[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF ILLINOIS INSTITUTE OF TECHNOLOGY]

A Kinetic Study of the Hydrolysis of Trimetaphosphates[1,2]

BY ROBERT M. HEALY AND MARY L. KILPATRICK

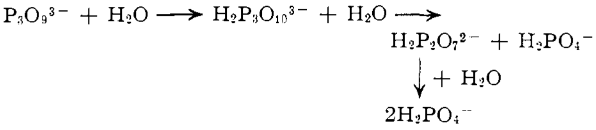
RECEIVED APRIL 6, 1955

Using P^{32} as an analytical tool, we have measured the rate of hydrolysis of sodium trimetaphosphate at temperatures from 50 to 70°, in solutions of such low trimetaphosphate concentration that the medium was sensibly unaffected by the progress of the reaction. The hydrolysis was rapid in acid solution, less rapid in alkaline solution, and negligible at *p*H 9. The kinetic data show that although $H_3P_3O_9$ has been classed as a strong tribasic acid, it is necessary to take into account the reactions of other trimetaphosphate species besides $P_3O_9^{3-}$: $HP_3O_9^{2-}$ and probably $H_2P_3O_9^-$, $NaP_3O_9^{2-}$, $CaP_3O_9^-$, etc. In alkaline solution reactivity increases with increase in (positive) charge of the species involved. The reaction was followed by precipitation of the products of hydrolysis with barium chloride at *p*H 10. Since precipitation occurred under constant conditions throughout an individual run, the coprecipitation of trimeta-, which was high, would have been without effect upon the first-order velocity coefficient. At *p*H 9, recommended by Jones, the precipitation of hydrolysis products was found to be incomplete, and the coprecipitation of trimetaphosphate not negligibly small.

Introduction

From its behavior upon electrometric titration, $H_3P_3O_9$ appears to be a strong tribasic acid in aqueous solution.[3] From its conductivity it appears to be a uni-trivalent strong electrolyte.[4] There is, however, evidence of formation of $HP_3O_9^{2-}$ as the concentration of acid increases,[4] and in the presence of alkali metal or alkaline earth salts, of formation of $NaP_3O_9^{2-}$, $CaP_3O_9^-$, etc.[4,5]

The hydrolysis may be written as



$$P_3O_9^{3-} + H_2O \longrightarrow H_2P_3O_{10}^{3-} + H_2O \longrightarrow H_2P_2O_7^{2-} + H_2PO_4^- \xrightarrow{+ H_2O} 2H_2PO_4^-$$

the products having been identified by Bell.[6] A few kinetic studies are reported in the literature; in them, the initial concentration of $H_3P_3O_9$ or $Na_3P_3O_9$ was of the same magnitude as that of the catalyzing acid or base, so that there was a considerable change in medium as the reaction progressed. For example, Brovkina[7] measured the rate in solutions initially *ca.* 0.1 *N* in NaOH and 0.1 *N* in $Na_3P_3O_9$, and reported first-order velocity coefficients

$$-\mathrm{d}[P_3O_9]/[P_3O_9]\mathrm{d}t = k \qquad (1)$$

(where $[P_3O_9]$ represents the stoichiometric concentration of trimetaphosphate) at 65, 75, 85 and 90°.

The present work was undertaken with P^{32} in order that such low phosphate concentrations might be used that the catalyst concentration and the medium would be sensibly unaffected by the progress of the reaction. It was assumed that, as in the cases of "hexameta-" and pyrophosphates,[8] there is in dilute solution no exchange between the hydrolysis product and the original phosphate species.

Experimental

Counting Apparatus. Thermostats.—These were the same ones used by Campbell and Kilpatrick.[9]

Materials.—Except as specified below, the reagents were C.P. or Analytical Reagent grade. Once-distilled water was used in preparing the solutions, since it gave the same results as redistilled in the kinetic experiments.

The radioactive phosphorus (P^{32}, S-3) was procured from the Oak Ridge National Laboratory as a solution of orthophosphate in dilute hydrochloric acid, of specific activity *ca.* 0.025 mg. P per mc. P^{32}.

The tetra-*n*-propylammonium hydroxide was obtained from Eastman Kodak Company as a 10% aqueous solution. Tetra-*n*-propylammonium perchlorate precipitated upon addition of perchloric acid to the solution of the base; it was purified by recrystallization from water, in which its solubility is *ca.* 0.01 *M* at 0 and 0.07 *M* at 70°. Sodium "hexameta-" and triphosphates were prepared in this Laboratory according to the directions of Jones[10] by Mr. H. Podall, whom we wish to thank. Inactive $Na_3P_3O_9$ for use as carrier was prepared by the thermal treatment of $NaH_2PO_4 \cdot H_2O$ which is described below.

Preparation of Radioactive Sodium Trimetaphosphate.—With some modifications, the directions of Jones[10] for preparing $Na_3P_3O_9$ by dehydration of sodium dihydrogen phosphate were followed in the preparation of the radioactive salt. Occasionally insoluble glasses were formed; their production seemed to be in line with some observations by Topley,[11] and in the later preparations, where the cooling period extended over 24 hours. they were not encountered.

The procedure finally adopted for small samples was as follows. A few drops of water and one of cresol red solution were put into a small platinum crucible. One or two mc. of the radiophosphate was added (usually less than 1 ml.), and the solution was adjusted to the yellow side of the endpoint (*p*H 7) with dilute NaOH and HCl. Then 50–100 mg. of $NaH_2PO_4 \cdot H_2O$ was added, and when it had dissolved, the solution was evaporated to dryness at 125°. The temperature of the furnace was next raised to 300°, where it was held for one hour, and to 610°, where it was held for three hours; then over a period of 24 hours it was gradually lowered to 390°, where it was held for 14 hours. Upon removal from the furnace the sample was dissolved in water, and the solution was transferred to a Pyrex flask, made just alkaline to phenolphthalein, diluted to 100 ml., and stored on ice.

It is to be expected that the small samples would contain appreciable amounts of hydrolysis products, since the radiophosphate solution was made more alkaline than required for conversion of H_3PO_4 to NaH_2PO_4; this was done to prevent formation of dehydration products of H_3PO_4. All samples were tested by determination of their rate of hydrolysis in dilute HCl solution at 70° and, as shown in Table II, the presence of hydrolysis products was found to have no effect upon the velocity constant. Samples 16 and 18, which contained relatively large amounts of hydrolysis

---

[1] Abstracted from the dissertation to be submitted by Robert Michael Healy to the Faculty of the Graduate School of Illinois Institute of Technology in Jan., 1956, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] Presented at the 125th Meeting of the American Chemical Society, Kansas City, Mo., March 31, 1954.

