REVIEW COMMENTARY

REACTIVE SPECIES: YNOLS AND YNAMINES

Y. CHIANG, A. J. KRESGE,* S. W. PAINE AND V. V. POPIK

Department of Chemistry, University of Toronto, Toronto, Ontario M5S 3H6, Canada

Acetylenic alcohols—ynols—and acetylenic amines—ynamines—have been generated in aqueous solution by flash phololytic decarbonylation of hydroxy- and aminocyclopropenones and their chemistry has been examined in that medium. This has revealed a remarkably strong acid-strengthening effect of the acetylenic group, which *ab initio* molecular orbital calculations suggest results from a combination of destabilizing inductive effects on the initial state and stabilizing resonance effects on the final state of the acid ionization reaction.
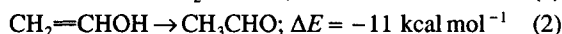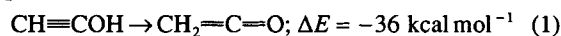
1. INTRODUCTION

Ynols are acetylenic alcohols—substances in which a hydroxyl group is attached directly to a carbon–carbon triple bond—and ynamines are their amine counterparts—substances in which an amino group is similarly attached. Both ynols and ynamines are quite reactive: they undergo facile rearrangement to ketenes and ketenimines, and their lifetimes in solution are consequently short. Fast reaction techniques must be used for their study. This review describes how we have been able to generate these substances and investigate their chemistry in aqueous solution using flash photo-lytic techniques. One of the products of this research has been our discovery of a remarkably strong acid-strengthening effect of the acetylic group: ynols, for example, are more acidic than the corresponding carboxylic acids!

YNOLS

Ynols are the tautomeric isomers of ketenes: they bear the same relationship to ketenes as enols do to alde-hydes and ketones. The energy difference in the case of the ketene-ynol pair, however, is much greater than that between the keto and enol forms of simple aldehydes and ketones. This is apparent, for example, from *ab initio* molecular orbital calculations that put hydrox-

yacetylene some 36 kcal mol^{-1} in energy above ketene, equation (1).[1]

$$CH{\equiv}COH \rightarrow CH_2{=}C{=}O; \quad \Delta E = -36 \text{ kcal mol}^{-1} \quad (1)$$

$$CH_2{=}CHOH \rightarrow CH_3CHO; \quad \Delta E = -11 \text{ kcal mol}^{-1} \quad (2)$$

Similar calculations give $\Delta E = -11$ kcal mol^{-1} for the conversion of vinyl alcohol inlo acetaldehyde, equation (2)[2] in good agreement with the experimentally deter-mined value for this reaction in the gas phase, $\Delta E = -10 \pm 2$ kcal mol^{-1}.[3] These same calculations, however, also predict a very high energy barrier of 73 kcal mol^{-1} for the unimolecular rearrangement of hydroxyacetylene to ketene, which suggests that hydroxyacetylene might be stable enough to be observed if it could be made.

This prediction was borne out 10 years ago by a tandem mass spectrometric investigation in which hydroxyacetylene was generated by the sequence of reactions shown in equation (3).[4]

$$CH{\equiv}CCO_2H \xrightarrow{70\,eV} CH{\equiv}COH^+ + CO + e^-$$
$$CH{\equiv}COH^+ + Xe \rightarrow CH{\equiv}COH + Xe^+ \quad (3)$$
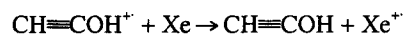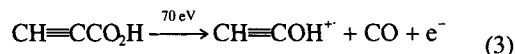
Hydroxyacetylene had been observed before in interstel-lar clouds and planetary atmospheres,[5] but this was the first time it had been seen on earth. This achievement was considered important enough to be cited by the Encyclopaedia Britannica as one of the outstanding scientific accomplishments of the year.[6] Shortly thereaf-ter, hydroxyacetylene was prepared again in a low-temperature argon matrix by two different methods,[7] one

---

of which involved photodecarbonylation of hydroxy-cyclopropenone, equation (4).[7a]

$$\text{(structure)} \xrightarrow{\text{hv}} CH{\equiv}COH + CO \quad (4)$$

Generation in solution

We have found that photodecarbonylation of hydroxy-cyclopropenones can also be effected in liquid solution at ambient temperature.[8] Flash photolysis of aryl-hydroxycyclopropenones in aqueous solution produces arylacetic acids as the ultimate reaction products, preceded by ultraviolet spectral changes that indicate the formation of two families of short-lived intermediate species, equation (5).
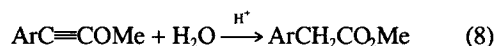
$$\text{(structure)} \xrightarrow[H_2O]{\text{hv}} X_1 \rightarrow X_2 \rightarrow ArCH_2CO_2H \quad (5)$$
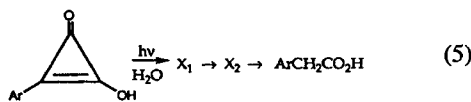
The longer lived of these two types of intermediates, X_2, were identified as ketenes from the rate profiles for their decay, the characteristic small solvent isotope effects that the decay reactions showed and, most conclusively, from the numerical identity of the rate laws for this decay with those for authentic ketenes produced by photo-Wolff reactions of the corresponding diazo compounds, equation (6).

$$\text{(structure)} \xrightarrow[-N_2]{\text{hv}} \text{(structure)} \xrightarrow{H_2O} ArCH_2CO_2H \quad (6)$$
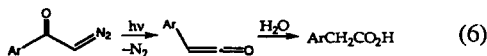
This identity is illustrated in Figure 1, which makes the comparison for the 1-naphthyl system. The rate profile shown in this Figure is typical of the hydration of aromatic ketenes in aqueous solution, having a long 'uncatalyzed' region representing nucleophilic attack at keto carbon by water plus a region of hydroxide ion catalysis that becomes apparent only at fairly high pH.[9]

