in this unsymmetrical azoalkane.

The dimethylallyl radical appears first, as one would predict on the basis that the weaker C–N bond to the dimethylallyl group (27 kcal/mol) should rupture before the stronger C–N bond to methyl (52 kcal/mol). The resulting methylidyazanyl radical persists for 10 to 14 ns under the collisional conditions used here before fragmenting into N₂ plus CH₃. This lifetime is remarkably consistent with the 11-ns value deduced for methylidyazanyl in hydrocarbon solution by Engel and Gerth on the basis of thermal activation parameters. Quantum chemical calculations predict that dissociation of methylidyazanyl is an exothermic but activated process with estimated barrier heights of 6.3–17.4 kcal/mol. Because of this barrier, we expect that the persistence of the methylidyazanyl radical will depend strongly on its internal energy content. In the gas phase, where collisional relaxation of vibrational energy is far slower than in solution, the methylidyazanyl at early times retains the nascent excitation level with which it is formed as the first C–N bond breaks. For MAMB, the large dimethylallyl fragment has 36 vibrational modes and is able to carry away a significant fraction of the excess energy available from the 80.6-kcal/mol excitation photon. This would leave the methylidyazanyl fragment with less vibrational energy, and thus a longer lifetime, than from a similar stepwise photodissociation of azomethane. We suspect that our failure to resolve a stepwise mechanism in previous azomethane vapor studies may therefore reflect a shorter lifetime for methylidyazanyl rather than a qualitatively different dissociation mechanism. Finally, we note that since photodissociation in azoalkanes is believed to proceed from high levels of the electronic ground state populated by internal conversion, the stepwise process observed in MAMB should also occur in thermolysis of this compound.

Conclusions

By using time-resolved detection of primary photoproducts, we have kinetically resolved the stepwise breakage of C–N bonds in the ultraviolet-induced dissociation of an unsymmetrical azoalkane. Although the intermediate methylidyazanyl radical was not directly observed, its lifetime was inferred to be 12 ± 2 ns under our gas-phase experimental conditions. We believe that the sequential mechanism applies to thermal as well as photoinduced dissociation of this compound, since both are thought to proceed on the S₀ electronic surface. In addition, it seems quite likely that the studied compound qualitatively represents the entire class of unsymmetrical azoalkanes and that these may now confidently be viewed as dissociating sequentially rather than simultaneously.

These results do not bear directly on the homolysis mechanism of symmetric azoalkanes, such as azomethane. However, if we are able to characterize the nascent rotational and vibrational distributions of the N₂ and CH₃ fragments formed from MAMB through dissociation of the methylidyazanyl radical, then these distributions may be compared to those from azomethane and the outcome used to establish or exclude a common intermediate for the two cases. These and related studies are planned for the future.

Acknowledgment. We are grateful to the National Science Foundation and the Robert A. Welch Foundation for research support. Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work. R.B.W. thanks the Alfred P. Sloan Foundation for a Research Fellowship; K.A.B. thanks the A.R.C.S. Foundation for a graduate scholarship.

Registry No. MAMB, 105018-56-2; AMB, 71647-31-9.

Pyrophosphate Formation from Acetyl Phosphate and Orthophosphate Anions in Concentrated Aqueous Salt Solutions Does Not Provide Evidence for a Metaphosphate Intermediate

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Contribution No. 1603 from the Graduate Department of Biochemistry, Brandeis University, Waltham, Massachusetts 02254. Received June 3, 1986

Abstract: The formation of pyrophosphate (PPi) from the anions of acetyl phosphate (AcP) and orthophosphate (Pi) in concentrated aqueous sodium perchlorate is approximately first order in each reactant. The pH dependence of the reaction in the presence of 0.25 M Pi monoanion and 6.4 M sodium perchlorate at 54 °C shows different yields of PPi from AcP mono- and dianion. This result is inconsistent with trapping of a free metaphosphate intermediate by Pi monoanion and water. The results are consistent with a concerted mechanism for PPI formation and yields of PPI from the different ionic species of 11.7% for AcP⁻ and Pi²⁻, 7.8% for AcP⁵⁻ and Pi⁷⁻, and 4.2% for AcP⁻ and Pi⁻. Measurement of rate constants and partitioning with AcP⁻, 0.25 M Pi⁻, and 6.4 M sodium perchlorate, in the presence and absence of pyridine, show that the phosphorylated pyridine monoanion yields 40% PPI, whereas AcP⁻ yields 10% PPI under the same conditions. The formation of PPI from AcP and PII diion is at least fourth order in sodium ion in concentrated sodium perchlorate solutions. The corresponding reaction of the monooanions is second order in sodium ion. The order of effectiveness of salts for facilitation of the formation of PPI from the diions of AcP and Pi is NaClO₄ > NaCl, KCl, CsCl, and NaCl > CsCl. However, increasing the concentration of sodium perchlorate from 0.1 to 6.6 M changes the rate constant for hydrolysis of AcP mono- and dianion by <30% at 39 and 54 °C. Values of ΔH* = 29 kcal mol⁻¹ and ΔS* = +12 eu for PPI formation from the diions of AcP and Pi and ΔH* = 19 kcal mol⁻¹ and ΔS* = -20 eu for PPI formation from the monoanions were obtained from the yields of PPI and the rates of hydrolysis at 39 and 54 °C. The high concentrations of sodium ion decrease electrostatic repulsion between the anions of AcP and Pi and may catalyze the formation of PPI by bridging the anions of AcP and Pi. These results provide no evidence for the existence of a metaphosphate intermediate in reactions in aqueous solution.

