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Anhydrous Sodium Polyuranates[1]

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The structure of anhydrous mixed uranium oxide–sodium oxide phases in which the ratio $UO_3:Na_2O$ varied from 2 to ~13 has been investigated using X-ray powder patterns and infrared absorption spectra. A phase with the approximate composition $Na_2O \cdot 13UO_3$ was identified and shown to be stable at high temperatures. Its cell parameters were found to be closely related to those for U_3O_8 and α-UO_3. A second, $Na_2U_2O_7$-related phase was also identified.

There have been a number of reported attempts to prepare anhydrous compounds of the type $Na_2O \cdot xUO_3$ where $x \geq 3$, the sodium polyuranates, but to date without success. Typically, mixtures of UO_3 and Na_2CO_3 in ratios calculated to give compounds in the polyuranate range have, upon ignition, yielded products whose X-ray diffraction patterns either were amorphous or were interpreted to represent $Na_2U_2O_7$ or a mixture of $Na_2U_2O_7$ and U_3O_8.[2-4] Differential thermal analyses of mixtures of Na_2CO_3 and UO_3 also failed to indicate polyuranate formation.[4]

These results are somewhat surprising. Lithium triuranate and compounds in the composition range $M_2O \cdot (3\text{–}6)UO_3$, where M = K, Rb, and Cs, have all been characterized.[2] Indeed, $Li_2U_3O_{10}$ and both $K_2U_3O_{10}$ and $K_2U_4O_{13}$ are reported to be thermally stable at >1000°.[5] Thus, one might have expected to obtain evidence at least for a sodium triuranate phase.

In contrast to the foregoing, there is considerable evidence for the formation of sodium polyuranates upon the addition of NaOH to solutions of uranyl salts. The product formed is pH dependent, and the equilibria involved appear to be reached rather slowly. There are some discrepancies between results reported in the literature; however, there is general agreement that near pH 6, practically complete precipitation of uranium can be achieved. A product of the approximate composition $Na_2U_7O_{22} \cdot xH_2O$, where x is probably near 7, has been reported, and under certain conditions evidence for polyuranates as high as $Na_2U_{16}O_{49} \cdot xH_2O$ has also been obtained.[6-12] Products resulting when hydrated polyuranate phases were heated at elevated temperatures were characterized as $Na_2U_2O_7$ or a mixture of $Na_2U_2O_7$ and U_3O_8.[10]

In a previous study of alkali metal uranates and neptunates, it was found that considerable structural information could be gleaned from the combined use of X-ray powder pattern data and infrared spectra.[13] We were, therefore, interested in determining whether the infrared spectra of possible anhydrous sodium polyuranate phases would substantiate the results arrived at primarily on the basis of powder diffraction patterns.

We have been able to show that an anhydrous high temperature stable sodium polyuranate phase can be prepared. However, the X-ray diffraction patterns were closely related to those of α-UO_3 and α-U_3O_8.[14] Thus, earlier work in which the diffraction patterns of sodium polyuranates heated at 750–850° were interpreted in terms of U_3O_8 formation is quite understandable. The differences between the pattern of the polyuranate and that of U_3O_8, while real, are indeed not striking. However, in contrast to the X-ray diffraction studies, the infrared spectrum of the sodium polyuranate phase proved to be quite distinct from that of either α-UO_3 or α-U_3O_8.

Experimental Section

Two different methods were used to obtain the compounds investigated. In one case mixtures of solid compounds such as Na_2CO_3 or Na_2O_2 and UO_3 were thoroughly ground and then slowly heated to 800–900°. They were maintained at this temperature for >24 hr and were removed and reground three times during the heating period. Alternatively, 0.1 *M* solutions of $UO_2(NO_3)_2$ were titrated potentiometrically to a desired pH with 0.1 *M* NaOH, and the resulting precipitates were washed, dried at 110°, and ignited at 850°. Analytical grade chemicals were employed throughout without further purification.

The UO_3 used in solid-state reactions was prepared by decomposing nitrate-free $UO_4 \cdot 2H_2O$ to amorphous UO_3 at 470°.[15,16] The sample of orthorhombic α-U_3O_8 was obtained by heating the amorphous UO_3 to 800° in air for 24 hr. Preparation of α-UO_3 followed the method of Cordfunke,[17] in which nitrate-containing $UO_4 \cdot 2H_2O$ was heated at 500° for 2 hr.

