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Generation of Free Radicals at Subzero Temperatures. I. Methanolyses of Thionyl Chloride and Methyl Chlorosulfite

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Rates of methanolysis of thionyl chloride and methyl chlorosulfite were measured conductimetrically at +1.0——91.6°C, and were compared with the rates of other acid chlorides. Activation enthalpies and entropies were obtained.

The generation of free radicals at subzero temperatures has been one of the objects of the investigations in our laboratories. It has been found that thionyl chloride produced free radicals by the reaction with some peroxides in alcoholic solvents. Obviously the alcoholysis of thionyl chloride has something to do with the reaction, and the methanolysis of thionyl chloride was investigated and reported on in this paper.

Experimental

Materials. The reagent grade methanol of Iwai Co. containing less than 0.02% water was distilled before use. Thionyl chloride was distilled just before use and the center fraction boiling at 77.5—77.8°C was collected for use.

Methyl chlorosulfite was prepared according to the method of Berti.[1)] 135 g of thionyl chloride (1.09 moles) and 32 g of methanol (1.00 mol) were let to react for 48 hr at room temperature. The fraction distilling at 103—104°C was collected and used for kinetic runs. $n_D^{20} = 1.4632$ (lit.,[2)] $n_D^{20} = 1.4629$). Dimethyl sulfite was prepared by the method of Vogel and Cowan.[3)]

Kinetic Procedure. The rates of methanolyses of thionyl chloride and methyl chlorosulfite were measured conductimetrically. In order to lessen the fractuation of the bath temperature, a conductivity cell was immersed in the cold bath of a Dewar bottle which was immersed in another cold bath. In order to set the temperature of the inner bath at −25.0°C, a carbon tetrachloride - dry ice mixture was used in the inner bath and a methanol - dry ice mixture was used in the outer bath. For +1.1, −73.0, −79.6 and −91.6°C, both the inner and the outer baths were filled with an ice-water mixture, a methanol - dry ice mixture, and acetone - dry ice mixture and a toluene - liquid nitrogen mixture, respectively.

The conductance was measured by a non-inductive bridge manufactured by Yanagimoto Seisakusho, Model MY-7. The cell constant of the cell used was about 1 cm^{-1}, and the content of the cell was about 25 *ml*. The platinum plates of the cell was galvanized with platinum black by the usual method.

Before the kinetic runs, the linear relationships between the concentration of hydrogen chloride and the conductance were checked at the reaction temperatures and the results were shown in Fig. 1. All the runs were conducted within the range where the linear relationship were held.

A small amount of thionyl chloride or methyl chlorosulfite was sealed in a small glass ampoule. The ampoule

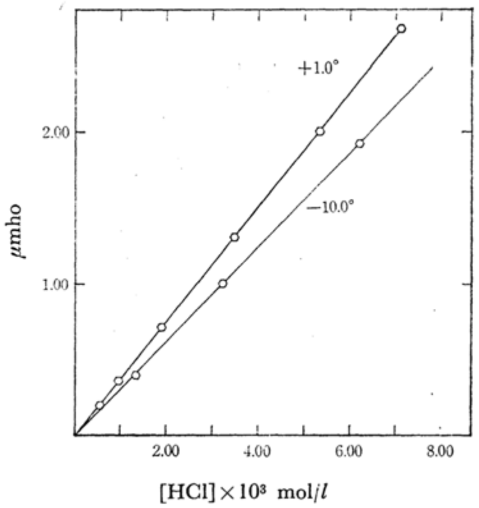

Fig. 1. Conductivity *versus* hydrogen chloride concentration.

TABLE 1. RATES OF METHANOLYSIS

	Temp., °C	$10^4 k_1$ (sec^{-1})
$SOCl_2$	−73.0	46.2±0.4
	−79.6	24.1±0.4
	−91.6	6.08±0.2
$ClSO_2Me$	+ 1.0	2.10 ±0.04
	−25.0	1.36 ±0.03
	−73.0	0.481±0.01

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1) G. Berti, *J. Am. Chem. Soc.*, **76**, 1213 (1954).

2) B. Trunel, *Compt. rend.*, **200**, 555 (1935).

3) A. I. Vogel and D. M. Cowan, *J. Chem. Soc.*, **1943**, 22.

and about 25 m*l* of methanol were placed in a conductance cell in a constant temperature bath. After about one hour, the temperature of the cell was equal to the temperature of the inner bath. Then, the ampoule was broken and the increase of the conductance was measured, and the concentration of thionyl chloride solvolyzed was determined by use of calibration curves. After a run was over, the chloride anions present were titrated with a 0.01 N silver nitrate solution.