The reactions of phosphate monoesters and related compounds with solvent and other nucleophilic reagents involve nearly complete bond breaking with the leaving group and little bond formation to the nucleophile. For example, the rapid hydrolysis of

0002-7863/86/1508-7938$01.50/0 © 1986 American Chemical Society
Pyrophosphate Formation from Acetyl Phosphate


phosphate monoester monoanions and some diatoms proceeds with entropies of activation near zero and no significant solvent isotope effect, as well as a large negative value of $\Delta_\text{shift}$ for the diatoms and a large bridge $^{17}Q$ isotope effect for 2,4-dinitrophenyl phosphate dianions. In addition, phosphate monoesters and phosphorylated guanidines exhibit low selectivity: the partitioning between components of mixed solvents (ROH/ROH) is often equal on a molar basis, and $\Delta_\text{shift}$ for the reaction of pyridines with dinitrophosphoryl phosphate diazonium is zero. The hydrolysis of the mono- and diatoms of AcP progresses with entropies and volumes of activation close to zero and no significant solvent isotope effect; the hydrolysis of the mono- and diatoms of AcP, as well as a large negative value of $\Delta_\text{shift}$ for the reaction of pyridines with dinitrophosphoryl phosphate diazonium is zero. The hydrolysis of the mono- and diatoms of AcP occurs with entropies and volumes of activation close to zero and no significant solvent isotope effect; these observations led workers to support the hypothesis that metastable phosphate is an intermediate in the hydrolysis of phosphate monoesters and related compounds.1,2 For example, DiSabato and Jencks, in 1961, concluded for the hydrolysis of AcP that: "While no single one of these considerations should be taken alone as conclusive proof of the monomolecular or bimolecular nature of a reaction, taken together they constitute strong evidence that the neutral hydrolysates of acyl phosphates occur via a meta-phosphate intermediate. Such conclusions are not justified by the data; transition states are not intermediates and the characteristics of a transition state do not usually demonstrate the existence of an intermediate. Reactions that exhibit "borderline" behavior proceed through transition states in which the bond to the leaving group is nearly broken, whether or not an intermediate is formed.1,3 Efforts to prove that metaphosphate exists as an intermediate have not been successful for reactions in aqueous solution. Phosphocreatine, the monoanion of phenyl phosphate, and the dianion of 2,4-dinitrophenyl phosphate form methyl phosphate in 50% aqueous methanol with inversion of configuration, and there is no positional isotope exchange of the $\alpha$-$\beta$ bridge oxygen atom of $\beta\text{-}[\text{OSO}_3\text{]}\text{ADP}$ with nonbridge $\alpha$-oxygen atoms concurrent with hydrolysis. Thus, these reactions are concerted and involve no hydrolysis, or are preassociation stepwise and involve an intermediate with a lifetime that is insufficient to allow rotation or diffusion in solution.1,4,5 Skoog and Jencks6 and Bourne and Williams7 have provided evidence that the reactions of pyridines with the monoanions of phosphorylated pyridines and isoquinoline do not involve metaphosphate intermediates, although the transition states are of metaphosphate-like character. However, in the gas phase, metaphosphate monoanion has been identified by mass spectroscopy8 and metaphosphate derivatives have been formed in the gas phase by pyrolysis.9 A metaphosphate intermediate with a significant lifetime could presumably be formed in a solvent with sufficiently low nucleophilicity. The observed low selectivity and absence of nucleophilic assistance in the Conant-Swan fragmentation10 would be expected if the reaction proceeded through a metaphosphate intermediate or if the reaction were concerted with a metaphosphate-like transition state and no intermediate. However, inversion of configuration for reaction with an alcohol in chloroform shows that there is no long-lived intermediate in this reaction.23 Reactions in acetonitrile and dioxane, such as the transfer of phosphoryl groups to nucleophile acceptors in the "three-phase test", the cleavage of phenyl phosphate and ADP with racemization, and the positional isotope effects of $\beta\text{-}[\text{PO}_4\text{]}\text{ADP}$, have been attributed to a requirement for a metaphosphate-like transition state or reaction with the solvent to form an adduct, as has been suggested for the Conant-Swan fragmentation;23 the adduct of SO$_3$ with dioxane is known.24 Phosphorylation of tert-butyl alcohol by a mono- or monosubstituted phosphoryl compounds25,26 could proceed through a metaphosphate intermediate, but could also proceed through an anionic intermediate. The formation of metaphosphate-like transition state participates in a second-order reaction with p-nitrophenyl phosphate diion,27 and inspection of CPK molecular models suggests that the steric hindrance for trimethylamine and tert-butyl alcohol is not grossly different. The fast reactions of 2,4-dinitrophenyl phosphate dianion and p-nitrophenyl phosphate mono- and diion reflect the stabilities of the transition states, but are not

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10. The $\Delta_\text{shift}$ of zero has been considered to represent the border between mono- and bimolecular reaction mechanisms (ref 5; Kirby, A. J. In Phosphorus Chemistry Directed Toward Biology; Scz, W. J., Ed.; Pergamon Press: New York, 1980; pp 79-83). However, negative values of $\Delta_\text{shift}$ have been observed for second-order reactions of quinuclidines with phosphorylated acetamides,28 such as has been suggested for the Conant-Swan fragmentation22 the adduct of SO$_3$ with dioxane is known.24 Efforts to prove that metaphosphate exists as an intermediate have not been successful for reactions in aqueous solution. Phosphocreatine, the monoanion of phenyl phosphate, and the dianion of 2,4-dinitrophenyl phosphate form methyl phosphate in 50% aqueous methanol with inversion of configuration, and there is no positional isotope exchange of the $\alpha$-$\beta$ bridge oxygen atom of $\beta\text{-}[\text{OSO}_3\text{]}\text{ADP}$ with nonbridge $\alpha$-oxygen atoms concurrent with hydrolysis. Thus, these reactions are concerted and involve no hydrolysis, or are preassociation stepwise and involve an intermediate with a lifetime that is insufficient to allow rotation or diffusion in solution.1,4,5 Skoog and Jencks6 and Bourne and Williams7 have provided evidence that the reactions of pyridines with the monoanions of phosphorylated pyridines and isoquinoline do not involve metaphosphate intermediates, although the transition states are of metaphosphate-like character. However, in the gas phase, metaphosphate monoanion has been identified by mass spectroscopy8 and metaphosphate derivatives have been formed in the gas phase by pyrolysis.9 A metaphosphate intermediate with a significant lifetime could presumably be formed in a solvent with sufficiently low nucleophilicity. The observed low selectivity and absence of nucleophilic assistance in the Conant-Swan fragmentation10 would be expected if the reaction proceeded through a metaphosphate intermediate or if the reaction were concerted with a metaphosphate-like transition state and no intermediate. However, inversion of configuration for reaction with an alcohol in chloroform shows that there is no long-lived intermediate in this reaction.23 Reactions in acetonitrile and dioxane, such as the transfer of phosphoryl groups to nucleophile acceptors in the "three-phase test", the cleavage of phenyl phosphate and ADP with racemization, and the positional isotope effects of $\beta\text{-}[\text{PO}_4\text{]}\text{ADP}$, have been attributed to a requirement for a metaphosphate-like transition state or reaction with the solvent to form an adduct, as has been suggested for the Conant-Swan fragmentation;23 the adduct of SO$_3$ with dioxane is known.25 Phosphorylation of tert-butyl alcohol by a mono- or monosubstituted phosphoryl compounds25,26 could proceed through a metaphosphate intermediate, but could also proceed through an anionic intermediate. The formation of metaphosphate-like transition state participates in a second-order reaction with p-nitrophenyl phosphate diion,27 and inspection of CPK molecular models suggests that the steric hindrance for trimethylamine and tert-butyl alcohol is not grossly different. The fast reactions of 2,4-dinitrophenyl phosphate dianion and p-nitrophenyl phosphate mono- and diion reflect the stabilities of the transition states, but are not
Evidence for a metaphosphate intermediate. In contrast, the partial racemization of the phosphoryl moiety upon reaction of an asymmetrical PPI derivative with 2-O-benzylpropane-1,2-diol in methylene chloride may provide evidence for metaphosphate mononanoanion in solution.

