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Mechanism study on the reactions between biphenyl and HNO_2 initiated by 355 nm irradiation in aqueous phase

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The reactions taking place in the mixed solution of biphenyl and nitrous acid after it was exposed to UV irradiation were studied in this research work. The transient species were identified with the nanosecond transient spectroscopic technique, and the final products were ascertained by GC-MS analysis. It was shown that the OH radical, generated by the direct photolysis of nitrous acid, would attack biphenyl molecule to form Bp-OH adduct with a rate constant of 9.5×10^9 $L\cdot mol^{-1}\cdot s^{-1}$. The Bp-OH adduct could either react with H^+ or be oxidized by nitrous acid to form nitrosobiphenol. The reactions between biphenyl and nitrous acid under UV irradiation in atmospheric aqueous phase were therefore suggested to be one promising source of nitrocompounds in the environment.

biphenyl, nitrous acid, laser flash photolysis, Bp-OH adduct, nitrosobiphenol

As the parent molecule of polychlorinated biphenyls (PCBs), biphenyl was one kind of important organic pollutant in the environment. The biphenyl in the environment came mainly from the manufacture and utilization of insulating liquids, plasticizing agents, antiseptic substances, dyes, organic heat carriers and high-energy fuels in the chemical and medical industry. In addition, the dechlorination process of PCBs under sunlight is regarded as another source of biphenyl in the environment[1,2]. What are the sinks of biphenyl in the atmosphere? Hitherto, most literature were limited to the elimination of biphenyl in the gas phase[3,4]. Rare research work reported its conversion pathway in the atmospheric condensed phase, such as cloud, fog, dew, and the surface water of aerosol and so on.

With the increasing release of NO_x, N-containing compounds, e.g., NO, NO_2, HNO_2, and HNO_3, were also recognized as main contaminants in the atmosphere. Atmospheric aqueous phase was recognized as an important reservoir of NO_2^-/HNO_2 because the gas phase HNO_2, with Henry's law constant up to 49 $mol\cdot L^{-1}\cdot atm^{-1}$[5,6], was readily dissolved in it. Could the widely distributed HNO_2 react with biphenyl under the sunlight with wavelength longer than 300 nm? If this reaction happened, would it contribute to the transformation of biphenyl in the atmosphere? These questions constitute one of today's public environmental concerns. In this paper, the reaction mechanism between biphenyl and nitrous acid initiated by 355-nm laser was studied by means of laser flash photolysis technique. GC-MS analysis was employed to identify final products. The results will be helpful to a better understanding of the fate of biphenyl in atmospheric water, as well as in the whole atmosphere.

1 Experimental

1.1 Reagents

The reagents used and their purity were as follows: bi-

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phenyl (99.0%, denoted as Bp) from Lancaster, HNO_2 (⩾99.0%), $HClO_4$ (AR), ethanol (⩾99.7%) from Shanghai Chemical Reagents Co., and N_2 (⩾99.999%) from Shanghai BOC Gas Indust. All the reagents were used as received. Solutions were prepared in three distilled water.

1.2 Laser flash photolysis apparatus and experimental method

The reaction between biphenyl and nitrous acid was studied by nanosecond laser flash photolysis apparatus. The 355 nm irradiation, which was used to initiate the photochemical reaction, was generated by the Qaunta-Ray GCR-150 Nd∶YAG laser (Spectra-Physics, laser energy 32.7 mJ/pulse, laser beam cross section 0.45 cm^2, HWFM 5—6 ns, repetition rate 10 Hz). A xenon arc lamp (OSRAM, XBO 150 W/CR-OFR), emitting light from 200 to 1000 nm at a vertical angle to laser beam, was employed as analyzing light. Before the flash, the optical signal was measured by a sample-and-hold circuit, and the change in absorption after the laser flash was detected by means of a differential amplifier (R928 photomultiplier, 5-stage). The electrical output from the photomultiplier was then transferred to a digitizing oscilloscope (Agilent 54820A, 2 GSa/s) connected to the work station (Acorn).

The UV-vis absorption spectra (Scinco, PDA, S-3100) of prepared sample were recorded in order to determine the solute concentration corresponding to Lambert-Beer Law.

