Volume 18
Number 11
November 1979

Inorganic Chemistry

Contribution from Atomic Energy of Canada Limited, Research Chemistry Branch,
Whiteshell Nuclear Research Establishment, Pinawa, Manitoba, Canada R0E 1L0

Sodium Oxide–Phosphorus(V) Oxide–Water Phase Diagram near 300 °C: Equilibrium Solid Phases

PETER TAYLOR,* PETER R. TREMAINE,* and M. GRANT BAILEY

Received November 27, 1978

The products of evaporation at 290 °C of sodium phosphate solutions with Na/P ratios ranging from 1.6 to 9 have been recovered under controlled humidities for examination by X-ray powder diffraction. The equilibrium solid phases inferred from these experiments are combined with previously reported solubility data to derive a detailed description of the Na_2O–P_2O_5–H_2O ternary phase diagram near 300 °C. X-ray diffraction data are reported for the following previously unreported or incompletely characterized phases: $Na_3PO_4{\cdot}NaOH$, $Na_{3-x}H_xPO_4{\cdot}xH_2O$ (three forms), $Na_{2.5}H_{0.5}PO_4{\cdot}zH_2O$, and a previously unreported polymorph of $Na_2HPO_4{\cdot}NaH_2PO_4$. The structural relationship between $Na_{3-x}H_xPO_4{\cdot}xH_2O$ and the high-temperature modification of Na_3PO_4 is discussed.

Introduction

A detailed knowledge of the compositions of saturated sodium phosphate solutions near 300 °C is important for optimizing chemistry control in steam-generating boilers.[1-8] Previous fundamental studies of the Na_2O–P_2O_5–H_2O system have been summarized by Broadbent et al.[1] Although three solubility studies of this system in the temperature range 250–365 °C have been reported,[1-3] the nature of equilibrium solid phases is still incompletely understood. A phase of variable composition, approximating to $11Na_2O{\cdot}4P_2O_5{\cdot}3H_2O$ (or $Na_{2.75}H_{0.25}PO_4{\cdot}0.25H_2O$), is the equilibrium solid over a wide range of saturated solution compositions[1-3] (molar ratios in the range $\sim 2.2 \leq Na/P <$ at least 9). Near Na/P = 2.0, Na_2HPO_4 and $Na_4P_2O_7$ are equilibrium phases at 250 and 300 °C, respectively.[1] The system near Na/P = 2.0 is further complicated by liquid immiscibility.[1]

Although diffraction studies of a very large number of sodium phosphates have been reported,[9] crystallographic information pertinent to this study is restricted to powder data for Na_3PO_4,[9-13] Na_2HPO_4,[9] $Na_2HPO_4{\cdot}NaH_2PO_4$,[9] $Na_4P_2O_7$,[9] $Na_3PO_4{\cdot}0.5H_2O$,[10] and $11Na_2O{\cdot}4P_2O_5{\cdot}3H_2O$.[1] Anhydrous trisodium phosphate undergoes a reversible, probably nonreconstructive transformation from a tetragonal (α) to a cubic ("γ") structure near 300 °C.[10-12] The latter is believed to be isostructural with Na_2CaSiO_4, but precise atomic positional parameters have not been determined.[10] Kizilyalli and Welch[13] reported two orthorhombic forms of Na_3PO_4, but these have not been observed by other workers.[10-12] Mair[10] and Hooper et al.[14] have shown that cubic Na_3PO_4 has a considerable capacity for solid solution formation by substitution of either anions or cations. These solid solutions tend to retain the cubic structure at room temperature. Polymorphism has not been reported for any other anhydrous sodium orthophosphates.

The reported solubility studies[1-3] are in good general agreement, but practical limitations in the accuracy of such studies restrict the information which they can provide about equilibrium solid phases. We therefore adopted an alternative, complementary approach in which sodium phosphate solutions in the composition range $1.6 \leq Na/P \leq 9.3$, including values near known congruent and invariant points, were evaporated to dryness near 300 °C, and the solid products were analyzed by X-ray powder diffraction. The equilibrium solid phases inferred from these "drying up" experiments could then be used to confirm or expand the details of the solubility-derived phase diagram.

Experimental Section

Careful humidity control during recovery of the precipitated phases was essential, in order to avoid the formation of polyphosphate or hydrated phases. The experiments were conducted in two independently controlled Parr Series 4601, 1 dm^3, 316 stainless steel autoclaves shown in Figure 1, each with its own Parr 4913 heater assembly, a Love 4821 temperature controller, and a 0–3000 psi pressure gage. The autoclaves were connected by stainless steel tubing wrapped in heating tape to prevent condensation and could be isolated from one another by two Whitey SS-3VS4 high-temperature valves. The sample autoclave was loaded with about 300 cm^3 of sodium phosphate solution whose composition was calculated to be about 20% below saturation at 300 °C.[2] The solutions were poured both inside and outside the Zircaloy 2 can which was then covered by a loose top to prevent water which had condensed on the autoclave head from entering the can during cool-down. With the more concentrated solutions of lower Na/P ratios, water, rather than solution, was poured outside the can, to reduce corrosion of the autoclave. The autoclave was left overnight at 300 °C before commencing the evaporation. The temperature was measured and controlled by a stainless-steel-jacketed, iron–constantan thermocouple which passed through a Conex MIC-062-AL thermocouple fitting in the autoclave head into a well at the bottom of the can. Solutions were evaporated to dryness by slowly releasing water vapor through the condenser. The autoclave temperature fell during the evaporation to 290 ± 5 °C and was consistent with the observed water vapor pressure as long as liquid solution was present. A brief overshoot (<15 min) of up to 50 °C occurred just as the abrupt fall in the vapor pressure indicated that the final traces of liquid had evaporated. This did not appear to cause appreciable decomposition of the samples. In general, the material which precipitated inside and outside the Zircaloy can had similar X-ray diffraction patterns, but the latter was visibly colored and more poorly crystalline.

The water autoclave contained doubly distilled water and was used to inhibit the decomposition of sodium hydrogen orthophosphates to pyrophosphates at Na/P ratios below 3.00 by maintaining a given partial pressure of water vapor in the sample autoclave. In practice, the second autoclave was maintained at a temperature about 15 °C

0020-1669/79/1318-2947$01.00/0 © 1979 American Chemical Society

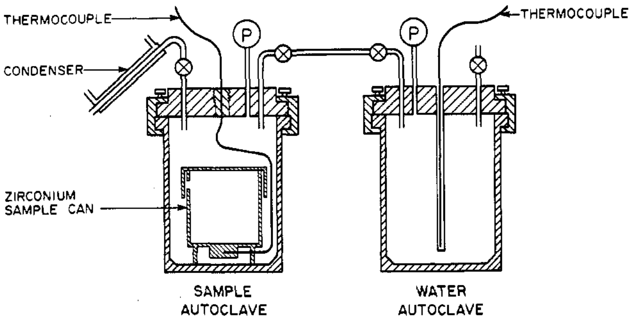

Figure 1. Autoclave assembly.

below the first during the evaporation and cooling steps. Water vapor from it was vented into the sample autoclave just as final evaporation occurred. As cooling proceeded below 150 °C, the sample autoclave was again isolated and was flushed overnight with dry nitrogen before removing the precipitated solids in a dry nitrogen atmosphere.

