= CHEMICAL KINETICS AND CATALYSIS =

Solvent Effects on Kinetics of an Heteroatomic Nucleophilic Substitution Reaction in Ionic Liquid and Molecular Solvents Mixtures¹

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Abstract—Rate constants, k_A , for the aromatic nucleophilic substitution reaction of 2-chloro-3,5-dinitropyridine with aniline were determined in different compositions of 2-propanol mixed with hexane, benzene, and 2-methylpropan-2-ol and 1-ethyl-3-methylimidazolium ethylsulfate ([Emim][EtSO₄]) with dimethyl sulfoxide at 25°C. The obtained rate constants of the reaction in pure solvents are in the following order: 2methylpropan-2-ol > dimethyl sulfoxide > 2-propanol > hexane > benzene > [Emim][EtSO₄]. Molecularmicroscopic solvent parameters corresponding to the selected binary mixtures were utilized to study the kinetics of a nucleophilic substitution reaction in order to investigate and compare the effects of the solvents

on a chemical process. The influence of solvent parameters including normalized polarity (E_T^N) , dipolarity/polarizability (π^*) , hydrogen bond donor acidity (α) , and hydrogen bond acceptor basicity (β) on the second-order rate constants were investigated and multiple linear regressions gave much better results with regard to single parameter regressions. The dipolarity/polarizability of media has a positive effect in all mixtures regarding zwitterionic character of the reaction intermediate and the hydrogen bond acceptor basicity of the solvent by stabilizing of activated complex increases the reaction rate.

Keywords: nucleophilic substitution, solvent effects, rate constants dipolarity/polarizability of media. **DOI:** 10.1134/S0036024413120297

INTRODUCTION

Interaction with other species in solution can permute the energetic level of molecules. Chemical and physical processes can be affected by solvents. Solvent effects are related to the kind and extent of solute-solvent interactions commonly developed in vicinity of solutes [1, 2]. Reaction rate, selectivity, equilibria, change in position and intensity of spectral absorption band are some kind of obvious phenomena which are influenced by solvents. In mixed solvents, solute–solvent interactions are more complex than in neat solvents because the solute can be solvated preferentially by any species in the system. Indeed, solute–solvent interactions can be affected drastically by solvent–solvent interactions [3, 4].

An ideal solvent should have a very low volatility and should be chemically and physically stable, recyclable, reusable, and eventually, easy to handle. Moreover, solvents that allow more selective and rapid chemical transformations will have a significant impact. Ionic liquids with interesting behavior and features have been recognized as a novel class of solvents in recent years [3–6]. To increase the efficiency of a process (e.g., separation, extraction, synthesis, etc.), one would like to "tune" the solvent or solvent mixture by adding cosolvents. It is beneficial in many ways to understand how added cosolvents (or impurities) affect the physicochemical properties of ionic liquids (ILs) or molecular solvents [4, 6]. When an ionic liquid (IL) is mixed with other solvents, physical and chemical properties will be tunable. Hence ILs can be used as cosolvents in binary or ternary solvents mixtures to increase the efficiency of the processes and change physicochemical properties of the solvents.

To interpret the behavior of solvents in chemical processes, understanding the solution interactions with solute is necessary. Solvatochromism that is a way to study solute–solvent interactions demonstrates specific and non-specific solute–solvent interactions [5]. Solvatochromic parameters and their measurements procedure have been reported elsewhere [6–9]. The effects of the polarity and solvophobicity on cycloaddition reactions and the effects of polarity and hydrogen bond donor acidity on aromatic nucleophilic substitution (ANS) reactions have previously

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been reported [10–13]. Therefore, it was interesting to study the influence of the media in other ANS reactions. The kinetics of nucleophilic heteroatomic substitution reaction of 2-chloro-3,5-dinitropyridine with aniline was studied in this work in 2-propanol/hexane, 2-propanol/benzene, 2-propanol/2methylpropan-2-ol and 1-ethyl-3-methylimidazolium ethylsulfate/dimethyl sulfoxide (DMSO) mixtures.

