Kinetic Studies of Spin-trapping Reactions. I. The Trapping of the *t*-Butyl Radical Generated by the Photodissociation of 2-Methyl-2-nitrosopropane by Several Spin-trapping Agents

Takahisa Doba, Tsuneki Ichikawa, and Hiroshi Yoshida
Faculty of Engineering, Hokkaido University, Kita-ku, Sapporo 060

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The photochemical reaction of 2-methyl-2-nitrosopropane (a spin-trapping agent) in benzene was studied at 299 K by monitoring the optical absorption intensity of the spin-trapping agent and the ESR signal intensity of the spin-adduct radical (di-*t*-butyl nitroxide). The observed kinetic feature was interpreted in terms of three elementary processes; the photodissociation of the spin-trapping agent giving a *t*-butyl radical, the spin trapping of the *t*-butyl radical by the trapping agent giving the spin adduct radical, and the reaction of the spin-adduct radical with the *t*-butyl radical giving diamagnetic products. The rate constant of the last process was found to be 10 times as large as that of the spin-trapping process, which was determined to be 3.3×10^6 mol^{-1} dm^3 s^{-1} based on the reported rate constant for the scavenging of the *t*-butyl radical by tributylstannane. The relative spin-trapping rate constants toward the *t*-butyl radical were also determined to be 0.07, 1.0, 41, 63, and much higher than 50 for 2,4,6-tri-*t*-butylnitrosobenzene, 2-methyl-2-nitrosopropane, pentamethylnitrosobenzene, nitrosodurene and nitrosobenzene, respectively. *C*-phenyl-*N*-*t*-butylnitrone was found to be much less reactive by a factor of less than 0.003.

The reaction of several nitroso compounds with short-lived free radicals giving stable nitroxide radicals (or anilino-type radicals) provides an indirect but convenient technique for detecting the short-lived free radicals by the conventional electron spin resonance (ESR) method.[1,2] This spin-trapping technique has been widely used in recent years to study radical intermediates in photochemical, radiation chemical, and even thermal reaction systems.[3-5] 2-Methyl-2-nitrosopropane, like nitrosobenzene derivatives, has been used very often as a spin-trapping agent because it gives an ESR spectrum of spin-adduct radicals (products of spin-trapping reactions) with a better-resolved hyperfine structure, facilitating the identification of the trapped radicals. However, one drawback of this spin-trapping agent is that it decomposes readily to give a *t*-butyl radical when irradiated by light.[2,6]

Naturally the observed yield of the spin-adduct radicals depends not only on the concentration of the trapped radicals in the reaction systems, but also on the rate constant of the spin-trapping process. The stability of the spin-adduct radicals is another factor determining the observed yield if they are unstable either in decomposing by themselves or in reacting with other radical entities. No quantitative information can, therefore, be drawn from spin-trapping experiments without knowing the kinetic features involved. However, there have been only a limited number of reports on the kinetic study of spin-trapping reaction systems. Although the figures available for the spin-trapping rate constant of the nitroso compounds have been very scanty,[7,8] it appears that the spin trapping is a comparatively slow process, and that it cannot always be the main reaction pathway of the short-lived free radicals. The accumulation of rate data on the spin-trapping is, therefore, desirable in order to extend the utility of this technique and to correlate more firmly the spin-adduct radicals with the actual reaction intermediates.

In the present study, the photochemical processes of 2-methyl-2-nitrosopropane in benzene were investigated mechanistically and kinetically. This photochemical reaction system was then used to determine the reaction rate constants of several spin trapping agents toward the *t*-butyl radical.

Experimental

Benzene and tributylstannane of analytical grade were used as received, without further purification. The benzene solvent was degassed by the freeze-pump-thaw technique, mixed with a spin-trapping agent (or agents) through a break seal under a vacuum of about 10^{-5} Torr in the dark, and sealed in a glass tube with a quartz-tip portion for ESR measurements at one end and a quartz optical-absorption cell at the other. The concentration of spin-trapping agents were usually from 0.01 to 0.1 mol dm^{-3}.