Solutions were prepared from Baker Analyzed reagent grade $NaH_2PO_4 \cdot H_2O$ and Na_2HPO_4 and from Fisher Certified standard NaOH solutions, with use of doubly distilled water. The NaOH standardization was checked by a potentiometric titration with HCl, and the phosphates' water of hydration was determined by drying at 120 °C. Carbon dioxide free water was used to prepare solutions with Na/P ratios greater than 2.00.

Powder X-ray diffraction data for isolated solids were obtained at temperatures from 20 to 285 °C with a Nonius Model FR553L Guinier-Simon variable-temperature focussing camera with quartz-monochromated Cu $K\alpha_1$ radiation, a Nonius Model FR508V Guinier film measuring device, and a Nonius Model II microdensitometer. Na_2HPO_4 was used as a calibration standard for the *d* spacings.[9] Some room-temperature diffraction studies were repeated, with larger samples, in a Philips Model PW1050 powder diffractometer to ensure that these results were representative of the bulk material. Relative amounts of Na_2HPO_4 and $Na_4P_2O_7$ in samples recovered from solutions with Na/P = 2.00 were estimated from relative major X-ray diffraction peak intensities by using standard mixtures.

The water content of some products was determined by thermogravimetric analysis with a Perkin-Elmer TGS-1 thermobalance purged with a dry nitrogen flow of about 30 $cm^3\ min^{-1}$ and a heating rate of 20 °C min^{-1}. The relative amounts of orthophosphate and polyphosphates in material recovered at Na/P = 1.6 were determined by gradient elution chromatography.[15]

The following methods were used in attempts to synthesize some of the solids recovered from solution. Tetragonal, anhydrous Na_3PO_4 was prepared by fusing Na_2HPO_4 and Na_2CO_3 in a Pt boat at 600 °C, in accordance with eq 1. This reaction was also performed in

$$2Na_2HPO_4 + Na_2CO_3 \rightarrow 2Na_3PO_4 + H_2O + CO_2 \qquad (1)$$

the presence of NaOH, NaF, and NaCl to test the possibility of adduct formation between Na_3PO_4 and those salts. The solid-state reaction between NaOH and tetragonal Na_3PO_4 was monitored between 20 and 285 °C by using the X-ray techniques described below. The double salt $Na_2HPO_4 \cdot NaH_2PO_4$ was prepared by evaporation of a solution with Na/P = 1.50 in a laboratory oven at 110 °C.

Results

The solid phases recovered from solutions of various compositions are listed in Table I and powder X-ray diffraction data for the previously unreported or partially characterized phases are given in Tables II–IV and in Tables V and VI in the supplementary material. The sodium to phosphate mole ratios, Na/P, which are used in Table I and the following discussion, refer to the initial compositions of the solutions.

At Na/P = 9.3 the major phases were α-NaOH and $NaOH \cdot H_2O$. A minor phase at Na/P = 9.3 (designated I) was identical with the major product at Na/P = 4.0 and 4.3. We recovered α-Na_3PO_4 as a major product at Na/P = 3.15, and it was also present at Na/P = 3.00. The previously unreported phase, I, was also observed in the reaction of solid NaOH with α-Na_3PO_4 at temperatures above 90 °C. We conclude that it is a double salt, $Na_3PO_4 \cdot x NaOH$, with *x* close to 1.0, since it was the major product (ca. 90%) of both solid-state reactions and autoclave experiments at Na/P = 4.0.

Table I. Precipitate Compositions (t = 290 ± 5 °C Unless Specified Otherwise[d])

Na/P[a]	major products	minor products	P_{H_2O}[b]/ MPa
9.30	NaOH, $NaOH \cdot H_2O$	I	
4.30	I	$NaOH \cdot H_2O$	
4.00	I	α-Na_3PO_4	
3.15	α-Na_3PO_4	I	
3.00	IIB	α-Na_3PO_4	
2.83	IIA		7
2.75	IIA	III	7
2.65	IIA, III	IIC	7
2.50	III	Na_2HPO_4, unident[c]	7
2.40	III, Na_2HPO_4	$Na_4P_2O_7$	7
2.15	Na_2HPO_4	III	7
2.00	Na_2HPO_4	$Na_4P_2O_7$ (~20%)	7
2.00[d]	$Na_4P_2O_7$	Na_2HPO_4 (~20%)	
1.80	Na_2HPO_4	unident	7
1.60	$Na_2HPO_4 \cdot NaH_2PO_4$	unident	7
1.60	$Na_4P_2O_7$, amorphous orthophosphate		4

[a] Na/P mole ratio in initial, unsaturated solutions. [b] Minimum water partial pressure during evaporation at temperature t when the second autoclave was used to control humidity. [c] unident = unidentified crystalline products. [d] $Na_4P_2O_7$ formed initially by evaporation at 330 °C, to test for formation of Na_2HPO_4 during recovery.

Table II. X-ray Diffraction Data for Phase I, $Na_3PO_4 \cdot NaOH$ at 22 °C[a]

hkl	d_{calcd}/ Å[b]	d_{obsd}/ Å	I/I_1[c]	*hkl*	d_{calcd}/ Å	d_{obsd}/ Å	I/I_1
101	5.954	5.952	17	031	2.302	2.303	15
011	5.354	5.355	8	203	2.287	2.287	46
111	4.592	4.588	42	312	2.266	2.266	7
200	4.464	4.464	7	400	2.232	2.233	40
002	3.994	3.990	22	321	2.206	2.206	45
201	3.897	3.897	32	230	2.117	2.118	4
210	3.796	3.795	46	123	2.083	2.084	32
102	3.646	3.643	7	132	2.007	2.008	18
020	3.606	3.603	6	322	1.990	1.992	35
211	3.429	3.427	<2	303	1.985	1.986	10
112	3.254	3.255	42	104	1.949	1.950	71
121	3.085	3.083	26	313	1.913	1.913	6
202	2.977	2.979	17	232	1.870	1.871	17
300	2.976			330	1.870		
220	2.805	2.805	11	421	1.847	1.846	<2
301	2.789	2.789	13	204	1.823	1.824	6
212	2.752	2.754	5	040	1.803	1.804	47
221	2.647	2.647	59	500	1.786	1.786	20
311	2.601	2.601	5	033	1.785		
122	2.564	2.564	100	140	1.768	1.769	20
103	2.552	2.551	15	214	1.768		
013	2.498	2.500	11	501	1.743	1.742	8
113	2.406	2.408	<2	124	1.715	1.716	16
				422	1.714		

[a] Weak lines due to traces of phase IIA and α-Na_3PO_4 were omitted; 34 further lines to d_{obsd} = 1.280 Å could not be uniquely indexed and are also omitted. [b] Orthorhombic; a = 8.929 (3), b = 7.213 (2), c = 7.989 (2) Å. [c] Determined photometrically.

