

Photo-induced electron transfer reaction between hexamethyldisilane and quinones as studied by a CIDNP technique

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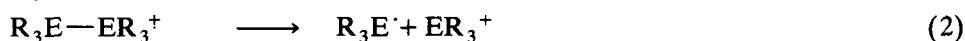
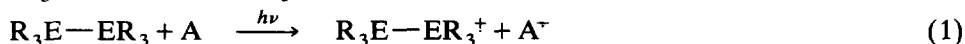
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Abstract

The reaction mechanism of photo-induced electron transfer reactions from hexamethyldisilane to quinones in chloroform solution was studied at room temperature by means of a CIDNP technique. With irradiation, the formation of the corresponding mono- and di-trimethylsilyl hydroquinones and trimethylsilyl chloride was confirmed by GC, GC-MS, and ^1H NMR spectra. The absorptive CIDNP phase of the mono-trimethylsilyl hydroquinone indicates that this reaction precursor is the triplet radical ion pair of the hexamethyldisilane cation radical and quinone anion radical, and that the former radical reacts with the latter prior to the fission of its Si–Si bond.

Introduction

The σ -bonds between group 14 elements (Si–Si, Ge–Ge, Sn–Sn etc.) have rather low ionization potentials [1,2]. These values are close to those of carbon–carbon π -bonds, not of their σ -bonds. For this advantage, these compounds ($\text{R}_3\text{E}-\text{ER}_3$) have been widely used as electron donors. Therefore, the photo-induced electron transfer between group 14 element compounds and electron acceptors has been studied due to interest in the reaction mechanism and the synthetic chemistry during the last decade [3–10]. After the photo-initiated electron transfer to the acceptor, the resultant cation radical ($\text{R}_3\text{E}-\text{ER}_3^+$) is considered to decompose quickly to a couple of group 14 element centered radical ($\text{R}_3\text{E}^\cdot$) and cation (ER_3^+) type species (eqs. 1 and 2).



(E = Si, Ge, or Sn)

However, there has been no report elucidating clearly the existence of the reaction intermediates for eqs. 1 and 2. In addition, almost all reports use nitriles like cyanobenzenes and cyanoethylenes as electron acceptors. There are few experiments with other electron acceptors [11–13].

It is well known that the interacting radicals induce the nuclear polarization in their products, which is observed as enhanced absorption or emission in the NMR spectra. This phenomenon is called chemically induced dynamic nuclear polarization (CIDNP). The polarization phase is dependent on several parameters, including the spin multiplicity of the pair and the magnetic parameters of the individual radicals [14]. One can construct the reaction scheme from the observed polarization using parameters which are easily obtained by other experiments.

In the present paper, we used quinones instead of nitriles as electron acceptors, and carried out the photo-induced electron transfer reactions of hexamethyldisilane with high potential quinones; 1,4-benzoquinone, chloro-1,4-benzoquinone, 2,5-dichloro-1,4-benzoquinone, 2,6-dichloro-1,4-benzoquinone, and tetrachloro-1,4-benzoquinone. Based on the CIDNP spectra and product analysis, we shall discuss their reaction scheme.

Results and discussion

The UV spectra of hexamethyldisilane ($\text{Me}_3\text{Si-SiMe}_3$) and 2,5-dichloro-1,4-benzoquinone (2,5-DCQ, 102 mM) were measured in chloroform. In solutions ranging in concentration of $\text{Me}_3\text{Si-SiMe}_3$ from 39 mM to 230 mM, the absorption band of the CT complex between $\text{Me}_3\text{Si-SiMe}_3$ and 2,5-DCQ was not observed.

