess of concentrated HCl to obtain a cloudy solution. Another part of the distillate was fractionally distilled, the first

## Table I

Rate Study Data
(concentrations on moles/liter of solution; time in hours)

Rate Study

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| #9 | | $[B]_o$=0.03320 $[H_2SO_4]$ = 0.000494 $[H_2O]$ = 0.0616 | | | | | | | | | |
| | t | .038 | .092 | .242 | .508 | 1.25 | 1.50 | 2.46 | 6.45 | 7.72 | 10.12 |
| | [B] | .03210 | .03205 | .03186 | .03134 | .03072 | .03053 | .02910 | .02510 | .02430 | .02190 |
| | t | 12.18 | 13.83 | 26.43 | 29.75 | 32.62 | 75.17 | 175.07 | | | |
| | [B] | .02012 | .01887 | .01312 | .01170 | .01113 | .00477 | .00217 | | | |
| #10 | | $[B]_o$ =0.03322 $[H_2SO_4]$ = 0.00556 $[H_2O]$ = 0.0616 | | | | | | | | | |
| | t | .46 | .184 | .392 | .534 | .850 | 1.02 | 1.50 | 1.84 | 3.15 | 6.25 |
| | [B] | .03139 | .02967 | .02896 | .02685 | .02310 | .02144 | .01878 | .01521 | .00984 | .00417 |
| | t | 8.18 | 10.22 | 12.37 | 36.64 | 40.17 | 43.09 | 46.28 | 73.62 | 169.15 | 265.35 |
| | [B] | .00293 | .00241 | .00207 | .00193 | .00217 | .00217 | .00203 | .00212 | .00217 | .00217 |
| #11 | | $[B]_o$=0.03304 $[H_2SO_4]$ = 0.0288 $[H_2O]$= 0.0616 | | | | | | | | | |
| | t | .029 | .075 | .217 | .437 | .629 | .791 | 1.00 | 1.34 | 1.61 | 2.24 |
| | [B] | .02671 | .02440 | .01770 | .01110 | .00731 | .00546 | .00385 | .00268 | .00225 | .00167 |
| | t | 2.83 | 7.79 | 19.76 | | | | | | | |
| | [B] | .00170 | .00163 | .00163 | | | | | | | |
| #12 | | $[B]_o$=0.03300 $[H_2SO_4]$ = 0.0172 $[H_2O]$= 0.0616 | | | | | | | | | |
| | t | .033 | .083 | .325 | .475 | .583 | .76 | 1.02 | 1.25 | 1.75 | 2.96 |
| | [B] | .02823 | .02643 | .01952 | .01651 | .01425 | .01175 | .00887 | .00665 | .00432 | .00219 |
| | t | 3.96 | 5.56 | 7.56 | | | | | | | |
| | [B] | .00182 | .00182 | .00182 | | | | | | | |
| #13 | | $[B]_o$= 0.09333 $[H_2SO_4]$ = 0.0849 $[H_2O]$ = 0.100 | | | | | | | | | |
| | t | .089 | .175 | .342 | .468 | .600 | .750 | 1.00 | 2.22 | 4.18 | |
| | [B] | .04379 | .01165 | .00954 | .00679 | .00556 | .00480 | .00442 | .00442 | .00437 | |
| #14 | | $[B]_o$ =0.09345 $[H_2SO_4]$ = 0.0170 $[H_2O]$= 0.100 | | | | | | | | | |
| | t | .058 | .138 | .413 | .567 | .742 | .958 | 1.25 | 1.52 | 1.78 | 2.20 |
| | [B] | .0818 | .0743 | .0614 | .04742 | .04217 | .03121 | .02420 | .01940 | .01365 | .01157 |
| | t | 3.38 | 3.95 | 4.48 | 5.08 | | | | | | |
| | [B] | .00645 | .00560 | .00499 | .00488 | | | | | | |

Table I (con't.)

Rate Study

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| #15 | $[B]_o$=0.09385 | $[H_2SO_4]$ = 0.00580 | $[H_2O]$ = 0.100 | | | | | | | |
| | t | .034 | .097 | .319 | .467 | .621 | .842 | 1.07 | 1.44 | 2.29 | 2.77 |
| | [B] | .0877 | .0862 | .0821 | .0752 | .0746 | .0701 | .0660 | .0574 | .04685 | .04079 |
| | t | 4.10 | 4.56 | 6.78 | 7.48 | 8.38 | 25.77 | | | | |
| | [B] | .02913 | .02625 | .01543 | .01346 | .01100 | .00437 | | | | |
| #17 | $[B]_o$=0.08425 | $[H_2SO_4]$ = 0.00873 | $[(CH_3CO)_2O]$ = 0.380 | | | | | | | |
| | t | .050 | .125 | .502 | .659 | .853 | 1.15 | 1.48 | 2.13 | 3.05 | 4.25 |
| | [B] | .0732 | .0695 | .0643 | .06295 | .06080 | .05740 | .05445 | .04795 | .04240 | .03503 |
| | t | 5.08 | 5.99 | 7.06 | 27.95 | | | | | | |
| | [B] | .03055 | .02685 | .01660 | .00990 | | | | | | |
| #18 | $[B]_o$=0.08695 | $[H_2SO_4]$ = 0.00898 | $[(CH_3CO)_2O]$ = 0.0995 | | | | | | | |
| | t | .042 | .142 | .396 | .592 | .825 | 1.07 | 1.83 | 2.56 | 3.69 | 4.51 |
| | [B] | .07290 | .07170 | .06785 | .06608 | .06355 | .06095 | .05355 | .04780 | .03990 | .03560 |
| | t | 5.65 | 76.31 | 83.14 | 95.59 | 110.44 | | | | | |
| | [B] | .03015 | .01180 | .01255 | .01252 | .01280 | | | | | |
| #19 | $[B]_o$=0.08420 | $[H_2SO_4]$ = 0.0228 | $[(CH_3CO)_2O]$ = 0.0963 | | | | | | | |
| | t | .042 | .317 | .550 | .775 | 1.30 | 1.85 | 3.00 | 26.90 | 40.90 | 59.00 |
| | [B] | .05895 | .05045 | .04680 | .04275 | .03485 | .02890 | .02470 | .01425 | .02115 | .02255 |
| | t | 72.01 | 87.30 | | | | | | | | |
| | [B] | .02395 | .02610 | | | | | | | | |
| #20 | $[B]_o$=0.07590 | $[H_2SO_4]$ = 0.0220 | $[(CH_3CO)_2O]$ = 0.0963 | | | | | | | |
| | t | .039 | .084 | .192 | .359 | .525 | 1.05 | 1.69 | 2.21 | 3.00 | 3.62 |
| | [B] | .05400 | .05325 | .05015 | .04650 | .04325 | .03535 | .02815 | .02330 | .01870 | .01610 |
| | t | 4.18 | 5.09 | 7.77 | 9.22 | 19.98 | 27.68 | 33.42 | 54.83 | 67.30 | 79.45 |
| | [B] | .01430 | .01225 | .01000 | .01005 | .01195 | .01435 | .01560 | .01900 | .01935 | .02025 |
| | t | 89.52 | | | | | | | | | |
| | [B] | .02185 | | | | | | | | | |

