Correlation of the Rate of Solvolysis of 2-Chloro-thioacetophenones

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According to the recent results of Kevill *et al.*[1-3] from kinetic data for solvolyses, they reported that the introduction of S-atom adjacent to a reaction center caused a partial shift away from the addition-elimination (Ad$_F$) through dual reaction channel (DC) to the ionization channel (IC) for solvolysis of acid chloride [ie: PhOCOCl[1](Ad$_F$) → PhSCOCl[1b,2] ≈ PhOCSCl[3] (DC) → PhSCSCl[3] (IC)].

And more recent results of Ryu *et al.*[4] the results of the rates of solvolysis of α-methylthioacetyl chloride (1) and phenylthioacetyl chloride (2) in more than 33 aqueous solvent system including 2,2,2-trifluoroethanol (TFE)-ethanol (EtOH) solvent can be explained by the same mechanism with the same structure of transition state (TS), controlled by the contribution from strong nucleophilic participation (third order reaction model for TFE-EtOH system)[5] by the molecule of solvent as well as weakly solvent polarity (ionization), regardless of the different neighboring groups containing an S-atom [even if these are far away the reaction center, (C−O)]

Results and Discussion

Accordingly, we have conducted the further research to investigate how S-methyl and S-phenyl groups influence the reaction center as well as the variation of reaction mechanism in solvolysis of 2-chloro-2-methylthioacetophenone (3)[6] and 2-chloro-2-phenylthioacetophenone (4)[7] (not acid chlorides), respectively at 25 °C and 50 °C, for more than 40 solvent mixtures containing hexafluoro-iso-propanol (HFIP)-water system and TFE-EtOH system (kinetic data in Table 1

and 2), by using the same regression analysis such as those of corresponding 1 and 2.

First of all, plot of log(k/k_0) for 3 at 25 °C *vs.* those of corresponding for 4 at 50 °C (rate-rate profiles) in 43 solvents was observed as phenomenon of dispersion (correlation coefficient, r − 0.928) due to the difference in solvation of the S-system between 3 and 4.

The reasonability of our interpretation for different solvation effects on the reaction site, with respect to the change in the position of an S-atom from an S-CH$_3$ to S-Ph group, can be confirmed by showing the a good linearity (r − 0.985, slope − 0.945)[4] in rate-rate profiles for solvolyses of 1 and those of 2 in the same solvent as these system.

Pure ethanol of the solvents investigated in our work has the highest probability of a bimolecular contribution (Ad$_F$) to solvolyses, because of the relatively high nucleophilicity and (or) relatively low ionizing power. Conversely, pure water is a suitable as solvent for the ionization pathway, so rate ratio,[8] $k_{S\text{-}CH_3}(4)/k_{S\text{-}Ph}(5)$ of 34(6.9) for ethanolyses (hydrolysis) of 3 and 4 in pure ethanol (water) at 50 °C (25 °C), which should not be ignored even if small observed rate effects (<100),[9,10] estimates that an S-CH$_3$ group attached reaction site is more favorable than an S-Ph group, in regard to bimolecular pathway compared with ionization pathway-solvolysis rate and $k_{S\text{-}CH_3}(1)/k_{S\text{-}Ph}(2)$−1.0(2.7), being relatively much smaller values, for ethanolysis (hydrolysis) of 1 and 2 in 100% ethanol (water) at 10 °C are obtained.

Consequently, we could not discover any evidence for the expected mesomeric interaction (1), which had been shown [by having a much higher rate ratio (>1700) of $k_{N,N\text{-}(CH_3)_2}/k_{N,N\text{-}Ph_2}$ in pure water] for solvolysis rates of N,N-substituted carbamoyl chloride containing a carbamoyl group (C−O) as a reaction center studied by Kevill *et al.*[11] for solvolyses of 3 and 4,
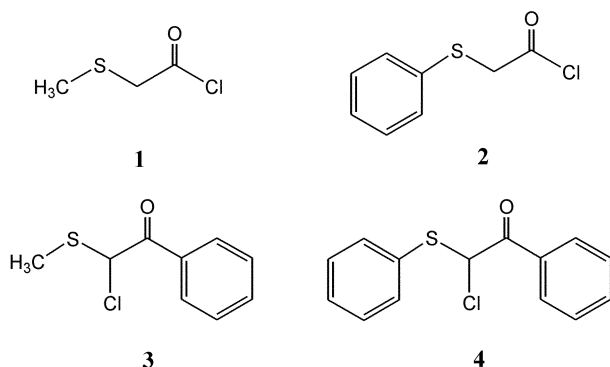
Scheme 1