Then the photoreaction was done in dichloromethane containing $\text{Me}_3\text{Si-SiMe}_3$ (44 mM) and 2,5-DCQ (0.65 mM). The spectra which were obtained after irradiation of the solution for 20 s with a 1-kW high pressure mercury lamp are shown in Fig. 1 for 2,5-DCQ. The absorption band of 2,5-DCQ around 330–360 nm decreased and a new band around 430 nm increased with the irradiation. This new

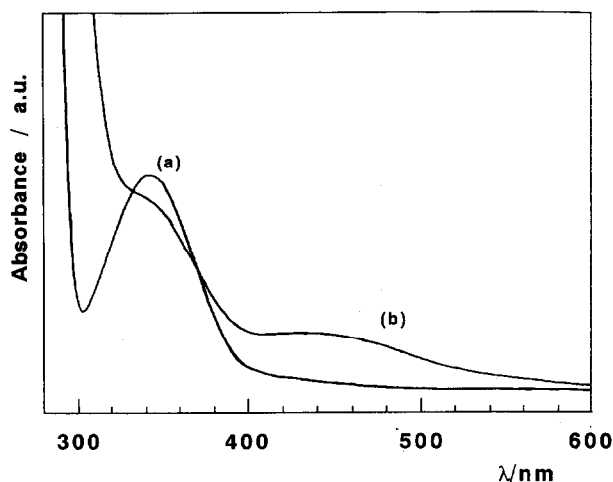
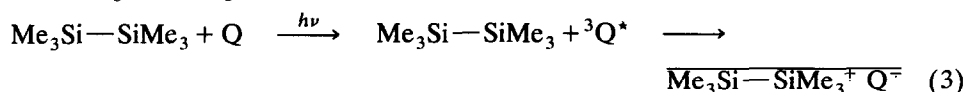


Fig. 1. UV spectral changes of $\text{Me}_3\text{Si-SiMe}_3$ (44 mM) and 2,5-DCQ (0.65 mM) in dichloromethane (a) before and (b) after irradiation for 20 s.

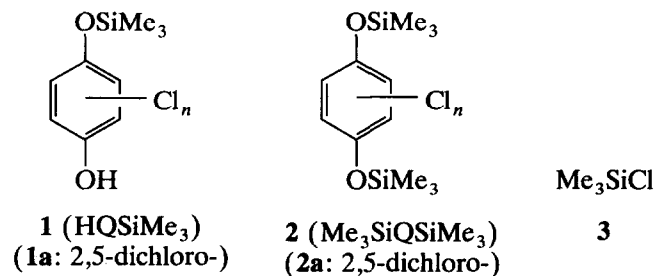
band can be assigned to the quinone anion radical (2,5-DCQ⁻) in comparison with that of 1,4-benzoquinone (410–460 nm) and tetrachloro-1,4-benzoquinone (420–450 nm) [15]. Since the light was selectively absorbed by quinone (Q) in the initial stage of the reaction, the triplet excited state of Q (³Q*) should be generated immediately after its intersystem crossing. The spectrum change suggests electron transfer from Me₃Si–SiMe₃ to ³Q* (eq. 3).



The absence of a CT absorption band eliminates the direct charge separation from the singlet excited state of the complex. The spectrum of Me₃Si–SiMe₃ and tetrachloro-1,4-benzoquinone (TCQ) after irradiation agreed well with that of the TCQ anion radical (TCQ⁻) reported in the literature [15]. Recently, the photoreaction of 2-(pentamethyldisilanyl)-5-tert-butyl-1,4-benzoquinone was investigated [16]. With irradiating its charge transfer band, the intramolecular electron transfer from the disilanyl moiety to the quinone moiety was reported to occur from the product analysis and UV spectra.

We measured the decrease of Me₃Si–SiMe₃ after irradiation for 4 min with several quinones. The decrease rates were found to be in the following order: TCQ > 2,5-DCQ ≈ 2,6-dichloro-1,4-benzoquinone (2,6-DCQ) > chloro-1,4-benzoquinone (MCQ) > 1,4-benzoquinone (BQ). This order is in good agreement with that of the half-reduction potentials of these quinones. They were measured to be +0.01, –0.18, –0.18, –0.34, and –0.51 V versus SCE in acetonitrile at 25 °C for TCQ, 2,5-DCQ, 2,6-DCQ, MCQ, and BQ, respectively [17]. Therefore, the more positive their reduction potential is, the larger the reaction rate with Me₃Si–SiMe₃ becomes. This correspondence between the reaction rate and the reduction potential implies that these reactions are driven by electron transfer.

