in 75 ml. of 48% hydrobromic acid and refluxed for 20 hours. The acid solution was freed completely of solvent *in vacuo*, and the residue was dissolved in 25 cc. of water, cooled to 5°, and transferred with 50 ml. of benzene to a separatory funnel. The following steps were carried out as quickly as possible to prevent too much quaternization in aqueous solution. To the cold mixture in the separatory funnel was added 20 ml. of 3 *N* sodium hydroxide. The mixture was shaken vigorously and the benzene layer separated. The aqueous portion then was extracted with two 50-ml. portions of benzene. The benzene extracts were combined, dried over anhydrous sodium sulfate for several minutes with swirling, and the benzene solution decanted into another flask. The benzene solution was refluxed for 45 minutes during which time a crystalline solid precipitated. The mixture was filtered, and the crystalline solid was recrystallized from acetone to give 1.10 g. (21% yield) of colorless crystals, m.p. 209–215°. Recrystallization from acetone (Norit) yielded material of m.p. 214–216°. The crude material, m.p. 209–215°, can be used for the oxidation to anagyrine.

Anal. Calcd. for $C_{15}H_{21}N_2Br$: C, 58.25; H, 6.85. Found: C, 58.35; H, 7.06.

dl-**Anagyrine.**—To a solution of 356 mg. (1.15 mmol.) of the tetracyclic quaternary salt XLI in 2 ml. of water was added a solution of 600 mg. of sodium hydroxide and 800 mg. (2.35 mmol.) of potassium ferricyanide in 4 ml. of water. The cloudy mixture was heated on a steam-bath and diluted with water until the total volume of solution was about 8.5 ml., at which point the solution became almost clear again. The solution was heated on the steam-bath (vessel should be stoppered to prevent evaporation of solvent) for one day, cooled and extracted with five 15-ml. portions of benzene. The combined benzene extracts were dried over anhydrous sodium sulfate, freed of solvent *in vacuo*, and the residue distilled in a 10 mm. diameter glass tube (sealed at one end), by heating in an appropriate aluminum block, to give 114 mg. (41%) of *dl*-anagyrine, b.p. 170–175° (0.1 mm.) a light yellow glass at room temperature.

A freshly prepared sample, 114 mg. (0.47 mmol.), was dissolved in 5 ml. of methanol and neutralized with 4.63 ml. of 0.101 *N* perchloric acid. The solution was evaporated to dryness, and the crystalline residue recrystallized from absolute methanol to give 114 mg. (81%) of colorless, cottony needles, m.p. 315°.

Anal. Calcd. for $C_{15}H_{21}O_6N_2Cl$: C, 52.25; H, 6.14. Found: C, 52.29; H, 6.12.

A sample of *dl*-anagyrine regenerated from pure *dl*-anagyrine perchlorate was distilled for analysis to give a colorless glass, b.p. 170° (0.1 mm.). The infrared spectra in carbon disulfide solution, and ultraviolet spectra in 95% ethanol, of *dl*-anagyrine and authentic *l*-anagyrine were indistinguishable.

dl-**Thermopsine.**—Thirty-five mg. (0.143 mmol.) of *dl*-anagyrine (regenerated from its perchlorate) was dissolved in 5 ml. of 5% aqueous acetic acid. To the solution in a 15-ml. graduated centrifuge tube was added 365 mg. (1.14 mmol.) of mercuric acetate. After the mercuric acetate dissolved, a slow, fine stream of nitrogen was passed through the solution, and the solution was heated on a steam-bath for two hours. The volume of solvent was kept constant by the addition of 5% acetic acid. After heating, the solution was cooled to 0° and the precipitated mercurous acetate (100 mg.) was centrifuged. The aqueous solution was then saturated with hydrogen sulfide, 5 drops of concentrated hydrochloric acid and 3 drops of concentrated sulfuric acid were added to the mixture, and the mixture was heated on a steam-bath until the mercuric sulfide coagulated. Then the mercuric sulfide was centrifuged, and the clear aqueous layer was evaporated to dryness *in vacuo*. The residue was dissolved in water and the solution made basic. Since the dehydrogenation product is unstable, the basic solution was rapidly extracted with four 15-ml. portions of chloroform, which were subsequently dried over anhydrous sodium sulfate for several minutes. The chloroform solution was filtered, evaporated under a stream of nitrogen, and 10 ml. of absolute methanol was added to the residue. The methanolic solution was shaken with two 50-mg. portions of Raney nickel, filtered, and hydrogenated over 30 mg. of 6% palladium-on-strontium carbonate at 1 atmosphere of hydrogen for 5 minutes. The hydrogenation mixture was filtered, the solvent evaporated completely, and the residue (31.5 mg.) was chromatographed on a column of 400 mg. of silicic acid in chloroform (ratio of height to width of column was 3:1). The mixture was placed on the column with 5 drops of chloroform solution and eluted with 1% methanol in chloroform. A band which immediately separated with 1% methanol in chloroform was collected and the residue obtained after evaporation of solvent was sublimed at 0.1 mm. to give 6 mg. of an oil, b.p. 150–170° (1 mm.). On scratching, the oil crystallized to material melting at 155–165°. The solid was recrystallized from a very small amount of acetone–ether and resublimed to give an oily solid, m.p. 160–168°. This solid was washed in the sublimation tube with a little ether and then resublimed to give 2 mg. of *dl*-thermopsine, m.p. 170–172°. A mixed m.p. with authentic *dl*-thermopsine was 170–172°. The infrared spectra in carbon disulfide solution, and the ultraviolet spectra in 95% ethanol of synthetic and authentic samples of *dl*-thermopsine were identical.

