The Menschutkin Reaction in Liquid Sulfur Dioxide*

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(Received September 13, 1962)

Liquid sulfur dioxide has been said to be one of the most ionizing solvents$^{1)}$. It has been previously reported that the cationic polymerization$^{2)}$ and the intramolecular rearrangements such as the Beckmann$^{3)}$ and Wagner-Meerwein rearrangements$^{4)}$ in liquid sulfur dioxide are carried out at extraordinarily fast rate. The reasons for such an accelerating effect of sulfur dioxide have also been discussed. Such a conspicuous property of sulfur dioxide perhaps is due to 1) the large ionizing power, 2) the solubility both to organic (olefin and aromatic compounds) and inorganic (aluminum chloride, stannic chloride and so on) materials, 3) the aprotic and protophobic nature with no affinity to proton or carbonium ion.

Among many nucleophilic reactions studied, the Menschutkin reaction is one of the most discussed and well established reaction$^{5)}$. Moreover, since the first kinetic study by Menschutkin appeared in 1890$^{5a)}$, the effect of the solvents on this reaction has been comprehensively studied and summarized in many articles and reviews$^{5)}$. Although the rate of solvolysis of alkyl halides depends upon the ionizing power of the solvent, that of the Menschutkin reaction does not. The plot of the specific rates of the latter reaction against the Z values$^{6)}$ of the corresponding solvents does not give a linear correlation.

The object of this investigation has been to study the effect of liquid sulfur dioxide as solvent on the Menschutkin reaction, since no kinetical comparison has been made between the rates in sulfur dioxide and other solvents by this time.

Study of the nucleophilic attack of fluoride anion, amines or pyridine on *m*-chlorobenzhydryl chloride in liquid sulfur dioxide was undertaken by Ingold et al.$^{7)}$, wherein they observed a peculiar phenomenon, the so-called borderline case, the reaction being classified neither as S_N1 nor S_N2. The aprotic and even protophobic character of liquid sulfur dioxide would be the reason why they performed the reaction in this solvent, though the reaction in liquid sulfur dioxide resulted in more complexity than was expected.

Ingold et al. used electric conductivity measurement of the reaction mixture to trace the kinetics. The organic halides in liquid sulfur dioxide have often been shown to have considerable conductivities$^{8)}$. In addition, the presence of a trace of water which could not be eliminated from liquid sulfur dioxide by the ordinary method$^{9)}$ may perhaps affect largely the results of the kinetic measurement.

The present authors have chosen a reaction, the Menschutkin reaction between methyl or ethyl halide and a base in liquid sulfur dioxide, in which the ionization of the alkyl chloride was surpressed in order to eliminate the S_N1 type reaction as much as possible. The kinetics was followed by a potentiometric titration of iodide ion produced. Dimethylaniline, dimethyl-*o*-toluidine or pyridine was used as a base. The reaction rate in liquid sulfur dioxide has been compared with those in other solvents, such as methanol, nitrobenzene, nitromethane, tetrahydrofuran, acetone, acetonitrile, dimethylformamide and dimethylsulfoxide.

Experimental

Materials. — Methyl, ethyl or isopropyl iodide was washed with sodium thiosulfate solution, water, sodium carbonate solution and water successively, dried and distilled: methyl iodide, b. p. 42.5∼43.0°C, ethyl iodide, b. p. 68∼72.3°C (impurity was below 1% by V. P. C.), isopropyl iodide, b. p. 88.2∼89.0°C. Dimethylaniline or dimethyl-*o*-toluidine was refluxed with acetic anhydride and distilled.

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* Substitution in Liquid Sulfur Dioxide, Part II. Preceding paper, N. Tokura, R. Tada and R. Igarashi, This Bulletin, 33, 1176 (1960).

1) S. G. Smith, A. H. Fainberg and S. Winstein, *J. Am. Chem. Soc.*, **83**, 618 (1961).

2) a) R. Asami and N. Tokura, *J. Polymer Sci.*, **42**, 545 (1960); b) N. Tokura, M. Matsuda and M. Iino, This Bulletin, in press.

3) N. Tokura and K. Shiina, ibid., **35**, 1779 (1962).

4) L. P. Hammett, "Physical Organic Chemistry", McGraw-Hill, New York (1940), p. 318.