The products in the photoreaction of Me₃Si–SiMe₃ with 2,5-DCQ or 2,6-DCQ were analyzed by GC and GC-MS. The main products were dichloro-4-trimethylsiloxyphenols (**1**, HQSiMe₃), dichloro-1,4-bis(trimethylsiloxy)benzenes (**2**, Me₃SiQSiMe₃) and trimethylsilyl chloride (**3**).



The typical product yields obtained for the reaction of Me₃Si–SiMe₃ and 2,5-DCQ were 32.1% (**1a**), 10.2% (**2a**), and 50.4% (**3**) based on the amount of consumed Me₃Si–SiMe₃ after irradiation for 10 min. The structure of **1** is seemingly derived by the addition of trimethylsilyl radical (Me₃Si[•]) and hydrogen to quinone, and **2** is by two Me₃Si[•].

These products could also be confirmed by ordinary NMR spectra. Hereafter, we describe mainly the reaction of 2,5-DCQ for its sufficient reactivity and

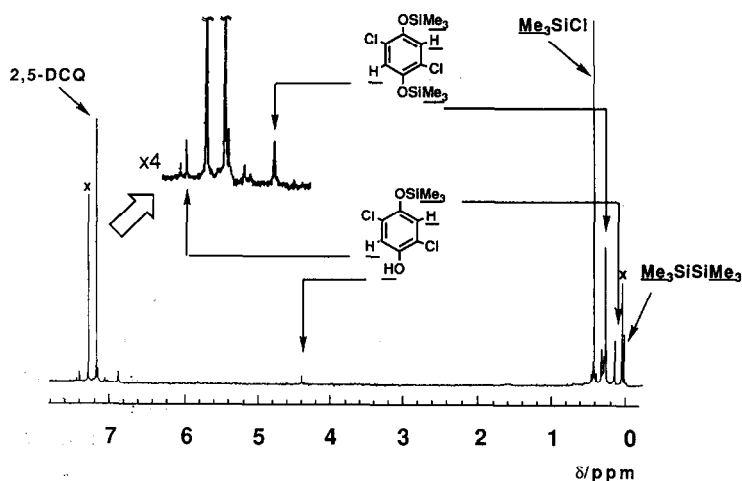


Fig. 2. ^1H NMR spectrum of $\text{Me}_3\text{Si-SiMe}_3$ (50 mM) and 2,5-DCQ (100 mM) in CDCl_3 after irradiation for 10 min. The signals denoted by $\times$ are due to hexamethyldisiloxane (0.07 ppm) and CHCl_3 (7.27 ppm). Hexamethyldisiloxane is a minor contamination of $\text{Me}_3\text{Si-SiMe}_3$.

molecular symmetry in ^1H NMR measurement. Figure 2 shows the NMR spectrum of $\text{Me}_3\text{Si-SiMe}_3$ (50 mM) and 2,5-DCQ (100 mM) in CDCl_3 after irradiation for 10 min. Here, the signals of the starting compounds were observed at 0.04 ppm (methyl-H of $\text{Me}_3\text{Si-SiMe}_3$) and at 7.16 ppm (ring-H of 2,5-DCQ). Several new signals in Fig. 2 appeared in the course of the irradiation with a concomitant decrease in the starting signals. The signals at 0.16, 4.38, and 7.40 ppm were assigned to the methyl-H, hydroxyl-H, and ring-H of product **1a**, respectively. The signals at 0.29 and 6.86 ppm were assigned to the methyl-H and ring-H of product **2a**. The signal at 0.46 ppm was assigned to the methyl-H of product **3**. The detail of the assignment is described in the experimental section.

