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The solvent effect and the structural effect of halides on the quaternization $Et_3N + RX \rightarrow Et_3RNX$

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Abstract

In this study, the solvent effect on the rate constant of the quaternization $Et_3N + BzCl \rightarrow Et_3BzNCl$ was studied. The used 20 solvents are, respectively, protic aliphatics, aprotic aliphatics, protic aromatics, and aprotic aromatics. The rate constant at 50 °C ranges from $0.23 \times 10^{-5}\,M^{-1}\,s^{-1}$ in benzene to $31.74 \times 10^{-5}\,M^{-1}\,s^{-1}$ in DMSO. For the solvents which possess normal characteristics among dipole moment (μ), solubility parameter (δ), and dielectric constant (ε), $\ln k$ is shown to be proportional to δ. The activation energy (E_a), Gibbs free energy ($\Delta G^{\neq}$), entropy ($\Delta S^{\neq}$), and enthalpy ($\Delta H^{\neq}$) in the various solvents were also obtained, and $E_a - \Delta H^{\neq} = RT$ was proved. On the other hand, the structural effect of the halides on the rate constants of the quarternization $Et_3N + RX \rightarrow Et_3RNX$ is shown by the two sequences $k(RI)/k(BuI) = 2193,\ 1170,\ 522,\ 5.3,\ 1.3,\ 1.1,$ and 1 when R = Bz, Me, allyl, Et, Pr, and Hex, respectively, where $k(BuI) = 3.37 \times 10^{-5}\,M^{-1}\,s^{-1}$ in acetonitrile at 30 °C; and $k(BzI){:}k(BzBr){:}k(BzCl) = 2200{:}243{:}1$, where $k(BzCl) = 3.36 \times 10^{-5}\,M^{-1}\,s^{-1}$ in the same solvent and at the same temperature. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Quaternization; Solvent effect; Structural effect; Triethylamine; Halides

1. Introduction

Quaternary ammonium compounds are often of the type $R^1R_3{}^2NX$ or R_4NX, which with $R^1 = C_nH_{2n+1}$, $n \geq 12$; $R^2 = CH_3$ are cationic surfactants; $R^1 = Bz$, $R^2 = C_nH_{2n+1}$, $n = 2 \sim 4$, and R = Bu are phase transfer catalysts [1]; and $R = C_nH_{2n+1}$, $n \leq 4$ can be used as supporting electrolytes [2]. The compounds are mainly synthesized by the quaternization of *tertiary* amines with halides. Because it is a very interesting reaction that the organic molecules result in an ionic compound, and both the solvent and the structure of the amine or the halide can affect the reaction rate up to 10^3-fold, numerous investigations have been carried out since Menshutkin [3] studied the reaction of triethylamine with ethyl iodide 110 years ago. For the purpose of the preparation of phase transfer catalysts, we have completed the studies of the quaternization of aliphatic *tertiary* amines and heterocyclic amines with benzyl chloride [4], the quaternization of *tertiary* amines with butyl iodide [5], the quaternization of tributylamine with butyl halides [6], the synthesis of quaternary ammonium hydroxides by electrolysis–electrodialysis [7], and the synthesis of a desired product QY by nucleophilic substitution ($RY + QX \rightleftarrows RX + QY$) [6,8] when QY is very difficult to be synthesized by quaternization.

The factors affecting the reactivity of the quaternization involve the structures of *tertiary* amines and halides, the free energies of solvation of the reactants and their activated complex, and the reaction temperature. The structural effect can be divided into the polar, the steric and the resonance effects as described by the Taft equation [9].

There are many studies concerning the reactivity of halide [6,10–17], the reactivity of *tertiary* amines [4,5,14,18], the solvent effect [4,5,19–29], and the temperature effect [4–6,12,22]. In this study, the solvent effect on the kinetic parameters k, $\Delta G^{\neq}$, $\Delta H^{\neq}$, $\Delta S^{\neq}$ and E_a of the reaction $Et_3N + BzCl \rightarrow Et_3RNCl$, and the structural effect of halides on the reactivity of the quaternization $Et_3N + RX \rightarrow Et_3RNX$ were investigated. Those results are also basic to the synthesis of phase transfer catalysts.