Final products were analyzed by using combined Gas Chromatogram and Mass Spectrum (Finnigan MAT ITD, 800GC/MS/DS).

To avoid secondary photochemical reaction, the sample mixture was refreshed after each pulse. All the experiments were carried out at (288 ± 1) K.

2 Results and discussion

2.1 The transient absorbance spectra recorded after laser photolysis of the aqueous solution of biphenyl and HNO_2

Figure 1 shows the transient absorbance spectra recorded after 355-nm laser flash photolysis of the N_2-saturated aqueous solution of 4.0×10^{-5} mol/L biphenyl and 2.0×10^{-3} mol/L HNO_2 at pH = 2.3. The spectrum recorded 0.5 μs after laser pulse exhibited major peaks centered at 310 and 360 nm, respectively. Both their absorption positions and peaks were identical to that of Bp-OH adduct acquired by Sehested et al.[7] and Chen et al.[8] through pulse radiolysis study.

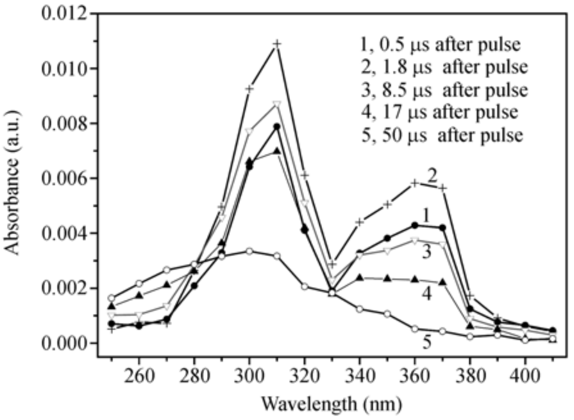


Figure 1 Time resolved transient absorbance spectra after the laser flash photolysis of aqueous solution containing 4.0×10^{-5} mol/L biphenyl and 2.0×10^{-3} mol/L nitrous acid.

The transient spectra were then recorded under identical conditions after the addition of 3.6×10^{-3} mol/L ethanol to scavenge OH radical[9]. The absorptions at 310 and 360 nm were found to decrease proportionally. There is no absorption in the range from 300 to 400 nm when the ethanol concentration was further increased to 3.0×10^{-2} mol/L, implying the transient species with absorption peaks at 310 and 360 nm stemmed from OH radical.

Based on the experimental results, it was concluded that biphenyl was able to react with nitrous acid when exposed to UV irradiation due to the generation of OH radical from HNO_2 photolysis.

$$\mathrm{HONO}\xrightarrow{h\nu}{}^{\bullet}\mathrm{OH}+\mathrm{NO}^{[10]} \tag{1}$$

$$^{\bullet}\mathrm{OH}+\mathrm{Bp}\xrightarrow{k_2}\mathrm{Bp\text{-}OH\ \ adduct} \tag{2}$$

Further study on the growth kinetics at 310 and 360 nm was performed by laser flash photolysis of aqueous solution containing 4.0×10^{-5} mol/L biphenyl and 2.0×10^{-3} mol/L HNO_2. As shown in Figure 2, both curves grew corresponding to first order kinetics with k_{obs} of $(1.88\pm0.03)\times10^{6}\ \mathrm{s}^{-1}$.

Except for reaction (2), the following reactions occurred at the same time.

$$^{\bullet}\mathrm{OH}+\mathrm{HNO_2}\xrightarrow{k_3}\mathrm{NO_2}+\mathrm{H_2O}^{[10]} \tag{3}$$

$$^{\bullet}\mathrm{OH}+{}^{\bullet}\mathrm{OH}\xrightarrow{k_4}\mathrm{H_2O_2} \tag{4}$$

Thus, OH radical decayed via three channels and the rate law expression of OH radical was:

$$-\frac{\mathrm{d[OH]}}{\mathrm{d}t}=k_2[\mathrm{Bp}][\mathrm{OH}]+k_3[\mathrm{HNO_2}][\mathrm{OH}]+2k_4[\mathrm{OH}]^2 \tag{5}$$

