[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF MICHIGAN]

O^{18} Study of the Reaction of Hydroxide with Mercury(II) Nitrate. Characterization of Basic Nitrates of Mercury(II)

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O^{18}-Tracer experiments have been carried out to investigate the source of the oxygen in HgO precipitated by the reaction of hydroxide ion with mercury(II) nitrate. In addition, an O^{16}/O^{18} isotope effect in the reaction was observed; O^{16} concentrates in the precipitated oxide. Three crystalline basic nitrates of Hg(II) were prepared and characterized by X-ray diffraction and infrared techniques. To elucidate the ionic species in mercury(II) nitrate solutions, Raman spectra were obtained. A band at 354 cm.$^{-1}$ was observed which disappeared upon adding nitric acid, suggesting the possibility of Hg–O linkages. The results of the present investigation indicate a mechanism whereby the reaction of mercury(II) nitrate with hydroxide ion proceeds *via* the formation of the basic nitrate $Hg_3O_2(NO_3)_2\cdot H_2O$, which upon hydrolysis yields HgO. The oxygen in the HgO is derived from the water which effects the hydrolysis.

Introduction

The behavior of concentrated mercury(II) solutions was known to be complex as early as 1839 when Kane[1] reported four basic nitrates of mercury(II), several of which were confirmed by Millon.[2]

Cox[3] made a systematic investigation of the phase equilibria involving solutions of mercury(II) nitrates and HgO. He studied the three component system HgO, N_2O_5, H_2O; when any two solid phases coexisted at a given temperature the composition of the solution was invariant. From his phase diagram (25°) the lower invariant concentration is 0.159 *N* in NO_3^-, corresponding to the equilibrium between HgO, solution and the basic salt designated "$3HgO\cdot N_2O_5$." Dilution results in complete conversion of basic salt to oxide; at higher concentrations of nitrate all oxide is converted to basic salt until the solution reaches the upper invariant composition (18.7 *N*), when the equilibrium between $Hg(NO_3)_2\cdot H_2O$ and basic salt is established; above this concentration the solid phase is solely $Hg(NO_3)_2\cdot H_2O$. No evidence on the existence of other basic nitrates was presented, and no reference was made to Millon's[2] work in which the compound "$2HgO\cdot N_2O_5\cdot H_2O$" was obtained by treatment of HgO with sirupy $Hg(NO_3)_2$. Hayek,[4] working in concentrated (2–4 *N*) mercury(II) perchlorate solutions suggested the existence of polynuclear cations, $Hg(HgO)_n{}^{++}$, because of the solubility of HgO in these solutions and because of the formation of the basic salt $Hg(HgO)_2(ClO_4)_2$.

The hydrolysis of mercury(II) ion in dilute solution (*ca.* 10^{-2} *N*) has been studied by Hietanen and Sillén,[5] who concluded that the main cationic species is the (hydrated) mercuric ion, with only a small equilibrium amount of the $HgOH^+$ ion present under any conditions. They found no evidence for polynuclear species.

Precise measurements of the solubility of HgO in water, in alkali and in HNO_3 were carried out by Garrett, *et al.*[6a,b] They found that the solubility was a minimum in pure water, increased linearly with alkali concentration (as expected from the equilibrium: $HgO + OH^- = H\,HgO_2^-$) and with added salts, *e.g.*, $NaNO_3$ (suggesting the equilibrium: $HgO + H_2O + NO_3^- = Hg(OH)_2NO_3^-$). They mention the "notoriously unpredictable characteristics of mercury compounds," which are manifested by the many different ionic equilibria known to occur in solutions of mercury(II).

The present study was an outgrowth of a preliminary O^{18} tracer investigation[7] which was intended to ascertain the source of the oxygen in precipitated HgO. In addition to tracer experiments, the O^{16}/O^{18} isotope effect in the reaction of OH^- with Hg(II) ion has been studied over a range of conditions. In an attempt at elucidating the nature of the ionic species present, Raman spectra of solutions of mercury(II) nitrate were obtained. Four crystalline mercury(II) nitrates were prepared, analyzed and characterized by means of X-ray diffraction and infrared techniques. Results of the present study have led to a reasonable understanding of the reaction of hydroxide ion with mercury(II) nitrate.

Results of Oxygen-18 Experiments

I. Exchange between HgO and H_2O.—In order to obtain meaningful results using O^{18} as a tracer it is necessary to determine the extent of exchange between HgO and H_2O. This exchange was found to be negligible at room temperature. Experiments consisted of (1) grinding small samples of HgO* under distilled water, followed by copious washing on the filter funnel, and (2) grinding small samples of HgO under H_2O^* (1.4% O^{18}), allowing them to stand, and filtering. Results are

System	Time, hr.	[a]$100 \times N^*_{HgO}$ Init.	Final
$HgO^* + H_2O$	0.5	0.353	0.341
	.5	0.453	0.443
	.5	1.430	1.425
$HgO + H_2O^*$	.8	0.204	0.207
	24	0.199	0.199

[a] $N^*_{HgO} = O^{18}$ atom fraction in HgO.

The negligible exchange is reasonable in view of the low solubility of HgO (2.4×10^{-4} mole/l. at 25°[6a]) and the very low degree of dissociation of $Hg(OH)_2$ in water (0.002% at 25°[6a]); it is known that dissolved HgO does not measurably increase the conductivity of water.[8]

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[1] M. R. Kane, *Ann. chim. phys.*, **72**, 236 (1839).

[2] M. E. Millon, *Ann. Chim.*, **3**, 333 (1846).

[3] A. J. Cox, *Z. anorg. Chem.*, **40**, 146 (1904).