5) a) N. Menschutkin, *Z. physik. Chem.*, **6**, 41 (1890); b) E. A. Moelwyn-Hughes, "Kinetics of Reaction in Solution", Sec. Ed., Oxford Univ. Press., London (1947), p. 207; c) E. L. Eliel, "Steric Effects in Organic Chemistry", Ed. by M. S. Neweman, John Wiley & Sons, New York (1956), Chapter 2, p. 70.

6) E. M. Kosower, *J. Am. Chem. Soc.*, **80**, 3253 (1958).

7) a) L. C. Batemean, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, **1940**, 1017; b) M. L. Bird, E. D. Hughes and C. K. Ingold, ibid., **1954**, 634; c) H. Greenstreet, E. D. Hughes and C. K. Ingold, ibid., **1954**, 642, 647.

8) Ref. 4, p. 53.

9) D. Murakami and N. Tokura, This Bulletin, **31**, 432 (1958).

The distillate was again treated with potassium hydroxide and distilled. Pyridine, rigorously dehydrated and distilled was donated by Ikenoue[10]. Liquid sulfur dioxide was dried with phosphorus pentoxide and distilled. Tetrahydrofuran, acetonitrile, nitromethane, acetone, dimethylformamide and dimethylsulfoxide were purified by known methods[11].

Kinetic Procedure.—The method and the apparatus used were demonstrated elsewhere[12]. An alkyl iodide (0.2∼0.6 mol./l.) was reacted with a base (0.2∼0.6 mol./l.) in liquid sulfur dioxide in a thermostat. After a definite time, reaction mixture was mixed with petroleum benzine (b. p. 60∼80°C) and the iodide ion produced was extracted thrice with water. After evaporation of sulfur dioxide gas from the aqueous extract in vacuo, the iodide ion in the solution was titrated with silver nitrate solution potentiometrically. A typical run of the reaction between methyl iodide and pyridine in liquid sulfur dioxide is listed in Table I. The reaction in acetone or other solvent was also conducted to compare with the result in liquid sulfur dioxide, which is indicated in Table II.

TABLE I. A TYPICAL RUN OF THE REACTION BETWEEN METHYL IODIDE AND PYRIDINE IN LIQUID SULFUR DIOXIDE AT 40°C

Methyl iodide 0.399 mol./l.		Pyridine, 0.359 mol./l.	
t, min.	$I^- \times 10^2$ mol. l^{-1}	$k_1 \times 10^3$ min^{-1}	$k_2 \times 10^2$ l. mol^{-1} min^{-1}
20	3.50	4.87	1.50
40	6.75	4.41	1.51
60	9.47	4.16	1.58
80	11.82	3.70	1.53
100	13.76	3.50	1.59
120	15.47	3.18	1.56
			1.55

TABLE II. THE RATE CONSTANT IN ACETONE AT 40°C

Methyl iodide 0.194 mol./l.		Pyridine, 0.292 mol./l.	
t, min.	$I^- \times 10^2$ mol. l^{-1}	$k_1 \times 10^3$ min^{-1}	$k_2 \times 10^2$ l. mol^{-1} min^{-1}
10	1.92	11.10	4.08
20	3.65	10.20	3.98
35	5.75	9.24	3.93
55	7.98	8.51	4.02
75	9.69	8.04	4.12
105	11.65	7.29	4.16
			4.05

Results

Reaction of Alkyl Iodide with Pyridine. — Alkyl iodide (0.2∼0.6 mol./l.) was reacted with a base (0.2∼0.6 mol./l.) in liquid sulfur dioxide. The reaction followed a second order rate law, being first order both in alkyl iodide and in pyridine. The second order rate constants were calculated according to the equation, $kt=\{1/(b-a)\}\ln[a(b-x)/b(a-x)]$ and the Arrhenius parameters were estimated as is listed in Table III.

TABLE III. THE RATE OF THE REACTION BETWEEN METHYL IODIDE AND PYRIDINE*

Reaction temp., °C	$k \times 10^5$ l. mol^{-1} sec^{-1}	$\Delta E^{\neq}$ kcal./mol.	$\Delta S^{\neq}$ e. u.
20	3.38		
30	9.00	17.8	−22.2(40°C)
40	24.70		

* The concentration of pyridine was equal to that of methyl iodide.

The similar reactions with the concentration range (0.2∼0.6 mol./l. of each reactant) have been conducted in acetone (Table II), dimethylformamide, dimethylsulfoxide, nitromethane, acetonitrile or tetrahydrofuran to find out that the reactions were all of the second order. A comparison of the second order rate constants in these solvents is listed in Table IV.