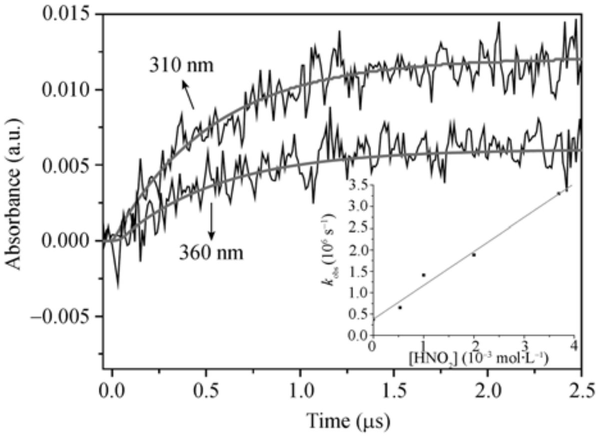


Figure 2 The build-up trends of Bp-OH adduct at 310 and 360 nm. Inset: linear dependence of the observed first-order growth rate of Bp-OH adduct on [HNO$_2$].

According to refs. [9, 11], k_3 and k_4 were 1.0×10^9 and 5.5×10^9 L·mol^{-1}·s^{-1}, respectively. The OH radical concentration was estimated to be no more than 4.0×10^{-6} mol/L by $\mathrm{Br}^{\bullet-}$ stoichiometry[12]. The rate of reaction (3) versus that of reaction (4) then could be expressed as

$$\frac{k_3[\mathrm{OH}][\mathrm{HNO_2}]}{k_4[\mathrm{OH}]^2}=\frac{k_3[\mathrm{HNO_2}]}{k_4[\mathrm{OH}]}\geqslant\frac{1.0\times10^9\times2.0\times10^{-3}}{5.5\times10^9\times4.0\times10^{-6}}$$
$$=90$$

The contribution of reaction (4) to OH radical decay was reasonable to be neglected with respect to reaction (3). Therefore,

$$-\frac{\mathrm{d}[\mathrm{OH}]}{\mathrm{d}t}=k_2[\mathrm{Bp}][\mathrm{OH}]+k_3[\mathrm{HNO_2}][\mathrm{OH}] \qquad (6)$$

Considering the concentration of HNO$_2$ and biphenyl were far more than that of OH radical, both reactions (2) and (3) could be regarded as a pseudo-first order one.

$$[\mathrm{OH}]=[\mathrm{OH}]_0\,\mathrm{e}^{-(k_2[\mathrm{Bp}]+k_3[\mathrm{HNO_2}])t} \qquad (7)$$

Meanwhile, the expression of Bp-OH adduct growth was

$$\frac{\mathrm{d}[\text{Bp-OH adduct}]}{\mathrm{d}t}=k_2[\mathrm{OH}][\mathrm{Bp}] \qquad (8)$$

The addition of eqs. (7) and (8) generated eq. (9)

$$\frac{\mathrm{d}[\text{Bp-OH adduct}]}{\mathrm{d}t}=$$
$$k_2[\mathrm{OH}]_0\exp(-(k_2[\mathrm{Bp}]+k_3[\mathrm{HNO_2}])t)[\mathrm{Bp}] \qquad (9)$$

$$[\text{Bp-OH adduct}]=$$
$$\frac{k_2[\mathrm{OH}]_0[\mathrm{Bp}]}{k_2[\mathrm{Bp}]+k_3[\mathrm{HNO_2}]}(1-\mathrm{e}^{-(k_2[\mathrm{Bp}]+k_3[\mathrm{HNO_2}])t}) \qquad (10)$$

The observed first-order rate constant of Bp-OH adduct (k_{obs}) could be given by

$$k_{obs}=k_2\,[\mathrm{Bp}]+k_3\,[\mathrm{HNO_2}] \qquad (11)$$

As the inset of Figure 2 presented, a linear plot of k_{obs} against [HNO$_2$] was obtained by varying HNO$_2$ concentration. The second order rate constant for the reaction between biphenyl and HNO$_2$ was then determined to be 9.5×10^9 L·mol^{-1}·s^{-1}, which was in good agreement with $(0.9\pm0.1)\times10^{10}$ L·mol^{-1}·s^{-1} reported by Sehested et al.[7] and $(1.04\pm0.05)\times10^{10}$ L·mol^{-1}·s^{-1} given by Chen et al.[8] using pulse radiolysis.

