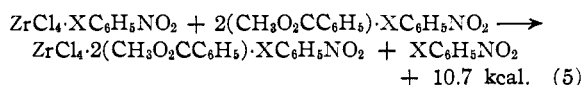
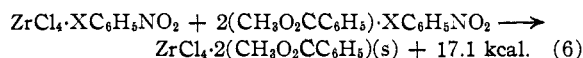


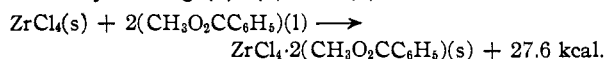
Add (2) and (4) we obtain



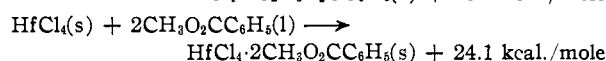
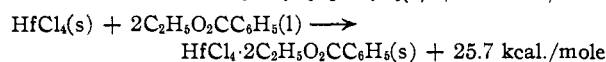
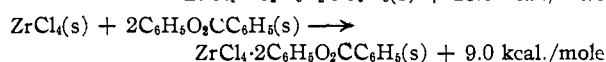
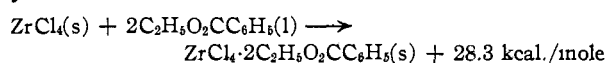
Add (3) to (5)



Then by adding (1), (2) and (6)



A similar operation with the other compounds yields



Crude measurements of the heat of formation of zirconium tetrachloride-2-ethyl benzoate were made in the absence of any solvent, by adding a weighed quantity of zirconium tetrachloride to a measured proportion of ethyl benzoate. The values obtained were in agreement with those calculated from the solvent system measurements within ± 2 kcal.

The points plotted in Fig. 1 are obtained by subtracting the heat of solution of ester from the gross heat measured. Thus these plots represent the heat effect of treating dissolved metal halide with dissolved ester without considering heats of dilution. The curves indicate compounds with ester-metal halide ratios greater than two to one are not stable under ordinary conditions. However, the slopes of the curves in the low ratio portions are such as to indicate the possibility of one to one addition compounds. There were indications that such compounds exist and a compound corresponding to a one to one addition was isolated when the reaction was carried out in a suspension of cyclohexane. However, the results were not reproducible.

Acknowledgment.—This investigation has been supported by the U. S. Atomic Energy Commission under Contract No. AT-(40-1)-234.

CHAPEL HILL, NORTH CAROLINA RECEIVED JUNE 27, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HARPUR COLLEGE]

A Kinetic Salt Effect on the Acid-catalyzed Decomposition of Trioxane¹

BY MARTIN A. PAUL

The rate of decomposition of trioxane into formaldehyde has been studied by a dilatometric method in solutions of perchloric acid and in solutions of perchloric acid mixed with sodium perchlorate at constant total ionic strength of 6 moles per liter, at 40°. At given perchloric acid concentration, the addition of sodium perchlorate markedly enhances the rate, an approximately sixfold increase being observed in 4 *M* HClO₄ + 2 *M* NaClO₄ as compared with 4 *M* HClO₄. The effect may be closely correlated with a similar effect found by Harbottle on the acidity toward simple basic indicators. The rates in solutions of other strong acids may likewise be correlated with the indicator acidity function *H*₀ of Hammett and Deyrup, the first-order rate constant *k* (in min.⁻¹) satisfying the empirical relationship: $\log k = -H_0 - 4.135$. These facts are consistent with the hypothesis that the rate-determining step consists of the slow rearrangement and decomposition of the acid ion conjugate to trioxane, which itself apparently functions as a simple weak base.

The author recently noted a correlation between the rate of decomposition of trioxane to formaldehyde in strongly acid solutions, measured by Walker and Chadwick, and the *H*₀ indicator acidity function of Hammett and Deyrup.²⁻⁴ The reaction has now been followed in solutions containing perchloric acid and sodium perchlorate in varying proportions at fixed total electrolyte concentration of 6 moles per liter. The *H*₀ indicator acidity of such solutions has been established by Harbottle,⁵ a quite marked progressive increase appearing in the acidity toward simple basic indicators of perchloric acid solutions as sodium perchlorate is added. Precisely the same effect is now reported on the rate of decomposition of trioxane.

