

Flash Photolytic Generation and Study of Reactive Species: From Enols to Ynols

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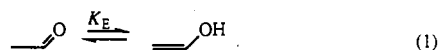
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Chemical transformations of one set of stable substances into another seldom take place in single reaction steps. They tend instead to occur as multistep sequences involving a number of reactive intermediates, and, if we wish to understand these transformations, and, through understanding, to control them, we must understand the chemistry of these reactive species.

We began our study of reactive species by investigating the chemistry of enol isomers of simple monofunctional aldehydes and ketones. That work, however, soon evolved into examination of other short-lived substances, such as the enols of carboxylic acids and esters, ketenes and ketene acetals, and, very recently, ynols and ynamines. This Account will describe some of the results we have obtained.

Simple Enols.¹ Enols and enolate ions are essential intermediates in many important chemical reactions, and a number of biological transformations also involve enol formation. Enolization, moreover, has long been of interest as an example of tautomeric rearrangement, and studies of enolization have played a fundamental role in the development of our ideas on acid-base catalysis.

One of the things that one would like to know about enols is the magnitude of equilibrium constants, K_E , for their formation from keto isomers, eq 1. The classic



way of determining such "enol contents" is by Kurt Meyer halogen titration.² This method works well when enol contents are high, as in the case of β -dicarbonyl compounds, but it fails badly when enol contents are low, as they are for most simple monofunctional aldehydes and ketones. Table I lists some values obtained in three different laboratories by three successive refinements of the Kurt Meyer method. The results for cyclopentanone and cyclohexanone vary by 2 or 3 orders of magnitude. Those for acetone show better consistency, but their common value is nevertheless 2 orders of magnitude greater than a result we obtained recently by a method that is free of the difficulties attending halogen titration of substances at low concentration.⁶

Our method is based upon the fact that an equilibrium constant for a chemical reaction is equal to the ratio of its forward to reverse rate constants: thus, $K_E = k_E/k_K$, where k_E is the specific rate of enolization of the carbonyl compound and k_K is that for ketonization of its enol.

Jerry Kresge received his undergraduate education at Cornell University and did graduate work at the University of Illinois. After postdoctoral research at University College, London, Purdue, and MIT, he joined the staff of Brookhaven National Laboratory. In 1960 he moved to the Illinois Institute of Technology and in 1974 took up his present position at the University of Toronto.

Table I
Some Enol Contents Determined by Kurt Meyer Halogen Titration^a

% enol			
cyclopentanone	cyclohexanone	acetone	ref
0.0048	0.02	0.00025	3
0.088	1.2	0.00015	4
0.0013	0.00041	<0.0001	5

^a Values for refs 3 and 5 are in aqueous solution, and those for ref 4 are for the neat ketones.

Rates of enolization are easy to measure, e.g., by halogen scavenging, and the literature contains values for many aldehydes and ketones. Rates of ketonization, on the other hand, present somewhat more of a problem, for their measurement requires generation of the enol in a greater than equilibrium amount under conditions where its conversion to carbonyl compound can be monitored accurately. Meeting this requirement may, in fact, appear to be an impossible task, because chemical dogma, as promulgated in introductory textbooks, has it that enols are highly labile substances that revert to their keto isomers "instantaneously". However, not all simple enols are highly reactive: some quite ordinary ones can persist for appreciable lengths of time. A good example is vinyl alcohol, the simplest enol of all: this substance was generated in aqueous acetonitrile solution recently, by a clever experiment, and was found to have a half-life of 10 min in that medium at 20 °C.⁷

Generation of Enols. Inspired by this observation, we set about devising techniques for generating enols in wholly aqueous solution and measuring their rates of reaction in that solvent. The first such method that we developed involved hydrolysis of alkali metal enolates. These were prepared in aprotic solvents by standard synthetic methods,⁸ and small quantities of

(1) Some recent reviews of enols are the following: (a) Hart, H. *Chem. Rev.* 1979, 79, 515-528. (b) Touleec, J. *Adv. Phys. Org. Chem.* 1982, 18, 1-77. Kresge, A. J. *CHEMTECH* 1986, 16, 250-254. Capon, B.; Guo, B.-Z.; Kwok, F. C.; Siddhanta, A. K.; Zucco, C. *Acc. Chem. Res.* 1988, 21, 135-140. (c) Rappoport, Z.; Biali, S. E. *Acc. Chem. Res.* 1988, 21, 442-449.

(2) Meyer, K. *Justus Liebigs Ann. Chem.* 1911, 380, 212-242. A modern discussion of the method and some representative results may be found in the following: Wheland, G. W. *Advanced Organic Chemistry*, 3rd ed.; Wiley: New York, 1960; pp 670-693.

(3) Schwarzenbach, G.; Wittwer, C. *Helv. Chim. Acta* 1947, 30, 669-674.

(4) Gero, A. *J. Org. Chem.* 1954, 19, 469-471; 1960-1970.