[3] (a) W. D. Treadwell and F. Leutwyler, *Helv. Chim. Acta*, **20**, 931 (1937); (b) H. Rudy and H. Schloesser, *Ber.*, **73**, 484 (1940); (c) W. Teichert and K. Rinman, *Acta Chem. Scand.*, **2**, 225 (1948).

[4] C. W. Davies and C. B. Monk, *J. Chem. Soc.*, 413 (1949).

[5] H. W. Jones, C. B. Monk and C. W. Davies, *ibid.*, 2693 (1949).

[6] R. N. Bell, *Ind. Eng. Chem.*, **39**, 136 (1947).

[7] I. A. Brovkina, *Zhur. Obshchei Khim.*, **22**, 1917 (1952).

[8] (a) R. C. Vogel and H. Podall, THIS JOURNAL, **72**, 1420 (1950); (b) D. E. Hull, *ibid.*, **63**, 1269 (1941).

[9] D. O. Campbell and M. L. Kilpatrick, *ibid.*, **76**, 893 (1954).

[10] L. T. Jones, *Ind. Eng. Chem., Anal. Ed.*, **14**, 563 (1942).

[11] M. Topley, *Quart. Rev.*, **3**, 345 (1949).

products, were treated as follows. The stock solution was divided into two parts, each part was evaporated in a vacuum desiccator to *ca.* one-tenth its volume, was made alkaline to thymolphthalein, and treated with $BaCl_2$ solution. The precipitate of barium phosphates was centrifuged out, the centrifugate was treated with an excess of Na_2CO_3 solution, and the $BaCO_3$ was centrifuged out. The centrifugate was then acidified and freed of carbonate by a stream of nitrogen.

Larger samples also were prepared. Here the amount of $NaH_2PO_4 \cdot H_2O$ used was 2–10 g. Hydrolysis products as a rule were not detectable by the usual qualitative tests on the larger samples, where the radiophosphate used in the preparation was a very small fraction of the total phosphate. The anhydrous trimeta- was in some cases dissolved in water, and crystallization brought about by the addition of saturated NaCl solution,[12] or of ethanol.[3c] When tests were made as described in the next section it was found that neither mode of purification brought the radioactivity of the barium precipitate below a few per cent., and it was concluded that coprecipitation of trimeta-, rather than the presence of hydrolysis products in the sample, was responsible.

The Analysis for Trimetaphosphate.—The analysis for trimetaphosphate was made by a modification of the method of Jones.[10] Jones determined trimeta- in mixtures of "hexameta-," trimeta-, tri-, tetra-, pyro- and orthophosphates in the following way. "Hexameta-" was precipitated from the freshly prepared solution at *p*H 2 with barium chloride. To the filtrate 1 *N* NaOH was added, with stirring, until the mixture remained definitely alkaline to phenolphthalein; the precipitated barium phosphates were filtered off, and the filtrate was boiled with nitric acid to convert trimeta- to orthophosphate for determination with ammonium molybdate reagent. In the absence of "hexameta-," the quantities recommended by Jones correspond to the following concentrations in the alkaline solution in which precipitation is to occur: total phosphate as P_2O_5, 0.005 *M;* $BaCl_2$, 0.03 *M*. It should be pointed out that the mixtures analyzed by Jones as a test of the method contained at most 6% of trimetaphosphate. Jones's method is based upon the assumptions that the precipitation of the other phosphates is complete at *p*H 9, and that coprecipitation of trimeta- is small enough to be neglected.

Although we found that under the conditions encountered in a hydrolyzing solution of trimetaphosphate these assumptions are not valid, we were able to adapt the method of Jones to serve our purpose. Some of the experiments leading to the procedure finally adopted are shown in Table I. In carrying out the tests, a 5-ml. aliquot of the solution to be analyzed was discharged into a 15-ml. centrifuge tube which already contained the carrier and, if necessary, enough acid or caustic to approximately neutralize the aliquot. Phenolphthalein or thymolphthalein was added, and the solution made just alkaline to the indicator. Next the $BaCl_2$ solution was added, with stirring, and in some cases the solution was readjusted to the alkaline side after formation of the precipitate. The mixture was centrifuged, the supernatant liquid was decanted, and the precipitate was washed twice with 1-ml. portions of a freshly made solution 3×10^{-4} *M* in $BaCl_2$, and just alkaline to the indicator. The precipitate was transferred to an aluminum counting pan with the aid of a medicine dropper and a minimum amount of water, and toward the end two drops of 0.1 *M* acid were used, with water, to clean the sides of the tube completely. A few drops of alcohol run onto the slurry gave an even distribution of the precipitate over the pan. The total radioactivity was determined by counting the evaporate of an aliquot of the original solution, or by evaporating the centrifugate, plus washings, and adding the count to that of the precipitate. Counting was carried out, except in a few cases, to a 0.9 error of 1%, or more than 27,000 counts.

TABLE I

THE COPRECIPITATION OF TRIMETAPHOSPHATE, AND THE EXTENT OF PRECIPITATION OF ITS HYDROLYSIS PRODUCTS, UNDER VARIOUS CONDITIONS

Sample	*p*H	$BaCl_2$, *M*	% of total activity in ppt. from $Na_3P^*{}_3O_9$ soln.	Soln. of hydrolysis products
15	10^{a}	0.03	5.2	
15	10^{a}	.05	5.1^{b}	
10	10^{n}	.1		95 ± 3 $(1:4:3)^{c}$
15	9^{d}	.03	11.6	
10	9^{d}	.03		98 ± 1 (0:0:1)
15	9^{d}	.3	14.1	
$H_3P^*O_4$	9^{d}	.3		98.5 ± 0.1 (0:0:1)
15	10^{d}	.3	16.4	
15	10^{d}	.3		99.7 ± 0.1 $(30:5:3)^{c}$
$H_3P^*O_4$	10^{d}	.3		99.6 ± 0.1 (0:0:1)

[a] Before addition of $BaCl_2$. [b] Done 20 days after experiment 1. [c] [tri-]:[pyro-]:[orthophosphate], estimated from the results of Bell.[6] [d] Solution readjusted to alkaline side after formation of precipitate.