Electron-withdrawing groups like nitro and cyano groups assist the ANS reaction drastically. Heteroatoms in heteroatomic compounds have activity as strong as the nitro group [13-15]. With the presence of an electronegative nitrogen atom in the aromatic ring, pyridine derivatives undergo nucleophilic substitution much easier than the corresponding benzenes [13]. This raised ability of pyridines towards the nucleophilic attack further reflects the electron-attracting character of the ring nitrogen.

EXPERIMENTAL

Materials. 2-Chloro-3,5-dinitropyridine (mp \approx 64°C) was obtained from Merck and purified by recrystallization from methanol—light petroleum as yellow needless. Aniline was purchased from Merck and purified by vacuum distillation. Spectroscopic grade high-purity hexane, benzene, and 2-methylpropan-2-ol, 2-propanol and dimethyl sulfoxide were

supplied by Merck (Darmstadt, Germany) (>99%). The ionic liquid was 1-ethyl-3-methylimidazolium ethylsulfate synthesized according to the literature and stored under anhydrous conditions [16]. Selection of the room temperature ionic liquid (RTIL) was mainly based on the fact that it can be obtained using a simple method at a relatively low price.

Kinetic measurements. A GBC UV-vis cintra 40 spectrophotometer coupled with a thermocell was used to study the reaction spectrophotometrically, by running the reactions in the thermostatted cells of spectrophotometer at 25°C. The absorbance variation with time was recorded at $\lambda = 350-360$ nm in different solvent compositions for the product of reaction [7, 14]. The kinetics of reactions was studied under pseudo-first-order conditions. In all the cases the infinity absorbance, A_{∞} , was determined experimentally for each kinetic run, and used to calculate the reaction rate constant from equation:

$$\ln(A_{\infty} - A_t) = -k_{\rm obs}t + \ln(A_{\infty} - A_0).$$
(1)

RESULTS AND DISCUSSION

In this work, we have assumed that the reaction proceeds by the two-step mechanism shown in Scheme 1:



The solvent effect on the reaction mechanism can evaluate the validity of such a mechanism. Equation (1) can be achieved by applying the steady state approximation for the concentration of ZH, d[ZH]/d[t] = 0 [7, 14]. By applying steady state approximation we obtain equation

$$k_{\rm A} = k_1(k_2 + k_3[{\rm B}])/(k_{-1} + k_2 + k_3[{\rm B}]),$$
 (2)

in which k_A is the observed second-order rate constant and B is a second molecule of the amine or an added base [14].

The second step which is the formation or decomposition of the intermediate in to product may be considered as a rate-determinating step. If the formation of the intermediate is the rate-determinating step, $k_{-1} \ll k_2 + k_3$ [B], then Eq. (2) is reduced to $k_A = k_1$, and the amine does not catalyze the reaction. But, if the condition is not obeyed, decomposition of the intermediate is rate limiting and base catalysis occurs. The

kinetic form of the catalytic reaction depends on the relative magnitudes of k_{-1} and $(k_2 + k_3[B])$ [7].

The mechanism of both the catalyzed and the uncatalyzed reaction has been discussed in the presence of the primary and secondary amines [7, 14–19]. The compound of 2-chloro-3,5-dinitropyridine has also a similar intermediate to 1-halo-2,4-dinitrobenzene. Moreover, the reaction rate of this compound is much faster than 1-halo-2,4-dinitrobenzene, because of (a) electron-withdrawing of aza group in addition to nitro groups and (b) the possibility of intramolecular hydrogen bonding between ammonium hydrogen and the aza in the intermediate (Scheme 2):



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The latter is confirmed with very negative activated entropy of the reaction [15-22].

The first step in investigating the reaction between 2-chloro-3,5-dinitropyridine and aniline is determination of the rate-determinating step. For this, various aniline concentrations as a base on the reaction rate were studied at different volume fraction of solvents. The second-order rate constants of the reaction at various concentration of aniline are reported in Table 1. As it can be seen, no significant variation in the second-order rate constants occurred with mutation of aniline concentration. According to our previous works [10–12, 14] and the above explanation the reaction was not catalyzed by base in all mixtures and the formation of the intermediate is the rate-determinating step of the reaction.