2. Theory

2.1. The characteristics among the solvent properties and the solvent polarity parameters

From the Gibbs phase rule, it is known that the degree of freedom of a pure substance is 2, so the solvent properties, dipole moment, dielectric constants, solubility parameter,

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Nomenclature

C	molar concentration (M)
E_a	activation energy (kJ/mol)
G	molar Gibbs free energy (kJ/mol)
ΔG	Gibbs free energy change (kJ/mol)
h	Planck's constant (6.626×10^{-34} J s)
ΔH	enthalpy change (kJ/mol)
k	second-order rate constant ($M^{-1}\,s^{-1}$)
k_B	Boltzmann constant ($1.38 \times 10^{-23}\,J\,K^{-1}$)
n	solvation number
N_A	Avogadro number (6.02×10^{-23} mol)
r	intermolecular distance (m)
ΔS	entropy change ($kJ\,mol^{-1}\,K^{-1}$)
t	reaction time (s)
T	absolute temperature (K)
X	conversion of a reactant

Greek letters

α	deformation polarizability ($C\,m^2\,V^{-1}$)
γ	activity coefficient
δ	solubility parameter $(cal/ml)^{1/2}$
ε	dielectric constant
ε_0	dielectric permitivity of vacuum ($8.85419 \times 10^{-12}\,C\,V^{-1}\,m^{-1}$)
μ	dipole moment, D (= Debye = 3.3357×10^{-30} C m)

Superscripts

$\circ$	standard state
$\neq$	activated complex, activation
ig	ideal gas

Subscripts

A	species A
0	initial
solv	solvation

and refractive index are not mutually independent. From the data of the book "Organic Solvents" by Riddick [30], we obtained the relations among, ε, μ, and δ as shown in Figs. 1 and 2. Fig. 2 reveals that the Debye equation, $\varepsilon - 1 = 4\pi n\alpha + 4\pi\mu^2/3k_BT$ [31], is roughly conformed. Fig. 2 shows ε is, respectively, proportional to δ for $0.0 \leq \mu \leq 0.5$ and $1.0 \leq \mu \leq 1.5$, and is approximately proportional to δ when $\mu \geq 3.0$.

A solvent polarity parameter is a measure of the overall effect of a solvent on a solute. There are many solvent polarity parameters derived from spectroscopic, enthalpy, basicity, NMR chemical shift, and rate constant measurements, respectively [32]. The most commonly used are E_T, δ, and the Kirwood dielectric constant function [25]. E_T is correlated with δ as $E_T = 5.98 + 3.13\delta$ with a correlation coefficient $r = 0.948$ [20].

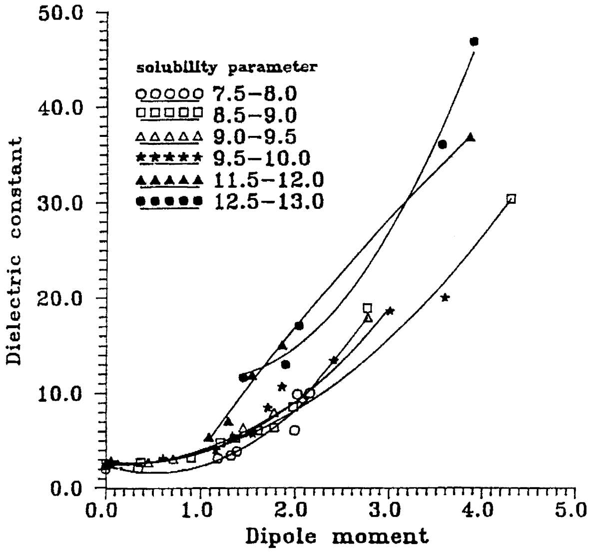

Fig. 1. The relation between the solvent properties of dielectric constant and dipole moment with solubility parameter as the parameter.

2.2. The transition state theory, the Arrhenius law and the rate equation

According to the transition state theory, the rate constant for a bimolecular reaction is

$$k = \frac{k_B T}{h} e^{-\Delta G^{\neq}/RT} \left(\frac{\gamma_A \gamma_B}{\gamma^{\neq}}\right) \tag{1}$$

The activity coefficient ratio is very closed to 1 when the solution is very dilute, then Eq. (1) becomes

$$k = \frac{k_B T}{h} e^{-\Delta G^{\neq}/RT} \tag{2}$$

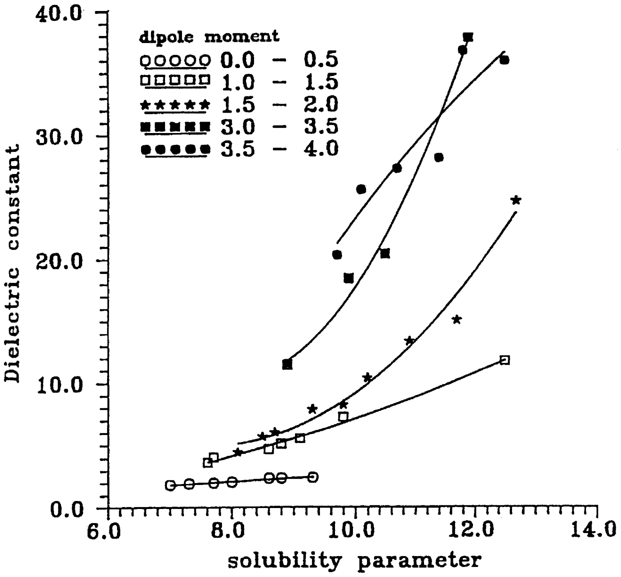

Fig. 2. The relation between the solvent properties of dielectric constant and solubility parameter with dipole moment as the parameter.

