

where ϕI_a and $\phi'' I_a''$ are the rates of production of Co(II) from the direct irradiation of $\text{Co}(\text{NH}_3)_6^{+3}$ and $\text{Co}(\text{NH}_3)_6^{+3} \cdot \text{I}^-$, respectively. After making the necessary correction for absorption of radiation by the several species present, we estimate that $k_{10}/k_{11} = 5$ in both experiments. Considering the approximations and differences in conditions, we feel that this compares very well with the ratio calculated from the literature values of k_{10} and k_{11} (~ 4).³⁵

Conclusions

(1) The quantum yields for photoreduction of Co(III) complexes at 2537 Å. are high even for complexes that are relatively inert to visible light. The relative values of the quantum yields at 2537 Å. often show the

(35) NOTE ADDED IN PROOF. Since writing this paper we have more exhaustively investigated photolysis of I⁻-Co(III) systems. This recent work has qualitatively confirmed the most important features of the discussion presented here; however, the very approximate treatment of the data and the limited number of experiments cited in this paper led to inaccurate values of k_{10}/k_{11} . The more correct result seems to be $k_{10}/k_{11} \approx 1.8$ for both $\text{Co}(\text{NH}_3)_6^{+3}$ and $\text{Co}(\text{NH}_3)_5\text{OH}_2^{+3}$.

reverse order of that reported for longer wave length irradiation. For example, we find the quantum yields decrease in the series: $\text{Co}(\text{NH}_3)_6^{+3} > \text{Co}(\text{NH}_3)_5\text{OH}_2^{+3} > \text{Co}(\text{NH}_3)_5\text{Cl}^{+2}$.

(2) The over-all quantum yields for Co(II) production are, for many of the complexes, found to vary with the acidity of the solutions. The sensitivity to pH and the type of variation observed depends on the kind of ligands in the first coordination sphere of the Co(III) center. For flexible bidentate ligands (en and tn) there is a maximum quantum yield at $[\text{H}^+] = 0.2 M$.

(3) The observed pH effects are best understood if the photoreduction of Co(III) complexes proceeds through a metastable excited state (which may be chemically stabilized) of sufficiently long life so that it can participate in the simple protolysis of the ligands.

(4) The photoreduction of the ion pair $\text{Co}(\text{NH}_3)_5\text{OH}_2^{+3} \cdot \text{Cl}^-$ resembles more the photoreduction of $\text{Co}(\text{NH}_3)_5\text{OH}_2^{+3}$ than that of $\text{Co}(\text{NH}_3)_5\text{Cl}^{+2}$.

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Preparation and Properties of Monoalkali Xenates

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Monosodium, -potassium, -cesium, and -rubidium xenates have been prepared by lyophilization of 0.1 M xenon trioxide and alkali hydroxides in 1:1 ratio. The existence of alkali xenates has been confirmed by infrared spectroscopy, X-ray powder diffraction patterns, and the determination of the oxidation equivalent by the "hi-lo" titration method. Sodium xenate has an apparent formula weight of 247 ± 4 . Sodium xenate is more stable than xenon trioxide and less stable than sodium perxenate. At room temperature, sodium xenate does not react readily with anhydrous methyl alcohol. The salt of sodium xenate is stable under anhydrous conditions, otherwise it disproportionates to xenon(0) and xenon(VIII).

In a recent publication, Appelman and Malm¹ questioned the preparation of barium xenate as reported by Kirshenbaum and Grosse.² Appelman and Malm observed that freshly precipitated barium xenate is readily converted to barium perxenate and that the transitory compound, barium xenate, is unstable under the preparative conditions. It has been observed and confirmed by Koch and Williamson³ that xenon(VI)

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

(2) A. D. Kirshenbaum and A. V. Grosse, *Science*, **142**, 3592 (1963).

(3) C. W. Koch and S. M. Williamson, *J. Am. Chem. Soc.*, **86**, 5439 (1964).

disproportionates and that the rate increases with the concentration of hydroxyl ion. In addition, it has been suggested by Appelman and Malm¹ that species such as HXeO_4^- and H_5XeO_6^- are possibilities at the first equivalence point when xenon trioxide is titrated with sodium hydroxide.

In the hope of shedding some light on the nature of the xenate ion, a project to prepare the mono- and dialkali xenate salts has been initiated.

Experimental

Chemicals and Apparatus. Solutions of xenon trioxide were obtained from the Argonne National Laboratory. Approximately 0.1 M xenon trioxide solutions were employed for the preparation of alkali salts. Sodium and potassium hydroxide solutions were prepared by routine methods. Rubidium and cesium hydroxides were prepared by the reaction of high purity chlorides (99.9%), supplied by Fisher Scientific Co., with freshly precipitated silver oxide. All preparations of xenate salts were done on a vacuum line. The normal operating pressure was about 10^{-5} mm.