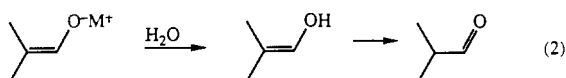
(5) Bell, R. P.; Smith, P. W. *J. Chem. Soc. B* 1966, 241-243.

(6) (a) Chiang, Y.; Kresge, A. J.; Tang, Y. S.; Wirz, J. *J. Am. Chem. Soc.* 1984, 106, 460-462. (b) Chiang, Y.; Kresge, A. J.; Schepp, N. P. *J. Am. Chem. Soc.* 1989, 111, 3977-3980.

(7) Capon, B.; Rycroft, D. S.; Watson, T. W. *J. Chem. Soc., Chem. Commun.* 1979, 724-725. Capon, B.; Rycroft, D. S.; Watson, T. W.; Zucco, C. *J. Am. Chem. Soc.* 1981, 103, 1761-1765.

(8) House, H. O.; Gzuba, L. J.; Gall, M.; Olmstead, H. D. *J. Org. Chem.* 1969, 34, 2324-2336. House, H. O.; Gall, M.; Olmstead, H. D. *J. Org. Chem.* 1971, 36, 2361-2371. Brown, C. A. *J. Org. Chem.* 1974, 39, 3913-3918.

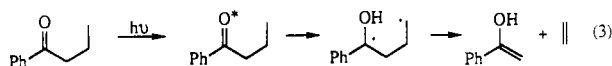
the solutions were then added to large amounts of water. This resulted in a very rapid proton transfer from water to enolate oxygen, which generated the enol in an essentially wholly aqueous solvent, eq 2. The enol



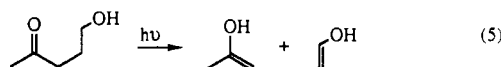
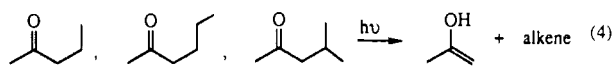
then ketonized at a slower rate, which could be measured by monitoring the UV absorbance change that accompanied the ketonization reaction. Because this absorbance change was quite pronounced, kinetic data of high quality could easily be obtained. We have used this technique to make the enols of isobutyraldehyde,⁹ isobutyrophenone,¹⁰ diphenylacetaldehyde,¹¹ and 2-indanone.¹²

This method, however, is limited by the time required to mix two solutions, and it consequently cannot be applied to investigation of the more reactive enols. We therefore developed other techniques which do not require mixing. All of these use flash photolysis to generate the enol directly in the reaction solution and then monitor its decay by fast spectrophotometric detection.

Flash photolysis was first employed to investigate enol chemistry by Wirz, who generated the enol of acetophenone through Norrish type II photoelimination of butyrophenone, eq 3.¹³ Working in collaboration



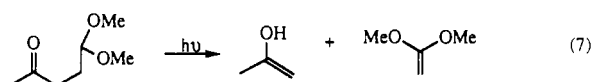
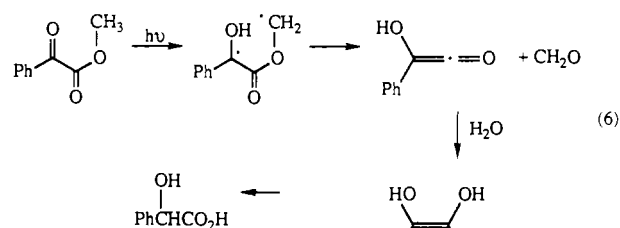
with Wirz, we subsequently used this reaction to make acetone enol from each of the three ketones shown in eq 4,^{6a} and also from the hydroxy ketone given in eq 5.¹⁴



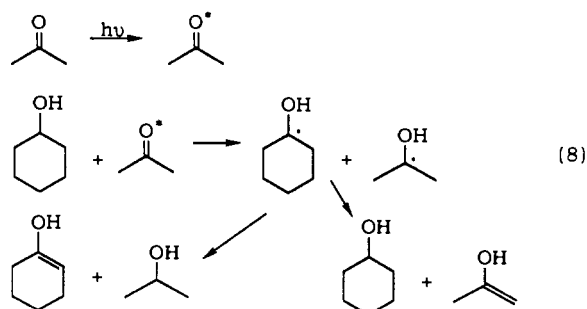
The latter reaction produces the enol of acetaldehyde as well, but this ketonizes 2 orders of magnitude more slowly than acetone enol, and well-determined rate constants for ketonization of both enols may consequently be obtained.

