카르보닐탄소원자의 친핵성 치환반응 (제13보). 메탄올-아세토니트릴
혼합용매에서 Thiochloroformate 의 가메탄올 분해반응

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Nucleophilic Displacement at a Carbonyl Carbon Atom (XIII). Methanolysis of Thiochloroformate in CH₃OH–CH₃CN Mixtures

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요 약. $CH_3O(CO)Cl$, $CH_3S(CO)Cl$ 및 $CH_3S(CS)Cl$ 의 가메탄올 분해반응속도를 메탄올-아세토니트릴 혼합용매하에서 결정하였다.

반응속도는 주로 벌크한 용매성질에 의해서만 아니라 일부 친전자적 특수용매화에 의해서도 영향을 받는다는 것이 실험결과로 알려졌다.

용매의 극성은 반응속도에 영향을 미치는 중요인자는 아니지만 S_N1형의 천이상태 안정화에 기여함을 알았다. $CH_3S(CS)Cl$ 의 가메탄올 분해반응은 메탄올에 의한 이탈기의 특수 용매효과 및 큰 유전상수를 가진 용매에 의한 천이상태 안정화가 중요한 S_N1형으로 진행됨을 알았다. $CH_3O(CO)Cl$ 의 가메탄올 분해반응은 위의 경우와는 반대로 S_N2형으로 진행됨을 알았다.

ABSTRACT. Methanolysis rate constants were determined for $CH_3O(CO)Cl$, $CH_3S(CO)Cl$ and $CH_3S(CS)Cl$ in CH_3OH–CH_3CN mixtures.
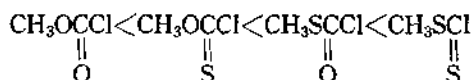
Results show that the rates are not predominantly influenced by the bulk solvent properties but are partly influenced by specific electrophilic solvation. Polarity of the solvent is not a dominant factor but it nevertheless plays a role in charge stabilization of the S_N1 like transition state.

The methanolysis proceeds through S_N1 mechanism for $CH_3S(CS)Cl$, for which both specific solvation of leaving group by methanol and charge stabilization by a high dielectric medium are important, while for $CH_3O(CO)Cl$ methanolysis occurs *via* S_N2 mechanism in which both of the solvent effects are unimportant.

INTRODUCTION

Our previous works have established that methylchloroformate (1; X=Y=O) solvolyzes much more slowly than other acid chlorides due to initial state stabilization[1], but this effect is diminished in compounds where the hetero- atoms, X or/and Y, have only a limited tendency to use its unshared electrons for π bond formation as in the thioanalogues of methylchloroformate (X=S, Y=O; X=O, Y=S; or X=Y=S).[2] Moreover it was found that the hydrolysis mechanism became increasingly more S_N1-like in the the order,[3]

$$CH_3OCCl < CH_3OCCl < CH_3SCCl < CH_3SCl$$
$$\quad\ \|\qquad\ \ \|\qquad\quad \|\qquad\quad \|$$
$$\quad\ O\qquad\ \ S\qquad\quad O\qquad\quad S$$

and this meant the cation[3] stabilization increased in that order as predicted by MO calculations.[4] We concluded based on rate changes with solvent composition that methylchloroformate(X= Y=O) reacted essentially *via* S_N2 mechanism while dithio compounds (X=Y=S) reacted *via* S_N1 and others (X=O, Y=S; X=S, Y=O) reacted with mechanism in between S_N1 and S_N2.[3]

$$CH_3-X-CY-Cl \quad CH_3-\overset{+}{X}\diagdown\overset{Cl}{\underset{C}{|}} \quad CH_3\diagdown$$

(1)   (2)   (3)
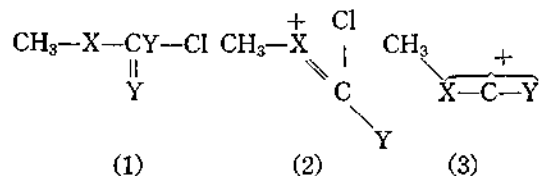
In this report we examine further the solvolysis of these compounds in methanol ($D=$ 32.70)-acetonitrile ($D=35.95$) mixtures which form an *iso*-dielectric series of solvent system.

We expect the nonspecific solvation (bulk solven effect) in this system to be unimportant since solvent polarity is nearly constant throughout the whole spectrum of solvent composition.

