

A STUDY OF THE SOLVENT EFFECT OF DIMETHYL SULFOXIMINE ON THE RATES OF  $S_N2$  REACTIONS

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Dimethyl sulfoximine was tested as a solvent in the  $S_N2$  reactions and was shown to have characteristic features of both protic and polar aprotic solvents. Dimethyl sulfoximine, when used as a mixed solvent with methanol, showed a large rate acceleration of the  $S_N2$  reaction likely DMSO or DMF.

Sulfoximines are isoelectronic to sulfones but have many interesting characteristic properties. A marked difference in behavior of sulfoximines from that of the corresponding sulfones is that sulfoximines of lower alkyl groups, such as dimethyl or tetramethylene sulfoximine dissolve inorganic salts substantially, like many well-known polar aprotic solvents and are freely soluble in such polar solvent as water or alcohols. Recently, sulfoximines were found to have larger pKa values than those of the corresponding sulfones or sulfoxides, suggesting that sulfoximines are more polar and basic than sulfones or sulfoxides.<sup>1)</sup> Furthermore, we found that  $CHCl_3$  was decomposed violently with NaOH in the presence of sulfoximines indicating that OH ion is activated by strong solvation of  $Na^+$  ion by sulfoximine and attacks  $CHCl_3$  to generate  $:CCl_2$ .<sup>2)</sup> Those dramatic behavior of sulfoximine suggest that the compound can be used as a solvent, like DMSO or DMF.<sup>3)</sup> Therefore, in order to find a new and useful application of sulfoximines, dimethyl sulfoximine(DMSOI), the simplest analog, was tested as a solvent. We wish to report here the excellent solvent properties of DMSOI in a few typical  $S_N2$  reactions.

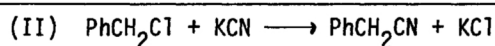
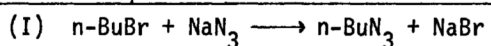
DMSOI prepared by conventional method<sup>1)</sup> is freely soluble in water or other organic solvents and also dissolves most of common inorganic salts considerably at its mp.<sup>4)</sup> At first, in order to compare the effect of sulfoximine as a solvent with those of the well-known organic solvents, we have measured the rates and determined the activation parameters of the reaction between n-BuBr and  $NaN_3$  (I) in DMSOI. The rates of the reactions in DMSOI were followed by the decrease of n-BuBr by g.l.c. by using toluene as an internal standard. The rates of the reaction as shown in Table I were nicely calculated by the 2nd order kinetic equation and the rate constant thus obtained was,  $k_2$ ;  $1.44 \pm 0.22 \times 10^{-1} \text{ l.m.}^{-1} \text{ sec.}^{-1}$  at 60°C. The activation parameters are,  $E_a$ ;  $18.56 \text{ kcal.mol.}^{-1}$  and  $\Delta S^\ddagger$ ;  $-8.90 \text{ e.u.}$  respectively ( $r=0.999$ ). The product obtained quantitatively was found as n-BuN<sub>3</sub>.

Earlier, Delpuech reported a kinetic study of the same reaction in a few common solvents.<sup>5)</sup> Following the same procedure, a typical  $S_N2$  reaction in DMSOI was found to be accelerated markedly. This effect of acceleration is larger than in such protic solvents as methanol or water and nearly equal or comparable to those in such polar aprotic solvents as DMSO or sulfolane.<sup>5)</sup> A comparison of the activation energy in DMSOI with those in other solvents reveals that the value falls between those in common polar aprotic and those in protic solvents. In polar aprotic solvents the activation energy is usually less than 17kcal, while in protic solvents it is generally more than 20

kcal in this reaction.<sup>5)</sup> According to this definition, DMSOI is a new type of solvent which is protic, yet has the characteristic features of most polar aprotic solvents. This may be due to both the NH group and the polar nature of sulfoximino function.<sup>6)</sup>

Table I Rate constants for the  $S_N2$  reactions of (I) and (II) in mixed solvents with methanol

		$k_{60^\circ}(\text{l.m.}^{-1}\text{sec.}^{-1})$ (% by weight of methanol)				
Solvent		100%	80%	50%	30%	0%
(I)	MeOH	$3.70 \times 10^{-4*}$				
	DMSOI		$7.27 \pm 0.47 \times 10^{-4}$	$2.09 \pm 0.27 \times 10^{-3}$	$5.96 \pm 0.30 \times 10^{-3}$	$\frac{1.44 \pm 0.22 \times 10^{-1}}{2.29 \times 10^{-1}*}$
	DMSO		$6.93 \pm 0.30 \times 10^{-4}$	$2.54 \pm 0.09 \times 10^{-3}$	$7.40 \pm 0.57 \times 10^{-3}$	$2.29 \times 10^{-1*}$
	DMF		$6.32 \pm 0.47 \times 10^{-4}$	$1.78 \pm 0.13 \times 10^{-3}$	$4.92 \pm 0.74 \times 10^{-3}$	$4.39 \times 10^{-1*}$
(II)	MeOH	$1.79 \pm 0.15 \times 10^{-4}$				
	DMSOI			$1.19 \pm 0.09 \times 10^{-3}$	$3.62 \pm 0.13 \times 10^{-3}$	
	DMSO			$7.99 \pm 0.73 \times 10^{-4}$	$2.17 \pm 0.04 \times 10^{-3}$	
	DMF			$5.04 \pm 0.05 \times 10^{-4}$	$1.39 \pm 0.11 \times 10^{-3}$	



\*) cited in the reference 5)

A mixed solvent of DMSOI with methanol was employed to examine the extent of acceleration in the  $S_N2$  reactions<sup>7)</sup> and the effect was compared with those of DMSO or DMF by changing the amount of solvents, partly because DMSOI is a solid mp.53°C and somewhat inconvenient to dissolve the inorganic salt at room temperature. The results are shown in Table I. Inspection of the data reveals clearly that the rate is accelerated even more than in DMF when both solvents were employed as a mixed solvent with methanol.

The rate acceleration in the  $S_N2$  reaction in mixed solvents was tested by another system between  $\text{PhCH}_2\text{Cl}$  and KCN (II). The rates of this reaction in various solvent compositions were measured by following the decrease of  $\text{PhCH}_2\text{Cl}$  by means of g.l.c. using PhBr as an internal standard. (Table I) In these reactions, the rates are enhanced markedly in a mixed solvent as compared to that in pure methanol. Here again, DMSOI showed the largest rate acceleration effect among others even in the solvent compositions of both 50% and 30%. Our preliminary investigation indicates also that marked acceleration in DMSOI is not limited to the  $S_N2$  reaction alone but other systems in which polar aprotic solvents enhance the rate.

#### References and Notes

- 1) S. Oae, K. Harada, K. Tsujihara, and N. Furukawa, *Int. J. Sulfur Chem., Part A*, **2**, 49 (1972).
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- 3) *Quarterly Reports on Sulfur Chemistry*, **3**, No. 2 (1968).
- 4) The solubilities of salts(g/100ml) in DMSOI at 65°C is, KSCN;15,  $\text{NaN}_3$ ;2, KI;27,  $\text{AgNO}_3$ ;4, KCl;1.
- 5) The rates at 60°C cited in the reference are,  $k_2$ ;  $2.59 \times 10^{-3} \text{l.m.}^{-1} \text{sec.}^{-1}$  ( $\text{H}_2\text{O}$ ),  $k_2$ ;  $4.95 \times 10^{-2} \text{l.m.}^{-1} \text{sec.}^{-1}$  (sulfolane). J. J. Delpuech, *Tetrahedron Lett.*, **25**, 2111 (1965).
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