The second-order rate constants of the reaction, k_A , at 25°C in mixtures of 2-propanol with hexane, benzene, and 2-methylpropan-2-ol and [Emim][EtSO₄] with DMSO are summarized in Tables 2–5. The solvatochromic parameters of media in binary mixtures are also indicated [17, 18]. Selection of the molecular solvents was based on the structures (2-propanol and 2-methylpropan-2-ol as polar protic solvents, DMSO as a polar aprotic solvent, hexane and benzene as aprotic solvents with low polarity and [Emim][EtSO₄] as a polar ionic medium).

The data variations are plotted in Fig. 1 which exhibits that the rate constants of reaction in 2-propanol/benzene mixtures decrease sharply with the benzene content. The second-order rate constant of the reaction follows the following sequence: 2-methylpropan-2-ol > DMSO > 2-propanol > hexane > benzene > [Emim][EtSO₄]. A decreasing profile is demonstrated for [Emim][EtSO₄]/DMSO system by increasing the ionic liquid content.

The normalized polarity parameter (E_T^N) values of the mixtures increase with 2-propanol content, thus it can be expected that the reaction rate constant is dependent on E_T^N . This prediction is acceptable for 2propanol/benzene mixtures. A single-parameter correlation of $\log k_A$ versus E_T^N gives reasonable results. The regression coefficient of $\log k_A$ versus E_T^N is 0.99. But there is no appropriate relationships for singleparameter correlations in other mixtures. For example in 2-propanol—hexane mixture, the regression coefficient of $\log k_A$ versus E_T^N is 0.673. Also, there is no acceptable correlation between $\log k_A$ and dipolarity/polarizability (π^*) in any of the solutions.

Although α value for pure [Emim][EtSO₄] is the highest, the obtained rate constant is lower than for the pure DMSO in [Emim][EtSO₄]/DMSO mixtures. Other solvatochromic parameters are the same: α parameters increase with addition of 2-propanol to 2-

Table 1.	Second-order rate constants ($k_A \times 10$, N	$\Lambda^{-1} \mathrm{s}^{-1}$	in
reaction	of 2-chloro-3,5-dinitropyridine with	aniline	in
mixtures	at 25°C		

~	[Aniline], mol l ⁻¹				
х	0.010	0.030	0.060		
	Propan-2-ol/hehane				
0.3	7.52	7.52	7.50		
0.6	7.80	7.84	7.80		
0.9	9.11	9.15	9.14		
	Pro	pan-2-ol/benz	ene		
0.3	1.22	1.31	1.45		
0.6	2.27	2.94	2.66		
0.9	5.81	5.56	5.86		
	Propan-2-ol/2-methylpropan-2-ol				
0.3	9.75	9.80	9.26		
0.6	8.27	8.17	8.26		
0.9	7.88	7.52	7.36		
	[Emin][EtSO ₄]/DMSO				
(0.3)	4.50	4.57	4.50		
(0.6)	3.50	3.59	3.63		
(0.9)	1.26	1.30	1.26		

Note: x is the volume fraction of propan-2-ol and (in parenthesis) and x_{IL} is the IL volume fraction.

Table 2. Second-order reaction rate constants $(10\times M^{-1}\,s^{-1})$ in mixtures at $25^{\circ}C$

<i>x</i> _{Hex}	$k_{\rm A} \times 10,$ ${\rm M}^{-1} {\rm s}^{-1}$	E_T^N	α	β	π*
0	6.86	0.54	0.67	0.90	0.49
0.1	9.15	0.53	0.66	0.88	0.48
0.2	9.15	0.52	0.66	0.89	0.45
0.3	11.11	0.51	0.65	0.92	0.43
0.4	7.84	0.49	0.65	0.91	0.39
0.5	7.19	0.048	0.66	0.90	0.35
0.6	6.54	0.46	0.66	0.91	0.30
0.7	7.52	0.46	0.71	0.92	0.23
0.8	7.52	0.43	0.75	0.83	0.15
0.9	5.23	—	—	0.68	0.06
1	4.58	0.00	0.10	0.03	-0.06

