Phenylynol, PhC≡COH: First Direct Detection in Solution via Time-Resolved Infrared Spectroscopy[1]

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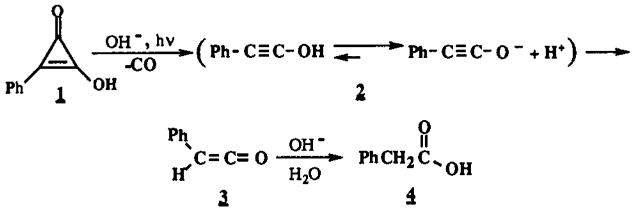
In this communication we report the first direct spectroscopic detection and some kinetic properties of a hydroxyacetylene, or ynol, in its neutral form in solution at room temperature. Ynols are the triple-bond analogues of enols and are tautomers of ketenes, just as enols are tautomers of ketones. Whereas the chemistry of enols has been well–studied, relatively little is known about ynols. In a search for direct spectroscopic evidence of ynol in ambient solution, Kresge *et al.* reported in a recent set of papers[3,4] the first UV detection of the deprotonated form of an ynol, the ynolate anion; under their experimental conditions the ynol–ynolate equilibrium was entirely shifted toward the ynolate. Previous to that work, the only observations of ynols were of the simplest example, hydroxyacetylene, in the gas phase (characterized by its mass spectrum)[5] and in a low-temperature argon matrix (characterized by its infrared spectrum: $\bar{\nu}_{C\equiv C}$ = 2202 cm^{-1}),[6] and of vinyl hydroxyacetylene in the gas phase ($\bar{\nu}_{C\equiv C}$ = 2250 cm^{-1}).[7]

Kresge *et al.*[4] used UV laser flash photolysis (LFP) to study the photochemistry of phenylhydroxycyclopropenone, **1**, in 0.1 M aqueous sodium hydroxide solution. They observed a transient absorption at 280 nm that decayed following two-exponential kinetics (τ_1 = 0.5 μs, τ_2 = 6.2 μs), superimposed on the bleaching of the absorption of **1**. This complex kinetic trace was assumed to indicate the presence of two successive intermediates, the second of which was firmly identified as phenylketene. The identification of the first intermediate as phenylynolate was based on the analogy to the photochemistry of other phenylcyclopropenones, and on the extremely large rate constant for protonation of this species (leading to formation of the ketene) of 1.4 × 10^{10} M^{-1} s^{-1}, far from the expected rate constant of ca. 1–10 M^{-1} s^{-1} for the protonation of the parent ynol.[4] Thus, Kresge *et al.*'s findings from LFP and product studies can be summarized in the following mechanism for the alkaline aqueous solution photochemistry of **1**:



LFP with infrared detection of transients[8,9] seemed to us to be perfectly suited for further exploration of the photochemistry of phenylhydroxycyclopropenone, particularly in neutral solvents with an aim of direct spectroscopic identification and kinetic characterization of the neutral phenylynol. The major advantage of this technique is that the ketene and ynol will have distinct and well-separated absorptions in the infrared, in the regions of 2100 and 2250 cm^{-1}, respectively. Thus, in principle, they can be spectroscopically identified and the kinetics of each species can be followed independently.

Upon 380-nm LFP of **1** in acetonitrile (MeCN), the instantaneous (*i.e.*, limited by the instrument response time) bleaching of the carbonyl band of the starting material, monitored at 1863 cm^{-1}, was observed accompanied by the growth, with a rate constant of 5.3 × 10^5 s^{-1}, of a strong absorption centered at 2110 ± 5 cm^{-1} readily assigned to phenylketene, **3**.[10] The growth rate of the ketene absorption was significantly slower than the instrument response time of *ca.* 2 × 10^6 s^{-1}, indicating the existence of a transient ketene precursor. The growth of the ketene absorption was not catalyzed by the addition of acid (trifluoroacetic, malonic, or sulfuric), suggesting that the intermediate species was the ynol, and not the ynolate anion (*vide supra*). On the other hand, the growth of the ketene was accelerated upon the addition of H_2O or methanol (MeOH). Interestingly, the quenching plots of k_{growth} *vs* [Q] showed significant upward curvature at [H_2O] ≥ 0.5 M and [MeOH] ≥ 2 M, suggesting that the H_2O or MeOH oligomers are better catalysts of the ynol to ketene conversion than the corresponding monomers.[11] Characteristics of the kinetics of formation of phenylketene indicate that its transient precursor is the ynol; unfortunately MeCN has a very strong absorption centered at 2253 cm^{-1}; hence any search for the absorption corresponding to the C≡C stretch of the ynol in this solvent was hopeless.