MADISON, WISC.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF DELAWARE]

Observations on the Mechanism of Addition Reactions of Olefins; Criteria for Mechanism in Mixed Aqueous Solvents

BY HAROLD KWART AND LEWIS B. WEISFELD[1]

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The rate of racemization of optically active 3-*p*-menthene has been found to be equal to the rate of addition to the double bond in highly acidic aqueous alcoholic solutions. These results are consistent with the hydration mechanism proposed by Taft and co-workers[2] and exclude a reaction sequence in which a carbonium ion is formed in a preliminary proton equilibrium step. The addition rates are well correlated by the activity postulate and the acidity scale suggested by Grunwald and co-workers.[7,9,10] This latter observation has been interpreted to establish a reaction mechanism whereby a π-complex is formed in a primary proton equilibrium followed by a rate-determining transition to carbonium ion with the exclusion of solvent from the major transition state. The acetoxylation of 3-*p*-menthene in glacial acetic acid with trifluoroacetic acid as catalyst is found to be mechanistically analogous to the hydration–etherification reaction. Criteria are developed for kinetic analysis of lyonium ion catalyzed reactions in other than purely aqueous media.

Introduction

A series of experiments reported by Taft and co-workers[2] constitute the most recent and most informative studies on the detailed mechanism of H^+ addition reactions of common olefinic substances.

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[1] E. I. du Pont de Nemours, Fellow 1955–1956.

[2] (a) R. W. Taft, Jr., THIS JOURNAL, **74**, 5372 (1952); (b) J. B. Levy, R. W. Taft, Jr., and L. P. Hammett, *ibid.*, **75**, 1253 (1953); (c) R. W. Taft, Jr., Abstracts of Papers, 125th Meeting A.C.S., Kansas City, Mo., March, 1954, p. 12P; (d) R. W. Taft, Jr., E. L. Purlee, P. Riesz and C. A. DeFasio, THIS JOURNAL, **77**, 1584 (1955); (e) P. Riesz, R. W. Taft, Jr., and R. H. Boyd, *ibid.*, **79**, 3724 (1957).

These workers report that unreacted 2-methyl-2-butene recovered after the first half-life of an acid-catalyzed hydration reaction with 50% deuterium oxide shows no deuterium uptake.[2c,3] 1-Methyl-1-cyclopentene shows parallel behavior. A corresponding series of experiments with trimethylethylene and *asym*-methylethylethylene reveals that neither of these olefins is measurably converted to the other after a half-life exposure to similar reaction conditions.[2b]

These observations exclude a reaction sequence in which a classical carbonium ion is formed in a preliminary reversible proton transfer. Furthermore, the rates of hydration of dissolved (in aqueous solution) isobutylene and others follow[3] the Hammett acidity function, H_0, with essentially unit slope.[2a,d] Consequently, applying the kinetic criterion of the H_0 function originally suggested by Zucker and Hammett[4] and widely developed by Long and co-workers[5] it was concluded that the hydration reaction major transition state must be free from firmly bound water molecules. A mechanism involving initial formation of a π-complex followed by a rate-determining transition to a carbonium ion was devised to explain these results.

This excellent work and the mechanism of reaction to which it leads appeared to have some possible limitations, however. For one, it seemed as though it might very well be a limiting case which applies only in water solution. Since the product-forming step is proposed as the reaction of water with the carbonium ion, no mechanistic detail suggests an explanation for the stereospecificity of the common addition reaction. If, in fact, the hydration reaction (in water solution) and other addition reactions of the double bond (in non-aqueous solution) are similar in mechanism, Hammond and Nevitt[6] appear to be in disagreement with Taft. These latter workers have observed that the addition of HBr glacial acetic acid solution in studies with various substituted cyclohexenes goes exclusively *trans*. They have postulated that the product-forming as well as the rate-controlling step occurs with attack of bromide ion upon an initially formed π-complex rather than upon a carbonium ion intermediate.

The objectives of the studies being reported here were to gain some understanding of the factors that control the addition mechanism in various media. More specifically, we have undertaken here to examine the kinetic factors involved in the addition reactions of substituted cyclohexenes other than (pure) hydration and in reaction media other than purely aqueous.[7] As an auxiliary problem we set ourselves to develop kinetic criteria to determine the involvement of solvent molecules and nucleophilic reagents in the major transition states of acid- and base-catalyzed reactions. This latter objective is made necessary by the demonstration[8a] that a Hammett acidity function often does not exist, as had been supposed,[8b] for other than purely aqueous media.

Results and Discussion

The selection of 3-*p*-menthene as the subject olefin was determined by several considerations; the presence of an asymmetric center in the reagent that is destroyed in the product affords an excellent test of the occurrence of a symmetrical intermediate in the addition reaction path and permits pursuit of the rate of reaction by a convenient polarimetric method. Furthermore, 3-*p*-menthene possesses the required alkyl substituted alicyclic double bond, wherein the steric course of addition has been thoroughly examined by Hammond and Nevitt[6] and which permits a desirable extension of Taft's[2] kinetic studies of the hydration reaction with purely aliphatic olefins and with small ring olefins.[2e]

All the rate measurements made showed good first-order obedience, even out toward completion (see Fig. 1), regardless of the addition reagent, the medium of reaction or the method of following the reaction rate. This result would be predicted by any mechanism in which the product-forming step was not rate determining. Several runs with varying concentrations of acid catalyst were followed both by iodimetric titration, used to estimate the formation of saturated product, and polarimetric means which measured the formation of a symmetrical intermediate. The observed equivalence (within 2%) between the polarimetric and the titrimetric rates in each case excludes a reaction sequence in which a planar carbonium ion of classical description is formed in a rapid, reversible, preliminary proton equilibrium.