[4] E. Hayek, *Z. anorg. allgem. Chem.*, **223**, 382 (1935).

[5] S. Hietanen and L. G. Sillén, *Acta Chem. Scand.*, **6**, 747 (1952).

[6] (a) A. B. Garrett and A. E. Hirschler, THIS JOURNAL, **60**, 299 (1938); (b) A. B. Garrett and W. W. Howell, *ibid.*, **61**, 1730 (1939).

[7] R. B. Bernstein and H. G. Pars, *ibid.*, **77**, 4433 (1955).

[8] G. A. Hulett, *Z. physik. Chem.*, **37**, 385 (1901).

In the course of the present investigation a large number of samples of HgO (prepared in different ways, washed and rewashed) were analyzed and found to differ significantly in O^{18}-content from that of the distilled water, confirming that no appreciable exchange occurred between HgO and water.

II. O^{16}/O^{18} Isotope Effect in the Reaction of OH^- with Hg(II).—The O^{16}/O^{18} isotope effect was studied using compounds containing natural O^{18}-abundance. The solution of one component (A) was delivered from a pipet into a beaker containing the solution of the other (B) at room temperature. The precipitate was collected on a sintered glass funnel, washed with distilled water and dried at 110° before O^{18}-assay. It was found that under all conditions O^{16} concentrated preferentially in the HgO.

Table I summarizes the data, given in terms of the observed % O^{16} enrichment of the HgO relative to the standard tank oxygen, defined $E = 100 \times [(O^{18}/O^{16})_{std}/(O^{18}/O^{16})_{HgO} - 1]$, and the calculated O^{16}/O^{18} fractionation factor relative to the water, $\alpha = (O^{18}/O^{16})_{H_2O}/(O^{18}/O^{16})_{HgO}$, (based on the 2.9%[9] O^{18}-enrichment of the standard tank oxygen relative to the distilled water; see Experimental section). It is noted that the conditions of precipitation did not significantly affect the results.

TABLE I

O^{16}/O^{18} ISOTOPE EFFECT

A	B	$[A]_0$ (moles/l.)	$[B]_0$ (moles/l.)	V_A (ml.)	V_B (ml.)	E	α
$Hg(NO_3)_2$	NaOH	1.8	1.0	5.0	100	4.3	1.014
$Hg(NO_3)_2$	NaOH	1.8	5.0	5.0	50^a	4.3	1.014
$Hg(NO_3)_2$	KOH	0.5	1.0	1.0	10^b	4.3	1.014
NaOH	$Hg(NO_3)_2$	1.0	1.8	5.0	50^a	4.1	1.012
NaOH	$Hg(NO_3)_2$	5.0	1.8	5.0	50^a	4.3	1.014
NaOH	$Hg(NO_3)_2$	1.1	0.9	2.0	10	4.3	1.014
NaOH	$Hg(NO_3)_2$	0.9	.9	1.0	10	4.0	1.011
NaOH	$Hg(NO_3)_2$	1.1	.9	1.0	10^c	3.6	1.007
NaOH	$Hg(NO_3)_2$	1.1	.9	1.0	10^c	3.3	1.004
NaOH	$Hg(ClO_4)_2$	1.1	.9	1.0	4.0	4.0	1.011
NaOH	$Hg(C_2H_3O_2)_2$	1.1	.5	1.0	4.0^a	3.9	1.010

[a] No stirring during precipitation; others stirred. [b] Reagents added simultaneously to boiling H_2O to form red HgO[6a]; all others gave yellow HgO. [c] Incomplete washing.

III. O^{18}—Tracer Experiments.—As a control tracer experiment, anhydrous $Hg(NO_3)_2$ (dried at 90° to constant weight) was dissolved in H_2O^* ($N^* = 0.0143$), the solution filtered and added to excess NaO^*H ($N^* = 0.0140$). The HgO^* was washed with distilled water, dried and analyzed. The result was $N^* = 0.0142$, essentially pure tracer with no contribution due to NO_3^- ion or wash water.

A series of experiments was carried out in which solutions of NaO^*H were added to (excess) $Hg(NO_3)_2$ solutions prepared with distilled water ($N^* = 0.00200$), the precipitates washed and treated as above. The HgO was the same or *depleted* in O^{18} relative to the distilled water, even though $O^{18}H^-$ was used as precipitant. The data (Table II) indicate an O^{16}/O^{18} effect similar to that described in section II, but of lesser magnitude.

Another series of experiments (Table III) was carried out in which $Hg(NO_3)_2$ solutions in H_2O^* ($N^* = 0.0143$ and 0.0081) were added to (excess) NaOH solutions (natural O^{18}-abundance, $N^* = 0.00200$); the precipitates were treated in the usual way. In another series $Hg(NO_3)_2$ solutions in normal H_2O ($N^* = 0.00200$) were added to (excess) NaO^*H solutions ($N^* = 0.0140$).

TABLE II

O^{18} TRACER EXPERIMENTS

(O^*H^- into excess Hg (II))

$[O^*H^-]_0$ (moles/l.)	$[Hg(NO_3)_2]_0$ (moles/l.)	V_{OH^-} (ml.)	$V_{Hg\ (II)}$ (ml.)	E	α
1.0	0.8	1.0	100^a	3.3	1.004
1.0	0.8	1.0	50	3.3	1.004
1.0	2.3	1.0	100^a	2.5	0.996
1.0	0.4	1.0	5.0^a	2.9	1.000
1.1	0.9	1.0	10	2.9	1.000
1.1	0.9	1.0	10	3.2	1.003

[a] No stirring during precipitation; others stirred.