The shorter lived of the two types of intermediates, X_1, were identified as ynol species on the basis of the expected ready isomerization of ynols to ketenes, the demonstrated formation of hydroxyacetylene from hydroxycyclopropenone, equation (4),[7a] and the observation that arylmethoxyacetylenes are formed upon flash photolysis of arylmethoxycyclopropenones, equation (7).

$$\text{(structure)} \xrightarrow{\text{hv}} ArC{\equiv}COMe + CO \quad (7)$$

$$ArC{\equiv}COMe + H_2O \xrightarrow{H^+} ArCH_2CO_2Me \quad (8)$$

The latter identification was made by showing that the rates of acid-catalyzed hydrolysis of authentic aryl-methoxyacetylenes, equation (8), which are stable substances that can be prepared by standard methods, are the same as those of the substances produced by photolysis of arylmethoxycyclopropenones, equation (7).[8,10] This is illustrated for the parent phenyl system in Figure 2.

Confirmation of our identification of the two intermediates as ynol and ketene species has come from a recent study in non-aqueous solvents using time-resolved infrared spectroscopic detection.[11] In this investigation, flash photolysis of phenylhydroxycyclo-propenone was found to produce a short-lived species, which was identified as phenylynol by its $C{\equiv}C$ stretching vibration at $\omega = 2245$ cm^{-1}, and a longer lived species, which was identified as phenylketene by its $C{=}O$ stretching vibration at $\omega = 2110$ cm^{-1}.
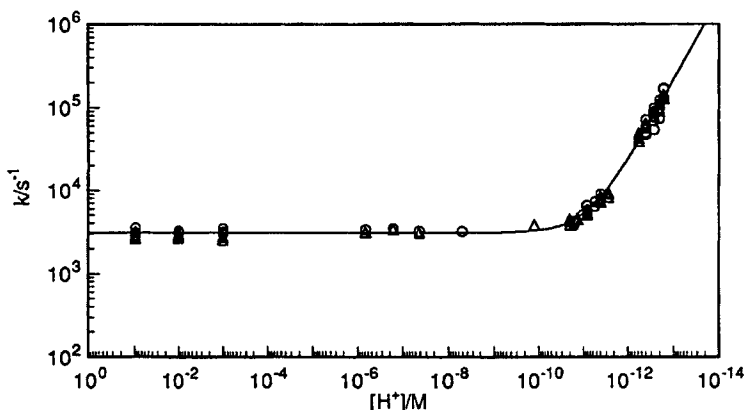

Figure 1. Rate profile for the hydration of 1-naphthylketene generated by photodecarbonylation of 1'-naphthylcyclopropenone (O) and by photo-Wolff reaction of diazo-1'-acetonaphthone (Δ)
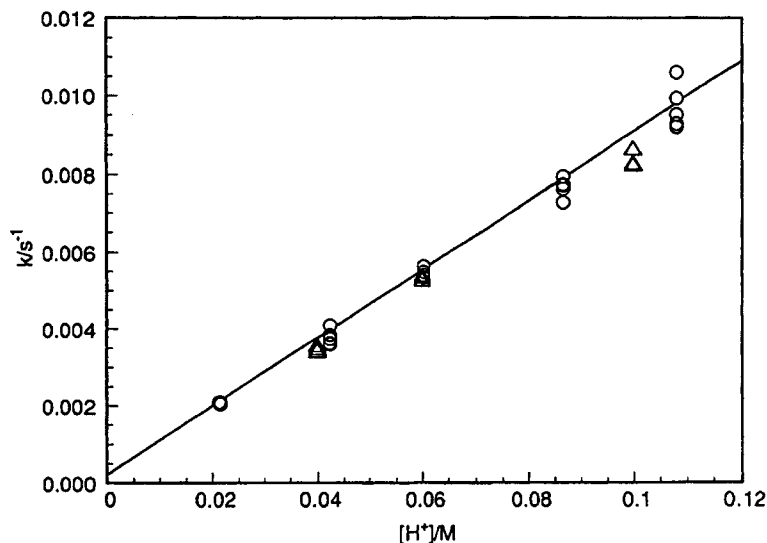
Figure 2. Rates of acid-catalyzed hydrolysis of phenylmethoxyacetylene generated by photolysis of phenylmethoxycyclopropenone (O) compared with those for an authentic sample of phenylmethoxyacetylene (Δ)

Reaction mechanism

We found that reaction of the ynol species to form ketenes showed general acid catalysis and gave hydronium-ion isotope effects in the normal direction, $k_{H^+}/k_{D^+} > 1$.[8] This is classic evidence for rate-determining proton transfer to carbon,[12] and it indicates that the reaction occurs, as expected, by simple protonation of the substrate on acetylenic carbon. We were also able to show that the substrates exist as ynolate ions rather than undissociated ynols under the reaction conditions by comparing observed rate constants with estimated values. These estimates were based on rate constants determined for the acid-catalyzed hydrolysis of methoxyacetylenes, equation (8), and the expectation that ynols (1) would be more reactive than their methyl ethers, (2) by the same factor, 10–100, that enols (3) are more reactive than their methyl ethers (4).[13] This leads to the prediction $k_{H^+} = 1–10\ 1\,\text{mol}^{-1}\,\text{s}^{-1}$ for phenylynol, which is much less than the observed rate constant, $k_{H^+} = 1\cdot3 \times 10^{10}\ 1\,\text{mol}^{-1}\,\text{s}^{-1}$. Enolate ions, however, are very much more reactive than enols, by factors as much as 10^{9},[14] and, when this increase in reactivity is applied to the estimate for phenylynol, a prediction for its ynolate ion consistent with observation is obtained. This indicates that the ynols existed as ynolate ions under the conditions of our study, and that the reactions observed
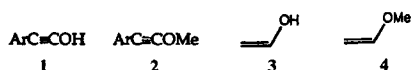
were simple protonation of these ions on β-carbon to produce ketenes, equation (9).

