

Stoichiometric Solvent Effect on S_N1 Solvolytic Reactivity Accounting for Phenomenon of Maximum Rates in Methanol-Nitromethane Mixtures

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Pseudo-first order rate constants (k_{obs}) are reported for the following solvolyses in approximately isodielectric mixtures: 3- and 4-methoxybenzyl chloride, bromo- and chlorodiphenylmethane, and 4-chloro-, 4,4'-dichloro- and 4-methyl-chlorodiphenylmethane in 0-80% v/v nitromethane-methanol mixtures; and bromo- and chlorodiphenylmethane and 4-methyl-chlorodiphenylmethane in various acetonitrile-methanol mixtures (in the range 0-50% v/v) at 25 °C. These data, and literature data for *t*-butyl halides (Cl, Br, and I), and for *p*-methoxybenzoyl chloride, show rate maxima in solvent compositions of *ca.* 30% aprotic cosolvent, explained by a stoichiometric solvent effect on electrophilic solvation. Linear relationships are observed between $(k_{\text{obs}})/[\text{MeOH}]^2$ and $[\text{AP}]/[\text{MeOH}]$, where [AP] refers to the molar concentration of aprotic cosolvent. The results are consistent with competing third order contributions to k_{obs} , $k_{\text{MM}}[\text{MeOH}]^2$ with hydrogen-bonded methanol as electrophile, and $k_{\text{MAP}}[\text{MeOH}][\text{AP}]$ with hydrogen-bonding disrupted by the aprotic solvent.

Key Words : Solvolysis, Third order kinetic model, Isodielectric mixture, Solvent effect

Introduction

Medium effects on rates of solvolytic reactions have often been discussed quantitatively in terms of empirical parameters for microscopic solvent properties. Correlations with single parameters for polarity (E_T),^{1a} ionizing power (Y),² or nucleophilicity (N)³ may be used. However, multiparameter equations are often required, *e.g.*, involving Y , N and an aromatic ring parameter (I).⁴ Alternatively, bulk solvent properties may be considered, such as dielectric constant (ϵ) for polarity,^{1b} solvent stoichiometry for nucleophilic⁵ or electrophilic catalysis.⁶

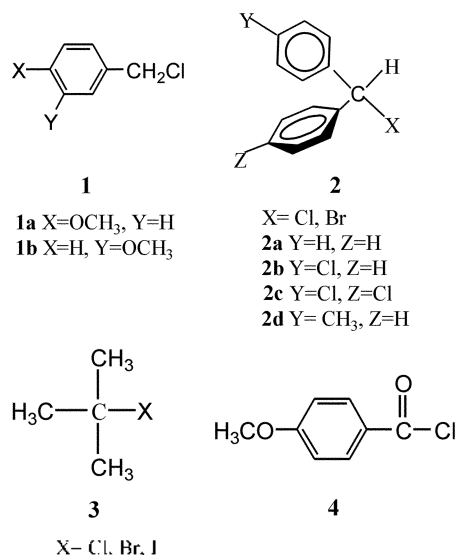
Rates of solvolyses of neutral substrates usually increase as solvent polarity increases, as expected for reactions in which charge develops in the transition state.^{1c} However, rate maxima in alcohol-water mixtures have also been observed, and explained by general base catalysed nucleophilic attack on carbonyl carbon (third order reactions in which changes in solvent stoichiometry are the dominant solvent effect).^{7,8} In addition to examples relevant to our work (see below), there are a few other examples of rate maxima for solvolyses in binary mixtures: *e.g.* S_N1 reactions of 1-adamantyl picrate in methanol-tetramethylene sulfone,⁹ and of 2-adamantyl perchlorate in methanol-acetone;¹⁰ S_N2 reactions of methyl perchlorate in methanol-acetone,¹⁰ acetone-water¹¹ and dioxane-water.¹¹

Surprisingly, rate maxima have also been observed for ' S_N1 ' reactions of *p*-methoxybenzoyl chloride^{11,12} and *t*-butyl halides^{13,14} in 'isodielectric' mixtures of methanol ($\epsilon = 33.6$) with nitromethane ($\epsilon = 35.9$) or methanol with acetonitrile (ϵ

$= 37.5$). We have investigated this phenomenon in more detail, using solvolyses of the classical S_N1 substrates, chlorodiphenylmethane (and related compounds) as model reactions. We now report new kinetic data, and a third order kinetic model for the role of solvent as electrophile.

