Solvent Effect on the Rearrangement of Cyclohexanoneoxime-p-toluenesulfonate. The Ionizing Power of Liquid Sulfur Dioxide[1,2]

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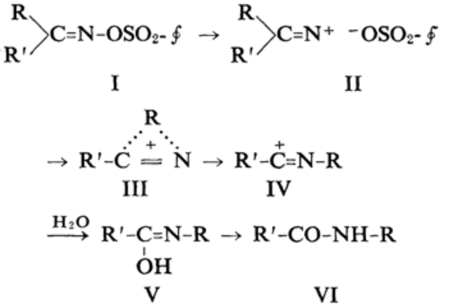
In liquid sulfur dioxide, the Beckmann rearragement has been reported to take place with unusual rapidnesss,[3] at a low temperature[4] and without any side reaction,[5] giving a product of an extreme purity.[3,4] The Beckmann rearrangement was elucidated first by Kuhara in 1906, when he observed that benzophenone-oxime-benzenesulfonate rearranges spontaneously and that the product formed is hydrolyzed to yield benzanilide.[6,7] He studied this rearrangement under varying conditions, thus finding out that the reaction rate depends both on the acid strength and on the easiness of the cleavage of the N–O bond of the oximeester to an ion-pair, $=N^+ \; {}^-O-$. Lately the mechanism of the reaction has been generally accepted as depicted in Chart 1, according mainly to the studies of Chapman,[7] Pearson[8] and Huisgen[9].



In a recent paper, Heldt[10] has found that the first order rate of the rearrangement of cyclohexanoneoxime-*p*-toluenesulfonate depends on the ionizing power of the solvents. The solvents used were acetic acid, chloroform, methanol and ethanol. The present authors have also attempted to study the solvent effect on the rearrangement, paying special attention to the ionizing power of liquid sulfur dioxide.

The results confirm that sulfur dioxide is an excellent solvent for the rearrangement,

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[1] The Beckmann Rearrangement in Liquid Sulfur Dioxide, Part XII.

[2] Part XI: N. Tokura, K. Shiina and T. Terashima, This Bulletin, 35, 1986 (1962).

[3] N. Tokura, R. Asami and R. Tada, *Science Report of Res. Inst., Tohoku University*, **A8**, 149 (1956).

[4] R. Tada, Y. Masubuchi and N. Tokura, This Bulletin, **34**, 209 (1961).

[5] N. Tokura and K. Shiina, ibid., **35**, 1779 (1962); N. Tokura, K. Shiina and T. Terashima, ibid., **35**, 1986 (1962).

[6] M. Kuhara and T. Kainosho, *Memoirs Coll. Sci. Kyoto*, **1**, 254 (1906).

[7] A. W. Chapmann et al., *J. Chem. Soc.*, **1933**, 806; **1935**, 1223; **1936**, 448.

[8] D. E. Pearson et al., *J. Org. Chem.*, **14**, 118 (1949); **17**, 1511 (1952); **19**, 957 (1954); **20**, 488 (1955); *J. Am. Chem. Soc.*, **81**, 612 (1959).

[9] R. Huisgen et al., *Ann.*, **604**, 191 (1957); **602**, 127 (1957); *Chem. Ber.*, **90**, 1844 (1957).

[10] W. Z. Heldt, *J. Org. Chem.*, **26**, 1695 (1961); *J. Am. Chem. Soc.*, **80**, 5972 (1958).

although no distinct solvent effect could be deduced to show the relationship between the rate of rearrangement and the ionizing power of the solvent. The ionizing powers of liquid sulfur dioxide, nitromethane, ethylenedichloride and ethyl methyl ketone have also been estimated according to the method of Kosower.[11]

Experimental

Materials.—Cyclohexanoneoxime was prepared according to the known method; m.p. 90.5∼91.0°C. Commercial *p*-toluenesulfonylchloride was dissolved in carbon tetrachloride and then precipitated by petroleum ether. Liquid ammonia was dried with sodium wire and distilled. Liquid sulfur dioxide was dried with phosphorus pentoxide and distilled. Benzene, carbon tetrachloride, petroleum ether (b.p. 30∼60°C), acetone and chloroform were purified according to the known methods.

