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Pulse Radiolysis Studies on Methyl Methylthiomethyl Sulfoxide in Aqueous Solutions

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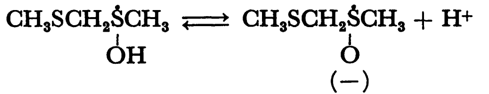
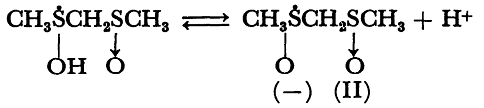
Reaction mechanisms between methyl methylthiomethyl sulfoxide (MTMSO) and hydrated electron (e_{aq}^-) or hydroxyl radical (OH· radical) have been studied in aqueous solutions with various pH values by means of pulse radiolysis technique. The acid and basic components of equilibrium



$$\underset{\displaystyle OH}{CH_3SCH_2\dot{S}CH_3} \rightleftarrows \underset{\displaystyle \overset{\displaystyle O}{(-)}}{CH_3SCH_2\dot{S}CH_3} + H^+$$

(I)

and



$$\underset{\displaystyle OH\ \ O}{CH_3\dot{S}CH_2SCH_3} \rightleftarrows \underset{\displaystyle \underset{(-)}{O}\ \ O}{CH_3\dot{S}CH_2SCH_3} + H^+$$

(II)

are formed for the reaction of $e_{aq}^- + CH_3SCH_2SOCH_3$ and OH· $+ CH_3SCH_2SOCH_3$, respectively. The pK_a values of the respective equilibrium are 10 and 9. The anion (I) and (II) have absorption maxima at 375 nm and 360 nm, respectively. The sulfinic acid $CH_3SCH_2SO_2^-$ is also formed in the reaction of $CH_3SCH_2SOCH_3$+OH·. The rate constants have been determined to be $k(e_{aq}^- + \text{MTMSO}) = 1.3\times10^8\ M^{-1}\ s^{-1}$ and $k\ (\text{OH}\cdot + \text{MTMSO}) = 3.1\times10^9\ M^{-1}\ s^{-1}$ ($1\ M = 1\ mol\ dm^{-3}$). Relative reactivities of OH· radical with thio-methyl bond and sulfinyl group are also discussed.

Two organic bonds involving sulfur atoms, thiomethyl bond (sulfide S–C bond) and sulfinyl-methyl bond (sulfoxide S–C bond), are known to change reactivities with pH of the solutions. Pulse radiolysis method has provided one of the most successful approaches to investigate dynamics of the compounds. Meissner, Henglein and Beck have reported the study on the primary processes for the irradiated aqueous solutions of dimethyl sulfide and dimethyl sulfoxide.[1] They suggested that the formation of the radical anion $CH_3SOCH_3^-\cdot$ and the radical cation complex $(CH_3SCH_3)_2^+\cdot$ for the reaction of the OH· radical with CH_3SCH_3, and that the formation of the radical anion $CH_3SOCH_3^-\cdot$ in the reaction of the hydrated electron with CH_3SOCH_3. The formation of sulfinic acid RSO_2^- for the reaction of the OH· radical with sulfoxide (R_2SO) have been found by Veltwisch, Janata and Asmus from a pulse radiolysis study with the conductivity detection method.[2] Although primary processes of the individual compounds have been fairly well studied, relative reactivities of the sulfide S–C bond and sulfinyl group with OH· radical are not known.

Methyl methylthiomethyl sulfoxide ($CH_3SOCH_2SCH_3$; MTMSO) possessing the sulfide S–C bond and the sulfinyl group within one molecule is expected to show interesting reactivities. In the present study we propose the primary processes for the reaction of e_{aq}^-+ MTMSO and OH·+MTMSO in aqueous solution in comparison with the dimethyl sulfide and the dimethyl sulfoxide. Spectral analysis of the transient absorption in the UV-Vis regions and an electrical conductivity analysis after pulse irradiation were two techniques to identify the transient species produced. Experimental results of reaction yields and reaction rate constants give information on the relative reactivities between the sulfide S–C bond and the sulfinyl group with OH· radical.