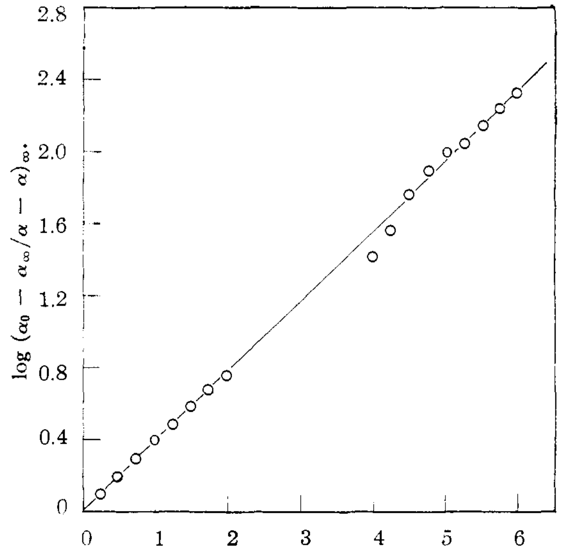

Fig. 1.—Acetoxylation of 3-menthene; polarimetric rate with 3.24 *M* trifluoroacetic acid at 44°.

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(3) E. L. Purlee and R. W. Taft, Jr., This Journal, **78**, 5807 (1956).

(4) L. Zucker and L. P. Hammett, *ibid.*, **61**, 2791 (1939).

(5) (a) J. G. Pritchard and F. A. Long, *ibid.*, **78**, 2667 (1956); F. A. Long and M. Purchase, *ibid.*, **72**, 3267 (1950); D. McIntyre and F. A. Long, *ibid.*, **76**, 3240 (1954); F. A. Long, W. F. McDevit and F. Dunkle, *J. Phys. Chem.*, **55**, 813, 829 (1951); (b) see also M. Paul and F. A. Long, *Chem. Revs.*, **57**, 935 (1957).

(6) G. S. Hammond and T. D. Nevitt, This Journal, **76**, 4121 (1954).

(7) A. G. Evans and J. Halpern, *Trans. Faraday Soc.*, **48**, 1034 (1952), have studied addition in methanol solutions to the conjugated double bond of various substituted styrenes.

(8) (a) B. Gutbezahl and E. Grunwald, This Journal, **75**, 559 (1953); (b) E. A. Braude and E. S. Stern, *J. Chem. Soc.*, 1982 (1948).

TABLE I

COMPARISON BETWEEN POLARIMETRIC RATES, k_p, AND TITRIMETRIC RATES, k_t, OF HYDRATION OF *d*-3-*p*-MENTHENE AT 44° (56 WT. % ETHANOL)

H_2SO_4 (equiv./l.)	$10^5\, k_p$, sec.$^{-1}$	$10^5\, k_t$, sec.$^{-1}$
2.99	1.95	1.99
3.24	2.60	2.57
3.48	3.28	3.25

It might be suggested, however, that the reaction consists of a rate-controlling transfer of proton from lyonium ion to olefin followed by a rapid reaction of the resultant carbonium ion with the hydroxylic solvent. Concerted proton donation and combination with solvent is yet another possibility that fits the observed pseudo first-order rate. Taft[2a,3] has distinguished these possibilities for the hydration reaction mechanism from the rate-controlling unimolecular rearrangement of the protonated olefin (*π-complex*) to carbonium ion by establishing the linear dependence of the log *k* and the Hammett acidity function as well as by means of other criteria, *e.g.*, solvent–isotope effects and I-strain theory applied to the effect of structure on rate and equilibrium.

It was our purpose to ascertain whether the π complex or A-1 mechanism[5] occurred in the mixed solvent composition (addition) reaction. However, while it appears from the plot in Fig. 2 that the addition rates in a given ethanol–water solvent composition vary linearly with an *apparent* H_0 function, a similar plot of log *k versus* log *I* has been demonstrated by Braude and Stern[8] for reactions in medium compositions in which Gutbezahl and Grunwald[7] (somewhat later) have shown an *actual* H_0 function does not exist. An acidity function H_0, in fact, exists only when the quantity f_B/f_{BH^+} is independent of the structure of the neutral base (B), and this condition often does not obtain in ethanolic solution.

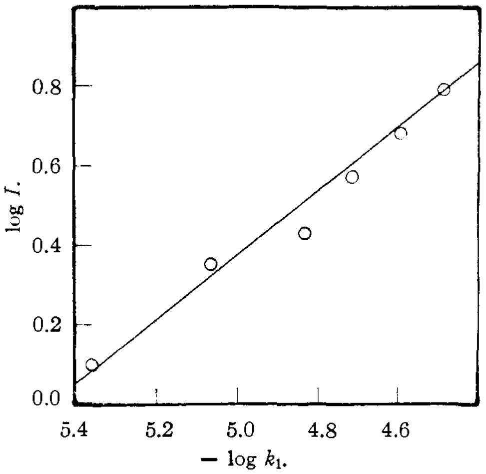

Fig. 2.—Variation of the polarimetric hydration rates of 3-*p*-menthene with indicator values of *p*-nitroaniline at constant medium composition (56 wt. % ethanol, 44°).

Dependence of Rate on Solvent Composition.—In this section we will try to show how the rate of reaction can be related to an empirical measure of hydrogen ion activity in any solvent medium. Also, we will attempt to verify the existence of a useful kinetic criterion for the A-1 mechanism under such circumstances.