$$\text{ArC}{\equiv}\text{CO}^- + \text{HA} \rightarrow \text{ArCH}{=}\text{C}{=}\text{O} + \text{A}^- \qquad (9)$$

These reactions are very fast. The data in Table 1 show rate constants in the range $k_{H^+} = (0\cdot6–1\cdot3) \times 10^{10}\ 1\,\text{mol}^{-1}\,\text{s}^{-1}$, and the value $k_{H^+} = 1\cdot3 \times 10^{10}\ 1\,\text{mol}^{-1}\,\text{s}^{-1}$ for phenylynolate ion is in fact the largest so far reported for protonation of a carbon pseudobase. Larger rate constants have been determined for the carbon protonation of cyanide ion[15] and the conjugate bases of some cyanocarbons and sulfones,[16] but these are believed to be normal[17] species whose basic electron pairs are localized on single (carbon) atoms and whose protonation is consequently not accompanied by much charge or structural reorganization. The negative charge in ynolate ions, on the other hand, must be situated largely on oxygen, and

Table 1. Rate constants for the conversion of arylynolate ions to arylketenes in aqueous solution at 25 °C[a]

Aryl group	$k_{H^+}/10^{9}\ 1\,\text{mol}^{-1}\,\text{s}^{-1}$
Phenyl	13·4
2,4,6-Trimethylphenyl	6·03
4-Methoxyphenyl	9·13
2,4,6-Trimethoxyphenyl	9·68
1-Naphthyl	8·77

[a] Ionic strength = 0·10 M

ArC≡COH   ArC≡COMe   3 $\overset{OH}{=\!\!/}$ 4 $\overset{OMe}{=\!\!/}$
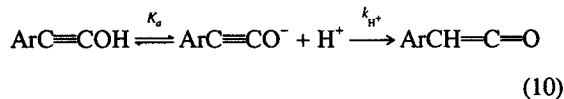
1   2

carbon protonation here thus involves charge movement as well as some bond angle and bond length changes.

The rate constant $k_{H^+} = 1\cdot3 \times x10^{10} \, l\,mol^{-1}$ for carbon protonation of phenylynolate ion is near the diffusion-controlled limit for a bimolecular process in aqueous solution, but the available evidence seems to suggest that this is nevertheless still an activation-controlled process. The isotope effect observed, $k_{H^+}/k_{D^+} = 2\cdot04 \pm 0\cdot05$, is greater than that expected for a diffusion-controlled process on the basis of the 20% difference in viscosity between H_2O and D_2O.[18] The Brønsted plot shown in Figure 3 is also inconsistent with a diffusion-controlled process: the Brønsted plot for a downhill reaction such as this, if it were diffusion-controlled, would have a slope of zero,[17] or perhaps even less than zero if desolvation of the acid proton donor is important,[19] but the slope of this plot is $\alpha a = 0\cdot21 \pm 0\cdot01$. Such a low value of α, on the other hand, is consistent with expectation for a very fast activation-controlled reaction. Such a process should have an early, reactant-like transition state in which proton transfer is not very far advanced[20] and, since Brønsted exponents are believed to indicate the extent of proton transfer at transition states,[21] α should consequently be small.

Acid strength

Although ynolate ions were the dominant substrate forms under the conditions of our investigation, in sufficiently strong acid these ions should undergo equilibrium protonation on oxygen, as shown in equation (10).

$$\mathrm{ArC\!\equiv\!COH} \overset{K_a}{\rightleftharpoons} \mathrm{ArC\!\equiv\!CO^-} + H^+ \overset{k_{H^+}}{\longrightarrow} \mathrm{ArCH\!=\!C\!=\!O}$$

$$(10)$$

That would convert a more reactive species into a less reactive species, causing saturation of acid catalysis of ketene formation. This change would appear as a break in the pH–rate profile for the reaction, with the break occurring at an acidity equivalent to the acid dissociation constant of the ynol. Such a break would therefore provide a measure of the acid strength of the ynol.

The rate profiles in Figure 4 show that, up to the highest acidities we could use, which were limited by the fastest reactions that our flash system could measure, no such breaks occurred for any of the systems we investigated. These rate profiles consist only of acid catalyzed portions, plus slower 'uncatalyzed' parts where water has taken over the role of the proton donor reacting with the ynolate ions. Since the highest acidities we used were $[H^+] \approx 10^{-3}$ M, this sets an upper limit of $pK_a \approx 3$ on the acid strength of the ynols we examined.