In addition to preparing simple enols by Norrish type II photoelimination, we have used this reaction to make hydroxyphenylketene, and that has led us to the enol of mandelic acid, eq 6.¹⁵ We have also prepared ketene dimethyl acetal by an analogous reaction, eq 7.¹⁶ Ketene acetals undergo acid-catalyzed hydrolysis to carboxylic acid esters through tetrahedral intermediates, but the great speed of the reaction hampered

previous investigation of this interesting process.¹⁷

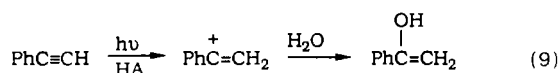


Norrish type II elimination, however, sometimes fails to produce enols in readily detectable quantity, and we have therefore developed still other flash photolytic methods. An especially useful one is photooxidation of alcohols, illustrated in eq 8 for the case of cyclohexanone enol. This process is an intermolecular



analogue of the Norrish type II reaction: the photoexcited ketone, having no suitably positioned C-H bond, cannot undergo intramolecular hydrogen atom transfer, and it therefore abstracts hydrogen from the alcohol instead. The ketyl radicals thus formed then disproportionate, in this case in two different directions to give two enols of sufficiently different reactivity to allow easy kinetic resolution of their ketonization reactions. We have used this reaction to prepare a number of aliphatic cyclic and acyclic enols.¹⁸

We have also made enols by the photohydration of acetylenes, eq 9.¹⁹ This reaction occurs thermally as well, but concentrated acids must be used, and under these conditions the enols ketonize faster than they are formed and thus are not observed.²⁰ Photoexcitation,



however, increases the reactivity of acetylenes enormously,²¹ enough to make formation of the enol more rapid than its ketonization; ketonization is therefore now rate determining and observable. The vinyl cationic intermediate in this reaction may also be produced

(9) Chiang, Y.; Kresge, A. J.; Walsh, P. A. *J. Am. Chem. Soc.* **1982**, *104*, 6122-6123; **1986**, *108*, 6312-6320.

(10) Pruszyński, P.; Chiang, Y.; Kresge, A. J.; Schepp, N. P.; Walsh, P. A. *J. Phys. Chem.* **1986**, *90*, 3760-3766.

(11) Chiang, Y.; Kresge, A. J.; Krogh, E. T. *J. Am. Chem. Soc.* **1988**, *110*, 2600-2607.

(12) Keefe, J. R.; Kresge, A. J.; Yin, Y. *J. Am. Chem. Soc.* **1988**, *110*, 1982-1983; 8201-8206.

(13) Haspra, P.; Sutter, A.; Wirz, J. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 617-619.

(14) Chiang, Y.; Hojatti, M.; Keefe, J. R.; Kresge, A. J.; Schepp, N. P.; Wirz, J. *J. Am. Chem. Soc.* **1987**, *109*, 4000-4009.

(15) Chiang, Y.; Kresge, A. J.; Schepp, N. P.; Wirz, J., unpublished work.

(16) Kresge, A. J.; Schepp, N. P.; Yousaf, T. I., unpublished work.

(17) Kankaanpera, A.; Touminen, H. *Suom. Kemistil. B* **1967**, *40*, 271-276.

(18) Keefe, J. R.; Kresge, A. J.; Schepp, N. P. *J. Am. Chem. Soc.* **1988**, *110*, 1993-1995.

(19) (a) Chiang, Y.; Kresge, A. J.; Capponi, M.; Wirz, J. *Helv. Chim. Acta* **1986**, *69*, 1331-1332. (b) Kresge, A. J.; Schepp, N. P. *J. Chem. Soc., Chem. Commun.* **1989**, 1548-1549.

(20) Bott, R. W.; Eaborn, C.; Walton, D. R. M. *J. Chem. Soc.* **1965**, 384-388. Noyce, D. S.; Schiavelli, M. D. *J. Am. Chem. Soc.* **1968**, *90*, 1020-1022; 1023-1026.

(21) Woolridge, T.; Roberts, T. D. *Tetrahedron Lett.* **1973**, 4007-4008. Wan, P.; Culshaw, S.; Yates, K. *J. Am. Chem. Soc.* **1982**, *104*, 2509-2515. Wan, P.; Yates, K. *Rev. Chem. Intermed.* **1984**, *5*, 157-181.

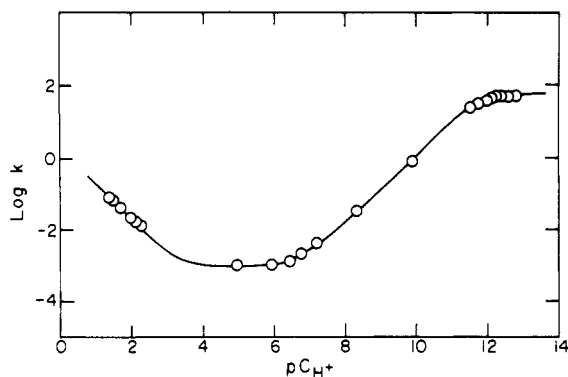


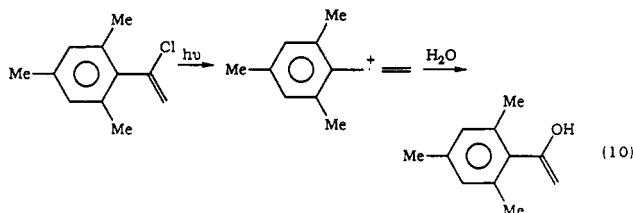
Figure 1. Rate profile for the ketonization of isobutyraldehyde enol by solvent-derived species in aqueous solution at 25 °C; $pC_{H^+} = -\log [H^+]$.