Results and Discussion

Rate constants for solvolyses of 4-methoxybenzyl chloride (**1a**), 3-methoxybenzyl chloride (**1b**), chlorodiphenylmethane (**2a-Cl**), bromodiphenylmethane (**2a-Br**), chloro(4-chlorophenyl)phenylmethane (**2b-Cl**), bis(4-chlorophenyl)chloromethane (**2c-Cl**) and chloro(4-methylphenyl)phenylmethane



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Table 1. Rate constants (k/s^{-1}) for solvolyses of (3- and 4-methoxybenzyl)chlorides (**1a** and **1b**) in methanol-nitromethane mixtures^a at 25 °C

solvent composition ^b	k/s^{-1}	
	3-OMe (1b)	4-OMe (1a)
100	$(9.84 \pm 0.05) \times 10^{-4}$	2.86×10^{-4c}
90	$(1.33 \pm 0.08) \times 10^{-3}$	$(4.51 \pm 0.01) \times 10^{-4}$
80	$(1.53 \pm 0.07) \times 10^{-3}$	$(5.44 \pm 0.11) \times 10^{-4}$
70	$(1.63 \pm 0.08) \times 10^{-3}$	$(5.53 \pm 0.18) \times 10^{-4}$
60	$(1.53 \pm 0.01) \times 10^{-3}$	$(5.24 \pm 0.18) \times 10^{-4}$
50	$(1.41 \pm 0.04) \times 10^{-3}$	$(4.42 \pm 0.08) \times 10^{-4}$
40	$(1.12 \pm 0.06) \times 10^{-3}$	$(3.54 \pm 0.01) \times 10^{-4}$
30	$(7.91 \pm 0.04) \times 10^{-4}$	$(2.40 \pm 0.04) \times 10^{-4}$
20	$(4.35 \pm 0.18) \times 10^{-4}$	$(1.42 \pm 0.01) \times 10^{-4}$

^aDetermined conductimetrically at least in duplicate, injected 10 mL of 10% (v/v) substrate in dry acetonitrile into the kinetic apparatus containing 5 mL of each solvent mixtures; errors shown are standard deviation. ^bv/v% methanol-nitromethane. ^cData from ref. 15

(**2d-Cl**) in methanol-nitromethane (NM) at 25 °C are given in Tables 1-3. Additional kinetic data for **2a-Cl**, **2a-Br**, and **2d-Cl** in methanol-acetonitrile are given in Tables 3-4.

According to these results, the phenomena of maximum rates were observed for solvolyses of **1** and **2** in 70 (60)-80% (v/v) MeOH-MeNO₂, for those of **2a-Cl** and **2a-Br** in 90% (v/v) MeOH-MeCN. Such phenomena were investigated further in terms of a third order reaction model. Observed pseudo first order rate constants (k_{obs}) can be expressed as a possible third order reaction [eq. 2 and 3] including third order rate constants as shown below.

$$-d[RX]/dt = k_{obs}[RX] \quad (1)$$

$$k_{obs} = k_{NM}[MeOH]^2 + k_{MAP}[MeOH][AP] \quad (2)$$

$$k_{obs}/[MeOH]^2 = k_{NM} + k_{MAP}[AP]/[MeOH] \quad (3)$$

AP: aprotic solvent (MeNO₂ or MeCN)

In equations (2) and (3), the k_{NM} term corresponds to a third order rate constant involving two molecules of methanol, and the k_{MAP} term corresponds to a third order rate constant involving methanol and the aprotic solvent. Plots of $k_{obs}/[MeOH]^2$ vs. $[AP]/[MeOH]$ (eq. 3) and the intercept and slope corresponding to the k_{NM} and k_{MAP} terms, are shown in Table 5.

To test equation 3, we need to show the results for a linear correlation, providing strong support for the validity of a third order reaction.

As typically shown in Figure 1, the result has been obtained to be two intersecting lines for solvolyses of **2a-Cl** in MeOH-MeNO₂ at 25 °C. The results showing parameters such as correlation coefficients and the position of maximum rates for all substrates (**1-4**) chosen are tabulated in Table 5.