TABLE III

O^{18} TRACER EXPERIMENTS (EXCESS ALKALI)

A	B	$[A]_0$ (moles/l.)	$[B]_0$ (moles/l.)	V_A (ml.)	$V_B{}^a$ (ml.)	100 × N^*_{HgO}
$Hg(NO_3)_2$ in H_2O	NaO^*H	0.4	1.1	1.0	2.3	0.907
$Hg(NO_3)_2$ in H_2O^*	NaOH	1.4	1.1	1.0	2.0	.560
$Hg(NO_3)_2$ in H_2O^*	NaOH	1.0	1.1	1.0	5.0	.480
$Hg(NO_3)_2$ in H_2O^*	NaOH	1.0	1.1	1.0	5.0	.475
$Hg(NO_3)_2$ in H_2O^{*b}	NaO^*H	1.2	1.1	0.5	2.0	1.32
$Hg(NO_3)_2$ in H_2O^{*b}	NaOH	1.2	1.1	0.5	2.0	0.317
$Hg(NO_3)_2$ in H_2O^{*b}	NaOH	1.2	1.1	1.0	5.0	0.315

[a] No stirring throughout entire series. [b] $100N^* = 0.81$ instead of the usual 1.43.

Tracer experiments on the hydrolysis of certain basic nitrates to the oxide were carried out as follows: (1) *ca.* 150 mg. of the salt was hydrolyzed by H_2O^*($N^* = 0.0143$) by heating briefly, or allowing to stand 12–24 hours at room temperature; (2) O^{18}-labeled basic nitrate (prepared by dissolving $Hg(NO_3)_2$ in H_2O^* and washing the precipitate with cold H_2O or adding O^*H^- to $Hg(NO_3)_2$ in H_2O^* and washing as above) was hydrolyzed with H_2O of natural O^{18} abundance. The results are shown in Table IV.

TABLE IV

TRACER EXPERIMENTS ON HYDROLYSIS OF BASIC NITRATES

Basic nitrate	Hydrolysis conditions	100 × N^*_{HgO}
$Hg_3O_2(NO_3)_2 \cdot H_2O$	5.0 ml. H_2O^*; room temp. 1 day	1.38
$Hg_3O_2(NO_3)_2 \cdot H_2O$	4.0 ml. H_2O^*; room temp. 1 day	1.35
$Hg_3O_2(NO_3)_2 \cdot H_2O$	5.0 ml. H_2O^*; wash in filter funnel[a]; rewash with 1.0 ml. H_2O^*	$(0.68)^a$ 1.24
$Hg_3O_2(NO_3)_2$	5.0 ml. H_2O^*; room temp. 1 day, then heat	1.34
$Hg_3O_2(NO_3)_2$	2.0 ml. H_2O^*; room temp. 1 day, then heat	1.03^b
$HgOHNO_3$	5.0 ml. H_2O^*; room temp. 2 days	1.27
$HgOHNO_3$	5.0 ml. H_2O; room temp. 1 day	0.196
$Hg_3O_2^*(NO_3)_2$	5.0 ml. H_2O; heat	0.198
$Hg_3O_2^*(NO_3)_2$	5.0 ml. H_2O; heat	0.198

[a] Initial value; sample incompletely hydrolyzed. [b] Sample incompletely hydrolyzed.

Discussion of Oxygen-18 Experiments

In a previous communication[7] the results of Table II (O^*H^- added to excess Hg(II); the O^{18}-content of the HgO essentially that of normal water) were interpreted in terms of a mechanism involving proton transfer from the hydrated mercury(II) cation to OH^-. The oxygen in the HgO was presumed to be derived exclusively from the original aquo-cation regardless of the isotopic composition of the added hydroxide solution. It was further suggested that the O^{16}/O^{18} isotope effect (Table I) was associated with preferential rupture of the O^{16}–H bond relative to O^{18}–H in the aquo-ion.

The above interpretation has proved to be incorrect when subjected to further experimental tests, *i.e.*, the tracer experiments summarized in Table III, where $Hg(NO_3)_2$ solutions were added to excess alkali. In all cases where the precipitate

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(9) The preliminary values of α (ref. 7) were high by 0.6% due to the use of an erroneous value (2.3%) for this difference.

was formed under alkaline conditions, the isotopic composition of the HgO was intermediate between that of the two reagent solutions. In an attempt to reconcile the apparent discrepancy between the two sets of O^{18}-tracer experiments (Tables II and III) it was necessary to make a detailed study of the nature of the precipitate obtained under the prevailing conditions.

In the present work it was found that with excess hydroxide ion the precipitate was indeed pure HgO, whereas excess $Hg(NO_3)_2$ solution resulted in the formation of a basic nitrate, $Hg_3O_2(NO_3)_2 \cdot H_2O$ (yield 95–100%). The preparation and characterization of this compound (and other basic nitrates) may be found in the Experimental section. This basic nitrate is readily hydrolyzed by water to give pure HgO. Tracer experiments on the hydrolysis of the basic nitrates (Table IV) showed that the oxygen in the resulting HgO was substantially[10] derived from the water used in the hydrolysis.

All the results thus far obtained may be explained satisfactorily by the following mechanism: the initial step in the reaction of mercury(II) nitrate with hydroxide ion is the formation of the basic nitrate $Hg_3O_2(NO_3)_2 \cdot H_2O$. In the presence of excess $Hg(NO_3)_2$, this compound may be isolated and subsequently hydrolyzed to the oxide; whereas in the presence of excess hydroxide the basic nitrate has only a transitory existence, being hydrolyzed immediately as it is formed to give the oxide. In both cases the oxygen of the HgO is derived from the water which effects the hydrolysis.