Experimental

MTMSO was purchased from Nisso LTD. and used without further purification. Solutions were prepared by dissolving *t*-BuOH, $HClO_4$, NaOH, and $NaClO_4$ in triply distilled water, and the pH values of the solutions were adjusted by adding perchloric acid or sodium hydroxide. For studies on the reaction of MTMSO with e_{aq}^-, solutions were bubbled with argon to remove oxygen. On the other hand, solutions for studies on the reaction with OH· radical were bubbled with dinitrogen monoxide in order to convert the e_{aq}^- into OH· radicals *via* the following reaction:

$$N_2O + e_{aq}^- \longrightarrow OH\cdot + OH^- + N_2. \qquad (1)$$

Pulse radiolysis measurements were performed with electron pulses (45 MeV) from a S-band linear accelerator (Mitsubishi) installed at Hokkaido University.[3] The half-width of the electron pulse used was 20 ns and dose per pulse was up to 14 krad. The optical detection system was basically the same as that designed by Hunt and Thomas.[4] Analyzing light from Xe arc lamp (1 kW, Wako Denki) was chopped by a rotating disk at 25 Hz and sent to a sample cell. The absorption signal, after passing through the monochromator (Shimadzu-Bausch and Lomb, 200 mm, f/3.5), was detected by a photomultiplier (Hamamatsu T. V. R446UR) system. The output signal was displayed on to an oscilloscope (National VP5405A).

The sample cell for the D-C conductivity analysis has two rectangular electrodes ($3\times5\ mm^2$), which were set 5 mm apart. By the conductivity method, charged species being produced after pulse irradiation are monitored *via* a variation of the signal voltage. The relation between the change in the concentration of *i*-th charged species ΔC_i and a signal voltage on the oscilloscope ΔV_s as a result of the formation or disappearance of the species in a solution is given by the following equation:[5]

$$\Delta V_s = \frac{VR}{k\,10^3}\sum \Delta C_i|Z_i|\Lambda_i, \qquad (2)$$

where V, R, and k indicate a voltage between two electrodes in the irradiation cell, a resistance and a cell constant (in $\mathrm{cm^{-1}}$), respectively. $|Z_i|$ and Λ_i represent the number of charges (1 for one electron oxidation) and the corresponding conductivities (in $\Omega^{-1}\,\mathrm{cm^2}$) for i-th charged species, respectively.

If only one acid species (XH) is produced by irradiation and G value of the species is given by G_{XH} which is directly proportional to ΔC_{XH}, then Eq. 2 is rewritten as

$$\Delta V_s \times K = G_{XH} \times (\Lambda_{X^-} + \Lambda_{H^+}), \qquad (3)$$

here K denotes certain constant determined experimentally.

Results and Discussion

Reaction of e_{aq}^- with MTMSO; Formation of Radical Anion. MTMSO aqueous solutions containing 1 M t-BuOH as a hydroxyl radical scavenger were irradiated to investigate the reaction mechanism of e_{aq}^- with MTMSO.

Figure 1 shows a representative decay curve for the transient absorption of e_{aq}^- which are produced after the pulse irradiation of the MTMSO aqueous solution. The decay curve fit a simple first-order kinetics as is shown in the figure. The pseudo-first-order rate for the absorption of the hydrated electron was plotted as a function of MTMSO concentration and the rate constant for the reaction e_{aq}^-+MTMSO was determined from the slope of the linear plot to be $(1.30\pm0.08)\times10^8\,\mathrm{M^{-1}\,s^{-1}}$. The rate constant values thus obtained are summarized in Table 1 as a function of pH values. The values were constant with respect to the pH (from pH 6 to 11) of the solutions.