All samples were analyzed for both alkali metal and uranium content—the former by use of a flame photometer and the latter either spectrophotometrically[18] or by titration with standard ceric solution after reduction of the uranium to U(IV).

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(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

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In attempting to determine the decomposition temperature of a sodium polyuranate phase, we placed appropriate anhydrous samples in small platinum boats and covered them with thin silica glass slides. In the absence of decomposition, the slide remained clear, but upon release of Na_2O from the sample the slide was visibly etched. This proved to be a sensitive indicator, since in some cases a small amount of etching was observed after short periods of heating without any noticeable change in infrared spectrum or X-ray pattern of the sample. However, repetition of the latter measurements after somewhat longer heating did reveal structural changes.

Infrared spectra were measured from 4000 to 166 cm^{-1} employing two different grating spectrophotometers. Samples ignited at >750° were anydrous; characteristic absorption bands were all found at <1000 cm^{-1}. The resolution from 1000 to 300 cm^{-1} was better than 3 cm^{-1} while that from 300 to 166 cm^{-1} was better than 2 cm^{-1}. Both Nujol mull and KBr disk techniques were employed from 1000 to ~250 cm^{-1}. Bands at <250 cm^{-1} were observed only in Nujol mulls using polyethylene windows.

X-Ray diffraction data were obtained using a 114.6-mm diameter camera (Straumanis film mounting) with nickel-filtered Cu $K\alpha$[19] radiation.

Results and Discussion

Compounds in the Composition Range $Na_2O \cdot xUO_3$, Where $x = 2.0$ to ~2.5.—We found that there was a definite change both in the X-ray diffraction patterns and the infrared spectra of samples analyzed as $Na_2O \cdot 2.1UO_3$ compared to those where the ratio $UO_3{:}Na_2O = 2.0$. However, as the ratio $UO_3{:}Na_2O$ increased from ~2.1 to 2.5, only small additional structural changes were noticed.

The preparation of several new samples and the reexamination of our previous results have led us to conclude that the length of the 3.93-A axis reported earlier[13] for the unit cell of $Na_2U_2O_7$ should be tripled to account for several weaker lines that are observed. Thus, the cell dimensions are $a = 6.812$, $b = 11.790$, $c = 17.742$ A.

A few of the lines in the diffraction patterns of $Na_2O \cdot 2.1UO_3$ were not well defined, even after samples had been annealed at 850° for several days. This definition improved as the ratio $UO_3{:}Na_2O$ increased; however, there was little if any corresponding change in the calculated lattice parameters. We found that the patterns obtained for $UO_3{:}Na_2O \geq 2.1$ did not appear to represent a mixture of $Na_2U_2O_7$ and a second phase, but rather a single new phase which showed a close structural relationship to the diuranate. The new phase could be indexed in an orthorhombic cell with approximate lattice constants $a = 6.68$, $b = 12.50$, $c = 9.18$ A. It will be noted that this c axis is approximately half that for $Na_2U_2O_7$, while the a and b axes of the two phases are comparable in magnitude.

The changes in the infrared spectra of samples in the composition range under consideration closely paralleled those found in examining X-ray diffraction patterns. As shown in Figure 1 (A–C), the spectrum of $Na_2O \cdot 2.1UO_3$ represents a considerable loss of definition and a shift both in energy and intensity of several bands compared to that observed for $Na_2U_2O_7$. In contrast, the spectra of $Na_2O \cdot 2.1UO_3$ and $Na_2O \cdot 2.5UO_3$ appear to be much more closely related.

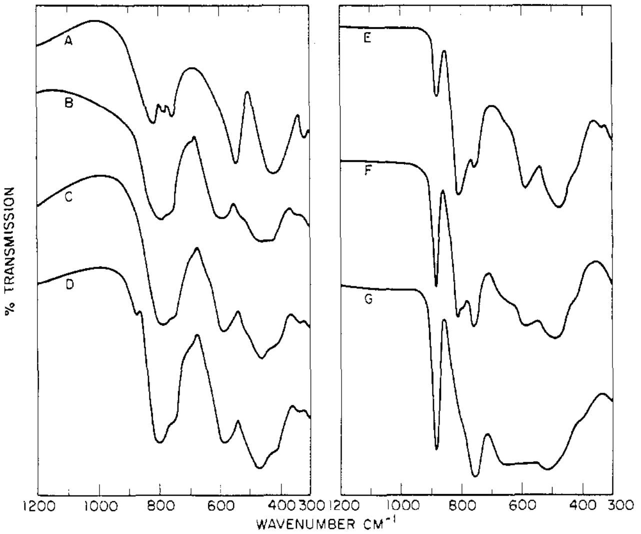

Figure 1.—Infrared spectra of sodium uranates ignited at 800–850°. $UO_3{:}Na_2O$: A, 2.0; B, 2.1; C, 2.5; D, 2.5; E, 3.0; F, 4.0; G, 5.0.

