136. Direct Observation of Acetophenone Enol Formed by Photohydration of Phenylacetylene

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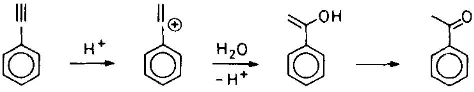
The photohydration of phenylacetylene yields acetophenone enol as a transient primary product which was detected by flash photolysis. The identification of the transient intermediate rests on a quantitative comparison of its decay kinetics with that of authentic acetophenone enol generated by *Norrish type-II* photoelimination from γ-hydroxybutyrophenone in aqueous HCl and aqueous AcOH buffer solutions.

It is generally accepted that enols are formed as intermediate species in the acid-catalyzed hydration of acetylenes, *e.g.* that the conversion of phenylacetylene to acetophenone occurs through the generation and subsequent ketonization of acetophenone enol [1]. When this reaction is conducted thermally, fairly concentrated acids must be used. The rate-determining step is protonation of the substrate to give a vinyl cation (*Scheme*), which then hydrates rapidly, and the enol so formed also ketonizes quickly. Photoexcitation, however, greatly increases the reactivity of acetylenes [2]. We wish to report that the resultant rate enhancement accelerates the initial substrate-protonation step so strongly that formation of the enol intermediate now becomes more rapid than its ketonization. In the photohydration reaction, therefore, the enol may be observed directly, and the rate of its ketonization may be measured accurately.

Scheme



We carried out the photohydration of phenylacetylene in a kinetic flash-photolysis system of conventional design, whose exciting flash was 20 µs wide at half-height. A transient species with strong absorbance at λ = 270 nm formed within the duration of the flash and then decayed more slowly. This decay followed the first-order rate law accurately. Observed first-order rate constants determined at 25° in aqueous HCl solutions over the concentration range [HCl] = 0.001 – 0.045M (ionic strength maintained at 0.10M with NaCl) were directly proportional to acid concentration, and linear least-squares analysis gave the hydrogen-ion catalytic coefficient $k_{\mathrm{H}^+} = (1.22 \pm 0.02) \times 10^3\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$, (91)¹); this is identical with the rate constant determined for the ketonization of aceto-

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¹) Error limits are standard deviations of the regression parameters. The degrees of freedom (number of measurements – 1) are given in brackets.

phenone enol generated by *Norrish type-II* photoelimination of γ-hydroxybutyrophenone under the same conditions, $k_{H^+} = (1.25 \pm 0.02) \times 10^3$ M^{-1} s^{-1}, (30) [3]. We also made measurements at 25° in AcOH buffer solutions of [AcOH]/[AcO$^-$] = 1.8 and ionic strength = 0.10M (maintained with NaCl) over the concentration range [AcOH] = 0.036 – 0.144M; these experiments provided the rate law shown in *Eqn. 1* for the transient formed from phenylacetylene and that shown in *Eqn. 2* for acetophenone enol generated by the *Norrish* reaction. These rate laws are also identical within the

$$k_{obs}/s^{-1} = (0.57 \pm 0.13) + (46.5 \pm 1.3)\,[\mathrm{AcOH}]/\mathrm{M},\ (32) \qquad (1)$$

$$k_{obs}/s^{-1} = (0.29 \pm 0.14) + (46.1 \pm 1.4)\,[\mathrm{AcOH}]/\mathrm{M},\ (20) \qquad (2)$$

(rather small) experimental uncertainty.

The results summarized above leave no doubt that the transient species formed in the acid-catalyzed photohydration of phenylacetylene is acetophenone enol. Several methods for the generation and observation of simple enols in aqueous solution have recently been developed, and they have provided direct insight into the chemistry of enols [4]. The present method might provide entry into entirely new regions of enol chemistry: into the chemistry of enols of carboxylic acid esters through the photohydration of alkoxy-acetylenes, and into the chemistry of enols of carboxamides through the photohydration of aminoacetylenes. Work along these lines is in progress.

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