constant can often be determined from data of the type shown in Figures 3 and 4. The large molar ratio of Eu(fod)$_3$ needed to reach this saturation point is indicative of the low basicity of these organic compounds and the extreme solubility of the fod complex. In the case of the ether, 2.0 mol equiv of the chelate was required to achieve complete coordination of the ether. This represents a solubility of over 200 mg of the europium complex in a 0.5-ml CCl$_4$ solution of the ether. Consequently, an important function of the fod ligand is to impart extremely high solubility to the resulting complex, enabling the attainment of larger induced shifts.

An equally important function of the fod ligand is to produce a species with relatively high Lewis acidity. Feibush, *et al.*,[19] have made extensive studies of the interactions of various weak donor organic ligands with many different coordinatively unsaturated lanthanide chelates. In these experiments the metal chelates were dissolved in nonpolar liquid stationary phases in gas chromatographic columns, and various organic donors were passed through the columns. The interactions were much greater (from relative retention volume data) with columns containing lanthanide–fod complexes than those with thd, providing clear independent experimental evidence for the greater Lewis acidity of the former.

It should also be mentioned that the chemistry of both the thd and fod complexes is not as straightforward as one might assume.[20-23] Everyone usually writes the formulas as simply M(thd)$_3$ and M(fod)$_3$ when in fact such simple unsolvated species may not exist as such. In the crystalline state the thd chelate of praseodymium is a dimer, (thd)$_2$Pr(thd)$_2$Pr(thd)$_2$, in which each of the metal atoms is surrounded by seven oxygens.[22] A single-crystal X-ray study has revealed that one of the oxygen atoms of each of the two bridging chelate rings is shared equally between Pr atoms. Some of the lanthanide–thd chelates have been isolated as hydrates,[23] but they do not undergo hydration as rapidly as the fod complexes.[18] A structure determination of the hydrated praseodymium complex has shown that it is a dimer with the formula, (fod)$_2$Pr(fod)$_2$(H$_2$O)Pr(fod)$_2$·H$_2$O.[23] Bridging of the two Pr atoms is provided by two carbonyl oxygen atoms as well as one molecule of water. The other water is apparently hydrogen bonded to two perfluoropropyl side chains in the ligand shell and is not bonded to the metal ion. This illustrates that two basically different types of interactions are operative with the same ligand; consequently perhaps even in solution similar complications can occur with organic donors when lanthanide chelates are used as shift reagents. In this complex each Pr is surrounded by eight oxygen atoms, again illustrating the variable coordination number of the lanthanides.

The anhydrous fod complexes pick up 1 mol of water per metal when allowed to stand unprotected in a moist atmosphere. Therefore it is recommended that fod samples be stored over P$_4$O$_{10}$ in a vacuum desiccator before use as shift reagents. In the present study, after the chelate samples were removed from the desiccator, no special care was taken to exclude moisture or to dry the solvents because we wanted to test the efficacy of the complexes under conditions of practical routine use. Since water acts as a competing donor, it may be necessary in special cases to exclude water insofar as is possible when very poor donors are under study.

We have examined several of the hundreds of lanthanide chelates synthesized in our laboratories and, while other complexes also produce shifts, the fod chelates of Eu(III) and Pr(III) are superior to all of the complexes so far studied.

Acknowledgment. We wish to thank Dr. K. J. Eisentraut, Col. J. W. Connolly, and Dr. Charles S. Springer, Jr., for synthesizing some of the samples used in this study.

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Solid-State Photochemistry of Ammonium Azides

Sir:

Modern theories of solid-state physics and chemistry have been applied to explain the mode of photochemical decomposition of certain solid inorganic ionic azides, and the mechanism is based on thermodynamic, kinetic, and spectroscopic evidence.[1,2] This investigation deals with the photolyses of ammonium azides underneath the surface of liquid cyclohexane at 2537 Å. The purpose of the hydrocarbon was to scavenge the reactive free radicals and intermediates produced on the surface of the solid azide during photolysis.

Freshly sublimed and powdered ammonium[3] or cyclohexylammonium[4] azides, covered by purified cyclohexane[5] (analyzed by uv, vpc, and mass spectroscopy) and under dry nitrogen or argon, in quartz vessels (50% or more transmission of uv at wavelengths longer than 2000 Å) were irradiated at 30° with a low-pressure mercury lamp (G. E. Germicidal G30T8, 30 W) having maximum emission at 2537 Å. The 1849-Å Hg emission is eliminated effectively by the Vycor lamp envelope (0% transmission < 2200 Å for a new lamp). The products and relative yields are given in Table I.