As shown in Table 5, the results analyzed from previous kinetic data for **1-4** by eq. 3 have shown good linear correlations (e.g., $r = 0.989-0.999$). The contribution of the k_{MAP} relative to the k_{NM} to solvolyses of **3**, which increases in the order I > Br > Cl according to the leaving ability, is

Table 2. Rate constants (k/s^{-1}) for solvolyses of ring-substituted chlorodiphenylmethane (**2a-2d**) in methanol-nitromethane Mixtures^a at 25 °C

solvent composition ^b	substituents	
	4-Me (2d)	4-H (2a)
100	1.94×10^{-2c}	8.33×10^{-4d}
90	$(3.25 \pm 0.04) \times 10^{-2}$	$(1.28 \pm 0.02) \times 10^{-3}$
80	$(3.82 \pm 0.07) \times 10^{-2}$	$(1.54 \pm 0.06) \times 10^{-3}$
70	$(4.26 \pm 0.05) \times 10^{-2}$	$(1.63 \pm 0.03) \times 10^{-3}$
60	$(4.25 \pm 0.04) \times 10^{-2}$	$(1.59 \pm 0.03) \times 10^{-3}$
50	$(3.51 \pm 0.02) \times 10^{-2}$	$(1.40 \pm 0.03) \times 10^{-3}$
40	$(3.07 \pm 0.09) \times 10^{-2}$	$(1.11 \pm 0.03) \times 10^{-3}$
30	$(2.20 \pm 0.03) \times 10^{-2}$	$(7.78 \pm 0.06) \times 10^{-4}$
20	$(1.25 \pm 0.04) \times 10^{-2}$	$(4.47 \pm 0.05) \times 10^{-4}$
	4-Cl (2b)	4,4'-Cl (2c)
100	2.97×10^{-4}	1.15×10^{-4e}
90	$(4.95 \pm 0.03) \times 10^{-4}$	$(1.90 \pm 0.03) \times 10^{-4}$
80	$(5.71 \pm 0.06) \times 10^{-4}$	$(2.46 \pm 0.04) \times 10^{-4}$
70	$(6.21 \pm 0.08) \times 10^{-4}$	$(2.52 \pm 0.02) \times 10^{-4}$
60	$(6.12 \pm 0.05) \times 10^{-4}$	$(2.42 \pm 0.07) \times 10^{-4}$
50	$(5.03 \pm 0.03) \times 10^{-4}$	$(2.00 \pm 0.06) \times 10^{-4}$
40	$(4.29 \pm 0.06) \times 10^{-4}$	$(1.74 \pm 0.06) \times 10^{-4}$
30	$(3.21 \pm 0.02) \times 10^{-4}$	$(1.21 \pm 0.02) \times 10^{-4}$
20	$(1.75 \pm 0.01) \times 10^{-4}$	

^aDetermined as described in Table 1 (footnote a), except for 4-Me, measured by using the kinetic apparatus with turbo-stirrer. ^bv/v% methanol-nitromethane. ^cData from ref. 16a. ^dData from ref. 17. ^eData from ref. 16b.

Table 3. Rate constants (k/s^{-1}) for solvolyses of bromodiphenylmethane (**2a-Br**) in methanol mixtures with nitromethane and acetonitrile^a at 25 °C

solvent composition ^b	methanol-nitromethane	methanol-acetonitrile
100	$(1.81 \pm 0.02) \times 10^{-2}$	$(1.81 \pm 0.02) \times 10^{-2}$
90	$(2.65 \pm 0.02) \times 10^{-2}$	$(1.96 \pm 0.07) \times 10^{-2}$
80	$(3.25 \pm 0.04) \times 10^{-2}$	$(1.75 \pm 0.06) \times 10^{-2}$
70	$(3.75 \pm 0.04) \times 10^{-2}$	$(1.59 \pm 0.03) \times 10^{-2}$
60	$(3.75 \pm 0.04) \times 10^{-2}$	$(1.38 \pm 0.02) \times 10^{-2}$
50	$(3.37 \pm 0.05) \times 10^{-2}$	$(1.08 \pm 0.01) \times 10^{-2}$
40	$(3.18 \pm 0.04) \times 10^{-2}$	–
30	$(2.46 \pm 0.01) \times 10^{-2}$	–
20	$(1.38 \pm 0.04) \times 10^{-2}$	–

