the endocyclic double bond in **1b** to initiate nucleophilic attack at C-7 during heterolysis of the allylic ester. The influence of the endocyclic double bond on the kinetically controlled product distribution is even more dramatic. Both **2b** and **3b**, which lack the double bond, yield virtually identical product mixtures, in which the primary alcohol **2a** predominates over the tertiary alcohol **3a** by a factor of 2:1. Since the equilibrium distribution (acid catalysis) of **2a** and **3a** favors the tertiary alcohol by a factor of at least 12:1, the observed product distribution is clearly kinetically controlled and must derive from nucleophilic attack by water on a common cation. The predominance of primary product would seem to indicate that, unlike most unsymmetrically substituted allylic cations,[3] this cation is possessed of greater positive charge density at the primary than at the tertiary position.

In sharp contrast, the product mixture derived from solvolysis of **1b** consists largely of the tertiary alcohol, 7-vinyl-*anti*-7-norbornenol (**4a**), which predominates over the primary alcohol **1a** by a factor of at least 43:1. No 7-vinyl-*syn*-7-norbornenol (**5a**) could be detected in the product mixture. Clearly the intermediate involved in solvolysis of ester **1b** must distribute a much greater percentage of the positive charge density to C-7 than does the intermediate derived from **2b** and **3b**. In addition, the absence of **5a** from the **1b** solvolysis product mixture is strongly reminiscent of results obtained with the 7-norbornenyl cation,[7] for which there is strong evidence for interaction between the endocyclic double bond and the vacant p orbital at C-7, but contrasts markedly with the lack of stereospecificity observed in the product distribution from the 7-*p*-anisyl-7-norbornenyl cation,[8] in which interaction between the double bond and the electron-deficient center appears to be absent. Both observations point to the interaction of the π electrons of the endocyclic double bond with the electron-deficient allylic π system in the cation resulting from ionization of ester **1b**. The fact that the rate of solvolysis of **1b** is accelerated by a factor of 18.8 strongly suggests that this interaction is already well developed in the transition state for bond heterolysis. For these reasons, we conclude that the endocyclic double bond does, indeed, participate during solvolysis of ester **1b** in a manner directly analogous to the behavior of the nucleophile in an S_N2' displacement reaction.

The solvolytic behavior of esters **4b** and **5b** is of interest in its own right and will be discussed elsewhere.

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A Kinetic Probe for Basicity and Its Application to Mixed Aqueous Solvents[1]

Sir:

The cyanocarbons constitute a class of RC–H acids of high stability and with widely varying acid strength.[2] Recent work with 1,4-dicyanobutene-2, a cyanocarbon acid of pK = 21, has demonstrated that the detritiation of a tritium-labeled species shows general base catalysis in the Brønsted sense which, along with other properties, establishes that the detritiation step measures the rate of proton removal from the weak acid.[3] Studies have now been made with two stronger acids of this series, malononitrile and *t*-butylmalononitrile. The detritiation of tritium-labeled molecules again exhibits general base catalysis. However, these acids are sufficiently strong (pK values of 11.2[4,5] and 13.10,[6] respectively) that, in addition to measurable detritiation rates with general bases and with hydroxide ion, there is an easily measured reaction with the solvent water. The consistency of the rate of this water reaction with that of other bases and the normal behavior of the rate of the reverse reaction make it clear that in this reaction water is acting as a base species attacking the acidic proton of the molecule and that the rate of detritiation, except for an isotope effect, measures the rate of this proton removal. At 25° the first-order rate coefficients for detritiation in aqueous solution by the "water" path are 3.2×10^{-4} sec^{-1} for *t*-butylmalononitrile and 8.5×10^{-3} sec^{-1} for malononitrile.

The existence of this slow reaction in which the solvent water is acting as a base offers the opportunity for a kinetic probe of the basicity of mixed solvents in which water is one component. This basicity probe has now been applied to three solvent mixtures: water–dioxane, water–ethanol, and water–dimethyl sulfoxide.

All studies were made with tritiated *t*-butylmalononitrile in solutions which were 0.001 *M* in hydrochloric acid, previous work having shown that at this acidity only the water reaction occurs; *i.e.*, the hydroxide ion reaction is negligible and there is no acid catalysis. The experimental procedure was to let the reaction proceed at 25°, remove aliquots at intervals, extract the *t*-butylmalononitrile and subject it to scintillation counting. Rates were reproducible to ±3%. The results are given in Figure 1 as plots of logarithm of the observed relative rates for detritiation *vs.* mole fraction of water in the two-component solvent system.

The gross over-all trend for all three systems is that, as expected, the replacement of water by the nonaqueous component leads to decreased basicity. However, there are two notable features. One is the very considerable specificity; the change in basicity with mole fraction of nonaqueous component is significantly different for each of the three solvent mixtures. The second remarkable feature is the rate maximum which is exhibited by each of the three systems, implying that initial addition of the nonaqueous components to water causes an *increase* in basicity.

