mination agent consisting of bromine adsorbed on 5-Å molecular sieves.[1] This selective reagent was claimed to be capable of differentiating between a double bond located in a sterically unhindered linear side chain and one in an inaccessible position, such as one within an alicyclic ring. As evidence the authors presented two observations: (1) the selective bromination of styrene in the presence of cyclohexene, and (2) the absence of bromoacetate product when run in the presence of a small amount of acetic acid.

It is most difficult to accept the interpretation of these observations as proposed by the authors, in view of the well established fact that 5-Å molecular sieves have pore openings too small to permit entry of branched hydrocarbons.[2] Accordingly, we have observed that secondary bromides such as 2-bromobutane are *not* sorbed inside 5-Å sieves at room temperature;[3] furthermore, if bromination were occurring within the sieve, the products would be retained by the sieve. We believe the observations reported can be most satisfactorily explained on the basis of the well-known dichotomy associated with olefin halogenation in general, namely the availability of competitive ionic and free-radical pathways. In the case of olefin chlorination, Poutsma[4] clearly demonstrated this duality of mechanism and identified the characteristics of each pathway. Bromination of olefins in low polarity media is also very sensitive to acceleration by light, hydrogen halides, and water and can be greatly affected by glass or silica surfaces.[5] Under ionic conditions, cyclohexene would be expected to halogenate faster than styrene, since styrene has been reported to brominate only at approximately the same rate as terminal olefins.[6] The reverse may be expected under free-radical conditions since thiyl radicals, which are considered to have reactivities similar to bromine atoms on the basis of the established bond dissociation energies of HSR and HBr, are known to add some 60 times faster to styrene than to cyclohexene.[7]

We have observed that, under competitive conditions in CCl_4 at room temperature, cyclohexene does in fact brominate ~5 times as rapidly as styrene. However, when a 10^{-2} M Br_2 solution was added dropwise to an equal volume of a CCl_4 solution, 0.02 M in styrene and in cyclohexene, while being illuminated by a photoflood lamp, the yield of 1,2-dibromoethylbenzene greatly exceeded (>10:1) that of 1,2-dibromocyclohexane. The free-radical nature of this reaction, performed in the presence of atmospheric oxygen, was confirmed by the detection of a third product, α-bromoacetophenone, formed by oxygen trapping of the intermediate β-bromobenzyl radical. Further support for a free-radical mechanism under these bromination conditions can be found in the observation of two other products by GC-mass spectroscopy: 1-chloro-2-bromoethylbenzene[8] and a trace amount of 3-bromocyclohexene. The former was formed by chlorine atom abstraction from CCl_4 by the β-bromobenzyl radical, while the latter undoubtedly derived from allylic hydrogen atom abstraction by radicals.

In view of these observations confirming the duality of mechanisms for olefinic halogenations, we believe the unusual reactivity of styrene reported for molecular sieve supported bromine to be due to free-radical reactions proceeding slowly in homogeneous solution with the small amount of soluble bromine in equilibrium with sorbed bromine. The absence of bromoacetate addition products is consistent with a free-radical mechanism, as such products would only be formed under ionic conditions.[9] The presence of 5-Å molecular sieves serves both to reduce drastically the concentration of bromine in solution and to initiate a free-radical chain reaction, which is not unexpected in view of its reported ability to catalyze the anti-Markownikoff addition of HBr to terminal olefins.[10]

Most convincing was the additional observation that, in the competitive 5-Å-supported bromination of cyclohexene and 4,4-dimethylhexene-1, a terminal olefin capable of partially penetrating the pores of the molecular sieve like styrene, but one much less susceptible to free-radical addition, the yield of dibromocyclohexene exceeded that of dibromodimethylhexane by a factor of 10. Since a similar ratio was observed in the absence of any sieves, the ionic bromination of olefins clearly is unaffected by the addition of 5-Å molecular sieves.