(1) Presented before the Physical and Inorganic Chemistry Division of the American Chemical Society, Cleveland, Ohio, April, 1951.

(2) J. F. Walker and A. F. Chadwick, *Ind. Eng. Chem.*, **39**, 974 (1947).

(3) L. P. Hammett and A. J. Deyrup, *THIS JOURNAL*, **54**, 2721 (1932); L. P. Hammett and M. A. Paul, *ibid.*, **56**, 827 (1934).

(4) M. A. Paul, *ibid.*, **72**, 3813 (1950).

(5) G. Harbottle, *ibid.*, **73**, 4024 (1951).

Materials and Procedure.—Trioxane was obtained through the courtesy of the Electrochemicals Division, E. I. du Pont de Nemours and Co. It was recrystallized from water, and redissolved in water to form an approximately 2 *M* stock solution. Stock solutions of the various acids of approximately 8 *M* concentration (perchloric acid by dilution of Merck and Co., Inc., 70-72% reagent grade) were analyzed by titrating weighed samples against 0.2 *M* sodium hydroxide, standardized with National Bureau of Standards potassium hydrogen phthalate. Sodium perchlorate was the Eimer and Amend C.P. monohydrate.

A dilatometric procedure was used, similar to that described by Long and Purchase.⁶ The dilatometer consisted simply of a glass bulb of about 60-ml. capacity, to which was attached a filling tube equipped with a stopcock, and a long open-ended capillary tube of about 1-mm. bore. In some of the dilatometers, a linear glass scale was affixed behind the capillary for determining the meniscus height. In others, the capillary tubes had linear scales engraved directly on them for greater convenience in reading and reduction of parallax error; these scales consisted of precision thermometer scales engraved by the Brooklyn Thermometer Co. on tubing previously selected for uniformity of bore. A droplet of mercury was placed above the solution meniscus to retard evaporation.

(6) F. A. Long and M. Purchase, *ibid.*, **72**, 3267 (1950).

All reactions were run at $40.00 \pm 0.002^\circ$, the initial trioxane concentration usually being about $0.25 M$. Solutions were prepared by weighing out the required quantities of $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ and acid into a 100-ml. volumetric flask, adding approximately 12.5 ml. of the $2 M$ trioxane solution, and bringing to mark in the thermostat at 40° . All final electrolyte concentrations therefore refer to a temperature of 40° . It was found essential that dissolved air be expelled from the solution before it is introduced into the dilatometer, as otherwise the gradual appearance of tiny air bubbles may invalidate the run; air was removed by placing the solution in a filter flask and exhausting the pressure over it by means of a good air-pump.

Although pure liquid trioxane has a density considerably greater than that of pure liquid formaldehyde (after allowance has been made for the difference between the temperatures at which these two phases normally exist), their partial volumes in dilute aqueous solutions are evidently such as to result in a significant volume decrease during the run. Calculations of the first-order rate constants, k , were usually made from the slopes of the least-squares straight lines fitted to the data in the form of $\log(r_\infty - r_t)$ vs. t , where r_∞ represents the final reading and r_t the reading at time t , in accordance with the equation

$$k = 2.3026 \frac{d \log(r_\infty - r_t)}{dt}$$

Comparable results were obtained also by Guggenheim's method,⁷ in which

$$k = 2.3026 \frac{d \log(r_2 - r_1)}{dt_1}$$

where r_2 and r_1 are dilatometer readings at times t_2 and t_1 differing by a fixed interval throughout the run. Figure 1 shows the data for a typical run plotted according to both methods. For all but the fastest runs, the values of k may be determined from the data within a precision of order $\pm 1\%$ or better. The limiting error governing the reproducibility of the results is the precision with which the acid concentration may be fixed, for the data of Walker and Chadwick¹ show that in sulfuric acid concentrations between $4 M$ and $6 M$, k increases by about 1% with $0.01 M$ increase in