The trapping agents used were 2-methyl-2-nitrosopropane (BNO), nitrosobenzene, nitrosodurene, pentamethylnitrosobenzene, 2,4,6-tri-*t*-butylnitrosobenzene, and *C*-phenyl-*N*-*t*-butylnitrone (*N*-*t*-butyl-α-toluenimine *N*-oxide). The BNO and nitrosobenzene were commercially purchased from the Aldrich Chem. Co., Inc., and Nakarai Chem., Ltd., and were used without further purification. The pentamethylnitrosobenzene was synthesized[9-11] and recrystallized from an acetone solution. The nitrosodurene, tri-*t*-butylnitrosobenzene, and *C*-phenyl-*N*-*t*-butylnitrone were kindly supplied by R. Konaka of Shionogi Pharm. Co., Ltd., M. Tabata of Hokkaido University, and K. Kuwata of Osaka University.

The solution was photolyzed with light from a Xe lamp through a band-pass filter (transmission maximum at 690 nm). The concentration of the spin-adduct radicals was monitored by means of an X-band ESR spectrometer (JEOL, JES-ME-2X), and that of BNO, by measuring its absorption at 680 nm by means of a recording spectrophotometer (Hitachi, EPS-3T). The photolysis and measurements were carried out 299 K.

Results and Discussion

Optical Absorption and Photodecomposition of BNO. The BNO solution in benzene shows, immediately after its preparation, an intense optical-absorption band with a maximum at 295 nm and a weak absorption band with a maximum at 680 nm, as is shown in Fig. 1. The latter band is attributed to the $\pi^*\leftarrow$n transition of

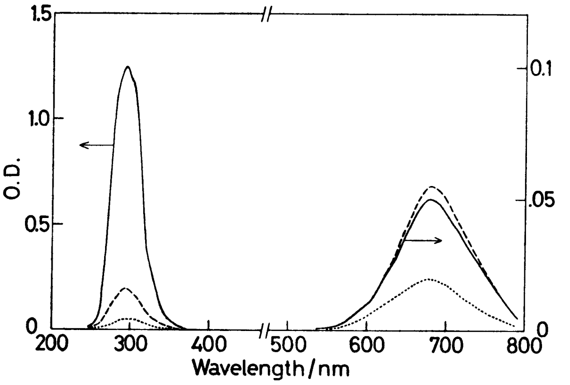


Fig. 1. The optical absorption spectra of BNO at 299 K (solid curves) immediately after dissolving it in benzene, (dashed curves) after 90 minutes when the monomer-dimer equilibrium was reached, and (dotted curves) after the photolysis for 200 minutes.

monomeric BNO, which is red-shifted by 15 nm compared with the band observed in the polar solvent of acetone.[12] The former band was found to decrease gradually in its intensity concomitantly with the increase in the band of monomeric BNO in the dark, as is shown in Fig. 1. Therefore, it is attributable to dimeric BNO. The monomer-dimer equilibrium was reached very slowly (in an hour) and was found to be shifted almost completely over to the monomer. Photoirradiation at the dimer band enhanced the dissociation of the dimer into the monomer.

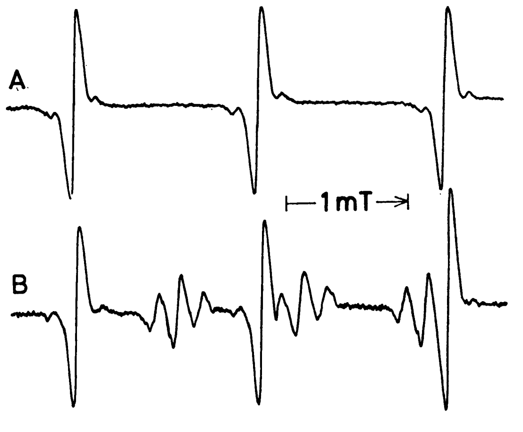


Fig. 2. The ESR spectra observed after the photolysis of BNO at 299 K. The upper spectrum was recorded from the benzene solution of BNO and is due to the di-*t*-butyl nitroxide formed by the spin trapping of *t*-butyl radical by BNO, and the bottom spectrum recorded from the benzene solution containing BNO and 2,4,6-tri-*t*-butylnitrosobenzene is due to both the di-*t*-butyl nitroxide and *N*-*t*-butoxy-2,4,6-tri-*t*-butylanilino radical formed from these two spin trapping agents.