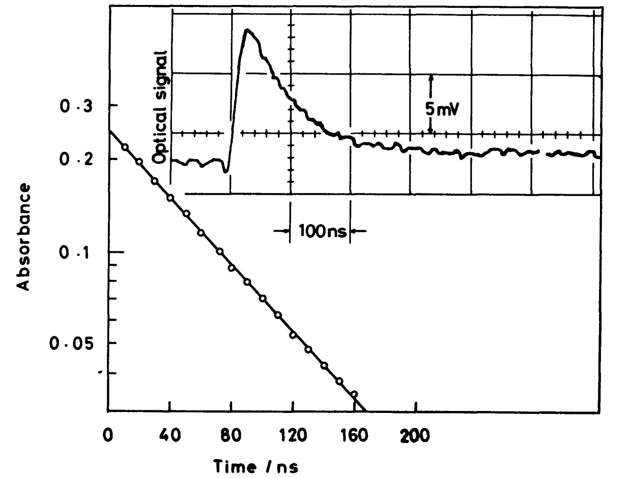


Fig. 1. First-order kinetic plot of log Abs. (e_{aq}^-) against time after the pulse irradiation of MTMSO aqueous solution ([MTMSO]=0.1 M, pH 7.1, monitoring wavelength; 600 nm). The solution was saturated with argon gas prior to the irradiation. Inset: an oscillogram trace of the decay curve for the absorption of e_{aq}^-. A change of 5 mV in the vertical axis corresponds to 22% transmittance.

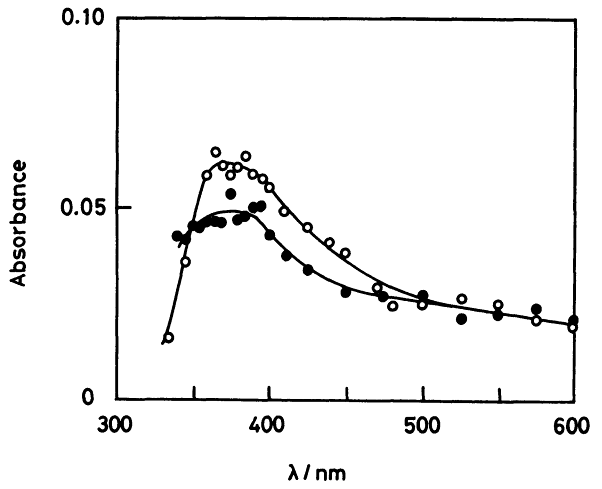


Fig. 2. Transient absorption spectra 2 μs after the pulse irradiation of MTMSO aqueous solutions ([MTMSO] =0.05 M, [t-BuOH]=1 M). Solutions were saturated with argon gas prior to the irradiation. ●: pH 6, ○: pH 10.

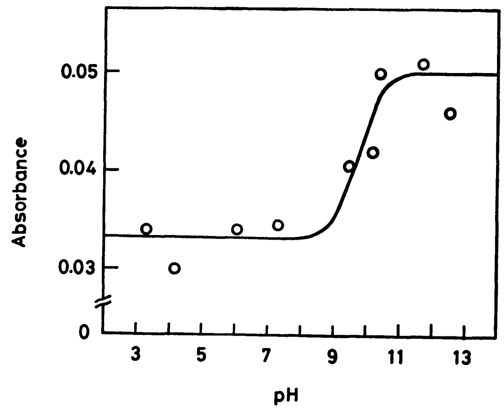


Fig. 3. Optical densities at 375 nm as a function of pH, 2 μs after the pulse. MTMSO aqueous solutions ([MTMSO]=0.05 M, [t-BuOH]=1 M) were saturated with argon gas prior to the irradiation.

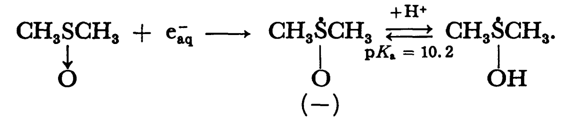
Figure 2 shows the transient absorption spectra observed for aqueous solutions containing MTMSO (0.05 M, pH 6 and 10) at 2 μs after the pulse where the absorption of e_{aq}^- is sufficiently diminished. The transient absorption spectrum thus obtained has a broad band with a λ_{max}=375 nm.