The acetonitrile of the first grade materials was dehydrated with phosphorus pentoxide and distilled; b. p. 82.0°C. Pyridine was dehydrated with potassium hydroxide and then with barium oxide, and distilled over barium oxide; b.p. 115.0°C. Ethylenedichloride was dehydrated with calcium chloride and then with phosphorus pentoxide, and distilled; b.p. 83.0∼83.7°C. Ethyl methyl ketone was dried over phosphorus pentoxide and fractionated; b.p. 79.3∼79.8°C.

Preparation of Cyclohexanoneoxime-*p*-toluenesulfonate.—The preparative method of Heldt,[10] was modified. Into a cooled, three-necked flask, 200 ml. of liquid ammonia was introduced. 3.26 g. of sodium wire was rapidly stirred in, and then a trace of ferric nitrate was added as a catalyst. The color of the solution changed from blue to dark green in 60 min. The excess ammonia was evaporated, and a solution consisting of 15.7 g. of cyclohexanoneoxime in 70 ml. of dry benzene was added to the mixture while the temperature of the flask was kept below 35°C. After the addition of the oxime, the mixture was stirred for a further 16 hr. at room temperature. Then the precipitate was filtered, washed eight times with dry benzene, and dried under reduced pressure; yield, 16 g.

To a slurry of 16 g. of sodium oximate thus prepared in 30 ml. of benzene, 17 g. of *p*-toluenesulfonyl chloride in 70 ml. of dry benzene was added, and the mixture was stirred for two hours at 25∼30°C. The precipitate was filtered, dissolved in dry carbon tetrachloride, treated with active carbon, and again filtered. Petroleum ether was added to the filtrate to cause a white clouding, and the mixture was allowed to stand in an ice box for 24 hr. The precipitate formed was separated and dried under reduced pressure; m.p. 57°C (lit.,[10] m.p. 56.8∼58°C).

Found: N, 5.28. Calcd. for $C_{13}H_{17}NO_3S$: N, 5.24%.

Apparatus and Procedure. — *Ionizing Power (Z-Value[11]) of Solvents, Including Liquid Sulfur Dioxide.* —The ultraviolet absorption spectra were measured by an Hitachi Model EPU-2A type spectrophotometer using 1-ethyl-4-carbomethoxypyridiniumiodide (m. p. 111°C) (lit.,[11] 111∼112°C) as the reagent. The c-t band was estimated in a quartz cell 10 mm. wide at 25°C. A specially-designed pressure cell with quartz windows (0.36 mm. wide) was used for liquid sulfur dioxide.

Kinetic Procedure.—The change of the concentration of oxime-*p*-toluenesulfonate was followed by the infrared spectrometry of Heldt.[10] An Hitachi Model EPI-S double beam spectrometer was used, with a specially-designed pressure cell (KCl width: 0.077 mm.) for liquid sulfur dioxide and with a cell (NaCl width: 0.1 mm.) for the other solvents. The absorption at 857 cm^{-1} (a frequency due to the N-O stretching vibration of oxime) was used.[10] Beer's law was obeyed throughout the experiment. The base line method was used for the estimation of the absorbancy.

The first order reaction dominated in each solvent, the rate constants of which were obtained from the linear plot of the time, t, vs. $\log a/(a-x)$, where a is the initial concentration of the ester and $(a-x)$ is the concentration at the time, t. The reaction was measured at 21.5°C. An example of the results obtained is shown in Fig. 1. From this plot, k (in acetone) is estimated as $1.92\times10^{-5}\cdot$ sec^{-1}. The maxima at 857 cm^{-1} showed little shift when solvents of different natures were used.

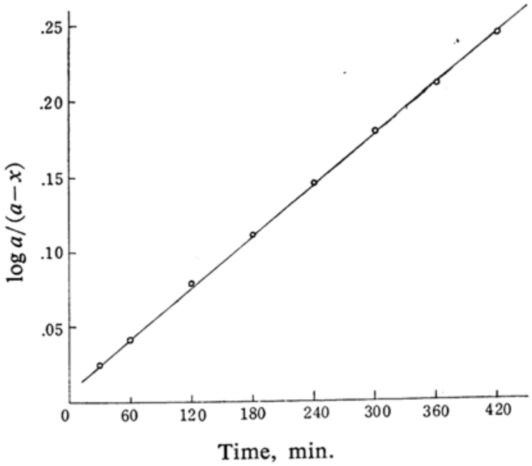

Fig. 1. A typical plot of $\log a/(a-x)$ vs. time. Rearrangement of cyclohexanoneoxime-*p*-toluenesulfonate in acetone at 21.5°C. Oxime-ester, 0.2260 mol./l.