While there is no convincing evidence for the existence of a metaphosphate intermediate in dilute aqueous solution, it has been suggested that the formation of PPI from AcP and from an amiphosphonate in concentrated aqueous sodium perchlorate provides evidence for a metaphosphate intermediate. We have examined the partitioning of AcP mono- and di-anions between reaction with water and with Pi anions and have obtained no evidence that supports the existence of a metaphosphate intermediate. Electrostatic repulsion between the anions of AcP and Pi is decreased in the presence of high concentrations of sodium ion, which allows the formation of PPI by a reaction that is first order with respect to both AcP and Pi. It is suggested that the formation of PPI involves concerted phosphoryl transfer from AcP to Pi in a complex of the reacting anions that is bridged by bound sodium ions.

**Experimental Section**

**Materials.** Aqueous solutions of AcP with potassium as the counterion were prepared in 95–100% yield by a modification of the method of Avison. Acetic anhydride, 1.7 mL, was added slowly to 8.2 mL of 1.95 M Pi (1:1 monopotassium/dipotassium salt) and 0.28 M pyridine at 0 °C with the pH maintained at >6.1 by addition of 4 M KOH; pyridine was removed by extraction with ether. A solution of the sodium salt was obtained by addition of sodium perchlorate followed by centrifugation. The lithium, potassium salt of AcP, Sigma Chemical Co., was used for pKₐ determinations. Sodium perchlorate (>99%) was from Aldrich, and solutions of sodium perchlorate were passed through Millipore filters. Pyridine was redistilled and acethyldihydroxamic acid was a standard. Reaction mixtures containing AcP and were assayed for PPi by a slight modification of a published procedure.

**Kinetic Studies.** Reactions of AcP were carried out at 39.0 °C. Pseudo-first-order rate constants for the disappearance of 6.4 M sodium perchlorate (O) or at a constant ionic strength of 7.6 maintained with sodium perchlorate ('). The final pH values were 6.7 to 7.2. The averages of the initial and final concentrations of Pi are used. The solid line is a linear least-squares fit to the open circles.

**Table 1. Effect of AcP Concentration on the Yield of PPI from AcP in the Presence of 7.0 M Sodium Ion and 0.25 M Pi Dianion at 54.4 °C**

<table>
<thead>
<tr>
<th>[AcP], M</th>
<th>PPI, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.023</td>
<td>8.7 (±0.3)</td>
</tr>
<tr>
<td>0.046</td>
<td>8.8 (±0.01)</td>
</tr>
<tr>
<td>0.091</td>
<td>9.3 (±0.2)</td>
</tr>
<tr>
<td>0.160</td>
<td>9.7 (±0.01)</td>
</tr>
</tbody>
</table>

*With perchlorate as the counteranion. The final pH values were 6.7 to 7.2. Average and range of values determined from two reaction mixtures.*

**Results**

Figure 1 shows that the yield of PPI from AcP dianion increases as the concentration of Pi dianion increases at constant sodium perchlorate concentration (solid line) and at constant ionic strength (dashed line); the intercepts are within experimental uncertainty of zero. Table I shows that the percent yield of PPI is almost independent of AcP concentration over the range 0.02 to 0.16 M in the presence of 0.25 M Pi dianion at constant sodium ion concentration. Thus, the formation of PPI is predominantly from a reaction involving AcP and Pi. The small increase in % PPI with increasing AcP concentration (Table I) can be accounted for by the release of Pi from the hydrolysis of AcP. The concave downward curvature in the yield of PPI with increasing concentration of Pi dianion (dashed line, Figure 1) may be attributed to the decrease in the concentration of sodium ion as the concentration of Pi increases at constant ionic strength (see Figure 3).

The dependence on pH of the yield of PPI from AcP and 0.25 M Pi in 6.4 M sodium perchlorate is shown in Figure 2. Apparent pKₐ values for AcP and Pi of 4.1 and 5.7, respectively, were determined by titration in 6.6 M sodium perchlorate at 25 °C.

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Pyrophosphate Formation from Acetyl Phosphate

The dependence on pH of the yield of PPi from AcP at 54.4 °C in 6.4 M sodium perchlorate, 0.09 M AcP, and 0.25 M Pi, as the di- and monosodium salts and as the acid. The pH was maintained throughout the reaction by addition of sodium hydroxide. Open and closed symbols are from different experiments. The lines are calculated for pK₂ values of 4.1 and 5.7 for AcP and Pi, respectively, as described in the Discussion.

Figure 2.

The effect of the concentration of sodium ion on the yield of PPi from the dianions of AcP and Pi at 54.4 °C.

Table II. Effect of Concentrated Salt Solutions on the Yield of PPi from the Dianions of AcP and Pi at 54.4 °C

<table>
<thead>
<tr>
<th>Conditions</th>
<th>PPI, %</th>
</tr>
</thead>
</table>
| A | 4.1 M NaCl, 0.1 M Na₂AcP, 0.1 M NaHAcP | 0.25 M Na₂HPO₄, 0.1 M NaH₂PO₄, 0.09 M AcP, 0.25 M Pi. The pH was maintained throughout the reaction by addition of sodium hydroxide. Open and closed symbols are from different experiments. The lines are calculated for pK₂ values of 4.1 and 5.7 for AcP and Pi, respectively, as described in the Discussion.