It is reasonable to assume that the same activity factors which govern the behavior of the olefinic substrate (S) proton equilibrium should be applicable to an indicator (B) acid–base equilibrium.[9] For any general base B and its conjugate acid BH^+ in the equilibrium

$$\mathrm{BH^+} \overset{K_a}{\rightleftarrows} \mathrm{B} + \mathrm{H^+}$$

a function H_ψ may be said to exist such that

$$H_\psi = -\log a_{H^+} - \log \frac{y_B}{y_{BH^+}} \text{ and} \quad (1)$$

$$(pK_a)_B = -\log a_{H^+} - \log \frac{a_B}{a_{BH^+}} \quad (2)$$

where y_B and y_{BH^+} are the molar activity coefficients referred to the infinitely dilute solution in a given solvent and a_{H^+} is the proton activity under the same conditions; *i.e.*, a_{H^+} = (lyonium ion)·y_{H^+}. Furthermore, since $y_B/y_{BH^+} = a_BC_{BH^+}/a_{BH^+}C_B$ and defining a quantity known[8] as the indicator ratio, $I = C_{BH^+}/C_B$, which is spectrophotometrically measurable, equations 1 and 2 can be transformed into

$$H_\psi = (pK_a)_B + \log \frac{C_B}{C_{BH^+}} = (pK_a)_B - \log I \quad (3)$$

The H_ψ function merely implies that, in a given solution in a chosen solvent, values of log y_B/y_{BH^+} are independent of the nature of B.[10] This is not at all to be taken for granted if the solution is moderately concentrated in acid. It will be clear, however, that this is a real relationship and the range of its applicability can be ascertained by direct measurements of acid-catalyzed reactions. Thus for the A-1 mechanism

$$\mathrm{S} + \mathrm{H^+} \overset{(K_a)_S^{-1}}{\rightleftarrows} \mathrm{SH^+}$$

$$\mathrm{SH^+} \xrightarrow{k} {}^*\mathrm{SH^+}$$

where $^*SH^+$ signifies some activated state of the conjugate acid of the substrate S formed in the rate-determining step. The terms $(K_a)_S$ and $(pK_a)_S$ can be defined in equations analogous to (2). It follows, then, that the velocity of an acid-catalyzed reaction of this mechanism is given by

$$v = kC_{SH^+}$$
$$= k(K_a)_S^{-1} \times \frac{y_S}{y_{SH^+}} \times a_{H^+} \times C_S \quad (4)$$

and, therefore, $k_1 = v/C_S = k(K_a)_S^{-1} \times (y_S/y_{SH^+})\cdot a_{H^+}$;

$$\log k_1 = \log k + (pK_a)_S + \log \frac{y_S}{y_{SH^+}} + \log a_{H^+} \quad (5)$$

It is apparent that, where it can be established that log k_1 (a function of y_S/y_{SH^+}) has a unit slope linearity with log *I* (a function of y_B/y_{BH^+}), the molar activity coefficient ratios are independent of the substrate and medium nature. Thus, on substi-

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[9] Where it has not been explicitly stated the symbols used here have the same significance as defined and applied by B. Gutbezahl and E. Grunwald, THIS JOURNAL, **75**, 565 (1953).

[10] Compare with the findings in several mixed solvents by C. A. Bunton, J. B. Ley, A. J. Rhind-Tutt and C. A. Vernon, *J. Chem. Soc.*, 2327 (1957).

tution into (5) from this corollary to (1) and (2) we get

$$\log k_1 = \log k + (pK_a)_S - H_\psi \qquad (6)$$

and

$$\log k_1 = \log I + \log k + (pK_a)_S - (pK_a)_B \qquad (7)$$

The last three terms of equation 7 are constant for a given solvent composition.

For variations of solvent compositions we invoke the activity postulates of Grunwald[11] in the form $(pK_a)_B = (pK_a^W)_B + \log f_H + m_B Y_0$. A similar set of expressions exists where S replaces B in pertinent terms and where m_B and m_S relate only to a property of B and S, respectively, and Y_0 is a function only of solvent composition. Hence, suitable substitution into (7) yields

$$\log k_1 = \log k + (pK_a^W)_S - (pK_a^W)_B + m_S Y_0 - m_B Y_0 + \log I \qquad (8)$$

$$= \log k + (pK_a^W)_{S-B} + \Delta m_{S-B} Y_0 + \log I$$

and, therefore, in any solvent composition

$$\log k_1 - \log I = \Delta m_{S-B} Y_0 + \text{constant} \qquad (9)$$

Thus, it is predicted that where the assumptions discussed in the above derivations hold, plots of $(\Delta m_{S-B} Y_0 + \log I)$ *versus* $\log k_1$ and $(\log k_1 - \log I)$ *versus* Y_0 should afford straight lines over the complete range of solvent compositions for which Y_0 values have been tabulated through independent determinations.

It is not at all necessary to the above argument that H_ψ be constant for a given acid concentration since it is not required that $y_S y_{H^+}/y_{SH^+}$ be the same at constant C_{H^+} in each mixed solvent composition. In the event that this constancy does exist, however, the values of m_S and m_B may be determined in several ways from the kinetic data and independently of the plot in eq. 9. Thus, substituting the Grunwald activity postulates into eq. 5 results in

$$\log k_1 = \log k + (pK_a^W)_S + \log f_H + m_S Y_0 + \log a_{H^+} + \log \frac{y_S}{y_{SH^+}} \qquad (10)$$

$$H_\psi = -\log a_{H^+} - \log \frac{y_S}{y_{SH^+}} \qquad (11)$$

The sum of these equations is given by

$$\log k_1 - \log f_H = m_S Y_0 + \log k + (pK_a^W)_S - H_\psi \qquad (12)$$

For rate data taken from runs at the same acid concentration but varying solvent composition the last three terms of equation 12 may be constant. Therefore, a plot of $(\log k_1 - \log f_H)$ *versus* Y_0 leads to a straight line whose slope determines m_S in solvent compositions for which $\log f_H$ and Y_0 are tabulated. In an entirely analogous fashion the relation

$$\log I - \log f_H = m_B Y_0 + \text{constant} \qquad (13)$$

can be derived, which affords a determination of m_B.

We have applied the principal equations in this development as kinetic criteria for the lack of involvement of the nucleophilic properties of the medium in the transition state for acid-catalyzed addition to olefins. Thus the applicability of equation (7) to the data on solvation of 3-*p*-menthene in ethanol–water solution is seen from the plot in Fig. 2 and the data entries 6–11 (constant medium composition) in Table II from which it was constructed.