Results and Discussion

The rates of methanolysis of both thionyl chloride and methyl chlorosulfite were proportional to the concentrations of the acid chlorides, and the pseudo-first order rate constants were calculated from the slope of the linear lines of plots between $\log C_0/C$ and time. A typical example was shown in Fig. 2, and the rate constants obtained were listed in Table 1. From the rate constants at three different temperatures, activation parameters were calculated by use of Fig. 3. For thionyl chloride, $\Delta H^{\neq}$ was 7.57 ± 0.27 kcal/mol and $\Delta S^{\neq}$ was $-30.4+1.6$ e. u. For methyl chlorosulfite, $\Delta H^{\neq}$ was 1.70 ± 0.06 kcal/mol and $\Delta S^{\neq}$ was -69.0 ± 6.8 e. u.

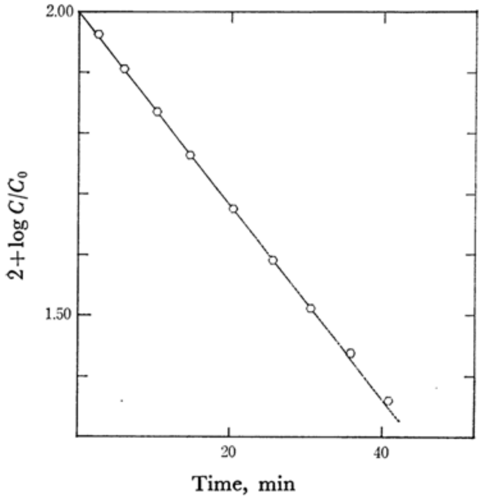

Fig. 2. Rate of methanolysis of $SOCl_2$ at -91.6°C. C_0 and C are the concentration of $SOCl_2$ at $t=0$ and $t=t$, respectively.

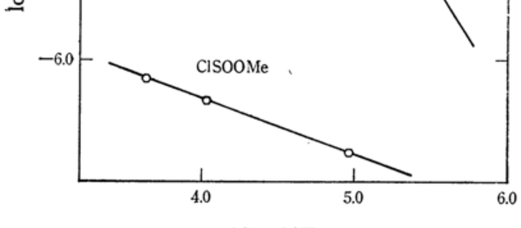

Fig. 3. $\log k/T$ *versus* $1/T$ for the methanolysis of $SOCl_2$ and $ClSO_2Me$.

The rates of solvolysis of some acid chlorides were compared in Table 2. It is clear that the rate of solvolysis of thionyl chloride is one of the fastest among various acid chlorides. It is interesting to note that the rate of methanolysis of methyl chlorosulfite is much faster than that of methyl chlorocarbonate. This difference may be due to the larger positive charge on the sulfur atom than on the carbonyl carbon atom. It was estimated that the ionic character of the S=O bond was about 30—40%.[4]

TABLE 2. RATES OF SOLVOLYSIS OF SOME ACID CHLORIDES

Acid chloride	Solvent	Temp., °C	10^4k_1(sec^{-1})	Ref.
$SOCl_2$	MeOH	−73.0	46.1	
$COCl_2$	1.6 vol% H_2O 98.4 vol% Me_2CO	−50.0	236	5
$ClSO_2Me$	MeOH	+ 1.0	2.10	
$ClCO_2Me$	MeOH	+25.0	1.64	6
CH_3COCl	5 vol% H_2O 95 vol% Me_2CO	+25.0	66.8	8

The activation enthalpies of thionyl chloride and methyl chlorosulfite were rather small, and the activation entropies were very negative values. However, these values should not be regarded as unusual. For the ethanolysis of acetyl chloride in 0.50 M ethanol in carbon tetrachloride, $\Delta H^{\neq}$ was 2.75 kcal/mol and $\Delta S^{\neq}$ was -69.4 e. u.[7] For the hydrolysis of acetyl chloride, $\Delta H^{\neq}$ was 7.6 kcal./mol and $\Delta S^{\neq}$ was -49.2 e. u.[8] For the hydrolysis of thionyl chloride and sulfuryl chloride in wet carbon tetrachloride at 25—45°C, the activation energies were 6.88 and 8.57 kcal/mol, respectively.[9]

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