June, 1982] © 1982 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 55, 1753—1755 (1982) 1753

Kinetic Studies of Spin Trapping Reactions. III. Rate Constants for Spin Trapping of the Cyclohexyl Radical

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(Received October 19, 1981)

In order to give a quantitative basis for the spin trapping technique, the spin trapping rate constants for the reactions between commonly-used spin traps and cyclohexyl radicals have been determined. The cyclohexyl radicals were generated by γ-irradiating cyclohexane solutions of the spin traps. The rate constants for nitrosobenzene, nitrosodurene, pentamethylnitrosobenzene, 2,4,6-tri-*t*-butylnitrosobenzene, and α-phenyl-*N*-*t*-butylnitrone at 299 K are 9×10^7, 1.4×10^7, 1.6×10^7, 2.4×10^4, and 8×10^3 mol^{-1} dm^3 s^{-1}, respectively. The results are qualitatively in accordance with previous data for *t*-butyl, 1-methyl-5-hexenyl, and 5-hexenyl radicals.

The spin trapping technique, that is, the transformation of short-lived free radicals into stable, persistent radicals by a reaction with a spin trap, such as a nitroso compound, and the subsequent observation of these persistent radicals by means of conventional electron spin resonance (ESR) measurements, has proved to be useful for the detection and indentification of free radical intermediates in liquid and gas-phase reaction systems. Before the method is utilized in mechanistic and kinetic studies of free radical reactions, its quantitative aspects should be further explored. The yields of the free radical intermediates, for example, cannot be derived by this technique without a knowledge of the rate constant for the spin trapping reaction between the spin trap used and the free radical in question. There has been relatively few rate date available for spin trapping reactions.

We have reported the first systematic study on the spin trapping rate constants for reactions between several spin traps (mostly nitroso compounds) and the *t*-butyl radical.[1] It was found that the rate constant varies over a wide range, from 10^4 to 10^8 mol^{-1} dm^3 s^{-1}, depending on the spin trap. Later, Ingold *et al.* have reported investigations on the spin trapping rate constant with 5-hexenyl[2] and 1-methyl-2-hexenyl radicals,[3] and have shown a general trend in the reactivity of several spin traps toward primary, secondary, and tertiary alkyl radicals.

In the present investigation, we have determined the spin trapping rate constants for reactions of commonly-used spin traps and another secondary alkyl radical, the cyclohexyl radical. We recently found that γ-radiolysis of cyclohexane containing a spin trap gave ESR spectra which were exclusively due to a cyclohexyl radical spin adduct.[4,5] This radiation-chemical technique has been used to generate authentic cyclohexyl radical spin adducts in the present investigation.

Experimental

Spectro-grade cyclohexane was used without further purification. Pentamethylnitrosobenzene (PMNB)[6] and α-phenyl-*N*-*t*-butylnitrone (PBN, *N*-*t*-butyl-α-toluenimine *N*-oxide)[7] were synthesized as has been described previously. Nitrosobenzene (NB) and 2-methyl-2-nitrosopropane (BNO) were purchased commercially and used as received. Nitrosodurene (ND) and 2,4,6-tri-*t*-butylnitrosobenzene (BNB) were kindly donated by Dr. R. Konaka of Shionogi Pharm. Co. Ltd. and Dr. S. Moriuchi of Mitsui Petrochemical Ind. Ltd.

Sample solutions of spin traps in cyclohexane were degassed by freeze-pump-thaw cycles nder a vacuumu of 10^{-5} Torr** and sealed in quartz ESR tubes. They were irradiated with ^{60}Co γ-rays at a dose rate of about 0.5 krad/min at 289—1 K, and subjected to ESR measurement with a Varian E-109 X-band spectrometer at the ambient temperature. Decay of the spin adducts during storage was avoided by freezing the irradiated samples at 77 K.