The first column of Table I gives the source of the radioactive phosphate. Sample 10 was prepared from 2 g. of $NaH_2PO_4 \cdot H_2O$ and 0.8 mc. of radiophosphate; sample 15 from 0.10 g. and 1.0 mc. The $H_3P^*O_4$ solution used in experiments 7 and 10 was diluted radiophosphate solution, acidified and boiled to ensure complete conversion to orthophosphate. The fourth column gives the percentage of the total activity found in the barium precipitate from a freshly prepared solution of $Na_3P^*{}_3O_9$, or in the case of sample 15 from a solution prepared by dilution of the stock solution, in which no measurable hydrolysis occurred over a period of three weeks (*cf.* experiments 1 and 2). In experiment 3 $Na_3P^*{}_3O_9$ was dissolved in 0.25 *M* NaOH and the solution kept at 100° for 17 hours; from the work of Bell[6] it can be seen that the resulting solution would contain tri-, pyro- and orthophosphates only, and that the relative concentrations would be [tri-]:[pyro-]:[ortho-] = 1:4:3, approximately. In experiment 5 the solution of $Na_3P^*{}_3O_9$ was acidified and heated; in experiment 9, it was made 0.25 *M* in NaOH and kept at 100° for one hour. In the experiments carried out with sample 15, the initial concentration of $Na_3P^*{}_3O_9$ was 1×10^{-4} *M;* in those with sample 10, *ca.* 4×10^{-4} *M*, and in experiments 7 and 10 the concentration of $H_3P^*O_4$ was 1×10^{-8} *M*. In most of the experiments a mixture of inactive ortho-, pyro-, tri- and trimetaphosphates was used as carrier, at concentrations of 5, 2, 2 and 2×10^{-3} *M*, respectively. In experiments 3 and 5 the carrier contained no trimetaphosphate.

It will be seen that in experiment 5, carried out under the conditions used by Jones, precipitation of orthophosphate was not complete. This experiment was performed after it had been found, in early kinetic runs carried out in acid solution, that toward the end of the run the activity of the barium precipitate passed through a maximum and thereafter decreased. If the centrifugate from the barium precipitate was treated with $(NH_4)_2MoO_4$ reagent,[9] and the activity of the phosphomolybdate precipitate added to that of the barium precipitate, the sum increased with time and approached a constant value. The conditions for formation of the barium precipitate were then made more drastic, in the hope of avoiding two precipitations, and it was found that under the conditions of experiments 8–10 of Table I precipitation of hydrolysis products was satisfactory, 99.7% of the activity appearing in the barium precipitate after conversion to tri-, and 99.6% after conversion to orthophosphate. But as the *p*H and the molarity of the $BaCl_2$ were increased, there was a corresponding increase in the activity of the barium precipitate from a $Na_3P^*{}_3O_9$ solution, indicating an increase in coprecipitation of trimetaphosphate (*cf.* column 4 of Table I).

The results given in Table I enable one to explain some observations made by Dewald and Schmidt,[13] who analyzed phosphate mixtures (including mixtures rich in trimeta-) by Jones' method. They found that in the presence of much pyro- the analysis for trimeta- was low, and that in the presence of ortho- it was erratic. Coprecipitation of trimeta- would lower the analysis, incomplete precipitation of orthophosphate would raise it, and the relative importance of the two errors would depend on the composition of the solution.

The Kinetic Experiments.—Although there is coprecipitation of trimeta- with the other barium phosphates, it is possible to evaluate the velocity coefficient from the counting data, provided the precipitation of the hydrolysis prod-

---

(12) R. N. Bell, "Inorganic Syntheses," Vol. III, McGraw-Hill Book Co., New York, N. Y., 1950, p. 104.

(13) W. Dewald and H. Schmidt, *Z. anal. Chem.*, **137**, 178 (1952).

ucts is complete, and provided the percentage of trimeta which coprecipitates remains constant throughout an individual run.

Let $\bar{A}$ be the radioactivity of the barium precipitate, corrected for coincidence loss, background, and decay; when all the trimeta- has hydrolyzed, $\bar{A}$ becomes $\bar{A}_\infty$. Let $\bar{A}_{\text{tm}}$ be the activity of the trimeta-, and X the fraction of the trimeta- which coprecipitates. Owing to coprecipitation of trimeta-, $\bar{A}$ is too high by $X\bar{A}_{\text{tm}}$, so $\bar{A}_{\text{tm}} = \bar{A}_\infty - (\bar{A} - X\bar{A}_{\text{tm}})$, or $\bar{A}_{\text{tm}} = (\bar{A}_\infty - \bar{A})/(1 - X)$. If the formation of the barium precipitate occurs under conditions which remain constant throughout an individual run, it would be expected that X would be constant throughout the run, that $\bar{A}_{\text{tm}}$ would be proportional to $(\bar{A}_\infty - \bar{A})$, and that a plot of log $(\bar{A}_\infty - \bar{A})$ *vs.* time would yield a straight line, since the reaction has been reported[7] to be of the first order with respect to trimetaphosphate. Figures 1 and 2 show our results for two typical runs. The solutions were at the start 9×10^{-5} and 1.5×10^{-5} M, respectively, in $Na_3P^*_3O_9$.

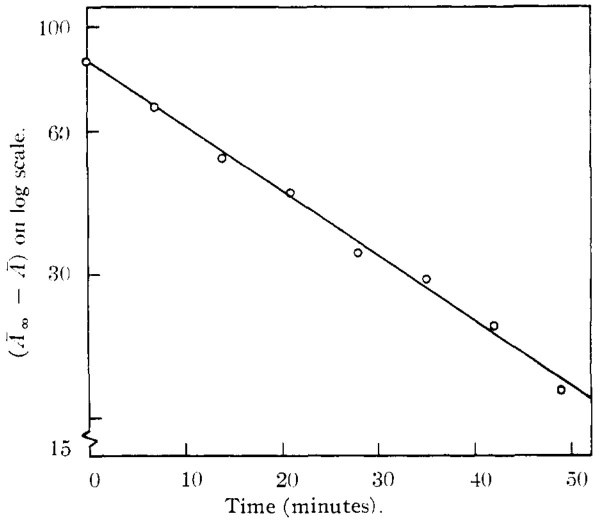


Fig. 1.—The reaction in 0.0200 M HCl solution at 69.40°.