Infrared spectra of these salts as well as of xenon trioxide, perxenates, and related iodine and tellurium compounds were run in a silver chloride matrix using the Perkin-Elmer 21 and KBr Infracord recording

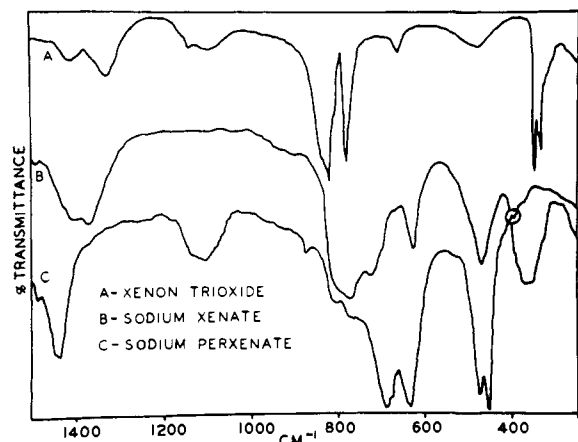


Figure 1. Infrared spectra of sodium xenate and perxenate and xenon trioxide in silver chloride matrix.

spectrophotometers. The 200–400-cm.⁻¹ region was scanned occasionally on a Perkin-Elmer 521 spectrophotometer. Pellets were pressed from powdered silver chloride according to a technique recently published.⁴ The spectrum of xenon trioxide was obtained by two methods: (1) either aqueous xenon trioxide was lyophilized and carefully mixed with powdered silver chloride or (2) powdered silver chloride was mixed with aqueous xenon trioxide solution before lyophilization.

X-Ray powder diffraction patterns of the alkali xenate salts were obtained on a Norelco instrument using a 114-mm. camera and the copper K α line with a nickel filter.

Preparation of Alkali Xenates. The monoalkali salts of xenon(VI) were prepared by lyophilization of solutions containing stoichiometric amounts of xenon trioxide and alkali hydroxide. In a typical preparation, 100 μ l. of 0.1 M xenon trioxide was mixed with 100 μ l. of 0.1 M sodium hydroxide in a small glass vial. The vial was placed in a tube fitted with a ground joint. A matching joint was attached to the vacuum manifold. The solution was frozen with liquid nitrogen before opening the vacuum chamber to the manifold. After 3 hr. lyophilization was complete as evidenced by the lack of further condensation of water in the liquid nitrogen cold trap. The sample thus prepared is in the form of a fluffy white powder.

Attempts were made to prepare xenate salts by slow dehydration over 95% sulfuric acid, but the analyses showed substantial sample decomposition and partial conversion to perxenate. At room temperature, xenon trioxide and sodium hydroxide solutions in a 1:1 ratio lost titer value at approximately 10%/hr. Following lyophilization of our samples, we had a loss of titer which ranged between 1 and 5%. Lyophilized samples can be kept under anhydrous conditions without decomposition. When the samples were hydrated, they decomposed slowly. Several attempts were made to vary the proportions of xenon to sodium. However, in no instance could a stable salt of xenon(VI) be prepared when the xenon-to-sodium ratio was significantly different from 1:1. Samples with as much as 20% excess of either component still showed infrared

spectral characteristics of the 1:1 salt. If the sodium-to-xenon ratio was 2:1, these spectral characteristics were entirely absent.

Potassium, cesium, and rubidium xenates can be prepared in a manner similar to sodium xenate. Sodium and potassium xenates yield white powders. Cesium and rubidium xenate salts are sometimes slightly yellow. Lithium xenate has not been prepared to date. All attempts have led to an unstable white powder containing only xenon(VI) but lacking any definite infrared pattern.

The amounts of xenon(VI) and xenon(VIII) in samples as well as in the standard xenon trioxide solution were established by the "hi-lo" titration method as described by Appelman and Malm.¹ For a typical analysis, three identical samples were prepared simultaneously. One sample was used for the infrared and the remaining two samples for "hi-lo" titration. The oxidation equivalent and the apparent formula weight of the sodium xenate were determined by "hi-lo" titration of weighed samples. The samples which showed no excess of xenon trioxide or perxenate were used for calculations.