The situation in the region of composition 2.00 < Na/P ≤ 3.00 is very complex, and two phases, one of which displays variable composition, have been observed in addition to Na_2HPO_4 (at Na/P ≤ 2.50) and α-Na_3PO_4 (at Na/P = 3.00). The phase of variable composition (here designated II) gives diffraction patterns similar to that reported by Broadbent et al.[1] for the material which they isolated from solutions with

Table III. X-ray Diffraction Data for Phase IIA, $Na_{3-x}H_xPO_4 \cdot xH_2O$, and Cubic Na_3PO_4[a]

	phase IIA (22 °C)[b]			phase IIA (285 °C)[b]				cubic Na_3PO_4 (25 °C)		
hkl	$d_{calcd}/Å$[c]	$d_{obsd}/Å$	I/I_1[d]	*hkl*	$d_{calcd}/Å$[e]	$d_{obsd}/Å$	*I*	*hkl*	$d_{calcd}/Å$[f]	I/I_1
$11\bar{1}$	4.368	4.372	40							
$1\bar{1}1$	4.281	4.278	30	111	4.375	4.371	m	111	4.279	70
$\bar{1}11$	4.232			$\bar{1}11$	4.300	4.296	s			
111	4.234	4.233	70							
200	3.760	3.763	20							
020	3.687	3.689	15	200	3.740	3.739	m, b	200	3.705	10
002	3.669	3.670	15							
220	2.653	2.653								
$20\bar{2}$	2.645	2.641	100							
$0\bar{2}2$	2.642			220	2.662	2.662	vs, b	220	2.620	100
$2\bar{2}0$	2.613	2.614	80	$\bar{2}20$	2.628	2.627	vs			
202	2.607	2.604								
022	2.561	2.560	40							
$13\bar{1}$[g]	2.258	2.257	15		(unobsd)			311	2.234	0
$3\bar{1}1$[g]	2.246	2.246	5							
$0\bar{3}2$[g]	2.072	2.072	8							
$\bar{2}30$[g]	2.072				(unobsd)			320	2.055	0
$\bar{2}03$[g]	2.064	2.063	8							
400	1.880	1.881	20							
040	1.843	1.843	15	400	1.870	1.871	s, b	400	1.853	20
004	1.834	1.835	15							
$42\bar{2}$	1.548	1.549	7							
$24\bar{2}$	1.537	1.535	11							
$22\bar{4}$	1.532									
$4\bar{2}2$	1.517	1.516	20							
422	1.516									
$\bar{4}22$	1.515			422	1.543	1.543	m			
$2\bar{4}2$	1.514			$4\bar{2}2$	1.524	1.524	m, b	422	1.513	20
$2\bar{2}4$	1.510	1.509	7	$\bar{4}22$	1.517	1.517	m			
$\bar{2}42$	1.497	1.495	10							
$\bar{2}24$	1.493									
$\bar{2}42$	1.489	1.489	5							
224	1.486	1.485	5							

[a] Square brackets indicate reflections which are degenerate in the higher symmetry phases; m = medium, s = strong, v = very, b = broad. [b] These diffraction patterns also contained a large number of weak lines, most of which could not be indexed. Many of these were shown to be due to minor phases, but some may be due to a superlattice structure. With the exception of one line at d_{obsd} = 3.110 Å (I/I_1 = 9), all unindexed lines had $I/I_1 \leqslant 5$. [c] Triclinic; a = 7.522 (3), b = 7.378 (3), c = 7.341 (3) Å; α = 91° 46 (3)′, β = 90° 49 (3)′, γ = 89° 4 (3)′. [d] Determined photometrically; the components of some barely resolved doublets were estimated visually on the basis of the integrated photometric intensity for the two lines. [e] Rhombohedral; a = 7.482 (2) Å; α = 89° 13 (2)′. [f] Cubic; a = 7.410 Å (from ref 10). [g] Tentative indexing.

initial compositions in the range $2.14 \leq Na/P \leq 9.05$ and reported as $11Na_2O \cdot 4P_2O_5 \cdot 3H_2O$. A reproducible, sharp diffraction pattern was obtained from material recovered from solutions of initial composition Na/P = 2.83, close to a known congruent point.[1-3] The same phase was the major component at Na/P = 2.75 and was also present at Na/P = 2.65; it is denoted IIA (Table III). A similar but not identical phase, IIB (Table IV), was the major product recovered at Na/P = 3.00. The diffraction patterns of IIB, and of some samples of IIA, displayed some diffuse scattering in the vicinity of major peaks, suggesting compositional heterogeneity. A third variant of phase II, denoted IIC (Table IV), was a minor product at Na/P = 2.65.

A minor component at Na/P = 2.75 was recovered in larger quantities at Na/P = 2.65 and was also obtained at Na/P = 2.50, 2.40, and 2.15 (together with increasing quantities of Na_2HPO_4). This material is referred to as phase III. Although phase III has not been isolated, and so could not be analyzed, it was recovered as the major component of a mixture with Na_2HPO_4 at Na/P = 2.4, so that its diffraction pattern could be distinguished (Table V in supplementary material). No variations in this diffraction pattern were observed with samples recovered from solutions with compositions in the range $2.15 \leq Na/P \leq 2.65$, indicating a narrow range of stoichiometry for III and a miscibility gap between II and III. The relative quantities recovered from different experiments indicate that III has a Na/PO_4 ratio close to 2.5, and we tentatively assign to III the formulation $Na_{2.5}H_{0.5}PO_4 \cdot zH_2O$, with z probably having a value between 0 and 0.5.

The only phases observed at Na/P = 2.0 were Na_2HPO_4 and $Na_4P_2O_7$. The relative quantities of these two phases were very sensitive to experimental conditions, as discussed in the following section. At Na/P = 1.6, the major phase was $Na_2HPO_4 \cdot NaH_2PO_4$,[9,16,17] and an unidentified minor phase was also observed. At Na/P = 1.8, we obtained a mixture of Na_2HPO_4, the same minor phase that was observed at Na/P = 1.6, and at least one other unidentified phase. Since suppression of polyphosphate formation becomes increasingly difficult with decreasing Na/P ratio (see Appendix in supplementary material), these unidentified phases may have been products of decomposition of equilibrium phases.