Applying this interpretation to the experiments in which O^*H^- was added to excess Hg(II) (Table II) the orginal precipitate was the basic nitrate (possibly enriched in O^{18}) which upon hydrolysis by the (normal) wash water gave HgO whose isotopic composition was that of the water, modified by the usual fractionation effect. For the experiments carried out in alkaline medium (Table III), the transitory basic nitrate is hydrolyzed in the existing medium of intermediate isotopic composition giving O^{18}-enriched HgO, which is unaffected by subsequent washing.

It is also noted that the HgO obtained from the hydrolysis of $Hg_3O_2^*(NO_3)_2$ with normal H_2O (Table IV) was actually depleted in O^{18} by a fractionation factor comparable to that observed for the case of O^*H^- added to excess Hg(II) (Table II). This shows that the O^{16}/O^{18} isotope effect is associated with the hydrolysis of the basic nitrate rather than with its formation.

Experimental

I. Analytical Procedures.—Mercury analyses were carried out using the standard thiocyanate titration procedure in 6 *N* HNO_3 solution with ferric alum indicator. Nitrate determinations were according to Leithe[11]; the sample is treated with excess $FeSO_4$ in concentrated H_2SO_4 solution, and back-titrated with standard $K_2Cr_2O_7$ using ferroin indicator.

Sevenfold O^{18}-enriched water (Stuart Oxygen Co.), designated H_2O^*, was the source of tracer O^{18}. NaO^*H was prepared by addition of sodium to H_2O^*.

O^{18}/O^{16} ratios were determined with an isotope-ratio mass spectrometer (Nier design); the 34/32 ratio for the unknown oxygen was compared with that of standard tank oxygen. The O^{18}/O^{16} ratio for the distilled water was compared with the ratio for a standard sample of water (prepared by the complete reaction of the standard oxygen with dry oxygen-free hydrogen over hot copper) by the conventional CO_2 equilibration technique.[12] It was found to be 2.9 ± 0.2% depleted in O^{18} (the "Dole effect"). All isotope abundances have been normalized so that the distilled water corresponds to 0.200% O^{18} (the O^{18} atom fraction, $N^* = 0.00200$).

The O^{18}-enriched water was analyzed (by CO_2 equilibration) to be 1.43 ± 0.01% O^{18}. The NaO^*H solution was analyzed (1) by distilling (*in vacuo*) a small sample to dryness, followed by equilibration of the water with CO_2 and (2) by electrolysis of a small sample and comparison of the O_2 evolved with the standard oxygen. The results were $N^* =$ 0.0140 and 0.0136, respectively.

The O^{18}-content of various preparations of HgO was determined by pyrolyzing small samples (50–75 mg.) quantitatively *in vacuo* and comparing the liberated oxygen with the standard oxygen. When intercomparing samples differing by <10% in the O^{18}/O^{16} ratio the probable error in the ratio of O^{18}/O^{16} ratios is less than ±0.1%.

II. Preparation of Mercury(II) Nitrates. (1) $Hg(NO_3)_2 \cdot H_2O$.—The starting material was B. & A. reagent grade. The hygroscopic nature of this compound presented some difficulties. The Karl Fischer method for assay of its water content failed due to interference from Hg(II). In order to prepare and store the pure monohydrate it was desirable to ascertain the equilibrium water vapor pressure for the system $Hg(NO_3)_2$–$Hg(NO_3)_2 \cdot H_2O$ so that an atmosphere of the proper relative humidity could be selected. A series of experiments was carried out with weighed samples of $Hg(NO_3)_2 \cdot H_2O$ using desiccators containing H_2SO_4 solutions of known vapor pressure. At values of the relative humidity below 22.2% ($p_{H_2O} = 5.28$ mm. at 25°) the sample lost weight; above 27.2% (6.47 mm.) it gained weight. Thus it is estimated that the equilibrium vapor pressure for the anhydrous–monohydrate system is about 5.3 mm. and that the monohydrate has a very short pressure range of existence.

Anal. Calcd. for $Hg(NO_3)_2 \cdot H_2O$: Hg, 58.6; NO_3, 36.2. Found: Hg, 59.0, 58.8; NO_3, 35.9, 35.7, 35.6.

(2) $HgOHNO_3$.—Mercury (*ca.* 25 g.) was dissolved in 16 *N* HNO_3 (*ca.* 25 ml.) and evaporated slowly. Large colorless crystals of $HgOHNO_3$ separated out; they were removed, washed with absolute ethanol and air-dried.

Anal. Calcd. for $HgOHNO_3$: Hg, 71.7. Found: Hg, 71.9, 71.8.

The compound did not appear to be hygroscopic, nor did it dissolve appreciably in or react with water at room temperature. After prolonged boiling it was hydrolyzed, yielding red HgO.

(3) $Hg_3O_2(NO_3)_2 \cdot H_2O$.—Approximately 85 g. of $Hg(NO_3)_2 \cdot H_2O$ was added to 500 ml. of H_2O; the finely divided white precipitate was filtered, washed with cold dilute (*ca.* 0.1 *N*) acetic acid and air-dried at room temperature.

Anal. Calcd. for $Hg_3O_2(NO_3)_2 \cdot H_2O$: Hg, 77.6; NO_3, 16.0; H_2O, 2.3. Found: Hg, 77.4, 77.5; NO_3, 16.8, 16.7, 16.6; H_2O, 3.0 (by weight loss at 110°).

