Oxidation of 2-Propanol by Bromine in Acid Solution[1]

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Abstract: The kinetics of the oxidation of 2-propanol by bromine in solutions of 3.0 M ionic strength have been measured as a function of both the $[Br^-]$ and perchloric acid concentration. The rate law found can be expressed as $-d[Br_2]/dt = k_2[Br_2]_T[ROH]/(1 + K_t[Br^-])(1 + K_c[H^+])$, where $K_t = [Br_3^-]/[Br_2][Br^-]$. Distribution measurements support the interpretation of the decrease in rate with increasing acid at constant ionic strength as an activity coefficient effect.

The oxidation of 2-propanol by aqueous bromine to form acetone has been the subject of several previous investigations.[3-6] Two areas of concern have been demonstrated by this previous work: (1) the mechanistic question of the structure of the transition state; and (2) the relative reactivities of the various possible bromine-containing species. Swain, *et al.*,[3] proposed a mechanism in which direct hydride abstraction by Br_2 from 2-propanol occurs and support for their point of view has been presented by Venkatasubramanian and Thiagarajan.[5] Deno and Potter[4] have presented arguments which support an ester mechanism, as well as a discussion of pH–rate profile. Perlmutter-Hayman and Weissmann[6] have discussed the pH–rate profile and concluded that the increase in rate with increasing pH was due to a path involving the oxidation of the basic anion of 2-propanol rather than HOBr and that the active oxidizing form of bromine is Br_2; no path involving Br_3^- was found. All previous detailed rate studies were performed in the pH region 2–8.

Our interest in this reaction was stimulated by coulometric kinetic studies of the oxidation of 2-propanol by electrogenerated bromine in sulfuric acid solutions which indicated that the reaction rate decreased with increasing acid concentration. Wells[7] has presented detailed evidence which indicates that substantial protonation of 2-propanol occurs in dilute acid solution. This work was undertaken to investigate the effect of acid concentration on the rate of oxidation of 2-propanol in solutions of $HClO_4$ and $NaClO_4$ of constant ionic strength.

Experimental Section

Reagents. The 2-propanol solutions were prepared from Fisher Spectranalyzed 2-propanol. Analyses of stock solutions were made by controlled oxidation with dichromate, followed by back titration of the excess dichromate with standard ferrous solution. Since the analyses agreed to better than 3% with the theoretical values calculated from the density, and previous work[8] indicated that this reaction was not perfectly stoichiometric, all concentrations were subsequently calculated from the volume–density relationship. Fresh stock solutions were prepared on alternate days to minimize losses due to the volatility of 2-propanol.

Stock sodium perchlorate solutions were prepared by careful neutralization of reagent grade sodium carbonate with 70% perchloric acid. Reagent grade sodium bromide and 70% perchloric acid were used to prepare stock solutions of sodium bromide and perchloric acid, respectively. All solutions had a total ionic strength of 3.0 M using $HClO_4$–NaBr–$NaClO_4$ in appropriate amounts.