X-ray diffraction of material recovered from a solution with Na/P = 1.6 under a lower partial pressure of water from the water autoclave (4MPa at 290 °C) revealed only $Na_4P_2O_7$. However, gradient elution chromatography[15] of this material revealed considerable amounts of orthophosphate as well as pyrophosphate. The orthophosphate was presumably present as an amorphous solid. This is consistent with the work of Edwards and Herzog,[16] who observed $Na_4P_2O_7$ and an amorphous orthophosphate as intermediate products of the dehydration of a sodium orthophosphate mixture with Na/P = 1.67. Autoclave corrosion became severe at $Na/P \leq 1.8$, due to the high solubility and low pH of the solutions, so that measurements below Na/P = 1.6 were not practical.

In the course of this work, we attempted to prepare $Na_2HPO_4 \cdot NaH_2PO_4$ by evaporation of a solution with Na/P = 1.5 at 110 °C. This material was found to have a diffraction pattern different from that reported for $Na_2HPO_4 \cdot NaH_2PO_4$[9] but to transform to that material without significant loss of

Table IV. X-ray Diffraction Data for $Na_{3-x}H_xPO_4 \cdot xH_2O$ Phases IIB and IIC[a]

	phase IIB (22 °C)[b]			phase IIB (285 °C)[c]		phase IIC (22 °C)[d]		
hkl	d_{calcd}/Å	d_{obsd}/Å	I/I_1[e]	d_{calcd}/Å	d_{obsd}/Å	d_{calcd}/Å	d_{obsd}/Å	I/I_1
$11\bar{1}$	4.330	4.329	45	4.353	4.358			
$\bar{1}11$	4.296	4.296	70	4.326	4.324			
$1\bar{1}1$	4.278	4.273		4.308	4.306			
111	4.229	4.229	35	4.267	4.265	4.308	4.308	s
200	3.751	3.751	20	3.775	3.775	3.731	3.732	m
020	3.733	3.732	20	3.755	3.757			
002	3.645	3.646	15	3.677	3.678			
$\bar{2}20$	2.650	2.651		2.666	2.666			
220	2.642	2.642	100	2.659	2.658	2.638	2.637	s
202	2.642			2.658				
$0\bar{2}2$	2.627	2.627	40	2.643	2.642			
022	2.589	2.588	65	2.612	2.612			
202	2.587			2.611				
$\bar{1}31$[f]	2.247	2.246	10	2.259	2.258			
$2\bar{2}2$[f]	2.139	2.141	10	2.154	2.154			
400	1.876	1.876	15	1.888	1.888	1.865	1.865	m
040	1.866	1.867	20	1.878	1.878			
004	1.823	1.823	20	1.839	1.839			
$\bar{4}\bar{2}2$	1.536	1.536	2	1.544				
$\bar{4}22$	1.531	1.530	5	1.541	1.540 vb			
$\bar{2}\bar{4}2$	1.530			1.539				
$2\bar{4}2$	1.523			1.532				
$\bar{2}42$	1.518	1.517 b	10	1.529				
$\bar{2}\bar{2}4$	1.518			1.527	1.528 b			
$4\bar{2}2$	1.517			1.528				
422	1.507			1.520				
242	1.505	1.505 b	5	1.517	1.517 b			
$\bar{2}24$	1.505			1.517				
$2\bar{2}4$	1.499	1.497	2	1.511	1.509			
224	1.483	1.482	2	1.498	1.498			

[a] Weak, unindexed lines ($I/I_1 < 5$), some of which may be superlattice reflections, have been omitted. [b] Triclinic; $a = 7.505$, $b = 7.467$, $c = 7.292$ Å; $\alpha = 90.8$, $\beta = 91.1$, $\gamma = 90.1°$. [c] Triclinic; $a = 7.552$, $b = 7.511$, $c = 7.357$ Å; $\alpha = 90.6$, $\beta = 91.0$, $\gamma = 90.1°$. [d] Cubic; $a = 7.461$ Å. [e] Determined photometrically for 22 °C data; relative intensities at 285 °C are similar. [f] Tentative indexing.

weight at ~120 °C. This transformation was irreversible, and we conclude that the initial product is a metastable polymorph of $Na_2HPO_4 \cdot NaH_2PO_4$. Its diffraction pattern is given in Table VI (supplementary material). Its formulation was confirmed by the weight loss on heating to 450 °C, according to eq 2. The identity of the products of reaction 2 was confirmed by X-ray diffraction.

$$2(Na_2HPO_4 \cdot NaH_2PO_4) \rightarrow Na_5P_3O_{10} + NaPO_3 + 3H_2O \quad (2)$$

Structural Inferences

Phase I. The X-ray diffraction pattern for I, $Na_3PO_4 \cdot NaOH$, in Table II was indexed on the basis of an orthorhombic unit cell: $a = 8.929$ (3), $b = 7.213$ (2), $c = 7.982$ (2) Å. The unit cell volume, 514.5 Å^3, is close to 530.3 Å^3, the value calculated from the volumes of α-Na_3PO_4 and α-NaOH, assuming four formula units of $Na_3PO_4 \cdot NaOH$ per unit cell. We believe this to be the first reported example of an anhydrous alkali metal phosphate hydroxide, although $Na_2Zn(PO_4)(OH)$ is known,[18] as are a great number of phases[19] of the types $(M^{II})_5(PO_4)_3(OH)$ and $(M^{II})_2(PO_4)(OH)$. Our attempts to prepare the analogous salts $Na_3PO_4 \cdot NaF$ and $Na_3PO_4 \cdot NaCl$ according to eq 3 were unsuccessful, consistent with phase diagram studies[20,21] in the systems Na_3PO_4–NaF and Na_3PO_4–NaCl.

$$Na_2HPO_4 + {}^1/_2Na_2CO_3 + NaX \xrightarrow[20\ h]{600\ °C} Na_3PO_4 \cdot NaX + {}^1/_2H_2O + {}^1/_2CO_2 \quad (3)$$

Phase II. The strong lines in the diffraction patterns of IIA and IIB (Table III) are grouped about the *d* spacings reported[10-12] for the high-temperature, cubic form of Na_3PO_4, suggesting a structural relationship between phase II and cubic Na_3PO_4. These diffraction patterns also bear a close resemblance to that reported by Kizilyalli and Welch[13] for "pseudo-cubic γ-Na_3PO_4". The strong reflections in the 22 °C diffraction pattern of IIA have been indexed on the basis of a triclinic unit cell with dimensions $a = 7.522$ (3) Å, $b = 7.378$ (3) Å, $c = 7.341$ (3) Å, $\alpha = 91° 46$ (3)′, $\beta = 90° 49$ (3)′, $\gamma = 89° 4$ (3)′, similar to the unit cell of cubic Na_3PO_4 in which $a = 7.410$ Å (Table III). The diffraction pattern also contained a large number of weak lines, many of which could not be indexed on the basis of this unit cell. Some of these lines could be assigned to traces of other phases, but some of them probably arose from a superlattice structure. The diffraction pattern of IIB was somewhat diffuse, but it was tentatively indexed on the basis of a second triclinic unit cell, with $a = 7.505$ (4) Å, $b = 7.467$ (4) Å, $c = 7.292$ (4) Å, $\alpha = 90° 34$ (4)′, $\beta = 91° 10$ (4)′, $\gamma = 90° 6$ (4)′ (Table IV). The four lines attributed to IIC correspond to a cubic unit cell with $a = 7.461$ Å (Table IV).