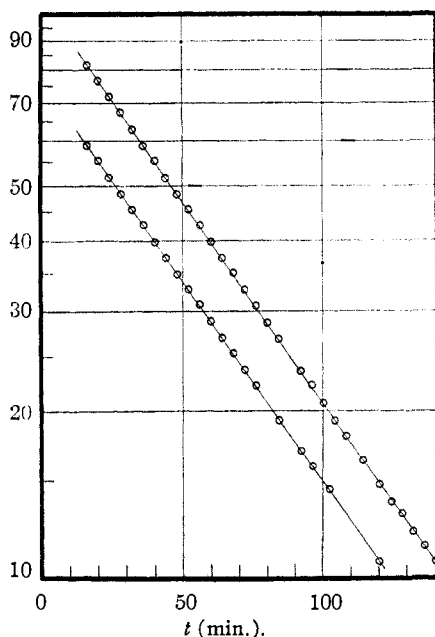


Fig. 1.—Dilatometer readings plotted against time for the decomposition of trioxane in $4 M \text{HClO}_4 + 2 M \text{NaClO}_4$ aqueous solution at 40° . Upper curve: ordinary plot, $(r_\infty - r)$ on logarithmic scale vs. t ; lower curve: Guggenheim plot, $(r_2 - r_1)$ on logarithmic scale vs. t_1 for constant $(t_2 - t_1) = 78$ min.

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

the acid concentration, and an effect of the same order of magnitude apparently applies to the perchloric acid concentration. The essential validity of the dilatometric technique is shown by the close agreement of the rate constant obtained in $6 M$ sulfuric acid (0.0298 min.^{-1}) with that obtained by Walker and Chadwick (0.029 min.^{-1}), who followed the reaction by iodimetric determination of the product, formaldehyde.

Results.—Table I presents first-order rate constants obtained in various acid solutions, all concentrations referring to 40° . In Fig. 2, $\log k$ has

TABLE I
FIRST-ORDER RATE CONSTANTS FOR THE DECOMPOSITION OF TRIOXANE IN AQUEOUS SOLUTIONS AT 40°

Composition	k , min.^{-1}	Half-life, min.
$6 M \text{HClO}_4$	0.0546	12.7
	0.0584	11.9
	0.0597	11.6
$5 M \text{HClO}_4 + 1 M \text{NaClO}_4$	0.0299	23.2
$4 M \text{HClO}_4 + 2 M \text{NaClO}_4$	0.0164	42.3
$3 M \text{HClO}_4 + 3 M \text{NaClO}_4$	0.00862	80.4
$2 M \text{HClO}_4 + 4 M \text{NaClO}_4$	0.00410	169.1
$1 M \text{HClO}_4 + 5 M \text{NaClO}_4$	0.00164	423
$4 M \text{HClO}_4$	0.00265	262
$6 M \text{H}_2\text{SO}_4$	0.0298	23.3
$6 M \text{HCl}$	0.00682	101.6

been plotted against $-H_0$; the H_0 values for HClO_4 - NaClO_4 mixtures are those of Harbottle,⁵ while the others are from work of Hammett and Deyrup, and Hammett and Paul.³ The indicator acidity data refer to 25° but since the rate data at other temperatures by Walker and Chadwick indicate an activation energy not particularly dependent on acid concentration, this should have no effect on the significance of the correlation. The correlation is indeed excellent, the straight line in the figure having been drawn with unit slope, satisfying the equation $\log k = -H_0 - 4.135$. One sees in particular that an approximately sixfold increase in the acidity of $4 M \text{HClO}_4$

