Molecular dynamics[14] free energy perturbation[15] (MD-FEP) simulations were performed in order to obtain a free energy of solvation curve (ΔG_{sol}). Bond, angle, and torsion parameters were chosen to make the $OH^-\cdots CO_2$ complexes rigid, the atomic point charges came from the ESP fitting procedure, and the Lennard-Jones parameters were tuned so that the experimental free energies of solvation of HCO_3^-, OH^-, and CO_2 were reproduced.[12] The TIP3P water model was used,[16] and the nonbonded cutoff[14,15] was 8.0 Å. SHAKE[17] was used to constrain all bond lengths, and the time step was 1.5 fs. Periodic boundary conditions were employed,[14,15] and the temperature and pressure were maintained at 298.15 K and 1.0 atm.[14d] A typical run involved minimization of the system, followed by 45.0 ps of equilibration. Electrostatic decoupling[18] was used in conjunction with a 180-ps slow-growth MD-FEP simulation. Both forward and backward runs were conducted to estimate the error, and longer test runs (360 ps) indicated that the free energies using the 180-ps runs were converged. Sixteen runs were carried out to assemble the free energy profile, and ~250 water molecules were used at the starting point (1.45 Å) and ~800 water molecules at the last point (9.9 Å). Procedures similar to ours have been utilized by others to study reactions in solution.[11,19,20]

The resulting ΔG_{sol} and total G_{aq} profiles are shown in Figure 1. The maximum in the ΔG_{sol} profile occurs at 1.8 Å, which is also the minimum point for the dipole moment of the complex along the reaction path. G_{aq} has a pure solvation-induced free energy barrier of 17 ± 2 kcal/mol at $R = 2.0$ Å. We analyzed the original experimental data[2] and obtained an experimental free energy barrier of 13.5 ± 0.2 kcal/mol at 298.15 K.[21] In light of the fact that we neglected solvent polarization[22] in this charged system, the agreement between experiment and theory is remarkably good. The position of the solution-phase transition state is similar to that observed by others for the reactions of OH^- with formaldehyde and formamide.[19,20d] Our results indicate that the energetic cost for the reorganization of the water molecules as the reaction proceeds is on the order of 40 kcal/mol. This solvation penalty combined with the activationless gas-phase potential yields the observed free energy of activation barrier. An interesting experiment that could be done in order to verify this conclusion would be to measure the $CO_2 + OH^-$ reaction rate in solvents less polar than water. Our results predict that the reaction would have a higher rate constant under these conditions.

In this work we have obtained molecular-level insights into the hydration of CO_2 by hydroxide. Given this information, we can now better understand how CA catalyzes the hydration of CO_2. CA accelerates this reaction by providing a relatively anhydrous environment,[23] which is accomplished by placing the active site in a hydrophobic region.[3,4] Furthermore, the reaction only requires one OH^- (unlike the reaction of CO_2 with water, which apparently requires two water molecules[24]), and CA provides this at physiological pH with the aid of a zinc ion, which reduces the pK_a of zinc-bound water.[3,25] Finally, the CA active site places the CO_2 and OH^- in such a way that the reaction is greatly facilitated.[26] Whether CA renders the hydration of CO_2 by OH^- activationless like the gas-phase reaction is an interesting issue and is the subject of current investigation.[27]

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Supplementary Material Available: Table of derived parameters for hydroxide, carbon dioxide, and bicarbonate (1 page). Ordering information is given on any current masthead page.

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Modulation of the Chain Conformation of Spiropyran-Containing Poly(L-lysine) by the Combined Action of Visible Light and Solvent

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In a previous paper[1] we reported clear CD evidence that poly(L-glutamic acid) containing spirobenzopyran units in the side chains can undergo reversible random coil ⇄ α-helix conversions upon exposure to sunlight and dark conditions, alternately.