Figure 3 shows the change in the absorbance of the transients at λ=375 nm with changing pH values of MTMSO solutions. The intensity of the transient absorption increases sharply at pH 10. It has been

TABLE 1. REACTION RATE CONSTANTS OF HYDRATED ELECTRON WITH MTMSO IN AQUEOUS SOLUTIONS AS A FUNCTION OF pH

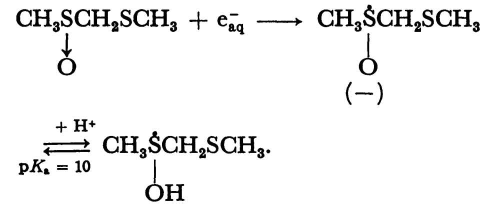
pH	6.1	7.1	9.0	10.4	11.0
k(e_{aq}^-+MTMSO)/$\mathrm{M^{-1}\,s^{-1}}$	1.30×10^8	1.38×10^8	1.28×10^8	1.30×10^8	1.23×10^8

reported for the reaction of e^-_{aq}+CH_3SOCH_3 that the following equilibrium between both species of acid and its conjugated basic form should be taken into consideration:[1)]



$$\mathrm{CH_3\underset{\underset{O}{\downarrow}}{S}CH_3} + e^-_{aq} \longrightarrow \mathrm{CH_3\underset{\underset{\underset{(-)}{O}}{|}}{\dot{S}}CH_3} \underset{pK_a=10.2}{\overset{+H^+}{\rightleftharpoons}} \mathrm{CH_3\underset{\underset{OH}{|}}{\dot{S}}CH_3\cdot} \qquad (4)$$

The pK_a value of the equilibrium (4) is 10.2. From our observation of the pH dependence for the transients and by analogy with the reaction scheme (4), we may reasonably assign the transients formed in the reaction e^-_{aq}+MTMSO to the radical anion which is in the following equilibrium:



$$\mathrm{CH_3\underset{\underset{O}{\downarrow}}{S}CH_2SCH_3} + e^-_{aq} \longrightarrow \mathrm{CH_3\underset{\underset{\underset{(-)}{O}}{|}}{\dot{S}}CH_2SCH_3}$$

$$\underset{pK_a=10}{\overset{+H^+}{\rightleftharpoons}} \mathrm{CH_3\underset{\underset{OH}{|}}{\dot{S}}CH_2SCH_3\cdot} \qquad (5)$$

Thus, from Fig. 3 the pK_a value of the equilibrium (5) is determined to be 10.

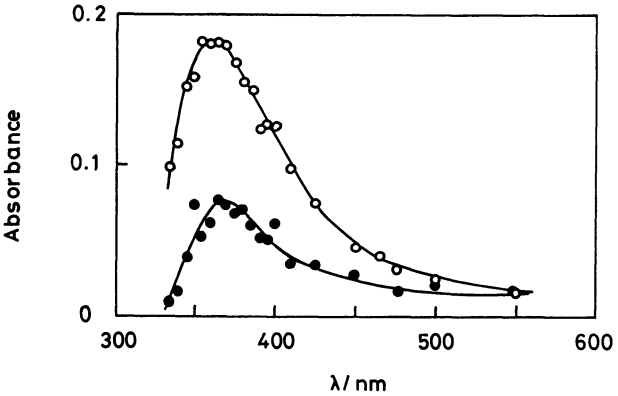


Fig. 4. Transient absorption spectra 500 ns after the pulse irradiation of MTMSO aqueous solutions ([MTMSO]=0.05 M). Solutions were saturated with N_2O gas prior to the irradiation. ●: pH 6, ○: pH 10.