This is a remarkable upper limit for the pk_a of an alcoholic hydroxyl group. However, an even lower upper limit can be set using information provided by the study of ynol chemistry employing flash photolysis with time-resolved infrared detection mentioned above.[11] No acid catalysis of ketene formation was found in that investigation, which means that the ynol–ynolate
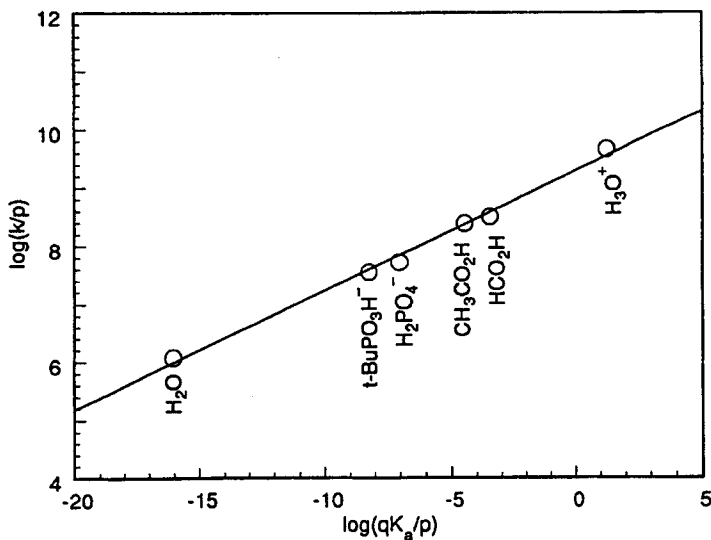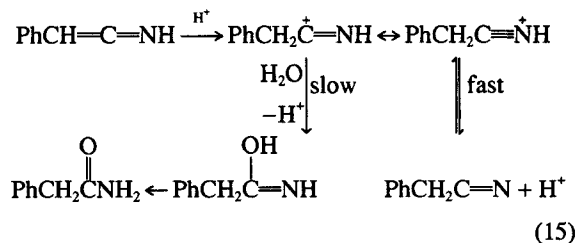

Figure 3. Brønsted plot for the carbon protonation of phenylynolate ion

Figure 4. Rate profiles for the carbon protonation of arylynolate ions in aqueous solution at 25 °C. Aryl group: (O) phenyl; (O) 4-methoxyphenyl; ($\triangle$)2,4,6- trimethoxyphenyl ($\triangle$)1-naphthyl; ()2,4,6 trimethylphenyl

equilibrium was on the side of ynol in the organic solvents used; this is consistent with the reduced acidity of neutral acids expected for such media. The rate law for ketene formation according to equation (10) under these conditions is $k_{obs} = K_a k_{H^+}$. The value of k_{H^+} is not known, but it is unlikely to be greater than $10^{10} \, l \, mol^{-1} s^{-1}$, and the rate constant reported for reaction of phenylynol in DMSO solution, $k_{obs} = 8 \cdot 7 \times 10^4 s^{-1}$, then leads to $K_a \geqslant 8 \cdot 7 \times 10^{-6}$ M, $pK_a \leqslant 5 \cdot 1$, in that medium. This value may be converted into an estimate for aqueous solution on the assumption that the medium effect in going from water to DMSO on the acid dissociation constant of phenylynol is similar to that for phenol, for which $pK_a = 18 \cdot 0$ in DMSO.[22] The result is $pK_a \leqslant -3$ for phenylynol in water. That makes this ynol ca 13 pK units more acidic than its double bond analog, the enol of phenylacetaldehyde, $PhCH{=}CHOH$, for which $pK_a = 9 \cdot 6$.[22]

YNAMINES

Generation in solution

The arylhydroxycyclopropenone substrates used in our study of ynols were prepared by hydrolysis of the corresponding arylchlorocyclopropenones, equation (11).

These chlorides are vinylogs of carboxylic acid chlorides and, like carboxylic acid chlorides, they react readily with amines, producing arylaminocyclopro-

penones, equation (12).

We have found that flash photolysis of phenylaminocyclopropenones in aqueous solution gives carboxylic acid amides as the ultimate reaction products via short-lived transient intermediates, which, from their behavior and also by analogy with the photolytic generation of ynols from hydroxycyclopropenones, we conclude are ynamines, equation (13).[24]

We have been able to make primary, secondary, and tertiary ynamines in this way. Tertiary ynamines are well known, stable substances whose chemistry in solution had been studied before,[25] but primary and secondary ynamines, because of their ready isomerization to ketenimines, equation (14),

$$PhC{\equiv}CNHR \rightarrow PhCH{=}C{=}NR \qquad (14)$$

had been observed previously only in the gas phase or in low-temperature matrices.[26]

We have found that primary and secondary ynamines produced in this way are transformed into yet other transient species, which we identified as ketenimines from their rates of reaction. The hydration of ketenimines to amides had been studied before and the rate constants reported,[27] e.g. $k = 100$ and $2200 \, l \, mol^{-1} s^{-1}$ for the hydrogen ion catalyzed reactions of phenylketene-N-phenylimine and phenylketene-N-

isopropylimine respectively, are in good agreement with our values, $k = 98$ and $2190 \, l \, mol^{-1} \, s^{1}$. It is interesting that the parent imine, phenylketenimine, is not hydrated to the corresponding amide directly but rather is first transformed into phenylacetonitrile, equation (15).

$$PhCH\!\!=\!\!C\!\!=\!\!NH \xrightarrow{\text{H}^+} PhCH_2\overset{+}{C}\!\!=\!\!NH \leftrightarrow PhCH_2C\!\!\equiv\!\!\overset{+}{N}H$$

$$\begin{array}{ccc} & H_2O \Big|_{\text{slow}} & \Big\|_{\text{fast}} \\ & -H^+ \downarrow & \\ O & OH & \\ \| & | & \\ PhCH_2CNH_2 \leftarrow PhCH_2C\!\!=\!\!NH & PhCH_2C\!\!\equiv\!\!N + H^+ \end{array}$$

$$(15)$$

This shows that the cation formed in the first step of this reaction loses its nitrogen-bound proton more readily than it reacts with water, which is consistent with the fact that the acid-catalyzed hydrolysis of nitriles is known to occur by an A-2 mechanism involving pre-equilibrium protonation of nitrogen followed by rate-determining attack of water on the cation so formed.[28]

Tertiary ynamines have no nitrogen-bound hydrogens and cannot isomerize to ketenimines. However, here again we were able to obtain literature support for our assignment of ynamine formation in the photoreaction of tertiary phenylaminocyclopropenones, as the hydration of some tertiary ynamines had been studied before.[29] The rate constants reported in this earlier investigation were consistent with our values, but the agreement was not exact because the previous measurements were made in a 1:10·6 dioxane–water mixture whereas we used a wholly aqueous solvent. We therefore also prepared authentic tertiary ynamines and measured rates of their reactions in wholly aqueous solution. As Figure 5 illustrates, good numerical agreement was obtained between these rates and values for tertiary ynamines obtained from arylaninocyclopropenones.