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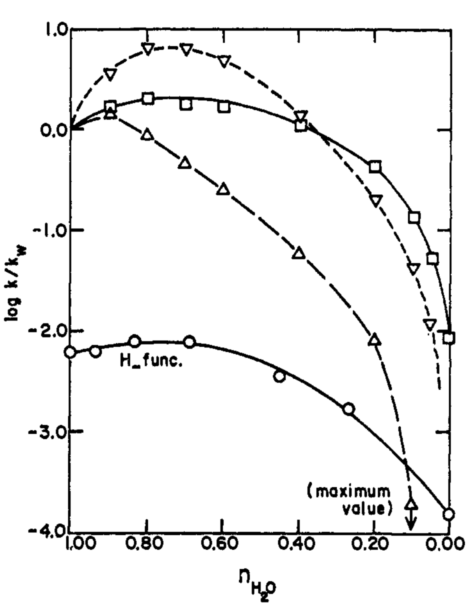

Figure 1. Dependence of relative rates of detritiation of *t*-butylmalononitrile-1-*t* on mole fraction of water for three solvent systems: water–dimethyl sulfoxide, ▽; water–ethanol, □; water–dioxane, △. The acidity function H_- for the water–ethanol system is plotted for comparison on a displaced scale.

It is tempting to interpret the initial rate acceleration which occurs upon addition of the nonaqueous component as due to the effect of these species on the structure of water. In terms of an explicit two-component interpretation of the structure of water, *i.e.*, "free" and bound water, of the kind discussed recently, for example, by Walrafen[7] and by Franks,[7] one could discuss the observed enhanced basicity qualitatively by postulating that the effect of the nonaqueous addition was initially to increase the amount of unbound water, with the further assumption that it is this component which is involved in the reaction with the tritiated acid species. However, other less specific considerations of structure change could also explain the rate acceleration. Since a number of thermodynamic and other properties of mixed water–nonaqueous solvent systems are known to go through maxima,[8,9] perhaps the kinetic maxima observed here are not surprising. The results do, however, demonstrate the existence of a probe of a somewhat different sort for studying these systems and suggest some significant further experiments.

Bates and Schwarzenbach[10] have studied the equilibrium acid–base properties of one of these solvent mixtures, water–ethanol, by several techniques. The set of systems of interest for comparison with the present studies contained 0.002 *M* HCl and 0.008 *M* NaCl; *i.e.*, the hydrogen ion concentration was held constant at a value close to that used here. Four different acidity functions were measured: two indicator acidity functions, H_0 and H_- and two electrometric functions, pH (conv) and $pW^{\ominus}$. Of these four, only one function, H_-, reasonably parallels the present kinetic measurements of basicity. This function is plotted in Figure 1 on a displaced scale for comparison, and it is evident that there is approximate parallelism with the kinetic data in the same solvent system.

Using BH and B^- for the two forms of the H_- indicator, 2,6-dinitro-4-chlorophenol, and using RCH and M* for the malononitrile and the transition state for hydrogen ion removal, the value of the activity coefficient ratio, $f_{BH}f_{M^*}/f_{RCH}f_{B^-}f_{H^+}$, is seen to be approximately independent of solvent composition. This is perhaps plausible in the high ethanol region since B^- and H^+ are probably extensively present as ion pairs and M* is itself essentially an ion pair of the type $RC^- \cdots H^+$. The rough parallelism between rate and acidity function in the high water region is, however, rather more surprising. Further solvent systems are under study.

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The Contribution of Circular Dichroism below 185 mμ to the Optical Rotatory Dispersion of Cytochrome b_2

Sir:

The optical rotatory dispersion (ORD) function of a substance, expressed as the molar rotation, $[M]_\lambda$, can be calculated[1] by means of the Kronig–Kramers relation (eq 1) from the circular dichroism (CD) function, in

$$[M]_\lambda = \frac{2}{\pi}\int_0^\infty [\Theta]_{\lambda'}\frac{\lambda'}{\lambda^2 - \lambda'^2}\,d\lambda' \qquad (1)$$

the form of the molar ellipticity, $[\Theta]_\lambda$. If the CD spectrum obtained in the observable range of wavelength, λ, extending down to a lower limit of approximately 185 mμ, gives on integration an ORD spectrum differing significantly from the observed spectrum, it is to be concluded that one or more bands of appreciable rotational strength lie outside the observable spectral region.

Schechter and Saludjian[2] reported that the ORD function for ferricytochrome *c* calculated from its CD spectrum lies below the observed function and concluded that the missing bands situated below 190 mμ are due to heme transitions. We have made similar observations[3,4] on another hemoprotein, cytochrome b_2. This enzyme contains one flavin mononucleotide and one protoheme group per 80,000 molecular weight. As shown by the data in Figure 1, obtained with a sample of enzyme having an activity[5] of 200 sec^{-1}, this protein exhibits a profusion of Cotton effects and CD extrema in the visible and ultraviolet regions of the spectrum. Both the ORD and CD data below 260 mμ, when interpreted in the usual manner,[6] indicate an apparent α-helical content of 17%.

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