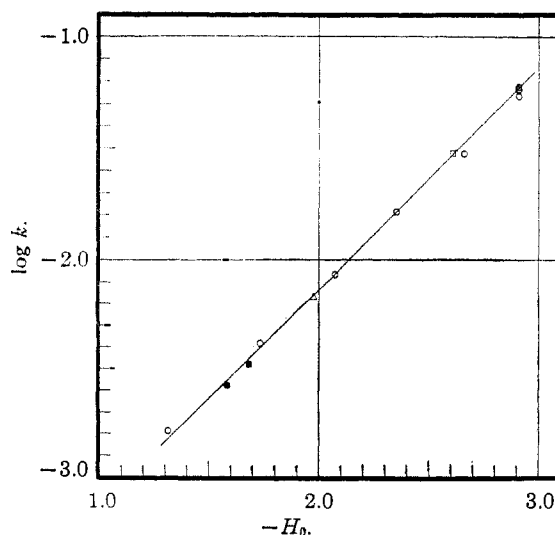


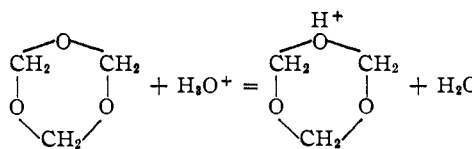
Fig. 2.— $\log k$ vs. $-H_0$ for the decomposition of trioxane: \circ , $\text{HClO}_4 + \text{NaClO}_4$ at constant total ionic strength of 6 moles/liter, $C_{\text{NaClO}_4} = 0, 1, 2, 3, 4, 5$ moles/liter; \bullet , $4 M \text{HClO}_4$; \square , $6 M \text{H}_2\text{SO}_4$; \blacksquare , $4 M \text{H}_2\text{SO}_4$ (rate data of Walker and Chadwick); Δ , $6 M \text{HCl}$.

toward simple basic indicators that accompanies the addition of 2 *M* NaClO₄, shown by Harbottle's data, is quite accurately reflected in an approximately sixfold increase in the reaction rate; a similar correlation (in 2 *M* HClO₄ + 4 *M* NaClO₄) has been observed by Long and Purchase in the hydrolysis of β-propiolactone.⁶ One will note also the significant spread at 6 *M* concentrations among the three "strong" acids, HClO₄, H₂SO₄ and HCl, the order of acid strength being plainly manifested by both the indicator acidity and the reaction rate.

These new results confirm and extend the correlation between log *k* and *H*₀ previously noted.⁸ They are consistent with the supposition that the mechanism of the reaction depends on a rapid equilibrium

(8) Ref. 4. The rate constants of Walker and Chadwick used in Fig. 1 or that note were expressed in sec.⁻¹; the present data indicate that the correlation line there drawn between log *k* and *H*₀ should be displaced upward by about 0.08 logarithmic unit.

between trioxane and its conjugate acid ion



followed by a rate-determining step consisting of internal rearrangement and decomposition of the ion. The reaction thus appears to be an unusually satisfactory one for the study of acid catalysis, and should be particularly valuable for the investigation of acidity in non-aqueous media.

The author takes pleasure in acknowledging his indebtedness to Professor F. A. Long of Cornell University for helpful suggestions concerning the dilatometric technique.

ENDICOTT, N. Y.

RECEIVED MAY 28, 1951

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

Acid Dissociation Exponents of Rutin and Xanthorhamnin¹

BY WILLIAM L. HOWARD² AND SIMON H. WENDER

Rutin is a polybasic acid with four dissociable groups measurable in aqueous solution of pH up to 12.5, while xanthorhamnin behaves as a dibasic acid in this range. Dissociation exponents are: for rutin, *pK*₁ 7.40, *pK*₂ 8.70, *pK*₃ 12.6, *pK*₄ 14.2; for xanthorhamnin, *pK*₁ 8.57, *pK*₂ 10.9.

During the investigation of the isolation and purification of flavonoid compounds by means of ion exchange procedures, it became desirable to know the dissociation behavior of some of these substances. Because of their pharmaceutical interest, relative water solubility, and availability, rutin and xanthorhamnin were chosen for this study.