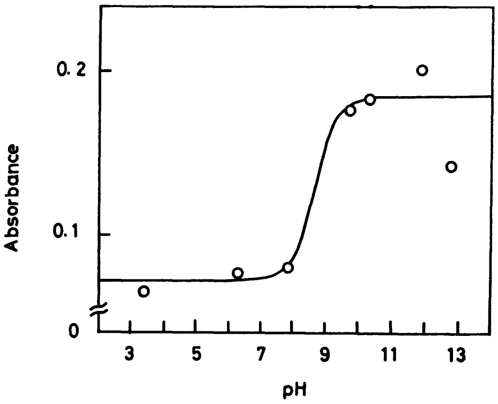
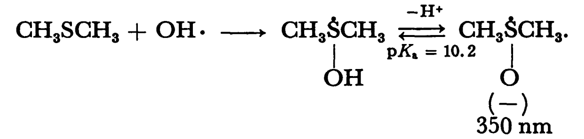


Fig. 5. Optical densities at 360 nm as a function of pH, 500 ns after the pulse. MTMSO aqueous solutions ([MTMSO]=0.05 M) were saturated with N_2O gas prior to the irradiation.

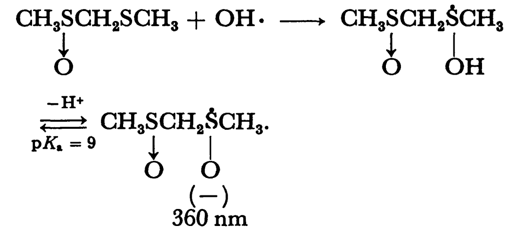
Reaction of OH· Radical with MTMSO. *a) Sulfide and OH· Radical*: Pulse radiolysis experiments of N_2O saturated MTMSO solutions (0.05 M, pH 6 to 10) were carried out in order to test the reaction mechanism of MTMSO with OH· radical. For N_2O saturated MTMSO solutions, no transient absorption being assignable to hydrated electron was observed. Figure 4 shows the transient absorption spectra observed at 500 ns after the pulse. Figure 5 shows the pH dependence of MTMSO aqueous solutions on the intensity of the transient absorption at 360 nm. The absorption intensity increases sharply at pH 9. The pH dependence indicates that the transients is in an acid-base equilibrium whose pK_a value is equal to 9. It has been reported that a radical anion $CH_3SOCH_3^-\cdot$ is formed in the reaction of the OH· radical with dimethyl sulfide, and that the radical anion is in an acid-base equilibrium:[1)]



$$\mathrm{CH_3SCH_3 + OH\cdot} \longrightarrow \mathrm{CH_3\underset{\underset{OH}{|}}{\dot{S}}CH_3} \underset{pK_a=10.2}{\overset{-H^+}{\rightleftharpoons}} \mathrm{CH_3\underset{\underset{\underset{\underset{350\,nm}{(-)}}{O}}{|}}{\dot{S}}CH_3\cdot} \qquad (6)$$

It is also known that the radical anion ($CH_3SOCH_3^-\cdot$) has the absorption with λ_{max}=350 nm.[1)]

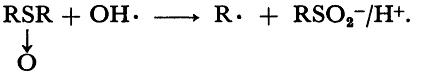
These facts suggest that the transient absorption spectrum observed here originates from the radical anion ($CH_3SOCH_2SOCH_3^-\cdot$) which is formed in the reaction between the OH· radical and sulfur atom of the thiomethyl bond of MTMSO. The radical anion is in an acid-base equilibrium with the pK_a=9:



$$\mathrm{CH_3\underset{\underset{O}{\downarrow}}{S}CH_2SCH_3 + OH\cdot} \longrightarrow \mathrm{CH_3\underset{\underset{O}{\downarrow}}{S}CH_2\underset{\underset{OH}{|}}{\dot{S}}CH_3}$$

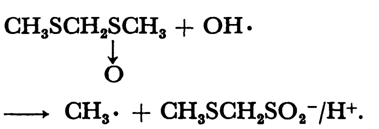
$$\underset{pK_a=9}{\overset{-H^+}{\rightleftharpoons}} \mathrm{CH_3\underset{\underset{O}{\downarrow}}{S}CH_2\underset{\underset{\underset{\underset{360\,nm}{(-)}}{O}}{|}}{\dot{S}}CH_3\cdot} \qquad (7)$$

b) Sulfoxide and OH· Radical: It is probable that the OH· radical attacks not only the sulfide S–C bond but also the sulfoxide S–C bond of MTMSO. The following route has been also suggested for the reaction between OH· radical and R_2SO:[2)]



$$\mathrm{R\underset{\underset{O}{\downarrow}}{S}R + OH\cdot} \longrightarrow \mathrm{R\cdot + RSO_2^-/H^+}. \qquad (8)$$