TABLE IV. COMPARISON OF SECOND ORDER RATE CONSTANTS

Solvent	k, (40°C) l. mol. sec^{-1}	Ratio $k_{\text{solvent}}/k_{SO_2}$
Tetrahydrofuran*	1.74×10^{-4}	0.7
Liq. SO_2	2.47×10^{-4}	1
Acetone	6.37×10^{-4}	2.6
Acetonitrile	1.13×10^{-3}	4.6
Nitromethane	1.48×10^{-3}	6.0
Dimethylformamide	3.12×10^{-3}	12.6
Dimethylsulfoxide**	6.85×10^{-3}	27.7

* The reaction was partly heterogeneous.

** However dimethylsulfoxide reacts with methyl iodide as,

$$CH_3I + (CH_3)_2SO = (CH_3)_3SO^+ + I^-$$

the Menschutkin reaction is so fast that the reaction of sulfonium ion formation is not competitive[13].

Reaction of Alkyl Iodide with Dimethylaniline or Dimethyl-*o*-toluidine. — In the series of these experiments, the reaction was also of the second order. The results are listed in Table V.

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[10] The present authors are indebted to Assist. Prof. Ikenoue for his courtesy.

[11] a) "Technique of Organic Chemistry", VII, "Organic Solvents", Ed. by A. Weissberger, Interscience Publisher, New York (1955); b) F. A. Cotton and R. Francis, *J. Am. Chem. Soc.*, **82**, 2990 (1960).

[12] N. Tokura, M. Matsuda and F. Yazaki, *Makromol. Chem.*, **42**, 108 (1960).

[13] a) S. G. Smith and S. Winstein, *Tetrahedron*, **3**, 317 (1958); b) R. Kuhn and Trischmann, *Ann.*, **611**, 117 (1958).

TABLE V. THE RATE CONSTANTS OF THE REACTIONS BETWEEN ALKYL HALIDES AND DIMETHYLANILINES

Reaction temp., °C	k l. mol^{-1} sec^{-1}	$\Delta E^{\neq}$ kcal./mol.	$\Delta S^{\neq}$ e. u.
(a) Dimethylaniline - methyl iodide			
30	1.72×10^{-5}		
40	4.77	17.2	-27.3(40°C)
50	9.93		
(b) Dimethyl-*o*-toluidine - methyl iodide			
40	1.65×10^{-5}		
50	3.62	15.9	-33.7(50°C)
60	7.81		
(c) Dimethylaniline - ethyl iodide			
40	3.41×10^{-6}		
50	8.63	17.9	-30.4(50°C)
60	21.80		
(d) Dimethylaniline - isopropyl iodide			
50	1.28×10^{-6}		
60	3.14	18.9	-31.0(60°C)
65	4.77		

As is seen in Table III, the reaction rate decreases as the alkyl halides varies from methyl to isopropyl iodide. When dimethyl-*o*-toluidine was reacted with methyl iodide in place of dimethylaniline, the rate depressed slightly. (Table VII).

Comparison of the reaction rate in liquid sulfur dioxide with that in methanol or in nitromethane is listed in Table VI.

TABLE VI

(a) Comparison of the second order rate constants

Dimethyl aniline - methyl iodide

$k_{\text{methanol}^{14)}}/k_{SO_2}=4.18$ (50°C)

$k_{\text{nitrobenzene}^{15)}}/k_{SO_2}=4.40$ (40°C)

(b) Comparison of the Arrhenius parameter

Solvent	$\Delta E^{\neq}$, kcal./mol.	$\Delta S^{\neq}$ e. s.
Liq. SO_2	17.2	-27.3
Methanol14)	15.2	-31
Nitrobenzene15)	12.8	-38

Among the three of the solvents, the rate in liquid sulfur dioxide is the least. The effect of the ortho-methyl group on the benzene ring of aniline derivative on the rate is described in Table VII.

TABLE VII. EFFECT OF *o*-METHYL IN DIMETHYLANILINE

Solvent	k_H/k_{o-Me}
Liq. SO_2	2.74 (50°C)
Methanol14)	28.5 (65°C)

k_H/k_{o-Me} is the ratio of the rate constant in the reaction of methyl iodide with dimethylaniline (k_H) against that with dimethyl-*o*-toluidine (k_{o-Me}). However the temperatures in the reaction in comparison are somewhat different, the ortho-effect in liquid sulfur dioxide (2.74) is very small as compared with that in methanol (28.5).