The rate of reaction (2) versus that of reaction (4) was equal to

$$\frac{k_2[\mathrm{OH}][\mathrm{Bp}]}{k_4[\mathrm{OH}]^2}=\frac{k_2[\mathrm{Bp}]}{k_4[\mathrm{OH}]}\geqslant\frac{9.5\times10^9\times4.0\times10^{-5}}{5.5\times10^9\times4.0\times10^{-6}}=17$$

Apparently, it is comprehensible to neglect reaction (4) when deriving k_2.

2.2 The fate of Bp-OH adduct

Ultraviolet light was able to initiate the reaction between biphenyl and HNO$_2$ to yield delocalized intermediate, namely Bp-OH adduct. Bp-OH adduct was observed to proceed bimolecular decay in the pulse radiolysis studies performed by Sehested et al.[7] and Chen et al.[8]. It took several milliseconds for Bp-OH adduct to vanish while Bp-OH adduct decayed on a time scale of merely tens of microseconds in this research work. Which pathway should be responsible for the fast decay of Bp-OH adduct? Further study was carried out to clarify this problem.

As illustrated in Figure 3, there still existed pretty strong absorbance at 310 nm 30 μs after the laser pulse while no significant absorbance signal could be observed at 360 nm. The absorbance at 310 nm would arrive at a constant with the time increased, indicating that one species (denoted as Prod.) generated during the

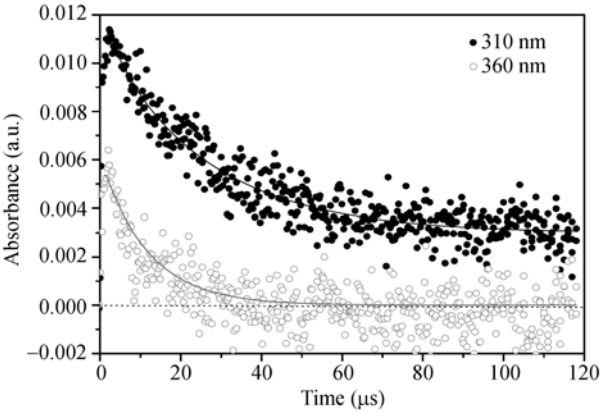


Figure 3 The decay curves recorded at 310 and 360 nm, respectively.

photochemical reaction must contribute to the absorbance at 310 nm. Therefore, only the kinetic trend recorded at 360 nm was appropriate for the study on Bp-OH adduct decay channel. The generated NO, NO_2 from HNO_2 photolysis, together with HNO_2 and H^+, had the possibility to influence the decay of Bp-OH adduct. In other words, other than the bimolecular decay channel, totally four channels might contribute to the decay of Bp-OH adduct:

Channel (1): NO + Bp-OH adduct
Channel (2): NO_2 + Bp-OH adduct
Channel (3): H^+ + Bp-OH adduct
Channel (4): HNO_2 + Bp-OH adduct

The laser energy was varied from 12.4 to 53.3 mJ for the purpose of examining the effect of NO and NO_2 concentration on Bp-OH adduct decay. The NO and NO_2 concentration would enhance with the increase of laser energy because the NO and NO_2 concentration were proportional to laser energy corresponding to ref. [12]. However, no detectable change in Bp-OH adduct decay rate was measured as the laser energy varied. Thus, channel (1) and channel (2) were not the main decay channels of Bp-OH adduct.

The Bp-OH adduct decay dependence on $[H^+]$ was investigated by varying pH value. When the pH value was lower than 1.5, in addition to the absorbance of Bp-OH adduct, two new strong absorption bands centered at 370 and 680 nm appeared (see Figure 4). These two absorption bands grew and decayed synchronously, and their growth rates were in accordance with the decay rate of Bp-OH adduct. As far as the absorption position and extinction coefficient were concerned, its spectrum resembled that of Bp^+[7]. Both of the absorption bands could be efficiently scavenged by ethanol, yet the presence of oxygen had no impact on their growth or decay. In light of these facts, these absorption bands were attributed to biphenyl cation radical produced by the interaction between Bp-OH adduct and H^+. The linear correlation was confirmed when plotting the observed first-order Bp-OH adduct decay rate ($k_{\text{obs dec}}$) against $[H^+]$. By reading the slope of the line, the second-order rate constant for the reaction of Bp-OH adduct and H^+ was derived to be 5.8×10^5 L·mol^{-1}·s^{-1}.