$$\left(R : \quad -CH_3, \; -ph \right) \tag{1}$$
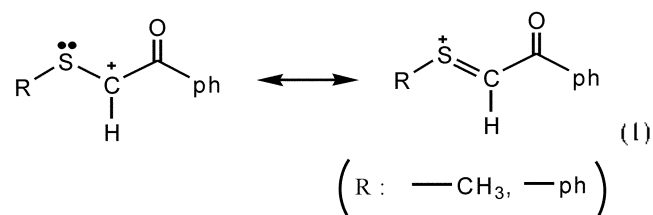
Equation (1) indicates the efficient the stabilization of the developing mesomeric cation by the molecule of water as high polarity.

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Table 1. Rate constants (k/s^{-1}) for solvolyses of **3** in binary solvent mixtures at 25 °C[a]

Solvent Composition[b]	k/s^{-1}		
	methanol-water	Ethanol-water	acetone-water
100	$(1.08 \pm 0.05) \times 10^{-3}$	$(1.70 \pm 0.10) \times 10^{-4}$	–
90	$(5.54 \pm 0.02) \times 10^{-3}$	$(1.49 \pm 0.01) \times 10^{-3}$	$(2.00 \pm 0.01) \times 10^{-5}$
80	$(8.09 \pm 0.04) \times 10^{-3}$	$(2.67 \pm 0.03) \times 10^{-3}$	$(2.00 \pm 0.01) \times 10^{-4}$
70	$(1.64 \pm 0.03) \times 10^{-2}$	$(5.71 \pm 0.01) \times 10^{-3}$	$(7.95 \pm 0.15) \times 10^{-4}$
60	$(3.02 \pm 0.03) \times 10^{-2}$	$(1.07 \pm 0.04) \times 10^{-2}$	$(7.79 \pm 0.02) \times 10^{-3}$
50	$(6.53 \pm 0.02) \times 10^{-2d}$	$(2.03 \pm 0.06) \times 10^{-2d}$	$(9.02 \pm 0.17) \times 10^{-3}$
40	$(1.57 \pm 0.01) \times 10^{-1d}$	$(5.27 \pm 0.09) \times 10^{-2d}$	$(2.96 \pm 0.10) \times 10^{-2d}$
30	$(3.27 \pm 0.02) \times 10^{-1e}$	$(1.51 \pm 0.06) \times 10^{-1e}$	$(6.00 \pm 0.02) \times 10^{-2d}$
20	$(6.03 \pm 0.02) \times 10^{-1e}$	$(4.61 \pm 0.07) \times 10^{-1e}$	$(2.62 \pm 0.08) \times 10^{-1e}$
10	$(9.55 \pm 0.04) \times 10^{-1f}$	$(6.81 \pm 0.00) \times 10^{-1f}$	$(8.17 \pm 0.01) \times 10^{-1e}$
0	$(1.21 \pm 0.02) \times 10^{-1f}$	$(1.21 \pm 0.02) \times 10^{-1f}$	$(1.21 \pm 0.02) \times 10^{-1f}$
	TFE-water[c]	TFE-ethanol	HFIP-water[c]
100	$(1.18 \pm 0.01) \times 10^{-3}$	$(1.18 \pm 0.01) \times 10^{-3}$	–
97	$(1.93 \pm 0.13) \times 10^{-3g}$	–	$(1.46 \pm 0.05) \times 10^{-2h}$
90	$(5.35 \pm 0.04) \times 10^{-3}$	–	$(1.35 \pm 0.01) \times 10^{-2}$
80	$(1.28 \pm 0.03) \times 10^{-2}$	$(1.69 \pm 0.03) \times 10^{-3}$	–
70	$(2.56 \pm 0.06) \times 10^{-2}$	–	$(3.43 \pm 0.09) \times 10^{-2}$
60	–	$(1.35 \pm 0.04) \times 10^{-3}$	–
50	$(5.14 \pm 0.01) \times 10^{-2}$	$(1.21 \pm 0.02) \times 10^{-3}$	$(6.02 \pm 0.03) \times 10^{-2}$
40	–	$(1.02 \pm 0.03) \times 10^{-3}$	–
20	–	$(7.55 \pm 0.15) \times 10^{-4}$	–