In dry dimethylformamide (DMF), a 308-nm LFP of **1** leads to a slow growth of the characteristic phenylketene absorption centered at 2110 cm^{-1}. In fact, the rate of the growth of the ketene absorption was too slow under these conditions to be accurately measured on our instrument (growth lifetime > 32 μs). As in MeCN, the formation of the ketene absorption was not acid-catalyzed, and hence it suggested that it is the long-lived ynol that is present as the phenylketene precuror in this solvent. The growth of the ketene was catalyzed by H_2O and MeOH, with the quenching plots displaying even greater upward curvature than that observed in the case of MeCN. The time-resolved IR absorption trace and spectrum observed for the phenylketene in a 0.30 M H_2O/DMF solution (which gives a growth in the proper range to be accurately measured on our system) are shown in Figure 1b. The rate of the observed ketene growth is 1.4 × 10^5 s^{-1}. On the basis of the very slow growth of the phenylketene and its lack of acid catalysis in DMF, it was expected that the ynol **2** should be observable in this solvent. Indeed, a transient IR absorption, *ca.* 12 times weaker than that concurrently observed for the ketene (our *ab initio* calculations yield a factor of 8.4), was observed in the expected C≡C stretching region, with a band maximum at 2245 ± 8 cm^{-1}. Its growth was instantaneous (*i.e.*, limited by the instrument response time), while its rate of decay was 1.6 × 10^4 s^{-1}, indicating a lifetime of 63 μs for phenylynol in this solvent. The decay of the observed signal was catalyzed by water; again a curved quenching plot was obtained, which matched that obtained from the growth of the ketene. For example, in a 0.30 M H_2O/DMF solution the rate of the observed ynol decay was 1.3 × 10^5 s^{-1}, in very good agreement with the observed rate of growth of the ketene, *i.e.*, 1.4 × 10^5 s^{-1} under the same conditions, confirming the suggested intermediacy of the ynol in the ketene formation in the phenylhydroxycyclopro-

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[8] A laser flash photolysis system with a Mütek MPS-1000 diode laser (output 1520–2314 cm^{-1}) as the monitoring source was used. A description of an earlier version of this instrument is given in ref 9; full details of the present system will be provided in an upcoming publication.

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[10] Asymmetric stretching frequency of phenylketene: 2115 cm^{-1} (Ar matrix). McMahon, R. J.; Abelt, C. J.; Chapman, O. L.; Johnson, J. W.; Kreil, C. L.; LeRoux, J.-P.; Mooring, A. M.; West, P. R. *J. Am. Chem. Soc.* **1987**, *109*, 2456-2469.

[11] Similar behavior has been reported, for example, for the reaction of MeOH with carbenes in acetonitrile solution. See: Griller, D.; Liu, M. T. H.; Scaiano, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 5549-5551.

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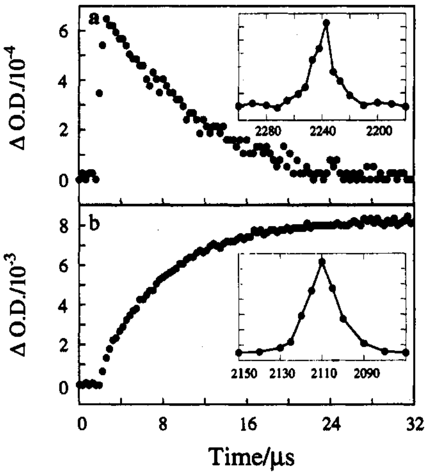

Figure 1. Time-resolved IR absorption traces and spectra observed following a 308-nm laser flash photolysis of 1 in 0.3 M H_2O/DMF: (a) Decay of phenylynol absorption monitored at 2240 cm^{-1}. The inset shows the corresponding time-resolved infrared spectrum in this region. (b) Growth of phenylketene absorption monitored at 2110 cm^{-1}. The inset shows the corresponding time-resolved spectrum in this region.

penone photolysis. The time-resolved IR absorption trace and spectrum observed for phenylynol under these conditions is shown in Figure 1a. In the presence of added hydroxide, no transient signal was observed in this $C\equiv C$ stretching region of the spectrum.