By the analogy with Reaction 8, the sulfinic acid ($CH_3SCH_2SO_2^-$) is expected to be formed for the case of MTMSO, when the OH· radical attacks the sulfoxide S–C bond of MTMSO:



$$\mathrm{CH_3\underset{\underset{O}{\downarrow}}{S}CH_2SCH_3 + OH\cdot}$$

$$\longrightarrow \mathrm{CH_3\cdot + CH_3SCH_2SO_2^-/H^+}. \qquad (9)$$

Detection of ionic species for the acidic solution of MTMSO will give a proof for the formation of the sulfinic acid. The conductivity detection method combined with the pulse radiolysis experiment was adopted for the acidic MTMSO (10^{-3} M) solution saturated by N_2O gas.

For the acid solution (pH 5.6), an increment in

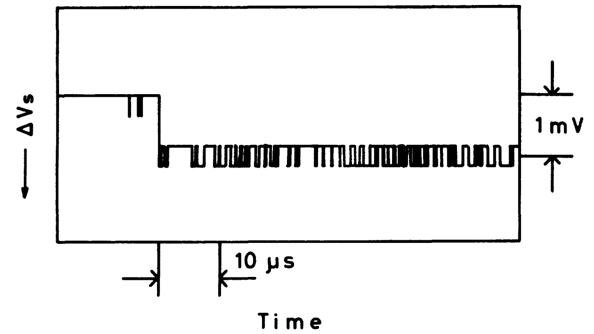


Fig. 6. Conductivity-time curve of pulse-irradiated aqueous N_2O saturated solutions of 10^{-3} M MTMSO at pH 5.6.

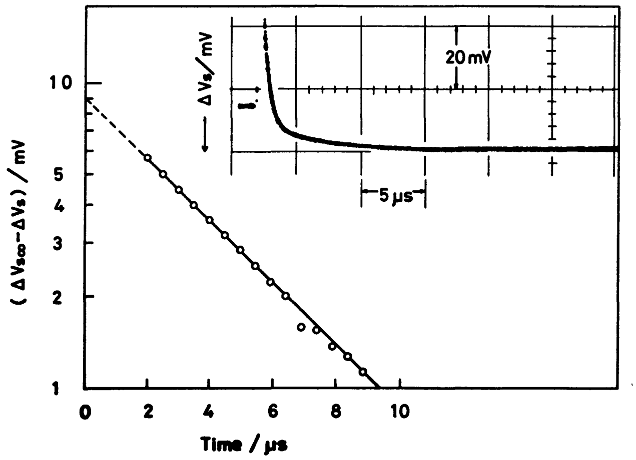


Fig. 7. First-order kinetic plot of $\log(\Delta V_{S\infty}-\Delta V)$ against time after the pulse irradiation of MTMSO aqueous solution ($[\mathrm{MTMSO}]=5\times10^{-5}$ M, pH 4.9, $V=-30$ V, $R=50\ \Omega$). The solution were saturated with N_2O gas prior to the irradiation. Inset: An oscillogram trace of the conductivity change as a result of the formation of sulfinic acid $CH_3SCH_2SO_2^-$.

conductivity was observed. The signal of the conductivity after the pulse was a step function since the $CH_3SCH_2SO_2^-/H^+$ ion pair is stable over the detection period (Fig. 6). From the signal in Fig. 6, the yield of sulfinic acid can be determined as:

$$0.99\times K=G_{\mathrm{CH_3SCH_2SO_2^-/H^+}}\times[\Lambda_{\mathrm{CH_3SCH_2SO_2^-}}+\Lambda_{\mathrm{H^+}}]. \quad (10)$$

