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RESEARCH ARTICLE

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Reaction mechanism studies on isoquinoline with hydroxyl radical in aqueous solutions

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Abstract The reaction mechanism between isoquinoline and ·OH radical in aqueous dilute solutions under different conditions was studied by pulse radiolysis. The main characteristic peaks in these transient absorption spectra were attributed and the growth-decay trends of several transient species were investigated. Under neutral or alkaline conditions, the reaction of ·OH radical and isoquinoline produces OH-adducts with respective rate constants of 3.4×10^9 and 6.6×10^9 $mol^{-1} \cdot dm^3 \cdot s^{-1}$ while under acidic conditions, the isoquinoline was firstly protonated and then ·OH added to the benzene ring and produced protonated isoquinoline OH-adducts with a rate constant of 3.9×10^9 $mol^{-1} \cdot dm^3 \cdot s^{-1}$. With a better understanding on radiolysis of isoquinoline, this study is of help for its degradation and for environmental protection.

Keywords isoquinoline, pulse radiolysis, transient absorption spectra, hydroxyl radical

1 Introduction

Along with the development of modern industry, heterocyclics are applied in chemical and pharmaceutical industry more and more widely. Heterocyclics will pollute the environment when their concentrations exceed a certain level, because they are difficult to destroy during the metabolic process. The nature makes them a category of refractory organics with a broad pollution area and large toxicity. Among numerous heterocyclic compounds, many of *N*-heterocyclics are considered toxic and/or mutagenic and carcinogenic [1–6], which were the main contaminations of many kinds of industrial wastewater, such as coking wastewater, dye industrial wastewater, rubber industrial wastewater, pharmaceutical industrial wastewater, and so on [7–9]. Hence, their degradation in surface water and ground water are concerned more and more. Isoquinoline is a kind of familiar *N*-heterocyclic compounds. It is an important material in chemical industry for the production of medicines, dyes, colorful film photosensitive intensifiers, rubber promoters and insecticides. Consequently, this kind of industrial wastewater contains a certain amount of isoquinoline. Isoquinoline is also one of the main contaminants in coking wastewater. Some processes of isoquinoline degradation, such as the active mud process [10], anaerobic process [11,12], anaerobic acidification-anoxic-aerobic membrane process [13], advance oxidation processes [14,15], and supercritical water-decomposition [16] were reported in the literature. However, because the degradation mechanism of isoquinoline was not investigated in these researches, they can not instruct the degradation of isoquinoline in wastewater. In this paper, the oxidation degradation of isoquinoline in aqueous solutions under various conditions was observed by pulse radiolysis. The result and conclusion will instruct the degradation of isoquinoline in practice wastewater effectively.

2 Experimental

Isoquinoline was purchased from Sigma-Aldrich (98% purity). All other chemicals were purchased from local chemical reagent company and were used without further purification. The pHs of the solutions were adjusted with $HClO_4$ (70%) and NaOH. The solutions were newly prepared by three-time distilled water before the pulse radiolysis experiment and saturated with N_2 or N_2O for 20 min. The purity of N_2 or N_2O was higher than 99.99%.

Pulse radiolysis experiments were carried out using the nanosecond-grade pulse radiolysis apparatus in Shanghai Institute of Applied Physics of Chinese Academy of Science. The energy of the linear accelerator was 10 MeV and the pulse length was 8 ns. The dosage of pulse radiation was

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continuously adjustable in the range of 10–50 Gy. Dosimetry was carried out with N_2O-saturated solutions of 0.01 mol·dm^{-3} KSCN. The resource of analytical light was 500 W Xe lamp, which can be increased 100 times in the duration of detection. The analytical light transferred through a quartz pool and then into the 44 W monochromator and detected by IP28 photomultiplier. The electrical signal was recorded by HP54510B digital oscilloscope and the data were analyzed by computer. [17,18] All of the experiments were performed at room temperature (about 25°C).