In several samples of composition near $Na_2O \cdot 2.5UO_3$, the X-ray diffraction patterns could be indexed with the parameters cited earlier, but the infrared spectra showed the presence of a new weak band at ~880 cm^{-1}, as shown in Figure 1D. In compounds where the ratio $UO_3{:}Na_2O$ was ~2.7, weak lines consistent with the presence of a U_3O_8-like phase were detected in addition to those of the $Na_2O.2.5UO_3$ phase. As the ratio increased, both the strength of the 880-cm^{-1} band and the intensity of the U_3O_8-like lines in the powder pattern also increased. It appeared that the infrared spectrum was more sensitive than X-ray diffraction patterns in detecting the presence of this phase.

Although a number of different methods of analysis including potentiometric titrations of uranyl salt solutions with NaOH have indicated the formation of compounds with the ratio $UO_3{:}Na_2O \geq 2$,[6,8,11,12,20] it is doubtful that such precipitates could be separated from solution without suffering some change in composition.[9,21] Baran[22] has summarized the evidence which demonstrates the capacity of the gelatinous, uranium-containing precipitate to exchange ions from solution for hydrogen ions. While equilibrium is reached rather slowly, washing the precipitate immediately changes its composition.

Wamser and co-workers[6] reported a hydrated orange phase obtained at pH ≥10 in which the ratio $UO_3{:}Na_2O$ was found to be 2.33. Subsequently, Maly and Vesely[8] confirmed this result and suggested that the X-ray diffraction pattern obtained was actually characteristic of a range of compounds in which the ratio $UO_3{:}Na_2O$ was ≤3. Pechurova and co-workers[10] also investigated compound formation in the $NaOH–UO_2^{2+}$ system at high pH. They reported a precipitate of

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the composition $Na_2O \cdot 2.21UO_3$ separated at pH 11.7 and also found lines which could be attributed to U_3O_8 in the powder diffraction pattern of a sample of composition $Na_2O \cdot 2.58UO_3$ which had been ignited at 800°.[10] They suggested that the diffraction pattern obtained with the sample which analyzed as $Na_2O \cdot 2.21UO_3$, after it had been heated at 800°, as well as the patterns obtained by Wamser, *et al.*, and Maly and Vesely, could be indexed with parameters nearly identical with those for $Na_2U_2O_7$. However, experimental details for the compound $Na_2O \cdot 2.21UO_3$ were not given.

The results of the present investigation are consistent with those cited above except with respect to indexing the patterns obtained from the $Na_2U_2O_7$-related samples.

One would not necessarily expect to find that a hydrated polyuranate phase had the same motif of uranium atoms as a corresponding anhydrous phase. However, a comparison of the X-ray diffraction data reported by Wamser, *et al.*, for $Na_2O \cdot 2.33UO_3$ and Maly and Vesely for $Na_2O \cdot \leq 3UO_3$ with those for the compound $Na_2O \cdot 2.5UO_3$, as shown in Table I, suggests that the structures involved are indeed related. Thus, while the present set of experiments was not designed to establish the stoichiometry of products isolated at any given pH in solution, it does provide a basis for systematizing the numerous reports of $Na_2U_2O_7$-type structures of varying analyses precipitated by NaOH.