In order to confirm the lack of H^+ catalysis of the ynol to ketene conversion, the experiment was repeated in DMSO, a solvent for which the pK_a's of several strong organic acids have been reported.[12] The ketene absorption was again observed at 2110 cm^{-1}, with a rate of growth of 8.6×10^4 s^{-1}. The ynol was observed with a band at 2253 ± 8 cm^{-1} and a decay rate of 8.7×10^4 s^{-1}. Both the ynol decay and ketene growth were unaffected by the addition of up to 0.10 M CH_3SO_3H ($pK_a = 1.8$ in DMSO;[12] $[H^+] = 2.9 \times 10^{-2}$ M), suggesting an upper limit for k_{H^+} of ca. 10^5 M^{-1} s^{-1}. This rate constant is ca. 5 orders of magnitude smaller than the value of 1.4×10^{10} M^{-1} s^{-1} reported by Kresge *et al.*[4] for the phenylynolate ion and is consistent with their estimated value of 1–10 M^{-1} s^{-1} for the protonation rate constant for the neutral ynol.

The assignment of the observed band at 2245 ± 8 cm^{-1} (H_2O/DMF) or 2253 ± 8 cm^{-1} (DMSO) to the $C\equiv C$ stretch of phenylynol is consistent with the IR frequencies previously reported for the following related acetylenes (room temperature liquid phase unless otherwise indicated, cm^{-1}): $HC\equiv COH$, 2202 (Ar matrix);[6] $CH_2{=}CHC\equiv COH$, 2250 (gas phase);[7] $PhC\equiv COMe$, 2277;[13] $PhC\equiv COEt$, 2258;[13] $PhC\equiv COPr^i$, 2253;[13] $PhC\equiv COBu^t$, 2238;[13] $Bu^tC\equiv COSiMe_2Bu^t$, 2270.[14] It is also well supported by our theoretical calculations that yield a frequency of 2255 cm^{-1} for the $C\equiv C$ stretch of phenylynol. This value was arrived at by calculating vibrational frequencies for phenylynol and related acetylene, $CH_2{=}CHC\equiv COH$, at the HF/6-31G* level of theory with the Gaussian 92 suite of programs[15] and then scaling them with a factor of 0.866[16] obtained by matching our theoretical frequency and the previously experimentally measured frequency for the $C\equiv C$ stretch of $CH_2{=}CHC\equiv COH$.[7] It is important to note that the same treatment yields the rather different frequency of 2042 cm^{-1} for the $C\equiv C$ stretch of phenylynolate,[16] thus further supporting the assignment of the transient species observed under our conditions as the neutral phenylynol molecule.

In conclusion, our studies provide the first experimental confirmation of the previous suggestion[4] that the dynamics of the ynol–ketene transformation is very different from that of the ynolate–ketene reaction although most likely in both cases ynolate is the immediate precursor of the ketene. Thus, the protonation of the ynolate is the rate-determining step in aqueous solution while the deprotonation of the ynol to ynolate determines the kinetics of ynol–ketene conversion in aprotic solvents.

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(16) The frequencies (scaled by a factor of 0.866, in cm^{-1}) of the modes with significant IR intensity (with the symmetry of the mode given in parentheses) computed for $CH_2{=}CHC\equiv COH$, $PhC\equiv COH$, and $PhC\equiv CO^-$[17] are as follows: for $CH_2{=}CHC\equiv COH$, 3522 (A′), 2250 (A′), 1210 (A′), 1177 (A′), 1007 (A′), 685 (A′), 931 (A″), 52 (A″); for $PhC\equiv COH$, 3517 (A′), 2939 (A′), 2255 (A′), 1195 (A′), 1001 (A′), 966 (A′), 745 (A′), 61 (A″); and for $PhC\equiv CO^-$ (HF/6-31+G*) 2042 (A_1), 1535 (A_1), 1364 (A_1), 1026 (A_1), 923 (A_1), 671 (A_1), 716 (B_1), 662 (B_1).

(17) Structural parameters obtained at the HF/6-31G* (neutral molecules) and HF/6-31+G* (anion) levels of theory for these molecules are as follows: for $CH_2{=}CHC\equiv COH$, $r(C{=}C) = 1.3217$ Å, $r(C{-}C) = 1.4385$ Å, $r(C\equiv C) = 1.1854$ Å, $r(CO) = 1.3055$ Å, $r(OH) = 0.9498$ Å, and $\angle(COH) = 110.47°$; for $PhC\equiv COH$ (C_s symmetry, with the plane of symmetry perpendicular to the phenyl ring), $r(PhC) = 1.4439$ Å, $r(C\equiv C) = 1.1850$ Å, $r(CO) = 1.3062$ Å, $r(OH) = 0.9500$ Å, and $\angle(COH) = 110.46°$; for $PhC\equiv CO^-$ (C_{2v} symmetry), $r(PhC) = 1.4160$ Å, $r(C\equiv C) = 1.2258$ Å, and $r(CO) = 1.2104$ Å.