

$B_{10}H_7(CN)_2 \cdot N_2^-$ .—A solution of  $Cs_2[\xi-B_{10}H_8(CN)_2]$  (4.0 g., 9.2 mmoles, prepared at 400° in 400 ml. of water was chilled in a water-ice bath. Sodium nitrite (5.0 g., 72.5 mmoles) and 12 *M* hydrochloric acid (10 ml.) were added, resulting in formation of a dark color. After 2 min. of stirring, with continued cooling in the ice bath, zinc dust (15 g., 230 g. atoms) was added. The cooling bath was removed, and an additional 10-ml. portion of 12 *M* hydrochloric acid was added. A vigorous reaction ensued, and the mixture became quite hot. After the reaction subsided, a final 10-ml. portion of 12 *M* hydrochloric acid was added, and the mixture was stirred until the supernatant liquid was light yellow, almost colorless. The mixture was filtered. The addition of excess tetramethylammonium chloride precipitated a white solid which was recrystallized from water. The recrystallization caused the development of a light yellow color, and the final product,  $(CH_3)_4NB_{10}H_7(CN)_2 \cdot N_2$ , was obtained as 0.4 g. (16%) of well-formed, light yellow crystals. *Anal.* Calcd. for  $(CH_3)_4NB_{10}H_7(CN)_2 \cdot N_2$ : B, 40.0; C, 26.0; H, 7.1. Found: B, 39.8; C, 26.1; H, 7.6. Ultraviolet showed  $\lambda_{max}^{CH_3CN-H_2O}$  395 ( $\epsilon$  38.8), 258 ( $\epsilon$  15,400), 218  $m\mu$  ( $\epsilon$  24,400).

$Cs_2[1,12-B_{12}H_{10}(CN)_2]$ .— $Cs_2[1,12-B_{12}H_{10}(CONH_2)_2]^{10}$  (4.3 g., 8.7 mmoles) was heated at 35–375° at 0.1 mm. nominal pressure for 5 days. Infrared analysis indicated complete dehydration of the amide groups and conversion to  $Cs_2[1,12-B_{12}H_{10}(CN)_2]$ . A small amount was recrystallized from water for analysis and was obtained as a hydrate as shown by its infrared spectrum. *Anal.* Calcd. for  $Cs_2B_{12}H_{10}(CN)_2 \cdot H_2O$ : B, 27.3; C, 5.0; H, 2.5; N, 5.9. Found: B, 27.4; C, 5.0; H, 2.5; N, 5.4. There was no maximum in the ultraviolet region. The infrared spectrum of a Nujol mull has absorption at 2515 (B–H str.), 2200 (C≡N), 3640, and 1630  $cm^{-1}$  (water of hydration), as well as fairly sharp absorptions of medium intensity at 1040 and 955 (shoulder at 970  $cm^{-1}$ ) and a somewhat broader one at 725  $cm^{-1}$  (shoulder at 737  $cm^{-1}$ ). The  $B^{11}$  n.m.r. spectrum in water consists of two peaks at 28.6 and 36.2 p.p.m. The 36.2-p.p.m. peak is more intense than the 28.6-p.p.m. peak because of coincidence of the

resonance from the boron atoms attached to CN with the high-field peak of the doublet caused by borons bonded to hydrogen. This is demonstrated by the decoupled spectrum which has a sharp peak at 32.3 p.p.m. with a high-field shoulder.

$Cs_2[\xi-B_{12}H_{10}(CN)_2]$ .— $Cs_2[1,12-B_{12}H_{10}(CONH_2)_2]$  (14 g., 28.3 mmoles) was heated to 500° for 1 hr. at 0.1 mm. nominal pressure. At the end of this time, the product was a clear straw-colored liquid which set to a very brittle glass on cooling. The infrared spectrum showed complete conversion of the amide groups to CN groups. *Anal.* Calcd. for  $Cs_2[B_{12}H_{10}(CN)_2]$ : B, 28.4; C, 5.2; H, 2.2; N, 6.1. Found: B, 29.1; C, 4.7; H, 2.6; N, 5.4. There was no ultraviolet maximum. The infrared spectrum of a Nujol mull had absorption at 2470 (B–H str.), 2190  $cm^{-1}$  (C≡N), and also had broad absorptions of moderate to weak intensity centered at 1190, 1020, 960, and 720  $cm^{-1}$ . The  $B^{11}$  n.m.r. spectrum was similar to that of the 1,12-isomer. In a similar preparation, characterization of evolved gases showed that 0.2 mole equiv. of hydrogen was formed. Noticeable gas evolution began at 450°.