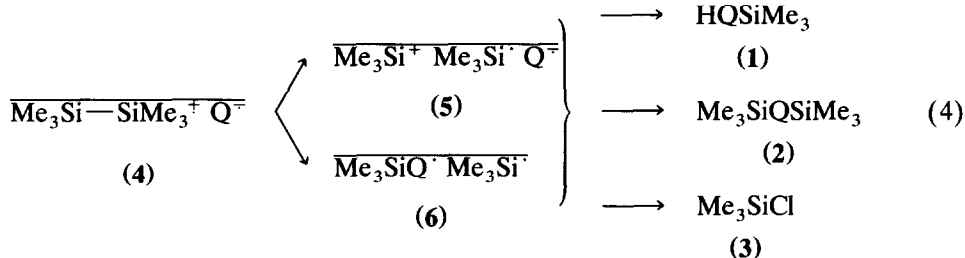
The hydroxyl-H of **1a** is not deuterium as shown in Fig. 2. The products of this reaction in CHCl_3 and in CDCl_3 were analyzed by GC-MS. The mass spectrum of **1a** formed in CDCl_3 showed the same parent m/e peak (M^+ 250) observed in CHCl_3 [18*]. Accordingly, the hydroxyl-H of **1a** as a final product is concluded not to be deuterium but to be hydrogen. In addition, the strong CIDNP signal of hydroxyl-H, as described later, stands against the formation of deuterated **1a** and the following D-H exchange by the contaminated H_2O in CDCl_3 . Consequently, the hydrogen of the solvent is not introduced to **1a**.

When 2,6-DCQ, MCQ, and BQ were used, the products were similar to those observed for the reaction of 2,5-DCQ. In the case of TCQ, $\text{Me}_3\text{Si-SiMe}_3$ was decreased by the irradiation, but **1** could not be observed. This may be due to the instability of **1** ($n = 4$) or due to some different reaction paths.

Here, we would like to construct the reaction scheme. The irradiation generates $^3\text{Q}^*$, and the triplet radical pair of $\text{Me}_3\text{Si-SiMe}_3^+$ and Q^- is formed by electron transfer from $\text{Me}_3\text{Si-SiMe}_3$ to $^3\text{Q}^*$. The products **1**, **2**, and **3** are produced by

* Reference number with asterisk indicates a note in the list of references.

succeeding reactions. Since **1** and **2** are mono- and di-trimethylsilyl adducts of quinones, the Si-Si bond fission of $\text{Me}_3\text{Si-SiMe}_3^+$ is necessary. This bond fission is considered to occur either by itself or by reaction as shown in eq. 4.



The initial radical pair **4** of $\text{Me}_3\text{Si-SiMe}_3^+$ and Q^- can be transformed to radical pair **5** of $\text{Me}_3\text{Si}^\cdot$ and $\text{Q}^\cdot$ by spontaneous Si-Si bond fission. The radical pair **6** of the trimethylsiloxylphenoxyl radical ($\text{Me}_3\text{SiQ}^\cdot$) and $\text{Me}_3\text{Si}^\cdot$ can be formed by the reactive fission of $\text{Me}_3\text{Si-SiMe}_3^+$ with Q^- . Although the protonation of Q^- by solvent may be expected, we eliminated this process since the hydrogen of the solvent is not introduced to the product.

At the initial stage, radical pairs are all in solvent cages. The formation of **1**, **2**, and **3** can occur either in the cage or after the separation of the component radicals from the pair. To elucidate the reaction scheme, we should classify the products into "in-cage" and "out-of-cage" reaction products. For this purpose, we scavenged escaping radicals by oxygen. The CDCl_3 solution containing $\text{Me}_3\text{Si-SiMe}_3$ (12.5 mM) and 2,5-DCQ (50 mM) was irradiated in the presence and in the absence of oxygen, and the yields of **1a** and **2a** were analyzed by ^1H NMR. The formation rates of **1a** and **2a** under nitrogen at the early stage were $0.154 \text{ mM min}^{-1}$ and $0.089 \text{ mM min}^{-1}$, respectively. On the other hand, those under oxygen were $0.122 \text{ mM min}^{-1}$ and $0.047 \text{ mM min}^{-1}$. The formation rate of **2** was much suppressed by oxygen compared with that of **1**. Thus, **2** is attributable to an "out-of-cage" reaction product. On the other hand, **1** is considered to be an "in-cage" reaction product. Since **3** is not included in the initial reaction, **3** must be an "out-of-cage" reaction product. The CIDNP technique is suitable to determine the reaction path, since this reaction includes a radical pair at its initial stage. Then we tried to measure the CIDNP spectra to decide the importance of radical pairs **4**, **5**, and **6**.