TABLE II

RATES OF HYDRATION OF 3-MENTHENE IN AQUEOUS ETHANOL AT 44.15, 0.03° (INDICATOR, *p*-NITROANILINE)

Entry	Ethanol, wt. %	H_2SO_4 equiv./l.	$-Y_0$[a]	log log f_H[a]	log I	$-\log k_1$ calcd.	$-\log k_1$ obsd.
1	79.42	2.20	0.575	1.130	0.378	5.28	5.28
2	74.13	2.20	.495	0.860	.346	5.22	5.24
3	69.15	2.20	.432	.665	.276	5.21	5.20
4	59.39	2.20	.330	.403	.254	5.10	5.05
5	50.03	2.20	.265	.250	.348	4.93	4.95
5a	40.79	2.20	.190	.115	.387	..	..
6	56.2	1.80	.300		.104	5.22	5.36
7	56.2	2.33	.300		.358	4.97	5.06
8	56.2	2.55	.300		.423	4.87	4.83
9	56.2	2.99	.300		.575	4.74	4.71
10	56.2	3.24	.300		.685	4.63	4.59
11	56.2	3.48	.300		.785	4.53	4.48

[a] Taken from reference 9.

An entirely similar plot for the analogous reaction in acetic acid catalyzed by trifluoroacetic acid is seen in Fig. 3, the data for which is derived from Table III.

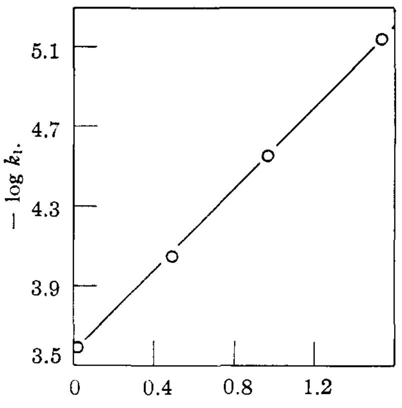

Fig. 3.—Variation of acetoxylation rates of 3-methene with indicator values for *p*-nitrobenzeneazo-(*p*′-nitro)-diphenylamine at 44°.

The most general equation, 9, is shown to encompass all the data entries in Table II by means of the plot in Fig. 4. The substrate and indicator parameters, m_S and m_B, are determined from the data in Table II, entries 1–5a (constant acid concentration), according to equations 12 and 13. The plot in Fig. 5 represents the determination of m_S in ethanol–water mixtures of varying proportion. The plot in Fig. 6 illustrates the method of determining m_B from equation 13. The difference $(m_S - m_B)$

TABLE III

ACETOXYLATION RATES OF 3-*p*-MENTHENE IN THE PRESENCE OF TRIFLUOROACETIC ACID AT 44° (POLARIMETRIC)

F_3CCOOH, moles/l.	$10^5 k_p$, sec.$^{-1}$	$-\log I$[a]	$\log k_p - \log I$
1.29	0.745	1.54	3.59
1.95	2.80	0.98	3.57
2.59	8.83	.49	3.56
3.25	24.4	.02	3.59

[a] Indicator, *p*-nitrobenzeneazo-(*p*′-nitro)-diphenylamine.

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(11) See references 7 and 9 as well as E. Grunwald and B. J. Berkowitz, *ibid.*, **73**, 4939 (1951).

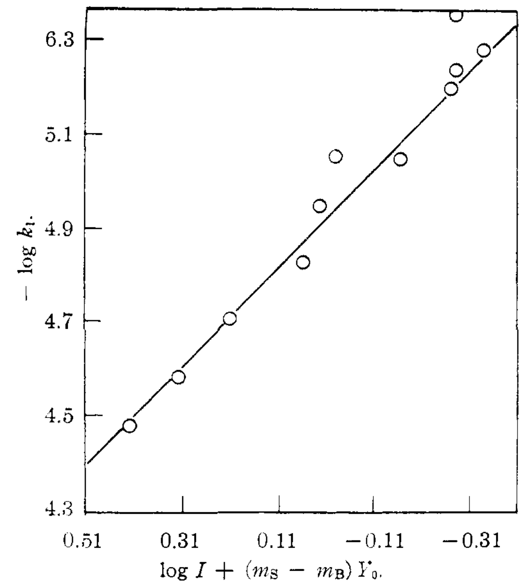

Fig. 4.—Polarimetric hydration rates of 3-*p*-menthene in ethanol–water at 44° plotted according to eq. 9 and Table II (all entries).

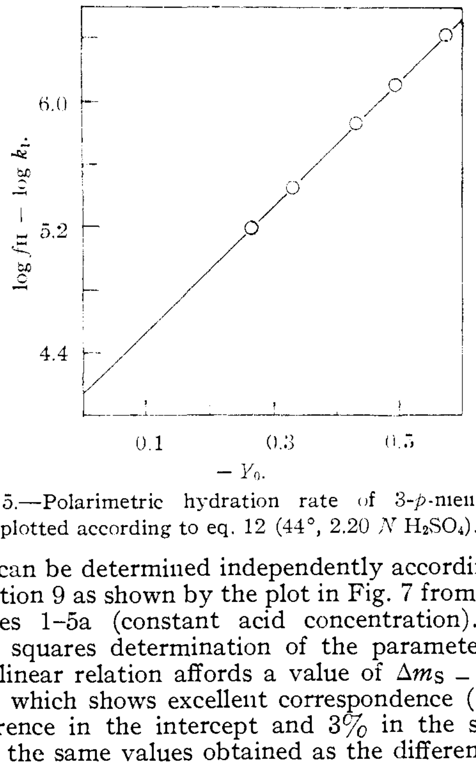

Fig. 5.—Polarimetric hydration rate of 3-*p*-menthene, plotted according to eq. 12 (44°, 2.20 N H_2SO_4).