As noted above, the phases corresponding to II, isolated by Broadbent et al.,[1] gave an average analysis close to the formulation $11Na_2O \cdot 4P_2O_5 \cdot 3H_2O$, or $Na_{2.75}H_{0.25}PO_4 \cdot 0.25H_2O$. Thermogravimetric analysis of our phase IIA, obtained from a solution of starting composition Na/P = 2.83, showed a weight loss above 250 °C of 2.8%, consistent with the total dehydration of $Na_{2.83}H_{0.17}PO_4 \cdot 0.17H_2O$ according to eq 4.

$$Na_{2.83}H_{0.17}PO_4 \cdot 0.17H_2O \rightarrow 0.255H_2O + 0.085Na_4P_2O_7 + 0.83Na_3PO_4 \quad (4)$$

The products of this analysis, which was terminated at 1000 °C, were confirmed by X-ray diffraction to be a mixture of $Na_4P_2O_7$ (minor) and α-Na_3PO_4 (major). It is therefore likely that the type II phases can be described by the general formula $Na_{3-x}H_xPO_4 \cdot xH_2O$. This could be envisaged as $[Na_{3-x}(H_3O)_xPO_4]$, $[Na_{3-x}(HPO_4)_x(PO_4)_{1-x} \cdot xH_2O]$, or $[Na_{3-x}(HPO_4)_{2x}(PO_4)_{1-2x}(OH)_x]$, or a dynamic equilibrium or intermediate composition between these forms. In view of the strong basicity of PO_4^{3-}, the first form is unlikely to contribute significantly to the true formulation. We suggest that the structure of phase II is formally derived from that of cubic Na_3PO_4 by the protonation of x of the phosphate ions per formula unit and the substitution of x sodium ions by water molecules, perhaps with some further redistribution of protons between water and phosphate moieties. The distortion of the structures of IIA and IIB from cubic symmetry and the possible existence of superlattice structures are probably due to hydrogen bonding interactions and/or ordering of sodium substitution sites.

The diffraction pattern of IIA was monitored as a function of temperature between 25 and 285 °C. With increasing temperature, the diffraction lines progressively shifted and coalesced, such that the 285 °C pattern can be indexed on the basis of a rhombohedral unit cell: $a = 7.482$ (2) Å, $\alpha = 89°$ 13 (2)′ (Table III). Slight broadening of some lines suggests a very slight distortion from true rhombohedral symmetry at this temperature, the upper limit of the Guinier-Simon system. Extrapolating the progression of the diffraction pattern, one observes that it is likely that the structure achieves true rhombohedral symmetry close to 300 °C. The rhombohedral cell is again closely related to the cubic Na_3PO_4 unit cell. The continuously monitored progress of the diffraction pattern with increasing temperature showed that $(11\bar{1})$ of the triclinic cell becomes $(11\bar{1})$ of the rhombohedral cell. We attribute the increase in symmetry to the disappearance of the orienting influence of hydrogen bonding; the process is reversible. We have observed a similar progressive change in the diffraction pattern of Na_2HPO_4, corresponding to transformation from a monoclinic low-temperature unit cell to an essentially isodimensional orthorhombic cell at 285 °C.

In a similar experiment with IIB, the structure remained triclinic at 285 °C (Table IV). The reason for this is obscure, but a different mode of modification of the cubic Na_3PO_4 structure may be involved. It is possible that IIB is a dehydrated phase, $Na_{3-x}H_xPO_4{\cdot}yH_2O$, with $y < x$. Unfortunately, no further discussion of the structures of type II phases is justified in the absence of single-crystal crystallographic structural data. Preliminary single-crystal studies of IIA have confirmed that the unit cell is related to that of cubic Na_3PO_4, but extensive twinning has so far prevented the acquisition of accurate structural data.

Phase III. Although the diffraction pattern of III bears some similarity to the phase II patterns, we have not been able to index it on this basis. On heating III dry to 285 °C, we observed that the diffraction pattern exhibits no changes other than those attributable to thermal expansion and partial decomposition.

Phase Diagram

The high-temperature equilibrium solid phases for the system $Na_2O-P_2O_5-H_2O$ have been deduced from Table I, the structural information in the preceding section, and literature solubility data.[1-3] The results of these deductions are illustrated in Figure 2, which is a schematic representation of Broadbent's phase diagram,[1] modified to account for the results of this study. To optimize the use of space in the triangular diagram, we chose the three components to be Na_2O, $P_2O_5{\cdot}1.5Na_2O$, and a 100-mol quantity of H_2O. The solubility isotherm in Figure 2 approximates to the literature data,[1-3] except for Na/P > 9, where the mole fraction of Na_2O was reduced for clarity because of the extremely high solubility of NaOH at 300 °C. The solubility studies[1-3] suggest that the isothermal phase diagram in Figure 2 is qualitatively correct from about 275 to 325 °C, except that the stability of $NaH_2PO_4{\cdot}Na_2HPO_4$ above 300 °C is unconfirmed. The detailed arguments presented below are based on Findlay's discussion[22] of the isothermal evaporation of ternary systems and proceed from right to left along the ternary diagram in Figure 2.

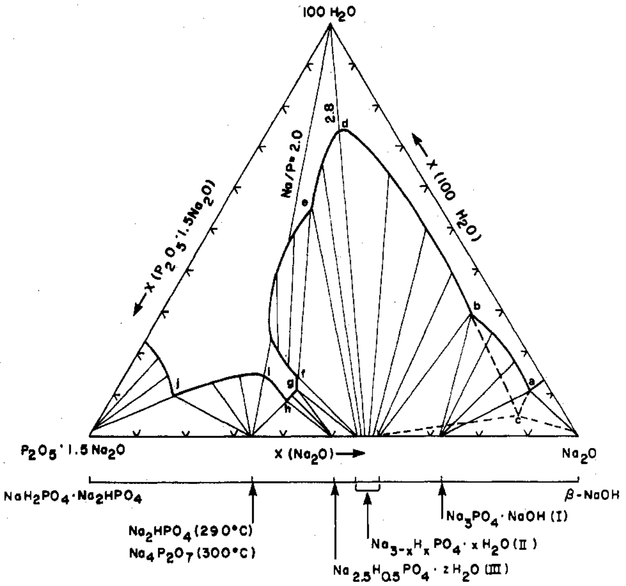

Figure 2. Schematic representation of part of the $Na_2O-P_2O_5-H_2O$ isothermal phase diagram near 300 °C. The water mole fractions for Na/P > 9.0 were distorted for clarity. The phase $Na_3PO_4{\cdot}NaOH$ may exist as an incongruently saturating equilibrium phase in the presence of liquid water when Na/P > 9.0, as shown by the dashed line.

