Nanosecond Time-Resolved Spectroscopic Study on the
Photochemical Conversion of 1,2-Naphthoquinonediazides

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1. Introduction

The photochemical conversion of 1,2-naphthoquinonediazides produces corresponding indenecarboxylic acids. This reaction has attracted much attention because of the interest both in wide application to the microlithographic process [1] and in fundamental research [2]. In spite of many investigations, its detailed mechanism is still a matter of some discussion and controversy [3-6].

The authors have recently studied the conversion mechanism for 1,2-naphthoquinonediazide-5-sulfonic acid (NQDS) in a solution by nanosecond time-resolved spectroscopy and observed a transient absorption with a peak around 350 nm [7]. The transient absorption was assigned to a ketene hydrate from the experimental results of its formation and decay kinetics. The ketene hydrate was found to be converted to 3-indenecarboxylic acid by acid catalysis.

In the present study, the authors have used non-substituted 1,2-naphthoquinonediazide (NQD) and several buffers to investigate the conversion mechanism over a wide pH range. This communication describes more detailed kinetics of the ketene hydrate than that reported previously.

2. Experimental

The apparatus for nanosecond time-resolved spectroscopy was slightly modified from that described in the previous paper [7]. The fourth harmonic pulse (266 nm, 5 ns) of a Q-switched Nd:YAG laser was used for excitation, and a xenon or tungsten lamp was used as a probe. NQD was purified by recrystallization from methanol. Several buffers were prepared by selecting the following systems: acetic acid-sodium acetate, for pH 3.2-6.2; potassium dihydrogenphosphate-disodium hydrogenphosphate, for pH 6.4-8.0; potassium dihydrogenphosphate-borax, for pH 8.2-9.2; and borax-sodium carbonate, for pH 9.4-10.0. All spectroscopic measurements were performed at room temperature for air-exchanged solutions with nitrogen. The solute concentration was between 5×10^{-5} and 7×10^{-4} M.

3. Results and Discussion

Figure 1 shows the transient difference spectra of NQD in water after 266 nm laser pulse excitation. The difference spectrum at 4 μ s after photoexcitation (solid curve with open circles) has a peak around 340 nm, which is due to the photoinduced transient species. The difference spectrum at 8 ms (dashed curve) has a negative peak around 400 nm, which indicates the photodecomposition of NQD. The transient species could not be detected in the dehydrated 1,4-dioxane, while it appeared in the mixed solvent of 1,4-dioxane:water=100:1 (v/v). Both the formation and decay kinetics of the transient species were apparently of the first order, and its life time was about 10^{-4} – 10^{-3} s. Such a behavior was consistent with that of the ketene hydrate detected in the previous experiment [7]; hence, the transient absorption observed here can be assigned to the ketene hydrate.

The formation kinetics of the ketene hydrate was studied in a mixed solvent of 1,4-dioxane/water. Figure 2 shows the dependence of the formation rate constant (k_f) on the molar concentration of water for NQD (solid curve with closed circles) and NQDS (dashed curve with open circles). Since k_f increased with increasing $[H_2O]$ for both NQD and NQDS, the ketene hydrate appears to be formed by the reaction between its precursor (ketene) and water. The relationship between k_f and $[H_2O]$, however, was not linear. This nonlinearity can presumably be ascribed to the solvent effect of the mixed solvent of 1,4-dioxane/water [8]. It also should be noted that k_f for NQDS was about 4–13 times larger than that for NQD at the same water concentration. The nature of the sulfonic acid group may explain such a difference between

Fig. 1 Transient difference spectra of NQD in water at 4 μ s (solid curve with open circles) and 8 ms (dashed curve) after photoexcitation

Fig. 2 Dependence of the formation rate constant for ketene hydrate on the molar concentration of water in the mixed 1,4-dioxane/water solutions of NQD (solid curve with closed circles) and NQDS (dashed curve with open circles)

Scheme I

NQD and NQDS. Since the sulfonic acid group is highly hydrophilic, the ketene for NQDS is more likely to be solvated by water than that for NQD. Furthermore, the electron-withdrawing sulfonic acid group is expected to facilitate the nucleophilic attack by a water molecule on the carbonyl carbon atom of the protonated ketene. The postulated hydration mechanism is shown in Scheme 1.

The decay kinetics of the ketene hydrate for NQD was studied in an acidic buffer (pH 3.2-4.6). Figure 3 shows the dependence of the decay rate constant (k_d) on the hydrogen ion concentration. The relationship between k_d and $[H^+]$ gave a straight line. Thus, one can conclude that the ketene hydrate is converted to 3-indenecarboxylic acid by acid catalysis. From the slope of this straight line, the acid catalytic constant (k_H) was determined to be $k_H = (3.7 \pm 0.2) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$.

The same experiment was extended to neutral and/or basic buffers. The common logarithm of k_d ($\log k_d$) is plotted as a function of pH in Figure 4. The $\log k_d$ value decreased rapidly with increasing pH in an acidic buffer (pH 3.2-6.2), while it was independent of pH in a neutral buffer (pH 6.2-7.5). These results indicate that the decay of the ketene hydrate is due to multiple catalysis, and led the authors to propose two types of reaction pathways, as shown in Scheme 2. Scheme 2a is an acid-catalyzed reaction. Taking into account the mesomeric effect and steric hindrance of two hydroxyl groups, it is predictable that proton will attack the 3-position of the ketene hydrate to result in 3-indenecarboxylic acid. On the other hand, Scheme 2b is a spontaneous (water-catalyzed) reaction, which is an intramolecular prototropy followed by a double-bond rearrangement. Such a rearrangement has been supported

Fig. 3 Dependence of the decay rate constant for ketene hydrate of NQD on hydrogen ion concentration in an acidic buffer (pH 3.2-4.6)

Fig. 4 Dependence of $\log k_d$ for ketene hydrate of NQD on pH of several buffers

Scheme 2

Ketene hydrate

3-indenecarboxylic acid

in the previous study on the base promoted 1,3-prototropy for 1-indene derivatives [9]. Furthermore, it is noticeable that $\log k_d$ varied again in the higher pH region (pH 7.5-10.0). This suggests that other species (negatively charged ions as the base) also play the role as a catalyst in this decay process.

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