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# Solvent Effect in the Base-catalyzed Hydrogen Isotopic Exchange Reaction of α-Deuteriodiphenylthioacetal[1]

Isao MINAMIDA, Kenji UNEYAMA, Waichiro TAGAKI[2] and Shigeru OAE

*Applied Chemistry, Faculty of Engineering, Osaka City University, Sugimotocho, Sumiyoshi-ku, Osaka*

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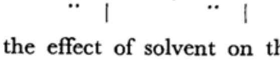
**Effect of Phenylthio Group.** Recently, we have shown that the divalent sulfide group assists the formation of α-carbanion due to its 3d-orbital resonance effect as shown below.[3-5)]

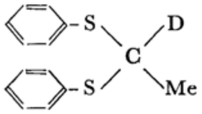
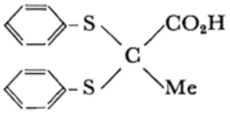
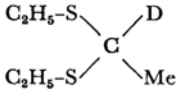
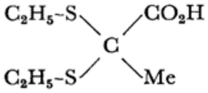


$$-\ddot{\underset{\cdot\cdot}{S}}-\overset{\ominus}{\ddot{C}}- \longleftrightarrow -\overset{\ominus}{\underset{\cdot\cdot}{\ddot{S}}}=C-$$

However, the effect of solvent on these α-thiocarbanion forming reactions has not received much attention, and deserves to be investigated in detail. This paper will describe the H-D exchange reactions of α-deuterio-1, 1-di(phenylthio)ethane (I) and α-deuterio-1,1-di(ethylthio)ethane (II) in MeOH-MeONa, EtOH-EtONa, *t*-BUOH - *t*-BuOK and *t*-BuOH - DMSO - *t*-BuOK in order to obtain clear-cut information on the solvent effect and also to compare the carbanion stabilizing effect of the phenylthio group with that of the ethylthio group. Each kinetic run for the hydrogen isotopic exchange was carried out in a solution containing 0.1 M of a base and 0.2 M of the substrate, while the rates were followed by measuring the intensity of the stretching frequency of the C–D bond by means of IR spectroscopy. The results are listed in Tables 1 and 2.

1,1-Di(phenylthio)ethane (I) reacts $1.4\times10^2$ times faster than 1,1-di(ethylthio)ethane (II) in *t*-BuOH - *t*-BuOK. This trend is consistent with that found in the triethanolamine-catalyzed decarboxylation of 1,1-di(phenylthio)propionic acid(III) and 1,1-di(ethylthio)propionic acid(IV).[4)] In the base-catalyzed elimination, β-chloroethyl phenyl sulfide reacts only 2.4 times faster than β-chloroethyl ethyl sulfide. This difference presumably comes from that of the carbanion character in the transition states of the two different reactions. In the former two reactions, the carbanion character develops substantially but in less extent in the elimination reaction, since this elimination is a typical E2 reaction.[5)] The relatively large electron-withdrawing effect of the phenylthio group arises undoubtedly both from the electron-withdrawing inductive effect of the phenyl ring and substantial delocalization of the lone pair electrons of α-carbanion into the phenyl ring. The appreciable Hammett ρ value (2.0) of the base-catalyzed decarboxylation of the substituted 1,1-di(phenylthio)acetic acids in DMSO also suggests this.[6)]

TABLE 1. RELATIVE EFFECT OF CARBANION STABILIZATION ABILITY OF PHENYLTHIO GROUP TO THAT OF ETHYLTHIO GROUP

| Base-catalyzed H-D exchange[a)] | | Base-catalyzed decarboxylation[b)] | |
|---|---|---|---|
| Compound | Rel. rate | Compound | Rel. rate |
|  | $1.4\times10^2$ |  | $2.7\times10^2$ |
|  | 1.0[c)] |  | 1.0 |

a) in *t*-BuOH - *t*-BuOK (see Table 2, this work)
b) in DMSO-triethanolamine (see Ref. 2)
c) Rel. rate at 158°C. Rate constant of this compound at 158°C was $5.95\times10^{-5}$ sec$^{-1}$.

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[1] Paper XIV on "3d Orbital Resonance in Divalent Sulfides".

[2] Present address: Faculty of Engineering, Gunma University Kiryu, Gunma.

[3] S. Oae, W. Tagaki and A. Ohno, *Tetrahedron*, **20**, 417, 427 (1964).

[4] S. Oae, W. Tagaki, K. Uneyama and I. Minamida *ibid.*, **24**, 5282 (1968).