EXPERIMENTAL

Materials. $CH_3O(CO)Cl$, $CH_3S(CO)Cl$ and $CH_3S(CS)Cl$ were synthesized and/or purified

as in the previous report.[3] Acetonitrile was purified as previously described.[3] Magnesium (10 g) and Iodine (0.5 g) were added to $2l$ methanol (Merck G. R.) and then refluxed for 30 min and distilled fractionally.
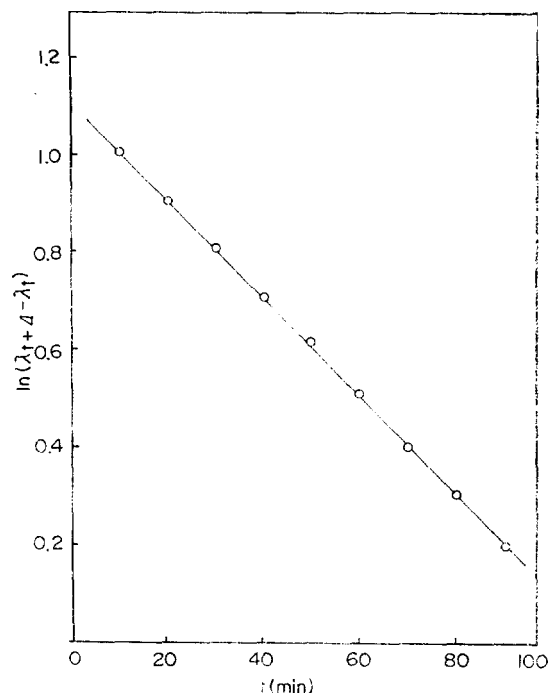

Fig. 1. Guggenheim plot for the methanolysis of $CH_3O(CO)Cl$ in CH_3OH-CH_3CN mixtures; $X_{MeOH}=$ 0.92, at 30°C.

Table 1. First order rate constants and activation parameters for the methanolysis of $CH_3O(CO)Cl$ in CH_3CN-CH_3OH mixtures.

X_{MeOH}	Rate constants ($k \times 10^4$) (sec^{-1})			$\Delta H^{\neq}$ (kcal·mole^{-1})	$-\Delta S^{\neq}$ (e. u.)
	20 °C	30 °C	40 °C		
0.655	0.48	1.23	2.60	14.8	27.7
0.715	0.568	1.42	2.98	14.2	29.5
0.742	0.621	1.53	3.20	13.9	30.1
0.786	0.719	1.70	3.45	13.7	30.7
0.832	0.818	1.88	3.99	14.2	28.7
0.879	0.908	2.06	4.36	13.7	30.2
0.919	0.980	2.21	4.70	13.7	30.1
0.960	1.05	2.35	5.04	13.7	29.9
1	1.15	2.51	5.30	13.4	31.0

Table 2. First order rate constants and activation parmeters for the methanolysis of $CH_3S(CO)Cl$ in CH_3CN-CH_3OH mixtures.

X_{MeOH}	Rate constatants $(k \times 10^5)$ (sec^{-1})			ΔH^* (kcal·mole^{-1})	$-\Delta S^*$ (e. u.)
	20°C	30°C	40°C		
0.655	1.25	2.83	6.25	14.1	32.8
0.715	1.27	2.99	6.85	14.8	30.5
0.742	1.27	3.05	7.10	15.1	29.3
0.786	1.28	3.15	7.50	15.5	27.9
0.832	1.28	3.25	7.95	16.1	26.1
0.879	1.30	3.35	8.40	16.4	24.8
0.919	1.31	3.55	8.80	16.8	23.6
0.960	1.31	3.65	9.15	17.1	22.4
1	1.31	3.75	9.55	17.5	21.0
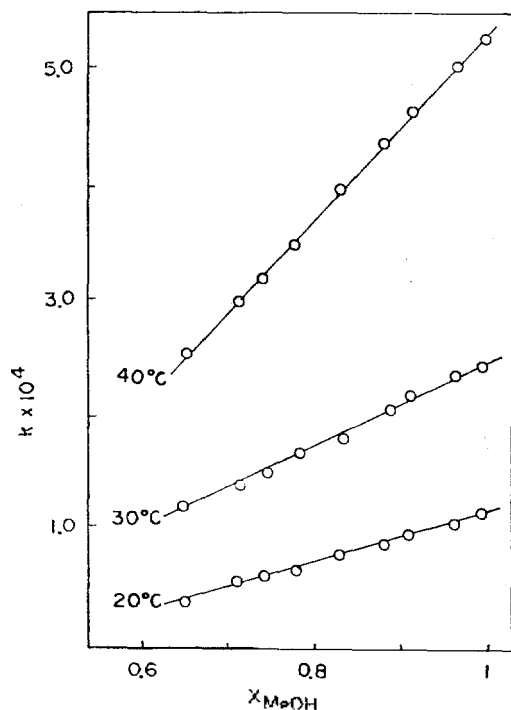
Fig. 2. Plot of k vs. MeOH for the methanolysis of $CH_3O(CO)Cl$ in CH_3OH-CH_3CN mixtures.

