Kinetic Study of the Reaction of Tetrakis(hydroxymethyl)phosphonium Cation with Urea

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Abstract: The reaction of the tetrakis(hydroxymethyl)phosphonium cation with urea has been investigated calorimetrically and by means of ^{31}P NMR spectroscopy. The heat of reaction amounts to $\Delta H = -24$ kcal/mol. The reaction involves the stepwise condensation of the methylol groups with urea, with at least four different phosphonium species present in the reaction mixture. The kinetics of the reaction can be analyzed in terms of the sequence in eq 4, with $k_1 = 3.0 \times 10^{-3}$, $k_2 = 2.25 \times 10^{-3}$, and $k_3 = 1.5 \times 10^{-3}$ s^{-1} at $T = 65$ °C. The onset of the gelation of a stoichiometric reaction mixture is in agreement with Flory's theory of gelation and corresponds to a conversion of $p = 0.587$. A reaction mechanism is proposed which involves the dissociation of the tetrakis(hydroxymethyl)phosphonium cation as the rate-limiting step.

The reaction between the tetrakis(hydroxymethyl)phosphonium cation, TK, and urea, U, is the basis for durable flame retardant treatments of cellulose-containing textile materials. An aqueous solution of the two components is padded on the textile fabric, which is then subsequently subjected to a heat cure to produce the flame retardant finish.[1,2] Although it is known that the reaction involves a polycondensation of the TK methylol groups with the amide groups of urea to form a highly cross-linked resin, the details of this condensation process are still unknown.

In order to increase the understanding of this important commercial process, we have studied the kinetics of the condensation reaction by means of ^{31}P NMR spectroscopy.

Experimental Section

Materials Used. The tetrakis(hydroxymethyl)phosphonium phosphate–acetate was Pyroset Fire Retardant TKP, American Cyanamid Co. Urea (American Cyanamid Co.), 1,3-dimethylurea (Aldrich), and formaldehyde (37% solution, Baker) were used as received. Dimethylolurea was synthesized from urea and formaldehyde.

Procedures. Calorimetry. The calorimeter was a 250-mL Dewar flask, fitted with a magnetic stirrer and a Hg thermometer. The Dewar flask was preheated with water to the desired reaction temperature. The two preheated reactant solutions were then introduced separately and mixed by means of the magnetic stirrer. After mixing, the stirrer was stopped and the reaction temperature monitored. The temperature rise was corrected for cooling; and the heat of reaction was then estimated from the maximum temperature rise of the reaction mixture, assuming a specific heat of 1.00 cal/g.

^{31}P NMR Spectroscopy. ^{31}P NMR spectra were measured with a HA-100 spectrometer at 40.5 MHz (23.5 kG) operating in the HR mode. P_4O_6 was used as the external standard; the solutions were used without dilution at the original concentrations. Instrument settings were as follows: rf attenuation, 10 dB; receiver gain, 2; recorder speed, 1000 s; scanning speed, 25 for normal spectrum, 3 for expanded regions of spectrum.

Kinetic Measurements. Since the reaction is sensitive toward changes of pH, the reaction mixture was buffered at pH 5.0 using 1.0 M acetate buffer. The reaction was initiated by immersing NMR tubes containing a stoichiometric solution of the reactants into a constant temperature bath, set at 65 ± 0.1 °C. Individual NMR tubes were then quenched in ice water at specified time intervals. The samples were kept at 0 °C until they were introduced into the NMR cavity. The actual measurements were carried out at room temperature.

Viscosimetry. The determination of the gel point was carried out viscosimetrically in a separate experiment. The viscosity of the thermostated reaction mixture was monitored by means of a "Rotovisco" rotating viscometer. The gel point coincides with the onset of the steep viscosity increase.

Results and Discussions

Dissociation Equilibrium of Tetrakis(hydroxymethyl)phosphonium Cation and the Reaction Stoichiometry. The dissociation of TK is described by the equation

$$^{+}P(CH_2OH)_4 \rightleftharpoons P(CH_2OH)_3 + CH_2O + H^+ \quad (1)$$

with an equilibrium constant of $K_1 = 8.70 \times 10^{-8}$ M^2.[3] At pH 5.0 and in the presence of excess formaldehyde, $[F]_{free} = 0.25[TK]_0$, the equilibrium is far to the left with practically all of the organic phosphorus in the phosphonium form. This assumption is supported by the ^{31}P NMR spectrum of the TK–phosphate–acetate depicted in Figure 1. The spectrum shows only the phosphonium and the phosphate absorptions, the latter being due to the presence of the $H_2PO_4^-$ anion, while the equilibrium concentration of the tertiary phosphine is below the detection limit.