TABLE I

COMPARISON OF X-RAY DIFFRACTION RESULTS FOR PHASES RELATED TO $Na_2U_2O_7$

$UO_3:Na_2O = 2.33$[6]		$UO_3:Na_2O = 3$[8]		Present study[a] $UO_3:Na_2O = 2.5$			
Intens	Obsd *d*, A	Intens	Obsd *d*, A	Intens	Obsd *d*, A	Calcd *d*, A	*h k l*
s	6.06	s	5.843	6	5.88	5.90	1 1 0
		ms	4.136				
vs	3.42	vs	3.397	6	3.35	3.34	2 0 0
vs	3.25	s	3.200	6	3.25	3.24	1 2 2
				7	3.16	3.14	2 0 1
w	3.02	vw	2.985	5	2.956	2.960	0 4 1
w	2.74	vw	2.699	6	2.71	2.71	1 1 3
		vw	2.505	2	2.506	2.508	2 3 1
		vw	2.260	3	2.434	2.414	0 5 1
s	2.01	s	1.985	5	1.982	1.984	2 3 3
				3	1.951	1.957	2 5 1
m	1.91	s	1.888	3	1.890	1.890	2 0 4
				5	1.849	1.849	0 4 4
w	1.72	w	1.729	1	1.728	1.726	1 7 0
				2	1.691	1.690	0 5 4
w	1.66			1	1.668	1.668	1 6 3
				5	1.630	1.630	4 1 1
				4	1.581	1.582	0 4 5

[a] The first 20 of 33 lines measured are shown.

Compounds in the Composition Range $Na_2O \cdot xUO_3$, Where $x > 2.5$.—In the investigation of compounds in this range, mixtures of Na_2O_2 (or Na_2CO_3) and UO_3 were ignited to give uranates in which the ratio, UO_3:Na_2O, was 2.5, 2.7, 3, 3.5, 4, 4.5, 5, and 5.5. Samples precipitated from solution were also studied. In general, the X-ray diffraction patterns were complex; however, only two phases could be identified. There were diffraction lines characteristic of the $Na_2O \cdot 2.5UO_3$ phase and those indicative of U_3O_8. As the ratio UO_3:Na_2O increased, the intensity of lines ascribed to the $Na_2O \cdot 2.5UO_3$ phase decreased, and those characteristic of a U_3O_8-type phase became more prominent.

The infrared spectra of products in the present composition range were considerably more revealing than the X-ray diffraction studies. By arranging the spectra in order of increasing ratio U:Na in the samples, it could be shown that, instead of a progressive transformation to a U_3O_8-type spectrum, a new set of bands developed which were quite distinct from those of either $Na_2U_2O_7$ or U_3O_8. These results are illustrated in Figure 1 (D–G). The intensity of the 820-cm^{-1} band of the diuranate-type phases decreased markedly in comparison with that of the 760-cm^{-1} band as the ratio of U:Na in the samples increased. The 820-cm^{-1} band could barely be detected in the preparation which analyzed as $Na_2O \cdot 5UO_3$. The 760-cm^{-1} band remained strong and did not appear to shift in energy. Concomitant with the decreasing intensity of the 820-cm^{-1} band was the growth of a new, sharp band at 880 cm^{-1}.

Since the results indicated that there were only two phases in samples corresponding to the molar ratio $UO_3:Na_2O > 2.5$, we attempted to selectively remove the diuranate-type phase from the mixture by means of an acid wash.

Sodium carbonate and UO_3 were mixed in the molar ratio $Na_2CO_3:UO_3 = 1:5$ and ignited at 850°. The product was then successively extracted three times with 0.5 *M* HCl at 60°. Each residue was washed twice with H_2O, then ignited at 850°. An average of 35% of the solid sample extracted was dissolved at each step. All extracts and solid residues were analyzed, and the infrared spectrum and powder diffraction pattern of each residue were obtained. The analytical results are recorded in Table II. The analysis of the original gross product, which accurately reflected the ratio of the starting materials, provided an additional check on the methods of determining Na and U. It is apparent that the first two acid extracts were rich in sodium in comparison to the solid samples extracted. Then a constant composition of $Na_2O \cdot \sim 13UO_3$ appeared to be attained.

TABLE II

ANALYSIS OF $Na_2O \cdot 5UO_3$ AFTER SUCCESSIVE EXTRACTIONS WITH 0.5 *M* HCl

	% U	% Na	Total[a] % acctd for	Indicated compn, $UO_3:Na_2O$
(1) Original product	80.1	3.07	100.4	5.0
(2) HCl extract of (1)	76.6	5.80	99.6	2.6
(3) Residue after HCl extraction of (1)	82.7	1.53	101.5	10.4
(4) HCl extract of (3)	80.4	2.44	98.3	6.4
(5) Residue after HCl extraction of (3)	82.6	1.26	100.9	12.7
(6) HCl extract of (5)	81.8	1.24	101.3	12.7
(7) Residue after HCl extraction of (5)	82.8	1.26	101.2	12.7

[a] Calculated assuming Na present as Na_2O and U as UO_3.