The solid phase in equilibrium with saturated aqueous NaOH at 290 °C is known to be β-NaOH.[23,24] Presumably the $NaOH{\cdot}H_2O$ observed at Na/P = 9.3 formed from traces of water in the apparatus on cooling. Phase I, $Na_3PO_4{\cdot}NaOH$, may be an equilibrium phase in the presence of the saturated aqueous solutions, or it may have been formed by a solid-state reaction between NaOH and phase II while the mixture was cooling down in the dry autoclave. The analogous reaction between NaOH and Na_3PO_4 solids yielded $Na_3PO_4{\cdot}NaOH$ rapidly above 90 °C. Broadbent's solubility data[1] indicate that I does not coexist with solution compositions Na/P ≤ 9. It might, however, coexist with incongruently saturated solutions[22] at still higher Na/P values. If so, the invariant points a and b (Figure 2) corresponding to the I/β-NaOH and II/I equilibria would exist at solution compositions with Na/P > 9. Otherwise, $Na_{3-x}H_xPO_4{\cdot}xH_2O$ and β-NaOH would form an invariant solution of composition c, as shown by the dashed lines.

Solubility studies[1-3] clearly show that variants of phase II are the equilibrium solids associated with saturated solutions with Na/P values from about 2.15 to at least 9.0. The data in Table I confirm that congruent precipitation occurs at Na/P = 2.80 ± 0.05, point d in Figure 2. Our recovery of phases other than II from solutions with starting compositions within the range 2.15 < Na/P < 9 is due to changes in the solution composition arising from incongruent precipitation during evaporation.[22] The α-Na_3PO_4 recovered at Na/P = 3.15 and 3.00 undoubtedly formed from variants of phase II close to the stoichiometric composition, γ-Na_3PO_4, at 300 °C. Mair[10] reported that solid solutions of Na_2CO_3 or Na_2SO_4 in Na_3PO_4 revert to the α-Na_3PO_4 structure on cooling only at solute concentrations below about 4 mol %. The solubility data of both Ravich and Shcherbakova[3] and Broadbent et al.[1] indicate that the equilibrium solid composition tends toward Na_3PO_4 as Na/P in solution is increased. Significant amounts of solid products with Na/P > 2.95 would thus have been precipitated in the experiments in which we observed α-Na_3PO_4.

Heating experiments in the Guinier-Simon X-ray camera did not reveal formation of III from IIA and Na_2HPO_4, dry,

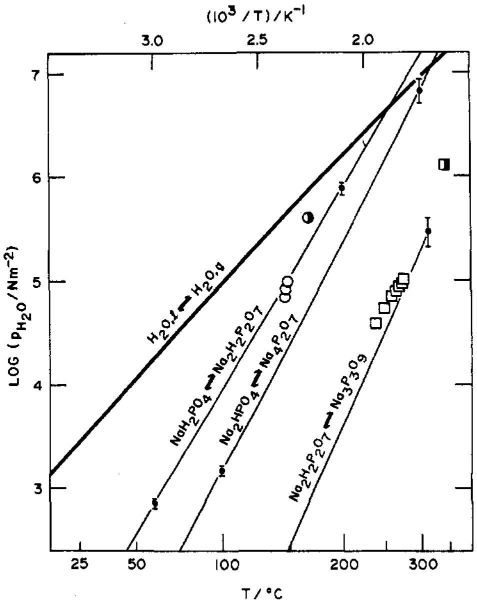

Figure 3. Vapor pressure data for condensation reactons of NaH_2PO_4, Na_2HPO_4, and $Na_2H_2P_2O_7$ and for vapor-saturated pure water. Experimental data for NaH_2PO_4 and $Na_2H_2P_2O_7$ are from ref 33 (○, □) and ref 34 (◐, ◧). Vertical bars refer to the standard deviations in the calculated vapor pressure curves.

at 285 °C. It is therefore unlikely that III formed by solid-state reactions subsequent to precipitation, and we conclude that it is an equilibrium phase. The solubility data[1,2] suggest that III forms an invariant solution with Na_2HPO_4 or $Na_4P_2O_7$ at Na/P ≈ 2.15, composition h in Figure 2, and that no congruently saturated solutions exist between point d and point h. It is likely that the incongruently saturating invariant solution[22] in equilibrium with II and III is also close to Na/P = 2.15, as shown by point g in the phase diagram. Otherwise, III would have been observed by other workers. The results of our study neither confirm nor contradict Broadbent's observation[1] of liquid-phase separation in the composition range 2.0 ≤ Na/P ≤ 2.15. The solubility data are not sufficiently precise to show which solid phase is in equilibrium with the two liquid phases at invariant compositions e and f. Figure 2 was drawn on the assumption that it is phase III, but it could equally well be phase II with the II/III invariant composition, g, occurring between e and d.

The major phase observed at Na/P = 2.00 was Na_2HPO_4 with traces of $Na_4P_2O_7$ which presumably formed at 290 °C via the condensation reaction (5) when the water vapor

$$2Na_2HPO_4 \rightleftarrows Na_4P_2O_7 + H_2O \qquad (5)$$

pressure was lowered below the saturation value. Broadbent et al.[1] demonstrated that $Na_4P_2O_7$ is the stable phase at 300 °C. To ensure that the Na_2HPO_4 which we observed was not formed from $Na_4P_2O_7$ by reaction with water vapor during cooling, we prepared $Na_4P_2O_7$ by evaporation at 330 °C (Table I) and then exposed it to 7 MPa of water vapor at 290 °C and cooled in the usual way. The small amount of Na_2HPO_4 (<20%) which formed during this and a similar run using finely ground anhydrous commercial $Na_4P_2O_7$ led us to conclude that the bulk of the Na_2HPO_4 recovered from solutions evaporated at 290 °C could not have formed by reaction of $Na_4P_2O_7$ with the vapor. Hence, Na_2HPO_4 is the equilibrium phase at 290 °C, and the transition from Na_2HPO_4 to $Na_4P_2O_7$ as the saturating phase occurs between 290 and 300 °C. The water vapor pressures corresponding to the $Na_4P_2O_7/Na_2HPO_4$ equilibrium were calculated from literature thermodynamic data[24-30] (see supplementary Appendix) and are plotted in Figure 3.[31,32] The calculated vapor pressure curve intersects the water vapor pressure line[30] at 320 ± 25 °C, in good agreement with our observation. The reliability of the vapor pressure calculations is confirmed by the agreement with experimental values[33,34] for the $NaH_2PO_4/Na_2H_2P_2O_7$ and the $Na_2H_2P_2O_7/(NaPO_3)_x$ equilibria at temperatures where the reactions are reversible (>145 °C and >245 °C, respectively). The lack of other products at Na/P = 2.00 in our experiments is consistent with other evidence of congruent precipitation from solution[1,7,8] at this composition.[35]