Kinetic Measurements. All rate data were collected under conditions of very low bromine concentration relative to the alcohol concentration so that pseudo-first-order conditions were rigorously maintained. The reaction vessel was a conventional coulometric titration cell painted black to exclude light and water-jacketed to control the temperature to ±0.1°. A Sargent Model IV Coulometric Current Source was used for the generation of bromine at a platinum anode. The working platinum cathode was isolated from the reaction solution by a glass frit. The anolyte and catholyte were identical in composition in a given run. The concentration of bromine as a function of time was monitored amperometrically using a rotating platinum electrode–sodium perchlorate salt bridge–sce circuit in conjuncton with a Leeds & Northrup Electrochemograph Type E. The potential (+0.168 V *vs.* sce) at which the current was monitored was determined from experimental current–voltage curves for the reduction of bromine. The linearity of the amperometric current as a function of bromine concentration was verified experimentally. Prior to initiating a kinetic run, the indicating electrode was pretreated according to the method described by Wooster, *et al.*[9] After pretreatment of the electrode and thermal equilibration of the solution, a kinetic run was initiated by oxidizing bromide ion at the rate of 1 μequiv-sec^{-1} with continuous stirring until the current in the indicating system reached *ca.* 40 μA. The concentration of Br_2 was approximately 10^{-4} M. Generation was discontinued, the solution was stirred with the magnetic stirrer for 30 sec to assure homogeneity, and the decay of the current was measured as a function of time. The solution was stirred except when a current measurement was being made. Currents were measured as deflections on the recorder chart, while times were measured with a precision timer. The measured currents were corrected for any residual currents after completion of the reaction. Pseudo-first-order rate constants were calculated from $-2.303 \times$ slope of log (corrected chart reading) *vs.* time. A typical plot is shown in Figure 1 confirming the pseudo-first-order character of the reaction. Check runs were made titrimetrically by the method of Perlmutter-Hayman and Weissmann[6] and spectrophotometrically. Spectrophotometric measurements were made using a thermostated Beckman DU spectrophotometer. In these runs, the spectrophotometric cell was filled almost to the top and one drop of concentrated bromine in the appropriate electrolyte solution was added, the solution was mixed, and the decrease in absorbance followed at either 270 or 350 nm. Pseudo-first-order rate constants were evaluated from $-2.303 \times$ the slope of log $(A_t - A_\infty)$ *vs.* time plots, where A_t is the absorbance at time t and A_∞ is the absorbance at infinite time.

For the amperometrically obtained data, second-order rate constants were obtained by plotting the pseudo-first-order rate constants *vs.* the 2-propanol concentration. A typical set of data is shown in Figure 2. Such plots were necessary because of the positive intercept, which indicated that a reaction independent of the alcohol concentration was occurring. Experiments on blank solutions

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[1] Work supported in part by VPI&SU-NASA Multidisciplinary Grant No. NGR47-004-006.

[2] Taken in part from the M.S. Thesis of L. G. B., Virginia Polytechnic Institute and State University, 1971.

[3] C. G. Swain, R. A. Miles, and R. F. W. Bader, *J. Amer. Chem. Soc.*, **83**, 1945 (1961).

[4] N. C. Deno and N. H. Potter, *ibid.*, **89**, 3555 (1967).

[5] N. Venkatasubramanian and V. Thiagarajan, *Tetrahedron Lett.*, **14**, 1711 (1968).

[6] B. Perlmutter-Hayman and Y. Weissmann, *J. Amer. Chem. Soc.*, **91**, 668 (1969).

[7] C. F. Wells, *Trans. Faraday Soc.*, **61**, 2194 (1965).

[8] F. H. Westheimer and A. Novick, *J. Chem. Phys.*, **11**, 506 (1943).

[9] W. S. Wooster, P. S. Farrington, and E. H. Swift, *Anal. Chem.*, **21**, 1457 (1949).

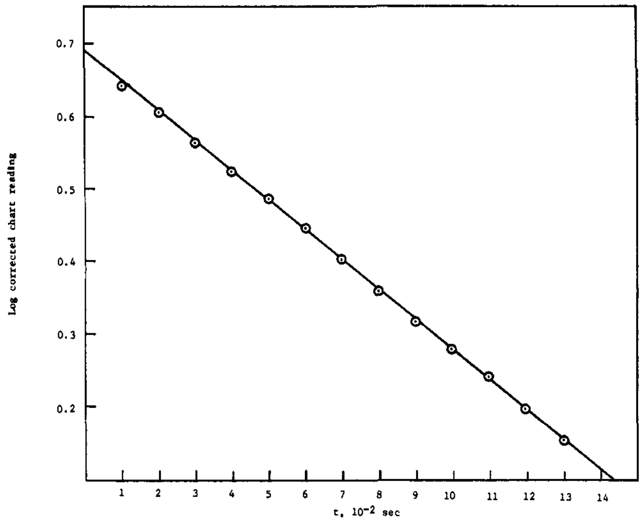

Figure 1. Typical first-order plot of the amperometric data: 0.1 M NaBr, 0.58 M $HClO_4$; 0.131 M 2-propanol, $\mu = 3.0\ M$, $T = 30°$.

containing no alcohol confirmed the first-order decay of the bromine concentration with time, as well as the magnitude of the intercept. The major factor determining the intercept is the volatilization of bromine into the air space above the solution in the cell. Reproducibility of the second-order rate constants determined in this manner was better than 10%. The addition of acetone to the solutions in quantities much larger than those produced during the runs had no effect upon the measured rates.