The increase in % PPI from reaction of the di-anions at very high concentrations of sodium ion is consistent with a rate constant for PPi formation that is fourth order in sodium ion concentration; the dashed line in Figure 3 was calculated from

\[
k_p = k'_p [Na^+]^4
\]  

(2)
calculated from eq 2 with \(k'_p = 1.3 \times 10^{-7} \text{ M}^{-2} \text{ s}^{-1}\). A better fit to the data for formation of PPi from the di-anions over the entire range of sodium ion concentration is obtained using a rate constant that depends on two sodium ions that bind with an association constant \(K_a\) and five additional sodium ions in the transition state. The upper solid line in Figure 3 was calculated for this stoichiometry from eq 3, with \(k_p = 3.9 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}, k'_p = 1.7 \times 10^{-4} \text{ M}^{-4} \text{ s}^{-1}, K_a = 0.25 \text{ M}^{-2}\), and \(K_p\) obtained using a rate constant

\[
k_p = k'_p [Na^+]^2 \left(1 + K_a [Na^+]^2 + k'_p [Na^+]^2 \left(1 + K_a [Na^+]^2\right)\right)
\]

(3)
Table III. Observed Rate Constants for the Hydrolysis of 0.03 M AcP Monoanion and Dianion in Concentrated Sodium Perchlorate Solutions at 39.0 and 54.4 °C

<table>
<thead>
<tr>
<th>[NaClO₄], M</th>
<th>AcP⁻</th>
<th>AcP²⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>39.0 °C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1</td>
<td>18.9⁺</td>
<td>7.2⁺</td>
</tr>
<tr>
<td>5.0</td>
<td>16.7⁺</td>
<td>7.2⁺</td>
</tr>
<tr>
<td>6.6</td>
<td>16.4⁺</td>
<td>7.1⁺</td>
</tr>
<tr>
<td>6.6</td>
<td>10.8⁺</td>
<td>6.8⁺</td>
</tr>
<tr>
<td>0.1 + 0.54 M pyr</td>
<td>15.0⁺</td>
<td></td>
</tr>
<tr>
<td>6.6 + 0.54 M pyr</td>
<td>12.4⁺</td>
<td></td>
</tr>
</tbody>
</table>

| 54.4 °C     |      |       |
| 0.1         | 11.8⁺ | 4.9⁺  |
| 4.9         | 8.7⁺  | 5.7⁺  |
| 6.6         | 7.8⁺  | 5.9⁺  |

*Buffer catalysis was estimated to be <10% in all cases, from the small effects of varying pH values and buffer concentration. *0.1 M NaH₂PO₄, 0.03 M sodium acetate, pH ~ 3.3. *0.1 M Tris, pH 8.5. *From ref 9. *pHfinal ~ 6.7. *Calculated from values of E₄ listed in Table V and rate constants for phosphorylation and hydrolysis in this table and in Table III. *pHfinal ~ 3.2.

Table IV. Effect of Temperature on the Yield of PPI from the Monoanions and from the Dianions of 0.07 M AcP and 0.25 M Pi in 5.7 M Sodium Perchlorate

<table>
<thead>
<tr>
<th>temp, °C</th>
<th>PPI, %</th>
<th>10⁴kₜ₁, M⁻¹ s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>AcP²⁻/Pi²⁻</td>
<td></td>
<td></td>
</tr>
<tr>
<td>38.5</td>
<td>6.1</td>
<td>0.15</td>
</tr>
<tr>
<td>54.4</td>
<td>7.1</td>
<td>1.5</td>
</tr>
<tr>
<td>75.0</td>
<td>8.1 (8.4)</td>
<td>0.86</td>
</tr>
</tbody>
</table>

| AcP⁻/Pi⁻ |      |                 |
| 38.5     | 3.4   | 0.19            |
| 54.4     | 2.8   | 0.86            |
| 75.0     | 1.8 (2.2) | 0.86        |

The data of Table III show that increasing the concentration of sodium perchlorate from 0.1 to 6.6 M changes the rate constants for hydrolysis of the mono- and dianions of AcP by <30% at 39.0 and 54.4 °C. The rate constants obtained at low ionic strength and 39 °C agree with those obtained previously under similar conditions. The observed rate constant for the reaction in the presence of 0.54 M pyridine is 32% lower in 6.6 M sodium perchlorate than in 0.1 M sodium perchlorate (Table III); it is possible that this decrease results from an increase in the self-association of pyridine in the presence of concentrated salt.

The effect of temperature on the yield of PPI from the mono- and from the dianions of AcP and Pi is shown in Table IV. The yields of PPI at 39 and 54 °C and the rate constants for hydrolysis under similar conditions (Table III) were used to calculate the rate constants for the reactions with Pi listed in Table IV. The small effect of the salt concentration on the rate constants for hydrolysis (Table III) allows calculation of the rate constants for phosphorylation using rate constants for hydrolysis obtained under similar, but not identical conditions. The observed yields of PPI at 75 °C show fair agreement with the yields calculated from the rate constants and energies of activation for hydrolysis and phosphorylation obtained at 39 and 54 °C (Table IV).

Table V lists activation parameters for hydrolysis and phosphorylation of the monoanion and the dianion of AcP. The rate constants for hydrolysis (Table III) allows calculation of the rate constants for phosphorylation using rate constants for hydrolysis obtained under similar, but not identical conditions. The observed yields of PPI at 75 °C show fair agreement with the yields calculated from the rate constants and energies of activation for hydrolysis and phosphorylation obtained at 39 and 54 °C (Table IV).

Table VI shows that pyridine catalyzes the formation of PPI from the dianions of AcP and Pi, as well as the hydrolysis of AcP in aqueous sodium perchlorate. Catalysis of AcP hydrolysis by pyridine involves a phosphorylated pyridine intermediate, and the data of Table VI suggest that the formation of PPI from AcP is also catalyzed via a phosphorylated pyridine intermediate, as shown in Scheme I. The yield of PPI from the dianion of phosphorolysis and 0.25 M Pi diation was calculated to be 40 and 41% at 0.14 and 0.21 M pyridine, respectively, from the rate and product data of Table VI and from Scheme I; the yield of PPI from the dianion of AcP is 10% under the same conditions. The ratio of the rate constant for PPI formation to that for PPI formation from the phosphorylated pyridine dianion of kₚ/kₚHOH is 2.7 M⁻¹s⁻¹ is six times larger than the corresponding ratio for PPI and Pi formation from AcP diation of kₚ/kₚHOH = 0.44 M⁻¹.

