TABLE I

COMPARATIVE SPECTRAL DATA FOR Nd^{3+} AND Er^{3+} AMINOPOLYCARBOXYLATE CHELATES

Chelate	$\epsilon_{max}/\epsilon^0_{max}$[a]	ν, cm^{-1}[b]
$Nd^{III}(aq)$	...	17,366
$Nd^{III}(CDTA)$	1.07	17,276
$Nd^{III}(EDTA)$	1.48	17,187
$Nd^{III}(TTHA)$	2.40	17,300
$Er^{III}(aq)$	...	26,533
$Er^{III}(CDTA)$	1.01	26,540
$Er^{III}(EDTA)$	1.33	26,463
$Er^{III}(TTHA)$	4.00	26,515

[a] Ratio of ϵ_{max} of chelate to that of aqueous ion, ϵ^0_{max}. [b] Observed values accurate to ±0.1%.

exhibit any shift in the position of their absorption maxima.

The results (Table I) for both Nd^{3+} and Er^{3+} chelates show that the intensity enhancements are in the order (relative to the ligands): TTHA > EDTA > CDTA. Any undisputable explanation of this observation will be rather tenuous, for the unique phenomenon of spectral hypersensitivity in rare earths has only recently received quantitative consideration.[2-4] Jørgensen and Judd[4] have given semiquantitative evidence supporting the suggestion that the hypersensitivity is most likely not pure electric dipole in origin, but rather electric quadrupole. These investigators have suggested that the electromagnetic field induces an asymmetrical distribution of dipoles in the medium surrounding the rare earth ion, thus inducing a large electric field gradient across the ion. The theoretical development leads to the quantum selection rule $\Delta J = \pm 2$ for such a pseudo-quadrupole transition, which is in complete accord with the data in Table I regarding the $^4I_{9/2} \rightarrow {}^4G_{5/2}$ and $^4I_{15/2} \rightarrow {}^4G_{11/2}$ transitions for Nd^{3+} and Er^{3+}, respectively. Thus, it would appear that this mechanism may indeed provide a logical explanation for the data, wherein the aminopolycarboxylate ligand induces a more or less permanent asymmetry about the rare earth ion with this asymmetry increasing in the order CDTA < EDTA < TTHA.

In the absence of detailed information regarding coordination number, geometry, and other essential structural details in these aminopolycarboxylate chelates and additional spectral data of a more detailed nature, it is impossible to ascertain which parameters are most specifically associated with the hypersensitivity. However, if the pseudo-quadrupole mechanism[4] is accepted as plausible, then one thing of importance is the polarizability of the solvent environment. Although this effect is an indirect one, the intensity of the transition should increase with increasing solvent polarizability.[4] Unfortunately, the aminopolycarboxylate Nd^{3+} and Er^{3+} chelates are not amenable to a spectral study involving solvents of widely varying polarity, since they appear to be formed only in highly polar solvents such as water. However, spectra of the analogous Nd^{3+} and Er^{3+} acetylacetonates have been obtained in benzene, toluene, carbon tetrachloride, and chloroform,[5] thus allowing at least a qualitative evaluation to be made. These solvents have effective molar polarizabilities, $(\alpha_m)_{eff}$,[6] of 10.5, 13.3, 11.1, and 17.8 A^3, respectively. Attempts to correlate the ϵ_{max} values of $Nd(acac)_3$ and $Er(acac)_3$ with these data were of no avail, thus suggesting that spectral hypersensitivity as a consequence of quadrupolar enhancement *via* dielectric inhomogeneity should perhaps be viewed with caution. In fact, it has recently been pointed out that the symmetry of the local environment also plays a major role in the enhancement of pseudo-quadrupole transitions.[7] This would seem to be more in line with these reported observations.

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Preparation and Properties of Barium Pernitride, Ba_3N_4[1]

BY Y. OKAMOTO AND J. C. GOSWAMI

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The thermal decomposition of many inorganic azides, especially those of heavy metals, proceeds explosively and results in the formation of the corresponding metal and nitrogen.[2] However, the thermal decomposition reactions of certain of these azides, such as those of barium, calcium, and strontium are accompanied, although to a small extent, by the formation of the corresponding nitrides.[3-6] According to Andrew,[5] in the thermal decomposition of barium azide, nuclei of metallic barium are first formed which then react with undecomposed barium azide to form the nitride. Harvey[7] has reported that, if partially decomposed crystals are removed from the sample during the period of acceleration of the decomposition, the product is found to consist only of metallic barium.