Table I (con't'd)

Rate Study

#21 $[B]_o$=0.03296 $[H_2SO_4]$ = 0.0224 $[(CH_3CO)_2O]$ = 0.151

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| t | .047 | .117 | .217 | .342 | .538 | .680 | 1.034 | 1.717 | 2.64 | 3.73 |
| [B] | .01176 | .01082 | .01082 | .01042 | .00983 | .00928 | .00842 | .00733 | .00626 | .00590 |
| t | 5.28 | 6.27 | 7.42 | 8.57 | 9.30 | 19.87 | 32.42 | 44.60 | 54.65 | 69.03 |
| [B] | .00576 | .00585 | .00580 | .00621 | .00660 | .01000 | .01236 | .01535 | .01708 | .01825 |

#22 $[B]_o$=0.03172 $[H_2SO_4]$ = 0.00452 $[(CH_3CO)_2O]$ = 0.426

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| t | .067 | .100 | .267 | .433 | .892 | 1.500 | 2.308 | 4.100 | 4.883 | 6.284 |
| [B] | .02745 | .02781 | .02718 | .02668 | .02577 | .02414 | .02305 | .01993 | .01866 | .01689 |
| t | 7.150 | 8.150 | 19.00 | 22.02 | 26.66 | 30.93 | 43.12 | 53.12 | | |
| [B] | .01545 | .01485 | .00824 | .00724 | .00674 | .00572 | .00530 | .00552 | | |

#23 $[B]_o$=0.03334 $[H_2SO_4]$ = 0.00996 $[(CH_3CO)_2O]$ = 0.150

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| t | 0.042 | .108 | .292 | .533 | .767 | 1.008 | 1.400 | 2.042 | 2.667 | 4.458 |
| [B] | .02495 | .02482 | .02364 | .02278 | .02164 | .02084 | .01979 | .01767 | .01689 | .01259 |
| t | 5.617 | 7.796 | 9.267 | 21.86 | | | | | | |
| [B] | .01124 | .00923 | .00824 | .00589 | | | | | | |

#24 $[B]_o$=0.03334 $[H_2SO_4]$ = 0.0136 $[(CH_3CO)_2O]$ = 0.150

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| t | .442 | .167 | .217 | .508 | .792 | 1.225 | 2.616 | 4.017 | 5.892 | 7.675 |
| [B] | .01852 | .01843 | .01707 | .01630 | .01527 | .01372 | .01046 | .00860 | .00671 | .00611 |
| t | 18.13 | 21.83 | 29.37 | 43.27 | 66.97 | 90.08 | 116.05 | | | |
| [B] | .00662 | .00773 | .00896 | .01059 | .01314 | .01368 | .01432 | | | |

#25 $[B]_o$=0.04426 $[H_2SO_4]$ = 0.00572 $[(CH_3CO)_2O]$ = 0.133

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| t | .043 | .104 | .338 | .605 | .912 | 1.238 | 1.925 | 2.595 | 3.104 | 3.808 |
| [B] | .03978 | .03891 | .03837 | .03733 | .03638 | .03538 | .03365 | .03171 | .03026 | .02917 |
| t | 4.758 | 5.442 | 6.267 | 7.425 | 9.100 | 10.02 | 10.68 | 11.91 | 12.58 | |
| [B] | .02640 | .02524 | .02350 | .02152 | .01943 | .01852 | .01721 | .01648 | .01522 | |

Table I (con't.)

Rate Study

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| #26 | | $[B]_o$=0.04412 | $[H_2SO_4]$ = 0.0110 | $[(CH_3CO)_2O]$ = 0.133 | | | | | | | |
| | t | .034 | .119 | .275 | .529 | .825 | 1.171 | 1.521 | 1.909 | 2.704 | 3.833 |
| | [B] | .03525 | .03460 | .03356 | .03229 | .03062 | .02840 | .02750 | .02564 | .02291 | .01943 |
| | t | 5.534 | 6.500 | 7.588 | 8.654 | 9.633 | 10.52 | 21.88 | 23.17 | | |
| | [B] | .01553 | .01381 | .01227 | .01110 | .01050 | .00982 | .00702 | .00706 | | |
| #27 | | $[B]_o$=0.04406 | $[H_2SO_4]$ = 0.0167 | $[(CH_3CO)_2O]$ = 0.132 | | | | | | | |
| | t | .042 | .043 | .280 | .634 | .972 | 1.329 | 2.300 | 2.942 | 3.583 | |
| | [B] | .03053 | .02935 | .02894 | .02654 | .02414 | .02260 | .01812 | .01612 | .01413 | |
| | t | 4.567 | 5.428 | 6.296 | 7.213 | | | | | | |
| | [B] | .01227 | .01078 | .00955 | .00878 | | | | | | |
| #28 | | $[B]_o$=0.04268 | $[H_2SO_4]$ = 0.0280 | $[(CH_3CO)_2O]$ = 0.132 | | | | | | | |
| | t | .038 | .104 | .256 | .483 | .841 | 1.001 | 1.285 | 1.695 | 2.028 | 2.501 |
| | [B] | .02142 | .02101 | .01952 | .01768 | .01621 | .01513 | .01377 | .01227 | .01110 | .01046 |
| | t | 3.000 | 3.582 | | | | | | | | |
| | [B] | .00907 | .00824 | | | | | | | | |
| #29 | | $[B]_o$=0.1368 | $[H_2SO_4]$ = 0.00560 | $[(CH_3CO)_2O]$ = 0.163 | | | | | | | |
| | t | .038 | .221 | .550 | .892 | 1.188 | 1.521 | 1.988 | 2.437 | 3.042 | |
| | [B] | 0.1358 | 0.1322 | 0.1288 | 0.1258 | 0.1220 | 0.1182 | 0.1136 | 0.1046 | 0.1052 | |
| | t | 3.535 | 4.050 | 5.096 | 6.821 | 7.933 | 9.225 | 10.42 | 11.42 | | |
| | [B] | 0.1005 | 0.0958 | 0.0883 | 0.0780 | .0723 | .06650 | .06150 | .05630 | | |
| #30 | | $[B]_o$=0.1328 | $[H_2SO_4]$ = 0.0275 | $[(CH_3CO)_2O]$ = 0.159 | | | | | | | |
| | t | .038 | .150 | .400 | .625 | .855 | 1.044 | 1.275 | 1.725 | 2.167 | 2.542 |
| | [B] | .1156 | .1102 | .09985 | .09095 | .08260 | .07715 | .07060 | .06030 | .05085 | 0.4624 |
| | t | 3.258 | 3.675 | 4.984 | 6.088 | 7.392 | 8.583 | 9.567 | | | |
| | [B] | .03608 | .03246 | .02443 | .02041 | .01685 | .01527 | .01530 | | | |