^aDetermined as described in Table 1 (footnote a), except for using the kinetic apparatus with turbo-stirrer. ^bPercentage of volume (v/v%) by methanol.

shown in Table 6. The cause for the k_{MAP}/k_{NM} ratio > 1 observed can be attributed to the dominance for a stoichiometric electrostatic solvation by a molecule of aprotic solvent. The shift for the position of maximum rates toward the higher aprotic solvent content, as the leaving group of **3** changes from -Cl through -Br to -I, is observed [e.g., Cl → Br → I: 40%MN (20An) → 50%MN (30%An) → 60%MN (50%An)] and the order of the k_{MAP}/k_{NM} ratios is consistent with the tendency of the shift for the position of maximum rates.

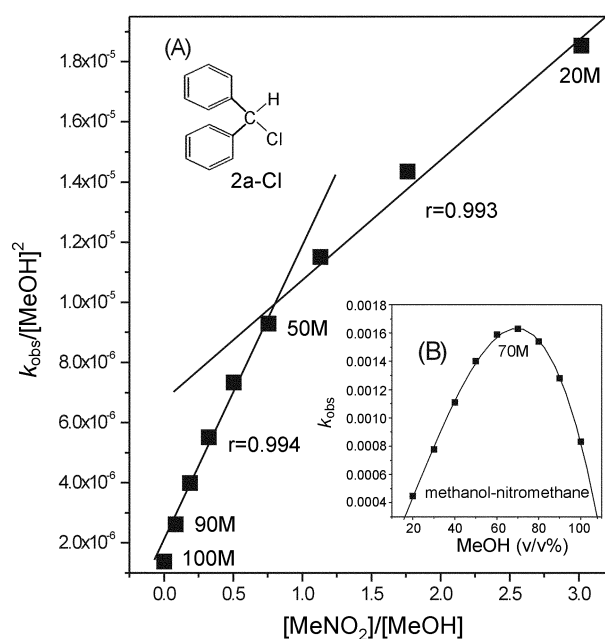
Vapour pressure measurements indicate that methanol is

Table 4. Rate constants (k/s^{-1}) for solvolyses of ring-substituted chlorodiphenylmethane (**2a** and **2d**) in methanol-acetonitrile mixtures^a at 25 °C

solvent composition ^b	substituents	
	4-Me (2d)	4-H (2a)
100	1.94×10^{-2c}	8.33×10^{-4d}
90	$(2.18 \pm 0.06) \times 10^{-2}$	$(8.95 \pm 0.06) \times 10^{-4}$
80	$(1.95 \pm 0.03) \times 10^{-2}$	$(7.89 \pm 0.08) \times 10^{-4}$
70	$(1.67 \pm 0.01) \times 10^{-2}$	$(6.77 \pm 0.18) \times 10^{-4}$
60	$(1.34 \pm 0.04) \times 10^{-2}$	

^aDetermined as described in Table 1 (footnote a). ^bv/v% methanol-acetonitrile. ^cLit. value as described Table 1 (footnote c). ^dLit. value as described in Table 2 (footnote d).

not associated in nitrobenzene ($\epsilon = 36.1$) up to 0.6 M solution,¹⁸ and first order rate constants for solvolyses of *t*-butyl bromide in nitromethane increase linearly with added ethanol (up to 1.6 M).¹⁹ Consequently, it is reasonable to expect solvolyses in nitromethane, containing small amounts of added methanol (*ca.* 10% v/v) to show a first order dependence on methanol concentration. As the methanol concentration increases, more complex kinetics would be expected. The importance of the second order terms in methanol concentration is indicated by the success of eq. 3 in accounting for the results (Table 5), and possible higher order terms can be ignored, because those terms were

**Figure 1.** Typical plot of $k_{\text{obs}}/[\text{MeOH}]^2$ against the molar concentration ratio of nitromethane and methanol (A), including plot of k_{obs} vs. solvent composition of methanol (B), for solvolyses of **2a-Cl** at 25 °C.

relatively unimportant for S_N1 solvolytic reactions.