**Isomerization of 1,2- and 1,6- $(CH_3)_2SB_{10}H_8N(CH_3)_3$ .**—Small samples of 1,2- (m.p. 268°) and 1,6- $(CH_3)_2SB_{10}H_8N(CH_3)_3^{14}$  (m.p. 204°) were placed in melting point capillary tubes and heated at various temperatures in a melting point apparatus. The products were subjected to t.l.c. on silica gel using 2% acetonitrile in ethylene chloride. At 236–240° (20 min.), the 1,2-isomer showed mostly unchanged starting material ( $R_f$  0.24) and a small amount of material with  $R_f$  0.36. Under the same conditions the 1,6-isomer showed mostly unchanged starting material ( $R_f$  0.59) with a smaller spot at  $R_f$  0.65 and very small spots at  $R_f$  0.17 and 0.37. Similar results were obtained at 258–261° except that the same minor products in each case became more pronounced.

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## A Study on the Stability of Xenon Trioxide in Basic Solutions<sup>1</sup>

BY CHARLES W. KOCH<sup>2</sup> AND STANLEY M. WILLIAMSON

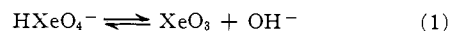
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The reaction of  $XeO_3(aq)$  with NaOH and KOH solutions in the range of 0.25 to 4.2 *M* and 2.0 to 3.6 *M*, respectively, at room temperature gives a 33% yield of the alkali perxenate. Higher  $[OH^-]$  and temperature increase the yield. Lowering the  $[OH^-]$  toward the neutral point leads to the direct decomposition of  $XeO_3$ . For comparable concentrations for LiOH, the yield of perxenate is 50% and higher. A yellow, mixed oxidation state complex with variable stoichiometry forms predominantly in the NaOH and KOH systems. It provides a mechanism by which Xe(VI) directly decomposes to  $Xe + 1.5O_2$ . In the KOH system, the complex is present as a solid during most of the course of the reaction. Subsequently,  $K_4XeO_6 \cdot 9H_2O$  has been isolated. The relative stabilities of the alkali and alkaline earth perxenates, a mechanism for the disproportionation-decomposition reaction of  $XeO_3$ , and the nature of the mixed oxidation state complex are presented.

### Introduction

The research of Appelman and Malm<sup>3</sup> has done much to elucidate the nature of the aqueous, oxygen-containing, xenon species. Since the earliest report on the preparation of Xe(VIII)<sup>4</sup> from the hydrolysis of  $XeF_6$  in NaOH solutions and with the observations at pH 7 that a secondary reaction interfered with the kinetic studies of the oxidation of iodide anion by aqueous xenon trioxide,<sup>5</sup> our interest in the disproportionation and de-

composition of Xe(VI) has been keen. Raman spectra in aqueous solution<sup>6</sup> have shown that xenon trioxide exists as a discrete, pyramidal molecule just as it does in the solid state.<sup>7</sup> From their titration experiments on aqueous xenon trioxide,<sup>3</sup> Appelman and Malm suggest that the Xe(VI) species that exists above pH 12 is  $HXeO_4^-$ . The end point that they and others have found is not well defined (see Fig. 2 in ref. 3), and we suggest that the change in slope of the graph need not be due entirely to<sup>3</sup>



Whether reaction 1 is fast or slow, the onset of the disproportionation reaction can complicate the titration

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(2) C. W. K. acknowledges support from the Lawrence Radiation Laboratory of the University of California.

(3) E. H. Appelman and J. G. Malm, *J. Am. Chem. Soc.*, **86**, 2141 (1964).

(4) J. G. Malm, B. D. Holt, and R. W. Bane, "Noble-Gas Compounds," H. H. Hyman, Ed., University of Chicago Press, Chicago, Ill., 1963, p. 167.

(5) C. W. Koch and S. M. Williamson, ref. 4, p. 181.

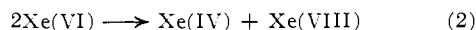
(6) H. H. Claassen and G. Knapp, *J. Am. Chem. Soc.*, **86**, 2341 (1964).

(7) D. H. Templeton, A. Zalkin, J. D. Forrester, and S. M. Williamson, *ibid.*, **85**, 817 (1963).

curve, since the disproportionation of Xe(VI) to Xe(VIII) consumes hydroxide anion. Data within the pH region of the questionable end point on the disproportionation-decomposition reaction will be given in a later section.

Our main concerns were the determination of the stability and stoichiometry of the reactions of Xe(VI) in basic solutions and whether these properties were influenced by different basic solutions.

The experiments of Appelman and Malm<sup>3</sup> on the hydrolysis of XeF<sub>6</sub> in 2.5 M NaOH gave a 50 mole % yield of Xe(VIII) and an equal amount of Xe gas. This stoichiometry is in accord with an initial disproportionation reaction



with the concomitant decomposition of Xe(IV) to Xe and one molecule of oxygen per Xe atom. This stoichiometry does not allow any other reaction from the Xe(IV).

We chose to use aqueous xenon trioxide that had been prepared by our original procedure,<sup>8</sup> *i.e.*, dissolving the recrystallized XeO<sub>3</sub>(s) in distilled water so that fluoride anion and trace amounts of other ions would not be present as would be so from any scheme that chemically separates the fluoride anion from the xenon trioxide.