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(1) Presented in part at the 141st National Meeting of the American Chemical Society, Washington, D. C., March 1, 1962.

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We have found that barium azide decomposes smoothly in organic solvents, such as decalin, xylene, or tetralin, near their respective boiling points to yield a fine black powder and nitrogen. No detectable amounts of barium azide and its black decomposition product have been found to dissolve in these solvents even at the boiling point.

Decomposition of barium azide was preceded by an induction period (10–20 min) at the decomposition temperature. After this induction period, the decomposition was first order (up to almost 97% decomposition). The rate constants in decalin and tetralin were $k_1 = 0.0271, 0.0258, 0.0250 \text{ sec}^{-1}$ (at 192°) and $k_1 = 0.0225, 0.0207 \text{ sec}^{-1}$ (at 202°), respectively. The infrared spectra of solvents used for the decomposition showed no change after decomposition.

X-Ray analysis of the black powder showed a hexagonal structure ($a = 5.22$ A and $c = 5.50$ A), which did not correspond to any reported barium compound. Elemental analyses of the black powder product and the amount of nitrogen evolved from the decomposition reaction suggested that the reaction proceeded as shown in eq 1.

$$3Ba(N_3)_2 \xrightarrow{\Delta} Ba_3N_4 + 7N_2 \qquad (1)$$

Calcium and strontium azides also decomposed smoothly in decalin and produced Ca_3N_4 and Sr_3N_4, respectively.[8]

Upon further heating in a nitrogen atmosphere, the barium pernitride decomposed (>250°) into barium nitride and additional nitrogen gas

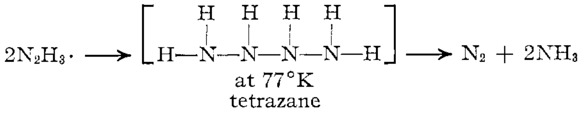
$$Ba_3N_4 \xrightarrow{\Delta} Ba_3N_2 + N_2 \qquad (2)$$

Barium pernitride was exceedingly reactive with water and air. With the former, products of the reaction, described by reaction 3, were barium hydroxide, ammonia, and nitrogen.

$$Ba_3N_4 + 6H_2O \longrightarrow 3Ba(OH)_2 + N_2 + 2NH_3 \qquad (3)$$

Rice and Scherber[9] observed that, when hydrazine was pyrolyzed, a yellow material was condensed at 77°K. Upon raising the temperature to 95°K, the material decomposed into nitrogen and ammonia (mole ratio of N_2 to NH_3 was 1:2). They suggested the yellow compound was tetrazane which formed during condensation at the low temperature by combination of two hydrazine radicals derived from the pyrolytic process

$$2N_2H_4 \longrightarrow 2N_2N_3\cdot + H_2 \qquad (4)$$



$$2N_2H_3\cdot \longrightarrow \underset{\substack{\text{at } 77°\text{K} \\ \text{tetrazane}}}{\left[H-\overset{H}{\overset{|}{N}}-\overset{H}{\overset{|}{N}}-\overset{H}{\overset{|}{N}}-\overset{H}{\overset{|}{N}}-H\right]} \longrightarrow N_2 + 2NH_3 \qquad (5)$$

The pernitrides of barium, strontium, and calcium yielded nitrogen and ammonium salt (mole ratio 1:2) when they reacted with aqueous acid. Therefore, in accordance with these results, although the structure of these compounds was not directly established, it might correspond to their tetrazane salts, $3M^{2+}(-\overset{|}{N}-\overset{|}{N}-\overset{|}{N}-\overset{|}{N}-)^{6-}$, where M is Ba, Sr, and Ca. Thus, when treated with water, the tetrazane salts of alkaline earth metals would be expected to produce tetrazane which would decompose immediately to form nitrogen and ammonia (mole ratio 1:2).

Experimental Section

Preparation of Alkaline Earth Azides.—Barium azide was prepared by neutralizing an aqueous solution of hydrazoic acid with barium hydroxide.[8] Metallic impurities have been found to influence the thermal decomposition.[2,10] Therefore, the azide obtained was repeatedly purified by recrystallization from the aqueous solution by adding ethanol or acetone. A typical spectrographic analysis[11] of barium azide (as the decomposition product, Ba_3N_2) is: Ba, major; Ca, 0.0*X;* Sr, 0.00*X;* Mg, 0.000*X;* Si, 0.000*X;* Al, 0.000*X*.

Calcium and strontium azides were prepared in a manner analogous to that of barium azide.