Determination of the Formation Constant of Tribromide Ion. The equilibrium constant, K_f, for the reaction $Br_2 + Br^- \rightleftharpoons Br_3^-$ was determined by measurements of the distribution of Br_2 between bromide ion containing solutions of the appropriate ionic composition and CCl_4. The solutions were sealed in glass bottles and stirred magnetically. Appropriate aliquots were removed from each phase and added to an iodide solution, and the resulting iodine was titrated with standard thiosulfate. Duplicate samples were taken after 30 min of additional stirring to ensure complete equilibration. Using the following definitions, $D = [Br_2]_o/[Br_2]_w + [Br_3^-]_w$, $K_f = [Br_3^-]/[Br_2][Br^-]$, and $K_D = [Br_2]_o/[Br_2]_w$, the relation between the experimental quantity, D, and K_f and K_D is $D = 1/K_D + K_f[Br^-]/K_D$. From plots of D *vs.* $[Br^-]$, both K_D and K_f can be evaluated. These plots are shown in Figure 3. Approximate values of K_f and K_D were obtained graphically; then using approximate K_f values, corrected values of $[Br^-]$ were obtained. These were utilized in a weighted least-squares computer program to obtain values of K_f and K_D. The values obtained are still subject to considerable uncertainty. Values of K_f and K_D were obtained for two series of solutions of 3.0 M total ionic strength: (a) 0.01 M $HClO_4$–variable $NaClO_4$–NaBr; and (b) 2.32 M $HClO_4$–variable $NaClO_4$–NaBr. The values of K_f and K_D for series a are 18 and 62 M^{-1}, respectively. For series b K_f is 20 M^{-1} and K_D is 40 M^{-1}. The relative uncertainty appears to be approximately 2%. The trend in K_f values with increasing $HClO_4$ is consistent with the measurements of the triiodide formation constant reported by Katzin and Gebert.[10]

Kinetic Results and Discussion

The Rate Law. Under the conditions studied, the rate for the oxidation of 2-propanol by Br_2 was found to be

$$\frac{-d[Br_2]_T}{dt} = k_m[Br_2]_T[ROH]$$

where $[Br_2]_T = [Br_2] + [Br_3^-]$ at fixed concentrations of Br^- and perchloric acid. The measured second-order rate constant, k_m, was found to be a function of both $[Br^-]$ and the stoichiometric acid concentration. Both of these effects are shown in Figure 4. The data shown for the pure $NaClO_4$–NaBr contained 0.01 M $HClO_4$ to suppress the hydrolysis of Br_2.