Under certain conditions with sodium hydroxide, especially at temperatures above that of the room, we also found that approximately 50% of the bound xenon originally as XeO<sub>3</sub> is liberated as Xe gas. However, after a more detailed study over wide ranges of base concentrations at room temperature, we have found the over-all reaction to be more complex than that described by reaction 2. The disproportionation of Xe(VI), which is accompanied by the decomposition of Xe(IV), is only one of two main steps in the over-all reaction. The other step is the formation of a mixed oxidation state complex of variable composition between the produced Xe(VIII) and the initially present Xe(VI). This complex in most cases does decompose with the liberation of the Xe(VIII), unchanged, and the decomposition of the Xe(VI) so that 1.5 oxygen molecules are liberated per xenon atom. This yellow compound<sup>3,4,9</sup> has been observed and mentioned before. With sodium hydroxide solutions, the complex forms but does not precipitate. With potassium hydroxide solution the yellow complex precipitates and leaves a solution with essentially no yellow color; with lithium hydroxide solution, no appreciable amount of the complex is ever formed. The course of the disproportionation and decomposition of Xe(VI) is therefore controlled by the relative stabilities of the alkali or alkaline earth perxenate and the mixed oxidation state complex. Experimental data will be given in a later section that will illustrate these reactions and the relative stabilities of the compounds formed from the reactions.

### Experimental

**Preparation of Pure, Aqueous XeO<sub>3</sub>.**—From the reaction of XeF<sub>4</sub>(s) and H<sub>2</sub>O(l) in Teflon-ware, XeO<sub>3</sub>(s) was obtained<sup>8</sup> after the resulting solution was allowed to evaporate at room tempera-

ture in a desiccator over Ascarite or barium oxide. This XeO<sub>3</sub> was always dissolved in distilled water and re-evaporated before the final dissolution was done for the stock solution. The recrystallization procedure gave extra certainty that traces of hydrofluoric acid were eliminated. Titration of an aliquot of the stock solution with standard sodium thiosulfate after the aliquot had been allowed to react with acidified potassium iodide solution gave the concentration. This procedure proved satisfactory and most of the experiments were done from a stock solution that was 0.1082 M in xenon trioxide. This solution was used over a period of 6 months and its concentration did not change. Room temperature storage was in an ordinary Pyrex volumetric glass-stoppered flask.

**Purification of the Bases.**—Purification of the bases was necessary to minimize the reducing agents that might react with Xe(VI) and Xe(VIII) since the amount of base used in some experiments was very large compared to the xenon trioxide.

Two recrystallizations of reagent grade NaOH from distilled water were sufficient to yield a reasonable material balance for xenon and oxygen in subsequent measurements. The concentration of the stock solution was 19 M. Reducing agents in the KOH and LiOH solutions were satisfactorily removed by digestion at 90° with small amounts of KMnO<sub>4</sub>(s) until a new increment did not change the color appreciably during an additional 1-lr. digestion period. Prolonged digestion of the excess permanganate eventually yielded colorless solutions and MnO<sub>2</sub>(s). The clear supernatant solutions were decanted, standardized *vs.* HCl using phenolphthalein indicator, and protected from other contamination for future use. The concentration of the stock KOH solution was 10.0 M; the LiOH solution was 4.98 M. No coloration due to manganate or permanganate could be detected in subsequent experiments that used the KOH and/or LiOH solutions. Therefore the concentration of dissolved lower oxidation states of manganese in the bases must have been very low.

**Gas-Handling Techniques.**—From a known amount of aqueous xenon trioxide, the stoichiometry of the disproportionation-decomposition reaction could be followed at any interval by directly measuring the number of moles each of xenon and oxygen evolved. Pressure-volume-temperature measurements on the gases were made. The evolved oxygen and xenon from the reaction vessel could be physically separated by means of a train of concentric tube Pyrex traps that were of a size to fit 1-pint dewar flasks, connected to an automatic Toepler pump<sup>10</sup> which was in turn fitted with a thermostated gas buret. We found that at nitrogen slush temperature, *ca.* 62°K., xenon samples of the size of our experiments, *ca.* 25–50 μmoles in a trap of the separation train, would not produce a blank in the buret after about a 20-min. pumping cycle larger than the blank due to the background pressure of the system. Oxygen gas could be quantitatively pumped from the trap at that temperature. So by use of a gas buret having several graduations and a total volume of 3 ml., pressure-volume measurements could be obtained on the separated gases. This apparatus had an established accuracy of ±0.2 μl. of gas. The principal uncertainty in the measurement of gas volumes is due to the outgassing procedure, since xenon is approximately five times more soluble in aqueous solutions than is oxygen. For maximum pressures in the buret of 0.5 atm., no ideality corrections were made.

