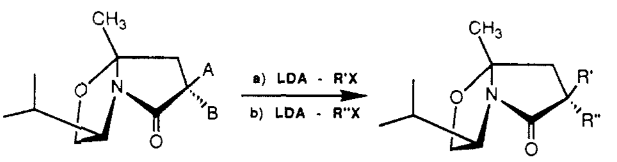

1 (A = B= hydrogen)
2 (A or B = methyl, B or A = hydrogen)

Figure 1. Alkylation of bicyclic [3.3.0] lactams.

counterion). The transition state (ts) for each reaction was located as a saddle point on the reaction surface and unequivocally identified by a FORCE calculation yielding one negative force constant with the major vibration along the axis of the S_N2 reaction. The endo ts was found to have a heat of formation of −69.9 kcal/mol while the exo was found to have a heat of formation of −70.2 kcal/mol. Within calculation error, these are essentially the same.

Since Meyers has observed generally higher selectivity in the addition of the second alkyl group, we considered the possibility that facial bias might be more manifest in these cases. The transition states for the endo and exo addition of methyl iodide to the monomethylated lactam **2** were located and found to have identical heats of formation at −75.9 kcal/mol. In looking for a possible steric bias, we also considered the modification to **1** where the ring juncture methyl group was replaced by hydrogen. The ts for the exo methylation was located and has a heat of formation of −58.1 kcal/mol. The corresponding endo ts has a virtually identical heat of formation of −58.4 kcal/mol. We therefore conclude that *no portion of the structural framework of these lactam enolates exerts any significant steric or electronic control on the diastereofacial selectivity observed in the alkylation reactions of these bicyclic lactams.*

We next considered the possibility that the observed diastereoselectivity stemmed from factors external to the enolate structure. In particular, if the counterion (lithium) exhibits preference for one of the enolate faces, it could interfere with the approach of an electrophile to that face. In order to probe this, an unsolvated lithium was included in the calculations.[10,11]

If the oxygen–lithium bond in the enolate of **1** is allowed to completely optimize, the lithium preferentially bridges the enolate carbon and oxygen atoms. This may result from the artificial lack of external solvation, since physical studies of lithium enolates show that the most stable species involves little interaction with the enolate carbon.[12] We do, however, notice an exo preference of 0.8 kcal/mol with the lithium out of plane by approximately 33°.

MOPAC[13] (MNDO) calculations involving lithium species solvated with 12-crown-4 resulted in transition-state geometries verified by FORCE calculations. The transition state for the endo addition of methyl iodide to the solvated lithium enolate of **1** was 0.7 kcal/mol more stable than the corresponding exo transition state. The same result was found for the transition states involving methyl iodide addition to the solvated lithium enolate of **2**, i.e., the endo transition state was found to be 0.7 kcal/mol more stable than the exo transition state. This difference clearly shows a preference for endo addition.

Assuming that the change in entropy is the same for each endo and exo reaction pair, a difference of 0.7 kcal/mol in the heat of formation for reactions run between −100 and −78 °C corresponds to a product ratio of 88:12. Thus, a great deal of the selectivity seen in these reactions can be explained solely through consideration of preferential exo solvation, presumably due to favorable electrostatic interactions between the lithium and the pyramidalized nitrogen.[14] In addition, the 12-crown-4 case is the one expected to give the lowest selectivity since the solvation of the lithium involves one of the least sterically encumbered solvation shells possible. In a solution enolate, in which the steric effects due to solvation are much greater, the facial bias could be more substantial. These results seem to confirm the conclusion that the diastereofacial selectivity results from the nature of the enolate solvation.

Acknowledgment. We thank Professor Albert Meyers of Colorado State University for helpful discussions. We also acknowledge the financial support of the National Science Foundation in the purchase of a Silicon Graphics Personal Iris.