Table II
Comparison of Keto-Enol Equilibrium Constants Determined in Acidic and Basic Solutions^a

substrate	pK_E	
	acid	base
	8.33 ± 0.02^b	8.22 ± 0.08^c
	8.01 ± 0.01^d	7.92 ± 0.03^e

^a Temperature 25 °C, wholly aqueous solvent. ^b Reference 6b. ^c Reference 6a. ^d Reference 24b. ^e Reference 24a.

by photosolvolysis,²² and we have used this process to generate enols as well, eq 10.^{19b}



Enol Chemistry. Using enols produced by these methods, we have made detailed measurements of rates of ketonization under a variety of conditions. The results, in combination with specific rates of enolization, have provided keto-enol equilibrium constants through the relationship $K_E = k_E/k_K$. The ketonization reaction, just as enolization, is catalyzed by both acids and bases, and both acid and base catalytic coefficients may be used in this expression for K_E to give replicate, independently determined values. The sample results listed in Table II show good agreement between determinations made in acidic and basic solution, and this provides assurance that the presently determined values, though very different from equilibrium constants measured by halogen titration (cf. Table I), are nevertheless authentic.

(22) Schnabel, W.; Naito, I.; Kitamura, T.; Kobayashi, S.; Taniguchi, H. *Tetrahedron* 1980, 36, 3229-3231. Kobayashi, S.; Kitamura, T.; Taniguchi, H.; Schnabel, W. *Chem. Lett.* 1983, 1117-1120. Kobayashi, S.; Zhu, Q. Q.; Schnabel, W. *Z. Naturforsch.* 1988, 43B, 825-829. van Ginkel, F. I. M.; Wisser, R. J.; Varma, C. A. G. O.; Lodder, G. *J. Photochem.* 1985, 30, 453-473. Verbeek, J. M.; Corenlisse, J.; Lodder, G. *Tetrahedron* 1986, 42, 5679-5684.

(23) Chiang, Y.; Kresge, A. J.; Walsh, P. A.; Yin, Y. *J. Chem. Soc., Chem. Commun.* 1989, 869-871.

(24) (a) Chiang, Y.; Kresge, A. J.; Wirz, J. *J. Am. Chem. Soc.* 1984, 106, 6392-6395. (b) Keeffe, J. R.; Kresge, A. J.; Toullec, J. *Can. J. Chem.* 1986, 64, 1224-1227.

(25) Kresge, A. J.; Schepp, N. P., unpublished work.

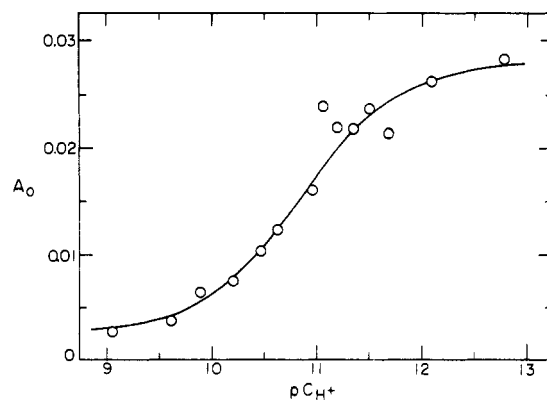


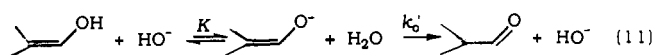
Figure 2. Spectrophotometric titration curve for the acid ionization of acetone enol in aqueous solution at 25 °C and ionic strength = 0.10 M.

Table III
Comparison of Enol Acidity Constants Obtained by Kinetic Analysis and by Spectrophotometric Titration^a

substrate	pK_a^E	
	kinetics	titration
	10.50 ± 0.02^b	10.42 ± 0.11^c
	10.96 ± 0.03^d	10.83 ± 0.06^d

^a In aqueous solution at 25 °C, ionic strength = 0.10 M; acidity constants are concentration quotients appropriate to this ionic strength. ^b Reference 14. ^c Chiang, Y.; Kresge, A. J.; Wirz, J., unpublished work. ^d Reference 6a.

Rate measurements made in basic solution also provide additional information about enol chemistry. As the typical rate profile provided in Figure 1 shows, hydroxide ion catalysis of the ketonization reaction eventually becomes saturated at sufficiently high pC_{H^+} . That is because this catalysis occurs through conversion of the enol to enolate ion followed by rate-determining protonation of the very much more reactive enolate ion by water, eq 11; eventually, however, at sufficiently high














HO^- concentrations, the equilibrium preceding the rate-determining step shifts over to the side of enolate, and hydroxide ion is then no longer effective in promoting the reaction. Standard analysis of rate data in the region of transition from catalysis to no catalysis produces both the equilibrium constant for the first step, K , and the rate constant for the slow step, k_0' , and, since K is a function of the dissociation constant of the enol ionizing as an oxygen acid, K_a^E , and the autoprotolysis constant of water, K_w , $K = K_a^E/K_w$, acidity constants of enols may be determined in this way.