Note: x_{Hex} is the volume fraction of hexane.

methylpropan-2-ol, but the reaction rate constants decrease. The increasing effect of π^* parameters is in contradiction with decreasing behavior of reaction rate constants in 2-propanol/benzene mixtures. The data in Table 6 confirm that single-parameter regression could not give a reasonable mathematical model

<i>x</i> _{benz}	$k_{\rm A} \times 10,$ $M^{-1} s^{-1}$	E_T^N	α	β	π^*
0	6.86	0.54	0.65	0.90	0.50
0.1	5.56	0.52	0.62	0.88	0.53
0.2	4.90	0.50	0.56	0.83	0.57
0.3	4.25	0.49	0.51	0.75	0.62
0.4	2.94	0.47	0.49	0.70	0.63
0.5	2.29	0.45	0.47	0.65	0.64
0.6	1.96	0.43	0.42	0.61	0.64
0.7	1.31	0.41	0.41	0.54	0.64
0.8	1.31	0.38	0.39	0.43	0.64
0.9	0.65	0.33	0.35	0.28	0.62
1	—	0.13	0.00	0.09	0.60

Table 3. Second-order reaction rate constants in mixtures at 25°C

Note: x_{benz} is the volume fraction of benzene.

Table 4. Second-order reaction rate constants in mixtures at 25°C

<i>x</i> _{2-M}	$k_{\rm A} \times 10,$ ${\rm M}^{-1} {\rm s}^{-1}$	E_T^N	α	β	π*
0	6.86	0.53	0.66	0.87	0.50
0.1	7.52	0.52	0.62	0.89	0.50
0.2	8.50	0.51	0.61	0.90	0.51
0.3	8.50	0.51	0.61	0.90	0.51
0.4	8.17	0.50	0.57	0.91	0.51
0.5	8.17	0.49	0.54	0.92	0.51
0.6	8.82	0.48	0.51	0.93	_
0.7	9.80	0.46	0.49	0.93	0.51
0.8	12.42	0.45	0.45	0.94	0.51
0.9	12.42	0.42	0.39	0.95	0.51
1	10.13	0.39	0.33	0.94	0.50

Note: x_{2-M} is the volume fraction of 2-methylpropan-2-ol.

to fitting data. Therefore, multiparameter linear regression (MLR) analysis was carried out. The dualparameter regression and corresponding correlation coefficients are listed in Table 6.

In 2-propanol/hexane mixtures dual parameter correlation of $\log k_A$ versus π^* and β could give a reasonable mathematical equation which is summarized in equation:

$$log k_{\rm A} = 0.669(\pm 0.075) + 0.115(\pm 0.33)\beta + 0.347(0.192)\pi^*$$
(3)
(n = 11, R = 0.815, s = 0.070, F = 7.91),

where *n*, *R*, *s*, and *F* are the number of data, regression error, standard deviation, and a statistical factor, respectively. The standard coefficient of β is 0.278, and the standard coefficient of π^* is 0.582. In mixture of 2propanol with 2-methylpropan-2-ol, similar correlation observes:

$$log k_{\rm A} = -2.289(\pm 1.376) + 3.047(\pm 0.561)\beta + 0.904(2.962)\pi^*$$
(4)
(n = 11, R = 0.917, s = 0.039, F = 18.50).

The standard coefficient of β is 0.895, and the standard coefficient of π^* is 0.050. In 2-propanol/benzene mixtures following equation was obtained (the standard coefficient of is 0.991):

$$\log k_{\rm A} = -1.832(\pm 0.106) + 4.954(\pm 0.232)E_T^N$$
(5)
(n = 10, R = 0.991, s = 0.045, F = 456.78).

The standardized coefficient is the estimate of an analvsis applied on variables that have been standardized, so that they have variance of 1. This is usually benefit to find which of the independent variables have greater effects on the dependent variables in the multiple regression analysis, when the variables are measured in different units of measurements [7, 14].