On the other hand, the Arrhenius law for the rate constant is

$$k = k_0\,\mathrm{e}^{-E_a/RT}\,(\partial(\Delta G^{\neq}/T)/2(1/T)) \tag{3}$$

By the Gibbs–Helmholtz equation, $(\partial\Delta G^{\neq}/\partial(1/T)) = \Delta H^{\neq}$, the temperature dependence of the rate constants of Eqs. (2) and (3) are

$$\frac{\mathrm{dln}\,k}{\mathrm{d}(1/T)} = -\frac{RT + \Delta H^{\neq}}{R} \tag{4}$$

$$\frac{\mathrm{dln}\,k}{\mathrm{d}(1/T)} = -\frac{E_a}{R} \tag{5}$$

respectively. Compare the above two equations, the relation between E_a and $\Delta H^{\neq}$ is

$$E_a = \Delta H^{\neq} + RT \tag{6}$$

With equimolar reactants A and B, the rate equation can be derived as

$$\frac{X_A}{1 - X_A} = C_{A,0}kt \tag{7}$$

Thus, the rate constant can be determined from the slope of the plot of $X_A/(1 - X_A)$ vs. t. Then, the Gibbs free energy of activation is calculated by Eq. (2), and then $\Delta S^{\neq}$ is obtained from the slope of the plot of $\Delta G^{\neq}$ vs. T, and $\Delta H^{\neq}$ is calculated by the equation $\Delta H^{\neq} = \Delta G^{\neq} + T\Delta S^{\neq}$. On the other hand, the activation energy, E_a, is obtained from the Arrhenius plot of $\ln k$ vs. $1/T$.

2.3. The solvent effect on the rate constant

Eq. (2) shows the dependence of the rate constant on the Gibbs free energy of activation which is defined as

$$\Delta G^{\neq} = G^{\neq,\circ} - G^{\circ}_{A} - G^{\circ}_{B} \tag{8}$$

From the definition of the standard Gibbs free energy of solvation

$$\Delta G_{\mathrm{solv}}{}^{\circ} = G^{\circ} - G^{\mathrm{ig},\circ} \tag{9}$$

Eq. (8) can be written as

$$\Delta G^{\neq} = \Delta G^{\neq,\circ}_{\mathrm{solv}} - \Delta G^{\circ}_{A,\mathrm{solv}} - \Delta G^{\circ}_{B,\mathrm{solv}} + \Delta G^{\mathrm{ig},\circ} \tag{10}$$

where

$$\Delta G^{\mathrm{ig},\circ} = G^{\neq,\mathrm{ig},\circ} - G^{\mathrm{ig},\circ}_{A} - G^{\mathrm{ig},\circ}_{B} \tag{11}$$

From Eqs. (2) and (10), the solvent effect on the rate constant is obviously shown by the difference between the Gibbs free energy of solvation of the activation complex and those of the reactants.

The activated complex of the quaternization of triethylamine with ethyl iodide is considered as a very strong polar molecule with the fraction of charge separation of about 0.4 and estimated dipole moment 8.2 Debye and solubility parameter 12.2 $(\mathrm{cal/ml})^{1/2}$ [27]. Thus, Kirkwood's equation [19]

$$\Delta G_{\mathrm{solv}} = -\frac{N_A}{4\pi\varepsilon_0}\frac{\mu^2}{r^3}\frac{\varepsilon - 1}{2\varepsilon - 1} \tag{12}$$

can be applied in the case of the quaternization of a *tertiary* amine with a halide. When $\varepsilon > 8$, the Kirkwood dielectric function can be simplified to

$$\frac{\varepsilon - 1}{2\varepsilon - 1} = \frac{1}{2} - \frac{3}{4\varepsilon} \tag{13}$$

Thus, ΔG_{solv} can be expressed as

$$\Delta G_{\mathrm{solv}} = A\mu^2 + \frac{B\mu^2}{\varepsilon} \tag{14}$$

where

$$A = -\frac{N_A}{8\pi\varepsilon_0 r^3} \tag{15}$$

$$B = \frac{3N_A}{16\pi\varepsilon_0 r^3} \tag{16}$$

From Fig. 1, ε is approximately proportional to μ^2, and from Fig. 2, ε is roughly proportional to δ for strong polar molecules. Then by Eq. (14), ΔG_{solv} is proportional to δ, and then by Eq. (2), $\ln k$ shall also be proportional to δ.