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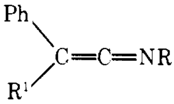
Rate-Determining Proton Transfer to Ketenimines

Sir:

We report here that *N*-alkylketenimines **1** undergo rapid reaction in aqueous solution to form the corresponding amides **5**, the slow step at all pH's being a proton transfer from acidic catalysts or the solvent. The ketenimine system can therefore even abstract a proton from such a weakly acidic species as water.

Ketenimines are heterocumulenes structurally related both to allenes and ketenes. Although chiral, they have not been resolved because of rapid nitrogen inversion.[1] They are highly reactive[2] undergoing inter alia cycloadditions and reactions with electrophilic and nucleophilic reagents and because of this they are usually generated and further reacted in situ.[3] We



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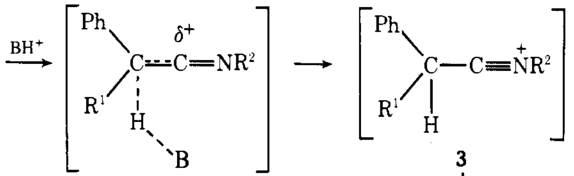

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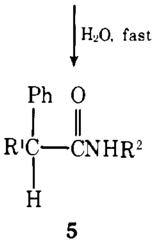

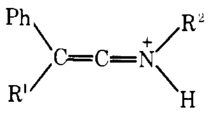

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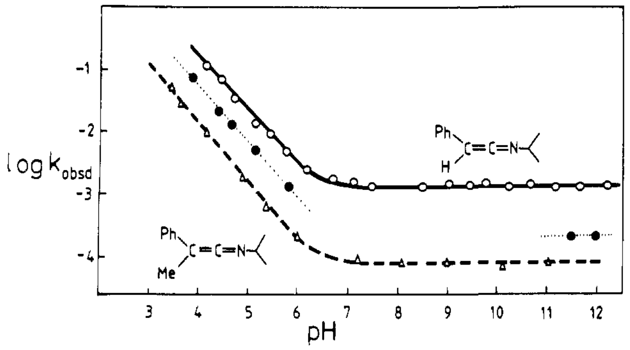


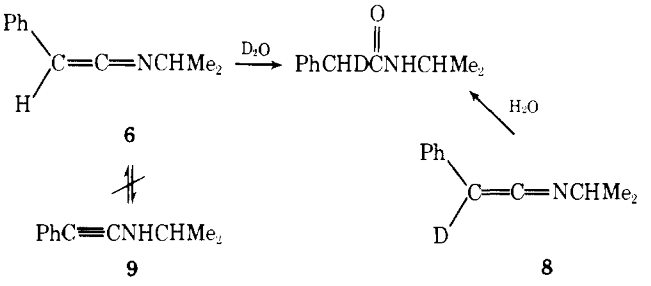
Figure 1. Log plot of the observed rates (in s^{-1}) of hydration of the ketenimines (**1** at 25 °C: $R^1 = H$, $R^2 = CHMe_2$ in H_2O (○) and in D_2O (●); $R^1 = Me$, $R^2 = CHMe_2$ in H_2O (△)).

have, however, found that many ketenimines can in fact be isolated and purified by distillation at low pressures (although this may be accompanied by extensive decomposition).[4] The synthetic route used involved careful dehydrohalogenation, usually by NEt_3 in benzene, of imidoyl chlorides, which were themselves prepared from the amides **5**.

Rapid and complete hydration of **1** to the corresponding amide **5** occurred at all pH's. A typical pH-rate profile that for reaction of **1** ($R^1 = H$, $R^2 = Me_2CH$) in H_2O at 25 °C is shown in Figure 1.[5] Clearly two distinct regions are observed: at pH <6, where acidic catalysis is noted and pH >7 where the rate of reaction is pH independent. Surprisingly, with this ketenimine, no base catalysis is observed even in the presence of 0.1 M HO^-.

We attribute the observed acid catalysis to the rate-determining proton transfer from H_3O^+ to the ketenimine **2** ($B = OH_2$) since the rate of hydrolysis is depressed ($k_{H_3O^+}/k_{D_3O^+} = 2.65$) in D_2O (Figure 1). If an alternative mechanism involving pre-equilibrium proton transfer to the ketenimine to form **3** were operative then the reaction would be faster in D_2O (owing to the greater acidity of D_3O^+ compared with H_3O^+).