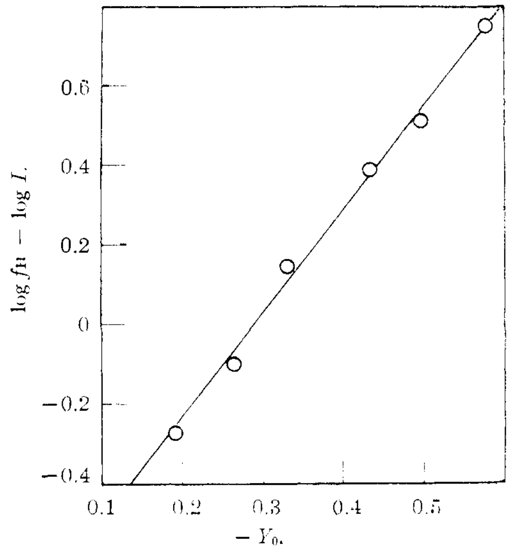

Fig. 6.—Polarimetric hydration rate of 3-*p*-menthene plotted according to eq. 13.

also can be determined independently according to equation 9 as shown by the plot in Fig. 7 from data entries 1-5a (constant acid concentration). A least squares determination of the parameters in this linear relation affords a value of $\Delta m_{S-B} = 1.28$, which shows excellent correspondence (0.4% difference in the intercept and 3% in the slope) with the same values obtained as the difference of the experimental values derived from the plots in Fig. 5 and Fig. 6. The data plotted in Fig. 7 also have a correlation coefficient, r_{xy}, equal to 0.980, which establishes considerable confidence in the existence of the relationship stated between the variables in eq. 9. The over-all kinetic relationship defining the acid-catalyzed solvation of 3-*p*-menthene in ethanol–water solutions of varying composition is expressed by

$$\log k_I - \log I = 1.28Y_0 - 4.93 \qquad (14)$$

The generally good consistency of the data of Table II, which represents a wide variation in reaction conditions, with all of the principal equations of the derivation above would seem to diminish the possibility of accidental fit. It can thus be deduced with some confidence that the assumptions on which the derivation have been based are generally useful in correlating rate and solvent composition.[12] In fact, it seems quite appropriate to propose that conducting acid catalysis studies in mixed solvents (as above) provides a more inquiring test of the A-1 mechanism than obtains in purely aqueous trials that assume the validity of the Zucker–Hammett treatment.[4] The mY function becomes the next higher approximation beyond the approximation inherent in the Zucker–Hammett treatment by allowing for possible structurally specific effects on the activity coefficient. Thus, by its successful application, the possibility that a correlation exists between mechanism and rate is increased. Furthermore, the possibility is decreased that a misfit due to accidental correspondence can occur; that is to say, failure to get a linear relationship as required for example by eq. 9 must mean with greater probability that the mechanism is not A-1. We may demonstrate this latter point by making reference to

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[12] It may be contended that this development suffers the same limitation of other attempts to correlate rate and solvent composition, namely, the k may not be a constant but would also have solvent dependence. Professor Grunwald, in a private communication has, demonstrated, however, that such a solvent dependence would be linear in Y_0 and, therefore, the mY_0 treatment developed above would still hold. Thus, we can write formally the general equations for the A-1 mechanism

$$\log K_A = \log K_A^W + mY_0 \qquad (I)$$

$$\log {}^*K_A = \log {}^*K_A^W + m^*Y_0 \qquad (II)$$

Thus

$$\log \frac{K_A}{{}^*K_A} = \log \frac{K_W}{{}^*K_W} + (m - {}^*m)Y_0 \qquad (III)$$

and

$$\log \frac{K_A}{{}^*K_A} = \log \frac{{}^*SH^+}{SH^+} = \log K^{\ddagger} \qquad (IV)$$

where $K^{\ddagger}$ is the equilibrium constant for the formation of the transition state as defined by Eyring and C is a collection of constant terms.

$$\log K^{\ddagger} = C + \log k \qquad (V)$$

On making suitable substitutions from III and IV into V, we obtain the linear relationship between k and Y_0, *viz.*

$$\log k = \log k^W + (m - {}^*m)Y_0 \qquad (VI)$$

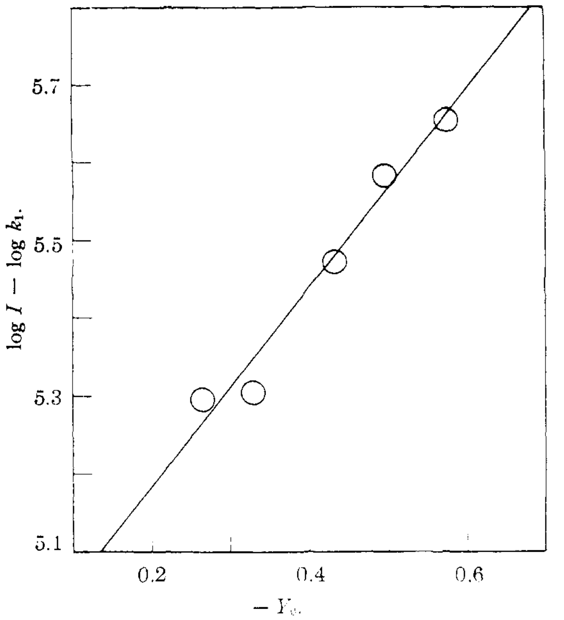


Fig. 7.—Polarimetric hydration rate of 3-*p*-menthene plotted according to eq. 9.

data computed from a report by Waters on the solvolysis of phenyl acetate in various ethanol–water compositions, as listed in Table IV.[13] As seen from Fig. 8, which represents a plot of these data according to eq. 9 and is to be compared for quality of fit with Fig. 7, a linear relation has not been achieved in accord with the well established A-2 mechanism of this acid-catalyzed reaction.[14]