Reaction mechanism

We found that decay of the transient species identified as ynamines formed by flash photolysis of phenylamino-cyclopropenones showed general acid catalysis and gave sizeable isotope effects in the normal direction, $k_H/k_D > 1$. This, again, is classic evidence for rate-determining proton transfer to carbon,[12] and it shows that ynamines react in a fashion completely analogous to ynols, by simple protonation of their acetylenic β-carbon atoms, equation (16).

$$PhC\!\!\equiv\!\!CNR_2 + HA \rightarrow PhCH\!\!=\!\!\overset{+}{C}NR_2 + A^- \quad (16)$$

These reactions, like the protonation of ynolate ions, are very fast, a property that may be attributed to the cation-stabilizing ability of amino groups. This stabilizing ability, and consequently the rate of reaction, should increase with the basicity of the amino substituent, and Figure 6 shows that this is indeed the case. The slope of the correlation shown in Figure 6 is $0·33 \pm 0·02$, which is consistent with the early transition states expected for these fast reactions.[20] The fact that primary, secondary and tertiary ynamines obey the same correlation, moreover, implies that proton loss from nitrogen is not
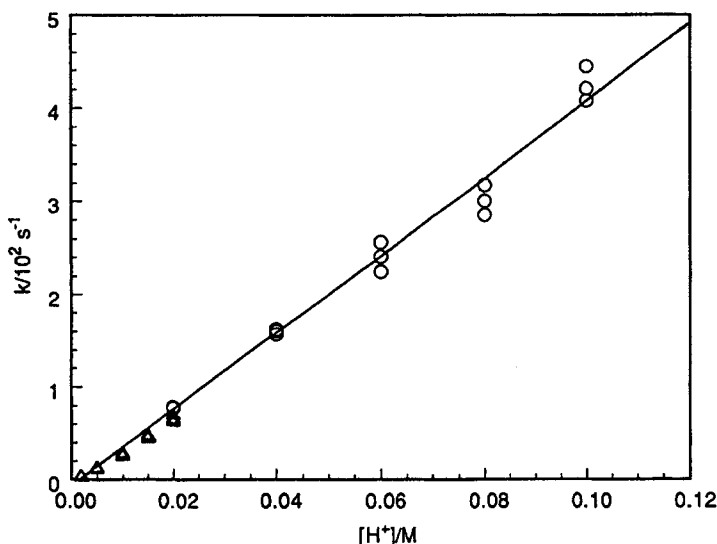

Figure 5. Comparison of rates of reaction of N-methyl-N-pentafluorophenylphenylynamine obtained by flash photolysis of the corresponding cyclopropenone (O) with those of an authentic sample of the ynamine (Δ)
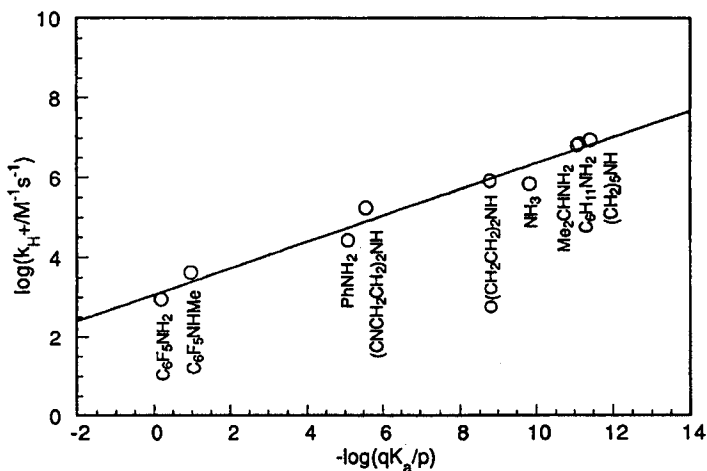
Figure 6. Correlation between rate constants for carbon protonation of phenylynamines by the hydronium ion and basicity of the amino portion of the ynamines as measured by the acidity constants of the conjugate acids of the corresponding amines

concerted with carbon protonation, as such proton loss cannot occur in the case of tertiary ynamines.

The carbon protonation of ynamines also gives good Brønsted correlations with low slopes: those for N-(isopropyl)phenylynamine and N-(pentamethylenyl)-phenylynamine, based on series of carboxylic acid proton donors, have $\alpha = 0\cdot29 \pm 0\cdot03$ and $0\cdot28 \pm 0\cdot02$ respectively.

Basic strength

It was shown above that the acetylenic group has a powerful strengthening effect on the acidity of ynols and consequently a powerful weakening effect on the basicity of ynolate ions. This group also exerts a strong base weakening effect in the case of ynamines. This is apparent from the fact that the carbon protonation of ynamines proved to be acid catalyzed even in the strongest acids we could use to study these reactions. In sufficiently strong acids, ynamines should undergo reversible equilibrium protonation on nitrogen in addition to nonreversible protonation on carbon, and that, just as in the case of ynolate ions, should be recognizable as a break in the reaction rate profile. We found no such breaks for any of the ynamines we examined up to acidities of the order of $[H^+] = 1$ M. This sets an upper limit of $pK_a \lessapprox 0$ on the acidity of ynamine conjugate acids and makes the base weakening effect of the acetylenic group greater than 10 pK units.