Here the value of $\Lambda_{\mathrm{H^+}}$ is known to be 315 Ω^{-1} cm^2 and $K=9.74\times10^2$ which is determined experimentally. Using these values and assuming that $\Lambda_{\mathrm{CH_3SCH_2SO_2^-}}$ is equal to $\Lambda_{\mathrm{CH_3SO_2^-}}=42\ \Omega^{-1}$ cm^2 which is determined by Veltwisch *et al.*,2) the yield of $CH_3SCH_2SO_2^-$ anion is calculated to be $G_{\mathrm{CH_3SCH_2SO_2^-}}=2.7$. The value of the yield is 45% of the total yield of the OH· radicals ($G_{\mathrm{OH\cdot}}=6.0$).6) This fact indicates that 45% of the OH· radicals produced after the pulse irradiation attack the sulfinyl group of MTMSO, and that the residual 55% attack the sulfide S–C bond. Thus, in this case if we can ignore other reaction routes of OH· radical, it has the same reactivity for both the sulfoxide S–C bond and the sulfide S–C bond of MTMSO.

c) Kinetics for the Reaction between OH· Radical and MTMSO: Two methods were adopted for the determination of the rate constant for the reaction of OH·+MTMSO. One is the conductivity method and the other is the KSCN method.

By the conductivity method, the rate constant was evaluated from a rise portion of build-up curve of the conductivity change after the pulse irradiation. Figure 7 shows a representative build-up curve in which the conductivity signal ΔV_S grows at short time and reaches a constant value $\Delta V_{S\infty}$. A plot of log $(\Delta V_{S\infty}-\Delta S_S)$ against time t gives a straight line, and the rate constant for the OH· radical with MTMSO was determined from the slope of the line to be 4.8×10^9 M^{-1} s^{-1}. The rate constant obtained from the conductivity method may correspond to the rate constant for the reaction of OH· radical with MTMSO.

By the KSCN method, the rate constant was determined utilizing the following competitive reaction of OH· radical with MTMSO.

$$\mathrm{MTMSO}+\mathrm{OH\cdot}\longrightarrow\mathrm{Products} \quad (11)$$

$$\mathrm{CNS^-}+\mathrm{OH\cdot}\longrightarrow\mathrm{CNS\cdot}+\mathrm{OH^-} \quad (12)$$

$$\mathrm{CNS^-}+\mathrm{CNS\cdot}\longrightarrow\mathrm{(CNS)_2^-\cdot}. \quad (13)$$

From the above reaction scheme, the concentration of $(CNS)_2^-\cdot$ after the pulse is obtained as follows:

$$[(\mathrm{CNS})_2^-\cdot]=\frac{k_C[\mathrm{CNS^-}][\mathrm{OH\cdot}]_0}{k_C[\mathrm{CNS^-}]+k_F[\mathrm{MTMSO}]}$$
$$[1-\exp\{-(k_F[\mathrm{MTMSO}]+k_C[\mathrm{CNS^-}])t\}], \quad (14)$$

where k_C and k_F denote the rate constants for Reactions 12 and 11, respectively, and $[\mathrm{OH\cdot}]_0$ represents initial concentration of OH· radical after the pulse. From Eq. 14, one can evaluate the rate constant values k_C and k_F by monitoring the growth for the absorption intensity of $(CNS)_2^-\cdot$ which has an absorption maximum at 475 nm. Figure 8 shows some representative rise-curve of $(CNS)_2^-\cdot$ absorption in the absence and the presence of MTMSO. Absorption intensities of $(CNS)_2^-\cdot$ increase