The normalized polarity parameter is a blend of π^* (polarity/dipolarizability) and α (hydrogen bond donor ability) of media [14]. Thus, the correlation of $\log k_{\rm A}$ versus α and π^* was considered and the results are demonstrated in equation:

$$\log k_{\rm A} = -3.650(\pm 1.376) + 4.544(\pm 0.436)\alpha + 3.058(0.842)\pi^*$$
(6)
(n = 11, R = 0.986, s = 0.062, E = 119.25)

$$(n = 11, R = 0.980, s = 0.002, F = 119.25).$$

Th d α is 1.378, and star coefficient of π^* is 0.480.

The intermediate of the reaction has zwitterionic character (Scheme 2), thus the activated complex of the reaction has higher polarity than reactant. Hence, the reaction rate increases with the polarity/dipolarizability of the solvent. As can be seen, the second-order rate constant of the reaction increases with an increase in the hydrogen bond acceptor (β) basicity. The activated complex leading to the zwitterionic intermediate is stabilized through hydrogen-bonding interactions of the media (solvent as acceptor with β parameter) with positive charge on the activated complex of the reaction. The activated complex stabilizes more than the reactant and an increase in the β parameters accelerate the reaction rate. It is clear that in solutions of 2-propanol with 2-methylpropan-2-ol, the effects of β on the increase in the reaction rate is higher than that of π^* , because the standardized coefficient of β is higher than that of π^* . The activated complex has the zwitterionic character with positive charge on nitrogen of aniline and negative charge on the pyridine ring. Hydrogen bonding interactions of media (donor and acceptor) with the charges on the activated complex stabilize the activated complex.

In [Emim][EtSO₄]/DMSO mixtures correlation with E_T^N and π^* have the best result with R = 0.87. As mentioned previously, E_T^N parameter can be divided in two other parameters. Hence, the correlation of $\log k_A$ versus α and π^* was done in IL mixtures. The results are shown in equation:

$$\log k_{\rm A} = -2.308(\pm 2.017) - 1.140(\pm 0.281)\alpha + 2.326(1.955)\pi^*$$
(7)
$$(n - 11 R - 0.820 s - 0.182 F - 8.23)$$

Standard coefficient of α is -0.844, and standard coefficient of π^* is 0.248.

In 2-propanol/benzene α parameter has a positive effect in reaction rate. This effect is related to stabilization of activated complex via hydrogen and electronic interaction between hydrogen bond donating structure of solvent and negative charge on the intermediate. The α parameter has a dual effect on reaction rate variations. Hydrogen bond donor ability of solvent could protonate the nitrogen in aniline molecule, hence the nucleophilic tendency of aniline decreased. With stabilization of intermediate by hydrogen bonding interaction, α parameter could increase the rate constants. In 2-propanol/benzene mixtures there is no hydrogen interaction between 2-propanol and benzene. So, 2-propanol as a protic and polar solvent can near the intermediate through hydrogen bonding formation with NO_2 group in pyridine ring and ultimately stabilize the intermediate with derealization of negative charge as electronic and hydrogen interactions. By adding small amounts of hydrogen-bond donor solvent, methanol to benzene in the reaction of phenyl 2,4,6-trinitrophenyl ether with primary and secondary amines [23] the reaction rate increased too.

In IL/DMSO, oxygen groups in the DMSO molecule and ethylsulfate anion can form strong hydrogen bonding with hydrogen of NH_2 group in aniline. Butting to intermediate because of steric hindrance and no hydrogen donor group in intermediate is impossible. Furthermore, aniline is a stronger hydrogen bond donator group more than intermediate. Hence, hydrogen bonding interaction between aniline and