Results and Discussion

The Ionizing Power of Liquid Sulfur Dioxide. —The absorption maximum of the charge-transfer band of 1-ethyl-4-carbomethoxypyridiniumiodide (7.27×10^{-4} mol./l.) in liquid sulfur dioxide was at 3650 Å, with an apparent ε value of 2.83×10^4. The Z-value of liquid sulfur dioxide was calculated from the E(kcal./mol.)$=2.859\times10^{-3}\times\tilde{\nu}$ equation[11] to be 78.3.

Charge Transfer Bands in Various Mixtures

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[11] E. M. Kosower, ibid., **80**, 3267 (1958).

[12] "Organic Syntheses," Coll. Vol. 2, 76 (1943).

of Liquid Sulfur Dioxide and Acetone.—As is shown in Fig. 2, the λ_{max}'s of the charge-transfer bands of 1-ethyl-4-carbomethoxypyridiniumiodide were estimated in various mixtures of liquid sulfur dioxide in acetone, from 0 (acetone only) to 100% surfur dioxide (21.38 mol./l.). The c−t band in acetone (4354Å) dropped abruptly upon the addition of a slight amount of liquid sulfur dioxide, a specific solvation by liquid sulfur dioxide being observed.

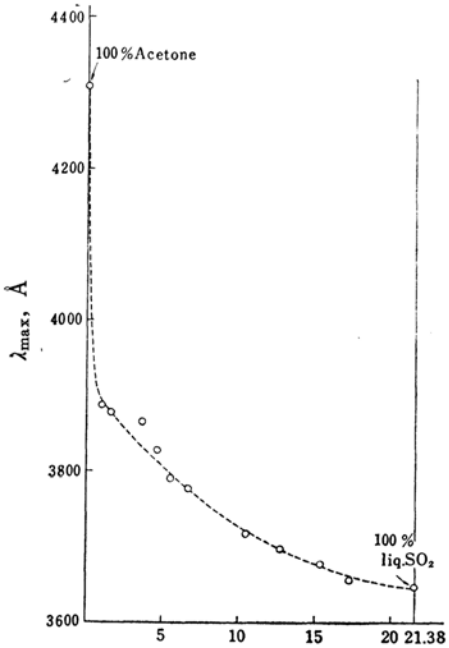

Fig. 2. Maxima of charge transfer band of 1-ethyl-4-carbomethoxypyridiniumiodide in various mixtures of acetone and liquid sulfur dioxide.

TABLE I. THE RATE CONSTANTS OF THE REARRANGEMENT IN MIXTURES OF LIQUID SULFUR DIOXIDE AND ACETONE AT 21.5°C

Concn. of liq. SO$_2$ mol./l.	k, sec^{-1}
0	1.92×10^{-5}
0.212	4.09×10^{-5}
0.491	4.37×10^{-5}
1.261	5.63×10^{-5}
2.212	8.40×10^{-5}
4.140	1.68×10^{-4}
7.811	5.02×10^{-4}
11.372	1.09×10^{-3}
12.385	1.38×10^{-3}
14.631	2.66×10^{-3}
16.406	3.84×10^{-2}

The Rate Constants in Various Mixtures of Liquid Sulfur Dioxide and Acetone.—The rate constants of the rearrangement of the oxime-ester in various mixtures of liquid sulfur dioxide and acetone, from 0 (acetone only) to

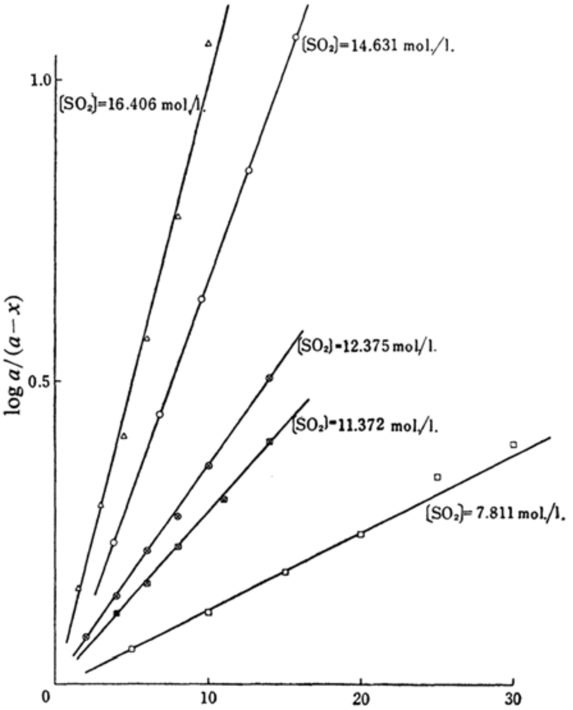

Fig. 3. Some examples of rate-runs in mixtures of acetone and liquid sulfur dioxide. 21.5°C