The NMR spectra of $\text{Me}_3\text{Si-SiMe}_3$ (12.5 mM) and 2,5-DCQ (50 mM) in CDCl_3 were measured on irradiation with the high pressure mercury lamp. Those obtained before, during, and after irradiation are shown in Fig. 3. Several new signals were observed during irradiation. Among them, the signals at 4.38, 6.65, 7.40 and 7.44 ppm disappeared after irradiation as shown in Figs. 3(b) and (c). Consequently, these signals are concluded to be due to CIDNP or due to unstable products. Since the signals at 4.38 and 7.40 ppm are assigned to **1a** as observed in Fig. 2, these signals are ascribed to the enhanced absorption (A) signals due to CIDNP. The yield of **1a** in $4 \text{ s} \times 32$ irradiation is so small that the signal for hydroxyl-H and ring-H of **1a** is not observed in Fig. 3(c). The polarization of hydroxyl-H is about ten times larger than that of ring-H. The other two signals are not assigned to the main products and will not be discussed further. No polarization was observed for the signals due to **2a** and **3**.

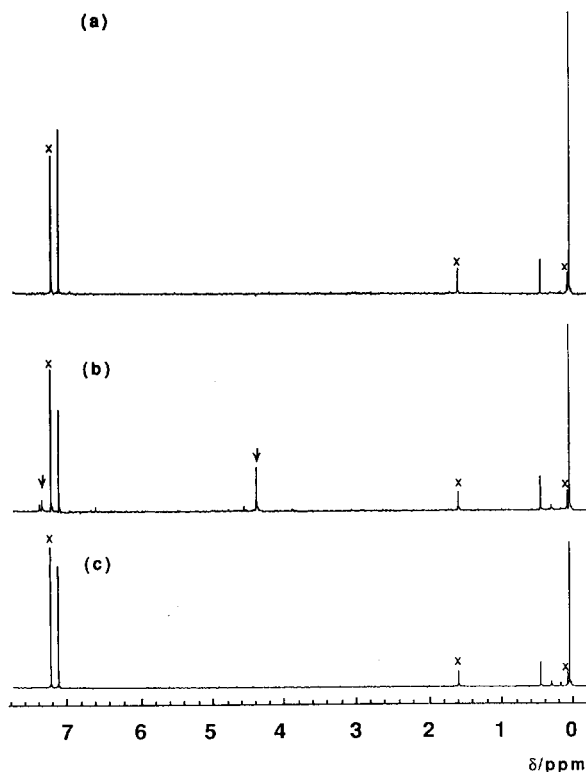


Fig. 3. ^1H NMR spectra of $\text{Me}_3\text{Si-SiMe}_3$ (12.5 mM) and 2,5-DCQ (50 mM) in CDCl_3 (a) before, (b) during, and (c) after irradiation. All of them are obtained by 32 times accumulation. Spectra (b) and (c) are obtained by 4×32 irradiation. The arrows denote the CIDNP signals of **1a**. The signals denoted by $\times$ are hexamethyldisiloxane (0.07 ppm), H_2O (1.59 ppm), and CHCl_3 (7.27 ppm).

The CIDNP measurements were also carried out with other quinones. 2,6-DCQ gave the same A polarization of ring-H and hydroxyl-H as 2,5-DCQ. MCQ gave also A phase of hydroxyl-H of **1**, but its polarization was too weak to observe that of ring-H. When BQ was used, we could not observe any CIDNP signal. This may be due to the low reactivity of BQ.

The reaction mechanism can be analyzed by Kaptein's CIDNP phase rule [14] (eq. 5).

$$\Gamma = \mu \cdot \epsilon \cdot \Delta g \cdot a \quad (5)$$

$\Gamma > 0$, enhanced absorption (A)

$\Gamma < 0$, emission (E)

Here the parameters μ and ϵ enter with the following signs: μ is the initial spin multiplicity of a given radical pair; +, triplet; -, singlet; ϵ is + for "in-cage" reaction products and - for "out-of-cage" reaction products. The parameter Δg is the difference between the g values of radical i containing the examined H atom and radical j , the partner of radical i ; $g_i - g_j$, the parameter a is the hyperfine coupling (hfc) constant of the examined H atom in radical i .

