Nitrous Oxide as a Radical Scavenger

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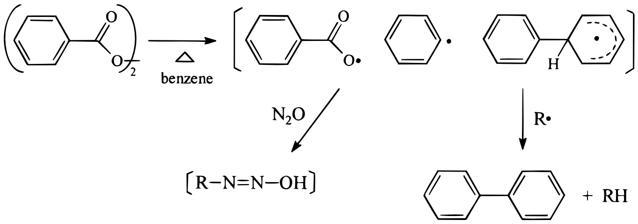
Nitrous oxide is known as a trapping agent for solvated electrons.[1] It has been used as a blocking agent for comparing reaction rates[2−4] as well as for selecting reaction pathways.[5] We recently and unexpectedly observed that a photochemical, radical-mediated reaction was retarded to some extent by the presence of nitrous oxide.[6] In view of this finding, it seemed important to clarify the possibility of nitrous oxide as a radical trapping agent by studying the effect of nitrous oxide on well-known radical-mediated reactions such as the thermal and photochemical reactions of benzoyl peroxide.

It has been reported that the thermal decomposition of a benzene solution of benzoyl peroxide produces a mixture of biphenyl, carbon dioxide, and benzoic acid in yields less than 50%, in addition to high-boiling materials.[7,8] There is no doubt that the radical species, such as benzoyloxyl, phenyl, and phenylcyclohexadienyl radicals, are involved in the decomposition.[7,8] It has been also reported that photochemical decomposition of benzoyl peroxide (10^{-3} M) in Freon 113 produced 8% of benzene and 7% of phenyl benzoate in the absence of cyclohexane and 35% of benzene in the presence of cyclohexane (0.06 M).[9] It has also been shown that phenyl and benzoyloxyl radicals are involved in the mechanism of formation of products in the photochemical reaction of benzoyl peroxide.[10]

A benzene solution of benzoyl peroxide (1.0×10^{-3} M, 25 mL) in a 50 mL, three-neck flask was heated under reflux for 30 min during purging with argon, nitrous oxide, or oxygen. Oxygen which is known as a radical scavenger[10c,11] was used to compare the extent of the trapping effect with nitrous oxide. The reaction mixture was analyzed by HPLC. The only three peaks at retention times 9.2, 14.0, and 16.9 min on theHPLC chromatogram were observed at the reaction condition and correspond to benzene (solvent), unreacted benzoyl peroxide, and biphenyl, respectively. The yields of biphenyl after 30 min reaction times were 7.4, 3.3, and 2.5% under argon, nitrous oxide, and oxygen, respectively. The formation of biphenyl was retarded by 60% and 66% under nitrous oxide and oxygen, respectively. The relevant results of the thermal reaction are summarized in Table 1. Reaction of a dilute benzene solution of benzoyl peroxide (1.0×10^{-4} M) shows that the biphenyl yield is also reduced to 60% both under nitrous oxide and oxygen. The ratio of biphenyl yields under nitrous oxide and oxygen is 1.3, indicating that the inhibition by nitrous oxide is a little less effective than oxygen.

Scheme 1



The reaction mechanism of the peroxide decomposition is shown in Scheme 1 as described elsewhere.[8,10c] The thermal decomposition produces radical intermediates, phenyl σ and phenylcyclohexadienyl radicals. Nitrous oxide presumably inhibits the formation of biphenyl by reacting competitively with benzene solvent for the same intermediate radicals to give R−N=N−OH. Several attempts to detect the adducts of the nitrous oxide radical such as benzenediazotic acid have failed in the thermal reaction by LC/MS and GC/MS. Probably the adduct of nitrous oxide radical is too labile to be detected by GC/MS and LC/MS.

A methanol solution of benzoyl peroxide (1.0×10^{-2} M, 2 mL) was irradiated by using monochromatic light (band-pass 274 ± 6 nm) from a Xe-lamp (450 W), and the reaction mixture was analyzed by HPLC. The HPLC profile (not shown) showed several products. Peaks with retention times of 9.2, 12.7, 14.0, and 16.9 min on a C-18 column [4.6 × 250 mm, CH_3CN:water (3:1) as eluent] are identified as benzene, phenyl benzoate, benzoyl peroxide, and biphenyl, respectively. The yields of benzene, phenyl benzoate, and biphenyl produced in the photochemical reaction under argon were 2.6, 1.2, and 0.04%, respectively. The ratio of benzene yields formed under argon and nitrous oxide is 0.7. The formation of benzene was retarded about 30% in the presence of nitrous oxide (Table 1). The formation of benzene in the presence of oxygen was extensively reduced, presumably because oxygen acted not only as the radical inhibitor but also as the triplet state quencher. The formation of other minor products such as phenyl benzoate and biphenyl was also reduced in the presence of nitrous oxide or