3 Results and discussions

3.1 Under neutral condition

A 1×10^{-4} mol·dm^{-3} isoquinoline solution was prepared and the pH value was adjusted to 7 by the addition of NaOH and $HClO_4$ aqueous solution, and then N_2O bubbled in the solution for 20 minutes. The solution of pulse radiolysis was performed right away. Figure 1 showed the transient absorption spectra recorded at different time after the pulse radiolysis of N_2O-saturated aqueous solution containing isoquinoline (1×10^{-4} mol·dm^{-3}) at pH = 7. The spectra showed that the maximum absorption was at the length of 330 nm.

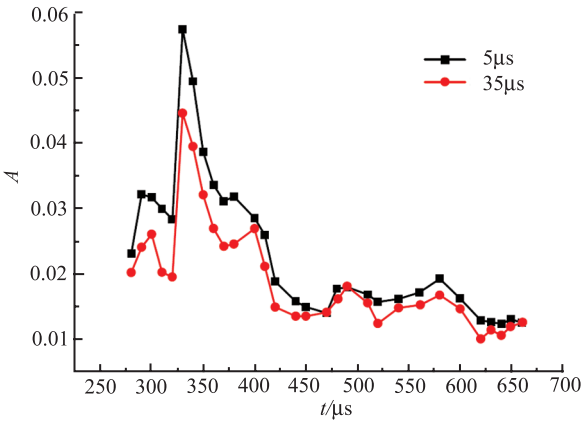


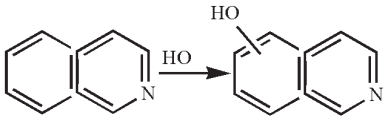
Fig. 1 Transient absorption spectra recorded at different time after the pulse radiolysis of N_2O-saturated aqueous solution containing isoquinoline (1×10^{-4} mol·dm^{-3}) at pH = 7

Under this condition, the quantum yield of hydrogen radical can be ignored after water radiolysis by electron beam. The main products were hydroxyl radical (HO·) and hydrated electron (e_{aq}^-) (Eq. (1)). However, e_{aq}^- can be eliminated by N_2O (Eq. (2)) and produced HO· (Eq. (3)). Hence, the main primary species were only HO· radicals in the system. Therefore, the absorption peak at the length of 330 nm could be considered as the absorption of the transient reaction products of isoquinoline and HO·. HO· was an electrophilic reagent and could be added to the rings of isoquinoline. While π-electron cloud density in the benzene ring was higher for the influence of N atom in the pyridine ring, the addition reaction mainly happened at the benzene ring. The main reactions happened in the system as follows

$$H_2O \xrightarrow{\text{electron beam}} e_{aq}^- + HO^{\cdot} \quad (1)$$

$$e_{aq}^- + H_2O \longrightarrow N_2O^- \quad (2)$$

$$N_2O^- + H_2O \longrightarrow N_2 + OH^- + HO^{\cdot} \quad (3)$$



(4)

Figure 2 showed the growth and decay curve of the absorption at 330 nm. Because the concentration of HO· produced instantaneously was far less than that of isoquinoline, the concentration of isoquinoline could be considered as a constant and the reaction could be dealt with as the first-order reaction. The observational reaction rate constant was 1.22×10^6 s^{-1}. A series of observational reaction rate constants were obtained by changing the concentration of isoquinoline. Figure 3 showed the dependence of observational reaction rate constant on the concentration of isoquinoline. The slope of the line were the absolute rate constant of the reaction between isoquinoline and hydroxyl radical of 3.4×10^9 mol^{-1}·dm^3·s^{-1}.