3. Experiment

3.1. Chemicals

The used solvents and the reactants BzCl, BzBr, RI, R = Me, Et, Pr, and Bu, were products of Merck. Their purity were 99%. BzI and HexI were also of Merck with purity 98%. The 98% allyl iodide was from Aldrich and 95% BzI was from Alfa.

3.2. Experimental apparatus

The reactor was a 300 ml three-necked round-bottom flask, which was immersed in a Lauda K20 temperature bath with accuracy ±0.1 °C. The central neck of the flask was fitted with a Teflon-jacketed stirrer. The stirring speed was controlled by a motor connected to a transformer. A side neck was connected to a condenser, and the other side neck was plugged with a glass plug. The instrument for analyzing the reaction products was a Dionex 4500i Ion Chromatography.

3.3. Experimental operation

The reactant Et_3N in a solvent was placed in the flask and stirred, and the reactant RX was placed in a tube. Both were

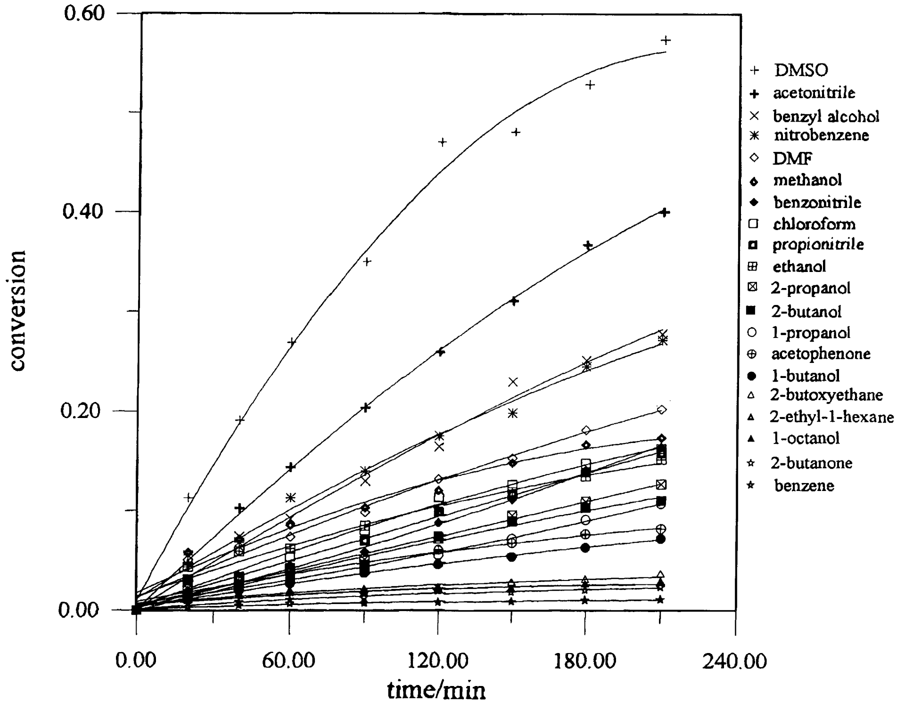

Fig. 3. The solvent effect on the relation between the conversion of Et_3N and the reaction time in the reaction of triethylamine with benzyl chloride. The reaction conditions are: initial mole ratio of Et_3N: BzCl: solvent = 1:1:38, initial amount of Et_3N = 0.05 mol and $T = 50\,^{\circ}C$.

heated simultaneously. When the desired reaction temperature was reached, the reactant RX was transferred into the flask to start the reaction. The reaction mixture was sampled at a suitable time interval. The sample was analyzed by the ion chromatography using the eluent 1.8 mN Na_2CO_3(aq) and 1.7 mN $NaHCO_3$(aq) with a flow rate of 2 ml/min, separation column Ion Pac As4-SC, and guard column Ion Pac AS4A-SC.