To select proper starting concentrations for TK and U, it is necessary to establish the reaction stoichiometry. Since the reaction is markedly exothermic, the stoichiometry can be determined calorimetrically: by increasing the initial ratio of [U]/[TK], the amount of heat liberated during the reaction increases until this ratio corresponds to the stoichiometry of the reaction. Beyond this point, the heat of reaction becomes constant. According to Figure 2, this leveling off occurs at a reactant ratio of [U]/[TK] = 2, which suggests a stoichiometry according to the equation

$$^{+}P(CH_2OH)_4\,X^- + 2H_2NCONH_2 = \text{product} \quad (2)$$

Therefore, the reaction occurs between a tetrafunctional phosphonium cation and a bifunctional amide. The bifunctionality of U is supported by the observation that 1,3-dimethylurea does not react with TK under identical reaction conditions: apparently, replacement of one amide hydrogen by a methyl group is sufficient to prevent the condensation reaction from occurring.

From Figure 2 one obtains a value for the heat of reaction of $\Delta H = -24$ kcal/mol TK, which corresponds to $\Delta H = -6$ kcal/mol CH_2OH group. This is in agreement with the reported heat of reaction for the condensation of F with U,[4] indicating that the exothermicity of the reaction between TK and U can be accounted for by the condensation of all four methylol groups of the TK cation with amide groups. The heat of reaction is, therefore, apparently the same, regardless whether the condensation involves free formaldehyde or a methylol group bonded to quaternary phosphorus.

^{31}Phosphorus NMR Spectra of Tetrakis(hydroxymethyl)phosphonium Phosphate–Acetate in the Presence of Urea.

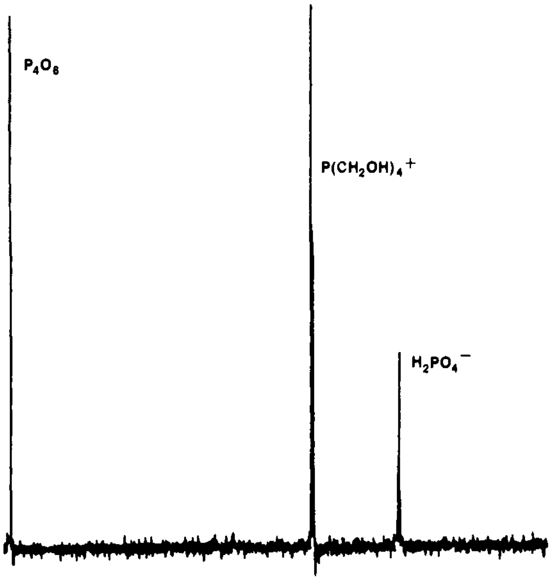

Figure 1. ^{31}P NMR spectrum of a 1.84 M aqueous solution of tetrakis(hydroxymethyl)phosphonium phosphate-acetate; pH 5.0, 1 M acetate buffer.

Table I. Relative Concentrations of Phosphorus Species at Different Reaction Times[a]

Reaction time, min	$[^+PR_4]/([^+PR_4] + [PR_3])$	$([^+PR_4] + [PR_3])/([^+PR_4] + [PR_3] + [H_2PO_4^-])$
0	0.892	0.71
6	0.832	0.71
13	0.818	0.71
18	0.799	0.72
21	0.838	0.72
Av	0.836 ± 0.035	0.71

[a] Conditions as in Figure 3.

Figure 3 shows the ^{31}P NMR spectra of a stoichiometric reaction mixture consisting of 1.84 M TK and 3.68 M U, buffered at pH 5.0, for different reaction times. Comparison with Figure 1 shows that the presence of U causes the appearance of a new absorption, which is assigned to $P(CH_2OH)_3$. The appearance of this species directly after mixing of the reactant solutions indicates a shift of the eq 1 equilibrium to the right side, which is obviously caused by the reaction of U with F according to the equation

$$CH_2O + H_2NCONH_2 \rightleftharpoons HOCH_2NHCONH_2 \quad (3)$$

which in turn has an equilibrium constant of $K_3 = 27.8\ M^{-1}$.[4] The sum of the integrated intensities of the phosphonium and the phosphine absorptions relative to that of the phosphate anion remains approximately constant throughout the reaction, which means that no appreciable amounts of other phosphorus species such as phosphine oxides are formed. Table I lists the distribution of organic phosphorus between phosphonium and phosphine species for different reaction times. One recognizes that this distribution remains likewise unchanged.