The major crystalline phase recovered at Na/P = 1.6 was $Na_2HPO_4 \cdot NaH_2PO_4$. Since it decomposed to $Na_4P_2O_7$ and an amorphous orthophosphate during recovery at somewhat reduced water vapor pressures, we conclude that it is an equilibrium precipitate whose upper limit of stability is not much higher than 290 °C. It probably precipitates congruently at Na/P = 1.5, but autoclave corrosion problems prohibited experimentation at this composition. The unidentified phases observed at Na/P = 1.6 and 1.8 may well have been metastable phases or products of partial decomposition. If so, there is an invariant composition, j, at which Na_2HPO_4 and $Na_2HPO_4 \cdot NaH_2PO_4$ coexist. If any of the unidentified solids are equilibrium phases, further invariant points must exist.

Acknowledgment. We are indebted to Mr. G. Wallace for performing several of the evaporation experiments, Mr. R. Portman for the gradient-elution chromatographic results, Mr. L. Hachkowski for the thermogravimetric analyses, and Dr. R. D. Heyding for single-crystal diffraction information. We also wish to thank Dr. J. R. Dean for encouraging us to undertake this project and Drs. P. V. Balakrishnan and E. A. M. Wetton for their critical appraisal of the manuscript.

Registry No. $Na_3PO_4 \cdot NaOH$, 70850-23-6; Na_3PO_4, 7601-54-9; $Na_{2.5}H_{0.5}PO_4$, 70659-31-3; NaOH, 1310-73-2; $Na_2HPO_4 \cdot NaH_2PO_4$, 65185-91-3; Na_2HPO_4, 7558-79-4; $Na_4P_2O_7$, 7722-88-5; NaH_2PO_4, 7558-80-7; $Na_2H_2P_2O_7$, 7758-16-9; $Na_3P_3O_9$, 7785-84-4; Na_2O, 1313-59-3; P_2O_5, 1314-56-3; H_2O, 7732-18-5.

Supplementary Material Available: Appendix, partial pressure data calculation; Table V, X-ray diffraction data for phase III; Table VI, X-ray diffraction data for the metastable polymorph of $Na_2HPO_4 \cdot NaH_2PO_4$; Table VII, thermodynamic data for selected Na_2O-H_2O solids (4 pages). Ordering information is given on any current masthead page.

References and Notes

(1) D. Broadbent, G. G. Lewis and E. A. M. Wetton, *J. Chem. Soc., Dalton Trans.*, 464 (1977).
(2) A. J. Panson, G. Economy, C.-T. Liu, T. S. Bulischeck, and W. T. Lindsay, Jr., *J. Electrochem. Soc.*, **122**, 915 (1975).
(3) M. I. Ravich and L. G. Shcherbakova, *Izv. Sekt. Fiz.-Khim. Anal., Inst. Obshch. Neorg. Khim., Akad. Nauk SSSR*, **26**, 248 (1955).
(4) V. M. Marcy and S. L. Halstead, *Combustion*, 45 (Jan 1964).
(5) K. W. Herman and L. R. Gelosa, *Power Eng.*, 64 (May 1973).
(6) G. M. W. Mann, *Br. Corros. J.*, **12**, 6 (1977).
(7) P. Goldstein and C. L. Burton, *J. Eng. Power*, **91**, 75 (Apr 1969).
(8) P. V. Balakrishnan, *Can. J. Chem. Eng.*, **55**, 592 (1977).
(9) Powder Diffraction File, Joint Committee on Powder Diffraction Standards, Swarthmore, Pennsylvania, 1978.
(10) A. D. Mair, *N. Z. J. Sci.*, **19**, 61 (1976).
(11) M. Palazzi and R. Francis, *Bull. Soc. Chim. Fr.*, 2795 (1971).
(12) M. Palazzi, F. Remy, and H. Guerin, *C. R. Hebd. Seances Acad. Sci., Ser. C*, **272**, 1127 (1971).
(13) M. Kizilyalli and A. J. E. Welch, *J. Inorg. Nucl. Chem.*, **38**, 1237 (1976).
(14) A. Hooper, P. McGeehin, K. T. Harrison, and B. C. Tofield, *J. Solid State Chem.*, **24**, 265 (1978).
(15) J. A. Grande and J. Beukenkamp, *Anal. Chem.*, **28**, 1497 (1956).
(16) J. W. Edwards and A. H. Herzog, *J. Am. Chem. Soc.*, **79**, 3647 (1957).
(17) B. Wendrow and K. A. Kobe, *Ind. Eng. Chem.*, **44**, 1439 (1955).
(18) Yu. K. Kabalov, M. A. Simonov and N. V. Belov, *Dokl. Akad. Nauk SSSR*, **202**, 823 (1972).
(19) J. R. Van Wazer, "Phosphorus and Its Compounds", Interscience, New York, 1966, Chapter 9, Appendix A.
(20) G. A. Bukhalova and I. V. Mardirosova, *Russ. J. Inorg. Chem. (Engl. Transl.)*, **12**, 1491 (1967).
(21) G. A. Bukhalova and I. V. Mardirosova, *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.*, **11**, 855 (1968).
(22) A. Findlay, A. N. Campbell and N. O. Smith, "The Phase Rule and Its Applications", 9th ed., Dover Publications, New York, 1951, Chapter 17.

(23) W. F. Linke and A. Seidell, "Solubilities—Inorganic and Metal-Organic Compounds", American Chemical Society, Washington, DC, 1965, p 1064.
(24) K. K. Kelly, "High Temperature Heat Content, Heat Capacity and Entropy Data for the Elements and Inorganic Compounds", *U.S., Bur. Mines, Bull.*, No. **584** (1960).
(25) R. J. Irving and H. M. McKerrill, *Trans. Faraday Soc.*, **63**, 2913 (1967); **64**, 879 (1968).
(26) R. J. L. Andon, J. F. Counsell, J. F. Martin, and C. J. Mash, *J. Appl. Chem.*, **17**, 65 (1967).
(27) T. R. Meadowcroft and F. D. Richardson, *Trans. Faraday Soc.*, **59**, 1564 (1963).
(28) S. J. Ashcroft, E. Keen, and C. T. Mortimer, *Trans. Faraday Soc.*, **66**, 2851 (1969).
(29) R. J. Irving and H. M. McKerrill, *Trans. Faraday Soc.*, **63**, 2582 (1968).
(30) H. C. Helgeson and D. H. Kirkham, *Am. J. Sci.*, **274**, 1089 (1974).
(31) Analogous calculations for reactions involving H_2 and O_2 are described by T. E. Rummery and D. D. Macdonald, *J. Nucl. Mater.*, **55**, 23 (1975).
(32) See also I. M. Klotz, "Chemical Thermodynamics", Benjamin, New York, 1964.
(33) S. J. Kiehl and G. H. Wallace, *J. Am. Chem. Soc.*, **49**, 376 (1927).
(34) G. W. Morey, *J. Am. Chem. Soc.*, **75**, 5794 (1953).
(35) E. A. M. Wetton (personal communication) has pointed out that both $Na_4P_2O_7$ and Na_2HPO_4 must coexist as equilibrium phases in the region hij, over a finite but probably very small temperature range, since the activity of water is not constant throughout this region. Invariant solution compositions corresponding to the $Na_4P_2O_7/Na_2HPO_4$ equilibrium would exist between i and j and/or between i and h in this temperature range.