TABLE IV

SOLVOLYSIS OF PHENYL ACETATE FROM DATA OF WATERS[13]

Mole % EtOH	10^6k	$-\log k$	$-\log I$	$-Y_0$
27.87	5.75	5.24	1.01	0.26
36.89	6.05	5.22	1.16	.34
47.72	5.50	5.26	1.27	.43
61.03	6.08	5.22	1.31	.57
76.12	7.90	5.10	1.25	.76
88.39	20	4.70	0.78	.88

In summarizing, then, we have in hand a useful criterion for nucleophilic participation of solvent in the transition state. Because this treatment involves the adjustable *m* parameter it seems clear that a fit is a highly possible but not a necessary condition for the A-1 mechanism. However, misfit is a sufficient condition for concluding the absence of this mechanism.[15]

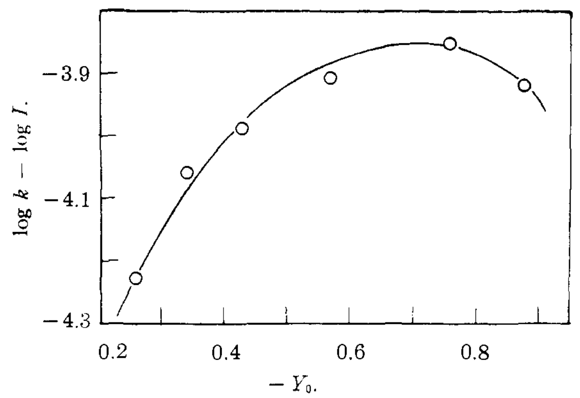
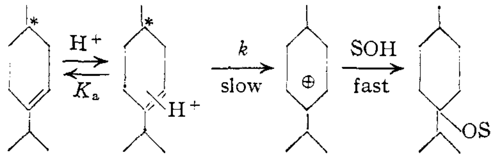


Fig. 8.—Solvolysis of phenyl acetate, demonstrating the failure of an A-2 reaction to fit the $H\psi$ relationship.

The Mechanism of Addition.—The results discussed above for an alicyclic non-aqueous and partly aqueous polar addition seem, on the whole, to be consistent with the conclusions of Purlee and Taft[3] derived from the entirely aqueous hydration reaction. Product formation involves the non-rate-determining reaction of nucleophiles and/or solvent with the carbonium ion.



The carbonium ion solvated by water in the hydration and etherification reaction is also seen from our results to be entirely similar to the carbonium ion solvated by glacial acetic acid in the acetoxylation reaction. It appears likely that the addition of HBr to olefin in glacial acetic acid medium possesses similar characteristics, if on the basis of our results on acetoxylation in glacial acetic acid, we can deduce that nucleophiles like the $Br^{\ominus}$ could not be involved in the transition state.[16] The observation by Hammond and Nevitt[6] that the latter reaction is strongly stereospecific would appear to indicate that interaction between the positive carbon and the acetic acid solvent molecules serves to retain the configurational identity of the carbonium ion; in other words, a classical carbonium ion which reacts stereospecifically. Steric effects governing the behavior of carbonium ions in highly branched aliphatic systems have been discussed by Brown and Kornblum.[17a] Recently, Zimmerman[17b] has demonstrated the marked disymmetry in the behavior of a substituted cycloalkane carbanion and has concluded that a *p*-orbital on the ring has a strong preference for reaction at one of its lobes dic-

[13] W. A. Waters, *J. Chem. Soc.*, 1014 (1936).

[14] C. T. Chmiel and F. A. Long, THIS JOURNAL, **78**, 3326 (1956). However, Waters' data show that the rate in ethanolic solvents increases with acidity faster than direct proportionality of ($H_3{}^+O$) requires and this might have been interpreted as approaching h_0 dependence, which the above analysis now excludes. See also D. P. N. Satchell, *J. Chem. Soc.*, 2878 (1957), on this point.

[15] A referee has suggested that many inconsistencies involved in the application of the Zucker-Hammett hypothesis may invalidate the use of acidity functions to ascertain factors in a reaction mechanism; (see "Annual Reports on the Progress of Physical Chemistry," 1957). We concur in the views expressed by F. A. Long, *Proc. Chem. Soc.*, 220 (1957), and by M. Paul and F. A. Long in reference 5b that comparison of rates with acidity functions constitutes an exceedingly useful tool for mechanism studies. In the present work the variation of rate with solvent composition at a fixed acid concentration leads to data that afford a more sensitive means of establishing such correlations than in the cases of H_0 dependence of the rates, where variation of acid concentration in aqueous media is the sole basis for mechanistic conclusions. This increased sensitivity has been adumbrated in the studies of D. P. N. Satchell (see ref. 14).

[16] This is to assume that the presence of $Br^{\ominus}$, a substance of considerably more nucleophilic properties than the solvents thus far investigated, does not alter the mechanistic features observed for hydration, etherification and acetoxylation of olefins. Clearly, this may be an unwarranted extrapolation and requires further study.

[17] (a) H. C. Brown and R. B. Kornblum, THIS JOURNAL, **76**, 4510 (1954); (b) H. E. Zimmerman, *J. Org. Chem.*, **20**, 549 (1955).

tated by the steric environment. Quite possibly in the addition reaction under consideration the solvation shell of the cationic intermediate is so oriented that collapse to form the covalent bond in the product can occur from only one direction, resembling in this respect the asymmetric carbanion discussed by Zimmerman. Taft and co-workers,[2e] on the other hand, have considered a possibility that also agrees with our results; *i.e.*, the transition state possesses carbonium ion character but not the molecular configuration of the carbonium ion. Since the product forms after the r.d.s., the involvement of solvent represents reaction with a carbonium ion which is symmetrical but not necessarily planar and permits this occurrence as a stereospecific step.