Discussion
Mechanism of Pyrophosphate Formation. The previously proposed mechanism for hydrolysis and phosphorylation of the anions of AcP, shown in Scheme II, predicts that the partitioning of a metaphosphate intermediate between reaction with Pi monoanion and with water will be the same for metaphosphate generated from the monoanion and from the dianion of AcP in concentrated sodium perchlorate solutions. The dashed line of Figure 2 was calculated according to eq 4 and

$$\frac{\% \text{ PPI}}{100} = \frac{k_p [\text{Pi}] + k_p'' [\text{Pi}^2]}{k_a + k_p [\text{Pi}] + k_p'' [\text{Pi}^2]}$$

the apparent pK₂ for Pi in 6.6 M sodium perchlorate of 5.7. Values of kₚ/kₚ = 0.18 M⁻¹ and kₚ''/kₚ = 0.53 M⁻¹ for eq 4 were determined from the formation of 4.2 and 11.7% PPI at low and high pH, respectively (Figure 2). The calculated yield of PPI for the mechanism of Scheme II, which invokes a free metaphosphate intermediate, is significantly less than the observed yield in the central pH region of Figure 2. Therefore, a common free metaphosphate intermediate is not responsible for the formation of PPI.

A concerted mechanism for PPI formation, shown in Scheme III, can account for the pH dependence of PPI formation. The solid line in Figure 2 was calculated for the concerted mechanism of Scheme III according to eq 5, with k₁/k₂ = 1.5 (Table III).
Table V. Activation Parameters for Hydrolysis and Phosphorolysis of the Monoanion and of the Dianion of AcP

<table>
<thead>
<tr>
<th>Reaction conditions</th>
<th>AcP</th>
<th>AcP2-</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrolysisb</td>
<td>0.1 M NaClO4, μ = 0.6 (KCl)b</td>
<td>24.1</td>
</tr>
<tr>
<td>Phosphorolysis</td>
<td>5.8 M NaClO4</td>
<td>22.1</td>
</tr>
</tbody>
</table>

*Calculated from the relationships ΔΗ* = E* + RT, ΔG* = ΔΗ* - RT In (kh/kT), and ΔS* = (ΔΗ* - ΔG*)/T. Values were calculated from the first-order rate constants unless otherwise noted. From the data of Table III. Calculated from the second-order rate constant for hydrolysis, using [H₂O] = 38 M in 6.6 M NaClO₄. From the data of Table IV at 39 and 54 °C.

Table VI. Effect of Pyridine on the Yield of PPI from the Dianions of AcP and Pi and on the Observed Rate Constant for Hydrolysis of AcP2- in Aqueous Sodium Perchlorate at 54.4 °C

<table>
<thead>
<tr>
<th>Pyridine, M</th>
<th>106k, a s⁻¹</th>
<th>PPI, a %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>5.7</td>
<td>9.0 (±1.0)</td>
</tr>
<tr>
<td>0.14</td>
<td>6.6</td>
<td>13.6 (±0.2)</td>
</tr>
<tr>
<td>0.21</td>
<td>15.0 (±0.4)</td>
<td></td>
</tr>
<tr>
<td>0.28</td>
<td>7.2</td>
<td>8.1</td>
</tr>
<tr>
<td>0.54</td>
<td>8.1</td>
<td></td>
</tr>
<tr>
<td>0.13 M dioxane</td>
<td>5.9</td>
<td>10.3</td>
</tr>
<tr>
<td>0.20 M dioxane</td>
<td>10.3</td>
<td></td>
</tr>
</tbody>
</table>

*Varying amounts of pyridine or dioxane were added to solutions with 0.1 M Tris·HCl, pH 8.5, 6.6 M NaClO₄, and 0.03 M Na₂AcP. When AcP was used, the concentration was high enough to overcome electrostatic repulsion. The selectivity between reaction of metaphosphate generated next to an acetate ion from AcP dianion would not differ greatly from the selectivity for metaphosphate generated next to pyridine, from phosphorylated pyridine monooanion. However, the selectivity for reaction with Pi compared to reaction with water, kpyr/kHOH, is sixfold larger for phosphorylated pyridine monooanion than for AcP dianion (Table VI; Results). This difference is consistent with nucleophilic involvement in the transition state and no metaphosphate intermediate, based on differences in selectivity for other reactions. The selectivity of kpyr/kHOH = 1.3 - 3.0 x 10⁴ for reactions of phosphorylated pyridine monooanions is greater than kpyr/kHOH = 1.1 x 10⁴ for reactions of AcP dianion, and values of kpyr for reactions of phosphorylated pyridine monooanions are larger than those for reactions of both p-nitrophenyl phosphate diester and 2,4-dinitrophenyl phosphate diester, which have oxyanion leaving groups of higher and lower pKa than AcP dianion. The rapid intramolecular attack of the carbonyl carbon of salicyl phenyl phosphate dianion on the phosphorylated pyridine monooanion shows that an anion is an effective nucleophile toward the phosphate diester anion if it is held in a reactive position. In fact, the rate acceleration from intramolecularity for the phosphate diester monooanion is greater than that estimated for a triester; the greater rate acceleration may be due to enforced proximity of the carboxylate anion nucleophile and the diester monooanion that overcomes the electrostatic repulsion.

Scheme III

(40) The reaction of AcP2- with Pi⁻ is kinetically indistinguishable from the reaction of AcP⁺ with Pi⁺.