Kinetic Measurements. Rates were followed conductometrically with Leeds and Northrup 4959 Electrolytic Conductivity Bridge and pseudo first order rate constans were obtained by Guggenheim method.[5] The concentration of substrate used was ~10^{-4}mole·l^{-1}. The typical plot is given in Fig. 1.

RESULTS AND DISCUSION

Pseudo first order rate constants for methanolysis of $CH_3O(CO)Cl$ and $CH_3S(CO)Cl$ are summarized in Tables 1 and 2 respectively together with activation parameters.

Rate constants increase linearly with mole fraction of methanol, X_{MeOH}, as shown in Fig. 2 and 3 respectively.

The rate constants for methanolysis of CH_3S (CS)Cl are given in Table 3. These data are presented graphically in Fig. 4 which shows that the rates are not linearly dependent on mole fraction of methanol and a rate maximum appears at $X_{MeOH} \simeq 0.85$.

The rate constant at a given mole fraction increasese in the order $CH_3S(CO)Cl < CH_3O$ $(CO)Cl < CH_3S(CS)Cl$.

This not consistent with our previous results where the hydrolysis rates are in the order $CH_3O(CO)Cl < CH_3S(CO)Cl \ll CH_3S(CS)Cl$. The sequence of methanolysis rate constants can be interpreted as methanolysis of $CH_3S(CS)Cl$ preceeding via S_N1 and the S_N1 character for methanolysis of $CH_3S(CO)Cl$ being smaller than for hydrolysis of $CH_3S(CO)Cl$.

In order to examine bulk solvent effect, we

Table 3. First order rate constants and activation parameters for the methanolysis of $CH_3S(CS)Cl$ in CH_3CN-CH_2OH mixtures.

X_{MeOH}	Rate constants ($\times 10^4$) (sec^{-1})			$\Delta H^{\neq}$ (kcal·mole^{-1})	$-\Delta S^{\neq}$ (e. u.)
	20 °C	30 °C	40 °C		
0.655	1.47	4.06	10.6	17.7	15.7
0.715	1.65	4.78	12.6	18.0	14.5
0.742	1.70	4.85	13.2	18.1	14.0
0.786	1.74	5.10	13.9	18.4	13.0
0.832	1.76	5.27	14.6	18.7	11.8
0.879	1.77	5.42	15.2	19.0	10.7
0.919	1.66	5.41	14.7	19.3	9.9
0.960	1.52	5.04	14.5	20.0	7.8
1	1.38	4.63	13.8	20.4	6.5
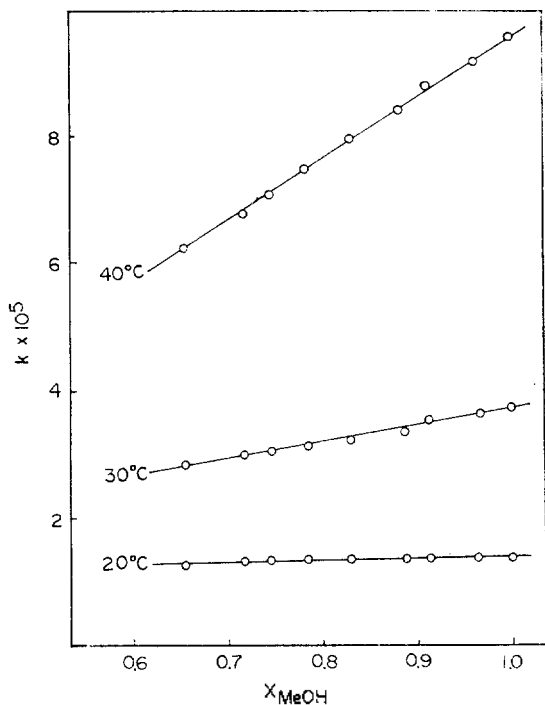
Fig. 3. Plot of k *vs.* X_{MeOH} for the methanolysis of $CH_3S(CO)Cl$ in CH_3OH-CH_3CN mixtures.
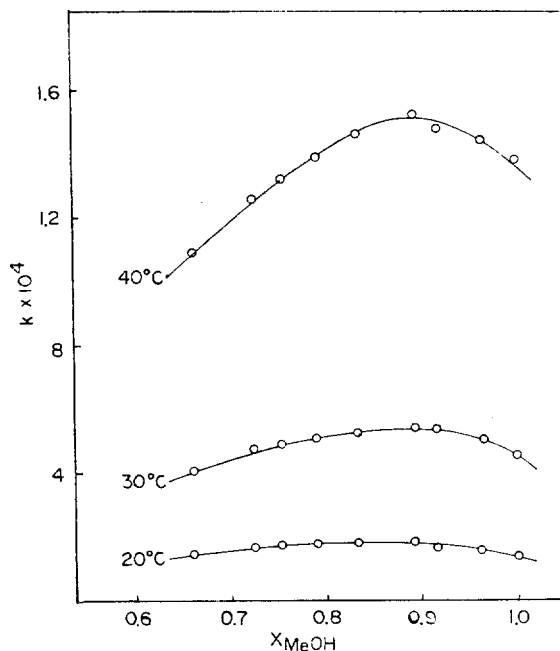
Fg. 4. Plot of k *vs.* X_{MeOH} for the methanolysis of $CH_3S(CS)Cl$ in CH_3OH-CH_3CN mixtures.