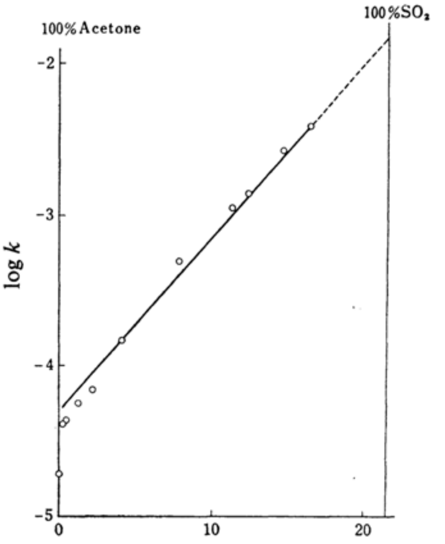

Fig. 4. The plot of log k vs. liquid sulfur dioxide concentration in acetone.

16.406 mol./l. (76.74 mol.%) of liquid sulfur dioxide in acetone are estimated and listed in Table I, some of the $\log a/(a-x)$ vs. t plots being shown in Fig. 3.

A linear plot of the $\log k$ vs. lquid sulfur dioxide concentration in acetone was obtained as in Fig. 4. The rate constant in liquid sulfur dioxide (100%) is obtained, by extrapolation of this plot to 100 % (21.38 mol./l.) liquid sulfur dioxide, as $k=1.6\times10^{-2}\ \mathrm{sec}^{-1}$.

The *Z*-Values of Nitromethane, Ethylenedichloride and Ethyl Methyl Ketone.—The same method was applied in estimating the *Z*-values of the solvents which were not measured in Kosower's papers. The results are listed in Table II.

TABLE II. *Z*-VALUES OF SOLVENTS

Solvent	$\lambda_{\max}$, Å	$\varepsilon_{\max}$	*Z*-Value
Nitromethane	3750	389	76.2
Ethylenedichloride	4400	703	64.4
Ethyl methyl ketone	4320	825	66.0

The Rate Constants in Various Solvents. The Correlation of the Rates with the Dielectric Constants. — The rearrangements were also carried out in various solvents, such as methanol, acetic acid, nitromethane, ethanol, acetonitrile, pyridine, chloroform, acetone, ethylenedichloride, ethyl methyl ketone and carbon tetrachloride. The rate constants were estimated from linear plots of $\log a/(a-x)$ vs. t, which are depicted in Fig. 5. These results, together with those with liquid sulfur dioxide, are listed in Table III; among them, the values of k at 21.5°C in chloroform, acetic acid, methanol and ethanol are calculated from the results of Heldt.[10] No correlation is found either between $\log k$ and the dielectric constant, D, or between $\log k$ and the dipole moment of

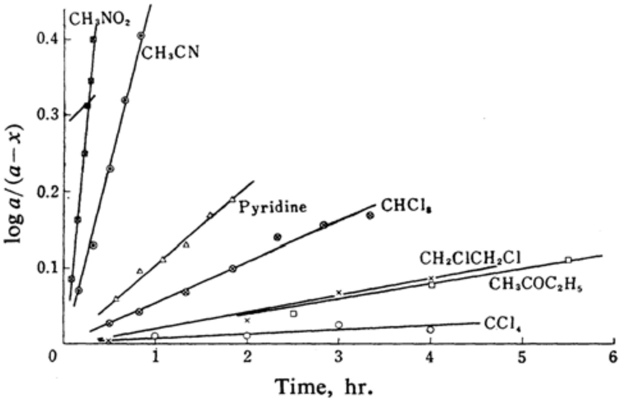

Fig. 5. The rate constants in various solvents. 21.5°C

TABLE III. THE FIRST ORDER RATE CONSTANTS OF THE REARRANGEMENT OF CYCLOHEXANONEOXIME-*p*-TOLUENESULFONATE IN SOLVENTS, 21.5°C