On irradiating the solution at the monomer band, the BNO disappeared gradually, while an ESR spectrum with the hyperfine splitting due to a nitrogen nucleus (1.57 mT) developed, as is shown in Fig. 2. The ESR spectrum is attributed to the di-*t*-butyl nitroxide radical, the spin-adduct radical of the *t*-butyl radical resulting from the photodissociation of the spin-trapping agent itself,[1,2]

$$(t\text{-Bu})\text{NO} \xrightarrow{h\nu} t\text{-Bu}\cdot + \text{NO} \tag{1}$$

$$t\text{-Bu}\cdot + (t\text{-Bu})\text{NO} \xrightarrow{k_2} (t\text{-Bu})_2\text{NO}\cdot \tag{2}$$

No other ESR spectrum was observed. No optical absorption other than that of the BNO was recorded down to 260 nm, either. The spin-adduct radical was found stable in the dark at room temperature.

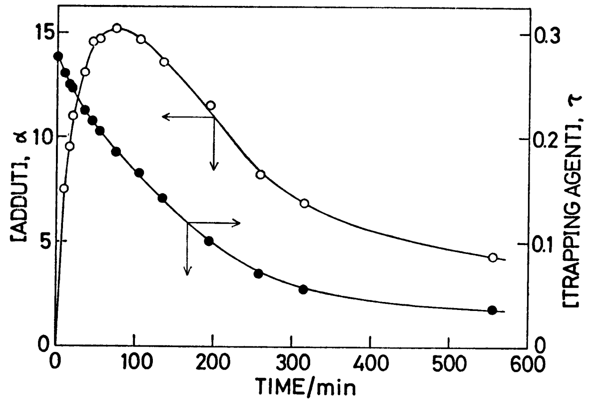


Fig. 3. The change in (●) the concentration of the spin trapping agent, BNO and (○) that of the spin adduct radical, di-*t*-butyl nitroxide, during the photolysis of BNO (2.7×10^{-2} mol dm^{-3}) in benzene at 299 K. The arbitrary units, α and τ are given in the text.

The change in the concentrations of the BNO and the spin adduct radical were followed by means of optical absorption and ESR measurements during the photolysis. The results are shown in Fig. 3. The spin-adduct radical initially increased in its intensity, reached a maximum, and then decreased gradually. By examining the effect of the initial BNO concentration, no indication was observed of the involvement of a second-order process with respect to the short-lived intermediates, such as a combination between the *t*-butyl radicals. The decay of the spin-adduct radical is, therefore, attributed to its reaction with the *t*-butyl radical, giving a diamagnetic product (or products) as:

$$(t\text{-Bu})_2\text{NO}\cdot + t\text{-Bu}\cdot \xrightarrow{k_3} (t\text{-Bu})_2\text{NO}(t\text{-Bu}). \tag{3}$$

The reaction between di-*t*-butyl nitroxide and the *t*-butyl radical was inferred to occur in the gas-phase reaction in pyrolyzing BNO.[13] The photodecomposition of the spin-adduct radical is not expected to occur, because the photolysis was carried out with light of selected wavelengths. The adduct radicals do not combine with themselves,[14] and so such a combination reaction cannot be a reason for their decay either.

Kinetic Features of the Photochemical Reaction of BNO. Based on the three elementary processes, Reactions 1 to 3, the photochemical reaction of the BNO can be totally described by the following rate equations:

$$\frac{d[\text{T}]}{dt} = -I\phi - k_2[\text{T}][\text{R}] \tag{4}$$

$$\frac{d[\text{R}]}{dt} = I\phi - k_2[\text{T}][\text{R}] - k_3[\text{A}][\text{R}] \tag{5}$$

$$\frac{d[\text{A}]}{dt} = k_2[\text{T}][\text{R}] - k_3[\text{A}][\text{R}] \tag{6}$$

where T, R, and A stand for the spin trapping-agent (BNO), the *t*-butyl radical, and the spin adduct radical (di-*t*-butyl nitroxide) respectively. In principle, the ratio of the rate constants, k_3/k_2, can readily be determined as $k_3/k_2=[T]/[A]$ at the time when [A] reaches the maximum. The assumption of the steady-state for [R] leads to:

$$\frac{d[A]}{d[T]} = \frac{(k_3/k_2)[A]-[T]}{(k_3/k_2)[A]+2[T]}, \tag{7}$$

which tests the validity of the presumed reaction mechanism by using the observed changes of [A] and [T] and the determined value of k_3/k_2.