Experimental

Reagent Preparation.—*d*-3-*p*-Menthene was prepared essentially by the method of Chugaev[18] by pyrolysis of menthyl xanthogenate (m.p. 38–39°), with U.S.P. (Japanese) *l*-menthol as the primary source. Menthyl methyl xanthate was pyrolyzed at approximately 240° under a nitrogen stream at slightly diminished pressure. The main fraction of pyrolysate passed over at about 120° (135 mm.) and was collected in a Dry Ice trap. After warming to room temperature, the residual liquid was washed well with potassium hydroxide solution and water, dried over anhydrous potassium carbonate, and finally distilled from metallic sodium at 100–101° (101 mm.). Based upon the amount of xanthogenate charged, the yield was about 70% of clear liquid, α^{25}_{D} 117.0° (*c* 3.88, ethanol). Cram has shown that the pyrolysis of xanthates proceeds for the most part in a stereospecific manner *via cis* elimination.[19] Although the redistilled pyrolysate undoubtedly was contaminated with small amounts of difficultly separated 2-*p*-menthene, no further purification was attempted since this does not react under the conditions of the following experiments.

Source of Other Reagents.—Ethanol, acetic acid and trifluoroacetic acid were all purified by conventional methods. *p*-Nitroaniline was recrystallized preliminary to use from ethanol. *p*-Nitrobenzeneazo-(*p*′-nitro)-diphenylamine was prepared in a method analogous to that of Walling[20] by coupling diazotized *p*-nitroaniline to *p*-nitrodiphenylamine in acetic acid solution. Coupling required several hours at room temperature and the product, which was slowly deposited from solution, was recrystallized twice from hot acetic acid before further use.

Reaction Kinetics.—Polarimetric rates were determined both with varying acid concentration and varying medium composition. This was achieved in the first cases by holding the initial ethanol concentration constant at about 56% (by weight) while varying the sulfuric acid from 1.8 to 3.5 *N*, and, in the second, by varying ethanol concentrations between 50 and 80% (by weight) while maintaining acidity at 2.20 *N*. The latter procedure is easily controlled while the former presents difficulties (a slight uncorrected variation in percentage alcohol) which account for small departures in the rate correlations discussed earlier. The reactions all took place in a specially designed 4-dm. tube with all glass optically parallel sealed windows (no gaskets). The tube charge was in most cases approximately 0.03 *M* in *d*-3-*p*-menthene, and reactions were followed over more than a one-degree range, in many runs essentially to completion. The residual, unchanging rotation was assigned to a small amount of unreactive 2-menthene contamination.

The absence of a solubility problem in acetic acid–trifluoroacetic acid mixtures permitted the use of a heavier menthene charge so that reactions in this case were followed over a six degree rotational change.

Polarimetric rates were all first order and were found to fit the expression

$$2.303 \log \frac{\alpha_0 - \alpha_\infty}{\alpha - \alpha_\infty} = k_{\mathrm{p}}t$$

where α_0 refers to the initial rotation of the reaction mixture, α is the rotation at time t in the reaction, α_∞ is the experimentally measured, calculated or theoretical rotation at infinite time, and k_{p} is the first-order rate constant. The "calculated" value is that obtained from the Tau method[21] of extrapolation to infinite time values, this method also serving as a check on other polarimetric runs. The "theoretical" rotation is that calculated from the initial concentration by correlation with previous runs using the same starting material. In all cases the characteristic linear first-order plot was obtained.

Several titrimetric rate experiments were carried out at "constant medium composition" using the same solutions as the corresponding polarimetric runs. Titration rates were followed by the Hanus Method,[22] using iodine monobromide. These rates also were found to fit a first-order equation analogous to that above, with each α and α_∞ corresponding to the respective thiosulfate titers. The proportions of residual unsaturation (as in the case of residual rotation previously) indicated that the amount of 2-menthene varied slightly with pyrolysis conditions. In the main, however, the contaminant accounted for about 20% of the total menthenes. All reactions were run at 44.15 ± 0.03°.

Indicator values were determined for each of the solutions by the usual methods.[8] *p*-Nitroaniline was used for the ethanol–water–acid solutions, while *p*-nitrobenzeneazo-(*p*-nitro)-diphenylamine was employed in the acetic acid–trifluoroacetic acid mixtures. This latter indicator was found to be color stable over an appreciable period of time in the strongly acid solutions, thereby indicating no significant acetylation of the amine function. A model B Beckman spectrophotometer was used for colorimetric determinations and the conjugate acid to base ratio, I, was computed from the relationship

$$I = C_{\mathrm{BH^+}}/C_{\mathrm{B}} = \frac{\epsilon_{\mathrm{N}} - \epsilon_{\mathrm{A}}}{\epsilon_{\mathrm{A}} - \epsilon_{\mathrm{S}}}$$

where ϵ_{N} is the molar extinction coefficient of the indicator in the neutral solvent system, ϵ_{A} the value for the acid solution and ϵ_{S} the extinction coefficient of nitrobenzene. For the azodiphenylamine in acetic acid, the ϵ_{S} term was omitted.

Acknowledgment.—The authors wish to thank Professors Ernest Grunwald and R. W. Taft, Jr., for their very helpful comments and stimulating discussions.

NEWARK, DEL.

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[18] L. Chugaev, *Ber.*, **32**, 3332 (1899).

[19] D. J. Cram, THIS JOURNAL, **71**, 3883 (1949).

[20] C. Walling, *ibid.*, **72**, 1164 (1950).

[21] E. Guggenheim, *Phil. Mag.*, [7], **2**, 538 (1926).

[22] "Official and Tentative Methods of Analysis of the Association of Official Agricultural Chemists," Henry A. Lepper, Chairman of Editorial Board, sixth ed., published by A.O.A.C., P. O. Box 54, Benjamin Franklin Station, Washington 4, D. C., 1945.