**The Reaction Vessel.**—The Pyrex reaction vessel is shown in Fig. 1. Part A is a 18/9 socket for convenient connection to the separation train. Part B is a 2-mm. bore high vacuum stopcock. Part C is a 19/38 standard taper joint through which the solutions were added to the two compartments D in the lower piece of the apparatus. The volume of each compartment without overflow was 1 ml., whereas the volume of the apparatus below the stopcock was 27 ml. This large volume allowed the reactions to occur under conditions where the partial pressures of the xenon and oxygen were always quite low. Since the two compartments were at a small angle to the axis through C, rotation of the apparatus about C provided a method for mixing after each separate solution had been thoroughly out-gassed. A was sealed to the train by means of Apiezon W black-wax, and B and C were lubricated with Apiezon N. When a measurement of the evolved oxygen and xenon was made, D was cooled with a solid-liquid acetone slurry and then B was opened. Outgassing was accomplished by closing B, warming D, rotating C, recooling D, and opening B.

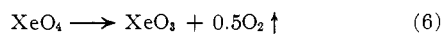
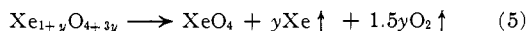
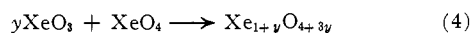
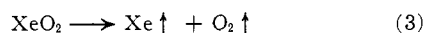
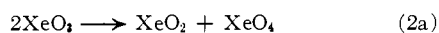
(8) S. M. Williamson and C. W. Koch, *Science*, **139**, 1046 (1963).

(9) A. Zalkin, J. D. Forrester, D. H. Templeton, S. M. Williamson, and C. W. Koch, *ibid.*, **142**, 501 (1963).

(10) C. W. Koch and E. E. Jones, *Mikrochim. Ichnoanal. Acta*, **4**, 734 (1963).

### Discussion

Instead of obtaining a 50% yield of perxenate from  $\text{XeO}_3$  and  $\text{NaOH}$  or  $\text{KOH}$ , we have observed that, when the reactions are completed, very nearly a 33% yield of perxenate is obtained over a  $\text{NaOH}$  range of 0.25 to 4.2  $M$  and a  $\text{KOH}$  range of 2.0 to 3.6  $M$ . The smaller yield is the result of an alternative reaction, other than reaction 2, by which  $\text{XeO}_3$  can decompose without giving rise to an increased amount of perxenate. With both reactions in force, the  $\text{O}_2/\text{Xe}$  values should be greater than unity. The following reactions are the ones that we propose to account for the over-all stoichiometry of the reaction of  $\text{XeO}_3$  with the different bases. To eliminate the possibility of further complications, the species will be written in the reactions as the oxides; *i.e.*, we shall not consider for this purpose the degree of hydroxylation of the species. The oxidation states of the species can easily be followed by use of the oxides.



Appelman and Malm<sup>3</sup> cite a datum on the composition of the complex compound of reaction 4 in the  $\text{KOH}$  system that supports  $2\text{XeO}_2 \cdot \text{K}_4\text{XeO}_6$  as the formula. We have found by analysis in the  $\text{KOH}$  system that  $y$  can vary between 4 and 0.1 when compared by algebraic difference to the total amount of xenon remaining in the solution. The data in Table I do support that for low concentrations of perxenate the value of  $y$  in reaction 5 is unity to give a total evolved  $\text{O}_2/\text{Xe}$  of approximately 1.25. But when  $\text{XeO}_3$  is allowed to react with perxenate at higher concentrations, the total evolved  $\text{O}_2/\text{Xe}$  is greater than 1.25 and approaches 1.50 so long as the  $[\text{OH}^-]$  is great enough to ensure stability of the perxenate, *i.e.*, to prohibit reaction 6. This observation suggests that the higher perxenate concentration suppresses reaction 2 and then reaction 3 which contributes an  $\text{O}_2/\text{Xe}$  of 1.0. A further observation on this point is that additional increments of  $\text{XeO}_3$  to solutions of perxenate produce subsequently smaller per cent yields of the perxenate based on the additional increment of  $\text{XeO}_3$  (see expt. 3 and 4). At higher  $[\text{KOH}]$  (see expt. 7), reaction 4 appears to have been suppressed, and more than 50% of the xenon remained in the solution as perxenate. This implies a reaction between  $\text{XeO}_3$  and a lower oxidation state to yield the perxenate. In expt. 7 there was not a precipitate that resembled the complex of reaction 4 as there was in the experiments with intermediate  $\text{KOH}$  concentrations.