Solvent	*Z*-Value	Dielectric[b] const., 20°C	Dipole[b] moment	k, sec^{-1}	$\log k$	$k/k_{\mathrm{CHCl_3}}$
Liq. SO_2	78.3[a]	12.35	1.61	1.6×10^{-2}	$\bar{2}.20$	480
Methanol	83.6	32.63	1.69	2.0×10^{-3} [c]	$\bar{3}.30$	61
Acetic acid	79.2	6.15	1.73	2.0×10^{-3} [c]	$\bar{3}.30$	61
Nitromethane	76.2	35.87	3.0	7.5×10^{-4}	$\bar{4}.88$	23
Ethanol	79.6	24.30	1.67	5.0×10^{-4} [c]	$\bar{4}.70$	15
Acetonitrile	71.3	37.5	3.2	3.1×10^{-4}	$\bar{4}.49$	9.4
Pyridine	64.0	12.3	2.30	8.5×10^{-5}	$\bar{5}.93$	2.6
Chloroform	63.2	4.80	1.05	3.3×10^{-5} [c]	$\bar{5}.52$	1.0
Acetone	65.7	20.7	2.83	2.0×10^{-5}	$\bar{5}.30$	0.6
Ethylenedichloride	64.4[a]	10.36	1.51	1.5×10^{-5}	$\bar{5}.18$	0.5
Ethyl methyl ketone	66.0[a]	18.51	2.75	1.2×10^{-5}	$\bar{5}.08$	0.4
Carbon tetrachloride		2.24	0	1.0×10^{-6}	6.00	0.03

a) Estimated by the present authors
b) "Organic Solvents, Technique of Organic Chemistry," Ed. by A. Weissberger, Interscience Publishers, New York (1955).
c) Calculated from the values of Heldt (Ref. 10)

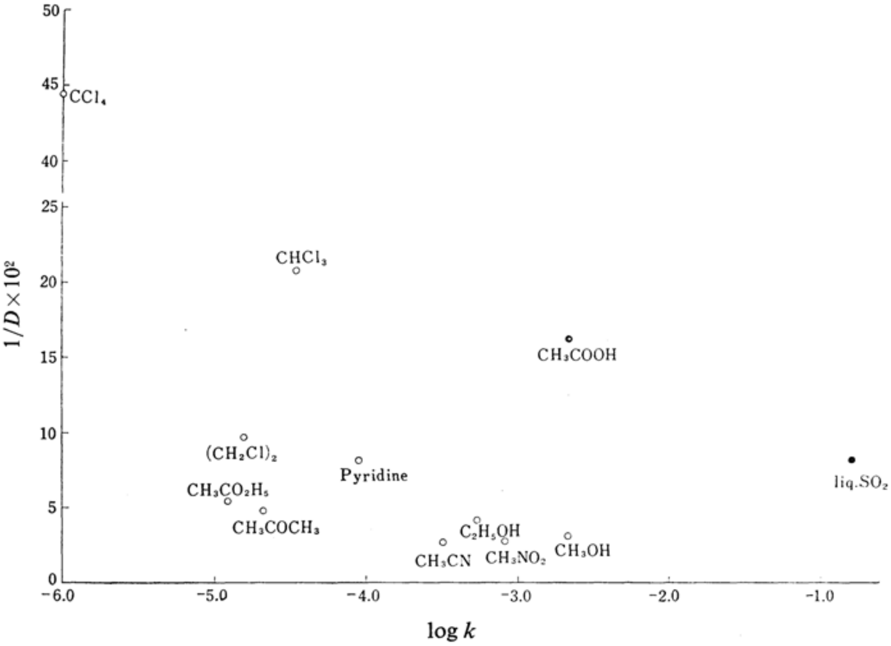

Fig. 6. Correlation of log k vs. $1/D$.