The compound is readily hydrolyzed; it may be quantitatively converted to yellow HgO by washing with water at room temperature. Single crystals of this basic nitrate were obtained by carefully adding 1 ml. of H_2O to 1 ml. of 1 *M* $Hg(NO_3)_2$ solution and allowing the two layers to interdiffuse. Crystals formed initially at the interface and after several days of growth were removed and washed with absolute ethanol. They were unaffected by prolonged exposure to the laboratory atmosphere.

This basic nitrate was also prepared in stoichiometric yield by the addition of 1 *N* NaOH to excess 5 *M* $Hg(NO_3)_2$ solution; the precipitate was then washed with cold ethanol. It was prepared (in less pure form) by the action of 5 *M* $Hg(NO_3)_2$ solution upon finely divided yellow HgO.

X-Ray powder patterns were used to compare different preparations made under widely varying conditions. Except for occasional evidence of traces of $Hg(NO_3)_2 \cdot H_2O$ (remaining from incomplete washing), or traces of HgO from hydrolysis, all preparations gave identical X-ray patterns.

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[10] For the cases where H_2O^* was used to hydrolyze the basic nitrates the percentage of O^{18} in the HgO is somewhat lower than the expected 1.4%; this probably is due to incomplete hydrolysis.

[11] W. Leithe, *Anal. Chem.*, **20**, 1082 (1948).

[12] M. Cohn and H. C. Urey, THIS JOURNAL, **60**, 679 (1938).

(4) $Hg_3O_2(NO_3)_2$.—This white, finely divided anhydrous salt is obtained readily by heating $Hg_3O_2(NO_3)_2 \cdot H_2O$ for *ca.* 1 hr. at 90–100° or by dehydrating a sample of $Hg_3O_2(NO_3)_2 \cdot H_2O$ at room temperature in a $CaCl_2$ desiccator.

Anal. Calcd for $Hg_3O_2(NO_3)_2$: Hg, 79.4; NO_3, 16.4. Found: Hg, 79.2, 79.4; NO_3, 17.0, 17.2.

The compound is hydrolyzed to the yellow HgO upon extended washing with water at room temperature. It is not especially hygroscopic. The equilibrium vapor pressure for the $Hg_3O_2(NO_3)_2$–$Hg_3O_2(NO_3)_2 \cdot H_2O$ system was estimated from a series of experiments similar to those described for $Hg(NO_3)_2$. At values of the relative humidity above 75% (p_{H_2O} = 17.8 mm. at 25°) the anhydrous compound gained weight. Thus the equilibrium vapor is *ca.* 17 mm. at 25°. Below this humidity the anhydrous salt is stable. In one experiment the anhydrous salt was exposed to an atmosphere of 94% relative humidity (22.3 mm.) and gained a total of 2.8% in weight (theor. 2.3%).

Raman Spectra.—Mathieu and Lounsbury[13] have reported the Raman spectra of solutions of a number of metallic nitrates, not including mercury. For most of the solutions the nitrate bands were complex, splitting into several components. Only for dilute solutions (<1 *N*) did the spectra show no more than the three lines corresponding to the three Raman-active fundamentals expected for the NO_3^- ion in the equilateral planar configuration. In concentrated solutions satellite lines appeared which were attributed to another (less symmetrical) form of the nitrate ion. The spectra of the concentrated solutions resembled those of the hydrated nitrate crystals.

In the present investigation Raman spectra were obtained for a number of solutions of $Hg(NO_3)_2$. The light source was a helical "Toronto" arc; the exciting line was 4358 Å. Sodium nitrite and either praseodymium or Rhodamine 5 GDN Extra filters were used. The spectrograph was an f/3.5 Gaertner instrument.[14] Exposures ranged from 1/4 to 11 hr.

Figure 1 shows a microphotometer tracing of the spectrum of a solution of $Hg(NO_3)_2$, whose concentration was 3.1 *N* with respect to Hg(II). A similar spectrum was observed for a 1.6 *N* solution. These solutions were prepared by dissolving $Hg(NO_3)_2 \cdot H_2O$ in distilled water and filtering off the precipitated $Hg_3O_2(NO_3)_2 \cdot H_2O$. Total Hg(II) was later determined by titration.

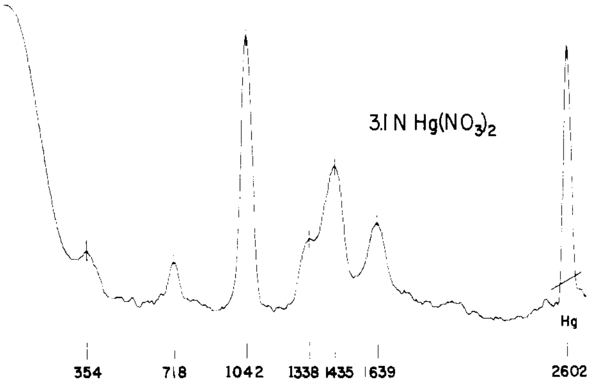

Fig. 1.—Raman spectrum of 3.1 *N* $Hg(NO_3)_2$ solution.

The data and the assignments of the bands are (for 1.6 *N* $Hg(NO_3)_2$ solution)

Δν (cm.⁻¹):	354w	718m	1042vs
Assignment:	Hg–O	$NO_3^-(\nu_4)$	$NO_3^-(\nu_1)$
	1338m	1435s	1639m
	$NO_3^-(\nu_3)$	$NO_3^-(\nu_3')$	$H_2O(\nu_2)$

The low frequency band (354 cm.⁻¹) is tentatively assigned to an Hg-O vibration. Mathieu[15] has reported a low frequency band in the range 350–400 cm.⁻¹ for a number of salt solutions and hydrated salt crystals; he attributes these bands to the totally symmetrical vibration of the octahedral $M(OH_2)_6^{Z+}$ groups.