The X-ray diffraction patterns of the residues could each be indexed in an orthorhombic cell with $a = 6.807$,

$b = 15.934$, $c = 8.257$ A. Their infrared spectra were also essentially identical. A representative tracing is shown in Figure 2C; the spectra of α-UO_3 and α-U_3O_8 are included for purposes of direct comparison. The further progression from $Na_2O{\cdot}5UO_3$ (Figure 1G) to that analyzed as $Na_2O{\cdot}{\sim}13UO_3$ (Figure 2C) represented primarily a clearer definition of structure that had previously been apparent. Of particular interest was the increase in intensity in the 880-cm^{-1} band such that in Figure 2C it had become one of the four most intense bands in the spectral region shown. There is some similarity to the spectrum of α-UO_3 but clearly none to α-U_3O_8.

In addition to igniting Na_2CO_3 and UO_3, samples of $Na_2U_2O_7$ and UO_3 or U_3O_8 were also prepared in the ratio calculated to give $Na_2O{\cdot}5UO_3$. In both of the latter cases the products had the same characteristics as those described for the sample prepared with Na_2CO_3 (Figure 1G).

As cited earlier, the precipitate formed by adjusting the pH of a $UO_2(NO_3)_2$ solution to approximately 6 with NaOH has been reported to have a composition near $Na_2O{\cdot}7UO_3$. Indeed, Maly and Vesely[8] found that the powder diffraction patterns of precipitates dried at 100° in which the ratio U:2Na varied from 16 to 5 were identical with that of the product Wamser, *et al.*,[6] identified as $Na_2O{\cdot}7UO_3$. However, these patterns were quite different from those obtained in the present investigation where anhydrous compounds of the indicated stoichiometry were formed by the fusion of uranium and sodium salts or oxides. We were, nevertheless, interested in directly comparing the characteristics of compounds obtained by precipitation from aqueous solution followed by ignition at 800° with those prepared by the fusion technique. Thus a number of samples were prepared by titrating $UO_2(NO_3)_2$ solution with NaOH to a given pH within the range 4.5–10. We made no effort to attain equilibrium conditions, since we were only interested in obtaining samples in which the ratio U:2Na varied from ~2.5 to ~8 or 9. The results showed, as expected, that in the pH range ~6–10, the products after ignition corresponded to compounds in the range $Na_2O{\cdot}{\sim}3UO_3$ to $Na_2O{\cdot}{\sim}7UO_3$, with infrared spectra of the phases that were richer in uranium corresponding quite closely to that of $Na_2O{\cdot}5UO_3$ (Figure 1G).

The characteristics of the precipitates formed at pH 4–5 (and washed) were in sharp contrast to those obtained in the pH 6–10 range. After ignition at 500°, the sample separated at pH 4.5 had an infrared spectrum that was quite similar to that of amorphous UO_3.[14] Its powder diffraction pattern at this temperature showed only a few very faint lines. Increasing the temperature to 800° produced a mixture in which lines characteristic of U_3O_8 were prominent, but the weak lines of the polyuranate phase could also be detected. Analysis gave a composition $Na_2O{\cdot}17.6UO_3$. Thus, the original precipitate was probably $UO_2(OH)_2$.

The precipitate obtained at pH ~4.8, after ignition at 850°, analyzed directly as $Na_2O{\cdot}12.4UO_3$. Its infrared spectrum and X-ray diffraction pattern were identical with those of the compound $Na_2O{\cdot}12.7UO_3$, Table II. These compositions are in very good agreement with the results reported by Paramonova and coworkers, where an indirect method of determining the U:Na ratio in solution at a given pH was employed.[9]

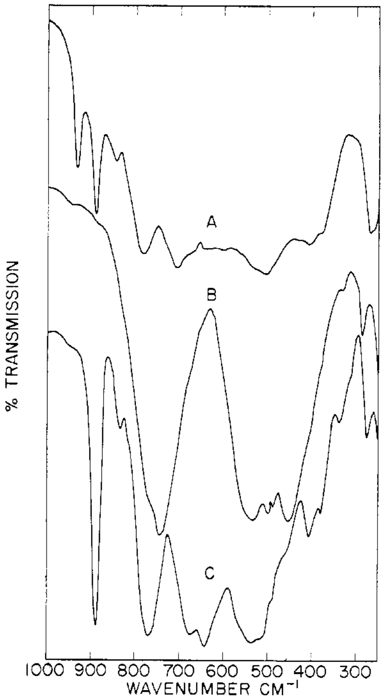

Figure 2.—Infrared spectra of (A) α-UO_3, (B) α-U_3O_8, (C) $Na_2O{\cdot}{\sim}13UO_3$.