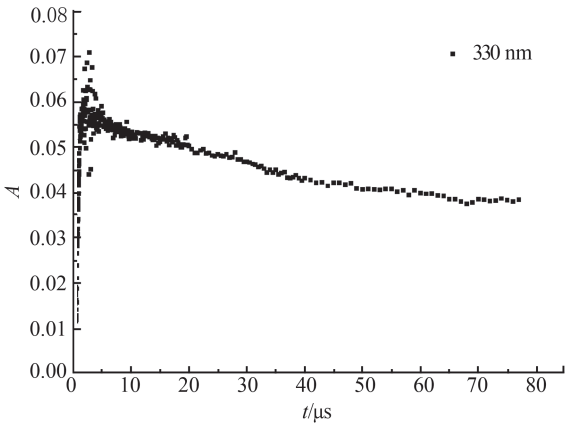


Fig. 2 Growth and decay curve of the absorption at 330 nm of N_2O-saturated aqueous solution containing isoquinoline (1×10^{-4} mol·dm^{-3}) at pH = 7 after the pulse radiolysis

3.2 Under alkaline condition

A 1×10^{-4} mol·dm^{-3} isoquinoline solution was prepared and the pH value was adjusted to 11 by the addition of NaOH aqueous solution, and then N_2O bubbled in the solution for 20 min. The solution of pulse radiolysis was performed right away. Figure 4 showed the respective transient absorption spectra recorded at 5 μs after the pulse radiolysis at pH = 11 and pH = 7. The figure showed that the transient spectra obtained under the alkaline condition were similar to that obtained under the neutral condition. The maximum absorption was at the length of 330 nm. Because HO· was the main species participating in the reaction under strong alkaline condition, the absorption band should attribute to the reaction

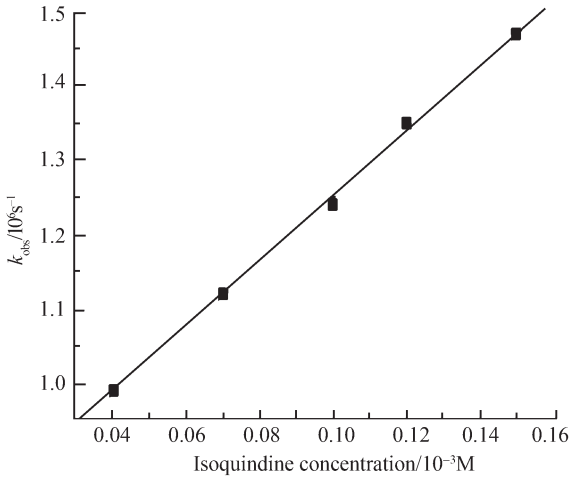


Fig. 3 Dependence of observational rate constant of the reaction between isoquinoline and hydroxyl radical on the concentration of isoquinoline at pH = 7

of HO· and isoquinoline. The growth curve of the absorption at 330 nm was in accordance with the first-order reaction equation. A series of observational reaction rate constants were obtained by the pulse radiolysis of isoquinoline solution with different concentration. Mapping the observational reaction rate constants with the concentration of isoquinoline, the slope was 6.6×10^9 mol^{-1}·dm^3·s^{-1}, which was the absolute rate constant of the reaction between HO· and isoquinoline at pH = 11.

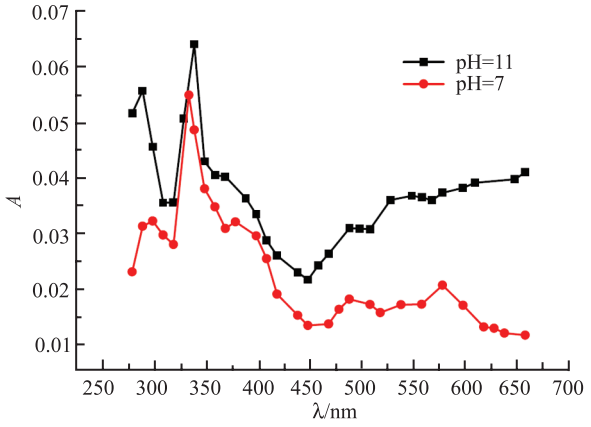


Fig. 4 Respective transient absorption spectra recorded at 5 μs after the pulse radiolysis of N_2O-saturated aqueous solution containing isoquinoline (1×10^{-4} mol·dm^{-3}) at pH = 11 and pH = 7