Results

Infrared Data. Infrared spectra of the alkali xenate salts were obtained under a wide range of conditions. These include incorporation in silver chloride and potassium bromide matrices, mulls in Nujol and perfluorohydrocarbon, water slurry, and deposition on silver chloride windows. In all cases, a characteristic pattern was evident. The infrared spectrum of sodium xenate in silver chloride matrix is shown in Figure 1. Besides weak bands at 3500 and 1600 cm.⁻¹, the spectrum shows the following bands (cm.⁻¹): 1360 (medium), 770–800 (strong and broad with a shoulder at 730 cm.⁻¹), 625 and 469 (strong and sharp), and 340–370 (medium broad). In many spectra, the 770–800 cm.⁻¹ band was resolved into two bands, 770–780 and 800–810 cm.⁻¹. The sodium xenate spectrum differs considerably from those of sodium perxenate and xenon trioxide as shown in Figure 1. The xenon trioxide spectrum is the same whether prepared by mixing dry xenon trioxide powder with silver chloride or by lyophilizing the aqueous xenon trioxide with silver chloride. Xenon trioxide slowly attacks silver chloride and the intensity of 780–820-cm.⁻¹ bands is reduced in time; also, the pellets show blistering. This blistering effect has also been noted with sodium xenate preparations containing an excess of xenon trioxide. Pellets containing a 1:1 ratio of sodium to xenon show no noticeable blistering or alteration of spectra even after several months of storage.

The characteristic spectrum of sodium xenate is almost the same for the salts of potassium, cesium, and rubidium, as shown in Figure 2. The characteristic sharp band at 625-cm.⁻¹ of sodium xenate is absent in the other alkali xenates.

X-Ray Powder Diffraction. The X-ray powder diffraction patterns of sodium xenate have been compared with those of sodium carbonate, sodium bicarbonate, sodium perxenate, and xenon trioxide. The principal *d*-spacings of these samples are listed in Table I. Some sodium carbonate contamination is apparent not only

(4) T. M. Spittler and B. Jaselskis, *Appl. Spectry.*, in press.

Table I. Principal *d*-Spacings of Sodium Xenate Compared with Other Possible Reaction Products Resulting from Mixture of Xenic Acid and Sodium Hydroxide Solutions

Sodium xenate		Sodium perxenate ^a		Xenon trioxide ^b	NaHCO ₃ ^c		Na ₂ CO ₃ ^c	
<i>d</i> , Å.	R.I. ^d	<i>d</i> , Å.	R.I.	<i>d</i> , Å.	<i>d</i> , Å.	R.I., %	<i>d</i> , Å.	R.I., %
10.3	A	5.07	A	4.91	5.9	5	3.43	8
5.65		4.01	B	4.40	4.83	5	3.22	12
4.81		3.86	F	4.06	3.49	14	2.96	80
3.99	E	3.16	C	3.99	3.27	8	2.70	20
3.64	D	3.13	G	3.58	3.08	24	2.60	60
3.49	G	2.97		3.39	2.94	100	2.54	60
3.22	B	2.70	D	3.21	2.68	10	2.36	100
2.96	C	2.58		3.08	2.61	48	2.25	40
2.72		2.38		2.88	2.31	20	2.18	60
1.98	F	2.18	E	2.84	2.21	32	2.02	14
1.86		1.73		2.75	1.97	14	1.95	40
1.75				2.39	1.87	2	1.88	40
1.68				2.20	1.74	11	1.71	25
1.62				2.07	1.69	8	1.67	12
					1.62	5	1.62	12 B

^a Sample supplied by Argonne National Laboratory. ^b Values calculated from published data: D. H. Templeton, A. Zalkin, J. D. Forrester, and S. M. Williamson, "Noble Gas Compounds," H. H. Hyman, Ed., University of Chicago Press, Chicago, Ill., 1963, p. 229. No intensity values available. ^c Selected relevant data from Hanawalt Powder File cards. ^d R.I. denotes relative intensity. Relative intensities visually estimated by authors ranging from A (strongest) to F (weakest).

by the infrared spectra, but also by the characteristic sodium carbonate *d*-spacings. The X-ray powder diffraction pattern of sodium xenate differs considerably from sodium perxenate and the likely contaminants. In particular, the strongest line, *d* = 10.3 Å., appears to be characteristic of sodium xenate and is absent in the other compounds used for the comparison. X-Ray patterns of cesium and rubidium xenates are also different from those in Table I and do not show a 10.3-Å. line.

Stability and Properties. When stored under vacuum, the sodium xenate salt proved to be stable up to several weeks. Open to the atmosphere and moisture, the sample lost much of its xenon(VI) strength in the course of a few days. Samples open to the atmosphere also seem to absorb carbon dioxide with consequent development of characteristic infrared absorption bands of sodium carbonate at 695, 878, and 1440 cm.⁻¹.

Preliminary tests of thermal stability indicate that samples containing sodium and xenon(VI) in an exact 1:1 ratio are stable above 160°. When an excess of xenon trioxide is present, samples explode around 100°. When excess of sodium hydroxide is present, the explosion temperature is about 140°. In many instances, samples (with an excess of xenon trioxide) show instability to mechanical shock. Occasionally the shock of inrushing air upon fracture of evacuated ampoules will detonate the samples. Care must always be exercised in admitting air to samples under vacuum. There is a rough correlation between the state of dehydration and the shock sensitivity. When samples are lyophilized for a very long time, the shock and thermal instability increases notably.