two milliliters being separated and KOH pellets were added to it. A second, lighter than water phase, separated. Using microtechnique, the upper layer was dried with $K_2CO_3$ and an ester test was made by the Davidson test (11), negative results being obtained. The boiling point by the Emich method was 80°C. This corresponds to t-butyl alcohol, b.p. 83°C.

The above procedure was repeated using a 1% water solution in acetic acid as solvent. The basic solution upon distillation gave 0.5 ml. of a second phase. This gave an Emich boiling point of 92°C and a positive Davidson ester test, corresponding to t-butyl acetate. The water phase from the steam distillation gave an immediate second phase on pouring into concentrated HCl.

Using acetic acid, that was made anhydrous by refluxing with an excess of C.P. redistilled acetic anhydride, as a solvent the above procedure was duplicated to obtain 1.6 ml. of a second phase on steam distillation. This gave a positive Davidson ester test.

These results indicate that there are two competing reactions; hydration and esterification, the hydration reaction overwhelming the esterification as the concentration of water is increased.

## ANALYZING DATA AND DISCUSSION

### Introduction

The reaction of isobutene and acetic acid was studied under two conditions, one in which water was present and the second

in which an excess of acetic anhydride was present. It was found that both gave smooth curves when the unsaturation was plotted against the time. Graphs No. 1 and No. 2 are representative of the two groups respectively. However, two distinct differences were noted: 1) In the solution containing some water a smooth curve was obtained, starting at the initial isobutene concentration; in anhydrous acetic acid a smooth curve was obtained, but it started at a value much below the initial isobutene concentration; 2) the water containing acetic acid solution showed a continual drop in unsaturation (after the initial drop) to a final constant value of the unsaturation; the anhydrous acetic acid solution showed a drop to a minimum unsaturation and then an increase.

Analysis of Data

Using the method of Lucas and Pressman (12), the unsaturation was plotted in the form of $\log_{10}\left[\frac{\text{Unsaturation} - [B]_e}{\text{Initial Unsaturation} - [B]_e}\right]$ against time, the constant $[B]_e$ being chosen to give the best straight line through the data points. The following symbols were used in the computations:

$[B]$ - concentration of isobutene in moles/liter of solution

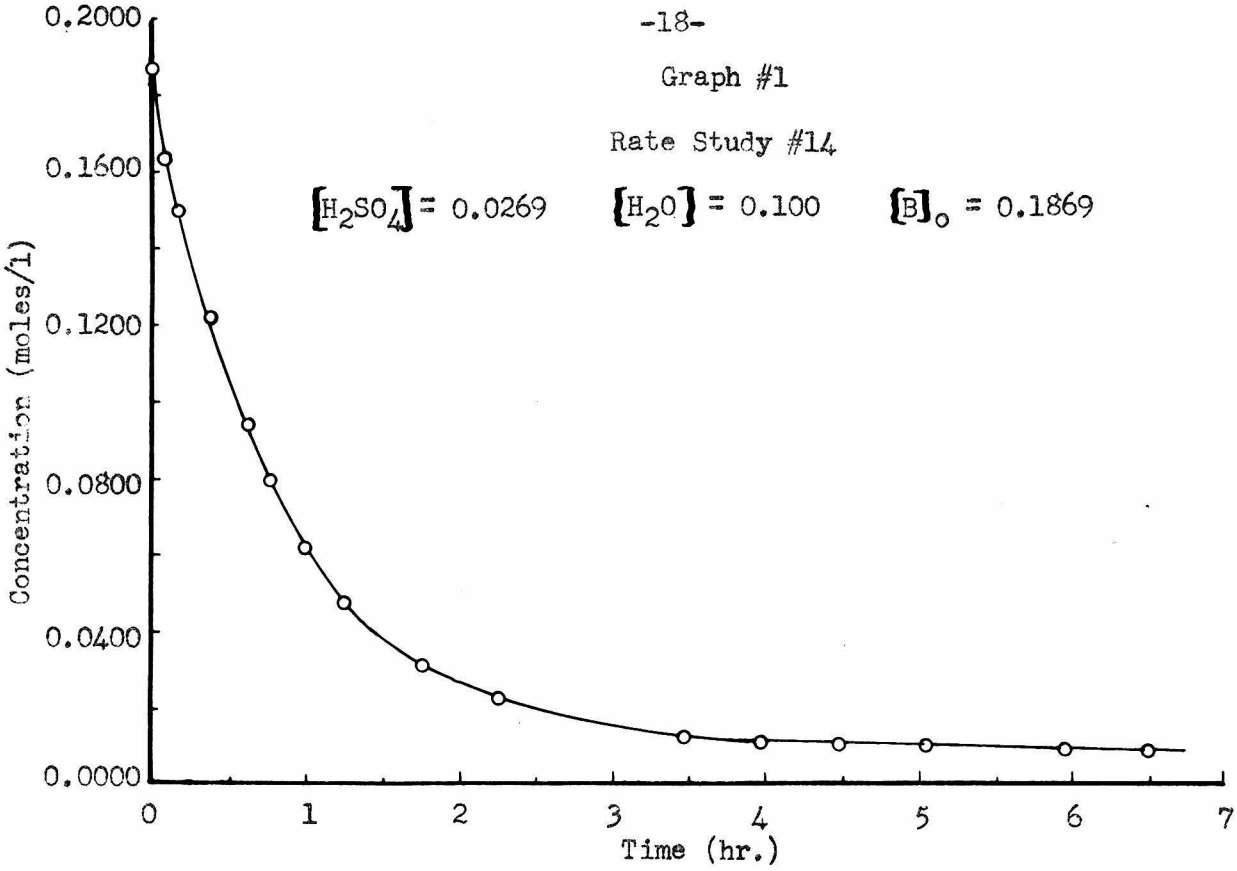
$[B]_o$ - concentration of isobutene at t = o, calculated from the B determined before the catalyst added, by allowing for the dilution of the reaction mixture by the catalyst and assuming no reaction has taken place: moles/liter of solution