ΔΗ* (39 °C) kcal mol⁻¹

<table>
<thead>
<tr>
<th>Reaction</th>
<th>AcP</th>
<th>AcP2-</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrolysisb</td>
<td>23.5</td>
<td>24.7</td>
</tr>
<tr>
<td>Phosphorolysis</td>
<td>21.4</td>
<td>26.8</td>
</tr>
</tbody>
</table>

ΔS* (39 °C) eu

<table>
<thead>
<tr>
<th>Reaction</th>
<th>AcP</th>
<th>AcP2-</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrolysisb</td>
<td>-0.5</td>
<td>+1.6</td>
</tr>
<tr>
<td>Phosphorolysis</td>
<td>-7.3</td>
<td>+8.4</td>
</tr>
</tbody>
</table>

constants for pyridines to $pK_a = -1.74$, the $pK_a$ of $\text{H}_2\text{O}^-$, to give $k_{py}$. The ratios for the diions of $n$-pentanitrophenyl phosphate and 2,4-dinitrophenyl phosphate of $k_{H2O}/k_{py}$ is $1 \times 10^{12}$ and $6 \times 10^{12}$, respectively, are not significantly larger than the ratios for the monoanions of methyl dinitrophenyl phosphate and bis(dinitrophenyl) phosphate of $8 \times 10^{3}$ and $6 \times 10^{4}$, respectively.

Thus, the available evidence supports, but does not rigorously demonstrate, a concerted mechanism for the phosphorolysis of AcP in aqueous sodium perchlorate solutions. Although we are not aware of any evidence that supports the existence of an intermediate but has a lifetime too short to allow diffusion, is not definitely excluded by the data. For example, the pH dependence of the yield of PPI formation from AcP should be consistent with a preassociation mechanism if the association constants for AcP and Pi increase with increasing charge on the anionic reactants because of bridging by sodium ions.

**Electrostatic Interactions.** The formation of PPI from AcP and Pi can be explained by direct binding of sodium ions to the anionic reactants to overcome electrostatic repulsion. At ordinary salt concentrations PPI is not formed in appreciable amounts from anions of AcP and Pi (Figure 3, see also ref 9). Other reactions of anions of AcP and Pi in aqueous solutions, the absence of such evidence does not disprove the existence of an intermediate. A preassociation stepwise mechanism, in which metaphosphate is formed as an intermediate but has a lifetime too short to allow diffusion, is not definitely excluded by the data. For example, the pH dependence of the yield of PPI formation from AcP should be consistent with a preassociation mechanism if the association constants for AcP and Pi increase with increasing charge on the anionic reactants because of bridging by sodium ions.

The dependence of the yield of PPI on the concentration of sodium ion (Figure 3) is consistent with a reaction of the monoanions of AcP and Pi that involves two sodium ions and a reaction of the diions of AcP and Pi that involves at least four sodium ions. This high sensitivity of PPI formation to the concentration of sodium ion suggests that sodium ions lower charge repulsion between the anions of AcP and Pi to catalyze the formation of PPI. Lowering of charge repulsion could occur by direct binding of sodium ions to the reactants or by an electrostatic field interaction of sodium ions that shields the repulsion between the reactants.

Although the dependence of the yield of PPI from the diions of AcP and Pi on the concentration of sodium ion is fit at very high concentrations of sodium ion by a model involving two sodium ions, a better fit over the entire range of sodium ion concentration is obtained by using a model involving two sodium ions with saturation and an additional five sodium ions (Figure 3). Smith and Albert estimated an association constant for sodium ion and the diion of Pi of $4 \times 10^{12}$ at $25^\circ C$ and ionic strength 0.2 from the dependence of the apparent $pK_2$ of Pi on the concentration of sodium ion, assuming that Pi and $n$-tetra- propylammonium ion do not associate. This value is in reasonable agreement with an association constant of $7.0 \times 2.4 \times 10^{12}$ (25°C, ionic strength 0), which was derived statistically from the effect of sodium chloride on $\text{CaHPO}_4$ solubility, with correction for activity coefficient effects by use of the Debye–Hückel equation. A similar association constant might be expected for the sodium ion and dianion of AcP. Saturation with two sodium ions or the formation of Pi dimers may prevent upward curvature in the yield of PPI with increasing concentration of disodium Pi (Figure 1).

More direct support for specific binding of sodium ions, rather than an electrostatic field effect, comes from the differences in the ability of different cations to promote the formation of PPI and from the entropy of activation for phosphorolysis. Smith and Albert obtained an order of binding affinities of monovalent cations for Pi diion of: $Li^+ > Na^+ > K^+ > (\text{CH}_3)_2\text{N}^+ > (\text{C}_2\text{H}_5)_4\text{N}^+ > (\text{CH}_3)_2\text{H}^+$. Cesium ion is expected to bind less strongly than potassium ion (and sodium ion), as seen in the Eisenman series XI for binding to anionic sites of strong field strength. The greater effectiveness of sodium than of cesium ions for catalysis of PPI formation from the dianions of AcP and Pi (Table II) is consistent with sodium ion serving as a preassociation agent for ion pairing.

The fact that the entropy of activation of $+12$ eu for phosphorolysis of AcP diions is large, positive, which is greater than the value of $+1.1$ eu for hydrolysis, suggests that ion-pair formation is involved in phosphorolysis (Table V). The change in entropy for ion-pair formation is expected to be positive as a result of the release of water of solvation from the ions, and the change in entropy upon association of sodium ion and the diion of Pi ($25^\circ C$, ionic strength 0.2) was estimated to be $+24$ eu by Smith and Albert from $pK_a$ measurements at 0 and 25°C. The observed value of the entropy of activation for formation of PPI should reflect both positive contributions from ion-pair formation and negative contributions from requirements for positioning of AcP and Pi ions in the transition state. The more negative entropy of activation for phosphorolysis of the monoanion of AcP by Pi monoanion than for phosphorolysis of the diion of AcP by Pi diion is consistent with involvement of fewer sodium ions in the reaction of the monoanions.

The enhanced ability of sodium perchlorate compared with sodium chloride to stimulate the formation of PPI (Table II) may reflect a greater availability of sodium ion for binding to the anionic reactants in the presence of perchlorate ion. The association constant of $0.37 \times 10^6$ at ionic strength 4.0 for ion-pair formation between sodium ion and perchlorate ion was determined by Raman spectroscopy, which is about fourfold smaller than that for sodium and nitrate ions. Raman spectra of nitrate ion in the presence of silver ion show no evidence for binding of perchlorate ion that competes with the association of nitrate ion with silver ion. In contrast, Raman spectra of nitrate ion in the presence of sodium ion suggest that the apparent association constant for contact ion-pair formation of sodium and nitrate ions decreases in the presence of chloride ion at constant ionic strength. This may result from competition between chloride and nitrate ions for association with sodium ion. Vieyra and co-workers have observed PPI formation from AcP and Pin anions that is sigmoidal dependent on the concentration of $Ca^{2+}$ and $Mg^{2+}$, suggesting that at least two divalent metal ions bind to the reactants and stimulate PPI formation. The formation of PPI in the presence of sodium ion may be catalyzed similarly. Ion pairs are also likely to be involved in PPI formation from AcP in 87% acetonitrile and 87% dioxane, which have lower dielectric constants than water.