However, it is a difficult task to determine precisely enough the absolute values of [A] by means of the ESR method. Therefore, the values were determined only relatively in the present experiment. Using the instrumental constants of a and b, [A] and [T] are expressed as $[A]=a\alpha$ and $[T]=b\tau$ respectively, α and τ being the recorded intensity of the ESR spectra of the spin-adduct radical and that of the optical-absorption spectra of the spin-trapping agent. Then, at the maximum α, this relationship:

$$(\tau/\alpha) = (k_3/k_2)(a/b) \tag{8}$$

is obtained. The results shown in Fig. 3 gave the value of 0.0123 for (k_3/k_2) (a/b). Equation 7 is transformed as:

$$\frac{d\alpha}{d\tau} = \frac{b}{a}\cdot\frac{(k_3/k_2)(a/b)\alpha-\tau}{(k_3/k_2)(a/b)\alpha+2\tau}. \tag{9}$$

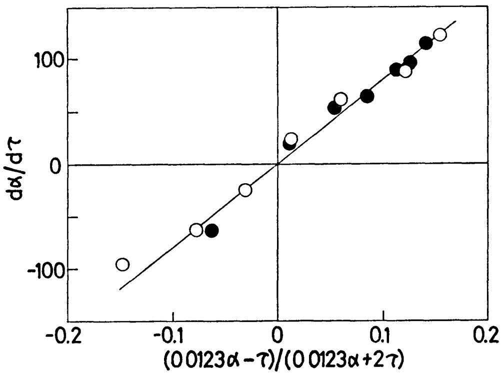


Fig. 4. The relationship between the ratio of the changing rate of the concentration of the spin trapping agent to that of the concentration of the spin adduct radical, $d\alpha/d\tau$, and the concentrations of the spin trapping agent and the spin adduct radical, $(0.0123\alpha-\tau)/(0.0123\alpha+2\tau)$, during the photolysis of (○) 2.7×10^{-2} mol dm^{-3} or (●) 1.2×10^{-2} mol dm^{-3} of BNO in benzene. The slope gives the value of 820 for b/a and, in turn, the value of 10 for k_3/k_2. See also the text.

The results in Fig. 3 are replotted in Fig. 4, where the expected linear relationship is observed between $d\alpha/d\tau$ and $(0.0123\alpha-\tau)/(0.0123\alpha+2\tau)$, and the slope gives the value of 820 for b/a. It turns out that $k_3/k_2=10$. The observed linear relationship gives a support to the presumed reaction mechanism comprised of Reactions 1, 2, and 3. Using the reported extinction coefficient of the monomer band[12] and the determined value of b/a, the concentration of the spin-adduct radical is found to have reached its maximum value of 1.8×10^{-3} mol dm^{-3} when the BNO concentration decreased to 1.9×10^{-2} mol dm^{-3} from its initial value of 2.7×10^{-2} mol dm^{-3} (*cf.* Fig. 3).

Equation 7 shows that d[A]/d[T] (or $d\alpha/d\tau$) is independent of the initial concentration of the spin-trapping agent. As a matter of fact, the data obtained for the initial BNO concentration half as much fall on the same straight line in Fig. 4. This result gives evidence that the second-order reaction with respect to the *t*-butyl radical concentration is effectively absent.

Although the available data on the rate constant of radical scavengers against the *t*-butyl radical has been very little, tributylstannane has been reported to react with the *t*-butyl radical at the constant of 7.4×10^5 mol^{-1} dm^3 s^{-1} in cyclohexane at 298 K.[15] If the radical scavenger is present in the solution, the radical-scavenging reaction:

$$t\text{-Bu}\cdot + (t\text{-Bu})_3\text{SnH} \xrightarrow{k_{10}} t\text{-BuH} + (t\text{-Bu})_3\text{Sn}\cdot \tag{10}$$

competes with Reaction 2 in the early period of the photolysis when Reaction 3 is effectively absent. An example of the observed scavenger effect is shown in Fig. 5. The linear increase of [A] is reduced in the presence of the radical scavenger. The reduction of the spin-adduct formation depends on the concentration of the radical scavenger, [S], as is shown in Fig. 6, and agrees with the normal competition kinetics:

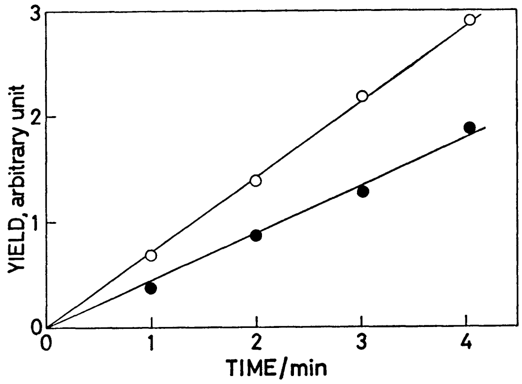


Fig. 5. The yield of the spin adduct radical in the benzene solution at 299 K as a function of the photolysis time, (○) in the presence of only 0.19 mol dm^{-3} BNO and (●) in the presence of 0.19 mol dm^{-3} BNO and 0.56 mol dm^{-3} tributylstannane.