The analysis for the solvolysis rates of **1-4** in MeOH-

Table 5. Correlation between $k_{\text{obs}}/[\text{MeOH}]^2$ and molar concentration ratio of aprotic solvent/methanol (eq. 3)^e

substrate	solvent ^b	solvent comp. ^c	slope ($k_{\text{MAP}} \times 10^{6d}$)	intercept ($k_{\text{MM}} \times 10^{5d}$)	N ^e	corr. coeff.
1a	0-40%NM	30%NM	3.78	5.93	5	0.993
	40-80%NM		1.35	19.4	5	0.993
1b	0-50%NM	30%NM	10.1	19.1	6	0.997
	60-80%NM		3.31	82.2	3	0.989
2a-Cl	0-50%NM	30%NM	10.4	18.0	6	0.993
	50-80%NM		3.99	67.7	4	0.993
	10-30%An	10%An	1.87	16.8	3	0.999
2a-Br	0-70%NM	30-40%NM	242	408	8	0.998
	10-50%An	10%An	47.7	361	5	0.992
2b-Cl	0-40%NM	30%NM	4.56	5.79	5	0.997
	40-70%NM		2.51	15.5	4	0.996
2c-Cl	0-30%NM	30%NM	2.06	2.11	4	0.995
	40-70%NM		0.904	6.81	4	0.991
2d-Cl	0-40%NM	30%NM	323	367	5	0.998
	30-70%NM		170	1117	4	0.995
	10-40%An	10%An	39.6	422	4	0.989
3-Cl^{f,g}	0-60%NM	40%NM	0.872	1.45	7	0.994
	0-30%An	20%An	0.0043	0.013	4	0.989
3-Br^f	0-70%NM	50%NM	0.865	0.265	8	0.999
	0-70%An	30%An	0.298	0.623	7	0.999
3-I^f	0-80%NM	60%NM	7.11	-7.04	9	0.996
	0-70%An	50%An	2.32	0.726	7	0.995
4^{h,i}	0-80%NM	20%NM	4.21	16.7	8	0.997

^aThe multiple regression analysis was performed using the Origin 6.0 program. ^bFor methanol-nitromethane (NM) solvent mixtures and for methanol-acetonitrile (An) solvent mixtures at 25 °C. ^cSolvent compositions having maximum rate constants (k_{obs}). ^dDimension: $\text{dm}^6\text{mol}^{-2}\text{s}^{-1}$. ^ePoint number of the line obtained from plot of eq. 3. ^fResults analysed by using kinetics data from refs. 13 and 14. ^gFor methanol-nitromethane solvent mixtures at 60 °C. ^hResults analysed by using kinetics data from ref. 12. ⁱFor methanol-nitromethane solvent mixtures at 0 °C.

Table 6. The contribution from k_{MAP} relative to the contribution from k_{MM} to rate reaction of compound (3) at 25 °C

k_{MAP}^a/k_{MM}^b	methanol-nitromethane			methanol-acetonitrile		
	Cl	Br	I	Cl	Br	I
	7.7 ^c	14.2	32.8	3.3	4.9	10.7

^aUsing slope values (k_{MAP}) to linear correlation obtained from eq. 3. ^b k_{MM} value calculated by using $k_{obs}^c/[MeOH]^2$ in solvolytic reaction (k_{obs}) in pure methanol ($k_{MM} = 1.13 \cdot 10^{-7} \text{ dm}^6\text{mol}^{-2}\text{s}^{-1}$ at 60 °C, $1.25 \cdot 10^{-9} \text{ dm}^6\text{mol}^{-2}\text{s}^{-1}$ at 25 °C for Cl, and $k_{MM} = 6.09 \cdot 10^{-8} \text{ dm}^6\text{mol}^{-2}\text{s}^{-1}$ for Br, $k_{MM} = 2.17 \cdot 10^{-7} \text{ dm}^6\text{mol}^{-2}\text{s}^{-1}$ for I). ^cData at 60 °C for Cl.