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Enhanced Photoacidities of Cyanonaphthols

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Received June 18, 1990
Revised Manuscript Received August 24, 1990

That the acidities of aromatic alcohols are enhanced upon photoexcitation has been recognized for several decades and has been the basis for several mechanistic and technological applications.[1] Among these are photopolymerization,[2] photodepolymerization,[3] pH jump experiments,[1d,4] and biological probes of the environment around proteins[5] and micelles.[6] Most of these studies have concentrated on the commercially available 1- and 2-naphthols, their sulfonated derivatives, and 8-hydroxy-1,3,6-pyrenetrisulfonate. Förster pK_a values[7] of substituted phenols have been determined,[8] but for many applications phenols are not suitable because their absorption frequency is too high and fluorescence is weak. Naphthols exhibit excited-state pK_a ($pK_a{}^*$) values in the range 0–3 and thus limit proton-transfer studies to aqueous solvents.[1] In fact, previous studies of naphthol derivatives in aqueous alcohols[9] and in the gas phase[10] indicate that a cluster

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Table I. Properties of Cyano-2-naphthols[a]

	2-naphthol	**5CN2**	**6CN2**	**7CN2**	**8CN2**
mp, °C		202–3	163–4	185.5–6.5	194–5
λ_{max} (neutral, abs)		337	338	350	342
λ_{max} (neutral, em)		419	380	405	424
λ_{max} (anion, abs)		371	360	380	382
λ_{max} (anion, em)		522	445	503	515
pK_a (H_2O)[b]	9.45	8.75	8.40	8.75	8.35
pK_a^* (Förster)[c]	2.8[e]	−1.2	0.2	−1.3	−0.4
pK_a^* (fluorescence)[d]	2.8[e]	1.7	0.5	2.0	0.7 (0.8)[f]
τ, ns (neutral, Me_2SO)[g]		2.6 ± 0.1	4.8 ± 0.1	6.0 ± 0.1	4.2 ± 0.1
τ, ns (anion, rise)[g]		2.50 ± 0.15	5.0 ± 0.5	6.5 ± 0.5	4.2 ± 0.1
τ, ns (anion, decay)[g]		25.9 ± 0.1	8.0 ± 0.5	38.5 ± 0.5	15.1 ± 0.2

[a] Spectral and acidity data are for 1×10^{-4} M aqueous solutions. Lifetime data are in Me_2SO. [b] From absorption titration. [c] Calculated from emission maxima using the Förster cycle. [d] From fluorescence titration. [e] Literature value (ref 1b). [f] Literature value (ref 16). [g] Errors represent standard deviations from "best fit" deconvolutions.

of four or more water molecules is necessary for excited-state proton transfer. This, along with the previous observation that proton transfer does not occur in Me_2SO,[11] suggests that excited-state proton transfer can only occur by a Grotthuss chain mechanism.[11,12] Such conclusions, however, may be based upon the readily available naphthols, which are only weakly acidic upon photoexcitation. Comparatively little effort has been directed toward the design and synthesis of substituted naphthols with high acidities suitable for nonaqueous environments.

Weller studied a series of 2-naphthol sulfonates.[13] The sulfonate group, with a σ value of 0.09,[14] is not the best electron-withdrawing group, and it is known that several sulfonate-substituted naphthols and 8-hydroxy-1,3,6-pyrenetrisulfonate do not transfer protons to alcohols[9b,e] or Me_2SO.[11] Although the nitro substituent is one of the most electron withdrawing groups, nitro-substituted aromatic compounds do not fluoresce,[15] which indicates that if deprotonation occurs in the excited state, the anion singlet state has a relatively short lifetime and would not be suitable for use as either an indicator or a catalyst. One cyanonaphthol, 8-cyano-2-naphthol, has been investigated and found to have a relatively low pK_a^* value of 0.8,[16] compared to 2.8 for 2-naphthol.[1] We have synthesized a series of cyano-2-naphthol compounds and found that, as expected, aqueous pK_a^* values were reduced compared to that of 2-naphthol. More importantly, these compounds exhibit efficient photopromoted proton transfer to neutral nonaqueous solvents, such as Me_2SO.