The reaction in the  $\text{KOH}$  system was run at three different temperatures, 0,  $25 \pm 1$ , and  $65 \pm 5^\circ$ . Experiments 1 and 2, for the first two temperatures, show very little difference in the over-all stoichiometry or per cent reaction. The rate is, however, much faster as the temperature is increased. The third temperature gave in a time less than 22 hr. 69.4%  $\text{Xe}$  recovery and 1.26 oxygen molecules per xenon atom to produce the perxenate. So over this temperature range, the reaction is

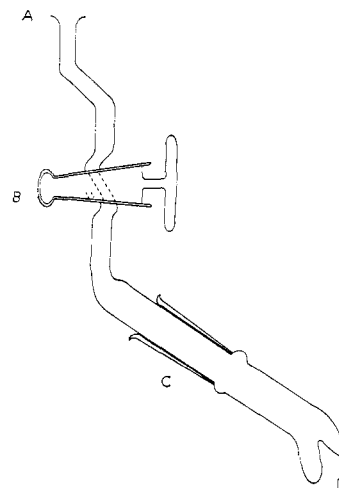


Fig. 1.—Reaction vessel for xenon trioxide and hydroxide solutions.

changed very little. This independence of temperature could be due to the heterogeneity of the reaction.

In expt. 6, where the initial  $[\text{KOH}]$  was 0.03  $M$ , it is seen that the gas evolution ratios are significantly higher than in the other experiments, and that essentially all of the  $\text{Xe}$  gas was recovered. This indicates that during the majority of the reaction most of the perxenate that was formed was unstable. The last gas measurement of expt. 6 shows that a small amount of perxenate remains stable. During the course of the reaction the  $[\text{OH}^-]$  goes through a minimum since perxenate formation consumes hydroxide, so at the end of the experiment the  $[\text{OH}^-]$  again approaches 0.03  $M$ . Also in this experiment, no yellow-colored solution or precipitate was formed.

During the course of the reactions, the remaining  $\text{O}_2/\text{Xe}$  values become less reliable, since the numerator and denominator of the number represent the differences between a constant and an increasing number. Also for experiments of long duration, the loss of oxidizing power to any reducing material will consequently give  $\text{O}_2/\text{Xe}$  remaining values in excess of 2.0. This phenomenon can be seen particularly in expt. 3 and 5. In the early stages of expt. 5, there did not seem to be any difference when compared with other experiments under comparable conditions, except that after 75% recovery of the  $\text{Xe}$ , the perxenate appears to be somewhat unstable.

In none of the seven experiments described so far was the perxenate concentration sufficiently high so that by cooling to  $0^\circ$  crystals of potassium perxenate were obtained. From expt. 3 after the second treatment of the perxenate solution with  $\text{XeO}_3$ , the efficiency of perxenate production became so poor that a third increment of  $\text{XeO}_3$  was not added. This resulting perxenate solution, which contained 33.81  $\mu\text{moles}$  of perxenate, 2008  $\mu\text{moles}$  of  $\text{K}^+$ , and 950  $\mu\text{l.}$  of  $\text{H}_2\text{O}$ , was reduced to about half-volume in a desiccator, and then slow chilling to  $5^\circ$  produced well-defined, colorless, transparent crystals. At  $5^\circ$  about one-half of the supernatant solution was withdrawn so that the crystals would not redissolve when brought back to room temperature. The X-ray crystal structure of this colorless compound has been determined and the formula established as  $\text{K}_4\text{XeO}_6 \cdot 9\text{H}_2\text{O}$ , potassium perxenate nonahydrate.<sup>11</sup> The crystals of

(11) A. Zalkin, J. D. Forrester, D. H. Templeton, S. M. Williamson, and C. W. Koch, *J. Am. Chem. Soc.*, **86**, 3569 (1964).