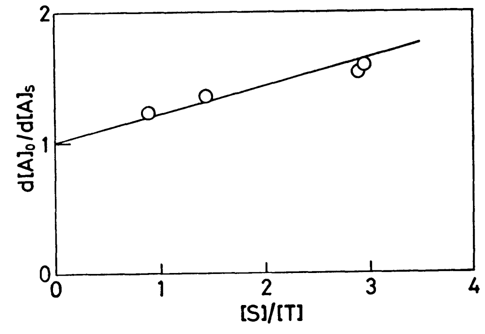


Fig. 6. The dependence of the rate of the spin adduct formation on the concentration of radical scavenger, tributylstannane, during the photolysis of BNO in benzene at 299 K.

$$\frac{d[A]_0}{d[A]_s} = 1 + \frac{k_{10}[S]}{k_2[T]}. \qquad (11)$$

On the basis of the reported k_{10},[15] k_2 is determined to be 3.3×10^6 mol^{-1} dm^3 s^{-1}.

Spin-trapping Rate Constants of Several Spin-trapping Agents. When BNO and another spin trapping agent (RNO) are present in the solution, and when the former is selectively photolyzed to generate the *t*-butyl radical, the spin-trapping rate constant of the latter can be determined relative to that of the former by the conventional treatment of competition reactions. As has been shown in the preceeding section, only the reaction:

$$t\text{-Bu}\cdot + \text{RNO} \xrightarrow{k_{12}} \text{RN}(t\text{-Bu})\text{O}\cdot \text{ or } \text{R}\dot{\text{N}}\text{O}(t\text{-Bu}) \qquad (12)$$

competes with Reaction 2 against the *t*-butyl radical in the initial period of the photolysis. The rate constant, k_{12}, can readily be determined from this relationship:

$$\frac{d[A']}{d[A]} = \frac{k_{12}[T']}{k_2[T]}, \qquad (13)$$

and the observed intensities of ESR spectra due to two kinds of spin-adduct radicals in the short photolysis time when they are increasing linearly. T′ stands for the second spin trapping-agent, from which the spin-adduct radical, A′, is generated.

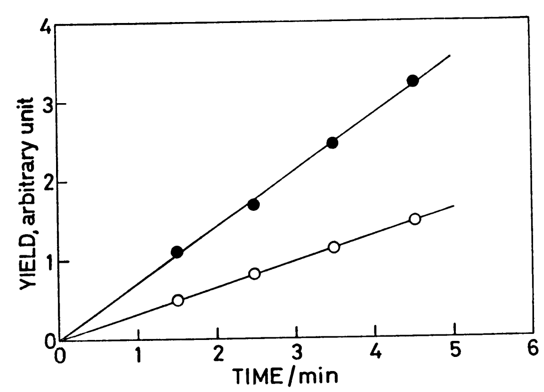
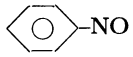
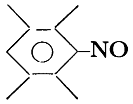
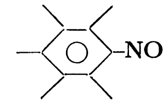
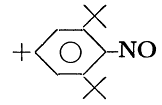
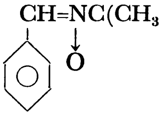


Fig. 7. The yields of the *t*-butyl radical adducts competitively formed (○) from 2.3×10^{-2} mol dm^{-3} BNO and (●) from 1.0×10^{-2} mol dm^{-3} nitrosodurene during the photolysis of BNO in the benzene solution at 299 K.