Table 7. The susceptibilities (ρ) obtained from Hammett plot using Okamoto-Brown equation⁹ for ring-substituted chlorodiphenyl-methane (2-Cl) at 25 °C and the comparison of bromide/chloride (Br/Cl) and iodide/bromide (I/Br) solvolysis rate ratios for bezhydryl (2) and *tert*-butyl halides (3), respectively, at 25 °C

	methanol-nitromethane		corr. coeff.	methanol-acetonitrile		corr. coeff.
ρ	-4.25 ± 0.03^b	$(-4.54 \text{ } 90\% \text{ acetone-H}_2\text{O})^{d,e}$	0.998 ± 0.001	-4.28 ± 0.11		0.999 ± 0.001
Br/Cl	25 \pm 4			26 \pm 4		
I/Br	5.0 \pm 1.8			5.2 \pm 1.2		

^aUsed Okamoto-Brown equation (ref. 20) [for these compound (e.g., Ar₁ Ar₂ CHCl) can be represented as $\log(k/k_0) = \rho(\sigma_1^+ + \sigma_2^+)$, where σ_1^+ and σ_2^+ are individual substituent constants of the substituents in groups Ar₁ and Ar₂, respectively] and the result analysed for the variation of the solvent composition chosen, respectively. ^bObtained $\rho = -4.23$ (-4.22) and corr. coeff. = 0.999 (0.998) in pure methanol, parenthesis; data from ref. 16a. ^cThe result for application of Hammett equation to the rate for the meta-substituted cumyl chlorides (ArMe₂Cl) with 6.2 kcal/mol free energy (refs. 20 and 21). ^dRef. 22.

MeNO₂ and/or MeOH-MeCN at 25 °C (eq. 3) shows a good linear correlation, indicating that eq. 3 is a useful linear relationship for interpreting solvolysis rates with maximum rates in specified solvent compositions.

However, considering the result obtained (Table 7) for the substituent effect and the leaving group effect,²³ unfortunately we have no evidence for the nucleophilic attack on carbocations by third order reaction model type (based on a general base catalytic reaction)^{7,8}

Therefore, the k_{MAP} terms may be estimated as 3rd order rate constant which depends on the number of free molecules of methanol caused by the cleavage of the H-bond, as a non-hydrogen bonding aprotic solvent (hydrogen bonding donor acidity, HBDA; $\alpha = 0.23$ for MeNO₂, 0.15 for MeCN)²⁴ is added to the bulk structure of methanol ($\alpha = 0.98$) and the k_{MM} , these values may be the only ones which are connected with a molecule of methanol without adding an aprotic solvent.

Thus the $k_{MN}[MeOH][AP]$ and the $k_{MM}[MeOH]^2$ terms can contribute to rate constants completely as described in eq. 2. In specified solvent compositions with bilinear correlation by eq. 3, the position of maximum rate constants could be explained as conversion of the k_{MAP} to the favorable k_{MM} term, even if two terms happen to cooperate in this reaction.

Conclusion

For the result as a whole, a stoichiometric solvent effect by relationship to solvent quantity (methanol and aprotic solvent) was very important for S_N1 solvolysis, having maximum rate constant in specified solvent composition of isodielectric mixtures. Linear relationships are observed between $(k_{obs})/[MeOH]^2$ and $[AP]/[MeOH]$, where $[AP]$ refers to the molar concentration of aprotic cosolvent. The results are consistent with competing third order contributions to k_{obs} , $k_{MM}[MeOH]^2$ with hydrogen-bonded methanol

as electrophile, and $k_{MAP}[MeOH][AP]$ with hydrogen-bonding disrupted by the aprotic solvent.

Experimental Section

Materials. Solvents used for kinetics were dried and distilled by a standard method. Compound 2c, 4,4'-dichlorodiphenylmethane obtained from the corresponding alcohol (Aldrich) by stirring with conc. hydrochloric acid²⁵ was recrystallized from light petroleum-chloroform [analytical data obtained: mp. 62 °C, H-NMR (CDCl₃) δ : 7.1-7.3 (8H, m, ArH) ppm, 5.8 (1H, s, CH) ppm]. 4-methyl-chlorodiphenylmethane (2d Y=CH₃, Z=H) was obtained using the same method²⁶ as above (2c). Other compounds used are obtained from Aldrich and used without distillation and/or recrystallization.

Kinetic method. Rates were determined conductimetrically as in previous work.^{6,27}

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