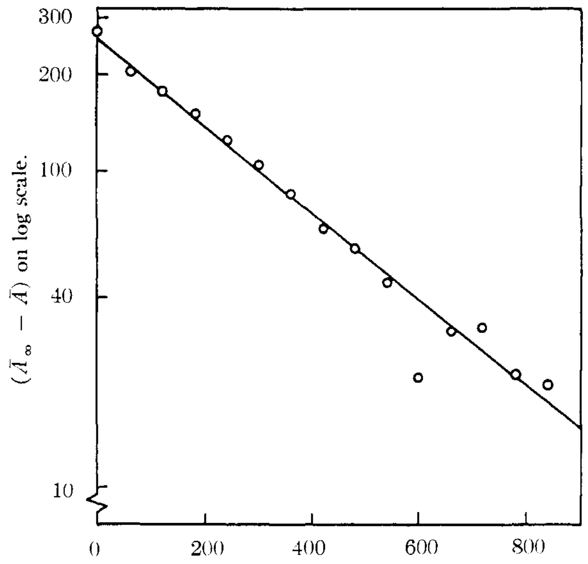


Fig. 2.—The reaction in 0.1750 M NaOH solution at 49.89°.

The linear relationships found here, as in most of the experiments, support the assumption that in any run the per cent. of trimeta- coprecipitating remains constant. The first-order velocity coefficient k was obtained from the slope of the line, usually determined by the method of least squares. Scattering of the points often appeared toward the end (*cf.* Fig. 2, where the reaction was 90% complete at 735 minutes). However, the error in k due to error in X becomes less serious as the reaction progresses.

As a further test of the effect of the high coprecipitation of trimeta- under the conditions of experiments 8–10 of Table I, a pair of duplicate runs was carried out, the reaction being followed in one member of the pair by precipitating the hydrolysis products under the conditions of experiments 8–10, and in the other by making two precipitations, one with $BaCl_2$ under the conditions of experiment 2 of Table I, the other with $(NH_4)_2MoO_4$ reagent, as described above. There was good agreement between the velocity coefficients obtained by the two methods, and the single precipitation with $BaCl_2$ at pH 10 was employed in the remainder of the work.

The procedure used in carrying out a kinetic run was as follows. The solution was prepared, at the temperature of the experiment, from measured volumes of $Na_3P^*_3O_9$ solution and standard acid or base and, in some cases, a known amount of salt. The reaction vessel was usually a 100-ml. Pyrex volumetric flask. Aliquots were removed at selected times with a 5-ml. pipet and run into 15-ml. centrifuge tubes set in cracked ice. Each tube already contained (1) 1 ml. of carrier solution which was 0.045 M in ortho-, and 0.015 M in pyro-, tri- and trimetaphosphates, (2) enough acid or base to approximately neutralize the aliquot, and (3) three drops of 0.001 M thymolphthalein solution. The acidity was carefully adjusted to the blue color of the indicator end-point with 0.1 M NaOH and HCl, and 2.5 ml. of 1.0 M $BaCl_2$ was added, with stirring, after which the solution was again brought to a definite blue. The solution was then centrifuged, the supernatant liquid decanted, and the precipitate washed and counted in the manner already described. The value of $\bar{A}_\infty$ was usually obtained by removing three aliquots, adding to each 0.5 ml. of concentrated hydrochloric acid, and placing the tubes in boiling water for 45 minutes to drive the reaction to completion; after this, the analysis was carried out in the same way as for the other samples. Whenever a sample was to stand for some time before analysis, it was brought to the thymolphthalein end-point and, for long standing, was frozen.

The Effect of Surface.—Campbell and Kilpatrick found in their study of the hydrolysis of pyrophosphates that, in HCl and $HClO_4$ solutions less concentrated than 0.04 M, curvature appeared in the plots of log ($Zn_2P_2O_7$ radioactivity) *vs.* time. The curvature was more pronounced at 70 than at 50 and 60°; it was about the same when the reaction vessel was polyethylene, as when it was glass; and it could be eliminated by adding inactive pyrophosphate to bring the initial concentration in the kinetic run up to 2×10^{-4} M. In the case of trimeta-, curvature was not observed at 70°

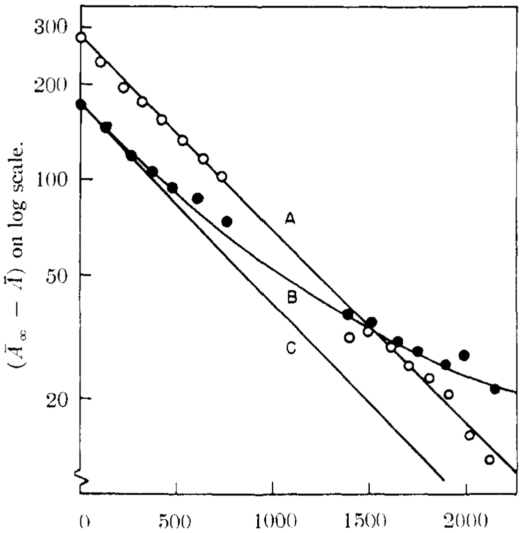


Fig. 3.—The effect of the container material on the linearity of the plot for the reaction in 0.00693 M HCl at 49.89°: A, polyethylene; B, glass; C, the initial slope of curve B.

except as noted below, but at 50 and to a lesser extent at 60° there was curvature in the plot of log $(\bar{A}_\infty - \bar{A})$ *vs.* time when the reaction vessel was glass and the acid concentration as low as 0.007 M (*cf.* curve B of Fig. 3). One difference between the two hydrolyses is that at the acid concentrations involved the reaction of trimeta- is *ca.* 10 times as fast as that of pyrophosphate, so that there is more opportunity for side reactions like adsorption to make themselves felt in the case of pyrophosphate.

A number of tests to determine the effect of surface were made by carrying out the reaction at 70° in 0.01 M HCl under various conditions. When the glass surface was increased by a factor of 5 by insertion of pieces of rod with fire-polished ends, curvature appeared in the log $(\bar{A}_\infty - \bar{A})$ *vs.* time plot, and the initial slope was about 3 times as large as in the absence of the pieces of rod. When a run was carried out in a 1000-ml. Pyrex flask, and care was taken to remove the aliquots from the center of the solution, the value of k was the same, within the experimental error, as obtained using 100-ml. Pyrex flasks, or 250-ml. polyethylene bottles, and the plots were linear in all cases. (For the technique used when a polyethylene bottle served as reaction vessel, see Campbell and Kilpatrick).[9] When the polyethylene surface was increased several-fold by insertion of strips of the material, there was no effect upon k.