These acidity constants are also available by another, completely independent method, based upon another property of the kinetic data. Enolate ions usually absorb light more strongly and at longer wavelengths than do the corresponding enols. Initial absorbance values, obtained by extrapolating flash photolytic kinetic traces back to zero time, therefore reflect the position of the enol-enolate equilibrium, and plots of such absorbances against pC_{H^+} describe sigmoid titration curves, Figure 2, whose inflection points correspond to pK_a^E .

Table III shows that results obtained by these two methods are in good agreement, which is gratifying in

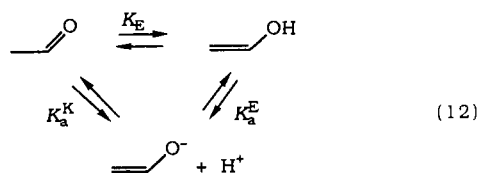
Table IV
Keto-Enol Equilibrium Constants and Acidity Constants of the Enol and Keto Forms for Some Simple Aldehydes and Ketones^a

substrate	pK_E	pK_a^E	pK_a^K	ref
	6.23	10.50	16.73	14
	3.86	11.63	15.49	9
 (cis enol)	3.35	9.76	13.11	23
 (trans enol)	3.07	9.46	12.53	23
	0.98	9.40	10.42	11
	8.33	10.94	19.27	6
	7.96	10.34	18.31	24
	6.48	11.78	18.26	10
	7.94			18
	6.39	11.70	18.09	18, 25
	8.00			18

^aIn aqueous solution at 25 °C, ionic strength = 0.10 M; constants are concentration quotients appropriate to this ionic strength.

view of the fact that enols generally have very short lifetimes in the basic solutions required for these measurements. For example, the lifetime of acetone enol under the conditions represented by Figure 2 is only 20–50 μ s.^{6a}

Keto-enol equilibrium constants and acid ionization constants of the enols form two legs of a thermodynamic cycle whose third member is ionization of the keto isomers as carbon acids, eq 12. Acidity constants of



carbonyl compounds, K_a^K , may therefore be calculated from the other two equilibrium constants: $K_a^K = K_E K_a^E$. Some representative results together with values of K_E and K_a^E are listed in Table IV. It may be seen that simple aldehydes and ketones are on the whole only weakly acidic and that their pK_a 's are generally too high to allow direct determination in dilute aqueous solution. This, however, is not invariably so:

in some cases, pK_a^K can be measured directly, and then this thermodynamic cycle affords a check on the internal consistency of the data. A particularly favorable example is provided by diphenylacetaldehyde,¹¹ for which we were able to measure each of the three constants by two independent methods; summing the pK 's around the cycle gave a result, 0.043 ± 0.046 , that is zero within the rather small ($\pm 10\%$) experimental uncertainty.

The enol contents we have obtained are uniformly smaller, often by several orders of magnitude, than those determined by halogen titration. Our results, on the other hand, are generally consistent with K_E , K_a^E , and K_a^K values estimated recently by a variety of approximate methods;²⁶ this shows that the assumptions upon which those methods were based are essentially correct. One of these methods derived values of K_E from rates of halogenation under conditions where reaction of the halogen with enol is partly rate determining.^{26b} This method requires an estimate of the rate constant for the halogen plus enol reaction, and, since this reaction was then believed to be encounter controlled, an appropriate but constant value was assumed for all enols. We have since learned that the process is not quite, though almost, encounter controlled and that its rate constant is consequently somewhat variable.²⁷

Our results (see Table IV for a sample) show that aldehydes generally have greater enol contents than ketones. This may be understood in the case of aliphatic ketones in terms of the effect of the additional alkyl group of ketones, which stabilizes the keto form through electron release to the partial positive charge on its carbonyl carbon atom. Phenyl substitution in the same position has a similar influence: the enol content of acetophenone resembles that of acetone. Methyl or phenyl substitution at the β -position, on the other hand, has the opposite effect: enol contents are higher because now the enol form is stabilized through the carbon-carbon double bond stabilizing effect of these groups.²⁸ This effect is especially pronounced in the case of diphenylacetaldehyde, whose keto-enol equilibrium constant is as great as 0.1. Such phenyl group effects provide much of the thermodynamic stability shown by a remarkable group of enols containing bulky aryl substituents prepared by Fuson some 40 years ago²⁹ and currently being investigated in detail by Rappoport.^{1c} Our results also show an interesting ring-size effect in cyclic ketones: the enol contents of cyclopentanone and cycloheptanone are similar to that of acetone, but that of cyclohexanone is considerably greater; the origin of this effect is not clear.