Finally, a large sample was prepared by titrating $UO_2(NO_3)_2$ to pH 6.1 with NaOH and igniting the washed precipitate to 860°. This solid was repeatedly extracted with 0.5 *M* HCl in the same manner as described earlier for the $Na_2O{\cdot}5UO_3$ sample. In this case a constant composition was achieved after the first extraction; otherwise, the results were identical with those reported in Table II. The composition of the original product, $Na_2O{\cdot}5.7UO_3$, compares reasonably well with the ratio U:2Na = 6.06, reported by Paramonova, *et al.*,[9] for a sample precipitated at pH 5.98.

The thermal stability of the product $Na_2O{\cdot}{\sim}13UO_3$ was particularly striking and rather unexpected in view of the formula. When samples were heated to temperatures in excess of 900°, it was found that decomposition to $UO_{2.6}$[23] usually occurred rapidly in the temperature range 1020–1070°. The change in infrared spectrum from that of Figure 2C to one closely resembling Figure 2B was clear evidence of the structural changes, but X-ray diffraction patterns also reflected the decomposition.

The results obtained for the system $Na_2O{\cdot}xUO_3$, where $x \geq 2$, are summarized in Table III. Thus we found evidence for only two types of phases—one related to $Na_2U_2O_7$ and a polyuranate type. The latter appears to approach a composition near $Na_2O{\cdot}13UO_3$ which corresponds closely to a short

[23] α-U_3O_8 is not stable at 900–1000°. A closely related phase of slightly lower oxygen content is formed, and denoted here by $UO_{2.6}$.[16]

TABLE III

Approx range of x	Structure obsd	
2.0	$Na_2U_2O_7$	
~2.1–~2.5	Type α	Related to but distinct from the $Na_2U_2O_7$ structure. Apparently a region of solid solution. Corresponds to Wamser's phase B[6]
~2.5–~6	Mixture	Phase α + polyuranate
~6–13	Polyuranate phase	Orthorhombic structure related to α-UO_3 and α-U_3O_8. Infrared spectrum indicative of a new phase

plateau in the plot of the ratio Na:U in the precipitate *vs.* pH of solution in the titration of UO_2^{2+} with NaOH.[9] Samples in which the ratio UO_3:Na_2O varied from ~6 to 13 could not be distinguished structurally. The X-ray diffraction patterns of α-UO_3, α-U_3O_8, and Na_2O·$13UO_3$ are compared in Figure 3, and the cell constants for compounds prepared in the course of this investigation are summarized in Table IV. The strong lines of α-UO_3 are seen in all three patterns in Figure 3, which indicates that the fundamental uranium structure is only distorted, not completely changed, within this group. Thus the indexing of the U_3O_8 pattern required tripling the b axis of a pseudo-cell with the dimensions a = 6.716, b = 3.988, c = 4.148 A. These parameters are basically those of α-UO_3 referred to orthorhombic indices. The main dimensional change upon transition from α-UO_3 to α-U_3O_8 is therefore a small contraction along the c axis. Similarly, the unit cell of the polyuranate structure requires a quadrupling of the b axis and a doubling of the c axis of an α-UO_3-related pseudo-cell. All but a few relatively weak lines in the polyuranate pattern could be indexed with c = 4.127 A which represents a further slight contraction of the c axis compared to α-UO_3.