Since there was no detectable effect of excess polyethylene surface at 70°, the reaction in 0.007 M HCl was remeasured at 50° using a polyethylene container; the data obtained are shown as curve A of Fig. 3. It will be seen that within the accuracy of the measurements there is no curvature, and that the slope of the line agrees with the initial slope of curve B. Attempts to eliminate the curvature found with the glass vessel by increasing $[P_3O_9]_i$ to 2×10^{-4} M, by addition of inactive salt, were unsuccessful.

The Kinetic Results

In Solutions of Strong Acids.—In Table II are collected the results of experiments carried out at 69.40° with samples of $Na_3P^*_3O_3$ prepared over a period of several years, and containing various amounts of hydrolysis products. The amount of hydrolysis products in the sample may be estimated roughly from the data in the second column, which give the per cent. of the total activity found in the barium precipitate when the sample was tested under the conditions of experiment 2 of Table I. The fourth column gives the initial stoichiometric molarity of trimetaphosphate, and the last column gives the second-order velocity coefficient $k_H = k/[H^+]$ where $[H^+]$ has been taken equal to the concentration of acid. It will be seen that k_H is constant, within the experimental error, over the range of acid concentration employed. In the later part of the work k_H was used as a criterion of acceptability of each preparation of $Na_3P^*_3O_9$; thus sample 18, which gave a low k_H, was found to contain "hexameta-" (3.6% of the total activity coming down with $BaCl_2$ at pH 2)[8a,10] and was discarded.

TABLE II

KINETIC EXPERIMENTS IN HCl SOLUTION AT 69.40°

Sample				
No.	% activity in Ba ppt.[c]	HCl, M	$[P_3O_9]$ ×	$k_H = k/[H^+]$ (mole/l.)$^{-1}$ min.$^{-1}$
15	5.2	0.00462	4×10^{-5}	1.50
15	5.2	.00462	4×10^{-5}	1.53
16a	8.0[d]	.00462	4×10^{-5}	1.52
16a	8.0[d]	.00462	1×10^{-5}	1.52
23	8.0	.00472	2×10^{-5}	1.45
24	20	.00472	2×10^{-5}	1.63
20	7.8	.00506	2×10^{-6}	1.47
16b	5.3[d]	.00693	1×10^{-5}	1.64
18a	10[e]	.00943	2×10^{-5}	1.31[f]
19	30	.00943	5×10^{-6}	1.46
19	30	.00943	5×10^{-6}	1.50
20	7.8	.00943	8×10^{-6}	1.54
22	25	.00943	8×10^{-6}	1.50
24	20	.00943	3×10^{-5}	1.48
20	7.8	.00943	5×10^{-5}	1.47[g]
14	7.1	.01062	2×10^{-4}	1.61
17	8.0	.01084	4×10^{-6}	1.61
20	7.8	.01500	9×10^{-5}	1.46[g]
17	8.0	.02000	9×10^{-5}	1.57

Av. 1.53 ± 0.05

[c] Under the conditions of experiment 2 of Table I. [d] After purification; initial value, 60%. [e] After purification; initial value, 75%. [f] Omitted from average. [g] Polyethylene vessel used.

The results obtained at 69.40° in acid–salt mixtures are given in Table III. Experiments 1–4 of Table III show that the rate of reaction is about the same in perchlorate solutions as in chloride. Experiments 6, 7 and 8 show that k_H increases as $[H^+]$ increases when the ionic strength is held constant by the addition of $(n\text{-Pr})_4NClO_4$. Experiment 6 and experiment 13, and experiment 5 and experiments 11 and 12 (interpolated) show that at $M_{HCl} = 0.00472$, the hydrolysis is slower in the presence of Na^+ than in the presence of $(n\text{-Pr})_4N^+$.

Experiments without added salt were also carried out at 59.95 and 49.89° at $M_{HCl} = 0.00693$, 0.01084 and 0.02000, respectively, with $[P_3O_9]_i$ ranging from 4×10^{-6} to 3×10^{-5} M. The velocity coefficients found were combined with the corresponding coefficients from Table II to obtain the parameters of the Arrhenius equation shown in Table V.

In Solutions of Strong Bases.—The results obtained in NaOH solution at 69.40° are given in Table IV, where the last column contains the second-order velocity constant $k_{OH} = k/[OH^-]$, $[OH^-]$ being taken equal to the concentration of base. For the runs without added salt log k_{OH} was plotted *vs.* $\sqrt{M_{NaOH}}$, and from the plot k_{OH} was estimated to be 0.3×10^{-2} at $M_{NaOH} = 0$, and 0.5×10^{-2} at $M_{NaOH} = 0.001$. Experiments 3–7 show that, at constant $[Na^+]$ and constant μ, Cl^- and OH^- have about the same effect on k_{OH}. On the other hand, when the ionic strength is increased by the use of anions of higher valence, k_{OH} decreases (*cf.* experiments 9–11). Experiments 12 and 13 are the last of a series of runs carried out to determine the effect of divalent cations. In the earlier experiments with alkaline earth chlorides there was a decrease in the activity of the solution with time, probably owing to precipitation of the salts of hydrolysis products, and in the later experiments lower concentrations of both base and chloride were employed. There was no decrease in the activity of the solution when aliquots were removed as the reaction proceeded in experiments 12 and 13; the curvature in the log $(\bar{A}_\infty - \bar{A})$ *vs.* time plots is probably to be attributed to uptake of CO_2.