The greater photoacidity of 1-naphthol over 2-naphthol has been attributed to population of the ^1L_a state in the former at the expense of the ^1L_b state, whereas in 2-naphthol the states are more nearly degenerate.[17] Both states are characterized by intramolecular charge transfer to the distal ring, but the former exhibits increased charge density at C-5 and C-8, as characterized by protonation at those positions within the lifetime of the excited state.[18] Thus substitution at those positions by electron-withdrawing groups should lower the energy of the ^1L_a state in 2-naphthol and further enhance the excited-state acidity. In order to test this hypothesis, we synthesized 2-naphthols substituted in the distal ring by the cyano group, i.e., 5-cyano-2-naphthol (**5CN2**), 6-cyano-2-naphthol (**6CN2**), 7-cyano-2-naphthol (**7CN2**), and 8-cyano-2-naphthol (**8CN2**). In each case, the naphthol was readily obtained by treatment of a methoxytetralone (e.g., 6-methoxy-1-tetralone for **5CN2**) with trimethylsilyl cyanide, elimination with $POCl_3$/pyridine, aromatization with sulfur/Pd–C,[19] and demethylation with sodium cyanide/Me_2SO.[20]

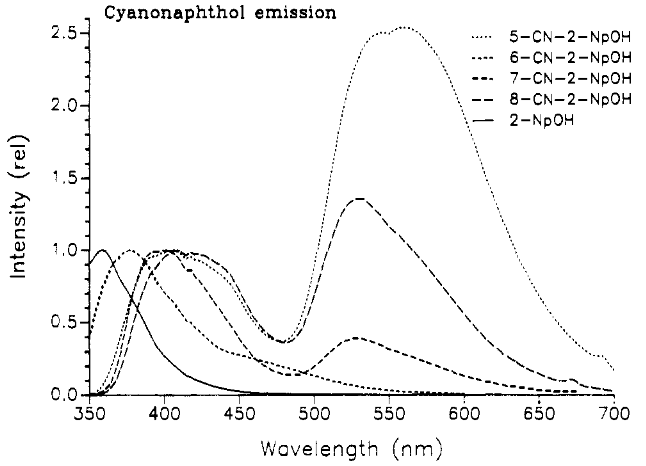

Figure 1. Emission from 2-naphthol and cyano-2-naphthols, normalized to neutral emission.

Absorption and emission studies as a function of pH revealed, as expected, significant Förster shifts and calculated excited-state acidities approaching over 4 pK_a units below that of 2-naphthol (see Table I). First approximations of the pK_a^* values in water were obtained from the inflection point of fluorescence titration curves, which yielded acidities significantly lower than the Förster acidities. As Krishnan, Lee, and Robinson[21] have pointed out, failure of the Förster formalism is expected when acidities approach 0 and entropic factors predominate.

In solutions acidic enough to prevent excited-state dissociation, the neutral fluorescence of these cyanonaphthols was largely quenched. This behavior, which is similar to that observed for 1-naphthol,[18b,d] indicates that dynamic quenching of neutral and anion fluorescence occurs, and as is the case for 1-naphthol, the pK_a^* values measured by fluorescence titration are probably higher than the true equilibrium values. Even so, the decrease in the excited-state pK_a value due to the cyano substituents was significantly greater than the decrease in ground-state pK_a values, reflecting the greater importance of the anion charge-transfer state upon excitation. Perhaps most dramatic were the emission studies in Me_2SO. Unlike 2-naphthol, the cyanonaphthols exhibited significant anion emission, identified by comparison with spectra of ground-state anions, indicating excited-state proton transfer to solvent (see Figure 1). This emission was particularly dramatic in the case of 5- and 8-cyano-2-naphthol, presumably reflecting population of the more acidic ^1L_a state. Excitation spectra in-

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dicated that all anion emission involved excitation of the neutral naphthols.

Time-resolved single photon counting fluorescence spectroscopy in Me_2SO enabled us to relate the steady-state observations to dynamic phenomena. In each case, the excited-state neutral lifetimes were attenuated and were within experimental error of the conjugate base rise times, indicating that deprotonation was the major source of neutral decay. Both **5CN2** and **8CN2** exhibited higher neutral decay rates than **6CN2** or **7CN2**, although the effect was not as dramatic as in the steady-state results due to the anomalously short lifetime for the 6-cyano-2-naphtholate anion.