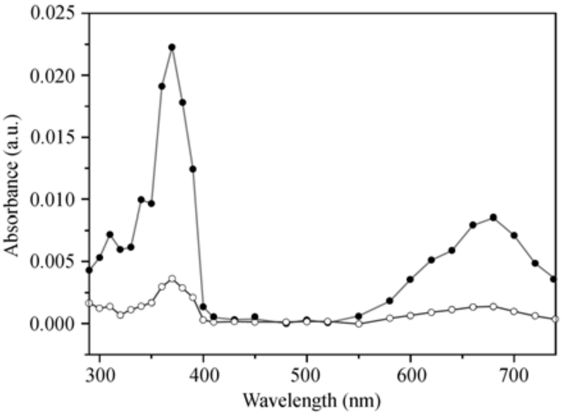


Figure 4 Transition absorbance spectra recorded 3.5 μs after laser pulse of aqueous solution of 4.0×10^{-5} mol·L^{-1} biphenyl and 2.0×10^{-3} mol·L^{-1} HNO_2 at pH = 0.5 in the presence (○) or absence of 3.6×10^{-3} mol·L^{-1} ethanol (●).

Provided that only decay channel (3) was taken into account, the half life of Bp-OH adduct would be 344 μs at pH = 2.3. This value was far higher than the measured one, implying the other channel must contribute to the decay of Bp-OH adduct. When $[HNO_2]$ was enhanced, the decay of Bp-OH adduct was remarkably accelerated. Hence, the reaction with HNO_2 was believed to be another decay channel of Bp-OH adduct. Figure 5 depicts the linear relationship between $k_{\text{obs dec}}$ and $[HNO_2]$, and gives a second-order rate constant for reaction between Bp-OH adduct and HNO_2 of 5.9×10^7 L·mol^{-1}·s^{-1}. The direct oxidation of Bp-OH adduct by HNO_2 ($E^{\Theta}_{HNO_2/NO}$ = 1.0 V) in acid condition was quite comprehensible considering a weaker oxidant, $Fe(CN)_6^{3-}$ ($E^{\Theta}_{Fe(CN)_6^{3-}/Fe(CN)_6^{2-}}$ = 0.56 V), was reported to be capable of oxidizing Bp-OH adduct in pulse radiolysis study[8].

In the following experiments, we moved our focus on the kinetics curves at the range from 250 to 350 nm. Figure 6 illustrated that in total two species, Bp-OH adduct and Prod., contributed to the absorption in this band. The pseudo-first order growth rate constant of Prod. was in accordance with the pseudo-first order growth rate constant of Bp-OH adduct, suggesting that Prod. originated from the reaction between Bp-OH adduct and

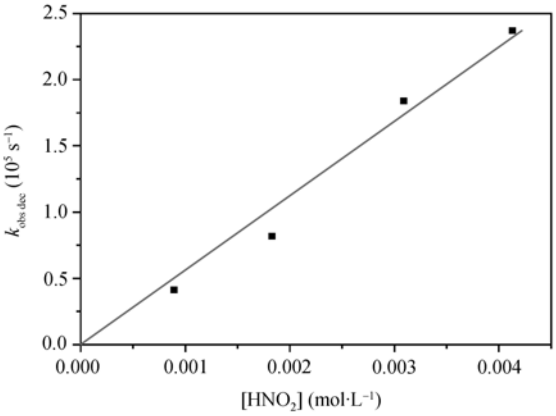


Figure 5 The plot of pseudo-first-order decay rate constant of Bp-OH adduct against $[HNO_2]$ with the best linear-fit.