Table 5. Second-order reaction rate constants in mixtures at $25^{\circ}C$

x _{IL}	$k_{\rm A} \times 10,$ ${\rm M}^{-1} {\rm s}^{-1}$	E_T^N	α	β	π*
0	7.18	0.44	0	0.76	1
0.1	7.18	0.52	0.34	0.79	1.05
0.2	5.55	0.55	0.4	0.76	1.05
0.3	4.57	0.57	0.45	0.76	1.06
0.4	5.55	0.6	0.5	0.78	1.06
0.5	3.92	0.61	0.54	0.77	1.06
0.6	3.59	0.63	0.58	0.78	1.05
0.7	3.59	0.67	0.66	0.76	1.06
0.8	2.28	0.67	0.68	0.77	1.03
0.9	1.30	0.68	0.66	0.69	1.1
1	0.98	0.69	0.76	0.78	0.99

Note: x_{II} is the volume fraction of [Emim][EtSO₄].

solvents (binary solvents) is more probable so that aniline cannot participate as a good nucleophile in the ASN reaction. In 2-propanol/benzene mixtures the effects of α on the reaction rate is higher than that of π^* , because the standardized coefficient of α is higher than π^* parameter.

The α parameter of ILs is largely affected by the nature of the cation, but there is also a smaller anion effect [4, 6]. It has been known that in [Emim][EtSO₄] all three imidazolium ring hydrogen atoms are acidic. The α value for [Emim][EtSO₄] is moderately high compared to molecular solvents. The β parameter of ILs is mainly dominated by the nature of the anion. By adding DMSO to 1-ethyl-3-methylimidazolium ethyl-sulfate, the rate constants increase signally. Despite this variation, there is no obvious change in π^* and β



Fig. 1. Second-order rate constants of reaction versus volume fraction of 2-propanol (*x*) in its mixtures with (*1*) hexane, (*2*) benzene, and (*3*) 2-methylpropan-2-ol; and (*4*) IL (x_{II}) with DMSO at 25°C.

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E_T	α	β	π^*	R		
2-Propanol/hexane						
0.345				0.673		
	0.395			0.693		
		0.303		0.726		
			0.474	0.795		
		0.115	0.347	0.815		
	2-Pr	opanol/ben	zene			
4.926				0.991		
	3.144			0.958		
		1.610		0.986		
			-4.622	0.729		
	4.544		3.058	0.986		
	2-Propanol	l/2-methylp	ropan-2-ol			
-1.516				0.818		
	-0.651			0.828		
		2.922		0.891		
			6.857	0.414		
		3.047	0.904	0.917		
[Emim][EtSO ₄]/DMSO						
-3.034				0.828		
	-1.059			0.784		
		4.391		0.409		
			0.411	0.044		
	-1.140		2.326	0.820		

 Table 6. Regression coefficients in different mixtures

parameters in IL system. The anion of $[Emim][EtSO_4]$ is known to have a compact structure, possessing much weaker basicity in comparison to alcohols. Then, $[Emim][EtSO_4]$ has higher hydrogen bond



Fig. 2. Plot of the calculated values of $\log k_{\rm A}$ versus the experimental values of it in mixtures of 2-propanol and IL at 25°C.

donor acidity relative to other molecular solvents. In [Emim][EtSO₄]/DMSO mixtures, standardized coefficient of α is higher than π^* parameter. According to these facts and negative effect of α parameter on reaction rate, it can be concluded that in ionic liquid, minimum rate constant should be obtained. Low rate constant for this aromatic nucleophilic substitution reaction was observed in 1-(1-butyl)-3-methylimidazolium terafluoroborate ([Emim]BF₄) too [14]. A study has been done by Habibi et al. [17] showed that in [Emim][EtSO₄]/DMSO mixtures, π^* and β parameters increase and α parameter decreases the rate of reaction of 1-chloro-2,4-dinitrobenzene with aniline which is in resemblance with our results.

In order to show the efficiency of the suggested dual-parameter correlations, predicted values of $\log k_A$ versus their experimental values were plotted in Fig. 2. There is good agreement between the experimental and calculated values of $\log k_A$ in all solvent mixtures.