Experimental

Method.—Weighed samples of the acids were titrated in accurately known volumes of water solution under carbon dioxide-free conditions maintained by passing nitrogen over soda lime and then through the solutions. After the addition of each increment of base, the pH was determined with a Beckman pH meter, Model H, using a type E glass electrode to minimize alkaline error. The data were interpreted by the method of Simms³ and by means of a method outlined by Glasstone.⁴ The measurements were made at room temperature which had a day to day variation from 22 to 24° but the temperature of the solutions remained constant to within 0.5° during a single titration.

For the determination of *K*₁ and *K*₂, accurately weighed samples of rutin of the order of 0.35 g. were titrated with 0.426 *N* NaOH in volumes of solution of the order of 500 ml. Xanthorhamnin samples of about 0.30 g. were titrated similarly in volumes of about 50 ml. To determine *K*₃ and *K*₄ of rutin, 0.35-g. samples were half-neutralized and titrated with 1.80 *N* KOH in 50-ml. volumes.

At low pH, the hydroxyl ion concentration could be taken as its activity, calculated from the pH and *K*_w, with negligible error. At higher pH values, it was determined by direct titration of water in the evaluation of *K*₁ and *K*₂. In evaluating *K*₃ and *K*₄ of rutin, the ionic strength was of the order of 0.1, so the hydroxyl ion concentration was deter-

mined by titrating a solution of Simms, *pK*' values were calculated from the average values of *pG*'.

The appropriate activity coefficients for appreciable concentrations by the equation $\log f = -Az^2\sqrt{\mu}/(1 + \sqrt{\mu})$, as given by Glasstone.⁵ The ionic strength was determined using the approximations mentioned by Glasstone,⁴ in interpreting the data for *K*₁ and *K*₂. In the calculations leading to *K*₃ and *K*₄ of rutin, the ionic strength was determined by making use of the known composition of the solutions, with the concentrations of the rutin anions being determined from the known values of *pK*₃' and *pK*₄' and utilizing the conditions for electroneutrality of the solutions.

In employing the method of Simms, *pK*' values were calculated from the average values of *pG*'. The appropriate activity coefficients at pH = *pK*' were then determined and utilized to calculate *pK* from the equation $pK = pK' - \log (f_b/f_a)$ where *f*_b and *f*_a are the activity coefficients of the basic and acid forms, respectively, of the substance involved in the equilibrium. In a similar manner, values of *pK*₃' and *pK*₄' of rutin, obtained from Fig. 3, were converted to *pK*₃ and *pK*₄.

Preparation of the Materials.—Rutin N.F. 1X (S. B. Penick and Co., New York) was recrystallized from water-alcohol solution and air-dried, then dried for several hours at 110°. By the method of Porter, *et al.*,⁶ the product was found to contain 94.5% rutin, a composition corresponding to that of rutin dihydrate.

Xanthorhamnin (S. B. Penick and Co.) was freed of a reddish impurity, which has the properties of an acid of lower equivalent weight, by recrystallizing several times from a mixture of ethyl and isopropyl alcohols. The bright yellow crystals were air-dried, then dried for several hours at 110°. Titration of this product indicated a molecular weight of 770, that of anhydrous xanthorhamnin.

Results.—Values of *X* and *Y* appropriate to the equation $Y = XK_1 + K_1K_2$ given by Glasstone⁴ were calculated from the titration data and plotted to give the straight lines from which *K*₁ and *K*₂ can be determined. The data for the first two dissociations of rutin are shown in Fig. 1 and those for xanthorhamnin in Fig. 2.

(5) S. Glasstone, ref. 4, p. 146.

(6) W. L. Porter, B. A. Brice, M. J. Copley and J. F. Couch, U. S. Dept. Agr., Circular AIC-159 (1947).

(1) This research was supported in part by a grant-in-aid from The Office of Naval Research (Project NR-059 226).

(2) Biological Department, Army Chemical Corps., Camp Detrick, Frederick, Maryland.

(3) H. S. Simms, THIS JOURNAL, 48, 1239 (1926).

(4) S. Glasstone, "An Introduction to Electrochemistry," D. Van Nostrand Co., Inc., New York, N. Y., 1942, p. 325.