While the total intensity of the phosphonium absorption remains constant, one observes at high reaction times, according to Figure 3, the appearance of up to four separate lines in the phosphonium region of the spectrum. The new lines appear downfield from the original $^+P(CH_2OH)_4$ line and are assigned to $^+P(CH_2OH)_{4-n}(CH_2NHCONH_2)_n$ species. Based on the variation of their relative intensities with reaction time, the four phosphonium lines are assigned as follows: $A_1 = {}^+P(CH_2OH)_4$, $A_2 = {}^+P(CH_2OH)_3(CH_2NHCONH_2)$, $A_3 = {}^+P(CH_2OH)_2(CH_2NHCONH_2)_2$, $A_4 = {}^+P(CH_2OH)(CH_2NHCONH_2)_3$. Apparently, the downfield shift is highest for the phosphonium species containing the largest number of P-C-N bonds.

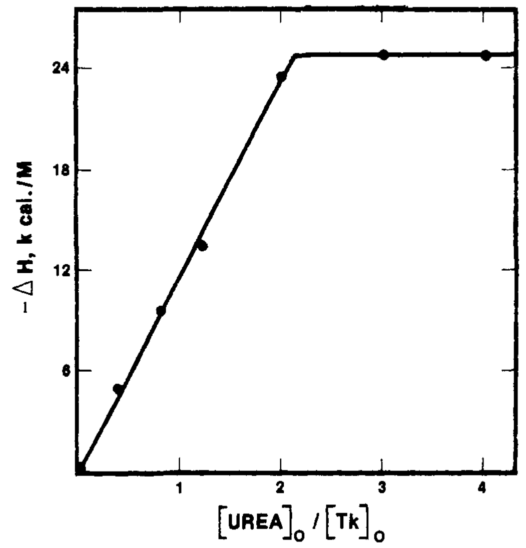

Figure 2. Calorimetric determination of the reaction stoichiometry. Conditions: $[TK]_0 = 0.92$ M; $[U]_0 = 0.4$-4.0 M; pH 5.0; $T = 65$ °C.

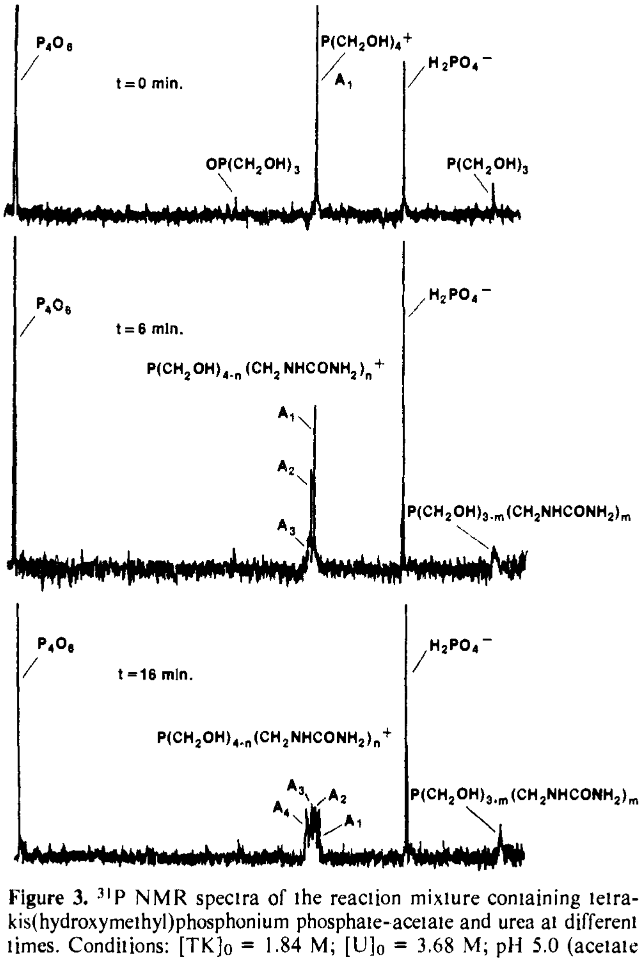

Figure 3. ^{31}P NMR spectra of the reaction mixture containing tetrakis(hydroxymethyl)phosphonium phosphate-acetate and urea at different times. Conditions: $[TK]_0 = 1.84$ M; $[U]_0 = 3.68$ M; pH 5.0 (acetate buffer); $T = 65$ °C.