CONCLUSIONS

Solvent effects on the aromatic nucleophilic substitution reaction of 2-chloro-3,5-dinitropyridine are similar to those of aromatic nucleophilic substitution reaction of 1-halo-2,4-dinitrobenzene. The reaction mechanism is also similar to ANS reaction of halonitrobenzens, and it confirms the suggested mechanism in Scheme 2. In all mixtures, formation of the zwitterionic intermediate is the rate-determining step of the reaction. Normalized polarity, hydrogen bond donor acidity, and hydrogen bond acceptor basicity of media have different effects on the rate of the reaction. Solvatochromic parameters of media can describe solvent effects on the reaction rate and represent a theoretical model for similar cases in the 2-propanol and [Emim][EtSO₄] mixed with other molecular solvents. The results of dual-parameter correlations of $\log k_{A}$ versus π^* and β (also α and β) in all of the solutions show some improvement with regard to the singleparameter models.

REFERENCES

- M. R. Gholami and A. Habibi-Yangjeh, J. Chem. Res. (S), 226 (1999).
- M. R. Gholami and A. Habibi-Yangjeh, J. Phys. Org. Chem. 13, 468 (2000).
- 3. M. Khodadadi-Moghadam, A. Habibi-Yangjeh, and M. R. Gholami, Monatsh Chem. **140**, 329 (2009).
- A. R. Harifi-Mood. A. Habibi-Yangjeh, and M. R. Gholami, J. Phy. Chem. B 110, 7073 (2006).
- C. Rafols, M. Rosés, and E. Bosch, J. Chem. Soc. Perkin Trans. 2, 243 (1997).
- H. Salari, M. Khodadai-Moghadam, A. R. Harifi-Mood, and M. R. Gholami, J. Phys. Chem. B 114, 9586 (2010).

- A. R. Harifi-Mood, M. Sadat Masumpour, and M. R. Gholami, Prog. React. Kinet. Mech. 31, 117 (2006).
- H. Salari, A. R. Harifi-Mood, and M. R. Gholami, J. Sol. Chem. 39, 1509 (2010).
- A. R. Harifi-Mood, A. Habibi-Yangjeh, and M. R. Gholami, J. Phys. Org. Chem. 21, 783 (2008).
- 10. M. R. Gholami and A. Habibi-Yangjeh, Int. J. Chem. Kinet. **32**, 431 (2001).
- 11. M. R. Gholami and A. Habibi-Yangjeh, Int. J. Chem. Kinet. **33**, 118 (2001).
- 12. M. R. Gholami and B. A. Talebi, J. Phys. Org. Chem. 16, 369 (2003).
- A. R. Harifi-Mood, M. Sadat Masumpour, and M. R. Gholami, Prog. React. Kinet. Mech. 31, 117 (2006).
- A. R. Harifi-Mood, A. Habibi-Yangjeh, M. R. Gholami, and A. Habibi-Yangjeh, Int. J. Chem. Kinet. 39, 681 (2007).

- 15. E. A. Hamed, Int. J. Chem. Kinet. 29, 515 (1997).
- 16. E. Gomez, B. Gonzalez, E. Calvar, E. Tojo, and A. Dominguez, J. Chem. Eng. Data **51**, 2096 (2006).
- 17. A. Habibi-Yangjeh, Y. Jafari-Tarzanag, and A. R. Banaie, Int. J. Chem. Kinet. **41**, 153 (2009).
- M. Rosés, C. Ràfols, J. Ortega, and E. Bosch, J. Chem. Soc. Perkin. Trans. 2, p. 1607 (1995).
- 19. D. J. Cram, B. Rickborn, C. A. Kingsbury, and P. Haberfield, J. Am. Chem. Soc. **83**, 3678 (1961).
- 20. M. Orozco and F. J. Luque, Chem. Rev. 100, 4178 (2000).
- E. A. Hamed, A. A. El-Bardan, E. F. Saad, G. A. Gohar, and G. M. Hassan, J. Chem. Soc. Perkin Trans 2, p. 2415 (1997).
- 22. F. M. Hegazy, A. Z. A. Fattah, E. A. Hamed, and S. M. Sharaf, J. Phys. Org. Chem. **13**, 549 (2000).
- 23. O. Banjoko and I. A. Babatunde, Tetrahedron **60**, 4645 (2004).