Figure 2B shows the ESR signal observed from the solution of BNO and 2,4,6-tri-*t*-butylnitrosobenzene. The *t*-butyl radical is added to the oxygen atom of tri-*t*-butylnitrosobenzene to form an anilino-type spin-adduct radical,[16] whose ESR spectrum is distinguished from that of the spin-adduct radical from BNO. Even when the nitroxide-type spin-adduct radical was generated from either the nitrosobenzene, nitrosodurene, or pentamethylnitrosobenzene coexisting with BNO in the solution, the ESR spectra of the two kinds of nitroxide radicals could readily be distinguished and their intensities determined relative to each other. In the presence of BNO and nitrosodurene in the solution, for instance, the concentration of the spin-adduct radicals increased linearly, as is shown in Fig. 7. The relative spin-trapping efficiency, k_{12}/k_2, was determined to be 63 from the observed slopes of the linear increases and the concentrations of the two spin-trapping agents dissolved in the solution. This shows that the spin-trapping rate constant of nitrosodurene is 2.0×10^8 mol^{-1} dm^3 s^{-1} toward the *t*-butyl radical. The spin-trapping rate constants were determined in the same manner for pentamethylnitrosobenzene,[11] tri-*t*-butylnitrosobenzene,

Table 1. The rate constants of the trapping *t*-butyl radical and the dimerization equilibrium constants of several spin-trapping agents at 299 K in benzene

		Relative rate constant k_{12}/k_2	Rate constant[a] (mol^{-1} dm^3 s^{-1})	Equilibrium constant, K (mol dm^{-3})	Monomer fraction[c]
2-Methyl-2-nitrosopropane	+NO	1.0	3.3×10^6	1.92[b]	0.99
Nitrosobenzene		>50	$>2.0 \times 10^8$	—	1.0
Nitrosodurene		63	2.0×10^8	1.6×10^{-4}	0.086
Pentamethylnitrosobenzene		41	1.4×10^8	3.6×10^{-4}	0.13
2,4,6-Tri-*t*-butylnitrosobenzene		0.07	2.3×10^5	—	1.0
Phenyl-*N*-*t*-butylnitrone		<0.003	$<1.0 \times 10^4$	—	1.0

a) The absolute values were determined with an experimental uncertainty of ±10%. b) From Ref. 21, the value determined at 299.5 K. c) The monomer fraction for 0.01 mol dm^{-3} of the total concentration based on the monomeric form.

and nitrosodurene, as is shown in Table 1. Nitrosobenzene was found to be too reactive toward the *t*-butyl radical for the rate constant to be determined precisely. The rate constants in Table 1 may include an experimental uncertainty, at the most, of 10% caused mainly in measuring the ESR intensities and in weighing the small amounts of spin-trapping agents.

The only data available to be compared with these results are those for BNO: the spin-trapping rate constant is 1.1×10^6 mol^{-1} dm^3 s^{-1} at 317 K toward the *t*-butoxycarbonyl radical[7] and 1.3×10^8 mol^{-1} dm^3 s^{-1} at 228 K toward the methoxyl radical.[8] The reactivity of BNO depends very much on the free radicals trapped, and the rate constant toward the *t*-butyl radical reasonably falls in between. The rate constant depends also very much on the spin-trapping agents used. Although tri-*t*-butylnitrosobenzene is exceptionally unreactive toward the *t*-butyl radical (it gives an anilino-type spin-adduct radical) because of the steric hindrance due to the ring substitution with bulky *t*-butyl groups, aromatic nitroso compounds are generally more reactive than BNO, the nitrosoalkane examined.

C-phenyl-*N*-*t*-butylnitrone, one of the most commonly used spin-trapping agents, was also examined in the same way. However, its concentration 30 times as high as the BNO concentration gave no detectable ESR spectrum of the spin-adduct radical from it in the competition reaction experiment. Thus, *C*-phenyl-*N*-*t*-butylnitrone was found to be less reactive than BNO by a factor of less than 0.003 toward the *t*-butyl radical. It turns out that the spin-trapping rate constant is as small as 1×10^4 mol^{-1} dm^3 s^{-1} or less. This is much smaller than the spin-trapping rate constants previously reported for *C*-phenyl-*N*-*t*-butylnitrone: 4×10^5 mol^{-1} dm^3 s^{-1} toward the benzyloxyl radical at room temperature,[17] 5.5×10^6 mol^{-1} dm^3 s^{-1} toward the *t*-butoxyl radical at 298 K,[18] and 1.2×10^7 mol^{-1} dm^3 s^{-1} toward the phenyl radical at 298 K.[19] This trapping agent seems to be exceptionally unreactive toward the *t*-butyl radical.