$[B]_i$ - the concentration of isobutene obtained by extrapolating to t = o, using the best straight line for the data points: moles/liter of solution

Graph #1

Rate Study #14

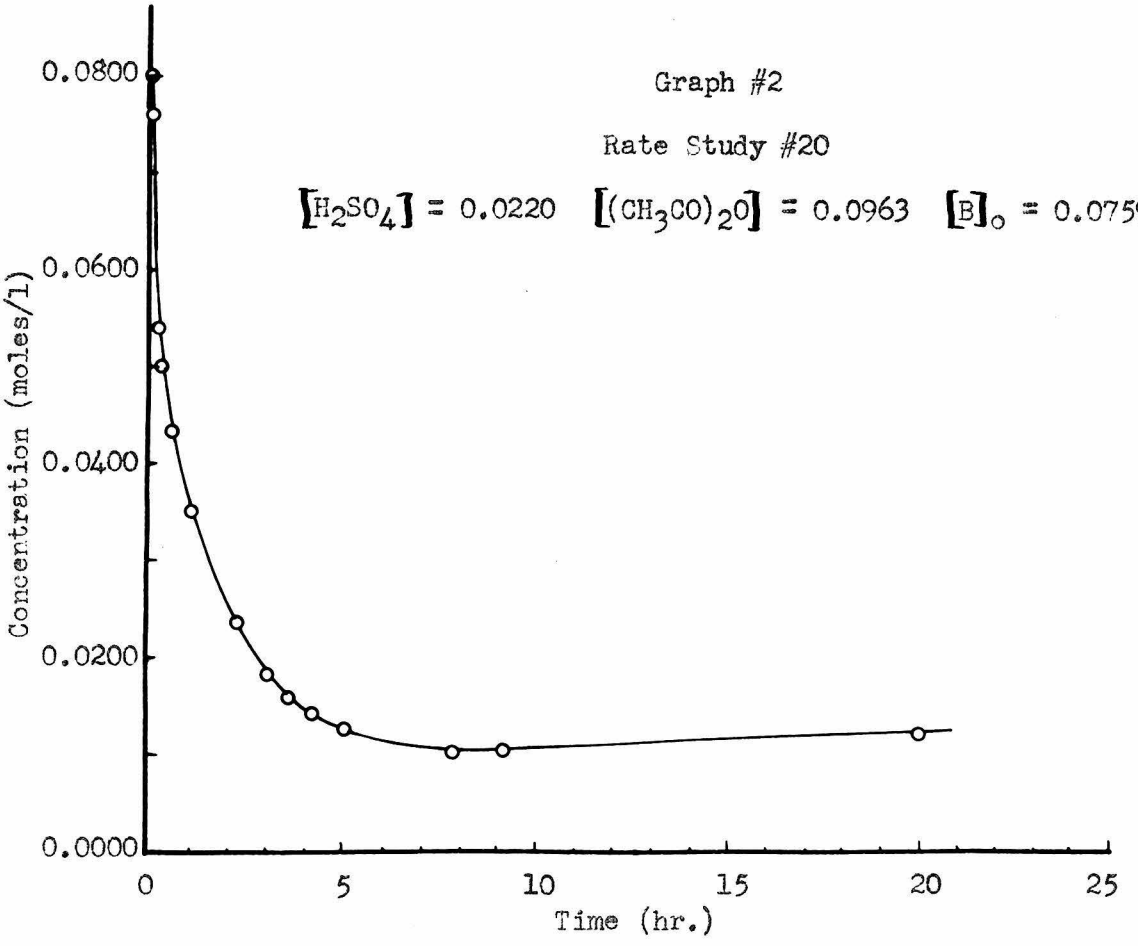
$[H_2SO_4] = 0.0269$ $[H_2O] = 0.100$ $[B]_o = 0.1869$




Graph #2

Rate Study #20

$[H_2SO_4] = 0.0220$ $[(CH_3CO)_2O] = 0.0963$ $[B]_o = 0.07590$



$[B]_e$ - the constant that gives the best straight line plot of the data points by the use of the formula

$$\log_{10}\left(\frac{[B] - [B]_e}{[B]_i - [B]_e}\right) = -kt$$

where t is the time in hours and k is the slope of the best straight line: moles/liter of solution

The values so obtained are tabulated in Table II.

These values again illustrate the marked difference in the reactions which take place with and without water. When water is present there are apparently two competing reactions, viz. hydration and esterification:

$$(CH_3)_2\ C = CH_2 + H_2O \rightarrow (CH_3)_3COH$$

$$(CH_3)_2\ C = CH_2 + CH_3CO_2H \rightarrow (CH_3)_3COCOCH_3$$

In the absence of water, the reactions are apparently esterification and polymerization:

$$(CH_3)_2\ C = CH_2 + CH_3CO_2H \rightarrow (CH_3)_3COCOCH_3$$

$$(CH_3)_2\ C = CH_2 \rightarrow \text{polymer}$$

Theoretical Development and Discussion

The marked difference in behavior between the water-containing and anhydrous acetic solutions is best understood in terms of the simpler anhydrous reaction conditions due to the complex set reactions that take place when water is present. For this reason the anhydrous system will be discussed kinetically and the results qualitatively applied to the water-containing reaction studies.