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Table 1. Effects of Nitrous Oxide on the Formations of the Products in the Thermal and Photochemical Reactions of Benzoyl Peroxide

reaction (solvent)	concn benzoyl peroxide (M) (reaction duration, min)	product	product yield (Y, %) under			yield ratio	
			Ar	N_2O	O_2	Y_{N_2O}/Y_{Ar}	Y_{N_2O}/Y_{O_2}
thermal at 80°C (benzene)	1.0×10^{-3} (30)	biphenyl	7.4	3.3	2.5	0.4	1.3
	1.0×10^{-4} (30)	biphenyl	2.5	1.0	0.9	0.4	1.1
photochemical[a] (methanol)	1.0×10^{-2} (30)	benzene	2.6	1.7	*b*	0.7	–
		phenyl benzoate	1.2	1.1	1.1	0.9	1.0
		biphenyl	0.04	0.03	0.02	0.8	1.5
	1.0×10^{-3} (30)	benzene	21.5	20.4	*b*	0.9	–
		phenyl benzoate	8.9	8.1	7.2	0.9	1.1
		biphenyl	0.7	0.6	0.4	0.9	1.5

[a] Monochromator light (274 ± 6 nm) from Xe-lamp. [b] Less than detecting limit.

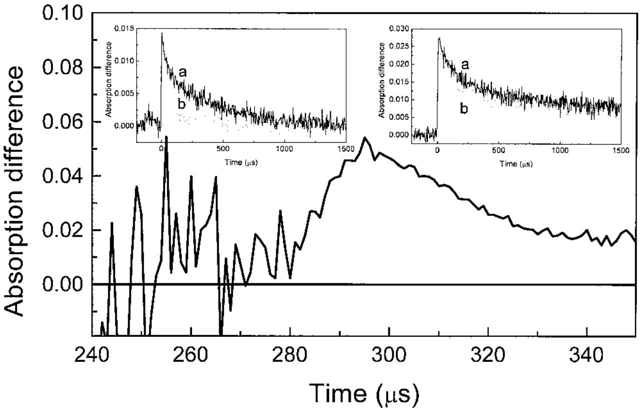
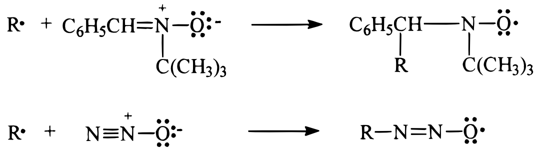


Figure 1. Transient absorption spectra 5 μs after the laser pulse for benzoyl peroxide (1.0×10^{-4} M) in methanol under argon. Inset: Temporal profiles of transients at 260 nm (left) and 295 nm (right) from the photolysis of benzoyl peroxide; curve a, under argon; curve b, under nitrous oxide.

oxygen. A similar result to the above was obtained for a dilute solution of benzoyl peroxide (1.0×10^{-3} M). It seems that the quenching selectivity of nitrous oxide toward carbon- and oxygen-centered radicals is not clear, although oxygen prefers a carbon-centered radical to an oxygen-centered one.

To examine the effect of nitrous oxide on the transients, benzoyl and phenyl σ radicals, benzoyl peroxide was irradiated using laser flash photolysis. A transient absorption spectra was obtained at a 5 μs delay after pulsing in the laser flash photolysis[12] of a methanolic solution of benzoyl peroxide (1.0×10^{-4} M). There are two absorption peaks at about 260 and 295 nm, and the lifetimes of these transients are 405 and 155 μs, respectively (Figure 1). They are regarded as different species because their lifetimes differ. The transient absorbing at 260 nm is assigned to the phenyl σ radical because the absorption wavelength and lifetime are similar to a reported phenyl-type radical of an *N*-benzylpyridinium salt.[6b] The temporal profiles of phenyl σ radical at 260 nm under argon (curve a) and nitrous oxide (curve b) are compared in the left inset of Figure 1. The lifetimes of phenyl radical in methanol are 405 and 136 μs under argon and nitrous oxide, respectively; the lifetime is shortened by about 66% in the presence of nitrous oxide. It is assumed that the transient species at about 295 nm is the benzoyloxyl radical because the lifetime and absorption wavelength are similar to those reported for benzoyloxyl radical.[13] The lifetime of benzoyloxyl radical is also quenched by 40% in the presence of nitrous oxide in the right inset of Figure 1.