Monomer-Dimer Equilibrium of Spin-trapping Agents. Nitroso compounds are often present in solutions in the dimeric form, which is inactive in trapping free radicals. Therefore, the dissociation constant, K ($=[\text{monomer}]^2/[\text{dimer}]$), of the spin-trapping agent used is an important parameter in the quantitative application of the spin-trapping technique.

Nitrosodurene showed optical absorption bands at 800 and 320 nm, the former being due to the monomer, and the latter, to the dimer. According to the well-known relationship between the total concentration of nitrosodurene, c, and the optical density of the monomer band:

$$\frac{c}{\mathrm{OD}} = \frac{1}{2\varepsilon} + \frac{1}{K\varepsilon^2}\mathrm{OD}, \tag{14}$$

the dissociation constant was determined to be 7.5×10^{-5} mol dm^{-3} at 298 K in benzene. It turns out that only 8% of the nitrosodurene is present in the monomeric form at the total concentration usually occurring in the spin-trapping experiments, 10 mmol dm^{-3}. The temperature dependence of K was also studied in the 293—313 K range, as is shown in Fig. 8, which gives the Arrhenius expression of $K = 10^{6.80}\exp(-61/RT)$ in kJ/mol unit. The molar extinction coefficient, ε, was found to be 91 mol^{-1} dm^3 cm^{-1}, almost unchanged in the temperature range examined.

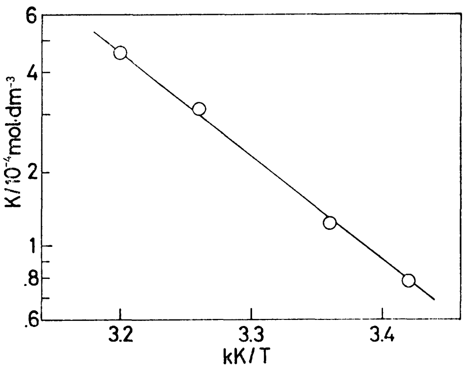


Fig. 8. The dependence of the monomer-dimer equilibrium constant of nitrosodurene in benzene on the reciprocal temperature.

For pentamethylnitrosobenzene, K was determined in the same way to be $10^{5.26}\exp(-50/RT)$, as has been reported previously.[11] Stowell reported the monomer-dimer equilibria for BNO at 288 and 298 K,[20] which were confirmed by the present observation that K is 1.31 at 290 K. Nitrosobenzene and tri-*t*-butylnitrosobenzene are already known to be totally monomeric in solutions.[21,22] *C*-phenyl-*N*-*t*-butylnitrone does not form the dimer at all, either.

The spin-trapping rate constants, k_{12}, shown in the preceeding section were determined on the basis of the monomer concentration calculated by using the dissociation constants obtained here. The dissociation constants used in the calculation and the monomer fractions for the total concentration of 10^{-2} mol dm^{-3} are also shown in Table 1.

In a practical sense, the efficiency of spin-trapping agents may be given by the product of the spin-trapping rate constant and the monomer fraction. Even though nitrosodurene and pentamethylnitrosobenzene are mostly in the dimeric form in benzene, they are more efficient in trapping the *t*-butyl radical than are BNO and tri-*t*-butylnitrosobenzene. Nitrosobenzene is an extremely efficient spin-trapping agent, though it gives a complicated hyperfine structure of the ESR spectrum of the spin-adduct radical.

Summary and Conclusion

The most significant results in the present investigation may be summarized as follows: (1) The *t*-butyl radical reacts with its spin-adduct radical formed from BNO more readily than with BNO itself, so that the yield of the spin-adduct radical cannot go above a certain level. (2) The spin-trapping rate constant depends very much on the nitroso compounds used as the spin-trapping agents; it varies from 2.3×10^5 to 2.0×10^7 or more toward the *t*-butyl radical in benzene at 299 K. Aromatic nitroso compounds are generally more efficient in trapping the *t*-butyl radical than the nitrosoalkane. *C*-phenyl-*N*-*t*-butylnitrone is less efficient in trapping the *t*-butyl radical than the nitroso compounds. (3) In some cases, the monomer-dimer equilibrium shifts well over to the dimer and reduces the practical effectiveness of the spin-trapping agents. Furthermore, the equilibrium was found to be reached extremely slowly (in about an hour) after mixing the spin-trapping agents with a benzene solvent.

These results are believed to give a clue to developing a quantitative utilization of the spin-trapping technique in the study of free radical reaction intermediates.

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