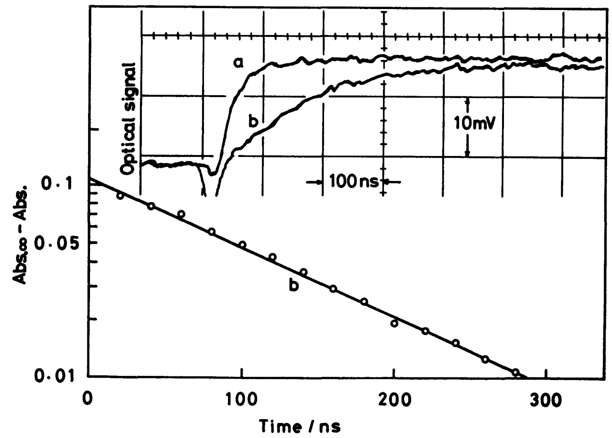


Fig. 8. First-order kinetic plot of log(Abs.$_\infty$−Abs.) against time after the pulse irradiation of MTMSO aqueous solution. Solutions were saturated with N_2O gas prior to the irradiation. Inset: a) an oscillogram trace for the absorption of $(CNS)_2^-$. after the pulse irradiation of KSCN (10^{-2} M) solution in the absence of MTMSO solution. b) An oscillogram trace for the absorption of KSCN (10^{-3} M) solution in the presence of MTMSO (10^{-3} M). A change of 10 mV in the vertical axis corresponds to 16% transmittance. The monitoring wavelength for all the solution is 475 nm.

Table 2. Reaction rate cosntants of OH· radical with MTMSO obtained from KSCN method

[MTMSO]/M	τ/ns$^{a)}$	k_F/M^{-1} s^{-1}
0	199	5.02×10^{6} $^{b)}$
0.5×10^{-3}	157	2.68×10^{9}
1×10^{-3}	118	3.43×10^{9}
3×10^{-3}	85	2.25×10^{9}
6×10^{-3}	33$^{c)}$	4.19×10^{9}

a) The lifetime τ is the reciprocal value of (k_c[CNS$^-$]+k_F[MTMSO]). b) The value represent that for k_c[CNS$^-$]. c) The value may not be very accurate since the pulse width used is ≈20 ns.

within a short period of time, reach maxima and decay slowly. As is shown in the figure, a plot of log (Abs.$_\infty$ − Abs.) against t gives a straight line, where Abs.$_\infty$ and Abs. represent a maximum value and a value at t of the absorbances of $(CNS)_2^{-}\cdot$, respectively. The rate constants k_C[CNS$^-$] and (k_C[CNS$^-$]+k_F[MTMSO]) are determined from a slope of the linear plots for KSCN aqueous solutions in the absence and the presence of MTMSO. k_F is then evaluated by the use of k_C[CNS$^-$] and [MTMSO]. Table 2 summarizes k_F values obtained as a function of MTMSO concentration. Thus, the observation of the rise-curve of $(CNS)_2^{-}\cdot$ absorption after the pulse irradiation of the KSCN (1×10^{-3} M) with the different concentration of MTMSO (0 to 6×10^{-3} M), gives the k_F value to be 3.1×10^{9} M^{-1} s^{-1}. The rate constant value represents the rate constant for all kinds of reaction between OH· radical and MTMSO.

As well as the results of the yield values for the transients which is discussed in the previous section, information on the rate constants which are obtained independently from two methods leads to the conclusion that the OH· radical has almost the same reactivities with both the sulfoxide S–C bond and the sulfide S–C bond of MTMSO.

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References

1) G. Meissner, A. Henglein, and G. Beck, *Z. Naturforsh., Teil B*, **22**, 13 (1967).

2) D. Veltwisch, E. Janata, and K.-D. Asmus., *J. Chem. Soc., Perkin Trans. 2*, **1980**, 146.

3) Y. Kondo, M. Aikawa, T. Sumiyoshi, M. Katayama and J. Kroh, *J. Phys. Chem.*, **84**, 2544 (1980).

4) J. W. Hunt and J. K. Thomas, *Radiat. Res.*, **32**, 149 (1967).

5) K.-D. Asmus, *Int. J. Radiat. Phys. Chem.*, **4**, 417 (1972).

6) R. H. Schuler, L. K. Patterson, and E. Janata, *J. Phys. Chem.*, **84**, 2088 (1980).