Experiments also were carried out in $(n\text{-Pr})_4NOH$ solution over the range 0.05–0.17 M. The values of k_{OH} obtained lay below those in NaOH solution, the difference appearing to increase with concentration of base. However, since different lots of the base gave somewhat different results, numerical

TABLE III

KINETIC EXPERIMENTS IN ACID-SALT MIXTURES AT 69.40°

Acid	Acid, M	Salt	Salt, M	$[P_3O_9]_i$	μ	k_H, (mole/l.)$^{-1}$ min.$^{-1}$
HCl	0.00462	NaCl	0.0151	1×10^{-5}	0.020	0.883
$HClO_4$	.00474	$NaClO_4$	.0151	1×10^{-5}	.020	0.937
HCl	.00472	NaCl	.0400	3×10^{-5}	.045	.703
$HClO_4$	.00472	$NaClO_4$	.0400	3×10^{-5}	.045	.725
HCl	.00472	$(n\text{-Pr})_4NClO_4$	.0200	3×10^{-5}	.025	1.03
HCl	.00472	$(n\text{-Pr})_4NClO_4$	.0400	3×10^{-5}	.045	0.790
HCl	.00943	$(n\text{-Pr})_4NClO_4$	.0356	3×10^{-5}	.045	0.865
HCl	.01886	$(n\text{-Pr})_4NClO_4$	.0265	3×10^{-5}	.045	1.12
HCl	.00943	$CaCl_2$	1.03×10^{-4}	3×10^{-5}	.010	1.32
HCl	.00472	NaCl	.0075	4×10^{-6}	.012	1.35
HCl	.00462	NaCl	.0151	1×10^{-5}	.020	0.883
HCl	.00472	NaCl	.0300	5×10^{-6}	.035	.727
HCl	.00472	NaCl	.0400	3×10^{-5}	.045	.703
HCl	.00462	NaCl	.0494	5×10^{-6}	.055	.567
HCl	.00470	NaCl	.0493	6×10^{-5}	.055	.564[a]
HCl	.00462	NaCl	.0935	5×10^{-6}	.098	.459

[a] Polyethylene vessel used.

TABLE IV

KINETIC EXPERIMENTS IN NaOH SOLUTION AT 69.40°

NaOH, M	Salt	Salt, M	$[P_3O_9]_i$	μ	10^2k_{OH}, (mole/l.)$^{-1}$ min.$^{-1}$
0.0100			4×10^{-5}	0.010	1.33
.0489			2×10^{-4}	.049	3.82
.1000			1×10^{-5}	.100	5.80
.0300	NaCl	0.0700	3×10^{-5}	.100	5.43
.1250			2×10^{-5}	.125	6.63
.1250			6×10^{-5}	.125	6.96[a]
.0300	NaCl	.0950	3×10^{-5}	.125	6.60
.1750			8×10^{-5}	.175	7.43
.0196	KCl	.0784	1×10^{-5}	.098	6.34
.0196	K_2SO_4	.0392	1×10^{-5}	.137	5.31
.0196	$K_3Fe(CN)_6$	.0262	1×10^{-5}	.177	4.95
.0010	$BaCl_2$	5.0×10^{-5}	4×10^{-6}	.001	19[b]
.0010	$CaCl_2$	1.0×10^{-4}	6×10^{-6}	.001	180[b]

[a] Polyethylene vessel used. [b] Calculated from initial slope.

values of k_{OH} are not reported. Replacement of Na^+ by $(n\text{-Pr})_4N^+$ in $(n\text{-Pr})_4NOH$–$(n\text{-Pr})_4NCl$–NaCl mixtures caused a decrease in k_{OH}.

Three experiments in NaOH solution were carried out at 59.95°, and three at 49.89°. The values of M_{NaOH} employed were 0.0489, 0.1250 and 0.1750, respectively, and $[P_3O_9]_i$ ranged from 8×10^{-6} to 2×10^{-5} M. The results are summarized in Table V.

The Water Reaction.—Assuming that there is an uncatalyzed reaction of trimetaphosphate with the solvent, one can write for the first-order velocity coefficient, in a very dilute solution of NaOH

$$k = k_0 + k_{OH}[OH^-] + k_H[H^+]$$

On substituting $k_{OH} = 3 \times 10^{-3}$ and $k_H = 1.5$ (mole/l.)$^{-1}$ min.$^{-1}$ and $K_w = 2 \times 10^{-13}$, one calculates that at 69.40° the minimum rate should be found at $[H^+] = 2 \times 10^{-8}$ M, and that in 1×10^{-5} M NaOH solution 0.1% of the trimetaphosphate should hydrolyze in 10 days in the absence of a water reaction.

Two-hundred and fifty ml. of solution 4.5×10^{-6} M in $Na_3P^*_3O_9$ was brought by addition of dilute caustic to *p*H 9.3, as measured with a Beckman *p*H meter, at room temperature. It was then kept at 69.40° for 17 days, samples being removed at intervals for determination of *p*H, and for analysis. By the end of the period the *p*H had fallen to 8.7, and from the log $(\bar{A}_\infty - \bar{A})$ *vs.* time plot k was estimated to be somewhat less than 4×10^{-6} min.$^{-1}$. In a second experiment a solution initially 1.5×10^{-5} M in $Na_3P^*_3O_9$, 0.1 M in NaCl, and 0.01 M in Na_2HPO_4 was kept for 8 days at 69.40°; here k was estimated to be less than 3×10^{-5} min.$^{-1}$. Thus in acid solution, at $[Na^+] \simeq 0.1$ M, any uncatalyzed reaction with the solvent would contribute less than 1.5% of the specific rate (*cf.* experiment 16 of Table III), and in alkaline solution less than 2% (*cf.* experiment 4 of Table IV).

Discussion

Any scheme proposed for the reaction must be in agreement with the following observations:

(1) In solutions of HCl, without added salt, the second-order constant k_H exhibits no electrolyte effect.

(2) On the other hand, k_H decreases when the ionic strength is increased by addition of $(n\text{-Pr})_4NClO_4$ or $NaClO_4$ or NaCl, at constant $[H^+]$.

(3) When the ionic strength is maintained constant by addition of $(n\text{-Pr})_4NClO_4$, k_H increases with increase in $[H^+]$.

(4) At a given acid concentration and ionic strength, k_H is higher in the presence of $(n\text{-Pr})_4N^+$ than in the presence of Na^+.

(5) In solutions of NaOH, the second-order constant k_{OH} increases with increase in M_{NaOH}.

(6) On the other hand, k_{OH} decreases when the ionic strength is increased by the presence of polyvalent anions, the cation concentration and M_{NaOH} remaining constant.

(7) In $(n\text{-Pr})_4NOH$ solution k_{OH} is smaller than in NaOH solution, and in $(n\text{-Pr})_4NOH$–$(n\text{-Pr})_4NCl$–NaCl mixtures replacement of Na^+ by $(n\text{-Pr})_4N^+$ causes a decrease in k_{OH}.

(8) Very small amounts of calcium (or barium) chloride cause a great increase in the rate of hydrolysis in basic solution; in acid solution, they cause a small decrease in rate.