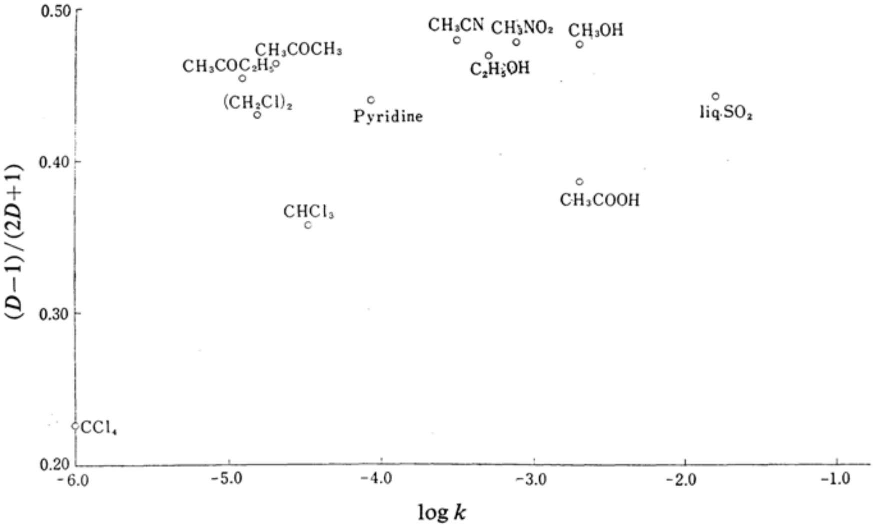

Fig. 7. Correlation of log k vs. $(D-1)/(2D+1)$.

the solvent. Figures 6 and 7 show the plots of log k vs. $1/D$ and log k vs. $(D-1)/(2D+1)$ respectively. The rate constants decrease in the following order: liquid sulfur dioxide> methanol>acetic acid>nitromethane>ethanol > acetonitrile > pyridine>chloroform>acetone >ethylenedichloride > ethyl methyl ketone > carbon tetrachloride. The fastest rate, in liquid sulfur dioxide, is eighty times that in methanol, 480 times that in chloroform and 1.6×10^4 times that in carbon tetrachloride at 21.5°C.

The rate in the mixtures of liquid sulfur dioxide in acetone was dependent on the molarity of liquid sulfur dioxide, as may be seen in Fig. 4, and relation 1 is observed:

$$\log k = \text{const.} \times [SO_2] \qquad (1)$$

which means that the higher the concentration of liquid sulfur dioxide in acetone, the smaller will be the activation free energy of the reaction.

The Ionizing Power of the Solvent. The

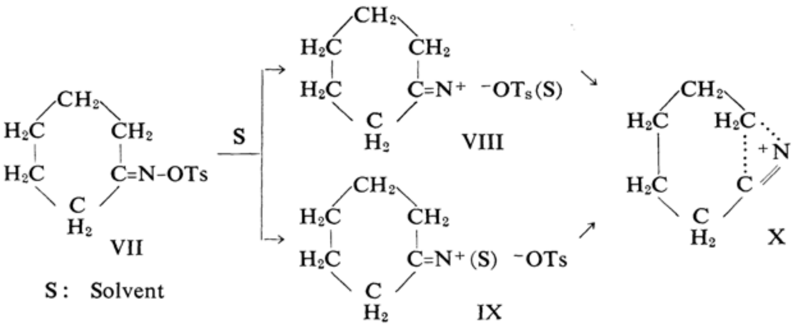

Chart 2

Correlation of *Z*-Values with the Rate Constants of the Rearrangement.—As is visualized in Figs. 6 and 7, no dependency of $\log k$ on $1/D$ or on $(D-1)/(2D+1)$, the latter relation being well-known as Kirkwood's relation,[13)] is observed. Although Chapman[14)] has revealed that the added solvents accelerated the Beckmann rearrangement in carbon tetrachloride and that the rates were dependent on the dipole moments of the added solvents, no linear correlation is seen between the $\log k$ and the dipole moment of any of the solvents used in this experiment. The relationship of $\log k$ against *Z*-value is also a disappointing one (Fig. 8).

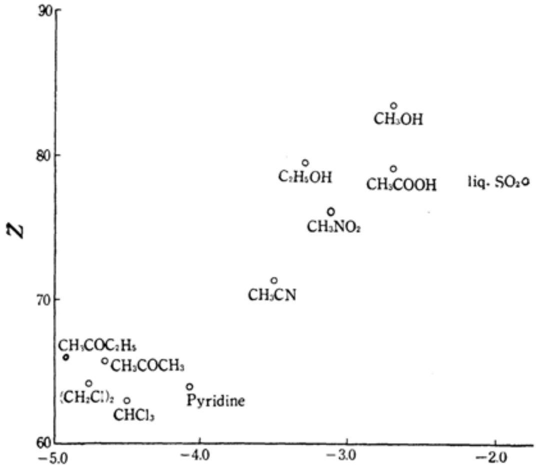

Fig. 8. Correlation of $\log k$ vs. *Z*-value.