[5] S. Oae and Y. Yano, *ibid.*, **24**, 5721 (1968).

[6] K. Uneyama and S. Oae, unpublished results. (1968).

TABLE 2. SOLVENT EFFECT OF BASE-CATALYZED D–H EXCHANGE REACTION OF $\alpha$-DEUTERIO-1,1-DI(PHENYLTHIO)ETHANE

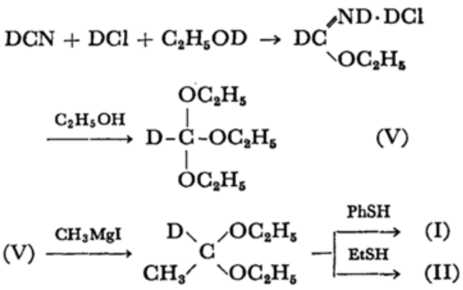
| Solv.-base | MeOH-MeONa | EtOH-EtONa | $t$-BuOH-$t$-BuOK | $t$-BuOH-DMSO[c] $t$-BuOK |
|---|---|---|---|---|
| $k \times 10^4$ sec$^{-1}$ | 0.228 | 0.774 | 3.18(120)[a] | 1.65 |
| (Temp °C) | (158) | (158) | 1,15(110) | (20) |
| | | | 0.395(100) | |
| Rel. rate[b] | 1.0 | 3.4 | $3.7 \times 10^2$ | $1 \times 10^8$ |

a) $\Delta E^* = 30.4$ kcal/mol, $\Delta S^* = 2.3$ cal/deg (120°C)
b) Relative rate at 158°C
c) DMSO : $t$-BuOH = 1:1 in mole

**Solvent Effects.** Solvents used were MeOH, EtOH, $t$-BuOH and DMSO. In alcohols the rate increases with the increase of base strength. The addition of DMSO to $t$-BuOH also enhances the rate markedly. This result is in line with those observed in both the base-catalyzed E2 reaction of $\beta$-chloroethyl phenyl[5] sulfide and the base-catalyzed decarboxylation of 1,1-di(phenylthio)acetic acid.[7] Potassium $t$-butoxide in $t$-butanol is a stronger base than sodium ethoxide in ethanol, hence the proton-removal from the substrate takes place faster in $t$-butanol with $t$-butoxide than in ethanol with ethoxide. Addition of DMSO to $t$-BuOH makes potassium butoxide more basic in this reaction medium, thus enhancing the rate.[8] The lone electron pair on the $\alpha$-carbon should be sufficiently delocalized both into the divalent sulfur atoms and phenyl ring due to the 3d orbital resonance, since the carbanion developing in the transition state is substantially stabilized by the two phenylthio groups. The carbanion is considered to be one of the soft bases as proposed by Pearson and Edwards.[9,10] Thus the $\alpha$-thio carbanion may be solvated well in the transition state by a dipolar aprotic solvent such as dimethyl sulfoxide.

## Experimental

Preparation of 1-deuterio-1, 1-di(phenylthio)ethane (I) and 1-deuterio-1,1-di(ethylthio) ethane (II) and kinetics were carried out in the same way as described previously.[3]



$$DCN + DCl + C_2H_5OD \rightarrow DC(=ND\cdot DCl)(OC_2H_5) \xrightarrow{C_2H_5OH} D\text{-}C(OC_2H_5)_3 \quad (V)$$

$$(V) \xrightarrow{CH_3MgI} (D)(CH_3)C(OC_2H_5)_2 \xrightarrow{PhSH} (I); \quad \xrightarrow{EtSH} (II)$$

Compounds (I) and (II) were finally distilled through an efficient column under reduced pressure. The boiling points of I and II are 168—169°C/1.7 mmHg and 79°C/15 mmHg respectively. Content of $\alpha$-deuterium was analyzed by NMR spectra and both I and II were shown to be deuterated by 95%.

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7) K. Uneyama, I. Minamida, W. Tagaki and S. Oae, *Tetrahedron*, **24**, 5271 (1968).

8) D. J. Cram, C. A. Kingsburg and B. Rickborn, *J. Am. Chem. Soc.*, **83**, 3688 (1961).
D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York and London (1965).

9) J. O. Edwards and R. G. Pearson, *J. Am. Chem. Soc.*, **84**, 16 (1962).

10) J. A. Parker, *Quart. Rev. (London)*, **16**, 163 (1962).