Thus, we conclude that nitrous oxide is a moderate radical-trapping agent, based on the results of the thermal and photochemical reactions as well as the results of laser flash photolysis: thermal and photochemical decompositions which are shown as radical-mediated reactions are retarded by the presence of nitrous oxide; the lifetimes of the transients assumed to be phenyl and benzoyl radicals (albeit not identified completely) are reduced by the presence of nitrous oxide. The trapping reaction might be similar to the known trapping reaction of *N*-*tert*-butyl phenylnitrone[14] which is structurally similar to the nitrous oxide:



$$R^\bullet + C_6H_5CH{=}\overset{+}{N}(C(CH_3)_3){-}O^- \longrightarrow C_6H_5CH(R){-}N(C(CH_3)_3){-}O^\bullet$$

$$R^\bullet + N{\equiv}\overset{+}{N}{-}O^- \longrightarrow R{-}N{=}N{-}O^\bullet$$

Experimental Section

Benzoyl peroxide (Fluka) was purified by recrystallization (methanol, twice). All solvents used were reagent grade unless otherwise specified. High-performance liquid chromatogaphy (HPLC, Rainin) was performed on a Rainin C-18 column for the thermal reaction mixtures. Argon was used as received from the supplier. Nitrous oxide was prepared by heating ammonium nitrate (50 g) to 250 °C in 200 mL in a three-neck flask. Water, an unwanted product in the reaction, was eliminated by passing the generated nitrous oxide gas through a Dewar flask containing dry ice and acetone and then through a tube of calcium chloride. A trace amount of nitric oxide (NO) side product was eliminated by passing the gas mixture through a aqueous ferrous sulfate solution in line before the Dewar flask.

Thermal Reaction.

A benzene solution of benzoyl peroxide (10^{-3} M, 25 mL) in a 50 mL, three-necked flask was deaerated with argon, nitrous oxide, and oxygen after purging with argon, for 30 min. After refluxing under the desired gas using a long introducing line of the gas (i.d., 5 mm; length, 1.5 m) for 30 min, the reaction mixture (1.0 μL) was chromatographed on Rainin C-18 column of Rainin HPLC (column size, 4.6 × 250 mm; mobile phase, $CH_3CN:H_2O(3:1)$; flow rate, 0.7 mL/min) to show three peaks at retention times of 9.2, 14.0, and 16.9 min with mixture eluent (CH_3CN and H_2O, 3:1) as a mobile phase. The peaks of retention times of 9.2, 14.0, and 16.9 min are assigned to solvent benzene, unreacted benzoyl peroxide, and biphenyl, respectively. The measurement of the yield of biphenyl was done by using a calibration curve of authentic sample.

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(12) The laser flash photolysis study should be safely carried out because of the decomposition property of benzoyl peroxide.

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Photochemical Reaction. A stock methanol solution of benzoyl peroxide (10^{-2} M, 2 mL) in a UV cuvette (1 cm path, 3 mL cuvette) was irradiated for 30 min using a monochromatic light (274 ± 6 nm) from Xe-lamp (450 W). The reaction mixture was chromatographed as the above thermal reaction to give several product peaks. The products, benzene, phenyl benzoate, and biphenyl, were assigned for the peaks of retention times 9.2, 12.7, 14.0, and 16.9 min, respectively, in reference to peaks of authentic samples. The yields of benzene, phenyl benzoate, and biphenyl were determined using calibration curves of authentic samples.

Laser Flash Photolysis. A detailed description of the experimental setup can be found elsewhere.[6] The fourth harmonic (266 nm) output from a Q-switched Nd:YAG laser (Spectron SL803G) was used as an excitation source (5 ns, 40 mJ/pulse). A cw Xe-arc lamp (Atago Bussan Co. XC-150) was used as a probe light source for the transient absorption measurement. The spectral resolution was obtained by using a 320 mm monochromator (Jobin-Yvon H*R*320) after the probe light passed through the sample solution. A boxcar signal averager (Stanford Research Sys. SR250) was used to record the photomultiplier output (Hamamatsu R955) which is attached on the exit slit of the monochromator. The temporal profile of the transient absorption signal was monitored by using a 500 MHz digital storage oscilloscope (Hewlett-Packard HP54503A). The sample solutions were circulated from a Teflon bottle (2.5 L in volume) to the fluorometer quartz cuvette of 10 mm in path length (flow type, Helma QS1.0) to reduce the effect by the accumulation of the reaction product and dilution of the reactant in the photolysis cell.

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