(9) The water reaction is negligible under the conditions of the present experiments.

The kinetic results in acid solution cannot be accounted for on the basis of a single reaction between $P_3O_9^{3-}$ and H_3O^+, since a reaction between ions of opposite sign is characterized by a negative primary kinetic salt effect,[14] and at low ionic strengths one would expect the effects of HCl, NaCl and $(n\text{-Pr})_4NClO_4$ on k_H to be about the same. Similarly, the kinetic results in alkaline solution cannot be accounted for on the basis of a single reaction between $P_3O_9^{3-}$ and OH^-. The great increase in rate in the presence of Ca^{++} or Ba^{++}, in alkaline solution; the difference between the effects of $(n\text{-Pr})N^+$ and Na^+; the decrease in k_{OH} with increase in μ observed in the presence of polyvalent anions—all argue against the existence of a single reaction between $P_3O_9^{3-}$ and OH^-. Instead, it appears that several trimetaphosphate species are participating in the measured reaction.

Let us assume that there is no formation of $(n\text{-Pr})_4NP_3O_9^{2-}$,[15] but that there is, at the temperatures of the experiments, formation of $HP_3O_9^{2-}$, $NaP_3O_9^{2-}$, $CaP_3O_9^-$, etc., as reported by Davies and co-workers for 25°, and that these ions, as well as $P_3O_9^{3-}$, are possible reactants. From the experiments on the water reaction, however, it can be concluded that the uncatalyzed reactions between $P_3O_9^{3-}$ and H_2O, and between $NaP_3O_9^{2-}$ and H_2O, are negligible here; the same is probably true of the uncatalyzed reactions of the complexes formed by the other metal cations.

Let us denote by K_j the jth dissociation constant of $H_3P_3O_9$, and to the reaction between $H_3P_3O_9$ and H_2O assign the velocity coefficient k_1, to that between $H_3P_3O_9$ and H_3O^+, the coefficient k_1', and so on. Then in dilute acid solution, in the absence of complexing metal ions, hydrolysis might take place *via* the reactions

$$HP_3O_9^{2-} + H_2O \xrightarrow{k_3} \text{Products}$$

$$HP_3O_9^{2-} + H_3O^+ \xrightarrow{k_3'} \text{Products}$$

$$P_3O_9^{3-} + H_3O^+ \xrightarrow{k_4'} \text{Products}$$

for which the second-order velocity coefficient is found to be

$$k_H = [k_3 + k_4'K_3 + k_3'[H^+]\}/[k_3 + [H^+]\} \quad (2)$$

It is assumed, in deriving (2), that K_1 and K_2 are so large, and $[H^+]$ so small, that the reactions of $H_2P_3O_9^-$ and $H_3P_3O_9$ may be neglected. In the presence of Na^+ hydrolysis might also take place *via* the reaction

$$NaP_3O_9^{2-} + H_3O^+ \xrightarrow{k'_{Na}} \text{Products}$$

If (2) applies, it follows that in acid solution at constant μ, in the absence of Na^+, k_H will increase with $[H^+]$ provided $k_3'K_3 > (k_3 + k_4'K_3)$. And when $(n\text{-Pr})_4N^+$ is replaced by Na^+ at constant $[H^+]$ and μ, it can be shown that k_H will decrease provided $k'_{Na} < (k_H)_{Na\ =\ 0}$, the second-order constant for the sodium-free solution.

Turning to the question as to why k_H exhibits no electrolyte effect in acid solution, in the absence of salt, let us examine (2) further. With increase in μ K_3 would increase, in dilute solution, and k_3' and k_4' would decrease; the change in k_3 would be expected to be small.[14] Moreover, since $k_4' = (k_4')_0 f_1 f_3/f_2$, and $K_3 = (K_3)_0/(f_1 f_3/f_2)$, where $(k_4')_0$ and $(K_3)_0$ are the limiting values of k_4' and K_3, respectively, and the f's are the activity coefficients of ions of valence shown by the subscript, $k_4'K_3$ should be nearly constant. Both numerator and denominator in (2) would increase with increase in M_{HCl}, and the observed constancy of k_H might thus be due to a balancing of the increase in $[HP_3O_9^{2-}]$ against the various electrolyte effects. On the other hand, with increase in $[H^+]$ the hydrolysis of $H_2P_3O_9^-$ might become a factor, so that

$$k_H = \frac{(k_4'K_3 + k_3) + (k_3' + k_2/K_2)[H^+] + (k_2'/K_2)[H^+]^2}{K_3 + [H^+] + [H^+]^2/K_2} \quad (3)$$

An argument in favor of the participation of $H_2P_3O_9^-$ is to be found in experiments 6, 7 and 8 of Table III. If (2) applies

$$(\partial k_H/\partial[H^+])_\mu = [k_3'K - (k_3 + k_4'K_3)\}/\{K_3 + [H^+]\}^2$$

so the slope of the curve obtained on plotting k_H *vs.* $[H^+]$ should decrease with increasing $[H^+]$. Davies and Monk found $(K_3)_0$ to be 0.009 at 25°. If K_3 is taken as $(K_3)_0/(f_1 f_3/f_2) = 0.009/0.25 = 0.036$ at $\mu = 0.05$, at 70°, the slope should decrease by 45% as $[H^+]$ increases from 0.005 to 0.02 *M;* actually, k_H for the highest $[H^+]$ lies well above the line drawn through the points for the two lower ones. It seems probable, therefore, that $H_2P_3O_9^-$ did participate in the hydrolysis in the acid solutions used.

Turning to the hydrolysis in alkaline solution, and assigning to the reaction between OH^- and $P_3O_9^{3-}$ the velocity coefficient k_4'', and to the reactions between OH^- and the complex ions $NaP_3O_9^{2-}$, $CaP_3O_9^-$, etc., the velocity coefficients k''_{Na}, k''_{Ca}, etc., one obtains for the second-order velocity coefficient the expressions below

In $(n\text{-Pr})_4NOH$ solution

$$k_{OH} = k_4'' \quad (4)$$

In NaOH solution, or NaOH solution containing a sodium salt

---

[14] J. N. Brönsted, *Z. physik. Chem.*, **102**, 169 (1922).