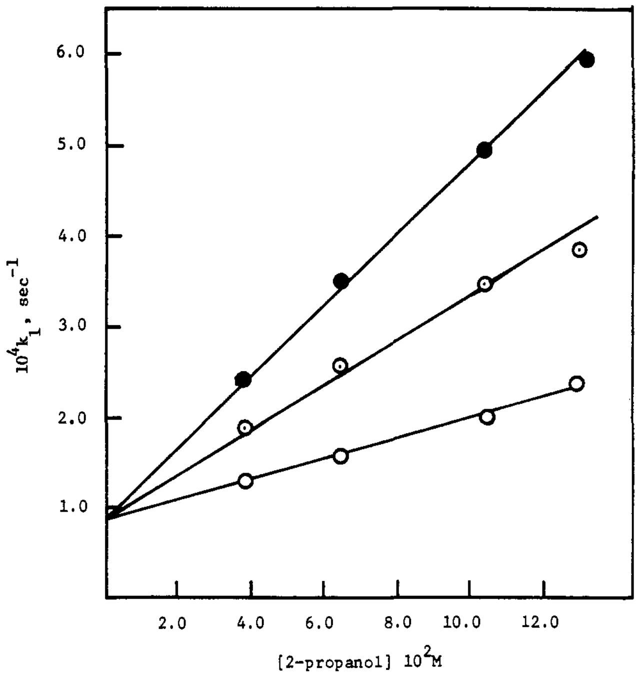

Figure 2. Evaluation of k_m: (●) $[Br^-] = 0.1\ M$; (⊙) $[Br^-] = 0.2\ M$; (○) $[Br^-] = 0.4\ M$.

The reduction in rate as the $[Br^-]$ is increased can be attributed to the formation of kinetically inactive Br_3^-. Using this interpretation, corrected rate constants were obtained by the relation $k_2' = k_m(1 + K_f[Br^-])$, where K_f is the formation constant of Br_3^-. For calculations of k_2', the experimentally determined values of 18 and 20 were used for the solutions of 3.0 M $NaClO_4$ and 2.32 M $HClO_4$–$NaClO_4$, respectively. Values of K_f as a function of acidity were obtained by linear interpolation.

The data shown in Figure 4 indicate an approximately linear reduction in rate constant as $HClO_4$ replaces $NaClO_4$ at constant total ionic strength. Within the expected experimental error the observed decrease can be described by several different empirical relations. For purposes of comparison with the data presented by Wells, a form of the rate law was assumed in which the protonation of 2-propanol was explicitly considered. It was found that k_2' could be described by $k_2 = k_2' \cdot (1 + K_c[H^+])$, where $K_c = [ROH_2^+]/[ROH][H^+]$ within the estimated error limits. This treatment of the data leads to the rate law

$$\frac{-d[Br_2]_T}{dt} = \frac{k_2[Br_2]_T[ROH]_T}{(1 + K_f[Br^-])(1 + K_c[H^+])}$$

where $k_2 = 1.96 \times 10^{-2}\ M^{-1}\ sec^{-1}$ and $K_c = 0.24\ M^{-1}$ at 30°. All data used are shown in Table I. The value of k_2 computed from the $NaClO_4$–NaBr solutions in the absence of substantial acid of $1.92 \times 10^{-2}\ M^{-1}\ sec^{-1}$ agrees well with that derived from the acid dependence data. This form of the rate law implies that the protonated alcohol is kinetically inactive.

Less extensive data were obtained at 25° and are shown in Table II. The values of k_2 and K_c obtained are $1.2 \times 10^{-2}\ M^{-1}\ sec^{-1}$ and $0.22\ M^{-1}$, respectively.

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[10] L. I. Katzin and E. Gebert, *J. Amer. Chem. Soc.*, 77, 5814 (1955).