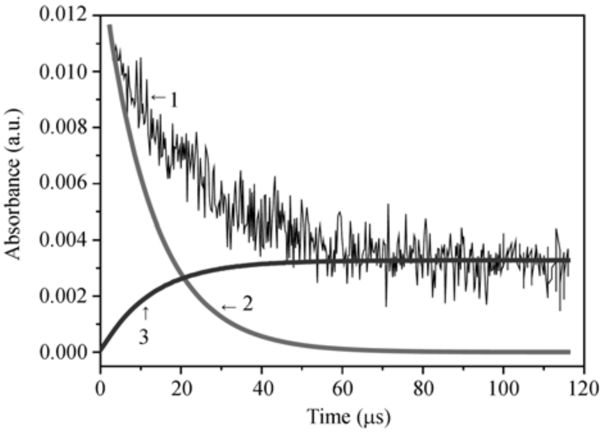


Figure 6 The measured decay trend at 310 nm (1) and the modeled kinetic curves of Bp-OH adduct (2) and Prod. (3) at 310 nm.

HNO_2. When Bp-OH adduct vanished, the obtained transient absorbance spectrum was attributed to Prod. (see Figure 1 curve 5).

We came to the conclusion that the Bp-OH adduct, generated from the reaction of biphenyl with HNO_2 under UV irradiation, decayed mainly via its reaction with H^+ and HNO_2.

$$Bp^+ \xleftarrow{H^+} \text{Bp-OH adduct} \xrightarrow{HNO_2} \text{Prod.}$$

2.3 Products analysis of the photochemical reaction between biphenyl and HNO_2

GC-MS analysis was performed for a further under-standing of the pathway and products of the photochemical reaction between biphenyl and HNO_2. One hundred milliliter aqueous solution, prepared in the same manner in Section 2.1, was exposed to 5 s of 355 nm irradiation. After the organic components were extracted by dichloromethane, anhydrous Na_2SO_4 was added to absorb the residual water in the sample. Twenty-four hours later, the sample was concentrated to 2 mL before GC- MS analysis for a better signal-to-noise ratio. By comparison with NIST database, a fraction of biphenyls were proved to convert to nitrobiphenyl (12.09, 12.28 min) and nitrobiphenol (12.22, 12.36, 12.55 min) after interaction with HNO_2 under UV irradiation (see Figure 7). Unfortunately, it is hard to distinguish isomers due to the shortage of analyzing methods.

Fisher[10] also detected the generation of nitrosophenol when studying the photochemical reaction between benzene and HNO_2. However, he assumed that nitrosophenol was produced by the further nitration of phenol, the direct product from the reaction between OH radical and benzene, by HNO_2. Contrarily, nitrobiphenol, instead of biphenol, was identified as the product of the reaction between biphenyl and HNO_2 under 355-nm irradiation. This phenomenon provided an important evidence for the decay channel of Bp-OH adduct proposed in Section 2.2. Due to the relatively slow rate for the conversion of Bp-OH adduct to biphenol, a majority of Bp-OH adduct would be oxidized to nitrosophenol by HNO_2. With respect to the unstable nature of nitrosobiphenol in air, not nitrosobiphenol but nitrobiphenol was detected by GC-MS analysis.

Nitrobiphenyl, as another byproduct, came mainly from the interaction between biphenyl cation radical and