[a]Determined conductimeterically at least in duplicate typically injected 4 μL of 10%(w/w) substrate in dry acetonitrile into the kinetic apparatus, with a turbo-stirrer containing 2 mL of each solvent mixtures: errors shown are average deviations. [b]Solvent composition v/v% by alcohol (trifluoroethanol). [c]Solvent composition w/w% by trifluoroethanol (water content were confirmed as errors ≤ 0.3% by using Karl Fisher Titrator). [d]Injected 4 μL of 5%(w/w) substrate in dry acetonitrile. [e]Injected 4 μL of 3%(w/w) substrate in dry acetonitrile. [f]Injected 4 μL of 1%(w/w) substrate in dry acetonitrile. [g]g footnote of Table 1 in ref. 5. [h]g footnote of Table 2 in ref. 5.

Therefore, it means that the stabilization of TS for solvolyses of **3** and **4** are not affected by the mesomeric effect, but by the solvation effect.

An evaluation of rates of solvolysis of **3** and **4** were also carried out in terms of the Grunwald-Winstein type equation[12,13] with ionizing power parameter (Y_{Cl}: based on the solvolyses of 1-adamantyl chloride, m = 1.00)[13] as shown in Table 3.

$$\log(k/k_o) = mY + c \qquad (2)$$

In equation (2), k and k_o refer to the specific rates of solvolysis in a given solvent and in 80 (v/v)% aqueous ethanol, respectively; m is the susceptibility to change in ionizing power (Y_{Cl}) and c is the intercept (residual term) and then these results, including dispersion patterns (r = 0.838-0.890) for plots of single parameter (Y_{Cl}), were summarized in Table 3.

Such phenomena of dispersion were further analyzed using dual Grunwald-Winstein correlation [equation (3)], considering solvent nucleophilicity terms, $l N_T$ (N_T: base on the solvolyses of S-methyl dibenzothiophenium ion.[14] l: the susceptibility to change in solvent nucleophilicity, N_T) from equation (1)

Table 2. Rate constants (k/s^{-1}) for solvolyses of **5** in binary solvent mixtures at 50 °C[a]

Solvent Composition[b]	k/s^{-1}		
	methanol-water	ethanol-water	acetone-water
100	$(4.65 \pm 0.05) \times 10^{-4}$	$(1.25 \pm 0.15) \times 10^{-4}$	
90	$(1.04 \pm 0.03) \times 10^{-3}$	$(2.15 \pm 0.15) \times 10^{-4}$	
80	$(2.81 \pm 0.04) \times 10^{-3}$	$(4.00 \pm 0.00) \times 10^{-4}$	
70	$(4.97 \pm 0.14) \times 10^{-3}$	$(8.05 \pm 0.05) \times 10^{-4}$	$(7.00 \pm 0.00) \times 10^{-5}$
60	$(6.28 \pm 0.01) \times 10^{-3}$	$(1.37 \pm 0.03) \times 10^{-3}$	$(2.30 \pm 0.30) \times 10^{-4}$
50	$(1.57 \pm 0.08) \times 10^{-2d}$	$(3.94 \pm 0.03) \times 10^{-3}$	$(9.25 \pm 0.05) \times 10^{-4}$
40	$(2.04 \pm 0.06) \times 10^{-2d}$	$(7.18 \pm 0.05) \times 10^{-3}$	$(2.97 \pm 0.03) \times 10^{-3}$
30	$(4.50 \pm 0.09) \times 10^{-2e}$	$(2.03 \pm 0.14) \times 10^{-2d}$	$(6.41 \pm 0.09) \times 10^{-3d}$
20	$(1.07 \pm 0.03) \times 10^{-1e}$	$(7.72 \pm 0.05) \times 10^{-2d}$	$(3.71 \pm 0.01) \times 10^{-2d}$
10	$(1.72 \pm 0.04) \times 10^{-1f}$	$(1.83 \pm 0.01) \times 10^{-1e}$	$(1.35 \pm 0.05) \times 10^{-1e}$
0	$(3.74 \pm 0.02) \times 10^{-1f}$	$(3.74 \pm 0.02) \times 10^{-1f}$	$(3.74 \pm 0.02) \times 10^{-1f}$
	TFE-water[c]	TFE-ethanol	HFIP-water[c]
100	$(1.68 \pm 0.03) \times 10^{-3}$	$(1.68 \pm 0.03) \times 10^{-3}$	–
97	$(1.35 \pm 0.04) \times 10^{-3}$	–	$(1.28 \pm 0.00) \times 10^{-2}$
90	$(2.76 \pm 0.05) \times 10^{-3}$	–	$(1.33 \pm 0.09) \times 10^{-2}$
80	$(4.82 \pm 0.02) \times 10^{-3}$	$(7.60 \pm 0.20) \times 10^{-4}$	–
70	$(7.93 \pm 0.30) \times 10^{-3}$	–	$(1.62 \pm 0.10) \times 10^{-2}$
60	–	$(5.75 \pm 0.15) \times 10^{-4}$	–
50	$(1.43 \pm 0.07) \times 10^{-2}$	$(4.20 \pm 0.10) \times 10^{-4}$	$(2.05 \pm 0.01) \times 10^{-2}$
40	–	$(3.33 \pm 0.15) \times 10^{-4}$	–
20	–	$(1.65 \pm 0.05) \times 10^{-4}$	–