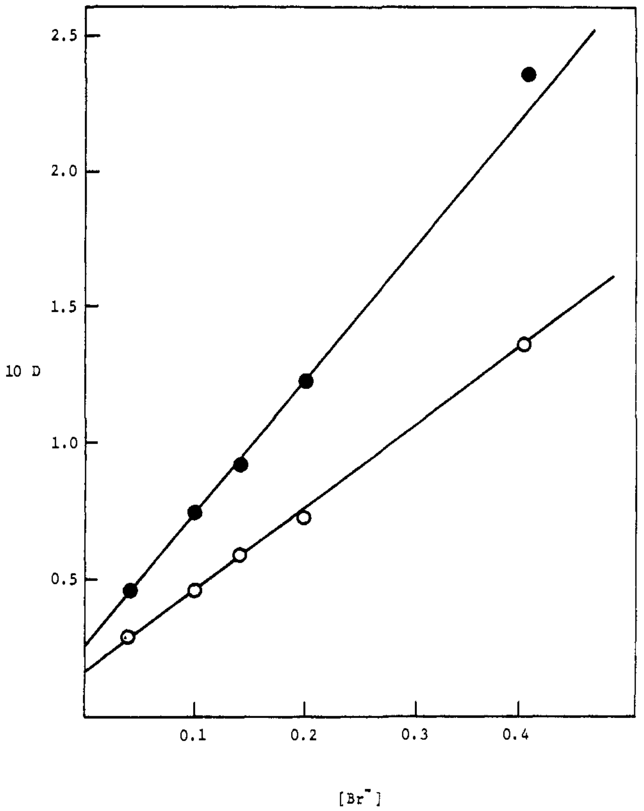

Figure 3. Graphical determination of K_f and K_D, μ = 3.0 *M*; (●) 2.32 *M* $HClO_4$; (○) 0.01 *M* $HClO_4$.

Table I. Kinetic Results at 30°, μ = 3.0 *M*

$[HClO_4]$, *M*	$[Br^-]$	10^3k_m, M^{-1} sec^{-1}	$10^2k_2'$, M^{-1} sec^{-1}
0.01	0.10	6.72	1.88
0.01	0.20	4.26	1.96
0.01	0.40	2.36	1.93
			Av 1.92 ± 0.03
0.58	0.10	6.34	1.81
0.58	0.20	3.64	1.71
0.58	0.40	2.05	1.72
			Av 1.75 ± 0.04
1.16	0.10	5.20	1.51
1.16	0.20	3.35	1.51
1.16	0.40	1.91	1.64
			Av 1.55 ± 0.03
2.32	0.10	3.90	1.17
2.32	0.20	2.42	1.21
2.32	0.40	1.25	1.13
			Av 1.17 ± 0.03

Table II. Kinetic Results at 25°, μ = 3.0 *M*

$[HClO_4]$, *M*	$[Br^-]$	10^3k_m, M^{-1} sec^{-1}	$10^2k_2'$, M^{-1} sec^{-1}
0.58	0.10	3.62	1.03
0.58	0.20	2.30	1.08
			Av 1.06 ± 0.03
1.16	0.10	3.15	0.91
1.16	0.20	2.05	0.98
			Av 0.95 ± 0.03

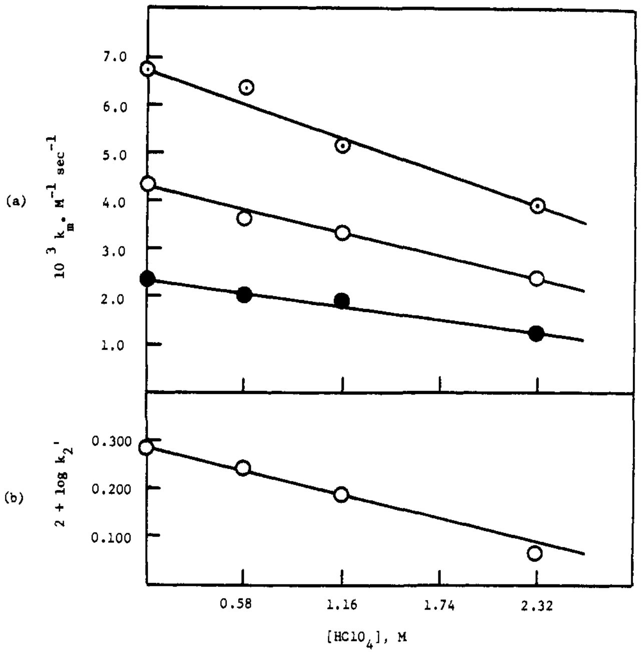

Figure 4. Effect of acidity on k_m and k_2': (a) (⊙) $[Br^-]$ = 0.1 *M*; (○) $[Br^-]$ = 0.2 *M*; (●) $[Br^-]$ = 0.4 *M*.

Other Results. Perlmutter-Hayman and Weissmann report $k_2 = 5.4 \times 10^{-3}$ M^{-1} sec^{-1} at 25° for solutions at 0.3 *M* KNO_3–KBr. The value determined here for k_2 at 25° is approximately twice that of Perlmutter-Hayman and Weissmann. Since there might be ambiguity associated with the measurement of the rate constants using the current-decay method, additional results were obtained by titrimetry, spectrophotometry, and current decay.