The following symbols are to be used in addition to those already defined:

Table II

Rate Study Data in moles/1. solution at 25.00 ± 0.05°C

| Rate Study | $[B]_o$ Concentration of Isobutene at t = o | $[B]_i$ Extrapolated initial concentration of isobutene | [B] Equilibrium Concentration Isobutene | $[(CH_3)_3COCOCH_3]$ Equilibrium concentration t-butyl acetate | $[H_2O]$ Mole/1 | $[(CH_3CO)_2O]$ Mole/1 | $[H_2SO_4]$ Mole/1 | $[B]_o-[B]_i$ Mole/1 | $K_\epsilon$ Equilibrium Constant | $k_1$ Forward Rate Constant |
|---|---|---|---|---|---|---|---|---|---|---|
| 9 | .03320 | - | .00217 | .03103 | .0616 | - | .000494 | - | 46.2 | 186 |
| 10 | .03322 | - | .00217 | .03105 | .0616 | - | .00556 | - | 46.2 | 180 |
| 11 | .03304 | - | .00263 | .03141 | .0616 | - | .0288 | - | 61.3 | 181 |
| 12 | .03300 | - | .00263 | .03137 | .0616 | - | .0172 | - | 61.3 | 176 |
| 13 | .09333 | - | .00355 | .08975 | .1000 | - | .0849 | - | 28.2 | 187 |
| 14 | .09345 | - | .00440 | .08905 | .1000 | - | .0170 | - | 22.5 | 144 |
| 15 | .09385 | - | .00440 | .08945 | .1000 | - | .00580 | - | 22.5 | 112 |
| 17 | .08425 | .0763 | .00875 | .07755 | - | .380 | .00873 | .0080 | 7.71 | 20.9 |
| 18 | .08695 | .0732 | .0100 | .07695 | - | .0995 | .00898 | .0137 | 6.32 | 18.7 |
| 19 | .08420 | .0582 | .0050 | .0532 | - | .0963 | .0228 | .0260 | 10.60 | 23.5 |
| 20 | .07590 | .0543 | .0080 | .0455 | - | .0963 | .0220 | .0216 | 5.27 | 19.2 |
| 21 | .03296 | .0118 | .0041 | .0077 | - | .151 | .0224 | .0212 | 1.88 | 19.5 |
| 22 | .03172 | .0279 | .0042 | .0237 | - | .426 | .00452 | .0038 | 5.64 | 27.9 |
| 23 | .03334 | .0253 | .0061 | .0192 | - | .150 | .00996 | .0080 | 3.15 | 27.3 |
| 24 | .03334 | .0190 | .0052 | .0138 | - | .150 | .0136 | .0143 | 2.65 | 18.8 |
| 25 | .04426 | .0396 | .0070 | .0326 | - | .133 | .00572 | .0047 | 4.66 | 17.9 |
| 26 | .04412 | .0355 | .0070 | .0285 | - | .133 | .0110 | .0086 | 4.07 | 16.0 |
| 27 | .04406 | .0309 | .0060 | .0249 | - | .132 | .0167 | .0132 | 4.15 | 14.8 |
| 28 | .04268 | .0217 | .0060 | .0157 | - | .132 | .0280 | .0210 | 2.62 | 13.9 |
| 29 | .1368 | .1360 | .0200 | .1160 | - | .163 | .00560 | .0008 | 5.80 | 15.6 |
| 30 | .061328 | .1162 | .0132 | .1030 | - | .159 | .0275 | .0166 | 9.84 | 18.7 |

It is not possible to calculate the reverse rate constant $k_{-1}$ because theory has shown that $K_\epsilon = \frac{k_1 k_2 k_3}{k_{-1} k_{-2} k_{-3}} [HOAc]$ so that as only $K_\epsilon$, $k_1$, [HOAc] are known $k_{-1}$ cannot be calculated unless some value for $\frac{k_2 k_3}{k_{-2} k_{-3}}$ could be determined, thus, is not possible here. (It could be assumed to be 1 then $K = \frac{k_1}{k_{-1}} [HOAc]$)

$[B]$ - concentration of isobutene at time t in moles/liter of solution

$[BH^+]$ —— carbonium ion ————————

$[AcOH]$ —— acetic acid ————————

$[AcOH_2^+]$ —— acetic acid-proton complex ————

$[BHOAc]$ —— t-butyl acetate ————————

$[BH_2OAc^+]$ —— t-butyl acetate proton complex ——

$k_1 k_2 k_3$ specific rate constants of the forward reaction

$k_{-1} k_{-2} k_{-3}$ reverse ————————→

In the anhydrous reaction mixture the following reactions are occurring:

$$B + AcOH_2^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} BH^+ + AcOH$$

$$BH^+ + AcOH \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} BH_2OAc^+$$

$$BH_2OAc^+ + HOAc \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} BHOAc + AcOH_2^+$$

thus $$\frac{-d[B]}{dt} = k_1 [B] [AcOH_2^+] - k_{-1} [BH^+] [AcOH]$$

but $$\frac{[BH_2OAc^+]}{[BH^+][AcOH]} = \frac{k_2}{k_{-1}} \quad \text{and} \quad \frac{[BHOAc][AcOH_2^+]}{[BH_2OAc^+][HOAc]} = \frac{k_3}{k_{-3}}$$

$$\frac{-d[B]}{dt} = k_1 [B][AcOH_2^+] - \frac{-k_{-1} k_{-2}}{k_2} [BH_2OAc^+]$$

$$= k_1 [B][AcOH_2^+] - \frac{k_1 k_2 k_{-3}}{k_2 k_3} \frac{[BHOAc][AcOH_2^+]}{[HOAc]}$$

but $[BHOAc] = [B]_i - [B]$ assuming $[BH^+]$ is very small, it being the reactive intermediate, and $[B]_i$, the initial isobutene concentration

$$= k_1 [B][AcOH_2^+] + \frac{k_1 k_2 k_{-3}}{k_2 k_3} \frac{[B][AcOH_2^+]}{[HOAc]} - \frac{k_{-1} k_{-2} k_{-3}}{k_2 k_3} \frac{[B]_i [AcOH_2^+]}{[HOAc]}$$

Let $K_\epsilon = \frac{k_1 k_2 k_3}{k_{-1} k_{-2} k_{-3}}$ $[HOAc]$ be the equilibrium constant for the addition reaction

$$\therefore \frac{-d[B]}{dt} = k_1 [B] [AcOH_2^+] + \frac{k_1}{K_\epsilon} [B][AcOH_2^+] - \frac{k_1}{K_\epsilon} [B]_i [AcOH_2^+]$$

$$= [B]\left(k_1 [AcOH_2^+] + \frac{k_1}{K_\epsilon} [AcOH_2^+]\right) - \frac{k_1}{K_\epsilon} [B]_i [AcOH_2^+]$$