This does not appear to be the correct interpretation of the band in the present case, however. It was found that the intensity of the 354 cm.⁻¹ band is decreased nearly to zero by the addition of strong acid (see Fig. 2). This behavior is suggestive of the presence in the original $Hg(NO_3)_2$ solutions of polynuclear cations such as $Hg(HgO)_n^{++}$, which are converted by hydrogen ions to the (hydrated) mercuric ion. Since the original solutions were in equilibrium with solid $Hg_3O_2(NO_3)_2 \cdot H_2O$ it is not unreasonable to expect a finite concentration of the cation $Hg(HgO)_2^{++}$ in the solutions. The possibility of $HgOH^+$ ions is not excluded, however.

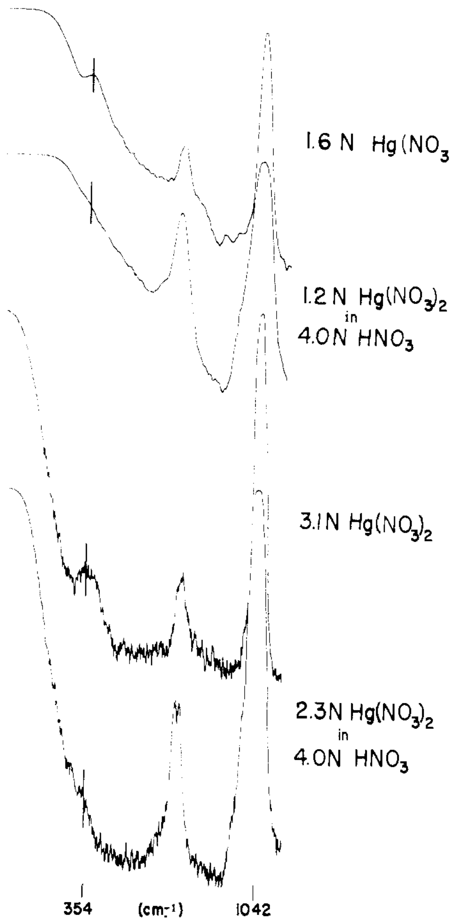

Fig. 2.—Effect of acid on Raman spectra of $Hg(NO_3)_2$ solutions.

One further change was noted upon addition of nitric acid. The nitrate ion band, ν_3, at 1338 cm.⁻¹ split into a doublet, ν_3 = 1317 and ν_3'' = 1361 cm.⁻¹, while the ν'_3 band remained unchanged at 1435 cm.⁻¹.

Infrared Spectra.—Infrared absorption spectra for each of five mercury compounds were obtained over the range 325–4000 cm.⁻¹. Nujol mulls of the solids were examined with a Perkin–Elmer Model 21 (NaCl) spectrophotometer above 610 cm.⁻¹ (see Fig. 3). Thin films of very finely divided solid samples were used for the spectra from 325–700 cm.⁻¹, obtained with a Model 112 (CsBr) spectrometer. Table V lists the infrared data for four of the compounds; for the fifth, HgO, the spectrum consisted only of two strong bands at 492 and 604 cm.⁻¹.

The fundamental frequencies of the nitrate ion are assigned according to the notation of Herzberg.[16] All the

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[13] J. P. Mathieu and M. Lounsbury, *Disc. Faraday Soc.*, **9**, 196 (1950).

[14] G. Vidale and R. C. Taylor, THIS JOURNAL, **78**, 294 (1956).

[15] J. P. Mathieu, *Compt. rend.*, **231**, 896 (1950).

[16] G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., New York, N. Y., 1945, p. 178.

principal bands agree fairly well with the "characteristic nitrate frequencies" listed by Miller and Wilkins[17] for ten other nitrates, except that the infrared-inactive symmetrical stretching frequency, $\nu_1(a'_1)$ is present for three of the mercury salts and is especially intense for the fourth, $HgOHNO_3$, presumably due to some loss of symmetry of the NO_3^- ion in the crystal.

The complexity of the ν_1, ν_2 and ν_3 nitrate bands has been noted in other cases. Mathieu and Lounsbury[13] have postulated two forms for the nitrate ion in concentrated aqueous solutions to account for the splitting of the intense Raman line near 1380 cm.$^{-1}$, $\nu_3(e')$, into a doublet.

TABLE V

INFRARED SPECTRAL DATA

$Hg(NO_3)_2 \cdot H_2O$	$HgOHNO_3$	$Hg_3O_2(NO_3)_2$	$Hg_3O_2(NO_3)_2 \cdot H_2O$	Assignment
		539w[a]	541w	Hg–O
	585s	571s	570s	
610wm	610w	617ms	616ms	?
		645s		
700w	706w	710vw	711vw	$NO_3^-(\nu_4)$
737vw		732vw		
	759wm	778vw		
806w	808ms	803,807m	807m	$NO_3^-(\nu_2)$
837m	835vw		835vw	
1036w	1037ms	1045,1050w	1037,1051w	$NO_3^-(\nu_1)$
1095vw	1096ms,b	1097wm,b	1100wm,b	
1300vs,b	1305vvs,b	1310vs,b	1300vs	
1375vs,b	1380,1412vvs,b	1375vs	1378vs,b	$NO_3^-(\nu_3)$
1460vs		1462s	1455ms	
1627m			1604wm	H_2O
1789w	1743w	1756w	1762w	$NO_3^-(\nu_1 + \nu_4)$
	1767w	1782w		
2435w	2430vw		2425vw	$NO_3^-(\nu_1 + \nu_3)$
		2670vw		
	3120ms,b			O–H
3505m			3390w,b	$\cdot H_2O$
			3500w	

[a] Symbols: s, strong; m, medium; w, weak; v, very; b, broad.