At 25°, titrimetric determination of k_2 was made at an ionic strength of 0.3 *M* maintained with KNO_3.[11] For comparison, spectrophotometric results were obtained at an ionic strength of 0.3 *M* maintained with KNO_3. These results are $k_{2(t)} = 5.8 \times 10^{-3}$ M^{-1} sec^{-1} and k_2(spec) = 6.2×10^{-3} M^{-1} sec^{-1}, in reasonable agreement with Perlmutter-Hayman and Weissmann. Spectrophotometry was used to determine k_2 in 3.0 *M* $NaClO_4$–NaBr–(0.01 *M* $HClO_4$) solutions at 25°. This value is 1.19×10^{-2} M^{-1} sec^{-1}, in excellent agreement with that determined by the current-decay method.

Finally, the current-decay method was used to evaluate both k_2 and K_f at 30° for 0.3 *M* KNO_3–KBr solutions. These values are 1.13×10^{-2} M^{-1} sec^{-1} and 20 M^{-1}, respectively. The value of K_f agrees reasonably well with that evaluated kinetically by Perlmutter-Hayman and Weissmann and the value of k_2 is consistent with the temperature dependence observed here.

Interpretation. The values of K_c found (0.24 M^{-1} at 30° and 0.22 M^{-1} at 25°) are in the range reported by Wells and could be used to support the arguments that: (1) 2-propanol is protonated in these solutions; and (2) that protonated 2-propanol is not easily oxidized by Br_2. However, comparison of our results with those of Perlmutter-Hayman and Weissmann indicates that on changing from 0.3 *M* KNO_3 to 3.0 *M* $NaClO_4$ there is a profound change in rate which can only be attributed to a salt effect. The distribution coefficients for Br_2 of K_D = 62 (3 *M* $NaClO_4$) and K_D = 40 (2.32 *M* $HClO_4$–0.68 *M* $NaClO_4$) show that the activity coefficient of Br_2 undergoes a significant change upon substitution

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[11] In our hands, rapid bromine loss required the same extrapolation technique as was used for the current-decay technique.

of $HClO_4$ for $NaClO_4$. For the general reaction between two molecules, the measured rate constant can be related to activity coefficients by $k_2 = k_0(\gamma_A\gamma_B/\gamma_\pm)$.[12] Assuming that the transition state is nonionic and that $\gamma_\pm$ approximates the activity coefficient of the alcohol leads to the relation that $k_2 = k_0\gamma_{Br_2}$. It is easily shown that the ratio of the experimentally determined distribution coefficients yields the ratio of the activity coefficients of Br_2 for the two salt solutions, 3.0 *M* $NaClO_4$ and 2.32 *M* $HClO_4$–0.68 *M* $NaClO_4$. This ratio is 1.55. The ratio of the rate constants for these solutions is 1.63. In view of both the assumptions and uncertainties involved, the two ratios are essentially the same, implying that the major factor determining the reduction in the second-order rate constant with increasing acidity is the effect of the change in medium on the activity coefficient of Br_2. While the activity coefficient of a nonpolar solute as a function of ionic strength can frequently be described by $\log \gamma = k_s\mu$,[13] the situation in mixed electrolyte solutions of constant ionic strength as a function of composition is less clear and quantitative. It is clear that if μ is constant and the k_s values for the electrolytes being considered are reasonably close, little effect will be observed upon the activity coefficient with replacement of one electrolyte for another. However, substantial differences in k_s values will materially alter the activity coefficient as one electrolyte is substituted for the other, and that at constant total ionic strength $\log \gamma$ may be approximately linear in the concentration of the electrolyte which is being substituted. The plot of $\log k_2'$ *vs.* $[HClO_4]$ shown in Figure 4b is linear and consistent with previously reported differences in the effect of $HClO_4$ and $NaClO_4$ on the activity coefficient of benzene.[14] On the basis of the results presented here, there would seem to be no necessity for the postulation of protonated 2-propanol and the effects observed can be described adequately by an activity coefficient effect.