In Table I, the extent of reaction depends on time and preparation batch, but the relative ratios of products are about the same for reactions proceeding 11–31% of completion. The product ratio varies noticeably at

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Table I. Relative Product Yields from the Photolyses of Ammonium Azides[a]

Reactants, 1 g/10 ml	Irradiation time, hr	Reaction extent,[b] %	Liquid product yields,[c] mol %						Gaseous product yields,[d] mol %			
			RNH_2	R_2NH	$RNHNH_2$	$(RNH)_2$	$R' = NH$[e]	R_2	H_2	N_2	NH_3	N_2H_4
A[f]/C[g]	12	11.4	71.4	Trace	Trace	0.00	0.00	28.6				
A/C[g]	12	17.8	65.6	Trace	Trace	0.00	0.00	37.3				
A[f]/C[h]	24	22.0	74.8	2.10	Trace	0.00	0.00	23.1	4.53	95.0	0.13	0.37
A/C[g]	24	31.2	72.2	1.50	Trace	0.00	0.00	26.3				
A[f]/C[g]	72	52.1	57.0	4.78	Trace	0.00	0.00	36.0				
B[f]/C[g]	12	26.7	67.5	0.00	10.3	8.63	3.06	00.0				
B[f]/C[h]	24	51.8	49.5	0.00	26.1	10.8	7.93	00.0	5.54	89.1	4.02	1.38
A[h]	96								1.81	83.7	14.4	0.09

[a] A = NH_4N_3; B = $C_6H_{11}NH_3N_3$; C = C_6H_{12}; R = cyclohexyl; R′ = cyclohexylidenyl. [b] Determined from unreacted azide salt. [c] Determined by vpc. [d] The yields were calculated from mass spectrometric data (H_2, *m/e* 2; N_2, *m/e* 28; NH_3, *m/e* 16, 17; N_2H_4, *m/e* 32, from ionizing voltages of 70 V and gas pressures at 50.81 μ) of products by standardization with the American Petroleum Institute Mass Spectral Catalog, Vol. 3, Pittsburgh, Pa., 1950, spectrum no. 452; Vol. 7, 1959, spectrum no. 1595; Vol. 2, 1948, spectrum no. 90; Vol. 5, 1955, spectrum no. 1110, respectively. [e] Detected as imine and isolated as cyclohexanone upon hydrolysis [f] The azide employed came from the same preparation batch. [g] Under N_2. [h] Under Ar.

about 50% of reaction or upon long periods of irradiation. All of the products reported in Table I and cyclohexane were found to be quite stable under reaction conditions of irradiation. No dissociation of the ammonium azides into base and acid was apparent on standing at room temperature for several days. Control experiments showed only 5% of the ammonium cation exchanged with cyclohexylamine.

The uv absorption spectra of thin films of ammonium azides (cast from methanol) showed a weak absorption band around 2250–2300 Å, and possessed an absorption edge that goes beyond 2537 Å, commencing at 2600–2650 Å. This weaker band is overlapped at its maximum by the edge of a strong band, designated as the first exciton band (λ_{max} ~1900 Å) in the spectra of NaN_3 and KN_3.[6]

In the irradiation of NH_4N_3, if the reaction occurred at the surface of the solid, heterogeneous attack of cyclohexane by reactive species is expected. No cyclohexyl azide was detected in the reaction mixture. When cyclohexyl azide was subjected to our photolytic conditions, this azide survived unchanged. The large quantities of dicyclohexyl are thought to arise from attack of cyclohexane by other radical intermediates rather than from hydrogen abstraction by azide radical.

The photolysis products, given in Table I, may be explained by Scheme I. The above reactions, involving intermediates N_2^-, N_4^-, and N, are based on esr studies at 77°K on irradiated (2537 Å) solid sodium, potassium, and barium azides, and recently N_3^{2-} has been detected in the barium salt.[1,2,7,8] Loosely bound odd electrons would be expected to be eventually solvated by the resulting ammonia and amine products formed in the solid.