Decomposition of Alkaline Earth Azides under Organic Solvents.—Decalin, xylene, and tetralin (Fisher Scientific Co.) were used as the solvents. All the solvents were dried by calcium hydride and distilled before being used in the experiment. A typical decomposition procedure is as follows. Barium azide (8.64 g) and 35 ml of decalin were placed in a 100-ml Pyrex round-bottom one-neck flask equipped with a Liebig reflux condenser. The air in the apparatus was replaced with dry nitrogen. The flask was heated slowly in an oil bath. The decomposition reactions in decalin or tetralin were found to take place within 20 min after the temperature of the solvents reached the boiling points. The nitrogen produced was measured using a wet test meter. The decompositions were completed after 30–40 min at their refluxing points. However, when the lower boiling solvent, xylene, was used, the decomposition was complete after about 8 hr at the boiling point. The rate of decomposition was followed by an accurate measurement of the nitrogen evolved. The data obtained from the decomposition of different samples of barium azide under various solvents are shown in Table I.

TABLE I

DECOMPOSITION OF BARIUM AZIDE IN ORGANIC SOLVENTS

Solvent vol, ml	Wt of $Ba(N_3)_2$, g	Theoret[a] amt of N_2, l.	Obsd[b] amt of N_2, l.
Decalin, 100	8.64	2.21	2.28
Decalin, 100	8.62	2.21	2.20
Decalin, 150	12.20	3.21	3.22
Decalin, 350	55.00	14.0	14.1
Decalin, 150	17.50	4.46	4.65
Xylene, 50	2.12	0.55	0.53
Tetralin, 60	5.47	1.41	1.58

[a] Calculated according to eq 1. [b] Measured at room temperature (21–26°).

Since finely divided black barium pernitride particles were exceedingly reactive with air, the compound was sealed under Ar atmosphere. The X-ray powder diffraction patterns of Ba_3N_4 [d (A), I/I_0] are: 3.96 w, 3.69 vw, 3.46 s, 2.87 mw, 2.29 m, 2.188 w, 2.096 mw, 1.913 m, 1.852 m, 1.741 m.

Analysis of Nitrogen and Barium in Ba_3N_4 and Ba_3N_2.—The nitrogen content in barium pernitride was determined by the Dumas method. The barium in the pernitride was determined

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[8] Hartmann, Fröhlich, and Ebert supposedly obtained strontium and calcium pernitrides (Sr_3N_4 and Ca_3N_4) from the corresponding amides by heating under high vacuum. However, they neither characterized nor isolated these compounds: H. Hartmann, H. J. Fröhlich, and F. Ebert, *Z. Anorg. Allgem. Chem.*, **218**, 181 (1934).

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[11] The analysis was carried out at Lucius Pitkin, Inc., New York, N. Y. 0.00*X*, 0.000*X* = concentration of the elements estimated to the nearest decimal place; 0.0*X* = 0.01–0.09% estimated. Elements checked but not found: Fe, Ti, Cu, Ag, Mn, Cr, Co, Mo, V, W, Bi, Sb, As, P, Pb, Sn, Tl, Ga, Ge, Zn, Cd, In, Na, K, and Li.

as $BaSO_4$. A typical result of the elemental analysis is: N, 12.00, 12.20, 12.10; Ba, 88.5, 87.0, 87.5%. Calculated values for Ba_3N_4 are: N, 11.95; Ba, 88.05%.

When barium pernitride (5.1 g) was slowly heated up to 250° under nitrogen atmosphere, 260 ml (at 24°) of nitrogen gas (identified by means of a mass spectrometer) was eliminated. Theoretical amount of nitrogen expected according to eq 2 is 270 ml.

The nitrogen content in a barium nitride sample produced according to eq 2 was analyzed by the Kjeldahl method and found to be 6.45 wt % (calculated value of nitrogen in Ba_3N_2 is 6.35%). The barium in Ba_3N_2 was found to be 92.9 wt % (calculated value is 93.6%).

The nitrogen contents in Sr_3N_4 and Ca_3N_4 were determined in a manner exactly analogous to that of Ba_3N_4.

Decomposition of Alkaline Earth Pernitride by Aqueous Acid.—The alkaline earth pernitrides (Ba_3N_4, Ca_3N_4, and Sr_3N_4) were found to react vigorously with aqueous acids and to form metal salts, nitrogen gas, and ammonium salts (eq 3).