Acid strength

Rate profiles for the carbon protonation of tertiary ynamines are similar to those for carbon protonation of

ynolate ions, showing only acid-catalyzed and 'uncatalyzed' regions representing protonation by the hydronium ion and by water molecules. The reaction of primary and secondary ynamines, on the other hand, also shows base catalysis. This is illustrated by the rate profile for N-(pentafluorophenyl)phenylynamine given in Figure 7.[30] Base catalysis eventually becomes saturated in this example, but saturation was not reached in the case of other ynamines with less strongly electron-withdrawing substituents on nitrogen.

Solvent isotope effects plus the form of catalysis by buffers lead us to believe that the basic part of the rate profile illustrated in Figure 6 represents ionization of N-(pentafluorophenyl)phenylynamine as an acid followed by rate-determining carbon protonation of the ionized species by water, as shown in equation (17).

$$PhC\equiv CNHC_6F_5 \overset{K_a}{\rightleftharpoons} PhC\equiv CNC_6F_5^- + H^+$$

$$k_0 \downarrow H_2O, -HO^- \qquad (17)$$

$$PhCH=C=NC_6F_5$$
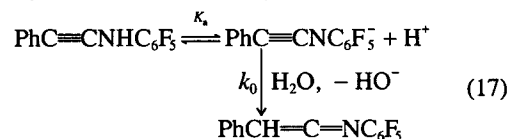
This scheme produces H^+ in the equilibrium before the rate-determining step, and the rate of the overall reaction will consequently be inversely proportional to $[H^+]$ or directly proportional to $[HO^-]$, thus producing the apparent hydroxide ion catalysis seen in the region $pC_{H^+} = 5-10$. Above $pC_{H^+} = 10$, the position of the prior equilibrium shifts from $PhC\equiv CNHC_6F_5$ to $PhC\equiv CNCC_6F_5^-$, and the concentration of the reactive form of the substrate is no longer inversely dependent upon $[H^+]$; base catalysis thus becomes saturated.

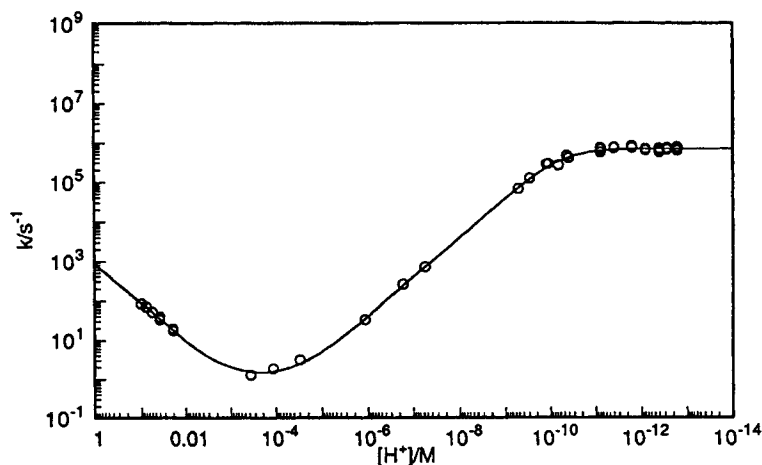The solvent isotope effect in the region of base catalysis saturation for this reaction is $k_H/k_D = 7\cdot9$.

Figure 7. Rate profile for the carbon protonation of N-pentafluorophenylphenylynamine in aqueous solution at 25 °C

This is a reasonable value for rate-determining proton transfer to carbon from a water molecule: such isotope effects tend to be large because the primary component is augmented by a secondary effect in the same direction, which is produced by formation of the solvation shell of the hydroxide ion being generated in this process.[31] In the region of apparent hydroxide ion catalysis, the isotope effect is much greater: $k_H/k_D = 30$.[32] In this region, however, the observed rate constant is the product of the acid dissociation constant of the ynamine and the specific rate constant for the slow step, $k_{obs} = K_a k_0$, and the observed isotope effect is consequently the product of isotope effects on K_a and k_0. Since $(k_0)_H/(k_0)_D = 7·9$ has been determined in the region of base catalysis saturation, the isotope effect on the acid dissociation constant can be evaluated. The result, $(K_a)_H/(K_a)_D = 3·8$, is a reasonable value for an acid of this strength.[33]

The break in the rate profile connecting the regions of apparent hydroxide ion catalysis and catalysis saturation corresponds to acid dissociation of the ynamine, and analysis of the data gives $pK_a = 10·3$ for N-(pentafluorophenyl)phenylynamine. This is a remarkably low value for the acid ionization of an amine, much lower than the estimate $pK_a = 35$ for the ionization of ammonia.[34]

A more meaningful comparison would be with the equilibrium constant for pentafluoroaniline ionizing as an acid, equation (18).

$$C_6F_5NH_2 \rightleftharpoons C_6F_5NH^- + H^+ \qquad (18)$$
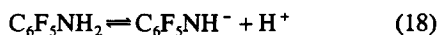
This constant has not been determined in aqueous solution, but an estimate can be made using $pK_a = 23·1$ in DMSO solution[35] and the assumption that the solvent

effect on this ionization is the same as that for aniline, for which $pK_a = 30·6$ in DMSO[22] and $pK_a = 27·7$ in water.[36] The result is $pk_a = 20·2$ for pentafluoroaniline in water, which gives an acid-strengthening effect of 10 pK units for the phenylynyl group in N-(pentafluorophenyl)-phenylynamine.
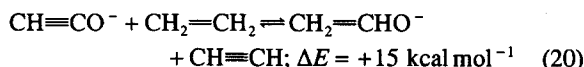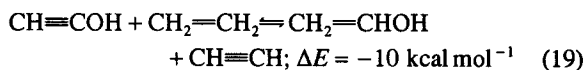
ORIGIN OF THE ACID-STRENTHENING EFFECT

This remarkable acid-strengthening effect of the acetylenic group is reminiscent of the greater acidity of acetylene over ethylene and ethylene over methane: These differences are cited in most introductory organic chemistry texts and are commonly attributed to differences in stability of the corresponding carbanions due to differences in s character of the orbitals occupied by their lone-pair electrons.[37] The s character increases from 25% to 33% to 50% for the sp^3, sp^2, and sp hybrid orbitals of CH_3-, $CH_2=CH^-$ $CH\equiv C^-$, respectively, and, since electrons in s orbitals have lower energy than those in p orbitals, the stability of the carbanions increases along this series.