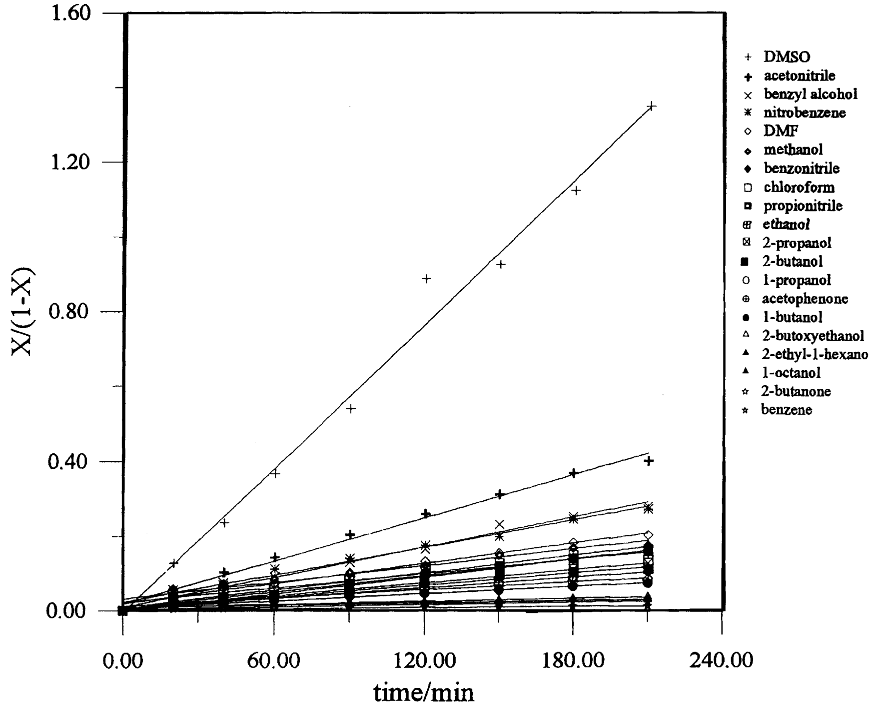

Fig. 4. The solvent effect on the second-order reaction kinetics. The data are from Fig. 3.

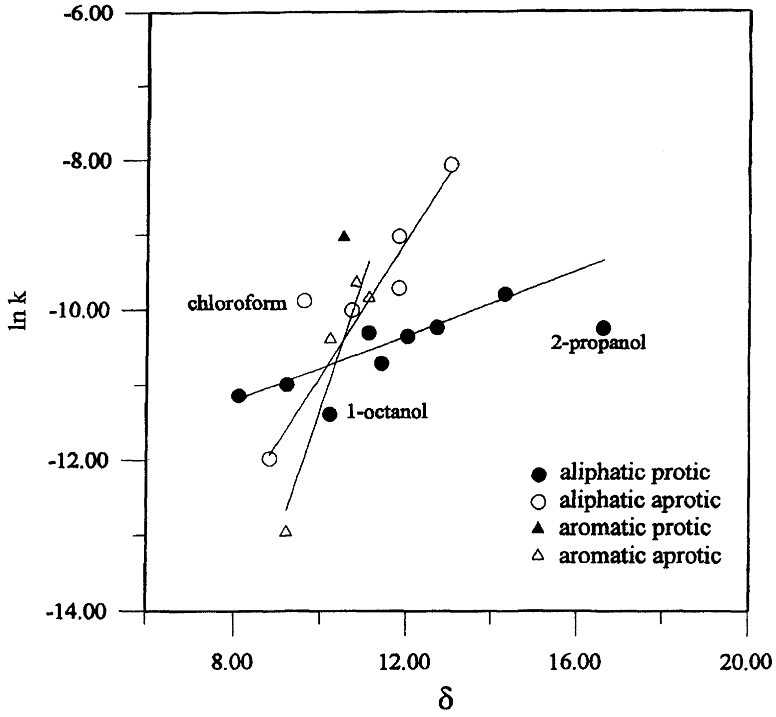

Fig. 5. The relation of $\ln k$ vs. δ for the quaternization of Et_3N with BzCl in the various types of solvents at 50 °C. Initial mole ratio of Et_3N: BzCl: solvent = 1:1:38, initial amount of Et_3N = 0.05 mol.

4. Results and discussion

4.1. The solvent effect on the rate constant of the reaction $Et_3N + BzCl \rightarrow Et_3BzNCl$

Under the reaction condition: mole ratio of Et_3N : BzCl : solvent = 1:1:38, and 50 °C, the solvent effect is shown by Figs. 3–5, and Table 1. From Fig. 5, it is seen that except chloroform, 1-octanol and 2-propanol, $\ln k$ is proportional to δ for each class of the solvents. This relation can be explained by Eqs. (2), (10) and (14). The exception is because the above solvents possess abnormal characteristics among μ, δ and ε as shown in Table 1. Both the dipole moment and the dielectric constant of chloroform are comparatively

Table 1

The effects of the various types of solvents on the rate constant and the activation Gibbs free energy of the reaction $Et_3N + BzCl \rightarrow BzEt_3NCl$ at 50 °C, initial mole ratio of Et_3N: BzCl: solvent = 1:1:38, initial amount of Et_3N = 0.05 mol