Table 1

The g values and signs of hyperfine coupling constants of component radicals in expected radical pairs

	g value [ref.]	The sign of proton hfc constants [ref.]
$\text{Me}_3\text{Si-SiMe}_3^+$	2.0075 [19]	+ [22]
$\text{Me}_3\text{Si}^\cdot$	2.0031 [20]	- [22]
$\text{Q}^\cdot$, $\text{Q} = 2,5\text{-DCQ}$	2.0055 [13]	- [23]
2,6-DCQ	2.0053 [13]	- [24]
MCQ	2.0058 [21]	
BQ	2.0050 [13]	- [23]
$\text{R}_3\text{EQ}^\cdot$, $\text{Q} = 2,5\text{-DCQ}$	2.0054 ^a [13]	- [25*]
2,6-DCQ	2.0053 ^a [13]	
BQ	2.0047 ^a [13]	
¹ Bu ₂ Q	2.0046 ^b [12]	

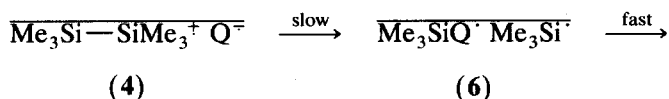
^a $\text{R} = ^n\text{Bu}$, $\text{E} = \text{Sn}$. ^b $\text{R} = \text{Et}$, $\text{E} = \text{Si}$. The g values of $\text{Me}_3\text{SiQ}^\cdot$ are expected to be similar to these values.

In the reaction of $\text{Me}_3\text{Si-SiMe}_3$ and Q , we found the A polarization on ring-H and hydroxyl-H of **1**. As mentioned above, the initial reaction proceeds via the triplet radical pair ($\mu > 0$), and **1** is the "in-cage" reaction product ($\epsilon > 0$). On the other hand, the signs of Δg and a are dependent on the radical pair, which enables us to discriminate the reaction mechanism. The g values and the signs of the hfc constants for the component radicals in each radical pair in eq. 4 are listed in Table 1.

We would like to consider the polarization for ring-H first. For radical pair **4**, $\text{Q}^\cdot$ is radical i because it has the proton to become the ring-H in **1**, and its partner radical j is $\text{Me}_3\text{Si-SiMe}_3^+$. Therefore, $\Delta g = g_{(\text{Q}^\cdot)} - g_{(\text{Me}_3\text{Si-SiMe}_3^+)} < 0$ and $a < 0$. For radical pairs **5** ($i = \text{Q}^\cdot$, $j = \text{Me}_3\text{Si}^\cdot$) and **6** ($i = \text{Me}_3\text{SiQ}^\cdot$, $j = \text{Me}_3\text{Si}^\cdot$), the sets of Δg and a are $(+, -)$ and $(+, -)$, respectively. Thus, the expected polarizations of ring-H should be A ($\Gamma > 0$), E ($\Gamma < 0$), and E ($\Gamma < 0$) for **1a** produced from radical pairs **4**, **5**, and **6**, respectively. Since the observed polarization was A, the reaction precursor is the radical pair **4** of hexamethyldisilane cation radical and quinone anion radical rather than the radical pairs **5** and **6**. The polarization phase for hydroxyl-H of **1a** can also be consistent with radical pair **4**. Since the hydroxyl-H of **1a** comes from the derivatives of $\text{Me}_3\text{Si-SiMe}_3$, this signal comes from the polarization for methyl-H of $\text{Me}_3\text{Si-SiMe}_3^+$. Therefore, the signs of Δg and a are both positive for radical pair **4** ($i = \text{Me}_3\text{Si-SiMe}_3^+$, $j = \text{Q}^\cdot$), hence the polarization for the hydroxyl-H of **1a** is also A ($\Gamma > 0$). The polarization observed with 2,6-DCQ or MCQ is similarly explained by radical pair **4**.