3.3 Under acidic condition

A 1×10^{-4} mol·dm^{-3} isoquinoline solution was prepared and the pH value was adjusted to 3 by the addition of $HClO_4$ aqueous solution, and then N_2O bubbled in the solution for 20 minutes. The solution of pulse radiolysis was performed right away. Figure 5 showed the respective transient absorption spectra recorded at 5 μs after the pulse radiolysis at pH = 3 and pH = 7. The figure showed that the maximum absorption in the transient spectra at pH = 3 was at the length of 360 nm, which was different from that under the neutral condition. The growth curve of the absorption at 360 nm was in accordance with the first-order reaction equation. The observational rate constant was 1.18×10^6 s^{-1}, which was obtained by the first-order reaction equation with the relative coefficient of 0.990. A series of observational reaction rate constants were obtained by the pulse radiolysis of isoquinoline solution with different concentrations. Mapping the observational reaction rate constants with the concentration of isoquinoline, the slope was 3.9×10^9 mol^{-1}·dm^3·s^{-1}, which was the absolute rate constant of the reaction between HO· and isoquinoline at pH = 3.

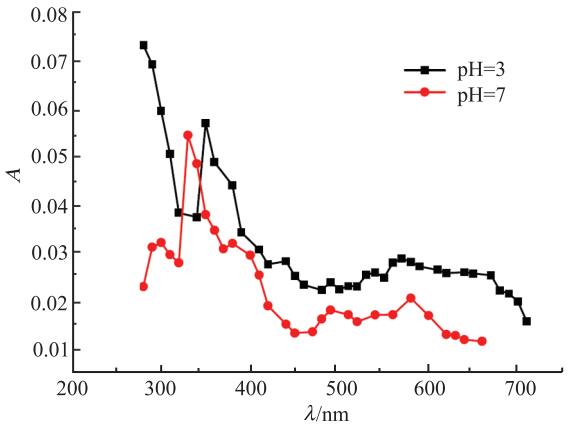
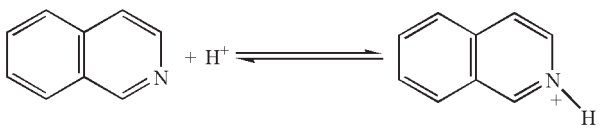


Fig. 5 Respective transient absorption spectra recorded at 5 μs after the pulse radiolysis of N_2O-saturated aqueous solution containing isoquinoline (1×10^{-4} mol·dm^{-3}) at pH = 3 and pH = 7

3.4 Comparison of transient absorption spectra obtained at different pHs

Isoquinoline is a weak base and the pKa of its conjugated acid was 5.23. In an aqueous solution, the following equilibrium occurs.



(5)

IQ representing isoquinoline, Equation (5) can be written as

$$IQ + H^+ \rightleftharpoons IQH^+ \tag{6}$$

while

$$K_a = \frac{[IQ][H^+]}{[IQH^+]} \tag{7}$$

$$\delta_{[IQ]} = \frac{[IQ]}{[IQ]+[IQH^+]} = \frac{K_a}{K_a+[H^+]} \tag{8}$$

$$\delta_{[IQH^+]} = \frac{[IQH^+]}{[IQ]+[IQH^+]} = \frac{[H^+]}{K_a+[H^+]} \tag{9}$$

Figure 6 showed the form distribution diagram of isoquinoline in an aqueous solution against pH protracting according to the calculation result from the data known above.