	Solvent	k ($\times 10^5$ M^{-1} s^{-1})	$\Delta G^{\neq}$ (kJ mol^{-1})	μ (Debye)	δ (cal/ml)$^{1/2}$	ε	η	T (°C)
Aprotic aliphatics	DMSO	31.74	101.00	3.9	13.00	46.68	2.00	25
	Acetonitrile	12.09	103.60	3.44	11.80	37.50	0.33	30
	DMF	6.04	105.46	3.86	11.80	36.71	0.80	25
	Chloroform	5.12	105.90	1.15	9.60	4.81	0.51	30
	Propionitrile	4.54	106.23	3.57	10.7	27.20	0.39	30
	2-Butanone	0.87	110.66	2.76	8.80	18.51	0.37	30
Protic aliphatics	Methanol	5.59	105.67	2.87	14.30	32.70	0.54	25
	Ethanol	3.61	106.84	1.66	12.7	24.55	0.99	30
	2-Propanol	3.58	106.87	1.66	16.6	19.92	1.77	30
	2-Butanol	3.37	107.02		11.1	16.56	3.18	30
	1-Propanol	3.21	107.16	3.09	12.00	20.33	1.72	30
	1-Butanol	2.24	108.12	1.75	11.4	17.51	2.27	30
	2-Butoxyethanol	1.69	108.89	2.08	9.2	9.30	3.15	25
	2-Ethyl-l-hexanol	1.45	109.29	1.74	8.1	4.41	9.80	20
	1-Octanol	1.13	109.95	1.76	10.2	10.34	6.13	30
Aprotic aromatics	Nitrobenzene	6.37	105.32	4.03	10.80	34.82	1.63	30
	Benzonitrile	5.33	105.80	4.05	11.1	25.20	1.11	30
	Acetophenone	3.09	107.26	2.96	10.2	17.39	1.51	25
	Benzene	0.23	114.19	0	9.20	2.29	0.56	30
Protic aromatics	Benzyl alcohol	11.84	103.65	1.66	10.50	13.10	4.65	30

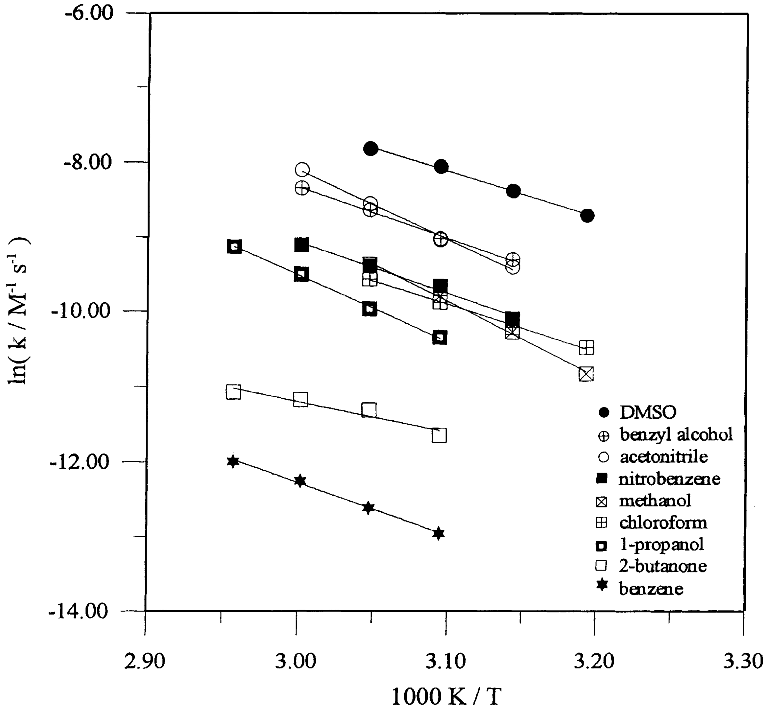

Fig. 6. The Arrhenius' plot of the reaction $Et_3N + BzCl \rightarrow BzEt_3NCl$ in the various solvents. The initial mole ratio of Et_3N/BzCl/solvent is 1/1/38, and the initial amount of Et_3N is 0.05 mol.