If the concentration of the spin traps was too low to be determined by weighing, it was determined from the intensity of their optical absorption. The optical absorption data which were used are summarized in Table 1.

Results and Discussion

When the sample solution contains one kind of spin trap, it generally shows an ESR spectrum which is due exclusively to a cyclohexyl radical spin adduct, as reported previously for PMNB.[4] An exception is BNO, which gave an ESR spectrum with 3×9 hyperfine lines. This spectrum cannot be due to the cyclohexyl radical spin adduct, but is probably due to the spin adduct of a secondarily generated free radical. Although BNO is one of the most commonly used spin adducts, it was omitted from the present investigation.

When two kinds of spin traps are present, the two corresponding spin adducts of the cyclohexyl radical are observed by ESR. This is shown in Fig. 1 for a pair of spin traps, PBN and BNB. The ESR signal is comprised of a triple doublet spectrum with a nitrogen hyperfine coupling, a_N, of 1.35 mT and a proton hyperfine coupling, a_H, of 0.25 mT and a triple quartet spectrum with a_N of 1.10 mT and a_H of 0.20 mT. The former spectrum is due to a nitroxide-type cyclohexyl radical-PBN spin adduct (*N*-*t*-butyl-α-cyclohexylbenzylaminoxyl), whereas the latter is due to an anilino-type cyclohexyl radical-BNB spin adduct (*O*-cyclohexyl-*N*-(2,4,6-tri-*t*-butylphenyl)hydroxylaminyl). This assignment is based on reported hyperfine coupling data.[8,9]

Assuming the absence of decay of the spin adducts once these have been generated, the relative yields of the spin adducts should be determined by a competition between the spin trapping reactions of the coexisting

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** 1 Torr ≈ 133.322 Pa.

Table 1. Optical absorption data and monomer-dimer equilibrium constants of spin traps in benzene determined at 299 K

Spin trap	Optical absorption[a)]		Monomer-dimer equilibrium const.[b)]
	λ_{max}/nm	ε/mol^{-1} dm^3 cm^{-1}	K/mol^{-1} dm^3
Nitrosobenzene (NB)	770	53[c)]	0
Nitrosodurene (ND)	800	36[d)]	1000[d)]
Pentamethylnitrosobenzene (PMNB)[e)]	790	52.6	1300
2,4,6-Tri-*t*-butylnitrosobenzene (BNB)	750	13	0
2-Methyl-2-nitrosopropane (BNO)	680	20	0.52
α-Phenyl-*N*-*t*-butylnitrone (PBN)	295	2.5×10^4	0

a) Absorption band due to $n\pi^*$ transition of the –NO group of monomeric form. b) Determined as [dimer]/[monomer]^2. c) Ref. 15. d) According to a recent experiment in a wider concentration range, values reported in Ref. 1 should be revised. e) Ref. 4.

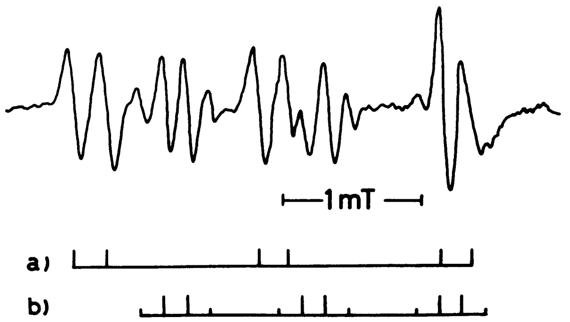


Fig. 1. ESR signal observed from γ-irradiated cyclohexane containing BNB and PBN. The stick diagrams show (a) the cyclohexyl radical-PBN spin adduct and (b) the cyclohexyl radical-BNB (anilino-type) spin adduct.