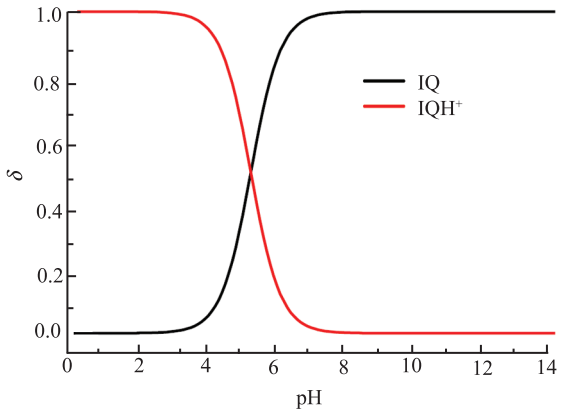
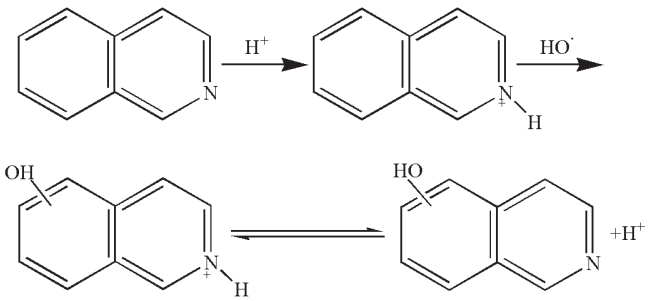


Fig. 6 Distribution diagram of δ against pH for isoquinoline (IQ) and its conjugate acid (IQH^+)

Figure 6 showed that isoquinoline occurs mainly in the form of protonated product at pH = 3 while in the form of isoquinoline molecule at pH = 7 and pH = 11. This fact was confirmed by the UV-Visible absorption spectra of isoquinoline at different pHs (Fig. 7). The figure implied that the spectra under the neutral and alkaline conditions were almost same while they were very different under acidic condition. A red shift occurred at the maximum absorption position and the absorption peak turned broader for the impact of proton to the pyridine ring.

According to the analysis above, we conclude that the followed reactions and equilibriums were occurred in the system under acidic condition



while the main reactions occurred under mediate or basic condition showed as Eq. (4).

Under neutral or alkaline condition, because isoquinoline exists in the same form, the primary species was the same. Therefore, the transient absorption spectra obtained under neutral and alkaline condition was similar. In the spectra, the absorption peak was at 330 nm and the change trend of the absorption at 330 nm was ultimately similar. However, under acidic condition, isoquinoline was firstly protonated and then performed addition reaction with hydroxyl radical. Because the reaction was different, the transient product was different.

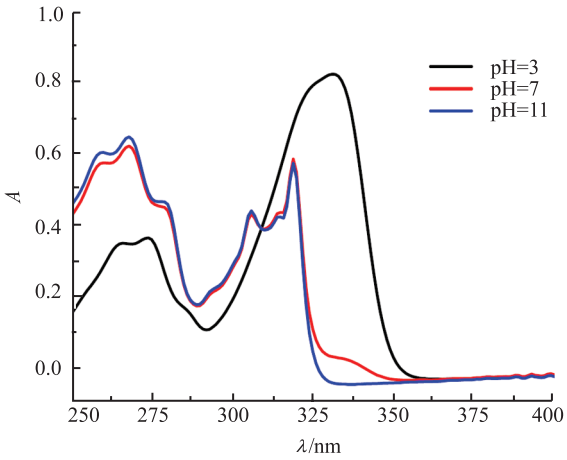


Fig. 7 UV absorption spectra of isoquinoline at different pH

Consequently, the transient absorption spectra were different. For the impact of proton to the pyridine ring, a red shift occurred in the transient absorption spectra obtained under acidic condition compared with that obtained under neutral and alkaline condition.

The pulse radiolysis of isoquinoline showed that hydroxyl radical reacts with isoquinoline and products OH-adducts under neutral and alkaline conditions with the respective rate constants of 3.4×10^9 and 6.6×10^9 $mol^{-1} \cdot dm^3 \cdot s^{-1}$. Hydroxyl radicals mainly add to the benzene ring. However, under the acidic condition, isoquinoline was firstly protonated and then additional reaction was performed with hydroxyl radical with the rate constant of 3.9×10^9 $mol^{-1} \cdot dm^3 \cdot s^{-1}$.

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