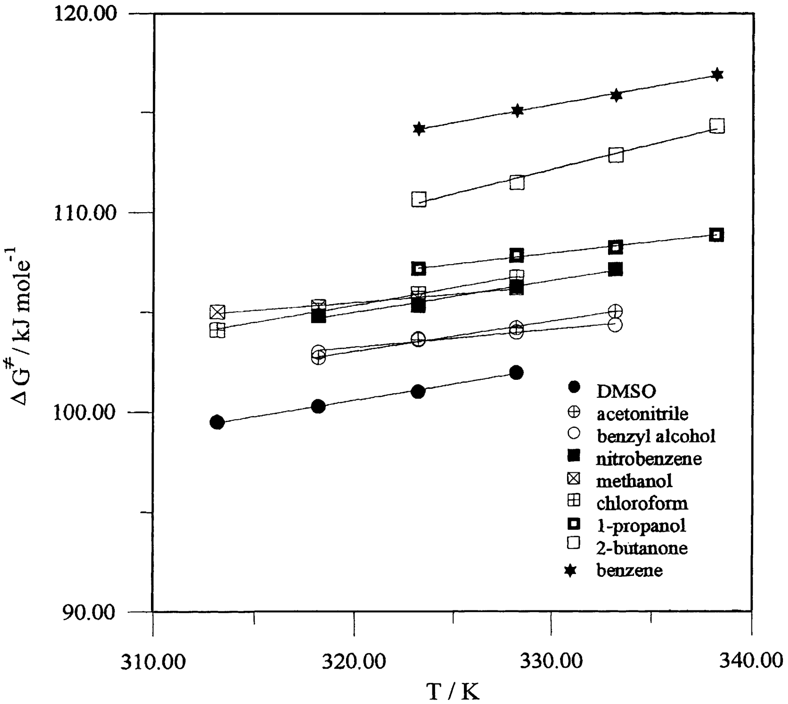

Fig. 7. The plot of the activation Gibbs free energy $\Delta G^{\neq}$ vs. the reaction temperature T. The data for the plot are the same as those of Fig. 6.

Table 2
The activation energy E_a and the activation Gibbs free energy $\Delta G^{\neq}$, enthalpy $\Delta H^{\neq}$ and entropy $\Delta S^{\neq}$ of the reaction $Et_3N + BzCl \rightarrow BzEt_3NCl$ in various solvents, initial mole ratio of Et_3N: BzCl: solvent = 1:1:38, initial amount of Et_3N = 0.05 mol[a]

	$\Delta G^{\neq}$ (kJ mol^{-1})						$\Delta H^{\neq}$ (kJ mol^{-1})	$-\Delta S^{\neq}$ (kJ mol^{-1} K^{-1})	E_a (kJ mol^{-1})	$(E_a - \Delta H^{\neq})/RT_a$
	40 °C	45 °C	50 °C	55 °C	60 °C	65 °C				
DMSO	99.49	100.27	101.00	101.95			48.52	0.162	51.25	1.024
Acetonitrile		102.71	103.60	104.19	105.01		55.05	0.150	57.73	0.991
Benzyl alcohol		102.98	103.65	103.97	104.33		75.23	0.088	77.82	0.957
Nitrobenze		104.81	105.32	106.26	107.12		54.61	0.157	57.46	1.053
Methanol	105.01	105.26	105.67	106.20			80.02	0.080	82.79	1.041
Chloroform	104.11	105.10	105.90	106.72			49.93	0.173	52.54	0.977
1-Propanol			107.16	107.83	108.23	108.86	71.74	0.110	74.46	0.992
2-Butanone			110.66	111.49	112.85	114.30	31.06	0.246	34.05	1.090
Benzene			114.19	115.07	115.84	116.89	56.66	0.178	59.48	1.024

[a] T_a in the last column is the average of the temperatures for obtaining the corresponding E_a.

very low, the solubility parameter of 2-propanol is comparatively very high, and the dielectric constant of 1-octanol is comparatively very low.

4.2. The temperature effect and the solvent effect on the kinetics of the reaction $Et_3N + BzCl \rightarrow Et_3BzNCl$

With the mole ratio of Et_3N : BzCl : solvent = 1:1:38, the temperature effect on the rate constant and the solvent effect on the activation Gibbs free energy of the reaction are shown in Figs. 6 and 7, respectively. The activation energy, E_a, is obtained from Fig. 6, and the activation entropy $\Delta S^{\neq}$, is from Fig. 7, and $\Delta H^{\neq}$ is calculated by the equation $\Delta H^{\neq} = \Delta G^{\neq} + T\Delta S^{\neq}$, together with $(E_a - \Delta H^{\neq})/RT$, they are shown in Table 2. The last column of the table shows that the values of $(E_a - \Delta H^{\neq})/RT$ are very close to 1. This is consistent with Eq. (6). It is worth noting that with 2-butanone as the solvent, the E_a is comparatively very low. However, the rate constant is only larger than that in benzene as shown in Fig. 6. This can be explained as follows: with the aid of the relation $E_a = \Delta H^{\neq} + RT$, the rate constant derived from the transition state theory can be expressed in the form of the Arrhenius law as $k = (k_B T/h)\exp(1 + \Delta S^{\neq}/R)\exp(-E_a/RT)$. Since the negative $\Delta S^{\neq}$ in 2-butanone is comparatively very large, the pre-exponential factor $(k_B T/h)\exp(1 + \Delta S^{\neq}/R)$ is 2.8 ×