From the stoichiometry according to eq 2, one should expect the appearance of a fifth line corresponding to the fully substituted phosphonium species. Failure to observe this line may be due to the fact that at high conversions the reaction mixture

Table II. Chemical Shifts of the Phosphorus Species Present in the Tetrakis(hydroxymethyl)phosphonium Cation–Urea System

Chemical shift, ppm[a]	Assignment
136.3	$P(CH_2OH)_3$
110.1	$H_2PO_4^-$
85.3	$^+P(CH_2OH)_4$
84.3	$^+P(CH_2OH)_3(CH_2NHCONH_2)$
83.2	$^+P(CH_2OH)_2(CH_2NHCONH_2)_2$
81.8	$^+P(CH_2OH)(CH_2NHCONH_2)_3$
62.9	$OP(CH_2OH)_3$

[a] Chemical shifts are upfield and relative to P_4O_6.

Table III. Relative Concentrations of the Phosphonium Species at Different Reaction Times[a]

Reaction time, min	Relative concn			
	A_1	A_2	A_3	A_4
0	1.00	0.00	0.00	0.00
2	0.63	0.31	0.06	0.00
4	0.45	0.41	0.14	0.00
6	0.33	0.45	0.22	0.00
8	0.24	0.39	0.32	0.05
10	0.19	0.41	0.33	0.07
12	0.16	0.35	0.38	0.11
14	0.12	0.34	0.41	0.13
16	0.09	0.31	0.40	0.20
18	0.08	0.30	0.35	0.27
20	0.07	0.28	0.33	0.32

[a] Conditions as in Figure 3.

undergoes gelation, which leads to a considerable broadening of the NMR absorptions, thus making the detection of the postulated species difficult.

The $P(CH_2OH)_3$ absorption is likewise found to broaden at higher reaction times, indicating the formation of substituted phosphines during the reaction. In this case, however, the new lines seem to appear upfield from the $P(CH_2OH)_3$ absorption. Since the differences of the chemical shifts are smaller and the total intensity is lower in this case, a resolution of the individual lines is not possible.

The chemical shifts for the various phosphorus species in the reaction mixture are listed in Table II.

Quantitative Determination of the Phosphonium Species in the Tetrakis(hydroxymethyl)phosphonium Cation–Urea System and Kinetic Analysis. By expanding the NMR spectrum in the phosphonium region it becomes possible to integrate separately each phosphonium line. Therefore, concentration–time data for the individual phosphonium species are obtained as shown in Table III.

Table III shows that A_1 steadily decreases as the reaction proceeds and A_2 and A_3 both go through a maximum, while A_4 keeps increasing until the gel point of the reaction mixture is attained. This behavior suggests that the time dependences of the concentrations of the four phosphonium species can be explained in terms of the consecutive reaction scheme:

$$A_1 \xrightarrow{k_1} A_2 \xrightarrow{k_2} A_3 \xrightarrow{k_3} A_4 \qquad (4)$$

Owing to the fact that the reaction leads to an insoluble cross-linked gel, this sequence can be considered as a series of irreversible reactions. While the time dependences of the species A_2, A_3, and A_4 are likely to be complex, the decay of A_1 is expected to obey a second-order rate equation, since the reaction is run under stoichiometric conditions. Rather surprisingly, the data of Table III suggest an exponential decay of the A_1 species instead, indicating that the reaction between TK and U cannot be rate determining for the conditions according to Figure 2, but must be preceded by a slower first-order process.