Discussion

In the preceding studies on the cationic reactions, i. e. both in the Beckmann rearrangement3) and in the cationic polymerization2), the reaction rates were found to be the fastest in liquid sulfur dioxide as compared with the organic solvents generally used. It is, therefore, a question why the Menschutkin reaction in liquid sulfur dioxide is so slow, whereas the rearrangement and the cationic polymerization in the same solvent are so fast.

Here, the role of the solvation as well as the ionizing power of the solvent in the nucleophilic substitution must be considered. A general survey of the solvation is indicated in Chart 1, in which RX may be either a covalent link compound such as alkyl halide or an ionophore16) such as tetraethylammonium chloride. In Chart 1, only a general feature of solvation is demonstrated and the detailed discussion on the extent of the ionization or the dissociation may be reserved for further investigation at the present stage. In addition, the number of the solvent molecules solvating on an ion is also not considered. The letter S in Chart 1 thus indicates an indefinite number of the solvent molecules solvating on a cation or an anion. However the strength of each solvation may also be varied as the solvent changes, the four models, A—D, used only to elucidate the role of the solvent on the solvation.

Chart 1

Classification of the solvation of a solvent on a substrate

$RX=R^{+}S+X^{-}S$	(A) Biphilic solvation
$RX=R^{+}+X^{-}S$	(B) Electrophilic solvation
$RX=R^{+}S+X^{-}$	(C) Nucleophilic solvation
$RX=R^{+}+X^{-}$	(D)

A, (biphilic solvation), is often the case in hydroxylic solvent (a solvent having the OH group) such as water or alcohol, where both ions are solvated by the solvent, the cation being coordinated with the O atom of the solvent and the anion being hydrogen bonded

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14) D. P. Evans, H. B. Watson and R. Williams, *J. Chem. Soc.*, **1939**, 1345, 1348.

15) K. Laidler, ibid., **1938**, 1786.

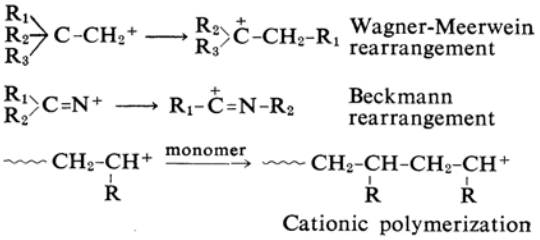
16) R. M. Fuoss, *J. Chem. Educ.*, **32**, 527 (1955).

by the solvent. This is the most popular and the most well established case of the solvation. D, (no solvent solvation) may be the case of no actual existence, but in gaseous state or in extremely inert solvent, a case close to D seems likely to take place. Special attention should be added to the cases, B and C, where either an anion (case B) or a cation (case C) is solvated, the counter ions (a cation in B and an anion in C) being unsolvated by the respective solvents and kept free. B (electrophilic solvation) is the case of liquid sulfur dioxide or sulfuric acid. C (nucleophilic solvation) is the case of the solvent of a basic character such as dimethylformamide, dimethylsulfoxide or acetone. The concept of the *unsolvated ion* or the *bare ion*[17] may be of some importance in the ionic reaction, since such a *bare ion* may be unstable and reactive, and could offer an appropriate driving force for the reaction.

Although sulfur dioxide is a strongly ionizing solvent, the ionizing power is due to the highly selective complexing of the solvent (sulfur dioxide) to the anion, thus the *bare caton* (unsolvated cation) is remaining as an unstable and reactive species. However, since the cation or the carbonium ion is surrounded by the cage of sulfur dioxide molecules which repel the ion, the cation is alive as long as no foreign substance is present in the solution and the counter anion is strongly solvated and supported by liquid sulfur dioxide. The unusual reactivity[2-4] is also consistent with the production of some new types of the nonclassical cations[18] in sulfur dioxide, because in both reactions strong solvation of anions is of utmost necessity.

Since sulfur dioxide is a Lewis acid, the affinity to proton or cation may be extremely small. There have been many evidences which support the denial of the proton affinity of sulfur dioxide[19,20], whereas anion or base is strongly solvated in this solvent. The *bare cation* (carbonium ion or immonium ion) produced in liquid sulfur dioxide as is depicted in Chart 1 may be quite useful to carry out the reactions (rearrangement and polymerization) in unusual speed.

Chart 2



The reverse situation may be found in the Menschutkin reaction. In this case the strong solvation of sulfur dioxide with anion or base may greatly retard the reaction velocity. It is worthy to note that the reaction favored by sulfur dioxide as listed in Chart 2 is a cationic intramolecular reaction or a cationic reaction in which a cation is reacting with a neutral molecule such as a vinyl monomer, the interfering anion being eliminated by complexing with sulfur dioxide.