Let $C = k_1 [AcOH_2^+] + \frac{k_1}{K_\epsilon} [AcOH_2^+] = k_1 [AcOH_2^+]\left(1 + \frac{1}{K}\right)$

and $D = \frac{k_1}{K} [B]_i [AcOH_2^+]$

If it is assumed that $[AcOH_2^+]$ is a constant, that is the "acidity" does not change during the reaction

$$\therefore -\frac{d[B]}{dt} = C[B] - D$$

$$\therefore \frac{d[B]}{C[B] - D} = -dt$$

$$\text{or} \int \frac{d[B]}{C[B] - D} = \int -dt = -t + \text{constant}$$

$$\text{but} \int \frac{d[B]}{C[B] - D} = \frac{1}{C} \int d\ln (C[B] - D) = \frac{1}{C} \ln (C[B] - D)$$

$$\ln (C[B] - D) = -Ct + \text{Constant} \times C$$

$$\text{or} \quad C[B] - D = \text{Constant} \times e^{-Ct}$$

Now $[B] = [B]_i$ at $t = o$

$$\text{Constant} = \frac{\ln (C[B]_i - D)}{C}$$

$$\ln (C[B] - D) = -Ct \quad \ln (C[B_i - D)$$

$$\text{or} \quad \ln \frac{C[B] - D}{C[B]_i - D} = -Ct$$

$$\frac{C[B] - D}{C[B]_i - D} = e^{-Ct}$$

$$\therefore \quad C[B] - D = (C[B]_i - D)e^{-Ct}$$

$$\text{or} \quad C[B] = (C[B]_i - D)e^{-Ct} + D$$

$$[B] = \left([B]_i - \frac{D}{C}\right)e^{-Ct} + \frac{D}{C}$$

$$\therefore \quad B = [B]_i e^{-Ct} + \frac{D}{C}(1 - e^{-Ct})$$

$$\text{thus since} \quad D = \frac{k_1}{K_\epsilon}[B]_i[AcOH_2^+]$$

$$\text{and} \quad C = k_1[AcOH_2^+]\left(1 + \frac{1}{K_\epsilon}\right)$$

$$\frac{D}{C} = \frac{\frac{k_1}{K_\epsilon}[B]_i[AcOH_2^+]}{k_1[AcOH_2^+]\left(1 + \frac{1}{K_\epsilon}\right)} = \frac{[B]_i}{1 + K_\epsilon}$$

Thus substituting back in

$$[B] = [B]_i e^{-k_1[AcOH_2^+]\left(1 + \frac{1}{K_\epsilon}\right)t} + \frac{[B]_i}{1 + K_\epsilon}\left(1 - e^{-k_1[AcOH_2^+]\left(1 + \frac{1}{K_\epsilon}\right)t}\right)$$

when t is large

$$[B] \rightarrow [B]_\epsilon \quad \text{and} \quad e^{-k_1[AcOH_2^+]\left(1 + \frac{1}{K_\epsilon}\right)t} \rightarrow 0$$

where $[B]_\epsilon$ is the equilibrium isobutene concentration

$$\therefore [B]_\epsilon = \frac{[B]_i}{1 + K_\epsilon}$$

$$\therefore [B] = [B]_i e^{-k_1[AcOH_2^+]\left(1 + \frac{1}{K_\epsilon}\right)t} + [B]_\epsilon\left(1 - e^{-k_1[AcOH_2^+]\left(1 + \frac{1}{K_\epsilon}\right)t}\right)$$

$$\text{or} \quad [B] = ([B]_i - [B]_\epsilon)e^{-k_1[AcOH_2^+]\left(1 + \frac{1}{K_\epsilon}\right)t} + [B]_\epsilon$$

$$\therefore [B] - [B]_\epsilon = ([B]_i - [B]_\epsilon)\, e^{-k_1[AcOH_2^+]\left(1 + \frac{1}{K_\epsilon}\right)t}$$

$$\text{thus} \quad \frac{[B] - [B]_\epsilon}{[B]_i - [B]_\epsilon} = e^{-k_1[AcOH_2^+]\left(1 + \frac{1}{K_\epsilon}\right)t}$$

$$\therefore \ln\left(\frac{[B] - [B]_\epsilon}{[B]_i - [B]_\epsilon}\right) = -k_1 [AcOH_2^+] \left(1 + \frac{1}{K_\epsilon}\right)t$$

$$\therefore \log_{10}\left(\frac{[B] - [B]_\epsilon}{[B]_i - [B]_\epsilon}\right) = \frac{-k_1}{2.303} [AcOH_2^+] \left(1 + \frac{1}{K_\epsilon}\right)t$$

Now since the initial reaction of $H_2SO_4$ is with the isobutene to give irreversibly (essentially)

$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!\diagdown\!\!\diagup C = CH_2 + H_2SO_4 \longrightarrow (CH_3)_3COSO_2OH$$

which then ionizes completely since it is a dilute solution and the solvent is a strong base, thus

$$(CH_3)_3COSO_2OH + AcOH \longrightarrow (CH_3)_3COSO_2O^- + AcOH_2^+$$

Thus $[AcOH_2^+] = [H_2SO_4]$

$$\therefore \log_{10}\left(\frac{[B] - [B]_\epsilon}{[B]_i - [B]_\epsilon}\right) = \frac{-k_1}{2.303} [H_2SO_4] \left(1 + \frac{1}{K_\epsilon}\right)t$$

Now after equilibrium (a steady state actually) is attained, the unsaturation increases due to the reaction

$$BH^+ + B \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} BH_2^+$$

$$B_2H^+ + AcOH \xrightarrow{k_5} B_2 + AcOH_2^+$$

where $k_4$, $k_{-4}$, $k_5$ are specific rate constants

and $[B_2]$ is the dimer concentration, which is irreversible and goes initially only to the dimer (because of decreased reactivity does not add HOAc or further polymerize rapidly), thus

$$\frac{d[B_2]}{dt} = k_5 [B_2][AcOH_2^+]$$

but $\frac{[B_2H^+]}{[BH^+][B]} = \frac{k_4}{k_{-4}}$

$$\therefore \quad \frac{d[B_2]}{dt} = \frac{k_4 k_5}{k_{-4}} [B][BH^+][AcOH]$$

However $$\frac{[BH^+][AcOH]}{[B][AcOH_2^+]} = \frac{k_1}{k_{-1}}$$

$$\therefore \quad \frac{d[B_2]}{dt} = \frac{k_1 k_4 k_5}{k_{-1} k_{-4}} [B]^2 [AcOH_2^+]$$