TABLE VI

X-RAY POWDER DATA (0.2 MMM. DIAM. CAPILLARY, CuK_α)

HgO	$Hg(NO_3)_2 \cdot H_2O$[a]	$HgOHNO_3$	$Hg_3O_2(NO_3)_2$	$Hg_3O_2(NO_3)_2 \cdot H_2O$
2.95s[b]	9.0vw	5.9s	5.7w	9.6s
2.83m	6.1w	3.84s	5.03s	6.0w
2.74m	5.8m	3.52m	4.05s	5.8w
2.40s	5.07w	3.20s	3.81w	5.08vw
1.81s	4.85s	3.07m	3.37w	4.79s
1.75w	4.61w	2.98m	3.33w	4.47vw
1.65w	4.40w	2.96w	3.08s	4.29w
1.63w	3.75s	2.60m	2.81s	3.70vw
1.60w	3.47w,d	2.57m	2.75s	3.28vw
1.49m,d	3.16m	2.41m	2.59w	3.19s
1.44w	3.05w	2.16m	2.53w	2.98m
1.42w	2.95w	2.10m	2.39s	2.88s
1.38w	2.88m	2.00m	2.26m,d	2.82m
1.20w	2.71w,d	1.96m,d	2.06m	2.59w
1.19w	2.58w	1.92w	2.04m	2.52m
1.16w	2.55w	1.90w	1.64m	2.21m
1.15w	2.45m	1.85w	1.61m	2.14m
1.10w	2.40w	1.79w	1.58m	1.92w
1.08vw	2.32w	1.76w	1.41w	1.86w
1.05vw,d	2.28w	1.74w	1.39w	1.74m,d

[a] 0.5 mm. diam. capillary used (sample hygroscopic). [b] Symbols: s, strong; m, medium; w, weak; v, very; d, doublet (unresolved).

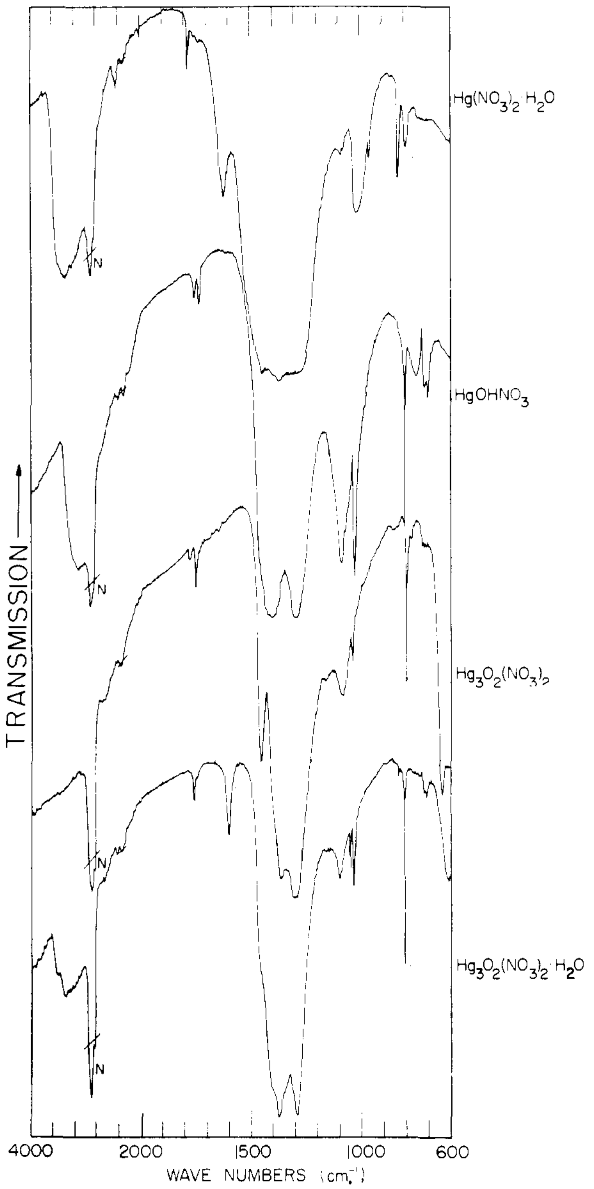

Fig. 3.—Infrared spectra of mercury(II) nitrate (Nujol mulls; N shows strong Nujol band).

The spectrum of a sample of $Hg(NO_3)_2$ (anhydrous) was identical with that of $Hg(NO_3)_2 \cdot H_2O$ except for the bands due to water of hydration at 1627 and 3505 cm.$^{-1}$. The absence of the hydrate–water band for $HgOHNO_3$ in the 1600 cm.$^{-1}$ region is to be noted. Also, the O–H stretching frequency in $HgOHNO_3$ is appreciably displaced relative to the O–H band in hydrate water. The bands in the 580 cm.$^{-1}$ region are tentatively assigned to an Hg–O stretching vibration.

X-Ray Data.—Powder diffraction photographs were obtained using a G. E. XRD-1 unit with Cu K_α radiation, a camera of 360 mm. circumference, and capillaries of 0.2 mm. diameter. Table VI lists *d*-values (Å.) and visually estimated intensities for the first 20 lines of each of five mercury compounds.

The results for HgO agree well with values calculated from the data of Zachariasen[18] and Roth[19] and the *d*-values listed in the A.S.T.M. diffraction data file, card no. I-2190. Because of the hygroscopic nature of the $Hg(NO_3)_2 \cdot H_2O$ which necessitated the use of the larger capillary, the results

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(17) F. A. Miller and C. H. Wilkins, *Anal. Chem.*, **24**, 1253 (1952).