It is of interest that these very concentrated salt solutions have little effect on the hydrolysis of acetyl phosphate, in spite of the fact that a large fraction of the water has been replaced by ions at a total concentration of up to $13 M$. The extraordinarily small effect of a very concentrated perchlorate on the rate constants for hydrolysis of AcP monoanion and diion (Table III) suggests that there is no change in reaction mechanism in these solutions and that the increased rate of PPI formation is not simply the result of electrophilic catalysis by sodium ions; in fact, the reaction with pyridine is slightly decreased in concentrated sodium perchlorate

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Scheme IV

Pyrophosphate Formation from Acetyl Phosphate

It is unlikely that a decrease in the activity of water accounts for the change in partitioning between reaction with Pi and water with increasing sodium perchlorate concentration because the activity of water in 4 M sodium perchlorate is 0.8.53 Acetonitrile also has very small effects on the rate constants for hydrolysis of AcP anions: 50% acetonitrile at 39 °C gives an 18% decrease and a change of <5% in the rate constants for mono- and dianion hydrolysis, respectively, compared to the rate constants in dilute aqueous solution.5

**Bridging by Sodium Ions.** The reaction of the dianions of AcP and Pi yields more PPi than the reaction of the monoanions of AcP and Pi, which provides a precedent for catalysis by sodium ion of the reactions in ion pair.

Phosphoryl oxygen atoms from different molecules are bridged by sodium ions in crystals of the salts of phosphoryl compounds such as ATP, β-glycerol phosphate, PiP, and phosphomamatide.54 The distances from the sodium ions to the coordinated phosphoryl oxygen atoms are 2.5 ± 0.4 Å, and the geometry about the sodium ions is that of a distorted octahedron. Scheme IV shows some of the possible structures for bridging sodium ions in the transition state for reaction of the dianions of AcP and Pi.

Several observations in the literature render bridging by sodium ions a reasonable mechanism for catalysis of PPI formation from the anions of AcP and Pi. The different effects of different cations on the osmotic coefficients of ADP and ATP in Me2SO suggest a role for the cation with specific geometrical constraints, rather than simple electrostatic shielding.55 Na+, K+, Cs+, and Rb+ ions catalyze the dismutation reaction, whereas Li+ and Mg2+ ions inhibit the reaction, presumably by competing with other cations for binding to ADP. Furthermore, rate data suggest that the Na+ ion binds more strongly than K+ ion to ADP, but that two molecules of ADP, each with one K+ ion bound to ADP, dismutate faster than those with bound Na+ ion. Thus, in addition to charge neutralization through binding, another factor, such as proper geometry for bridging together of reactants, is required for this phosphoryl transer reaction.

The self-association of Pi anions in solution to form dimers of net charge −2 and −4 is consistent with data from Raman spectroscopy and other techniques56 and suggests that even hydrogen bonds are sufficient to overcome the electrostatic repulsion in the complex.57 The results of potentiometric titrations of Pi in the presence of divalent metal ions, including Mg2+ and Ca2+, are consistent with the formation of dimers with net charges of 0 and −1 and bridging of Pi by the divalent metal ion.58 Metal ion catalysis of the departure of oxygen anion leaving groups provides a precedent for catalysis by sodium ion of the nucleophilic addition of Pi oxyanions in the reverse direction. The reaction of pyridines with p-nitrophenyl phosphate diester, which has a partial negative charge on the leaving group in the transition state, is catalyzed by Ca2+ and Mg2+, whereas the reaction with phosphorolylated morpholinopyridine monoaon, which has a partial positive charge on the leaving group in the transition state, is inhibited by Ca2+ and Mg2+. The catalysis of the p-nitrophenyl phosphate reaction has been attributed to a favorable electrostatic interaction of the divalent metal ion with the oxygen atom of the leaving group in the transition state, in addition to the interaction with phosphoryl oxygen atoms.59 The value of β = −0.7 for the p-nitrophenyl alkoxy intermediates of salicylate O-aryl phosphate diesters catalyzed by Zn+ ion, compared with β = −1.2 in the absence of divalent metal ions,60 suggests that the charge on the leaving group is partially neutralized in the transition state by an interaction with the divalent metal ion.

The facilitation of nucleophilic attack by Co(III) coordination of p-nitrophenyl phosphate diester and OH− or NH2− shows that bridging of reactants can increase rates of reaction by inducing intramolecularity.61 In addition, monodentate ammines chloride provide rate enhancements of two orders of magnitude for the hydrolysis of AcP, presumably because the phosphoryl anion binds to the positively charged ammonium moieties of the micelle, which induces intramolecularity of the carbonyl moiety of AcP and the amine nucleophile of the micelle.62

The enhanced reactivity of the monocations of primary and secondary amines with the anion of mononuclear phosphoryl compounds appears to be another example of bridging, in this case through hydrogen bonding of the protonated amine to one or more phosphoryl oxygen atoms. These monocations react with p-nitrophenyl phosphate diester and with phosphorolylated isoquinoline and substituted pyridine monoaon, about twofold faster than predicted from Bronsted-type correlations for a series of primary amines.63,64 Kirby and Jencks originally suggested that the rate enhancements with primary alkylamine monocations result from an indirect electrostatic attraction, rather than from hydrogen bonding, because the reaction of p-nitrophenyl phosphate diester with the monocation of Dabc, which cannot hydrogen bond to the substrate in the transition state, is faster than predicted from the rate constant for the free base of Dabc and β = 0.1.65 However, the finding of a negative value of β for attack by quinolines on PNPP has removed the basis for the conclusion.66 Comparisons of the reactivity of charged and uncharged nucleophilic reagents in several systems indicate that charged groups which are separated by several atoms from the nucleophile have little or no effect on observed rate constants for reaction with phosphoryl groups as the result of electrostatic interaction, at least for reactions in water at moderate ionic strength. This suggests that the rate enhancement observed with flexible dianion monocations is the result of hydrogen bonding to the anionic phosphoryl group.