The polarization phase of **1** derived from radical pair **4** indicates that radical pair **4** has a long lifetime, namely the Si-Si bond fission of $\text{Me}_3\text{Si-SiMe}_3^+$ is not so fast. To obtain the polarization for hydroxyl-H, the hydrogen must come from the initial radical pair. To generate **1**, the reaction must proceed via radical pair **6**, but the polarization due to radical pair **6** was not observed. The appearance of the polarization due to radical pair **4** instead of radical pair **6** is explained by the "memory effect" [28]. Consequently, the lifetime of radical pair **6** is considered to

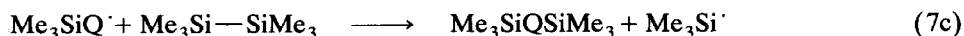
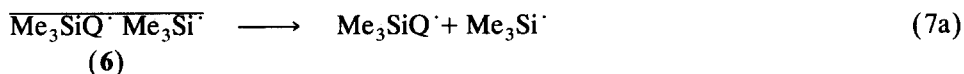
be short owing to disproportionation (eq. 6).



(1)

The $\text{Me}_3\text{SiQ}^\cdot$ in radical pair 6 may escape and abstract hydrogen from $\text{Me}_3\text{Si}-\text{SiMe}_3$ or escaping $\text{Me}_3\text{Si}^\cdot$. In this case, the hydroxyl-H can have no CIDNP. Therefore, the polarization for hydroxyl-H of 1 is by itself strong support that 1 is the "in-cage" reaction product.

Product 2 is formed by "out-of-cage" reaction after the separation of the component radicals from radical pair 6 (eq. 7a). Consequently, the nuclear polarization on the escaping radicals should be relaxed before the termination reaction (eqs. 7b and 7c).



(2)

Product 2 may also be formed as an "in-cage" reaction product by recombination from radical pair 6. This process is, however, a minor path, because the disproportionation/recombination ratio for the radical pairs of tert-butyl radical and alkoxy radical were reported to be 19–77:1 [29].

Product 3 can be generated through several processes. Free $\text{Me}_3\text{Si}^\cdot$ is obtained after several steps from the separation of radicals from radical pairs 4, 5, and 6, and the reaction of this free $\text{Me}_3\text{Si}^\cdot$ with chloroform generates 3 (eq. 8). Therefore, the polarization of 3 is unexpected.



3

The whole reaction mechanism of the photo-induced electron transfer reaction between $\text{Me}_3\text{Si}-\text{SiMe}_3$ and Q is represented by eqs. 3, 6, 7, and 8.

In conclusion, the reaction mechanism of the photo-induced electron transfer reaction from hexamethyldisilane, a group 14 element compound, to halogenated quinone was explained clearly by means of a CIDNP technique. In a chloroform solution of hexamethyldisilane and quinone, mono- and di-trimethylsilyl hydroquinones and trimethylsilyl chloride are formed on irradiation. We have proved that the reaction precursor is the ion radical pair of the hexamethyldisilane cation radical and quinone anion radical. In the formation of mono-trimethylsilyl hydroquinone, the former radical reacts with the latter prior to the fission of its Si-Si bond.

Experimental

Apparatus

^1H NMR spectra and CIDNP spectra were recorded with a JEOL JNM-FX100 FT NMR spectrometer. UV absorption spectra were measured with a Hitachi 320 spectrophotometer and a quartz cell of 1 cm path length. Gas chromatography was performed with a Shimadzu GC-8A equipped with a 2 m 10% SE30 column. GC-MS spectra were recorded with a JEOL JMS-DX 303 mass spectrometer.

Materials

1,4-Benzoquinone (Tokyo Kasei), chloro-1,4-benzoquinone (Aldrich), 2,5-dichloro-1,4-benzoquinone (Kanto Chemical), 2,6-dichloro-1,4-benzoquinone (Kanto Chemical) and tetrachloro-1,4-benzoquinone (Tokyo Kasei) were purified by vacuum sublimation after recrystallization from petroleum ether. Hexamethyldisilane (Kanto Chemical; > 97%), chloroform (Kanto Chemical; HPLC grade), chloroform- d_1 (Merck; > 99% deuteration), and dichloromethane (Kanto Chemical; optical grade) were obtained commercially and used without further purification.