TABLE I  
 KOH + XeO<sub>3</sub> DATA

Expt.	Initial $\mu$ moles		$\mu$ moles evolved		$[\text{O}_2/\text{Xe}]_{\text{collected}}$	$[\text{O}_2/\text{Xe}]_{\text{remaining}}$	Reaction, %	Total time, hr.
	XeO <sub>3</sub>	KOH	O <sub>2</sub>	Xe				
1	51.90	2540	4.05	3.65	1.11	1.53	7.0	63.2
	(total vol., 700 $\mu$ l.; 0°)		6.52	5.66	1.15	1.58	17.9	154.8
			9.56	7.50	1.27	1.65	32.4	319.7
			14.66	10.94	1.34	1.78	53.5	461.5
			13.54	10.14	1.34	2.11	73.0	630.6
$[\Sigma\text{O}_2/\Sigma\text{Xe}]_{\text{collected}} = 1.275$								
2	20.50	2540	2.66	2.19	1.22	1.53	10.7	2.3
	(total vol., 700 $\mu$ l.; 25 $\pm$ 1°)		4.12	3.39	1.21	1.61	27.2	4.8
			12.06	9.28	1.30	2.11	72.5	21.4
3	27.05	2008	8.34	7.26	1.15	1.63	26.9	6.2
	(total vol., 950 $\mu$ l.; 24 $\pm$ 1°)		14.53	10.96	1.33	2.01	67.6	19.4
Added additional 54.00 $\mu$ moles of XeO <sub>3</sub> and 500 $\mu$ l. of H <sub>2</sub> O after removing $\sim$ 500 $\mu$ l. of H <sub>2</sub> O from the reaction vessel								
54.00			7.35	6.13	1.20	1.54	11.4	1.8
			22.53	17.19	1.31	1.67	43.2	7.2
			22.71	16.23	1.40	1.97	73.2	18.9
Added additional 54.00 $\mu$ moles of XeO <sub>3</sub> and 500 $\mu$ l. of H <sub>2</sub> O after removing $\sim$ 500 $\mu$ l. of H <sub>2</sub> O from the reaction vessel								
54.00			11.19	9.62	1.16	1.57	17.8	3.5
			31.15	23.51	1.33	1.85	61.4	20.3
			14.37	10.28	1.40	2.29	80.4	44.2
4	80.82	2008	45.10	38.00	1.19	1.78	47.0	68.5
	(total vol., 950 $\mu$ l.; 26 $\pm$ 2°)		12.21	8.85	1.38	1.88	57.9	145.9
			8.93	6.00	1.49	1.97	65.4	237.4
$\sim$ 400 $\mu$ l. of H <sub>2</sub> O pumped off; 21.64 $\mu$ moles of XeO <sub>3</sub> + 200 $\mu$ l. of H <sub>2</sub> O added								
21.64			4.23	3.30	1.28	1.54	15.2	21.2
(total vol., 750 $\mu$ l.)			11.49	8.67	1.32	1.73	55.3	87.5
			5.60	4.06	1.38	1.99	74.1	159.3
5	27.05	250	9.13	7.79	1.17	1.63	28.8	6.7
	(total vol., 775 $\mu$ l.; 25 $\pm$ 2°)		8.46	6.32	1.34	1.78	52.2	40.1
			9.65	6.22	1.55	1.99	75.2	162.1
			7.21	4.55	1.59	2.83	92.0	281.0
6	27.05	25	2.55	1.56	1.63	5.9	97.7	493.9
	(total vol., 850 $\mu$ l.; 24 $\pm$ 1°)		8.81	6.22	1.42	1.53	23.0	21.6
			25.61	17.20	1.49	1.70	86.6	69.2
			2.94	2.12	1.39	2.13	94.4	166.8
7	27.05	6350	0.08	0.06	1.3	2.2	94.6	260.5
	(total vol., 750 $\mu$ l.; 25 $\pm$ 1°)		1.47	2.06	0.71	1.57	7.6	4.0
			5.65	6.81	0.83	1.84	32.9	31.0
		2.96	2.99	0.99	2.01	44.0	68.9	

the potassium perxenate were found to be considerably more stable in X-rays than was Na<sub>4</sub>XeO<sub>6</sub>·6H<sub>2</sub>O, but less so than was Na<sub>4</sub>XeO<sub>6</sub>·8H<sub>2</sub>O. In none of these salts has any explosive character been observed.

In Table II it can be seen for the room temperature expt. 10 and 13 at 4.2 and 0.25 *M* NaOH, respectively, that the stoichiometries at a given per cent reaction are very similar. The reaction rate at higher [OH<sup>-</sup>] is considerably faster. The elapsed time for the last measurement of an experiment may not be meaningful, because the reaction could have essentially stopped before the last measurement was made. In expt. 10 and 13 the O<sub>2</sub>/Xe collected values begin close to unity and increase as the reactions proceed. The observations are again in accord with a sequence of reactions such as 2-5 above. In both cases it is seen that close to a 33% yield of perxenate has been obtained.

From the data for expt. 11 and 12, it can be seen that at higher temperatures, the yield of perxenate is increased at the given hydroxide concentrations, and the data for the stoichiometry suggest that reactions 2 and 3 are the predominant ones. As has been mentioned above, higher temperature in the KOH system did not

increase the yield of perxenate. The solid, yellow, mixed oxidation state complex was present in the KOH reaction at 65°, whereas, in the NaOH system, no compound of that nature was ever precipitated; thus reactions 4 and 5 cannot be significant, whereas they are with the KOH system.

Another way to increase the yield of perxenate in the NaOH system is to increase the concentration of NaOH. The disadvantage is that the rate of the reaction is decreased (see expt. 9). (A correlation between [OH<sup>-</sup>] and rate does not seem to exist because of the heterogeneity of the reaction.) Experiment 8 shows that increased [OH<sup>-</sup>] and temperature both increase the yield of perxenate, even though the data for expt. 8 are not complete. The better than 50% yield of perxenate must involve the reaction of XeO<sub>3</sub> with a stabilized xenon species having an oxidation state less than 6. Experiment 7 was an example in the KOH system.