Here we describe the photochromic behavior of polypeptides obtained by attaching spirobenzopyran units to the side chains of poly(L-lysine). In contrast to the analogous polymers derived from poly(Glu), the spiropyran-modified poly(Lys) do not give photoresponse effects in pure hexafluoro-2-propanol (HFP). However, when appropriate amounts of triethylamine are added to the HFP solutions, exposure to sunlight produces reversible helix

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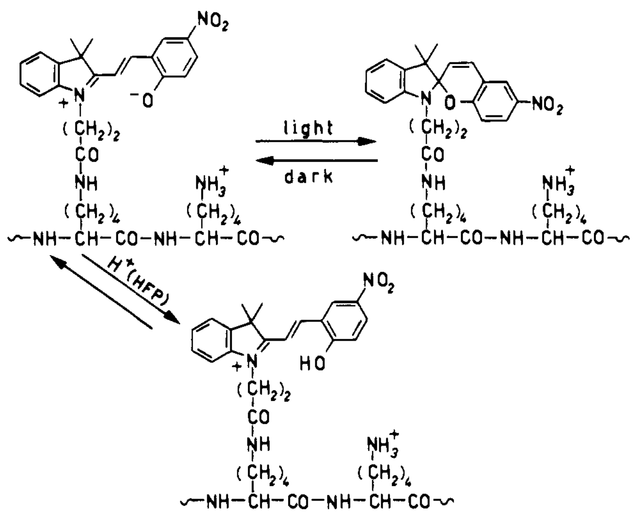

Figure 1. Negative photochromic reactions of spiropyran-modified poly(L-lysine) in HFP.

formation by the polypeptide chains; the combination of base and light effects allows modulation of the extent of the photoresponse.

1-(β-Carboxyethyl)-3,3-dimethyl-6′-nitrospiro[indoline-2,2′-[2*H*-1]benzopyran] (I) (2.6 mmol), prepared as described for the 1-(β-hydroxyethyl) derivative,[1,2] was reacted with pivaloyl chloride (2.6 mmol) and NEt_3 (2.6 mmol) in anhydrous dimethylformamide at 0 °C. The mixed anhydride was added to poly(Lys·HCl)[3] ($\bar{M}_v = 3 \times 10^5$) in DMF/water (10/1), the apparent pH was adjusted at pH 8 with NEt_3, and the solution was stirred at room temperature for 24 h. The polymer was precipitated in ethanol, any unreacted reagents were removed by repeated dissolutions and precipitations, and finally the polymer was washed with water. The dried polymer was soluble in HFP and contained 46 mol % spiropyran units, as determined by comparing the absorption spectrum with that of the *n*-butylamide derivative of I, taken as low molecular weight model compound II (spiro form: λ_{max} = 350 nm; ϵ_{max} = 11 200, in HFP).

Poly(Lys) and poly(Glu) containing spirobenzopyran side chains,[1] as well as their low molecular weight model compounds, exhibit intense "negative" photochromism in HFP.[4] In the dark the solutions are orange with two absorption maxima at about 470 (ϵ_{mol} = 31 700) and 370 nm (ϵ_{mol} = 32 000). Exposure to sunlight[5] is accompanied by prompt bleaching, with a shift of the absorption maxima to 353 (ϵ_{mol} = 11 200) and 270–272 nm (ϵ_{mol} = 16 200). The original spectrum is reversibly restored on stopping illumination. Decay in the dark at 25 °C follows first-order kinetics for the model compound II with a rate constant of 5.7 $\times 10^{-3}$ min^{-1} and a half-life of about 122 min. For the polymer, the kinetics slightly deviates from a monoexponential and a biexponential decay; the time necessary to restore half of the original absorbance is about 80 min.[6]

The perfect analogy of these reversible processes with those observed in spiropyran-modified poly(Glu) suggests the occurrence of similar photochromic reactions. Accordingly, HFP stabilizes the colored ionic merocyanine structure, while irradiation gives the colorless spiro structure. Moreover the absorption spectra, and particularly the presence of the maximum at 370 nm, are indicative of a protonated species formed between the zwitterionic form and HFP,[4,7] with this last acting as an acid (pK_a = 9.30)[8] (Figure 1).