[a-f]Determined as described footnote a in table 1.

$$\log(k/k_o) = l N_T + mY_{Cl} + c \qquad (3)$$

According to the previous results[4] reported for solvolyses of **1** and **2**, these are very similar m-values (0.39-0.45) and l-values (1.02) with r to be acceptable value (r ≈ 0.963), when used dual regression analysis, as the linear correlation for 33-35 aqueous solvent systems including TFE-EtOH solvent system.

For solvolysis of **3** with S-CH₃ group, as exhibited in Figure 1, the observation of one good linear dual Grunwald-Winstein plot (equation 3), over the full range of the 38

Table 3. Correlation analyses of $\log(k/k_o)$ for solvolyses of various compound studied with single or dual parameter Grunwald-Winstein equation [(2), (3) and (4)][a]

Compound	Parameter	n[b]	r[c]	m[d]	d	h[d]	c[e]
3 (25 °C)	Y_{Cl}	39[f]	0.884	0.52			-0.245
		43	0.838	0.46			-0.215
	Y_{Cl}, N_T	38	0.980	0.71	0.66		0.029
		43	0.979	0.70	0.60		0.001
4 (50 °C)	Y_{Cl}	38[f]	0.890	0.47			0.045
		42	0.877	0.44			0.070
	Y_{Cl}, N_T	38[f]	0.931	0.59	0.37		0.176
		41	0.932	0.58	0.33		0.159
	Y_{Cl}, N_T, I	27	0.936	0.63	0.47	0.66	0.130

[a]Origin 6.0 program were used to for the multiple regression analysis. [b]Number of solvents. [c]Correlation coefficient. [d]Sensitivity to each solvent parameter chosen. [e]Constant value obtained from correlation. [f]Except for hexafluoro-iso-propanol systems.

Notes

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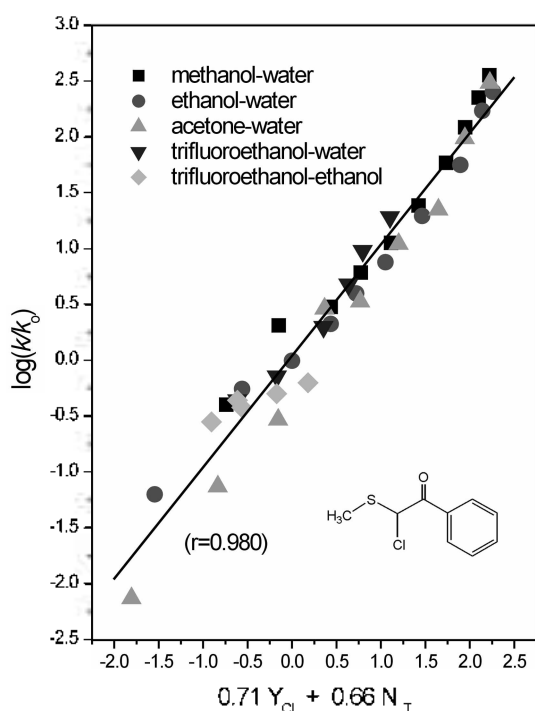
Figure 1. Correlation of logarithms of rate for solvolyses of **3** in various solvent system at 25 °C.

solvents chosen, with $l = 0.66$ and $m = 0.71$ values ($r = 0.980$) suggests that these solvolysis rates of **3** depend on two solvation parameters (Y_{Cl}, N_T) and imply a unity of mechanism, involving solvent nucleophilic participation by solvent molecule from the rear side in TS of ionization (as expected for S_N2 reaction of α-haloketones).[15]