have plotted log k against the polarity parameter $\frac{D-1}{2D+1}$ in *Fig.* 5. *Fig.* 5 shows clearly that the rate constants are not related with the bulk solvent properties, especially for $CH_3S(CS)Cl$. We can therefore conclude that the specific solvent effect plays an important

role in methanolysis of $CH_3S(CS)Cl$.

The maximum rate behaviour shown by $CH_3S(CS)Cl$ is also observed by other workers for several reactions in mixed solvents. [6] They have ascribed the maximum rate to the break up of the protic solvent structure with the cosolvent addition; thus the addition of the

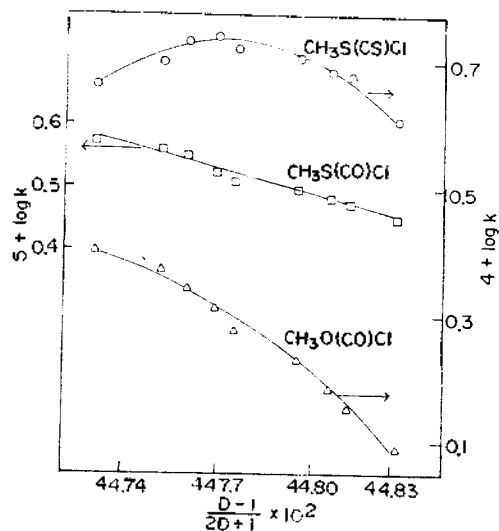cosolvent to methanol breaks up polymer chain of methanol and increases the amount of free

Fig. 5. Plot of log k vs. $\frac{D-1}{2D+1}$ for the methanolysis of $CH_3O(CO)Cl$, $CH_3S(CO)Cl$ and $CH_3S(CS)Cl$ at 30°C.

protic solvent available to make hydrogen bonds with the leaving group, but a further addition of the aprotic solvent decreases the electrophilic solvating power of the medium making the reaction rate lower.

Fig. 6 shows the plot of log k vs. log (CH_3OH). Three curves are similar to those of k vs. X_{MeOH} in *Figs.* 2, 3 and 4. For $CH_3O(CO)Cl$, there is a good linearity with a slope of 1.2. This can be interpreted as approximately one methanol molecule being involved in the transition state, i.e., the rate is first-order with respect to methanol. This is reasonable since methylchloroformate is known to react with a neutral nucleophile, H_2O, CH_3OH and C_2H_5OH, by the S_N2 mechanism,[4] in which bond formation preceedes bond breaking at the transition state and hence the electrophilic solvation of leaving group, Cl^-, by a methanol molecule is not important.