(1) Dabcmonocation shows the same 3.2-fold rate increase as uncharged quinuclidines for reaction with the 2,4-dinitrophenyl phosphate diester/Ca2+ complex compared with free dinitrophenyl phosphate.1 (2) Piperazine monocation and three uncharged cyclic secondary amines follow the same Bronsted correlation (β = 0) for reaction with phosphorolylated isoquinoline monoaon.17 (3) The rate constants for reactions of cyclic dianion monocations with other monosubstituted phosphate compounds are smaller than predicted by Bronsted correlations for structurally related amines.67,68 (4) Glycine falls on the same Bronsted correlation


57) The association constants for hydrogen-bonded complexes measured by Stahl and Jencks suggest that multiple hydrogen bonds are necessary to explain the observed association constant for reaction of the Na+ ion with PiP: Stahl, N.; Jencks, W. P. J. Am. Chem. Soc. 1986, 108, 4196-4205.

line as other primary amines for reaction with p-nitrophenyl phosphate dianion and phosphorylated isoquinoline monoanion.\textsuperscript{1,2,6}

(5) Nicotinate anion falls on the same Brensted correlation line as uncharged pyridines for reaction with phosphorylated pyridine monoanions.\textsuperscript{10} An apparent exception is the 8-fold decrease in the reactivity of nicotinate anion compared with uncharged pyridines for reaction with 2,4-dinitrophenyl phosphate dianion.\textsuperscript{5,6}

(65) It has been suggested that rate constants for reactions of phosphoryl compounds with monocations of Dabco and piperazine may be greater than expected, as a result of electrostatic attraction: Lloyd, G. J.; \textit{et al.}, \textit{J. Am. Chem. Soc.} 1971, 93, 4839-4892; ref 64. However, Brensted-type correlations that support rate constants that are greater than predicted have not been reported.

The reason for this is not clear, but it may involve an unfavorable interaction between an oxygen atom of the constrained meta phosphoryl group of nicotinate with an oxygen atom of the phosphoryl group. Inspection of CPK molecular models suggests that the distance between the phosphoryl oxygen atoms and the carboxylate oxygen atoms of glycinic and of nicotinate is nearly the same in the two transition states, but the glycine carboxylate group is free to move to a position in which it is pointed away from the phosphoryl group.

Neutron Profile Refinement of the Structure of FeOCl and FeOCl(TTF)\textsubscript{1/8.5}

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Contribution from the Department of Chemistry, University of Virginia, Charlottesville, Virginia 22901, Department of Chemistry, Michigan State University, East Lansing, Michigan 48824, and Argonne National Laboratory, Argonne, Illinois 60439. Received April 11, 1986

Abstract: Neutron diffraction studies on powder samples of FeOCl and FeOCl(TTF)\textsubscript{1/8.5} establish that TTF intercalated into FeOCl contributes to the diffraction pattern and exhibits long-range order. Room-temperature time-of-flight diffraction results are reported. The structure of FeOCl was refined in a space group \textit{Pmn2}_1 with \(a = 3.7730\) (1), \(b = 7.9096\) (1), and \(c = 3.3010\) (1) \(\AA\). Least-squares Rietveld refinement (21 parameters, 3296 degrees of freedom) yielded \(R = 0.0115\), \(R_B = 0.0203\), and \(R_{E{\text{xp}}} = 0.0111\) (28 parameters, 1894 degrees of freedom).

Indicating that the structure of the host layers has not changed significantly. Powder X-ray diffraction data confirm the existence of the four possible sites, to give \(R = 0.0203\), \(R_w = 0.0289\), and \(R_{E{\text{xp}}} = 0.0111\) (28 parameters, 1894 degrees of freedom).


(2) \textit{Rietveld refinement (21 parameters, 3296 degrees of freedom) yielded \(R = 0.0115\), \(R_B = 0.0203\), and \(R_{E{\text{xp}}} = 0.0111\) (28 parameters, 1894 degrees of freedom).}

(3) \textit{Rietveld refinement (21 parameters, 3296 degrees of freedom) yielded \(R = 0.0115\), \(R_B = 0.0203\), and \(R_{E{\text{xp}}} = 0.0111\) (28 parameters, 1894 degrees of freedom).}

(4) \textit{Rietveld refinement (21 parameters, 3296 degrees of freedom) yielded \(R = 0.0115\), \(R_B = 0.0203\), and \(R_{E{\text{xp}}} = 0.0111\) (28 parameters, 1894 degrees of freedom).}

(5) \textit{Rietveld refinement (21 parameters, 3296 degrees of freedom) yielded \(R = 0.0115\), \(R_B = 0.0203\), and \(R_{E{\text{xp}}} = 0.0111\) (28 parameters, 1894 degrees of freedom).}

(6) \textit{Rietveld refinement (21 parameters, 3296 degrees of freedom) yielded \(R = 0.0115\), \(R_B = 0.0203\), and \(R_{E{\text{xp}}} = 0.0111\) (28 parameters, 1894 degrees of freedom).}

(7) \textit{Rietveld refinement (21 parameters, 3296 degrees of freedom) yielded \(R = 0.0115\), \(R_B = 0.0203\), and \(R_{E{\text{xp}}} = 0.0111\) (28 parameters, 1894 degrees of freedom).}

(8) \textit{Rietveld refinement (21 parameters, 3296 degrees of freedom) yielded \(R = 0.0115\), \(R_B = 0.0203\), and \(R_{E{\text{xp}}} = 0.0111\) (28 parameters, 1894 degrees of freedom).}

(9) \textit{Rietveld refinement (21 parameters, 3296 degrees of freedom) yielded \(R = 0.0115\), \(R_B = 0.0203\), and \(R_{E{\text{xp}}} = 0.0111\) (28 parameters, 1894 degrees of freedom).}

(10) \textit{Rietveld refinement (21 parameters, 3296 degrees of freedom) yielded \(R = 0.0115\), \(R_B = 0.0203\), and \(R_{E{\text{xp}}} = 0.0111\) (28 parameters, 1894 degrees of freedom).}

(11) \textit{Rietveld refinement (21 parameters, 3296 degrees of freedom) yielded \(R = 0.0115\), \(R_B = 0.0203\), and \(R_{E{\text{xp}}} = 0.0111\) (28 parameters, 1894 degrees of freedom).}

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