Let $Kp = \frac{k_1 k_4 k_5}{k_{-1} k_{-4}}$ , the polymerization constant

$$\therefore \quad \frac{d[B_2]}{dt} = Kp\,[B]^2 [AcOH_2^+]$$

However $$[B] = ([B]_i - [B]_\epsilon) e^{-k_1 [AcOH_2^+] (1 + \frac{1}{K_\epsilon})t} + [B]_\epsilon$$

so that

$$[B]^2 = \left[([B]_i - [B]_\epsilon) e^{-k_1 [AcOH_2^+] (1 + \frac{1}{K_\epsilon}) t}\right]^2 + 2([B]_i - [B]_\epsilon) e^{-k_1 [AcOH_2^+](1 + \frac{1}{K})t} + [B]_\epsilon^2$$

But since the polymerization rate is low, at large t (near equilibrium)

$$[B]^2 = [B]_\epsilon^2 \qquad \text{as} \quad e^{-k_1 [AcOH_2^+] (1 + \frac{1}{K_\epsilon})t} \to 0$$

$$\therefore \quad \frac{d[B_2]}{dt} = K_p [B]^2 [AcOH_2^+]$$

thus $$\int_0^{[B_2]} d[B_2] = \int_{t_\epsilon}^{t} K_p [B]_\epsilon^2 [AcOH_2^+]\, dt$$

where $t_\epsilon$ is time at which equilibrium is attained

$$\therefore [B_2] = K_p [B]_\epsilon^2 [AcOH_2^+] (t - t_\epsilon)$$

Thus the measured unsaturation will be for large t $\quad t$

$$[\text{Unsaturation}]_t = [B]_\epsilon + [B_2]$$

$$= [B]_\epsilon + K_p [B]_\epsilon^2 [AcOH_2^+] (t - t_\epsilon)$$

Since $[AcOH_2^+] = [H_2SO_4]$

$$\therefore \quad K_p = \frac{[\text{Unsaturation}]_t - [B]_\epsilon}{[B]_\epsilon^2 [H_2SO_4] (t - t_\epsilon)}$$

The theory indicates that the relation between [B] and t should be

$$\log_{10}\left(\frac{[B] - [B]_\epsilon}{[B]_i - [B]_\epsilon}\right) = -\frac{k_1}{2.303}\,[H_2SO_4]\,(1 + \frac{1}{K_\epsilon})\,t$$

which, when compared with

$$\log_{10}\left(\frac{[B] - [B]_\epsilon}{[B]_i - [B]_\epsilon}\right) = -Kt$$

that was used in the analysis of the data, shows that

$$K = \frac{k_1}{2.303}\,[H_2SO_4]\,(1 + \frac{1}{K_\epsilon})$$

and predicts that

$$K' = \frac{K}{[H_2SO_4]} = \frac{k_1}{2.303}\,(1 + \frac{1}{K_\epsilon})$$

should be a constant as was experimentally found. The mechanism presented also permits the polymerization to be studied semi-quantitatively. Thus, since

$$[B_2] = K_p\,[B]_\epsilon^2\,[AcOH_2^+]\,(t - t_\epsilon) = [B] - [B]_\epsilon$$

which predicts that

$$K_p = \frac{[B] - [B]_\epsilon}{[B]_\epsilon^2\,[H_2SO_4](t - t_\epsilon)}$$

should be a constant. This is indeed found to be true as shown by Table III.

The presence of excess acetic anhydride has no effect upon the equilibrium constant, $K_\epsilon$, or the forward rate constant $k_1$. This is shown on Table II by Rate Studies #17 and #18 where a four-fold variation in its concentration did not effect $K_\epsilon$ or $k_1$.

There seems to be no trend in the values of $K_\epsilon$ and $k_1$ with respect to the initial isobutene concentration and the sulfuric acid concentration. The average values of the equilibrium and the

Table III

Rate Study #20 $[H^+] = 0.0220$ moles/l $[B]_\epsilon = 0.0088$

| $t - t_\epsilon$ | $[B]-[B]_\epsilon$ | $\frac{[B]-[B]_\epsilon}{[H^+]}$ | $\frac{[B]-[B]_\epsilon}{[H^+][B]_\epsilon^2}$ | $\frac{[B]-[B]_\epsilon}{[H^+][B]_\epsilon^2}(t-t_\epsilon)$ |
|---|---|---|---|---|
| 9.9 | .0064 | .291 | 950 | 96 |
| 17.7 | .0112 | .510 | 1670 | 94 |
| 23.4 | .0137 | .623 | 2040 | 87 |
| 44.8 | .0205 | .923 | 3050 | 68 |
| 57.3 | .0212 | .963 | 3150 | 55 |
| 69.4 | .0230 | 1.046 | 3420 | 49 |
| 79.5 | .0260 | 1.181 | 3860 | 48 |

Rate Study #21 $[H^+] = 0.0224$ moles/l $[B]_\epsilon = .0041$

| $t - t_\epsilon$ | $[B]-[B]_\epsilon$ | $\frac{[B]-[B]_\epsilon}{[H^+]}$ | $\frac{[B]-[B]_\epsilon}{[H^+][B]_\epsilon^2}$ | $\frac{[B]-[B]_\epsilon}{[H^+][B]_\epsilon^2}(t-t_\epsilon)$ |
|---|---|---|---|---|
| 5.9 | .0042 | .188 | 2900 | 490 |
| 5.7 | .0050 | .223 | 3310 | 490 |
| 23.2 | .0119 | .523 | 7900 | 340 |
| 36.7 | .0175 | .782 | 11600 | 320 |
| 47.9 | .0245 | 1.093 | 16300 | 340 |
| 57.9 | .0259 | 1.156 | 17200 | 300 |
| 72.3 | .0283 | 1.262 | 18800 | 260 |