Experiment 14 shows at an initial [OH<sup>-</sup>] of 0.067 *M* that perxenate is formed but that it is not stable. This instability is also seen at the end of expt. 13, so for the NaOH system the approximate lower limit of the hydroxide for perxenate stability is 0.1 *M*; whereas, for the

TABLE II  
 XeO<sub>3</sub> + NaOH DATA

Expt.	Initial $\mu$ moles		$\mu$ moles evolved		[O <sub>2</sub> /Xe] <sub>collected</sub>	[O <sub>2</sub> /Xe] <sub>remaining</sub>	Reaction, %	Total time, hr.
	XeO <sub>3</sub>	NaOH	O <sub>2</sub>	Xe				
8	51.45	19,000	5.23	5.97	0.88	1.58	11.6	3.3
	(total vol., 1050 $\mu$ l.; 53 $\pm$ 5°)		5.14	5.14	1.00	1.66	21.6	15.3
			4.07	5.78	0.70	1.82	32.8	64.4
9	51.29	4750	2.29	2.84	0.81	1.54	5.5	5.1
	(total vol., 500 $\mu$ l.; 25 $\pm$ 2°)		3.85	5.08	0.76	1.63	15.4	44.2
			7.86	10.32	0.76	1.90	35.5	143.6
10	51.31	1900	1.83	2.22	0.82	1.98	39.9	279.3
	(total vol., 450 $\mu$ l.; 26 $\pm$ 1°)		2.37	2.53	0.93	1.53	4.9	1.0
			19.14	16.37	1.17	1.71	36.8	7.3
11	51.51	900	20.02	15.03	1.33	2.04	66.1	17.5
	(total vol., 400 $\mu$ l.; 60 $\pm$ 5°)		20.43	19.80	1.03	1.79	38.4	6.7
			7.02	6.32	1.11	1.96	50.7	23.1
12	51.51	300	21.44	19.83	1.08	1.76	38.4	3.9
	(total vol., 400 $\mu$ l.; 60 $\pm$ 5°)		10.14	8.62	1.18	1.98	55.0	19.4
13	51.29	125	8.97	9.14	0.98	1.61	17.8	6.1
	(total vol., 500 $\mu$ l.; 26 $\pm$ 1°)		10.32	8.83	1.17	1.73	35.0	21.2
			12.97	9.41	1.38	1.87	53.4	46.8
			11.72	7.44	1.58	2.00	67.9	93.3
14	51.31	50	3.52	2.09	1.68	2.04	71.9	119.4
	(total vol., 750 $\mu$ l.; 26 $\pm$ 1°)		18.84	13.51	1.40	1.54	26.3	2.5
			41.31	27.47	1.50	1.63	79.9	18.7
			10.60	7.21	1.47	1.99	93.9	41.7
		4.40	3.00	1.47	...	99.8	87.3	

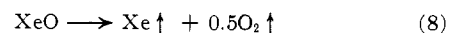
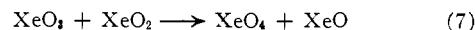
 TABLE III  
 XeO<sub>3</sub> + LiOH DATA

Expt.	Initial $\mu$ moles		$\mu$ moles evolved		[O <sub>2</sub> /Xe] <sub>collected</sub>	[O <sub>2</sub> /Xe] <sub>remaining</sub>	Reaction, %	Total time, hr.
	XeO <sub>3</sub>	LiOH	O <sub>2</sub>	Xe				
15	26.94	2491	2.48	2.97	0.83	1.58	11.1	22.8
	(total vol., 750 $\mu$ l.; 25 $\pm$ 2°)		1.75	1.87	0.93	1.64	18.0	69.8
			1.88	2.16	0.87	1.72	25.9	165.3
			3.64	4.51	0.81	1.99	39.5	428.8
16	27.05	124.6	2.65	3.21	0.83	1.59	11.9	15.3
	(total vol., 475 $\mu$ l.; 23 $\pm$ 1°)		2.44	2.92	0.84	1.70	22.7	86.4
			3.74	4.43	0.84	1.93	39.1	178.2
			1.55	1.84	0.84	2.06	45.9	250.0
17	21.64	49.8	1.92	1.76	1.10	2.19	52.3	345.3
	(total vol., 460 $\mu$ l.; 24 $\pm$ 1°)		3.04	2.84	1.07	1.56	13.1	19.3
			6.23	5.60	1.11	1.76	39.0	97.4
			3.11	2.72	1.14	1.92	51.6	166.2
		1.42	1.66	0.86	2.11	59.2	234.4	

KOH system, it is 0.3 M. These values are in good agreement with the hydrolysis data on XeO<sub>6</sub><sup>-4</sup> that Appelman and Malm<sup>3</sup> report. This difference in the alkali hydroxide concentrations also qualitatively supports the relative stability of the respective alkali perxenates.

Table III shows some data for the lithium hydroxide system. It is seen for expt. 15 and 16 with initial [LiOH] of 3.32 and 0.262 M, respectively, that there is again the reaction with XeO<sub>3</sub> and a lower oxidation state of xenon throughout the entirety of the experiments except for the last measurement of expt. 16.