The formation of NH and N, derived from N_3^-, is supported by the stoichiometry of the reaction of $C_6H_{11}NH_3N_3$. The actual total yields of all basic products, calculated on the basis of each nitrogen being derived solely from the cation, exceed theory (from $C_6H_{11}NH_3N_3$, 99–108% yield of amines, imines, and hydrazines, plus a quantity of NH_3 and N_2H_4, in Table I). A similar calculation for NH_4N_3 results in only 1.3–16% yield of amines and trace amounts of NH_3 and N_2H_4 in Table I, based on the products arising from NH_4^+. The rapid reaction of NH_3 with e⁻ and NH,[9,10] and reaction of N_2H_4 with e⁻, NH,[9] and N,[11] in the solid to produce H_2 and N_2, explain the low yields of amines, NH_3, and N_2H_4 obtained from the irradiated NH_4N_3.

Scheme I

$$N_3^- \xrightarrow{h\nu} N_3^{-*}$$
$$N_3^{-*} \longrightarrow N + N_2^-$$
$$N + N_3^- \rightleftharpoons N_4^- \longrightarrow N_2^- + N_2$$
$$N_3^{-*} + NH_4^+ \longrightarrow NH_3 + HN + N_2$$
$$N_2^- + NH_4^+ \longrightarrow H\cdot + NH_3 + N_2$$
$$N_2^- + NH_3 \longrightarrow N_2 + NH_3^-$$
$$NH_3^- + NH_4^+ \longrightarrow 2NH_3 + H\cdot$$
$$N + H\cdot \longrightarrow NH$$
$$2NH \longrightarrow N_2 + H_2$$
$$NH + NH_3 \longrightarrow NH_2NH_2$$
$$2N \longrightarrow N_2$$
$$NH_3 + R\cdot \longrightarrow NH_2\cdot + RH$$
$$C_6H_{12} + R\cdot \longrightarrow C_6H_{11}\cdot + RH$$
$$C_6H_{11}NH_2 + R\cdot \longrightarrow C_6H_{11}NH\cdot + RH$$
$$2R\cdot \longrightarrow R_2$$
$$R\cdot = H\cdot,\ NH_2\cdot,\ C_6H_{11}\cdot,\ \text{or}\ C_6H_{11}NH\cdot$$

In irradiation of $C_6H_{11}NH_3N_3$ covered by cyclohexane, the products (Table I) indicate that the radical intermediates, subsequent to electron capture by $C_6H_{11}NH_3^+$, form products below the crystal surface or form stable products by rapid reaction with other radical species or nitrogen bases derived from the salt at the solid surface. The cyclohexyl bases arise from electron transfer to the cation and by radical attack on cyclohexylamine, and not by radical attack on cyclohexane at the crystal surface. The lack of formation of detectable amounts of dicyclohexyl or dicyclohexylamine strongly supports this view. The insertion and abstraction reaction of NH with cyclohexylamine does account for the formation of cyclohexylhydrazine,

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NH_3, and cyclohexylimine, since only the imine can be readily explained by radical attack on the parent amine.

$$2C_6H_{11}NH_2 + 2HN \longrightarrow C_6H_{11}NHNH_2 + C_6H_{10}NH + NH_3$$

The difference in chemical behavior between the two azide salts may be ascribed to the difference in structure and ease of diffusion through the crystal lattice of the two initially formed radicals, amino and cyclohexylamino, and the corresponding bases. The large and structurally complex cyclohexylamino radical results in stable products, such as imine and cyclohexyl-substituted hydrazines, while surfacing. Heterogeneous reaction depends upon the ability of survival or regeneration of reactive species, like the amino radical, within the solid azide such that they can finally diffuse to the surface and react.

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An Unusual Rate Enhancement in Metal Ion Catalysis of Phosphate Transfer

Sir:

Although divalent metal ions are required as cofactors in many enzyme-catalyzed phosphate transfer reactions,[1] the structural constraints necessary for catalytically active metal ion–substrate complexes remain largely undefined so that efforts to create suitable models have been unproductive. We wish to report a model reaction in which a dramatic rate acceleration has been observed.

The pH–rate profile for the hydrolysis of 2-(4(5)-imidazolyl)phenyl phosphate (I) in the presence and absence of Cu^{2+} is shown in Figure 1. At pH 6, Cu^{2+} at a $[Cu^{2+}]:[substrate] \cong 2$ leads to an acceleration of $>10^4$ compared to the noncatalyzed reaction. This may be compared to the metal ion effects observed in the hydrolysis of salicyl phosphate[2] at a metal ion–ester ratio of unity, which finds Cu^{2+} increasing k_{obsd} sevenfold at pH 5.1, and VO^{4+} increasing k_{obsd} 28-fold at pH 4.5. A more analogous system, 2-pyridylmethyl phosphate,[3] finds Cu^{2+} leading to an 18-fold rate acceleration at pH 4.93 ($[Cu^{2+}]:[substrate] = 1$).