Rate Study #24 $[H^+] = 0.0136$ moles/l $[B]_\epsilon = .0285$

| $t - t_\epsilon$ | $[B]-[B]_\epsilon$ | $\frac{[B]-[B]_\epsilon}{[H^+]}$ | $\frac{[B]-[B]_\epsilon}{[H^+][B]_\epsilon^2}$ | $\frac{[B]-[B]_\epsilon}{[H^+][B]_\epsilon^2}(t-t_\epsilon)$ |
|---|---|---|---|---|
| 8.1 | .0028 | .206 | 2060 | 255 |
| 11.8 | .0051 | .375 | 3610 | 306 |
| 19.4 | .0075 | .551 | 5300 | 274 |
| 33.3 | .0112 | .824 | 7930 | 238 |
| 57.0 | .0158 | 1.160 | 11200 | 197 |
| 80.1 | .0169 | 1.242 | 12000 | 150 |
| 106 | .0182 | 1.339 | 12900 | 121 |

rate constants are

$$K_\epsilon = 5.31 \pm 2.01 \qquad k_1 = 19.5 \pm 3.1$$

The high deviation in $K_\epsilon$ comes from

$$K_\epsilon = \frac{[(CH_3)_3COCOCH_3]}{[(CH_3)_2C = CH_2]} = \frac{[B]_i - [B]_\epsilon}{[B]_\epsilon}$$

where $[B]_i$ depends on $[B]_\epsilon$, a quantity that is chosen to give the best straight line. The equilibrium isobutene concentration, $[B]_\epsilon$, can have a relatively large effect since it is small and sensitive to errors. The relatively low deviation of $k_1$ comes from

$$k_1 = \frac{K}{[H_2SO_4](1 + \frac{1}{K_\epsilon})2.303}$$

where K is the slope of the straight line obtained with the best $[B]_\epsilon$. Since K is comparatively insensitive to moderate variations in $[B]_\epsilon$ and $k_1$ depends on $(1 + \frac{1}{K_\epsilon})$, any slight variation in K will have a small influence on $k_1$.

The treatment of the very complex equilibrium mixture that exists with water present was not possible due to the lack of information as to the final concentration of t-butyl alcohol and the distribution constant of the proton between water and acetic acid:

$$B + H_3O^+ \rightleftharpoons BH^+ + H_2O$$

$$B + AcOH_2^+ \rightleftharpoons BH^+ + AcOH$$

$$BH^+ + H_2O \rightleftharpoons BOH_3^+$$

$$BH^+ + AcOH \rightleftharpoons BAcOH_2^+$$

$$BOH_3^+ + H_2O \rightleftharpoons BHOH + H_3O^+$$

$$BOH_3^+ + AcOH \rightleftharpoons BHOH + AcOH_2^+$$

$$BH_2OAc^+ + H_2O \rightleftharpoons BHOAc + H_3O^+$$

$$BH_2OAc^+ + AcOH \rightleftharpoons BHOAc + AcOH_2^+$$

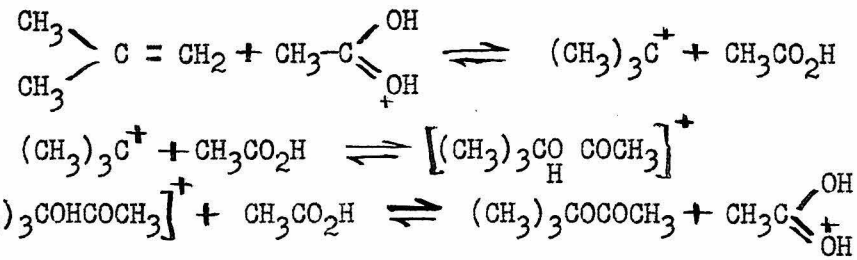
Qualitatively it is possible to predict that the hydration reaction should be much more rapid due to the greater basicity of water relative to acetic acid. This is indeed reflected in the larger values of the forward rate constant for Rate Studies #9 to #15 on Table II. The "equilibrium constants" also show a larger value which is understandable in terms of the greater stability of tertiary butyl alcohol. There are no observable systematic trends on the data, thus $K_\epsilon = 41.2 \pm 10.0$, for Rate Studies #9 to #15 as compared with $K_\epsilon = 5.3 \pm 2.0$ for Rate Studies #17 to #30. The $K_\epsilon$, $k_1$, and $[B]_\epsilon$ values for the two sets of conditions show no correlation with $[H_2SO_4]$, $[B]_o$, $[H_2O]$ or $[(CH_3CO)_2O]$. The $K_\epsilon$ values for #9 to #15 (water containing) were not reproducible from experiment to experiment whereas the $K_\epsilon$ for #17 to #30 (anhydrous) gave values that were more duplicatable, although being as sensitive to experimental errors. This lack of reprodubibility reflects the extreme complexity of the reaction system when water is present and is understandable in terms of the equations given above.

## CONCLUSIONS

Using Whitmore's (13) concept of the carbonium ion as an intermediate in acid catalyzed reactions, it has been possible to treat in a quantitative manner the kinetics of the addition of acetic acid to isobutene and to semi-quantitatively treat the polymerization. When water is present the reaction

kinetics become very complicated and were only treated qualitatively.

The successful quantitative treatment of the reaction, assuming the following mechanism



and putting in the assumption that $(CH_3)_3C^+$ is present only in small concentrations, leads to

$$\log_{10}\left(\frac{[B] - [B]_\epsilon}{[B]_i - [B]_\epsilon}\right) = -\frac{k_1}{2.303}\,[H_2SO_4]\,(1 + \frac{1}{K_\epsilon})\,t$$

and $[B_2] = K_p\,[B]_\epsilon^2\,[H_2SO_4]\,(t - t_\epsilon)$

where $k_1 = 19.5 \pm 3.1$, $K_\epsilon = 5.3 \pm 2.0$ and $K_p \simeq 200$. The semiquantitative results obtained in treating the polymerization on the basis of Whitmore's carbonium ion, further strengthens the evidence for its existance.

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Dear Professor Lucas;

I am enclosing the original and 1st carbon copy of my thesis – I included all the suggestions you made to me in your last letter in the final draft. I hope that I have done everything correctly – I have several more copies here, one being for you as soon as I hear whether this will be acceptable in its present form. I sincerely hope that everything is in order as it about broke me to get the typing and drawings made.

I hope to hear from you as soon as possible as it will be a big load off my shoulders to get things completed. I was happy to hear about Frank Dickey (that was an interesting note on his work on adsorption in Chem Eng. News) and the post-doctoral fellowship, about Garner and Henry and Ned.

My best to you Professor Lucas,

John