No yellow color was observed at any time during the course of expt. 15 and 16, but in both cases a white gelatinous precipitate grew in from the homogeneous solutions after about 2 hr. So with no yellow complex which reduces the activity of the XeO<sub>3</sub>, a reaction between the XeO<sub>3</sub> and a lower oxidation state will become more probable than in the NaOH and KOH systems at comparable base concentrations. This reaction of XeO<sub>3</sub> and a lower oxidation state may be represented as



It seems unlikely that the Xe(II) undergoes reaction other than decomposition, since the O<sub>2</sub>/Xe collected values do exceed 0.5 significantly.

The only difference in the reaction of XeO<sub>3</sub> with KOH, NaOH, or LiOH solutions at comparable base concentrations seems to be the relative stability of the respective alkali perxenate solids and the mixed oxidation state complexes that decompose into perxenate and xenon plus oxygen in the ratio that corresponds to the direct decomposition of XeO<sub>3</sub>.

In the KOH system, the complex easily precipitates, and as long as the complex is present, no solid potassium perxenate was observed. From the viewpoint of relative solubility, it appears that there is a reversal from potassium to lithium for the complex and the solid perxenate; *i.e.*, the potassium complex is more insoluble than is the lithium complex, and the lithium perxenate is more insoluble than is the potassium perxenate

at the same initial concentrations. With the increased insolubility of lithium perxenate over that of the lithium complex, the best yield of perxenate from the three alkali bases that were studied is obtained from lithium hydroxide. Three experiments from the tables support this statement. From 3.6 *M* LiOH, 4.2 *M* NaOH, and 3.6 *M* KOH, the room temperature yields of perxenate are 41, 34, and 27%, respectively, based on the initial XeO<sub>3</sub>.

If the initial relative amount of LiOH to XeO<sub>3</sub> is sufficiently low, as is found in expt. 17, the stability of the alkali perxenate is not sufficiently great to suppress reactions 4 and 5; thus the O<sub>2</sub>/Xe collected values tend to be greater than unity. In expt. 17, the solution after mixing did have a yellow color. No yellow solid was observed and the yellow color in the solution faded as the reaction proceeded toward completion.

We have not yet been successful in recrystallizing the gelatinous lithium perxenate into crystals that would be suitable for a X-ray structure determination. We do have a rough estimate on the solubility and the solubility product from the data of expt. 16. By means of an iodometric titration, the solution over the solid perxenate at room temperature was  $1.88 \times 10^{-3}$  *M* in XeO<sub>6</sub><sup>-4</sup>; *i.e.*, it contained 0.89 μmole of XeO<sub>6</sub><sup>-4</sup>. Of the 12.89 μmoles of perxenate in the total, 12.00 made up the precipitate which would have removed 48.00 μmoles of Li<sup>+</sup> from the solution, and 76.6 μmoles would be left for a [Li<sup>+</sup>] of 0.16. For an upper limit, we estimate that

$$K_{sp} = [\text{Li}^+]^4[\text{XeO}_6^{-4}] = 1.3 \times 10^{-6} \text{ mole}^5 \text{ l.}^{-5} \quad (9)$$

If the stability of the solid metal perxenate is the controlling feature on the probability of other reactions

that can consume XeO<sub>3</sub> *via* direct decomposition or reaction with other xenon species, then a test will be the behavior of XeO<sub>3</sub> in alkaline earth hydroxide solution. The doubly charged cation would be expected to form more insoluble perxenates than the alkali cations, and consequently reaction 2 should be favored over the other XeO<sub>3</sub>-consuming reactions given in this paper. With reaction 2 predominating, reaction 3 should provide the stoichiometry of decomposition to the extent that reaction 2 proceeds.

Data on an experiment at 0° using XeO<sub>3</sub> and Ba(OH)<sub>2</sub> reported by Appelman and Malm<sup>3</sup> completely support the idea stated in the above paragraph. They found for an initial [Ba(OH)<sub>2</sub>] = 0.08 *M* and [XeO<sub>3</sub>] = 0.004 *M* that a nearly quantitative precipitation of the xenon occurs, but that 49.6% of the original xenon and 65.7% of the original oxidizing power was retained, and a residue of entirely Xe(VIII) remained. In addition to confirming their experiment, we have found for the calcium hydroxide system with XeO<sub>3</sub> at 0° that the alkaline earth perxenate is formed from the initial precipitate, and the O<sub>2</sub>/Xe values evolved at 19, 31, and 37% reaction were 0.99, 1.06, and 1.06, respectively; the initial [Ca(OH)<sub>2</sub>] = [XeO<sub>3</sub>] = 0.0181 *M*. The reaction was not followed to completion. In our experiments, this initial hydroxide ion concentration of 0.0362 *M* is the lowest at which we have observed the stability of the perxenate anion. The [OH<sup>-</sup>] of 0.16 *M* from the barium hydroxide experiment is certainly not a lower limit. We saw above for the NaOH system that 0.10 *M* was the lower limit, whereas 0.30 *M* was for the KOH system. Neither is the [OH<sup>-</sup>] of 0.108 *M* for the LiOH system a lower limit.