In the case of $CH_3S(CS)Cl$ there is a rate

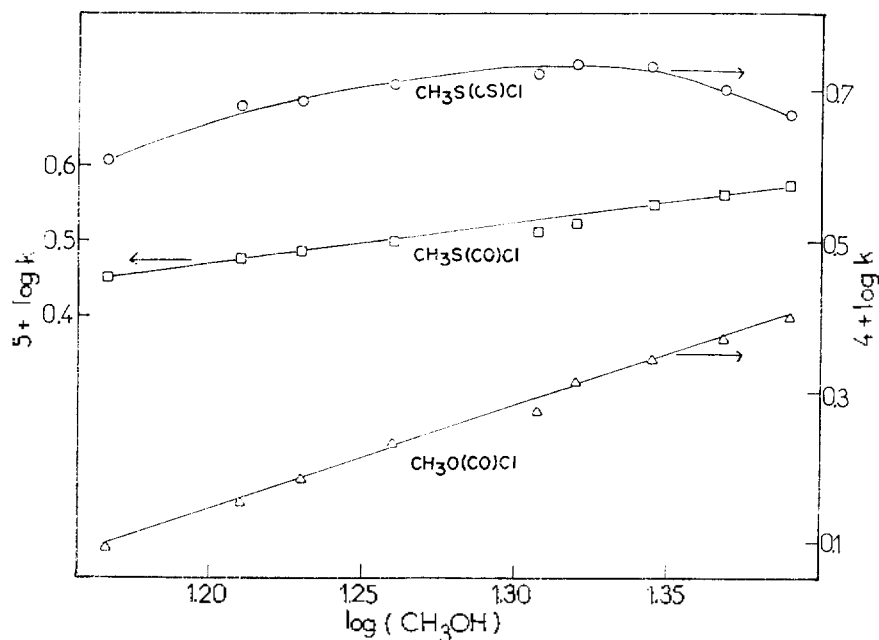*Fig.* 6. Plot of log k vs. log(CH_3OH) for the methanolysis of $CH_3O(CO)Cl$, $CH_3S(CO)Cl$, and $CH_3S(CS)Cl$ in CH_3OH-CH_3CN mixtures at 30°C (log(CH_3OH) is calculated from ref. (7)).

maximum and the linearity is not good. Although the linear part of curve is very small, it is approximately~0.5. This is contrary to our expectation since $CH_3S(CS)Cl$ has more charge separation at the transition state i.e., S_N1-like, and hence the electrophilic solvation power of the medium should become important (see Fig. 7).

Therefore hydrogen bonding of the leaving group by methanol molecule at the transition state is important and hence the role of free protic solvent increases with break up of polymer structure of methanol. This means that now the bond breaking is more important than the bond formation.

However the partial charge separation of the S_N1 transition state can also be stabilized by the more polar acetonitrile molecules. * Thus the rate decrease with the decrease of methanol content of the solvent mixture will not be great in the S_N1 reaction as in the S_N2 reaction. The bond breaking greatly advanced at the transition state for $CH_3S(CS)Cl$, therefore electrophilic solvation of leaving group by methanol molecule becomes very important and also stabilization of charged transition state by a more polar solvent, CH_3CN, becomes important. This is exactly the opposite for $CH_3O\cdot(CO)Cl$, for which the bond formation preceedes bond breaking, and hence no such speific and nonspecific solvation effects become apparent (Fig. 7).

For $CH_3S(CO)Cl$, Fig. 6 shows that the slope is approximately~0.5. This value is similar to the linear part of $CH_3S(CS)Cl$.

It seems that the situation is intermediate where the reaction mechanism is somewhere in the spectrum of $S_N1 \sim S_N2$. The similarity of the slope for $CH_3S(CO)Cl$ with that of $CH_3S(CS)Cl$ implies an S_N1 character and the absence of the specific solvent effect, i.e., electrophilic solvation by methanol, implies an S_N2 character.

The activation parameters in Tables 1, 2, and 3 are also consistent with our proposed mechanism; relatively large ΔH^* and small $-\Delta S^*$ (S_N1 like)[9] for $CH_3S(CS)Cl$, and relatively small ΔH^* and large $-\Delta S^*$ (S_N2 like)[9] for $CH_3O(CO)Cl$. Here again $CH_3S(CO)Cl$ shows the intermediate behaviour.
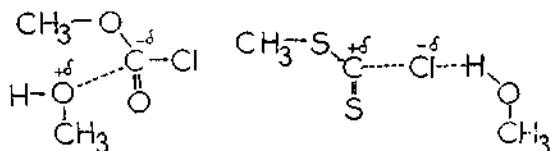
We conclude that for S_N1 mechanism both specific solvation of leaving group by methanol and charge stabilization by a higher D solvent are important, while for S_N2 mechanism both of these are unimportant in comparison with the concentration effect of a nucleophile.

ACKNOWLEDGEMENT

S_N2 Transition state S_N1 Transition state

Fig. 7. Two types of transtion state models.

*Although CH_3OH-CH_3CN solvent mixtures can be treated as quasi isodielectric solvent mixtures, it is known that solvation of large cation by acetonirile is larger than in methanol.[8]

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