By extending the range of excited-state acidities, cyanonaphthols provide further opportunities for proton-transfer studies in nonaqueous solvents and may provide entry into new photopolymerization catalysts. The observation that excited-state proton transfer from cyanonaphthols to Me_2SO solvent can occur without benefit of a Grotthuss chain-transfer pathway if the excited-state acidity is high enough indicates that other mechanisms of excited-state proton transfer are possible. Further studies are currently underway.

Acknowledgment. Support of this work by the National Science Foundation through Grant No. CHE8805577 is gratefully acknowledged. We also thank Prof. Kirk Schanze for use of his fluorescence lifetime apparatus and Mr. Tom Perkins for expert assistance.

Effect of Reactant Rotation on Hydrogen Atom Transfer

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Received February 26, 1990

We report gas-phase quasiclassical trajectory calculations of reaction cross sections for the transfer of a light atom between two heavier atoms on potential energy surfaces which possess a barrier to reaction. It is found that reactant rotational energy is more efficient at promoting reaction than either translation or vibration, regardless of the reaction energetics.

Investigation of the role played by each possible mode of reactant energy in enhancing the rates of elementary gas-phase exchange reactions has been an active area of research for the last three decades.[1-7] In particular, the propensity rules for comparing the relative efficacy of translation and vibration have been exhaustively investigated both experimentally and theoretically[1,2] and are summarized in the so-called "Polanyi rules".[1,2,8] The possible role of rotational energy in enhancing reaction rate has not been studied in comparable detail; indeed it is often summarily dismissed as ineffective. The most recent review of rotational effects[9] suggests that, in the most optimistic case, rotation may be comparable to translation in enhancing reaction, but that it will usually be much less effective than vibration. (However, one case[10]—a light-atom transfer—where rotation is comparable to vibration was reported.) Intuitively, it is often felt that rotational motion is "perpendicular" to the reaction coordinate and hence cannot assist in crossing the barrier to reaction. However, recent theoretical work[11,12] has clearly shown that rotational motion can couple to translation if there is significant stretching of the bond under attack. Several calculations have been published that confirm that rotation can increase reaction cross sections.[9,13-18]

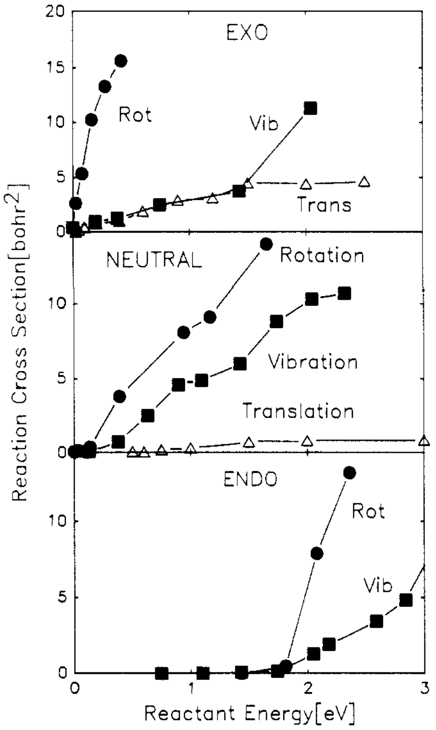

Figure 1. Reaction cross section as a function of reactant energy for the hydrogen-transfer reaction, A + HB → AH + B, on three different potential energy surfaces. Atoms A and B both have mass 19 amu; H has mass 1 amu. Note that translational energy is ineffective on the ENDO surface.

The transfer of a light atom has traditionally[19,20] served as a model for hydrogen atom transfer and (although less appropriately) for proton and hydride transfer. We have compared the relative effectiveness of reactant translational, vibrational, and rotational energy on an exoergic, and endoergic, and a thermoneutral potential surface. For our model exoergic surface we used the potential number 5 of Muckerman,[21] designed for $F + H_2$, and for our endoergic system we used the $I + H_2$ potential of Perry et al.[22] Neither of these potentials is now considered to be of chemical accuracy. However, they have the advantage of being easily programmed, are readily accessible, and have already been the subject of several trajectory studies. For the thermoneutral system we used the accurate LSTH potential[23] for $H + H_2$.

The reaction cross sections for the three systems are shown as a function of energy in Figure 1. In all cases, the zero of internal

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