Photolysis

The chloroform solution of hexamethyldisilane and a quinone was irradiated with a 1-kW high pressure mercury lamp after bubbling pure nitrogen gas. As a typical case, the solution containing hexamethyldisilane (273.4 mM) and 2,5-dichloro-1,4-benzoquinone (252.0 mM) was irradiated for 10 min. The resultant products were analyzed by GC and GC-MS. The main products were **1a**, **2a**, and **3** in yields 32.1%, 10.2%, and 50.4% on the basis of the amount of consumed hexamethyldisilane, respectively. Product **1a** was identified by GC-MS. For its instability, its NMR signals were assigned in comparison with those of the substituted phenols. **1a**: ^1H NMR δ (CDCl_3) 0.16 (s, 9H); 4.38 (s, 1H); 7.40 (s, 2H). MS (EI, 70 eV) m/z (%) 252/250 (M^+ , 53, 86), 237 (90), 234 (100), 202 (19), 201 (23), 200 (43), 199 (51), 173 (9), 171 (17), 141 (6), 117 (11), 95 (37), 93 (86), 73 (75). HR-MS $\text{C}_9\text{H}_{12}\text{O}_2\text{SiCl}_2[\text{M}^+]$ calc.: 249.9984. Found: 249.9983. Product **2a** was isolated with GC. ^1H NMR δ (CDCl_3) 0.29 (s, 18H), 6.86 (s, 2H); MS (EI, 70 eV) m/z (%) 324/322 (M^+ , 79, 100), 309 (19), 307 (26), 274 (32), 272 (56), 199 (27), 93 (51), 73 (56). HR-MS $\text{C}_{12}\text{H}_{20}\text{O}_2\text{Si}_2\text{Cl}_2[\text{M}^+]$ calc.: 322.0379. Found: 322.0367. Product **3** was identified in comparison with the authentic sample by GC and GC-MS.

CIDNP measurement

The CDCl_3 solution of hexamethyldisilane and quinone was deoxygenated in a sample tube by bubbling pure nitrogen gas for 10 min before irradiation. NMR spectra were measured before, during (immediately after) and after irradiation. The scheme of CIDNP measurement is shown in Fig. 4. The irradiation of the 1-kW high pressure mercury lamp was focused onto the NMR detecting region of a sample cell through a water filter and quartz lenses as shown in Fig. 4(a). The sampling and the irradiation time were controlled by a DG535 pulse generator (Stanford Research Systems, Inc.) with an electrical shutter. As shown in Fig. 4(b), the irradiation period was 4 s prior to the applied RF pulse. The total interval

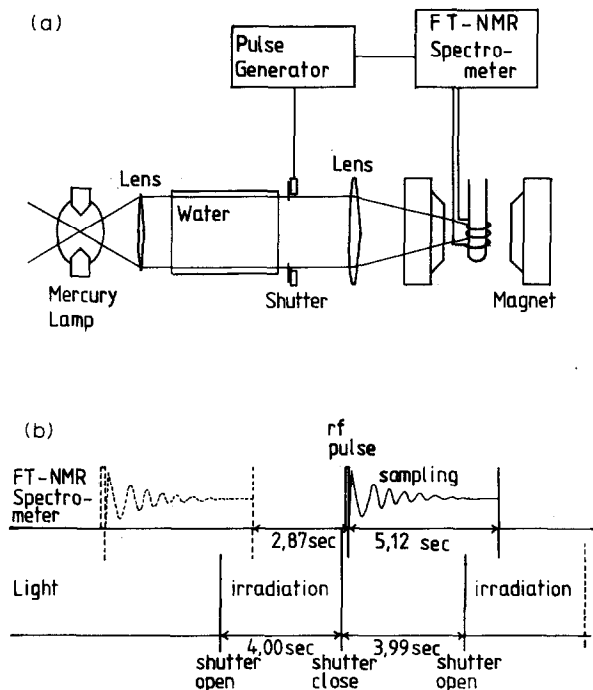


Fig. 4. (a) Set-up of and (b) the timing diagram of irradiation and sampling for CIDNP measurement apparatus.

including the signal sampling was 7.99 s. Usually, the signal was accumulated 32 times.

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