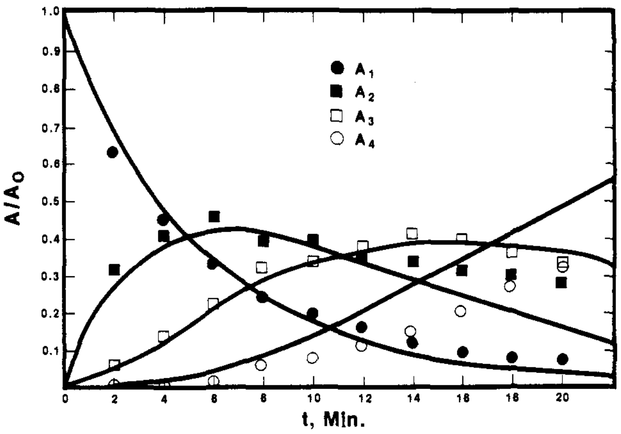

Figure 4. Calculated and experimental time dependences for the different phosphonium species according to the sequence given in eq 4.

The decay of A_1 according to Table III is satisfied by a rate constant of $k_1 = 3.0 \times 10^{-3}\ s^{-1}$. Assuming that the time dependences of the remaining species are likewise governed by first-order processes, the reaction sequence can be treated as a series of three first-order processes with A_2 and A_3 as intermediates and A_4 as the reaction product. This system has been integrated;[5] the concentration–time integrals for all four species are listed in Table IV.

While k_1 can be readily determined, the evaluation of k_2 and k_3 is possible only by iterative methods. However, if one makes the ad hoc assumption that the condensation of each free methylol group occurs with the same velocity and is not affected by the structure of the phosphonium species to which it is attached, the rate constant for the consumption of every phosphonium species should be proportional to the number of free methylol groups attached to it. Considering the structures assigned to the four species according to Table II, the ratios of the three rate constants should, therefore, be: $k_1/k_2/k_3 = 4{:}3{:}2$. With this assumption one obtains $k_1 = 3.00 \times 10^{-3}$, $k_2 = 2.25 \times 10^{-3}$, and $k_3 = 1.50 \times 10^{-3}\ s^{-1}$, respectively. Using the integrals from Table IV, the time dependence of the concentrations of the four phosphonium species is plotted in Figure 4 together with the experimental points taken from Table III. One recognizes that the fit of the experimental data to the kinetic model is satisfactory. Significant deviations are encountered only at higher reaction times, particularly for A_4. This is probably due to integration errors caused by increased line broadening at higher degrees of conversion.

Infinite Network Formation in the System Tetrakis(hydroxymethyl)phosphonium Cation–Urea. The reaction between stoichiometric amounts of the tetrafunctional TK and the bifunctional U eventually leads to the formation of an infinite polymer network. The appearance of this network is characterized by a sharply defined gel point, which in turn can be determined viscosimetrically.

According to Flory's theory of gelation,[6] the critical degree of branching, α_c, at the point of gelation is given by $\alpha_c = 1/(f - 1)$. Since the functionality, f, of the branching unit is four in the case of TK, the theoretical branching coefficient of $\alpha_c = 0.333$ is obtained. For stoichiometric concentrations of the reacting groups, the branching coefficient is related to the extent of reaction, p, by $\alpha_c = p^2$. Hence, for the reaction between a tetrafunctional and a bifunctional unit, the theoretical extent of reaction at the gel point is $p_c = 0.577$.

Experimentally, the time to gelation for the experimental conditions according to Figure 3 is $t_g = 21.5$ min. Using the

Table IV. Concentration–Time Functions for the System

$$A_1 \xrightarrow{k_1} A_2 \xrightarrow{k_2} A_3 \xrightarrow{k_3} A_4{}^a$$

$$A_1/A_0 = e^{-k_1 t}$$

$$A_2/A_0 = \frac{k_1}{k_2 - k_1}(e^{-k_1 t} - e^{-k_2 t})$$

$$A_3/A_0 = k_1 k_2 \left\{\frac{e^{-k_1 t}}{(k_2 - k_1)(k_3 - k_1)} - \frac{e^{-k_2 t}}{(k_2 - k_1)(k_3 - k_2)} + \frac{e^{-k_3 t}}{(k_3 - k_2)(k_3 - k_1)}\right\}$$

$$A_4/A_0 = 1 - \frac{k_2 k_3 e^{-k_1 t}}{(k_2 - k_1)(k_3 - k_1)} + \frac{k_1 k_3 e^{-k_2 t}}{(k_2 - k_1)(k_3 - k_2)} - \frac{k_1 k_2 e^{-k_3 t}}{(k_3 - k_2)(k_3 - k_1)}$$

[a] Conditions for $t = 0$: $A_1 = A_0$; $A_2 = A_3 = A_4 = 0$.