[15] J. R. Van Wazer and D. A. Campanella, THIS JOURNAL, **72**, 655 (1950).

$$k_{\mathrm{OH}} = \{k_4''K_{\mathrm{Na}} + k''_{\mathrm{Na}}[\mathrm{Na}^+]\}/\{K_{\mathrm{Na}} + [\mathrm{Na}^+]\} \quad (5)$$

where $K_{\mathrm{Na}} = [\mathrm{Na}^+][\mathrm{P_3O_9}^{3-}]/[\mathrm{NaP_3O_9}^{2-}]$.

In NaOH containing a salt of a metal other than sodium

$$k_{\mathrm{OH}} = \{k_4''K_{\mathrm{Na}}K_{\mathrm{M}} + k''_{\mathrm{Na}}K_{\mathrm{M}}[\mathrm{Na}^+] + k''_{\mathrm{M}}K_{\mathrm{Na}}[\mathrm{M}]\}/\mathrm{D} \quad (6)$$

where $D = K_{\mathrm{Na}}K_{\mathrm{M}} + K_{\mathrm{Na}}[\mathrm{M}] + K_{\mathrm{M}}[\mathrm{Na}^+]$, and K_{M} is the dissociation constant of the new complex.

At a given μ, replacement of Na^+ by $(n\text{-Pr})_4\mathrm{N}^+$ causes a decrease in k_{OH}, so $k''_{\mathrm{Na}} > k_4''$. At constant $[\mathrm{Na}^+]$ and constant $[K^+]$, k_{OH} decreases with increasing μ (*cf.* experiments 9–11 of Table IV); this is to be expected from (6) if $k''_{\mathrm{Na}} > k_4''$ and $k''_{\mathrm{K}} > k_4''$, since

$$\frac{\partial[\mathrm{P_3O_9}^{3-}]/[\mathrm{P_3O_9}]}{\partial\mu} = \left\{[\mathrm{K}^+](K_{\mathrm{Na}})^2\frac{\partial K_{\mathrm{K}}}{\partial\mu} + [\mathrm{Na}^+](K_{\mathrm{K}})^2\frac{\partial K_{\mathrm{Na}}}{\partial\mu}\right\}/D^2$$

and K_{K} and K_{Na} would increase with increasing μ in dilute solution.

The great increase in k_{OH} in the presence of Ca^{++} or Ba^{++} enables one to estimate the magnitudes of k''_{Ca} and k''_{Ba} if one assumes that K_{Ca}, K_{Ba} and K_{Na} are about the same at 70 as at 25°. (In this connection, the dissociation constant of the ion $\mathrm{CaP_3O_{10}}^{3-}$ is reported to be 2.1×10^{-7} at 60 and 3.1×10^{-7} at 30°.)[16] The value of k_{OH} in 0.001 M NaOH alone is 0.5×10^{-2}, as compared with 180×10^{-2} when the solution is made 1×10^{-4} M in $\mathrm{CaCl_2}$, so

$$180 \times 10^{-2} \simeq k''_{\mathrm{Ca}}[\mathrm{CaP_3O_9}^-]/[\mathrm{P_3O_9}]$$

and taking $K_{\mathrm{Na}} = 6.8 \times 10^{-2}$,[4] and $K_{\mathrm{Ca}} = 3.6 \times 10^{-4}$,[5] k''_{Ca} is estimated to be 800×10^{-2}. Similarly

$$19 \times 10^{-2} \simeq k''_{\mathrm{Ba}}[\mathrm{BaP_3O_9}^-]/[\mathrm{P_3O_9}]$$

and taking $K_{\mathrm{Ba}} = 4.5 \times 10^{-4}$,[5] k''_{Ba} is estimated to be 200×10^{-2}. Thus the rate of reaction of the $\mathrm{MP_3O_9}^-$ complexes is several powers of ten greater than that of $\mathrm{P_3O_9}^{3-}$, since k_4'' in 0.001 M NaOH should lie between 0.3×10^{-2} and 0.5×10^{-2}. According to the data the rates of reaction of the several trimetaphosphate species stand in order of charge: $\mathrm{MP_3O_9}^- > \mathrm{M'P_3O_9}^{2-} > \mathrm{P_3O_9}^{3-}$. Similarly, Topley[11] attributed to decrease in the negative field of the anion the tenfold increase observed in the hydrolysis of potassium polymetaphosphate, in dilute $\mathrm{Na_2CO_3}$ solution at 100°, upon the addition of 5×10^{-4} mole of $\mathrm{MgSO_4}$ per liter; in contrast, $\mathrm{MgSO_4}$ had no effect on the rate of hydrolysis in dilute $\mathrm{NaH_2PO_4}$ solution. And similarly, Van Wazer, Griffith and McCullough[17] attributed the increase in rate of hydrolysis of pyro- and triphosphates upon replacement of $(\mathrm{CH_3})_4\mathrm{N}^+$ by Na^+, at $p\mathrm{H} \geqq 4$, to the formation of complexes with Na^+.

Since the hydrolysis of trimetaphosphate in either HCl or NaOH solution is composite, the frequency factors and energies of activation obtained from k_{H} and k_{OH} (*cf.* Table V) are composite. The value of E in 0.175 M NaOH solution may be compared with Brovkina's 20 kcal./mole, obtained from five experiments over the range 65–90°, with solutions initially 0.1 N in NaOH and 0.1 N in $\mathrm{Na_3P_3O_9}$.

TABLE V

THE ENERGY OF ACTIVATION OF THE NET REACTION IN HCl AND IN NaOH SOLUTION

Moles per liter HCl	Moles per liter NaOH	E,[a] kcal./mole	$\log_{10} A$[a, b]
0.00693		23.4	16.1
.01084		22.8	15.8
.02000		24.0	16.5
	0.0489	15.5	11.4
	.1250	17.5	13.0
	.1750	16.1	12.1

[a] Calculated from k_{H} (or k_{OH}) at 49.89, 59.95 and 69.40°. [b] A is in units of liters per mole per minute.

Acknowledgment.—We wish to express our gratitude to Dr. Richard C. Vogel, with whose help this problem was begun.

We also wish to thank the Office of Ordnance Research for support of the work of the senior author (M.L.K.) under Contract No. DA-11-022-ORD-1598.

CHICAGO 16, ILLINOIS

---

[16] O. T. Quimby, *J. Phys. Chem.*, **58**, 603 (1954).

[17] J. R. Van Wazer, E. J. Griffith and J. F. McCullough, THIS JOURNAL, **77**, 287 (1955).