spin traps (denoted as 1 and 2). This means that the relationship

$$\frac{d[A_1]/dt}{d[A_2]/dt}=\frac{k^T{}_1[T_1]}{k^T{}_2[T_2]} \tag{1}$$

should hold between the concentrations of spin traps and spin adducts, T_i and A_i. $k^T{}_i$ is the spin trapping rate constant of the *i*-th spin trap, and *t* is the time of the γ-irradiation. The rate constant ratio $k^T{}_1/k^T{}_2$ has been determined for several pairs of spin traps at 289 K by irradiating the sample solutions to a low dose so that $[A_i]$ increased linearly with the irradiation time.[4)] Pairs of spin traps were chosen for which overlapping spectra of spin adducts can be separated from each other. A typical example of the observed results, that of the PMNB-BNB pair, is shown in Fig. 2.

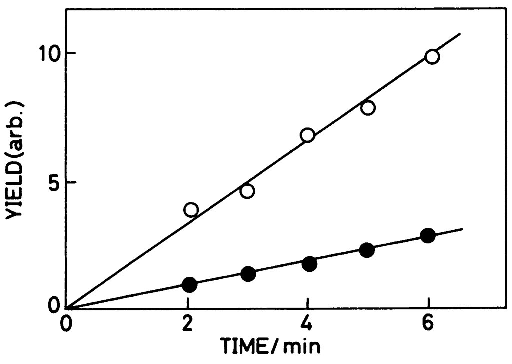
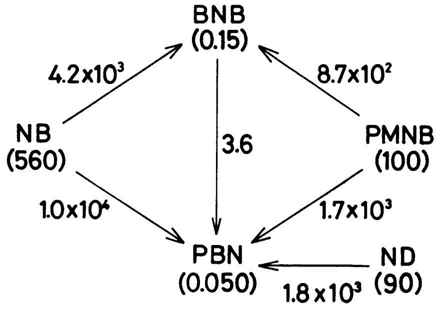


Fig. 2. Yields of (○) cyclohexyl radical-PMNB and (●) cyclohexyl radical-BNB spin adducts as a function of γ-irradiation time observed from cyclohexane containing 1.9×10^{-4} mol/dm^3 PMNB and 5×10^{-2} mol/dm^3 BNB.

The rate constant ratio was determined according to the following scheme, where arrows connect the pairs of the spin traps examined, pointing from the more reactive to the less reactive trap. The observed ratio is given above each arrow. It is the average of two to five individual competitive measurements at various trap concentrations. The numbers in parentheses show the relative spin trapping rate constants determined with respect to PMNB by averaging all possible paths with a weight factor inversely proportional to the number of arrows along the path. For example, the rate constant for NB is $100\times[(4.2\times10^3/8.7\times10^2+1.0\times10^4/1.7\times10^3)/2+(1.0\times10^4/3.6\times8.4\times10^2+3.6\times4.2\times10^3/1.7\times10^3)/3]\times(6/10)=560$. The values thus determined show the validity of the scheme by their internal consistency. These values seem to be correct with an uncertainty of 20%.



The absolute value of the spin trapping rate constant can generally be determined from competition experiments using a reference reaction with a known rate constant. We previously determined the spin trapping rate constant for the reaction of PMNB and the cyclohexyl radical to be 1.6×10^7 mol^{-1} dm^3 s^{-1} at 299 K. This was done by using

$$\dot{C}_6H_{11} + (C_4H_9)_3SnH \longrightarrow C_6H_{12} + (C_4H_9)_3\dot{Sn}, \tag{2}$$

as a reference reaction.[10)] The temperature was 10 K higher than that in the present experiment. The activation energy of k^T has been reported to be so small (1—3 kcal/mol)[2)] that the experimental $k^T{}_1/k^T{}_2$ ratio