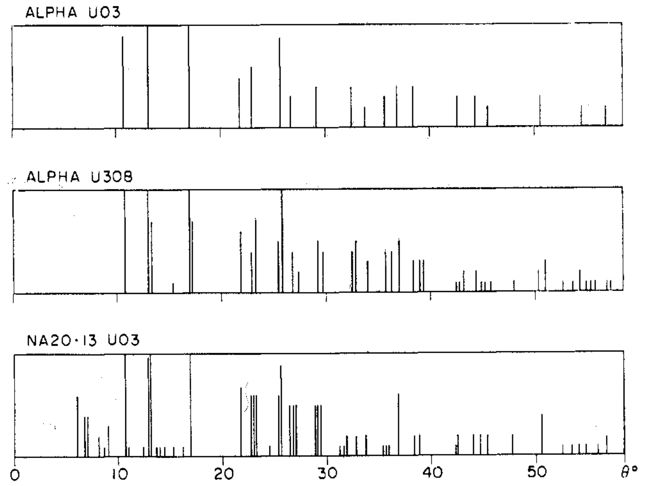

Figure 3.—Comparison of powder diffraction patterns of α-UO_3, α-U_3O_8, and Na_2O·$13UO_3$.

TABLE IV

STRUCTURAL DATA OBTAINED FROM POWDER DIFFRACTION PATTERNS

	Cell parameters, ±0.003 A					
	a	b	c	$\rho_{X\text{-ray}}$	$\rho_{meas d}$	Z
α-UO_3[a]	3.958	...	4.166	8.4	(7.04)[14]	1
α-U_3O_8	6.716	11.966	4.148	8.4	7.9	2
Na_2O·$2.5UO_3$	6.68	12.50	9.18	...	...	...
Na_2O·$13UO_3$	6.807	15.934	8.254	7.1	7.2	1
$Na_2U_2O_7$	6.812	11.790	17.742	6.6	6.4	9

[a] According to the results of Wheeler, *et al.*[16] this sample was slightly oxygen deficient, although the hexagonal α-UO_3 structure can be maintained under such conditions. The method has been reported to give the stoichiometric trioxide.[17]

The polyuranate demonstrated a remarkable degree of thermal stability; no decomposition was indicated upon prolonged heating at 900°, whereas α-UO_3 decomposes at ~650°.[14] A rapid transformation from the polyuranate to the $UO_{2.6}$ phase was observed near 1000°. Unfortunately, attempts to grow single crystals of the polyuranate by heating for several weeks at high temperature were unsuccessful.

The identical polyuranate phase was produced *via* several different reactions including ignition of Na_2CO_3 or $Na_2U_2O_7$ with UO_3 or U_3O_8 and precipitation from $UO_2(NO_3)_2$ solution with NaOH. In the latter case, the gross composition of the ignited precipitate obtained near pH 4.8 corresponded directly to the "pure" polyuranate phase. Precipitates formed at higher values of pH, as well as the products obtained by fusing solid mixtures, were washed with acid to remove a varying amount of a second phase (which resembled $Na_2U_2O_7$) before the pure polyuranate structure was apparent. We found no evidence for stoichiometric compounds such as Na_2O·$3UO_3$ or Na_2O·$4UO_3$.

The infrared spectrum characteristic of products in the Na_2O·(6–13)UO_3 range resembles that of α-UO_3. The two intense bands in the polyuranate at ~640 and 760 cm^{-1} have counterparts at slightly higher energy in α-UO_3, while both the polyuranate and α-UO_3 exhibit slight shoulders at 830 cm^{-1} and a sharp band at ~880 cm^{-1}. A comparison of the bands for the polyuranate phase, α-UO_3, and α-U_3O_8 in the 600–166-cm^{-1} range is given in Table V. The results for the latter two compounds are similar to those reported by Tsuboi, *et al.*[24] We have previously discussed[13] the

TABLE V

ABSORPTION BANDS OBSERVED IN THE 600–166-CM^{-1} REGION

Na_2O·$13UO_3$		α-U_3O_8		α-UO_3	
ν, cm^{-1}	Rel[a] intens	ν, cm^{-1}	Rel intens	ν, cm^{-1}	Rel intens
520	10.0	524	9.7	616	9.8
455	8.2 sh	444	10.0	520	10.0
396	7.1	280	8.7	395	9.0
370	6.7 sh	241	8.1	246	8.0
328	4.6	219	8.4	189	4.8 sh
306	4.0	200	7.5 sh		
268	5.7				
260	7.3 sh				
240	5.7				
218	5.1				
188	3.8				

[a] Approximate arbitrary scale (0–10), where 10 is assigned to the strongest band in the region observed.

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(24) M. Tsuboi, M. Terada, and T. Schimanouchi, *J. Chem. Phys.*, **36**, 1301 (1962).