Sodium xenate is soluble in water and immediately begins to decompose upon rehydration. Effervescence is frequently observable and definite amounts of xenon and oxygen can be detected if this is done in a vacuum system. The sodium salt shows no solubility in dry methanol, ethanol, *t*-butyl alcohol, chloroform, and carbon tetrachloride. Tests made by "hi-lo" titration indicate that no notable reaction occurs with these sol-

vents in a short period of time. Sodium xenate decomposes slowly in warm methanol and in a 10% solution of methanol in *t*-butyl alcohol. When an excess of xenon trioxide is present, the decomposition is explosive. This can serve as a test for an excess of xenon trioxide. Xenon trioxide dissolves readily in *t*-butyl alcohol with no observable reaction. When an excess of

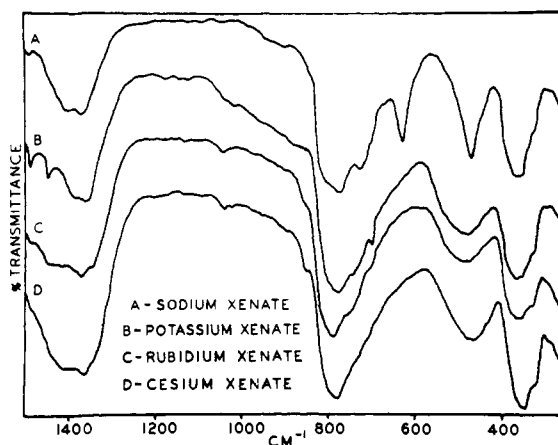


Figure 2. Infrared spectra of monoalkali xenates in silver chloride matrix.

xenon trioxide is used to prepare sodium xenate (3–5%), this excess can be almost quantitatively destroyed by washing the salt several times with a 1% solution of methanol in *t*-butyl alcohol. A similar but much slower reaction is found with ethanol solution. This agrees well with the observations reported by Jaselskis and Vas.⁵

Formula Determination. Five determinations by the "hi-lo" titration method on samples which had been lyophilized for 2 to 3 hr. yielded an average oxidation equivalent of 41.3 ± 0.7. This corresponds to an apparent formula weight of 247 ± 4 (NaHXeO₄ · 1.5H₂O)

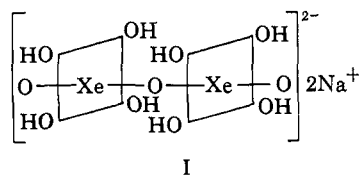
(5) B. Jaselskis and S. Vas, *J. Am. Chem. Soc.*, **86**, 2078 (1964).

or to a dimeric species, 494 ± 8 ($\text{Na}_2\text{H}_8\text{Xe}_2\text{O}_{11}$). Samples which had been lyophilized for a long period of time yielded formula weight values slightly lower than the above. This suggests the possibility of further dehydration.

Discussion

A series of relatively stable monoalkali salts of xenon(VI) have been prepared and have been examined by infrared spectroscopy, X-ray powder diffraction, and by the "hi-lo" titration method. The infrared data do not give definite grounds for drawing parallels between these salts and the various para- and metaperiodates, iodates, and tellurates. The presence of hydroxyl groups in the sodium xenate salt is indicated by absorption bands at 3500 and 1630 cm^{-1} . Although the sodium xenate is insoluble in *t*-butyl alcohol, it cannot be prepared by mixing equivalent amounts of xenon trioxide in *t*-butyl alcohol with sodium *t*-butoxide unless some water is added. This fact suggests that the neutralization reaction proceeds through a hydrated species.

The presence of a strong *d*-spacing of 10.3 Å., the absence of direct infrared parallels between periodates and orthotellurates, and the apparent formula weight determinations suggest that sodium xenate under our preparative conditions has a possible dimeric structure (I). A *d*-spacing of 10.3 Å. may result from adding four xenon-to-oxygen bonds of about 1.87 Å. each⁶ and two sodium-to-oxygen distances. The cesium and rubidium



xenates have no *d*-spacing of 10.3 Å. and no infrared band at 625 cm^{-1} . A structural difference between sodium xenate and the heavier alkali xenates is indicated.

The possibility that sodium xenate exists as the tetra-coordinated, NaHXeO_4 , rather than the hexacoordinated species has been considered. To obtain the oxidation equivalent weight of 41.3 as suggested for the dimeric species, $\text{Na}_2\text{H}_8\text{Xe}_2\text{O}_{11}$, it would be necessary to have approximately 12.5% of sodium hydroxide or sodium carbonate impurity in the NaHXeO_4 . This is impossible considering stoichiometric conditions imposed and has not been confirmed by infrared or X-ray powder diffraction patterns.

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(6) W. C. Hamilton, J. A. Ibers, and D. R. Mackenzie, *Science*, 141, 532 (1963).