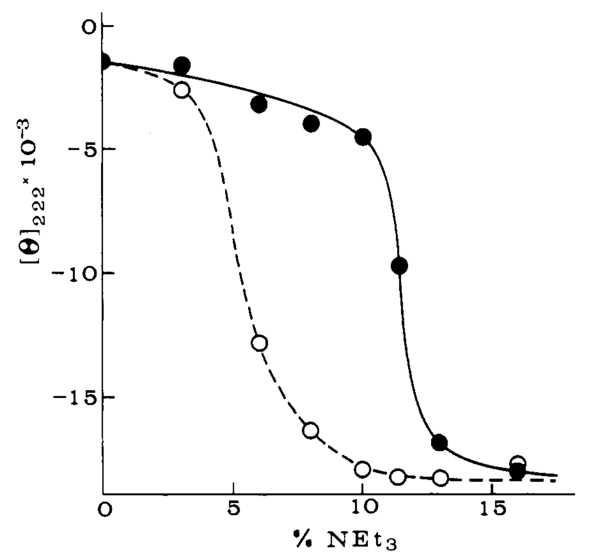

Figure 2. Variation of ellipticity at 222 nm with % NEt_3 (v/v), at 25 °C, for poly(L-lysine) containing 46 mol % spiropyran units in HFP/NEt_3: (—) dark adapted; (···) irradiated.

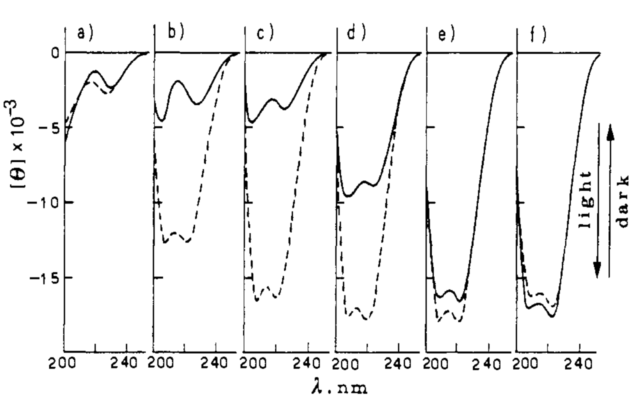

Figure 3. Effect of irradiation on CD spectra in various HFP/NEt_3 solvent mixtures, at 25 °C (*c* = 1.13 g/dL), for poly(L-lysine) containing 46 mol % spiropyran units: (—) dark adapted; (---) irradiated samples. % NEt_3 (v/v): (a) 3%; (b) 6%; (c) 8%; (d) 10%; (e) 13%; (f) 16%. Molar ellipticity values are based on the mean residue molecular weight.

In pure HFP, the CD spectra are consistent with those of random coil polypeptide chains and the photoisomerization reaction does not affect the polymer conformation at all. Addition of triethylamine to the HFP solution induces the coil → helix transition, but the amount of base necessary to induce the transition is different for the dark-adapted sample (15% v/v) with respect to the irradiated one (3% v/v) (Figure 2). Thus, at any composition in the range 3–15% v/v NEt_3, exposure to sunlight produces reversible variations of the helix content. Combination of the effects due to the photochromic behavior with appropriate amounts of NEt_3 allows modulation of the extent of the photoresponse (Figure 3). In a 93/7 HFP/NEt_3 mixture, up to 40% of helix content was induced by visible-light (575–525-nm) irradiation of the random coil polypeptide.[9,10]

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This result can be interpreted by assuming that in pure HFP the conformation is determined by the unmodified Lys side chains protonated by the acid solvent; as a consequence, the polypeptide assumes a coil conformation which is not affected by the isomerization of the photochromic groups. Addition of a moderate amount (3–15%) of NEt$_3$ removes protons from Lys side chains, whose basicity depends on the isomeric composition of the photochromic moieties.[11] In the range between the transition curves of the dark-adapted and irradiated sample (Figure 2), the chain folding $\rightleftarrows$ unfolding is then controlled by the isomerization of the photochromic side chains: when these last are in the charged merocyanine form, the polypeptide chains are in the random coil arrangement; photoconversion to the apolar spiropyran form causes the macromolecules to assume a helical conformation. At NEt$_3$ content greater than 15%, the high concentration of a NEt$_3$·HFP saline complex[12] can probably exert a shielding effect of the charged side chains, allowing the polypeptide to stay in the helical conformation at any photoisomeric composition.[13]

The subject system provides a well-defined example of the combined action of light and environment on the secondary structure of polypeptides. Thus it can be considered as a macromolecular model resembling the behavior of naturally-occurring photoreceptors.[14]

Registry No. I, 55779-26-5; I (*n*-butylamide), 139168-54-0; poly(Lys·HCl) homopolymer, 26124-78-7; poly(Lys·HCl) SRU, 28575-12-4.