A typical experiment can be described as follows. Barium pernitride (7.7 g) was placed in a 50-ml three-neck flask under a dried nitrogen atmosphere and cooled with ice. A large excess of 5% aqueous HCl solution was added slowly dropwise to the flask with stirring. The decomposition of pernitride started immediately, and 385 ml of nitrogen gas was evolved at 27°. The calculated value according to eq 3 is 370 ml. After the decomposition, the ammonia content of the solution was determined by the Kjeldahl method and found to be 0.027 mole (calculated value using eq 3 is 0.030 mole).

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Thermochemistry of Aqueous Pervanadyl and Vanadyl Ions

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In 1952 Latimer[2] was able to list only free energies of formation for the species of V(IV and V) in aqueous acid. These values were based on a free energy calculated from the solubility of V_2O_5 and the oxidation potential for the $V(IV) = V(V) + e^-$ half-reaction. Subsequent measurements by LaSalle and Cobble[3] have provided data for the heat of solution of V_2O_5 and more data for its solubility. Mah and Kelley[4] have reported a new $\Delta H_f°$ and derived $\Delta G_f°$ for V_2O_5 (c).

We have remeasured the heat of solution of V_2O_5 in aqueous acid and have also measured the heat of reduction of V(V) to V(IV), with results being used in several thermodynamic calculations.

Experimental Section

The calorimeter used was patterned after one previously described,[5] except that a Leeds and Northrup Mueller G-2 bridge and H.S. galvanometer were used with a nickel resistance thermometer. Also, the thermometer and calibration heater were contained in a glass spiral filled with mineral oil. All of the work reported here was carried out with 950 ml of solution in the calorimeter at 25.0 ± 0.2°.

Fisher Certified reagent V_2O_5 (100.0%) was leached with 1 *M* $HClO_4$ for periods from 1 hr to 1 month. After filtering and washing, the products were dried at 450° and stored in a vacuum desiccator with P_2O_5. Other samples were prepared by leaching with nitric acid and by thermal decomposition at 450° of ammonium metavanadate from Fisher and Mackay. Direct titration with standard $KMnO_4$ solution showed that these samples had less than 0.1% vanadium in lower oxidation states. Similar titration after reduction of V(V) to V(IV) with HSO_3^- led to calculated compositions in the range 100.1 ± 0.3% for all samples. Our heat measurements disclosed no thermochemical differences between any of these samples.

Results and Calculations

Although there is poor agreement on values of equilibrium constants relating important species of V(V) and V(IV) in acidic solutions, it does appear that below pH $\cong$2 the principal species are the pervanadyl and vanadyl ions represented by $VO_2^+(aq)$ and $VO^{2+}(aq)$. The reaction equation for our measurements of the heats of solution of $V_2O_5(c)$ in $HClO_4$ is written as

$$V_2O_5(c) + 2H^+(aq) = 2VO_2^+(aq) + H_2O(l) \qquad (1)$$

All measurements were made with approximately 1-g samples of V_2O_5 being dissolved in 950 ml of $HClO_4$ to yield solutions about 0.01 *M* in $VO_2^+(aq)$. Solution times varied from 10 to 20 min, depending on concentration of acid and method of preparation of V_2O_5. Most of the estimated uncertainties (~0.1 kcal/mole of V_2O_5) in results given in Table I stem from rather long extrapolations associated with these long reaction times.

TABLE I
HEATS OF SOLUTION OF $V_2O_5(c)$ IN AQUEOUS $HClO_4$

$[H^+]$, *M*	$-\Delta H$, kcal/mole of V_2O_5	$[H^+]$, *M*	$-\Delta H$, kcal/mole of V_2O_5
0.25	8.25	0.60	7.90, 7.85, 7.88
0.35	8.09	0.70	7.94
0.40	7.98, 8.09	0.80	7.79
0.50	7.90, 8.15	1.00	7.67, 7.51

Extrapolation to infinite dilution of the data in Table I leads to $\Delta H° = -8.4$ kcal/mole of V_2O_5 for reaction 1. Because of uncertainties associated with this extrapolation to the reference state, the uncertainty in $\Delta H°$ is several times that derived from purely experimental uncertainties, possibly being ~±0.3 kcal/mole of V_2O_5.

LaSalle and Cobble[3] have also determined heats of solution of V_2O_5 (about the same total vanadium concentrations as in our measurements) in $HClO_4$ from 0.16 to 0.63 *M*. They reported an extrapolated $\Delta H° = -5.78 \pm 0.09$ kcal for reaction 1. Their $\Delta H°$ differs from ours by 2.6 kcal. Also, their measured heats became less exothermic with increasing dilution of acid while ours became more exothermic. We are

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[1] National Science Foundation Research Participation for High School Teachers.

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