In the case of solvolysis of **4** with S-Ph group, analysis of the rates of solvolysis, using the identical set of solvents and solvent parameters [equation (3)] as used in **3**, obtained unsatisfactory results with $r = 0.931$ ($m = 0.59$, $l = 0.37$) as a linear correlation and manifested the same results such as above (no change in r-values) when performed 41 solvents including HFIP-water system and the application of multiple Grunwald-Winstein parameter involving the aromatic ring parameter (I)[16] proposed by Kevill was performed,

$$\log(k/k_o) = l N_T + m Y_{Cl} + hI + c \qquad (4)$$
(h: susceptibility to I parameter)

Our results analyzed so far are listed in table 3 and c-value corresponding residual term of equation (3) for **1**, **2** and **3** were observed to be very small (c − -0.016-0.032)[4] except for **4** with the relatively large value of c − 0.176. These mean that the rates of solvolysis of **1**, **2** and **3** for all solvent systems chosen in this work can be evaluated by dual parameter correlation analyses (equation 2), but are different from that of **4**.

Solvolysis rates of **4** at 50 °C exhibits a nicely linear relation ($r − 0.991$) with Y_{Cl} for 15 solvents in Figure 2, being more than 2.85 of corresponding Y_{Cl} value of 97%(w/w) TFE-water system, and obtain the m-value of corresponding slope − 1.24 to be considered to proceed by limiting mechanism ($m − 1.00$ for 1-adamantyl chloride

established as S_N1-standard compound).[13]

Positive activation entropy ($\Delta S^{\neq} = 9.17$ cal mol⁻¹)[17] provide additional support for the validity of S_N1 mechanism in high polar solvent systems.

Consequently, in Figure 2, the solvent systems deviated from the corresponding correlation line of the rationalization as favoring the ionization channel, leading to carbocationic intermediates, can be responsible for favoring a bimolecular the reaction channel and the different slopes of the dotted lines to each solvent system may reflect the degree of the nucleophilic solvation at the reaction site. Solvent composition of pure ethanol lies on the straight dotted line for methanol-water solvent system, this may be another expression for the predominance of ethanol as a nucleophilic solvent in this solvolysis.

Finally, kinetic solvent isotope effect (KSIE) have been performed satisfactorily as an additional tool for mechanistic identification in solvolyses under favor of the values of solvolysis rate ratio 40%(v/v) ethanol-water and 97%(w/w) TFE-water solvent system [$k_{40L}/k_{97T}]_Y$, so that these values observed and the additional kinetic data were ascribed together in Table 4. For **1**[4] and **2**[4], the values (≥ 1.49) for KSIE are within the range predicted for the bimolecular solvolysis which is accompanied by general base catalysis and [$k_{40L}/k_{97T}]_Y$ values of < 215-254 are also within the range of favoring nucleophilic solvation, even if these values are less than 500 of corresponding methyl tosylate (MeOTs)[18] at 25 °C known as model compound for the bimolecular reaction. These results ($l = 1.02$-1.03)[4] are closely consistent with those previously analyzed in terms of dual Grunwald-Winstein parameters [equation (2)].
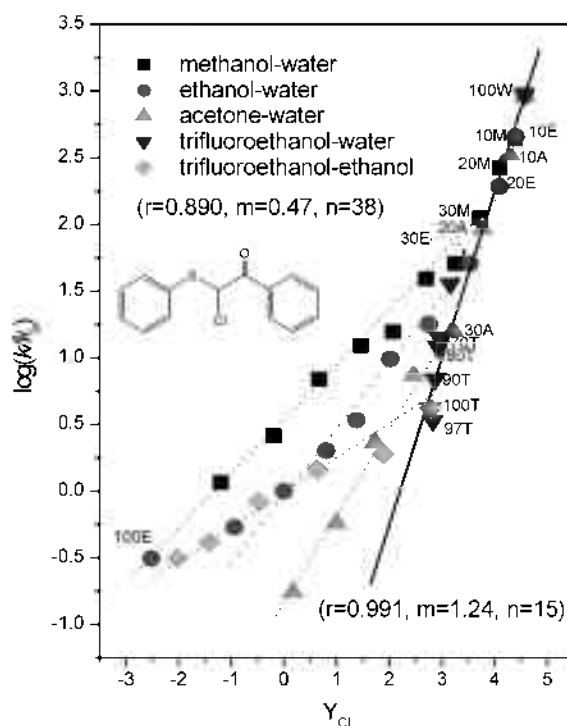
Figure 2. Correlation of logarithms of rate constants for solvolyses of **5** with Y_{Cl}.