Table V. Calculated Concentrations of the Different Phosphonium Species at the Gel Point[a]

Species	Calcd concn at $t_g = 21.5$ min	Concn of reacted methylol groups
$^+P(CH_2OH)_4$	0.021	0.000
$^+P(CH_2OH)_3(CH_2NHCONH_2)$	0.136	0.136
$^+P(CH_2OH)_2(CH_2NHCONH_2)_2$	0.333	0.666
$^+P(CH_2OH)(CH_2NHCONH_2)_3$	0.510	1.530
$\sum CH_2OH_{reacted}$ =		2.330
$\sum CH_2OH_{reacted}/\sum CH_2OH_{initial}$ =		2.330/4.000 = 0.583

[a] Conditions as in Figure 3.

integrated rate expressions of Table IV, one can calculate the concentrations of the various phosphonium species and hence the extent of conversion of the initially present methylol groups at the gel point. As shown in Table V, the total conversion at the gel point amounts to $p = 0.583$, which is in good agreement with the requirements of Flory's theory, thus supporting the validity of the kinetic model based on equal reactivities of the free methylol groups.

The fact that the calculated composition of the reaction mixture at the gel point correctly reflects the theoretical requirements suggests that the experimental deviations apparent in Figure 4 are caused by experimental error rather than by an incorrect kinetic model.

In order to reconcile the stoichiometric requirements with the extent of reaction at the gel point, one has to assume that the reaction progresses beyond this point. This is supported by the fact that the heat evolution of the reaction mixture continues after gelation has taken place, indicating that further condensation is occurring. Quantitative NMR measurements of closely spaced absorptions beyond the gel point are, however, not feasible owing to increased line broadening.

The Reaction Mechanism. A possible pathway for the polycondensation of TK with U is the direct reaction of CH_2OH groups attached to quaternary phosphorus with urea NH_2 groups. This simple picture is compatible with the observed statistical ratio of $k_1/k_2/k_3 = 4{:}3{:}2$. However, it is not capable of explaining the observed first-order kinetics for the disappearance of the $^+P(CH_2OH)_4$ species in a stoichiometric reaction mixture. A direct condensation of methylol groups attached to phosphorus should moreover result in a shift of the eq 1 equilibrium to the left side, thus decreasing the equilibrium concentration of the tris(hydroxymethyl)phosphine in the presence of urea even further, which is the direct opposite of the observed behavior.

A reaction sequence which is in better agreement with the experimental results is given by Scheme I:

Scheme I

$$^+P(CH_2OH)_4 \xrightarrow{k_A} P(CH_2OH)_3 + CH_2O + H^+ \quad (A)$$

$$CH_2O + H_2NCONH_2 \xrightarrow{k_B} HOCH_2NHCONH_2 \quad (B)$$

$$HOCH_2NHCONH_2 + H^+ \xrightarrow{k_C} {}^+CH_2NHCONH_2 + H_2O \quad (C)$$

$$^+CH_2NHCONH_2 + P(CH_2OH)_3 \xrightarrow{k_D} {}^+P(CH_2OH)_3CH_2NHCONH_2 \text{ etc.} \quad (D)$$

Since the reaction is buffered, the $[H^+]$ terms in Scheme I are constant. If the reaction is run at a lower pH, a decrease of the reaction rate is noted, which indicates that reaction A is reversible, i.e., that the equilibrium according to eq 1 is operative. On the other hand, addition of formaldehyde causes a slight increase of the reaction rate rather than leading to the expected decrease. This apparent inconsistency can be resolved, if one assumes that the dissociation of the phosphonium cation occurs in two stages according to eq 5[3] and that only the first step, eq 5a, represents a mobile equilibrium while the second step, eq 5b, is virtually irreversible due to the rapid consumption of formaldehyde according to reaction B of Scheme I.