The data of Table IV show further that the acid strength of enols is comparable to that of phenols. There is not as much variation in the enol acidity

(26) (a) Guthrie, J. P.; Culimore, P. A. *Can. J. Chem.* **1979**, *57*, 240–248. Guthrie, J. P. *Can. J. Chem.* **1979**, *57*, 797–802; 1177–1185. Guthrie, J. P.; Cossar, J.; Klym, A. *J. Am. Chem. Soc.* **1982**, *104*, 895–896; **1984**, *106*, 1351–1360. Guthrie, J. P.; Cossar, J. *Can. J. Chem.* **1986**, *64*, 2470–2474. Guthrie, J. P.; Cossar, J.; Klym, A. *Can. J. Chem.* **1987**, *65*, 2154–2159. (b) Dubois, J. E.; El-Alaoui, M.; Toullec, J. *J. Am. Chem. Soc.* **1981**, *103*, 5393–5401. (c) Tapuhi, E.; Jencks, W. P. *J. Am. Chem. Soc.* **1982**, *104*, 5758–5765.

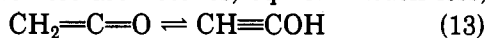
(27) Hochstrasser, R.; Kresge, A. J.; Schepp, N. P.; Wirz, J. *J. Am. Chem. Soc.* **1988**, *110*, 7875–7876.

(28) Hine, J. *Structural Effects on Equilibria in Organic Chemistry*; Wiley-Interscience: New York, 1975; pp 270–276.

(29) Fuson's work has recently been well reviewed by Hart.^{1a}

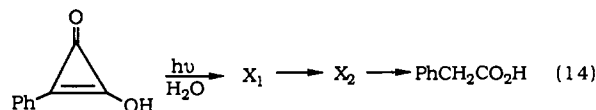
constants (pK_a^E) presented there as in the acidity constants of the keto isomers ionizing as carbon acids (pK_a^K). Changes in pK_a^K values, moreover, parallel those in pK_a^E , and there is in fact a good linear correlation between the two quantities;³⁰ structural effects on pK_a^K thus appear to reflect structural effects on K_E .

Ynols and Ynamines. Ynols or hydroxyacetylenes are the triple-bond analogues of enols. Like enols, they are tautomers of carbonyl compounds; in this case, the tautomeric isomers are ketenes, eq 13. Much less,

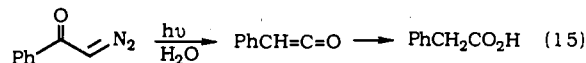


however, is known about ynols than about enols. High-level ab initio calculations predict that they are considerably less stable relative to their keto isomers than is the case with enols,³¹ and the first ymol to have been prepared, hydroxyacetylene itself, was made, in the gas phase, only three years ago.³² It has also been made again, very recently, in an argon matrix.³³

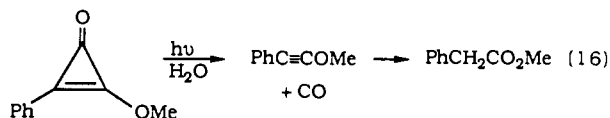
We wished to examine the chemistry of ynols in aqueous solution, and we therefore developed a method of generating these substances in that medium.³⁴ Our technique involves flash photolysis of phenylhydroxycyclopropenone.³⁵ Phenylacetic acid is formed when this process is carried out in aqueous solution, and two transient species may be seen during the course of this reaction, eq 14. We have identified the longer lived



of these transients as phenylketene from the rate law for its decay, which is identical with that for the hydration of phenylketene prepared independently by a photo-Wolff reaction, eq 15.³⁶ We have also found that



flash photolysis of phenylmethoxycyclopropenone³⁷ gives phenylmethoxyacetylene, eq 16, a stable molecule



which we have prepared independently and have characterized kinetically.³⁸ This evidence, plus the fact that photodecarbonylation of cyclopropenones to acetylenes is a well-known reaction,³⁹ indicates that the shorter lived of the two transients observed in the flash

(30) Keeffe, J. R.; Kresge, A. J. In *The Chemistry of Enols*; Rappoport, Z., Ed.; Wiley-Interscience: New York, in press.

(31) (a) Bouma, W. J.; Nobes, R. H.; Radom, L.; Woodward, C. E. *J. Org. Chem.* **1982**, *47*, 1869-1875. (b) Smith, B. J.; Radom, L.; Kresge, A. J. *J. Am. Chem. Soc.* **1989**, *111*, 8297-8299.

(32) von Baar, B.; Weiske, T.; Terlouw, J. K.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 282-284.

(33) Hochstrasser, R.; Wirz, J. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 181-183.

(34) Chiang, Y.; Kresge, A. J.; Hochstrasser, R.; Wirz, J. *J. Am. Chem. Soc.* **1989**, *111*, 2355-2357.

(35) Chickos, J. S.; Patton, E.; West, R. *J. Org. Chem.* **1974**, *39*, 1647-1650.

(36) Allen, A. D.; Kresge, A. J.; Schepp, N. P.; Tidwell, T. T. *Can. J. Chem.* **1987**, *65*, 1719-1723.