Table 4. Rate constants (s^{-1}) in methanol kinetic solvent isotope effect (KSIE) and values of solvolyses rate ratio in 40(v/v)% ethanol/water compared with 97(w/w)% trifluoroethanol/water for **3** and **4**[a]

Compound	MeOH	MeOD[b]	(k_H/k_D)[c]	$[k_{40E}/k_{97T}]_Y$[d]
3 (25 °C)	$(1.08 \pm 0.05) \times 10^{-3}$	$(1.05 \pm 0.10) \times 10^{-3}$	1.03	27
5 (50 °C)	$(4.65 \pm 0.05) \times 10^{-4}$	$(3.85 \pm 0.25) \times 10^{-4}$	1.21	5.3

[a]Determined conductimetrically at least in duplicate. [b]MeOD was Aldrich > 99.5% = D). [c]Kinetic solvent isotope effect. [d]Subscribed Y symbol means very similar ionizing power (Y_{Cl}) but different nucleophilicity (N_T) (Y_{Cl} of 2.75. N_T of -0.75 for 40(v/v)% ethanol/water and Y_{Cl} of 2.85. N_T of -3.30 for 97(w/w)% trifluoroethanol/water.

In contrast, small values of KSIE for **3**(1.03) and for **4**(1.21) are very similar to those reported for MeOTs(1.11)[19] at 49.8 °C and in case of $[k_{40E}/k_{97T}]_Y$ values for **3** and **4**, the value of 5.3 for **3** is analogous to that of 4.7 for 2-naphthoyl chloride.[20] estimated as a dual reaction mechanism and those for **3**(27) show higher than those of **4**, but smaller that these for **1** and **2**.

Conclusions

Our research have conducted to obtain further information on the possible effect of adjacent group including S-atom to reaction center [ie: S-CH$_3$ or S-Ph group]. Consequently, the change from a unit of mechanism indicating S_N2 type [S-CH$_3$ (**3**)]. involving solvent nucleophilic participation by a molecule of the solvent from the rear side in TS of ionization. to the dual reaction channel [S-Ph (**4**)] with S_N1-S_N2 type by means of a specific solvent effect has shown in solvolyses of 2-chloro-2-thioacetophenone (**3** and **4**). Such phenomenon can be explained as a difference in the solvation between CH$_3$- and Ph-group, considering previous the result[21] reported as a quite different solvation between alkyl groups (CH$_3$-) and aromatic rings (Ph-) in solvolyses of substituted acetyl chloride in fluorinated alcohol systems.

Experimental Section

Materials. 2-Chloro-2-methylthioacetophenone (**3**)[6] was prepared from the reaction of α-(methylthio)acetophenone (4.5 g. 0.027 mole) in 40 mL of carbon tetrachloride (CCl$_4$) with N-chlorosuccinimide (NCS: 3.61 g. 0.027 mole) at room temperature during 6 hours and then the product was purified by distillation under reduced pressure (b.p: 135 °C/6 mmHg) after filtering the residue (succinimide) [analytical data obtained: oil phase. ^{1}H-NMR (CDCl$_3$) δ: 2.24 (3H. s. SCH$_3$). 6.34 (1H. s. CH). 7.46-8.08 (5H. m. ArH)]. 2-Chloro-2-phenylthioacetophenone (**4**)[7] was also prepared from the reaction of α-(phenylthio)acetophenone (6 g. 0.026 mole) in CCl$_4$ (40 mL) with NCS (3.47 g. 0.026 mole) and then the residue was purified by column chromatography (SiO$_2$. C$_6$H$_6$) by the same method as ref. 6 [analytical data obtained: oil phase. ^{1}H-NMR (CDCl$_3$) δ: 6.41 (1H. s. CH). 7.21-8.10 (10H. m. ArH)]. All solvents used for kinetics in this work were dried and distilled by standard methods.

Kinetic methods. The rate constants for solvolytic reaction proceed as pseudo-first type were determined using a general conductimetric method[5] and calculation of those were performed by the Origin 6.0 program using the Guggenheim equation[22] from data monitored automatically.

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