Consistent with this, just one deuterium was incorporated at the benzylic position when the ketenimine **6** was reacted with D_2O at low pH;[7] this rules out a pre-equilibrium which would be characterized by extensive D exchange at this position. Moreover the same monodeuterated product **7** was obtained when the deuterioketenimine **8** was reacted in H_2O in the presence of acid.



The position of protonation of the ketenimine could be carbon or nitrogen (to ultimately give the nitrilium ion **3** or the keteniminium ion **4**). Substituent effects in R^2 are not informative as to the protonation site since the transition state for the formation of either ion is expected to have most of the charge localized on nitrogen.[8] However, we found that on replacement of the hydrogen by a methyl group at carbon (**1**, $R^1 = Me$ compared with $R^1 = H$) produced a marked rate depression (~11-fold, see Figure 1). This is a good indication of proton transfer to carbon in the slow step, inhibited by the steric effect of the Me group. A similar slowing in the rate of a proton transfer was previously noted in acid-catalyzed hydration of diazo ketones, where a change in the substituent at carbon from H to Me resulted in a change in mechanism from specific acid to general acid catalysis.[9]

A special mechanism for the rapidly reacting ketenimine **6**, involving prior tautomerism to the ynamine **9** (which is known to undergo rapid hydration),[10] can be ruled out on the basis of the D-labeling experiments.

As regards the pH independent hydration observed at high pH, a mechanism involving direct nucleophilic attack by $(H_2O)_n$ on the ketenimine can be ruled out by the observation of the very large deuterium isotope solvent effect ($k_{H_2O}/k_{D_2O} = 4.8$). It is, of course, also highly unlikely that rate-determining nucleophilic attack by water would be observed when attack by HO^- does not occur to an appreciable extent (Figure 1) even at high pH.

We therefore favor a mechanism involving rate-determining proton transfer from the solvent H_2O in this pH region (**2**, $B = -OH$). Consistent with this is the large negative entropy value obtained ($\Delta S^{\ddagger} = -28 \pm 0.5$ eu at 298 K) for hydration at pH 10. The substituent effects in the pH independent region also appear to parallel those for the acid-catalyzed reaction; e.g., introduction of a methyl group at carbon (**1**, $R^1 = Me$ vs. $R^1 = H$) causes a 17-fold reduction in the rate of pH independent hydration.

Other weak general acid catalysts including HPO_4^{2-}, HCO_3^- and the conjugate acids of amines such as morpholine and piperidine are also very effective catalysts for the hydration of **1** ($R^1 = H$, $R^2 = Me_2CH$), giving a Brønsted α value of 0.53. The only amine for which direct nucleophilic attack on the ketenimine is detectable is piperidine ($pK_a = 11.1$), but, remarkably, the second-order rate constant for nucleophilic attack is less than half that for proton transfer from the very weak conjugate acid. In all cases when amines were used as buffer species, the products obtained were amidines, formed by trapping of the nitrilium ions **3** after the rate-determining step.

It thus appears that the ketenimine system reacts via a slow proton transfer to form a stabilized nitrilium ion at all pH's. There is therefore a similarity between the behavior of ketenimines and vinyl ethers[11] (although the ketenimines studied react more rapidly than even the most highly reactive (cyclopropyl substituted) vinyl ethers[12]). When nucleophiles other than H_2O are present, the products formed depend upon selective trapping of the nitrilium ion.

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(5) The reactions were followed by UV spectroscopy at suitable wavelengths; e.g., phenylketene-*N*-isopropylamine has an absorption at 270 nm (ϵ_{max} 8050) which disappears on conversion to the amide (λ_{max} 225 nm (ϵ_{max} 340)). A pH stat combined with a Cary 14 spectrophotometer was used to measure rates of reaction in the absence of buffer species.[6]
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