(37) Farnum, D. G.; Chickos, J.; Thurston, P. E. *J. Am. Chem. Soc.* **1966**, *88*, 3075-3081.

(38) Banait, N.; Hojatti, M.; Findlay, P.; Kresge, A. J. *Can. J. Chem.* **1987**, *65*, 441-444.

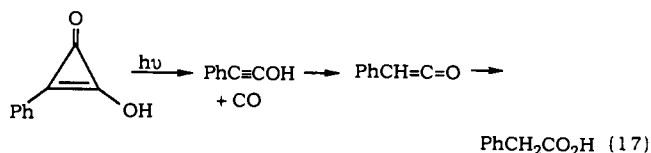
(39) See, e.g.: Sander, W.; Chapman, O. L. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 398-399.

Table V
Comparison of pK_a Values

substance	pK_a
PhC≡COH	<2.8
PhCH=CHOH	9.6 ^a
PhCH ₂ CH ₂ OH	15.5 ^b
CH=CH	24 ^c
CH ₂ =CH ₂	44 ^c

^a Average of values for cis and trans enols; ref 23. ^b Estimated by using correlation of ref 42. ^c Reference 43.

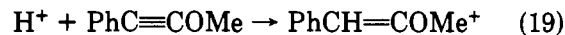
photolysis of phenylhydroxycyclopropenone is phenylhydroxyacetylene, and that the reaction proceeds as shown in eq 17.



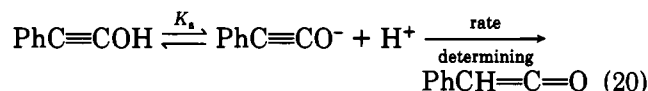
The conversion of phenylhydroxyacetylene to phenylketene is subject to general acid catalysis and gives a hydronium ion isotope effect in the normal direction, $k_{H^+}/k_{D^+} > 1$. This is classic evidence for rate-determining proton transfer from catalyst to substrate, and it suggests that the ymol to ketene reaction occurs by simple protonation of the ymol on acetylenic carbon, eq 18. However, the rate constant that may be estimated



for such a process, $k_{H^+} = 1-10 \text{ M}^{-1} \text{ s}^{-1}$, from the known hydronium ion catalytic coefficient for the corresponding reaction of phenylmethoxyacetylene, eq 19,³⁸



and from the fact that enols are usually 1-2 orders of magnitude more reactive than analogous methyl enol ethers,^{24a,26b,30,40} is many orders of magnitude less than the observed rate constant, $k_{H^+} = 1.4 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$. Enolate ions, on the other hand, are very much more reactive than enols, by factors as great as 10^9 ,⁴¹ and ymolate ions should also be correspondingly more reactive than ynols. The rate constant observed is thus consistent with a process involving rate-determining protonation of the ymolate ion, rather than ymol, on acetylenic carbon, eq 20.



Such a process requires the rate of reaction to be proportional to H^+ concentration as long as the position of the ymol-ymolate equilibrium is on the side of ymolate. When the H^+ concentration becomes greater than the acidity constant of the ymol and the position of equilibrium shifts over to the side of ymol, the rate will become independent of the concentration of H^+ . We have monitored this reaction up to an H^+ concentration of 0.0016 M—above this point the rate becomes too fast

(40) Capon, B.; Zucco, C. *J. Am. Chem. Soc.* **1982**, *104*, 7567-7572.

(41) Chiang, Y.; Kresge, A. J.; Santaballa, J. A.; Wirz, J. *J. Am. Chem. Soc.* **1988**, *110*, 5506-5510.

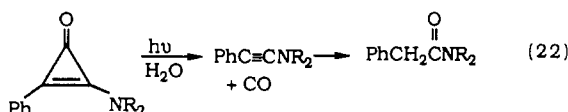
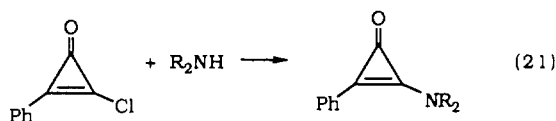
(42) Perrin, D. D.; Dempsey, B.; Serjeant, E. P. *pK_a Predictions for Organic Acids and Bases*; Chapman and Hall: London, 1981; p 60.

(43) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 3rd ed.; Harper and Row: New York, 1987; p 294.

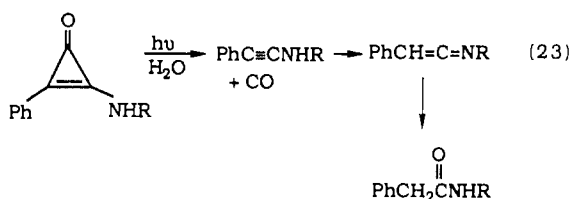
for us to measure—without seeing such a change in H^+ concentration dependence. This indicates that the position of equilibrium has remained on the side of ynolate, and that implies that the pK_a of the ynol is less than 2.8 ($=-\log 0.0016$).