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Role of d and f Orbitals in the Geometries of Low-Valent Actinide Compounds. Ab Initio Studies of U(CH$_3$)$_3$, Np(CH$_3$)$_3$, and Pu(CH$_3$)$_3$

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While organoactinide compounds are traditionally characterized by high oxidation states and coordination numbers, the synthesis, chemistry, and electronic properties of low-valent actinide complexes have been receiving greater attention in recent years.[1-4] Specific examples of complexes in the AnL$_3$ family are represented by U[N(SiMe$_3$)$_2$]$_3$,[1] U[CH(SiMe$_3$)$_2$]$_3$,[2] and Np and Pu analogues,[3] for which cases the ligands adopt a pyramidal arrangement around the actinide. In this communication, we report the results of one of the first studies of such low-valent complexes to be carried out using ab initio electronic structure techniques. Related molecules include lanthanide species of the form LnX$_3$, which also adopt pyramidal geometries[5] and which have been the subject of semi-empirical theoretical investigations.[6] Transition metal MX$_3$ species, by contrast, can exhibit either planar or pyramidal forms, depending on the nature of the metal and the ligand.[7]

Table I. Calculated Structural Parameters for An(CH$_3$)$_3$ Complexes

compd	R (Å)	α (deg)[a]	β (deg)[a]	E_{rel} (kcal/mol)[b]
	Pyramidal Structures (**1**)			
UMe$_3$	2.543	113.1	105.6	0
NpMe$_3$	2.536	111.7	107.2	0
PuMe$_3$	2.523	110.2	108.7	0
U[CH(SiMe$_3$)$_2$]$_3$ exptl[c]	2.48	111.2	107.7	
	Planar Structures (**2**)			
UMe$_3$	2.586	90[d]	120[d]	3.7
NpMe$_3$	2.577	90	120	3.3
PuMe$_3$	2.558	90	120	2.4

[a] The C–An–C angle is denoted by β and the angle between the An–C bond and the 3-fold axis is denoted by α. [b] $E_{\mathrm{rel}} = E(\text{planar}) - E(\text{pyramidal})$. [c] Reference 2. [d] Angles α and β held fixed for planar structures.

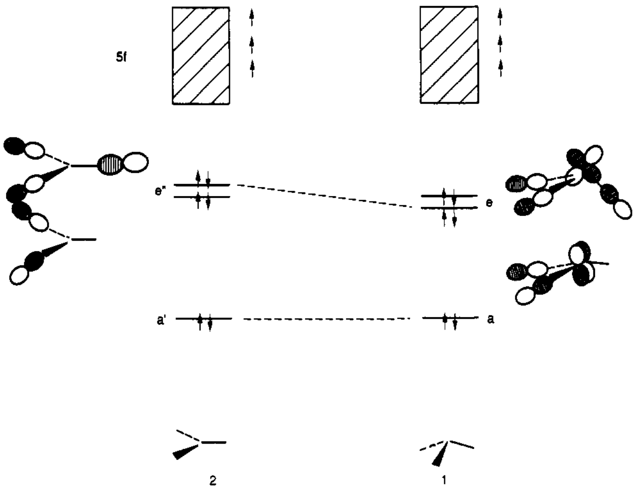

Figure 1. Schematic diagram of the changes in the bonding orbitals in UMe$_3$ for planar (**2**) and pyramidal (**1**) structures.

Complete active space (CAS-SCF) calculations[8] were carried out in a valence double zeta basis set employing relativistic effective core potentials (RECPs) for the actinide atoms.[9,10] In this type of calculation, the electronic structure for UMe$_3$, for example, can be described in terms of the open-shell configuration $[\varphi_1\bar{\varphi}_1 \ldots \varphi_n\bar{\varphi}_n)$ [5f^3], where φ_1 through φ_n denote the doubly oc-

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