$$^+P(CH_2OH)_4 \rightleftharpoons {}^+P(CH_2OH)_3CH_2O^- + H^+ \quad (5a)$$

$$^+P(CH_2OH)_3CH_2O^- \rightarrow P(CH_2OH)_3 + CH_2O \quad (5b)$$

The fact that step B is indeed fast and therefore kinetically not important is established by the observation that using dimethylolurea instead of urea does not increase the reaction velocity. Since for the reaction conditions employed [urea] ≫ [formaldehyde], reaction B should obey pseudo-first-order kinetics. The corresponding pseudo-first-order rate constant for the conditions of Figure 3 can be estimated from the reported values $k^{35°C}$ (U + F) $\approx 4.4 \times 10^{-4}$ M^{-1} s^{-1} and E = 14 kcal/mol;[4] one obtains $k_B \approx 12 \times 10^{-3}$ 3 s^{-1}, which is four times as large as the experimentally obtained value of $k_1 = 3 \times 10^{-3}$ s^{-1}, indicating that $V_B > V_A$ is indeed valid. Finally, to account for the fact that the equilibrium concentration of $P(CH_2OH)_3$ is increased in the presence of urea, one has to assume that $V_B > V_D$ throughout the course of the reaction.

These considerations, therefore, suggest that the rate of reaction between TK and U under stoichiometric conditions is controlled by the dissociation of the zwitterion, $^+P(CH_2OH)_3CH_2O^-$, according to eq 5b. To explain the statistical ratios of the rate constants for the consecutive condensation steps, one has to assume that the velocity of the dissociation is not affected by the presence of N-substituted methylol groups at the reacting phosphorus atom.

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Cobalt(III)-Promoted Hydrolysis of a Phosphate Ester

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Abstract: Chelated *p*-nitrophenylphosphatobis(trimethylenediamine)cobalt(III) perchlorate hydrolyses in the pH range 6.5–13.5 to ~35% *p*-nitrophenol and ~65% monodentate *p*-nitrophenylphosphate with a rate law, $k_{\mathrm{obsd}} = k_1 + k_2[\mathrm{OH}^-]$, $\mu = 0.5$, 25 °C where $k_1 = 7 \times 10^{-5}\ \mathrm{s}^{-1}$ and $k_2 = 5.1\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$. Tracer studies indicate that ester cleavage and chelate opening on the metal ion occur by different paths, through the chelated five-coordinate phosphorane intermediate and the conjugate base hydrolysis mechanism for Co(III) amine complexes, respectively. The ester hydrolysis is accelerated 10^9-fold relative to the uncoordinated ester in basic solution. Evidence for strain in the four-membered ring of the chelated ester is adduced from an x-ray crystallographic analysis of phosphatobis(ethylenediamine)cobalt(III) which is also reported. The results are discussed in relation to alkaline phosphatase activity.

One of the striking observations in biological phosphate chemistry is that it all appears to be metal ion catalyzed. However, the role of the metal ion in promoting biological hydrolysis reactions of phosphate derivatives including phosphate esters has been the subject of considerable speculation.[2-6] Some experimental approaches have involved model systems in which the relationship between the metal ion and the phosphate derivative has been difficult to define and in which the catalytic effects have been modest.[3]

The idea that chelate formation between a phosphate ester and a metal ion could result in greatly enhanced hydrolysis rates was conceived at least by Farrell, Kjellstrom, Spiro,[3] and ourselves after the extraordinarily high reactivity for five-membered cyclic phosphate esters was observed.[7] However, a tractable and unequivocal system to demonstrate this hypothesis has proved difficult to find and characterize. The experiments in this area,[3] with methyl phosphate and ethylenediamine and triethylenetetraminecobalt(III) complexes have displayed relatively small acceleratory effects over free methyl phosphate and there are many mechanistic ambiguities. We report here on the hydrolytic reactivity of *p*-nitrophenylphosphate in the chelate (*p*-nitrophenylphosphato)bis(trimethylenediamine)cobalt(III) cation, $[\mathrm{Co(tn)_2O_3PO\text{-}C_6H_4NO_2}]^+$, a complicated but tractable system.

We have not discovered any structural studies of bidentate covalently bound phosphate complexes. Consequently we report an x-ray crystal structure analysis of phosphatobis(ethylenediamine)cobalt(III) which defines the geometry of the four-membered chelated phosphate ring and is relevant to the hydrolysis study.

Experimental Methods

Visible-UV spectra and rate data were collected on a Cary-118 recording spectrophotometer. ^1H NMR spectra were obtained at 100 MHz on a JEOL Minimar spectrometer. pH measurements were made with a Radiometer pH meter 26 using a sodium chloride salt bridge, with standardizations before and after measurements.