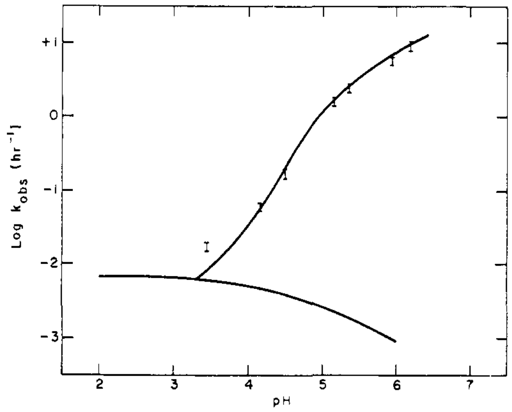

Figure 1. The pH–rate profiles for the spontaneous and Cu^{2+}-catalyzed (I) hydrolysis of 2-(4(5)-imidazolyl)phenyl phosphate; conditions: Cu_{total} (3.8×10^{-4} *M*), substrate (2.0×10^{-4} *M*), 55°, $\mu = 0.2$.

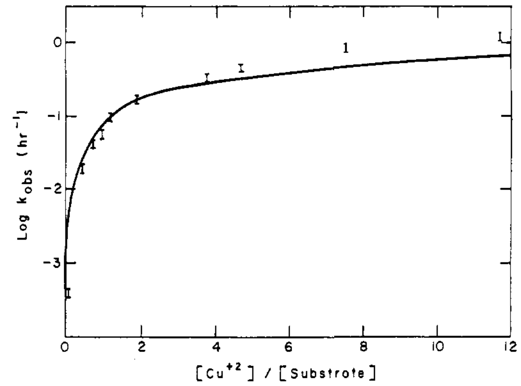

Figure 2. Log k_{obsd} *vs.* $[Cu^{2+}]$/[2-(4(5)-imidazolyl)phenyl phosphate] at 35°, pH 5.37, $\mu = 0.2$; substrate = 2.0×10^{-4} *M*.

The noncatalyzed reaction of I proceeds *via* pseudo-first-order kinetics, with concomitant formation of inorganic phosphate and 4-(2′-hydroxyphenyl)imidazole. This reaction, like those of most simple phosphate monoesters, is presumed to proceed through expulsion of a highly reactive monomeric metaphosphate species, which is quickly solvated.[4] The observed rate of hydrolysis of the monoanionic form of I is identical with that predicted by a structure–reactivity correlation for a series of phosphate monoester monoanions (based on a $pK_a = 8.62$ for a phenolic leaving group ortho to an imidazolium ion[5]). Thus, the noncatalyzed hydrolysis appears to be "normal," and not subject to any unusual steric or electronic effects.

The influence of Cu^{2+} on the observed hydrolytic rate of I increases with conversion of both the imidazolyl and phosphoryl moieties to their free base forms ($pK_{IM} = 5.8$; pK_{a_2} phosphate = 6.6) but decreases with the dissociation of $Cu(H_2O)_6{}^{2+}$ to $Cu(H_2O)_5OH^+$ ($pK_a \cong 5.0$). The theoretical curve of Figure 1 is generated from eq 1 where

$$v = k'[Cu(H_2O)_6{}^{2+}][I^{2-}] \qquad (1)$$

with $k' = 1.4 \pm 1.0 \times 10^6\ M^{-1}\ hr^{-1}$. A plot of log k_{obsd} *vs.* $[Cu^{2+}]:[substrate]$ is shown in Figure 2. The theoretical curve is calculated from eq 2 based on a scheme assuming preequilibrium formation of a reactive 1:1 ester–metal ion complex. Given the scheme

$$Cu^{2+} + I \overset{K}{\rightleftharpoons} Cu\text{-}I \xrightarrow{k_r} \text{products}$$

it can be shown that

$$k_{obsd} = \frac{Kk_rCu_T}{(Cu_TK + 1) + E_TK(1 - k_{obsd}/k_r)} \qquad (2)$$

where Cu_T and E_T are the initial stoichiometric quantities and the terms K and k_r are valued at $4.2 \pm 0.4 \times 10^2\ M^{-1}$ and $1.25 \pm 0.25\ hr^{-1}$, respectively. Deviation at higher metal ion:substrate ratios is attributed to the

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