In a nucleophilic substitution, S_N1 or S_N2, whichever the reaction may be, the attacking reagent, an anion or a base, may be strongly seized by liquid sulfur dioxide. The number of the reacting anion or base available for the reaction must then be reduced greatly. The complexed base may sometimes be able to participate in the reaction, but the reaction rate may be far more depressed. The consideration on the diffusion velocity or on the steric effect of the bulky complexes may also support this view. That a borderline case[7] is observed in a substitution which may otherwise be an S_N1 reaction is accordingly easily understood, since the rate-determining step (the ionization of RX) is not followed by a fast step of the combination of the R^+ (carbonium ion) with an anion or a base. In liquid sulfur dioxide the anion or the base is complexed with sulfur dioxide, so the rate of the second step is not so fast and even a case in which the second step is rate-determining may also be probable. Even if the alkyl halide may be a strong ionizing substrate such as *t*-butyl iodide, the situation that the reaction is very slow will not be improved. In the experimental conditions applied, isopropyl iodide reacted in the slowest rate among the alkyl iodides obeying the second order rate law as is seen in Table VI, which may be attributed to the steric effect[21]. The observed, comparatively small ortho-effect (Table VII) in liquid sulfur dioxide as compared to that in methanol in the reaction of methyl iodide with dimethyl-*o*-toluidine may perhaps due to the smaller solvation of dimethyl-*o*-toluidine by sulfur dioxide.

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[17] N, Tokura, *Kagaku*, **17**, 575 (1962). The present authors would like to use the term "*bare ion*" instead of the frequently used, "*free ion*", since the latter term has been confusedly adopted both for unsolvated and solvated ions.

[18] a) H. Dauben, F. A. Gadecki, K. M. Harmon and D. L. Pearson, *J. Am. Chem. Soc.*, **79**, 4577 (1957); S. Winstein and C. Ordonneau, ibid, **82**, 2084 (1960); c) R. R. Story and M. Saunders, ibid., **82**, 6199 (1960).

[19] H. Hart and G. Levitt, *J. Org. Chem.*, **21**, 921 (1956).

[20] The view suggested earlier by Sidgwick (W. A. Waters, "Physical Aspect of Organic Chemistry", Routledge and Kogan, London (1950), p. 230.) that liq. SO_2 may have solvations both for cation and anion must be amended.

[21] See Ref. 5c), p. 75.

Among the solvents used, the Menschutkin reaction in liquid sulfur dioxide was the slowest (Tables IV and VI). However, the Menschutkin reaction may be greatly favored by the solvent in which a *bare base* is permitted. This is the reason why the reaction in dimethylformamide or in dimethylsulfoxide is very fast. Of course, the quaternization reaction may be facilitated by the ionizing power of the solvent as may be seen by the fact that the rate constant in dimethylformamide is larger than in acetone (Table IV), since the product of the reaction is an ion pair.

Inspection of Table VI reveals that activation energy increases and the activation entropy also increases in liquid sulfur dioxide, the solvation being decreasing in approach to the transition state. The reaction in tetrahydrofuran was slow and comparable to the rate in sulfur dioxide, however, the reaction was heterogeneous owing to the lower solubility of the reactants in this solvent and the rate can not be discussed on the same basis.

The rate in nitromethane was six times faster as that in liquid sulfur dioxide. No adequate explanation has been prepared for the rate increase except that nitromethane is a very ionizing solvent and the solvation to the base may not be so large by steric reason.

Summary

1) The Menschutkin reaction (reaction of methyl, ethyl or isopropyl iodide with pyridine, dimethylaniline or dimethyl-*o*-toluidine) has been carried out in liquid sulfur dioxide. The reaction rate has been compared with those in other commonly used solvents.

2) The reaction rate in liquid sulfur dioxide is the slowest, whereas the previously performed reactions such as the Beckmann rearrangement and the cationic polymerization in this solvent were the fastest among the solvents ordinarily used.

3) The reason for such a discrepancy has been discussed. Importance of the *bare* (or unsolvated) ion or species in an ionic reaction is presented.

The authors are indebted to the Seitetsu Kakagu K. K. for the denotion of liquid sulfur dioxide. Part of the expensed for this study has been defrayed by the grant-in-aid from the Ministry of Education.

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