It is not clear that a similar explanation can apply to ynols and ynamines, as the state of hybridization of the orbitals of the O—H and N—H bonds undergoing ionization here does not change in going from acetylenic to vinylic to saturated systems. Recent high-level *ab initio* molecular orbital calculations,[38] in fact, suggest a different origin for the acidifying effect of the triple bond in ynols and ynamines. The results of these calculations, which agree well with experimental values wherever experimental data are available, can be formulated into isodesmic reactions such as those of equations (19) and (20). The first of these reactions

transfers an OH group from acetylenic to vinylic carbon;

$$CH{\equiv}COH + CH_2{=}CH_2 \rightleftharpoons CH_2{=}CHOH$$
$$+ CH{\equiv}CH; \Delta E = -10 \text{ kcal mol}^{-1} \quad (19)$$

$$CH{\equiv}CO^- + CH_2{=}CH_2 \rightleftharpoons CH_2{=}CHO^-$$
$$+ CH{\equiv}CH; \Delta E = +15 \text{ kcal mol}^{-1} \quad (20)$$

the calculations show this to be an exoergic process, $\Delta E = -10 \text{ kcal mol}^{-1}$ (1 kcal = 4·184 kJ), which indicates that a hydroxyl group is more stable when attached to vinylic carbon. This difference may be understood in terms of the inductive effects of the groups involved. The OH group is electron withdrawing, as are also the CH≡C and CH₂=CH groups. Juxtaposition of these groups in ynols and enols will therefore be destabilizing, but it will be more destabilizing in ynols than in enols because the inductive effect of CH≡C is stronger than that of CH₂=CH; this is apparent, for example, from the substituent constants $\sigma_I = 0{\cdot}29$ for CH≡C and $\sigma_I = 0{\cdot}11$ for CH₂=CH.[39]

The second isodesmic reaction transfers O⁻ from acetylenic to vinylic carbon; the calculations show this to be an endoergic process, $\Delta E = +15 \text{ kcal mol}$, which indicates that O⁻ is more stable when attached to acetylenic carbon. Resonance effects are likely to be more important than inductive effects here because of the strong conjugative effect of O⁻, and conjugation of O⁻ will be stronger with CH≡C than with CH₂=CH because the former has two π systems but the latter has only one and also because the CO bond in CH≡CO⁻ is shorter and can provide better overlap than that in CH₂=CHO⁻.

These effects are summarized in the energy diagrams in Fig. 8. They suggest that ynols are more acidic than enols because non-ionized ynols are less stable than non-ionized enols and also because ynolate ions are more stable than enolate ions; the acid-strengthening effect of the acetylenic group here is consequently a combination of initial state and final state effects.
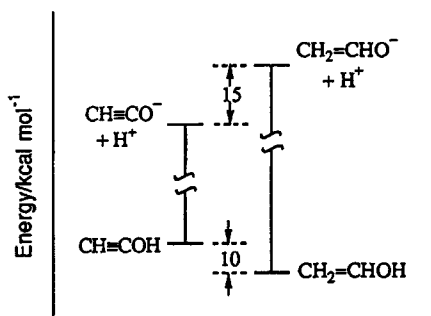

Figure 8. Energetic relationships comparing the ionization of hydroxyacetylene and vinyl alcohol. Energies are based on the calculations of Ref. 38a

Similar consideration of the energies of ynamines and enamines and the anions formed by their ionization[38b] leads to the same conclusion, i.e. that both initial state and final state effects are also responsible for the enhanced acidity of ynamines.