(18) W. Zachariasen, *Z. physik. Chem.*, **128**, 421 (1927).

(19) W. L. Roth, *Acta Cryst.*, **9**, 277 (1956).

are subject to greater error due to the absorption effect; some of the higher *d*-values may be low by 0.01–0.05 Å.

Single crystals of $HgOHNO_3$ and $Hg_3O_2(NO_3)_2 \cdot H_2O$ were studied by Dr. C. E. Nordman of this Department. The crystal structure of $HgOHNO_3$ will be reported separately by him at a later date. In the case of the $Hg_3O_2(NO_3)_2 \cdot H_2O$, his results are as follows: the unit cell is triclinic with a, b and c = 6.92, 10.10 and 6.87 Å. and α, β and γ = 97° 39′, 119° 31′ and 100° 07′, respectively. The volume of the unit cell is 398 Å.^{3} and the calculated density is 6.48 g. cm.$^{-3}$, assuming two formula units of $Hg_3O_2(NO_3)_2 \cdot H_2O$ per unit cell. The density of a powder sample of this compound was determined with a pycnometer using both CCl_4 and "Halocarbon" oil, resulting in values of 6.37 and 6.34 g. cm.$^{-3}$, respectively.

Using Nordman's values for the cell parameters of $HgOHNO_3$ and $Hg_3O_2(NO_3)_2 \cdot H_2O$ a number of *d*-values were computed, all of which agreed (within experimental error) with the powder data.

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[Contribution from the Chemistry Department, Oregon State College]

Radiosulfur Exchange Reactions between Sulfur Oxyhalides[1]

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The sulfur-35 exchange reaction between thionyl chloride and thionyl bromide has been studied at −20 and −50°, both in liquid sulfur dioxide solution and in the two pure mixed compounds. The exchange is rapid and complete, except for the pure compounds at −50°, where a measurable rate is observed. The results are interpreted as demonstrating the probable existence of ionic dissociation processes for thionyl halides, both pure and in liquid sulfur dioxide solutions. The sulfur-35 exchange between thionyl chloride and sulfuryl chloride is insignificant in five days at 0°, in line with the lack of a readily available ionization pathway. A further reason for the slowness of this type of exchange is suggested.

The rapidity of radiochlorine exchange reactions between solute chloride salts and thionyl chloride, both as a solvent and dissolved in liquid sulfur dioxide,[3] attests to the participation of thionyl chloride, under such circumstances, in some type of ionization processes. Although these results seem to suggest a dissociation equilibrium[4] to $SOCl^+ + Cl^-$, it is possible that they could alternatively be explained in terms of an association equilibrium to $SOCl_3^-$. We have now undertaken to distinguish between these two possibilities by studying the radiosulfur exchange between thionyl chloride and thionyl bromide. In such solutions, containing no halide salts, no association equilibrium could occur (except possibly by virtue of dissociation-produced halide ions). A rapid exchange, taken to imply an ionization process, would then indicate the occurrence of dissociation to SOX^+ for one or both of the thionyl halides (the apparently unstable species $SOClBr$[5] being assumed as an intermediate). Continuing the earlier work,[3] we have studied this exchange both between the two pure mixed compounds and between the two dissolved together in liquid sulfur dioxide.

As a related system, but one in which ionization would not lead directly to exchange, the radiosulfur exchange between sulfuryl chloride and thionyl chloride (pure liquids, no other solvent) has also been investigated. Besides their pertinence in the present context, the results in this case are of interest in their relation to earlier observations[6] on exchange in the related S(IV)–S(VI) system, sulfur dioxide–sulfur trioxide.

Results and Discussion

Thionyl Bromide–Thionyl Chloride Exchange.—The results are summarized in Table I. In the case of the experiments done in liquid sulfur dioxide solutions, although the separation method was such as to make difficult calculation of precise exchange percentages, it seems certain that the exchange was substantially complete within a few minutes, even at −50°, either with excess of thionyl bromide or of chloride. With the two pure mixed compounds the exchange is also fast, being essentially complete within a few minutes at ∼ −20°. However, the rate does appear to be somewhat lower than in sulfur dioxide solutions, only partial exchange occurring at −50°.

The rapidity of the exchange appears to support, at least so far as sulfur dioxide solutions are concerned, the previously indicated[3] occurrence of some type of ionization process involving the thionyl halide solutes. It further satisfies the initial objective of this research by demonstrating the probable formation in these solutions of dissociated ionic species of the type SOX^+. Thus the ionization process might consist either of a simple dissociation of one or both of the thionyl halides (*e.g.*, $SOCl_2 \rightleftarrows SOCl^+ + Cl^-$), or alternatively of a direct halide ion transfer between two thionyl halides (*e.g.*,

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[1] Oregon State College, Research Paper No. 308, School of Science, Department of Chemistry.

[2] Taken from the M.S. thesis of LeRoy F. Johnson, Jr., at Oregon State College, June, 1956.

[3] B. J. Masters, N. D. Potter, D. R. Asher and T. H. Norris, This Journal, **78**, 4252 (1956).

[4] Dissociation to $SO^{++} + 2Cl^-$ has previously been shown not to occur, R. E. Johnson, T. H. Norris and J. L. Huston, *ibid.*, **73**, 3052 (1951).

[5] H. A. Mayes and J. R. Partington, *J. Chem. Soc.*, 2594 (1926).

[6] J. L. Huston, This Journal, **73**, 3049 (1951).