The assertion of Heldt[10)] that $\log k$ was dependent on the *Z*-value must be amended, for only four solvents were used in his work. An inspection of Fig. 8 will enable us to understand that the $\log k$ vs. Z relation is not linear but consists of a broad zigzag band; the explanation of such a result must await further study. For instance, the *Z*-value of ethanol is larger than that of acetonitrile, and that of methanol is larger than the *Z*-value of acetic acid; the $\log k$'s of ethanol and acetonitrile or those of methanol and acetic acid are very close to each other. In chloroform the rate is faster than in acetone, whereas the *Z*-value of acetone is larger than that of chloroform. The comparatively small *Z*-value of liquid sulfur dioxide (78.3) is unexpected in view of the largest rate constant in this solvent.

In a preceding paper[15)] by one of the present authors, a proposal has been made regarding the reasons for the unusual rapidness of the Beckmann rearrangement and the cationic polymerization, and for the unexpected dullness of the Menschutkin reaction in liquid sulfur dioxide, in which the presence and the importance of the unsolvated *(bare)* carbonium ion in liquid sulfur dioxide have been emphasized. The rapidness of these reactions is largely a result of the ability of the solvent, (1) to ionize the covalent linkage to an ion-pair and (2) to prevent the harmful attachment (association) of counter anion or nucleophilic species to carbonium ions or cations by the strong solvation of the solvent (liquid sulfur dioxide) on anions or nucleophiles.

It is generally accepted that the formation of an aza-cyclopropenium cation (X) is the intermediate step in the Beckmann rearrangement.[8,9)] The fact that the rearragement is always a *trans*- and intramolecular-migration supports this view. Since the results indicated here suggest that the ionizing power of the solvents is important but not the final word in the elucidation of the solvent effect on the rearrangement, another source for such behavior should be sought.

As is illustrated in Chart 2, to attain the intermediate X, two extreme cases of the solvent solvation may be considered. When the solvent is an electrophile, the anion

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[13)] J. G. Kirkwood, *J. Chem. Phys.*, **2**, 351 (1934).

[14)] A. W. Chapman, *J. Chem. Soc.*, **1934**, 1550.

[15)] N. Tokura and Y. Kondo, This Bulletin, **36**, 200 (1963).

($^-$OTs anion) may be strongly solvated and the intermediate X may easily be formed concertedly or by ionization via VIII. However, when the solvent used is a nucleophile, the solvation of the cation (=C=N$^+$) by the solvent may be predominant, as is seen in IX, the formation of X being thus retarded or inhibited. If such is the case, the migrating group (α carbon atom) should have enough driving force to push away the nucleophilic solvent to obtain the intermediate X. Acetone, pyridine and acetonitrile are to be classified as nucleophilic solvents, whereas sulfur dioxide is to be considered an electrophilic solvent. However, the ionizing powers of ethanol and methanol are large; these solvents are biphilic (both electrophilic and nucleophilic), and the behavior of these solvents towards the oximeester is of a complicated nature. The effect of the strong ionizing power on the rate of the rearrangement may perhaps be compensated for partly by the nucleophilicity of these hydroxyl solvents. There remain many problems to be solved concerning the ionizing power of solvents. Many suggestions which have intended to classify the solvents by their ionizing powers such as dielectric constants, Y-values(16) or Z-values are not satisfactory. The consistent relations between such ionizing powers of the solvents and the rate of the reactions in the solvents are only observed among the solvents with similar natures. Meanwhile, the superiority of liquid sulfur dioxide as the solvent in many reactions is probably largely due to its electrophilic and non-nucleophilic nature.

Summary

The Beckmann rearragement of cyclohexanoneoxime-*p*-toluenesulfonate has been carried out in various solvents and the results have been discussed. The rate in liquid sulfur dioxide is the fastest among the solvents examined. The plots of the log k vs. ionizing powers of the solvents are not linear. The electrophilic solvation of liquid sulfur dioxide on the *p*-toluenesulfonate anion is important if the reaction is to be carried out rapidly and if an intermediate bridged cation, an azacyclopropenium cation, is to be obtained.

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16) S. Winstein, E. Grunwald and H. W. Jones, *J. Am. Chem. Soc.*, 73, 2700 (1951).