REFERENCES

1. W. J. Bouma, R. H. Nobes, L. Radom and C. E. Woodward, J. Org. Chem. 47, 1869–1875 (1982).
2. B. J. Smith, M. T. Nguyen, W. J. Bouma and L. Random, J. Am. Chem. Soc. 113, 6452–6458 (1991).
3. J. H. Holmes and F. P. Lossing, J. Am. Chem. Soc. 104, 2648–2649 (1982).
4. B. van Baar, T. Weiske, J. K. Terlouw and H. Schwarz, Angew. Chem., Int. Ed. Engl. 25, 282–284 (1986).
5. D. J. DeFrees and A. D. McLean, J. Phys. Chem. 86, 2835–2837 (1982).
6. Encyclopaedia Britannica Yearbook of Science, p. 334. (1988).
7. R. Hochstrasser and J. Wirz, Angew. Chem., Int. Ed. Engl. (a) 28, 181–183 (1989); (b) 29, 411–413 (1990).
8. Y. Chiang, A. J. Kresge, R. Hochstrasser and J. Wirz, J. Am. Chem. Soc. 111, 2355–2357 (1989); Y. Chiang, A. J. Kresge and V. V. Popik, J. Am. Chem. Soc. 117, 9165–9171 (1995).
9. A. D. Allen, A. J. Kresge, N. P. Schepp and T. T. Tidwell, Can. J. Chem. 65, 1719–1723 (1987); T. T. Tidwell, Acc. Chem. Res. 23, 273–279 (1990).
10. N. Banait, M. Hojatti, P. Findlay and A. J. Kresge, Can. J. Chem. 65, 441–444 (1987).
11. B. D. Wagner, M. Z. Zgierski and J. Lusztyk, J. Am. Chem. Soc. 116, 6433–6434 (1994).
12. J. R. Keeffe and A. J. Kresge, in Techniques of Chemistry, Vol. VI, Investigations of Rates and Mechanisms of Reactions, edited by C. F. Bernasconi, Chapt. XI. Wiley, New York (1986).
13. J. R Keeffe and A. J. Kresge, in The Chemistry of Enols, edited by Z. Rappoport, Chap. 7, Wiley, New York (1990).
14. Y. Chiang, A. J. Kresge, J. A. Santaballa and J. Wirz, J. Am. Chem. Soc. 110, 5506–5510 (1988).
15. R. A. Bednar and W. P. Jencks, J. Am. Chem. Soc. 107, 7117–7126 (1985).
16. F. Hibbert, in Comprehensive Chemical Kinetics, edited by C. H. Bamford and C. H. F. Tipper, Chap. 2. Elsevier, New York, (1977).
17. M. Eigen, Angew. Chem., Int. Ed. Engl. 3, 1–72 (1964).
18. W. J. Albery, in Proton Transfer Reactions, edited by E. F. Caldin and V. Gold, Chap. 9. Chapman and Hall, London (1975).
19. C. J. Murray and W. P. Jencks, J. Am. Chem. Soc. 110, 7561–7563 (1988); 112, 1880–1889 (1990); M. W. Washabaugh, J. T. Stivers and K. A. Hickey, J. Am. Chem. Soc. 116, 7094–7097 (1994).

20. J. E. Leffler, *Science* **117**, 340–341 (1953); G. S. Hammond, *J. Am. Chem. Soc.* **77**, 334–338 (1955).
21. A. J. Kresge, in *Proton Transfer Reactions*, edited by E. F. Caldin and V. Gold, Chap. 7. Chapman and Hall, London (1975).
22. F. G. Bordwell, *Acc. Chem. Res.* **21**, 456–463 (1988).
23. Y. Chiang, A. J. Kresge, P. A. Walsh and Y. Yin, *J. Chem. Soc., Chem. Commun.* 869–871 (1989).
24. Y. Chiang, A. S. Grant, A. J. Kresge, P. Pruszynski, N. P. Schepp and J. Wirz, *Angew. Chem., Int. Ed. Engl.* **30**, 1356–1358 (1991).
25. H. G. Viehe, in *Chemistry of Acetylenes*, edited by H. G. Viehe, Chap. 12. Marcel Dekker, New York, (1969); J. M. Z. Gladych and D. Hartley, in *Comprehensive Organic Chemistry*, edited by D. Barton and W. D. Ollis, pp. 75–79. Pergamon Press, Oxford (1979).
26. H.-W. Winter and C. Wentrup, *Angew. Chem., Int. Ed. Engl.* **19**, 720–721 (1980); J. M. Buschek and J. L. Holmes, *Org. Mass Spectrom.* **21**, 729–731 (1986); B. van Baar, W. Koch, C. Lebrilla, J. K. Terlouw, T. Weiske and H. Schwarz, *Angew. Chem. Int. Ed. Engl.* **25**, 827–828 (1986); C. Wentrup, H. Briehl, P. Lorencak, U. J. Vogelbacher, H. W. Winter, A. Maquestiau and R. Flammang, *J. Am. Chem. Soc.* **110**, 1337–1343 (1988).
27. D. G. McCarthy and A. F. Hegarty, *J. Chem. Soc., Perkin Trans. 2.* 579–591 (1980).
28. M. Liler, *Reaction Mechanisms in Sulfuric Acid*, pp. 205–208. Academic Press, New York (1971).
29. W. F. Verhelst and W. Drenth, *J. Am. Chem. Soc.* **96**, 6692–6697 (1974).
30. J. Andraos, Y. Chiang, A. S. Grant, H.-X. Guo and A. J. Kresge, *J. Am. Chem. Soc.* **116**, 7411–7412 (1994).
31. A. J. Kregse, R. A. More O'Ferrall and M. F. Powell, in *Isotopes in Organic Chemistry*, edited by E. Buncel and C. C. Lee, Vol. 7, Chapt. 4. Elsevier, New York (1987).
32. This isotope effect refers to rates determined at the same hydron ion concentration, *i.e.*, at $[H^+] = [D^+]$.
33. P. M. Laughton and R. E. Robertson, in *Solute–Solvent Interactions*, edited by J. F. Coetzee and C. D. Ritchie, Chapt. 7. Marcel Dekker, New York, (1969).
34. R. P. Bell, *The Proton in Chemistry*, 2nd ed. pp. 86–87. Cornell University Press, Ithaca, NY (1973).
35. V. M. Vaslov, M. I. Terekhova, E. S. Petrov, A. I. Shatenshtein and G. G. Yakobson, *J. Org. Chem. USSR* **17**, 1807–1813 (1982).
36. R. Stewart, *The Proton: Applications to Organic Chemistry*, p. 70. Academic Press, New York (1985).
37. See, *e.g.* A. Streitwieser, C. H. Heathcock and E .M. Kosower, *Introduction to Organic Chemistry*, 4th ed., pp. 302–303, Macmillan, New York (1992).
38. (a) B. J. Smith, L. Radom and A. J. Kresge, *J. Am Chem. Soc.* **111**, 8297–8299 (1989); (b) B. J. Smith and L. Radom, *J. Am. Chem. Soc.* **114**, 36–41 (1992).
39. M. Charton, *Prog. Phys. Org. Chem.* **13**, 119–251 (1981).