This is a remarkable result. It makes phenylhydroxyacetylene more acidic than a carboxylic acid! Phenylhydroxyacetylene is also at least 7 orders of magnitude more acidic than its double-bond analogue, the enol of phenylacetaldehyde, and at least 13 orders of magnitude more acidic than the fully saturated analogue, β -phenylethanol (cf. Table V). This striking acid-strengthening effect of the carbon-carbon triple bond is reminiscent of the greater acidity of acetylene over ethylene (Table V).

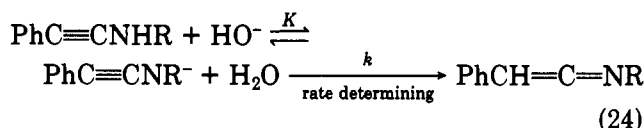
We have recently seen this remarkable effect in yet another system.⁴⁴ We have found that phenyl(*N,N*-dialkylamino)cyclopropenones, prepared by treating phenylchlorocyclopropenone with secondary amines, eq 21, when subjected to flash photolysis in aqueous solution, undergo decarbonylation to tertiary ynamines, eq 22, which we have identified by their known rates



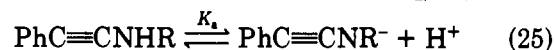
of hydration to phenylacetamides.⁴⁵ When the phenylaminocyclopropenone is derived from a primary amine or ammonia, flash photolytic decarbonylation also occurs, but now the ynamines are converted to ketenimines, eq 23, which we have also identified from the known rate laws for the hydration of these substances.⁴⁶



The conversion of primary or secondary ynamines to ketenimines is catalyzed by the hydroxide ion but not by general bases. This indicates that the reaction occurs by rapid preequilibrium ionization of the ynamine to its anion, followed by rate-determining protonation of the latter on acetylenic carbon by water, eq 24. We do



not know the rate constant for this rate-determining step, but a reasonable upper limit would be a value corresponding to the rotational diffusion (dielectric relaxation) time of liquid water, $\tau \approx 10^{-11}$ s.⁴⁷ Use of this value, plus the experimentally determined hydroxide ion catalytic coefficient for the overall reaction of eq 24, then allows us to set a lower limit for the preequilibrium constant, K , and therefore also a lower limit for the dissociation constant of the ynamine ionizing as an acid, eq 25, inasmuch as $K = K_a/K_w$, where



K_w is the (known) autoprotolysis constant of water. For phenylamine itself, $\text{PhC}\equiv\text{CNH}_2$, this treatment gives $pK_a \leq 18$, which makes this amine at least 17 pK units more acidic than NH_3 ($pK_a = 35$).⁴⁸

Some insight into the origin of this striking acid-strengthening effect of carbon-carbon triple bonds is provided by recent ab initio calculations.^{31b} These pertain to the gas phase, and they predict that hydroxyacetylene is more acidic than vinyl alcohol in that medium, just as we have observed for aqueous solution. The calculations show further that transfer of a hydroxyl group from an acetylenic carbon to an olefinic one, eq 26, is an exoergic process, consistent with σ - $\text{CH}\equiv\text{COH} + \text{CH}_2=\text{CH}_2 \rightarrow \text{CH}\equiv\text{CH} + \text{CH}_2=\text{CHOH}$ (26)

electron withdrawal by OH from $\text{CH}\equiv\text{C}$ being more unfavorable than from $\text{CH}_2=\text{CH}$,⁴⁹ and they also show that transfer of a negatively charged oxygen atom from acetylenic to olefinic carbon, eq 27, is an endoergic $\text{CH}\equiv\text{CO}^- + \text{CH}_2=\text{CH}_2 \rightarrow \text{CH}\equiv\text{CH} + \text{CH}_2=\text{CHO}^-$ (27)

process, consistent with better π -electron donation by O^- to $\text{CH}\equiv\text{C}$ than to $\text{CH}_2=\text{CH}$.⁴⁹ These calculations thus suggest that the remarkable acid-strengthening effect of the carbon-carbon triple bond in ynols is due to a combination of destabilization of the ynol and stabilization of the ynolate ion.

I am grateful to many skilled collaborators who have contributed so much to this research, especially Professor J. Wirz, who introduced me to flash photolysis and without whose continued assistance much of this work could not have been done. I also thank the Natural Sciences and Engineering Research Council of Canada, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Shell Development Company for their financial support.

(47) Caldin, E. F. *Fast Reactions in Solution*; Blackwell: Oxford, 1964; p 103.

(48) Bell, R. P. *The Proton in Chemistry*, 2nd ed.; Cornell University Press: Ithaca, NY, 1973; pp 86-87.

(49) Radom, L.; Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* 1971, 93, 289-300.

(44) Chiang, Y.; Kresge, A. J., unpublished work.

(45) Verhelst, W. F.; Drenth, W. *J. Am. Chem. Soc.* 1974, 96, 6692-6697.

(46) McCarthy, D. G.; Hegarty, A. F. *J. Chem. Soc., Perkin Trans. 2* 1980, 579-591.