TABLE 2. SUMMARY OF RATE CONSTANTS FOR THE SPIN TRAPPING OF ALKYL RADICALS

Spin trap	$k^T/10^5$ mo^{-1} dm^3 s^{-1}			
	t-Butyl[a] (299 K)	Cyclohexyl[b] (299 K)	1-Methyl-5-hexenyl[c] (313 K)	5-Hexenyl[c] (313 K)
Nitrosobenzene (NB)	>2000	900	—	—
Nitrosodurene (ND)	900[d]	140	406	407
Pentamethylnitrosobenzene (PMNB)	900[e]	160	—	—
2,4,6-Tri-*t*-butylnitrosobenzene (BNB)	2.3[f]	0.24[f]	3.3[g]	4.7
2-Methyl-2-nitrosopropane (BNO)	33	—	61	90
α-Phenyl-N-*t*-butylnitrone (PBN)	<0.1	0.08	0.68	1.3

a) Reference 1. b) This work. c) Refs. 2 and 3. d) Revised value, see Ref. 4. e) Recalculated using the revised value of $\varepsilon = 36$ mol^{-1} dm^3 cm^{-1}. f) Anilino-type spin adduct is generated. g) 3.1 and 0.18 for anilino- and nitroxide-type spin adduct formations.

is expected to be almost temperature-independent in a small temperature range, such as that from 289 to 299 K. A difference of 1 kcal/mol in activation energy leads to a difference of 12% in the ratio. Actually, no temperature-dependence could be found experimentally for the PBN-ND pair. The spin trapping rate constant for each spin trap was calculated from the rate constant ratio determined in the present study and the absolute rate constant for PMNB reported previously.[4]

The results of the present study are shown in Table 2 together with the rate constants for spin trapping primary (5-hexenyl), secondary (1-methyl-5-hexenyl), and tertiary (*t*-butyl) radicals as reported by Ingold *et al.*[2,3] and by ourselves.[1] Alkyl radicals are efficiently spin-trapped by all of the aromatic nitroso compounds examined except BNB. The rate constants for the spin trapping reactions of the different nitroso compounds decrease in the order $k^T_{NB} > k^T_{ND} \approx k^T_{PMNB} \gg k^T_{BNB}$. This shows that substituting ortho hydrogens in the aromatic ring for bulky groups has a significant effect on the spin trapping reactions. It also supports the previous suggestion[2] that the spin trapping reaction of BNB is slow because formation of the adduct requires a fairly exact configuration of the reactions, even though the potential energy barrier to be surmounted is small. The type of trapping reaction BNB undergoes depends on the free radical trapped. For primary alkyl radicals, the result is a nitroxide-type spin adduct which many other spin traps also give. But for tertiary alkyl radicals the results is an anilino-type spin adduct. Secondary alkyl radicals are on the borderline between these two types of the trapping reactions. For the 1-methyl-5-hexenyl radical, both the anilino- and nitroxide-type spin adducts are found,[3] whereas for the cyclohexyl radical only the anilino-type spin adduct is observed.[4,9] Although the nitrone is not an efficient spin trap for alkyl radicals, including the cyclohexyl radical, it is efficient in trapping phenyl[11] and alkoxyl radicals.[12–14] It should be stressed that the spin trapping rate constants of commonly-used spin traps differ over a wide range of four orders of magnitude.

Although the overall picture for primary, secondary, and tertiary alkyl radicals has revealed that $k^T_{prim} > k^T_{sec} > k^T_{tert}$,[3] the spin trapping rate constants determined for the cyclohexyl radical in this paper are generally smaller than those for *t*-butyl radical as previously determined by ourselves.[1] This unexpected result may stem from an experimental artifact caused by an improper choice of reference reactions. Nevertheless, the results summarized in this paper gives a clue to the quantitative application of the spin trapping technique to mechanistic and kinetic studies of free radical reactions.

The authers wish to thank Dr. R. Konaka of Shionogi Pharm. Co. Ltd. and Dr. S. Moriuchi of Mitsui Petrochemical Ind. Ltd. for their kindness in donating spin traps, and Dr. K. U. Ingold of the National Research Council, Canada, for the suggestion, which enabled us to improve the data shown in Table 1.

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