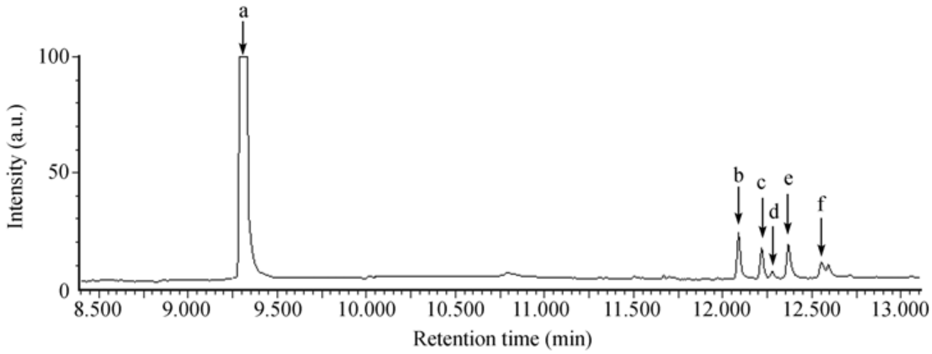
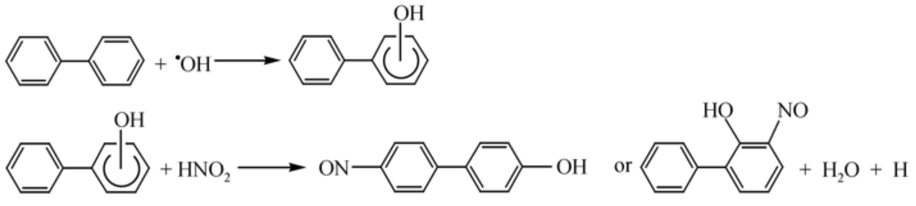
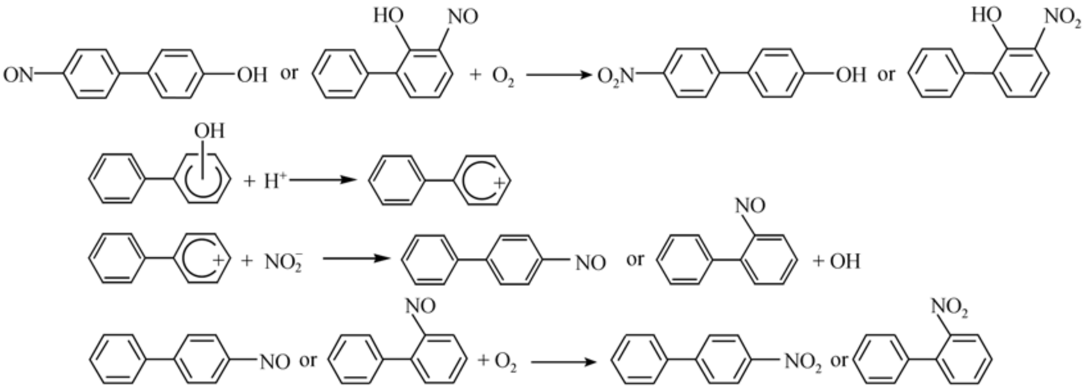


Figure 7 Gas chromatogram of the solution extracts with CH_2Cl_2 of biphenyl-HNO_2 after 5 s of 355-nm irradiation. Peak a, biphenyl; b, 2-nitrobiphenyl; c, *o*-nitro-biphenol; d, 4-nitrobiphenyl; e, *p*-nitro-biphenol; f, *p*-nitro-biphenol.





nitrite.

3 Conclusions

The chemical reactions occurring in the atmospheric condensed water (e.g., cloud, fog, rain, dew, haze and surface water of aerosols) have a pronounced influence on the atmospheric composition and the transport and conversion of pollutants in the atmosphere[13]. Recent research work has demonstrated a wide distribution of HNO_2 and NO_2^- in the atmospheric water, with a concentration ranging from 0 to 4.6 μmol/L[6,14−16]. Meanwhile, biphenyl was detected in raindrops at times[17,18], which provided the possibility for interaction of HNO_2/NO_2^- with biphenyl.

In this paper, to explore the interaction of biphenyl with HNO_2 under UV irradiation, the pH value of the mixed solution was adjusted to 2.3 to ensure a distribution fraction of $[HNO_2]([HNO_2]/([HNO_2]+[NO_2^-])$ exceeding 0.9. This pH value was slightly lower than the actual pH of the atmospheric condensed water, usually varied between 2.0 and 6.0[13], yet the photochemical reaction pathway between biphenyl and HNO_2 was all the same. No essential difference was found between the transient absorbance spectra after the laser flash photolysis of air-saturated and N_2-saturated aqueous solution of biphenyl and HNO_2, indicating that oxygen did not participate in the reaction. The experimental results also showed that Bp-OH adduct was formed by the reaction of biphenyl with $^{\bullet}OH$ radical generated from photolysis of HNO_2 under 300−400 nm irradiation and followed by oxidation to nitrosobiphenyl by HNO_2. As compared with the original reactants, the toxicity of nitrosobiphenyl was even greater. Nitrosobiphenyl could be subsequently oxidized by air to nitrobiphenyl, which contributed to the source of nitro compounds in the atmosphere.

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