Analytical reagents were used in kinetic studies, except where otherwise specified. *p*-Nitrophenylphosphate, disodium salt, hexahydrate (Gold Label, 99%) was obtained from Aldrich Chemical Co. Sodium hydroxide solutions were freshly prepared from May and Baker "Volucon" concentrate, using carbon dioxide free water.

***trans*-[Co(tn)₂(OH)(OH₂)](ClO₄)₂** was prepared from $[\mathrm{Co(tn)_2CO_3}]\mathrm{ClO_4}$ in accord with the procedure of Jonasson et al.[8]

Anal. Calcd for $\mathrm{CoC_6H_{23}N_4Cl_2O_{10}}$: C, 16.34; H, 5.26; N, 12.70. Found: C, 16.3; H, 5.2; N, 12.5.

***trans*-[Co(tn)₂Cl₂]ClO₄** was prepared by heating excess ~6 M aqueous hydrochloric acid and *trans*-$[\mathrm{Co(tn)_2(OH)(OH_2)}](\mathrm{ClO_4})_2$ on a steam bath for ~30 min. After cooling, aqueous perchloric acid (~4 M) was added. The green product was collected and washed with dilute aqueous perchloric acid followed by ethanol and then ether before drying it over phosphorus pentoxide in vacuo.

[Co(tn)₂O₃POC₆H₄NO₂]ClO₄. Stoichiometric quantities of silver perchlorate (BDH, LR) and *p*-nitrophenylphosphate, disodium salt, hexahydrate, were mixed in aqueous solution to precipitate $\mathrm{Ag_2[O_3POC_6H_4NO_2]}$. The product was washed with cold water and dried, in the dark, in vacuo over phosphorus pentoxide (~80% yield). $\mathrm{Ag_2[O_3POC_6H_4NO_2]}$ (2.02 g, finely ground), *trans*-$[\mathrm{Co(tn)_2Cl_2}]\mathrm{ClO_4}$ (1.76 g), and $\mathrm{Me_2SO}$ (30 mL) were stirred (in a stoppered flask) at 20 °C in the dark. After ~10 min the solution became violet. Stirring was continued for ~18 h before removing the AgCl. The product was precipitated with dry ethanol and ether, filtered with minimum exposure to air, and washed with ethanol and then ether. Purification was achieved by dissolving it in a small volume of $\mathrm{Me_2SO}$ (~5 mL) and reprecipitating with aqueous $\mathrm{NaClO_4}$ (0.25 M, 50 mL). The violet crystalline product was washed with aqueous $\mathrm{NaClO_4}$, then with ethanol followed by ether, after which it was dried in vacuo over phosphorus pentoxide (~30% yield).

Anal. Calcd for $\mathrm{CoC_{12}H_{24}N_5PClO_{10}}$: C, 27.52; H, 4.62; N, 13.37; P, 5.91; Cl, 6.77. Found: C, 27.6; H, 4.7; N, 13.2; P, 5.6; Cl, 6.5.

The ^1H NMR spectrum of $[\mathrm{Co(tn)_2O_3POC_6H_4NO_2}]\mathrm{ClO_4}$ in $\mathrm{Me_2SO}$-d_6 gave the following chemical shifts (parts per million downfield from external $\mathrm{Me_4Si}$; relative peak areas in parentheses): α-$\mathrm{CH_2}$, 1.49 (8); β-$\mathrm{CH_2}$, 2.47 (4); $\mathrm{NH_2}$, 3.65 and 3.89 (overlapping, total 4); $\mathrm{NH_2}$, 4.88 (2); aromatic H, doublet centered at 7.23 (2); $\mathrm{NH_2}$, 7.89, and aromatic H, doublet centered at 8.10 (overlapping, total 4).

Analysis of *p*-Nitrophenylphosphate. A sample of $[\mathrm{Co(tn)_2O_3PO\text{-}C_6H_4NO_2}]\mathrm{ClO_4}$ (0.027 g) was dissolved directly in 2 M NaOH (10 mL). After 2 min ($>8t_{1/2}$ for hydrolysis) the solution was diluted 25-fold and a spectral measurement on an aliquot showed 7% *p*-nitrophenolate released, (based on the weight of complex). The re-