Contribution from the Department of Chemistry,
University of Alberta, Edmonton, Alberta, Canada T6G 2G2

Kinetics and Thermodynamics of Dissociation of Nickel(II)–Isoquinoline Complexes in Water, Ethanol, and 1-Propanol

P. K. CHATTOPADHYAY and B. KRATOCHVIL*

Received November 2, 1978

Rate constants and associated activation parameters for the dissociation of $(solv)_5Ni(isoquin)^{2+}$ (solv = solvent, isoquin = isoquinoline) in ethanol, 1-propanol, and water and of $(solv)_5NiSCN^+$ in 1-propanol have been measured kinetically by stopped-flow spectrophotometry using H_3O^+ as the decomposing ion for $(solv)_5Ni(isoquin)^{2+}$ and copper(II) for $(solv)_5NiSCN^+$. These data are compared with previously reported results on dissociation of $(solv)_5Ni(isoquin)^{2+}$ and $(solv)_5NiSCN^+$ in several donor solvents. Pathways for dissociation of both $(solv)_5Ni(isoquin)^{2+}$ and $(solv)_5NiSCN^+$ in the solvents studied are accommodated within an I_d-type mechanism.

Introduction

An improved understanding of solvent properties can be obtained from studies of reactions in which solvent molecules are direct participants, such as in the solvolysis of ligand-substituted complexes. It has been shown[1,2] that measurements of dissociation rates of $(solv)_5Ni(isoquin)^{2+}$ (solv = solvent, isoquin = isoquinoline) in water, methanol, acetonitrile, and dimethyl sulfoxide and of $(solv)_5NiSCN^+$ in water, methanol, acetonitrile, dimethyl sulfoxide, and dimethylformamide can be interpreted through an I_d-type mechanism represented by eq 1, where solv is a solvent molecule and L is either iso-

$$LNi(solv)_5 + solv \rightleftarrows solv,(solv)_5Ni{-}L \rightleftarrows solv{-}Ni(solv)_5,L \qquad (1)$$

quinoline or thiocyanate ion (charges omitted). It has also been shown that dissociation rate constants at a single temperature do not bear a systematic relation to the donor properties of the solvent, but enthalpies of activation for dissociation of both $(solv)_5Ni(isoquin)^{2+}$ and $(solv)_5NiSCN^+$ bear an inverse linear relation to solvent donor properties as expressed by the Gutmann donor number.[3]

We report in this work studies of the dissociation of $(solv)_5Ni(isoquin)^{2+}$ in water, ethanol, and 1-propanol and of $(solv)_5NiSCN^+$ in 1-propanol over a range of temperatures. Enthalpies and entropies of activation for dissociation in these solvents have been calculated; the results, in conjunction with previous work on these systems in other solvents,[1,2] are discussed in terms of mechanisms and solvent donor properties.

Experimental Section

Solvents. Commercial 1-propanol (Baker Analyzed, assay 99%) was refluxed for 12 h over BaO and fractionally distilled in the absence of air. The middle fraction, collected over alumina previously baked 24 h at 550 °C, was shaken for 12 h and then fractionally distilled. The middle cut from the second distillation was fractionally distilled twice more from metallic sodium in the absence of air. The purified solvent was used within 24 h of the final distillation. Pure ethanol, USP (U.S. Industrial Chemicals), was used as obtained without further treatment. Singly distilled water was redistilled from alkaline $KMnO_4$ before use.

Reagents. Nickel(II) was introduced as the perchlorate salt. In all solvents, nickel(II) perchlorate monohydrate, prepared as previously described,[4] was used. Copper(II) was introduced as hexakis(acetonitrile)copper(II) perchlorate and was prepared as before.[5] Perchloric acid (Mallinckrodt, analytical reagent, 70%) was used as received. Isoquinoline (Aldrich, mp 26–28 °C, bp 252 °C) was purified as described before.[4] Potassium thiocyanate (J. T. Baker, Baker Analyzed, assay 100%) was dried at 60 °C under vacuum for 3 days.

Instruments and Experimental Procedure. All nonaqueous solutions were prepared and dispensed in a drybox (Kewaunee Scientific) under dry nitrogen by using glassware that had been oven-dried at 100 °C for several days. All standard procedures for handling nonaqueous solutions were followed. The first-order dissociation rate constant of $(solv)_5Ni(isoquin)^{2+}$ in perchloric acid was determined by measuring the rate of formation of $isoquinH^+$ by following the rate of change of transmittance upon mixing of a solution of $(solv)_5Ni(isoquin)^{2+}$ with $HClO_4$ at a wavelength where $isoquinH^+$ absorbs strongly and $(solv)_5Ni(isoquin)^{2+}$ and $HClO_4$ absorb but little. A stopped-flow spectrophotometer (Durrum Instrument Co., Model D110) was used for all kinetic measurements. A description of the instrument along with modifications for better temperature control has been given.[6] Solutions of $(solv)_5Ni(isoquin)^{2+}$ were prepared in dry volumetric flasks by adding measured volumes of a standard nickel(II) solution to a known volume of a stock isoquinoline solution and diluting to volume with solvent. In all solutions, the concentration of nickel(II) was in 50- to 100-fold excess of the isoquinoline concentration to ensure the formation of the mono complex only. The total concentration of perchloric acid in the final mixed solution was held higher than the total concentration of nickel(II) by a ratio of 2 to 1 in water and 1-propanol and 6 to 1 in ethanol. In 1-propanol, kinetic measurements were done in both the presence and absence of acetic anhydride, the concentration of acetic anhydride being held equal to the concentration of perchloric acid or held at double the concentration of perchloric acid. Absorbance measurements were made at 332 nm in water and 1-propanol and at 334 nm in ethanol. Dissociation rate constants of

0020-1669/79/1318-2953$01.00/0 © 1979 American Chemical Society