While the uncertainties in the rate constants and the limited temperature range make meaningful calculations of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ impossible, $\Delta H^\ddagger$ can be crudely estimated as approximately 18 kcal and $\Delta S^\ddagger \cong -8$ eu in 3.0 *M* $NaClO_4$ solutions.

[12] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, Wiley, New York, N. Y., 1961, p 132.

[13] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd ed, Reinhold, New York, N. Y., 1958, p 532.

[14] W. F. McDevit and F. A. Long (*J. Amer. Chem. Soc.*, 74, 1774 (1952)) report from studies of the solubility of benzene in $NaClO_4$ solutions and $HClO_4$ solutions values of k_s of +0.119 and −0.041, respectively.

Interaction of Acylating Agents and Phosphorus(III) Sources. I. Intermediacy of Condensed Species in the Formation of Ethane-1-hydroxy-1,1-diphosphonic Acid

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Abstract: This work determines the main sequence of intermediates formed when acetylating agents react with phosphorus(III) compounds under anhydrous conditions. The capacity of the reactants to scavenge water is shown to be the driving force for such reactions. Under anhydrous conditions, the initial products are condensates; *i.e.*, two or more molecules of ethane-1-hydroxy-1,1-diphosphonic acid condensed *via* the removal of water. Five such condensates have been isolated and characterized. The existence of three others is inferred from ^{31}P nmr data. Three of the isolated condensates have been shown to be involved in the complex rearrangements which occur during reaction of acetyl groups and phosphorus(III) species. Interconversions among the isolated condensates are discussed. The condensed intermediates are quantitatively converted to $CH_3C(OH)(PO_3H_2)_2$ upon heating in water. One condensate not observed is the cyclic dimer containing a $\underline{\mathrm{C{-}O{-}P{-}C{-}O{-}P}}$ ring. This is thought to be due to the instability of such a diester relative to the C–O–C and P–O–P bonded condensates.

Chemistry is seldom as simple as it seems at first sight. A prime example of this is the preparation of ethane-1-hydroxy-1,1-diphosphonic acid (EHDP) from acetylating agents and phosphorus(III) sources. EHDP and its salts have been known since the classic studies of von Baeyer and Hofmann,[1] who correctly represented the structure of the acid as $CH_3C(OH)(PO_3H_2)_2$, calling it "acetodiphosphorous acid." The metal binding ability of EHDP, suggested by the studies of von Baeyer and Hofmann, has encouraged a closer examination of its preparation[2] and properties.[3]

Recently papers[4,5] have appeared describing cyclic condensates isolated from the reaction of acetylating agents with phosphorous acid, the usual reagents for EHDP synthesis. This prompts us to report our ex-

[1] H. von Baeyer and K. A. Hofmann, *Ber.*, **30**, 1973 (1897).

[2] (a) Henkel et Cie., Belgian Patents 619,619; 619,620; 619,621 (1962); (b) Albright and Wilson, Belgian Patent 672,168 (1966); (c) Procter and Gamble, U. S. Patents 3,366,675; 3,366,677; 3,400,147 (1968); Canadian Patents 770,173; 777,198 (1968); Monsanto, French Patents 1,521,961; 1,521,962; 1,521,963 (1968); and others.

[3] (a) Henkel et Cie., Belgian Patent 579,012 (1959); (b) *ibid.*, 591,066 (1960); (c) Procter and Gamble, U. S. Patent 3,159,581 (1964); and others.

[4] (a) B. Blaser, K.-H. Worms, H.-G. Germscheid, and K. Wollmann, *Z. Anorg. Allg. Chem.*, **381**, 247 (1970); (b) G. Brun and C. Blanchard, *C. R. Acad. Sci., Ser. C*, 272 (1970); *Chem. Abstr.*, **75**, 110372d (1971).

[5] Procter and Gamble U. S. Patents, 3,387,024; 3,400,151; 3,400,149 (1968); 3,621,081 (1971).

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