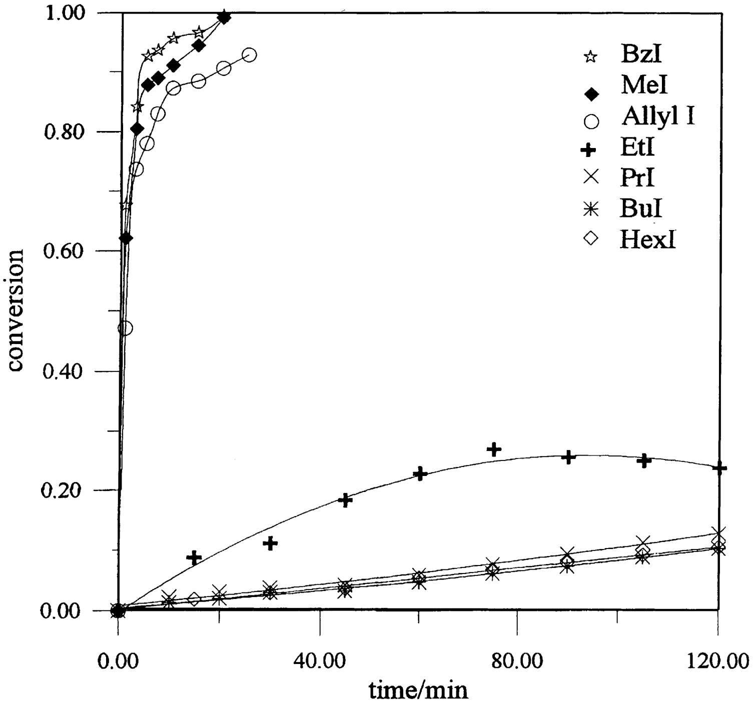

Fig. 8. The conversion of triethylamine vs. time in the reactions with various iodides in acetonitrile at 30 °C. The initial mole ratio of Et_3N: RI: acetonitrile = 1:1:38, and the initial amount of triethylamine is 0.05 mol.

10^{-4} times that of benzene. Therefore, the rate constant of 2-butanone is only 3.78 times that of benzene as shown in Table 1.

4.3. The structural effect on the reactivity of halides

The structural effect of R on the reactivity of RI with Et_3N in acetonitrile is shown in Fig. 8 and Table 3. In which the reaction condition is: initial mole ratio of Et_3N : RI : acetonitrile = 1:1:38, initial amount of Et_3N is 0.05 mol, and reaction temperature is 30 °C. The figure reveals that the conversion of EtI declines after 80 min of reaction time. This is because that beyond the reaction period of 80 min, more and more Et_4NI crystallized out of the solution that was taken as samples for analyzing the iodide ions by ion chromatography. When crystallization occurs, the conversion thus determined is less than its true value. So, only the data without the crystallization were used for obtaining the rate constant. The relative reactivity of BzI : AllI : BuI = 2193:522:1. The reason that benzyl and allyl groups are far more reactive than butyl group is due to their resonance effects as below [8]:

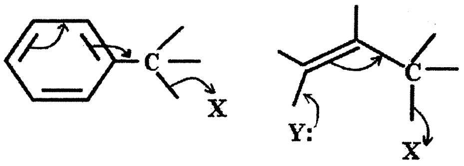

Table 3
The rate constant k and the relative reactivity k_{RI}/k_{BuI} of the reaction $Et_3N + RI \rightarrow REt_3NI$ in acetonitrile at 30 °C. The initial mole ratio of Et_3N: RI: acetonitrile = 1:1:38, and initial amounts of Et_3N = 0.05 mol

RI	k ($\times10^5$ M^{-1} s^{-1})	k_{RI}/k_{BuI}
BzI	7391	2193
MeI	3942	1170
AllI	1758	522
EtI	17.8	5.3
PrI	4.22	1.3
HexI	3.70	1.1
BuI	3.37	1

Due to the resonance effect, the bond dissociation energy of Bz–Cl is 68 kcal/mol, this is lower than that of Ph–Cl by 18 kcal/mol, and that of All–Cl is 60 kcal/mol, lower than CH_2CH–Cl by 44 kcal/mol. The reason for $k(\text{MeI})/k(\text{BuI}) = 1170:1$ is due to the steric effect. That is, butyl group is more bulkier than methyl group and then the nucleophile Et_3N is more difficult to reach the reaction center (the carbon atom bonded to the iodide atom), and why the reactivity ratio k(PrI):k(HexI):k(BuI) is equal to 1.3:1.1:1 is that their differences in polar effects and steric effects are small and have opposite effects [4].

The effect of the leaving group (X) on the reactivity of BzX with the same reaction condition as above is shown in Fig. 9 and Table 4. The relative reactivity of BzI:BzBr:BzCl is equal to 2200:243:1. This can be explained by the bond

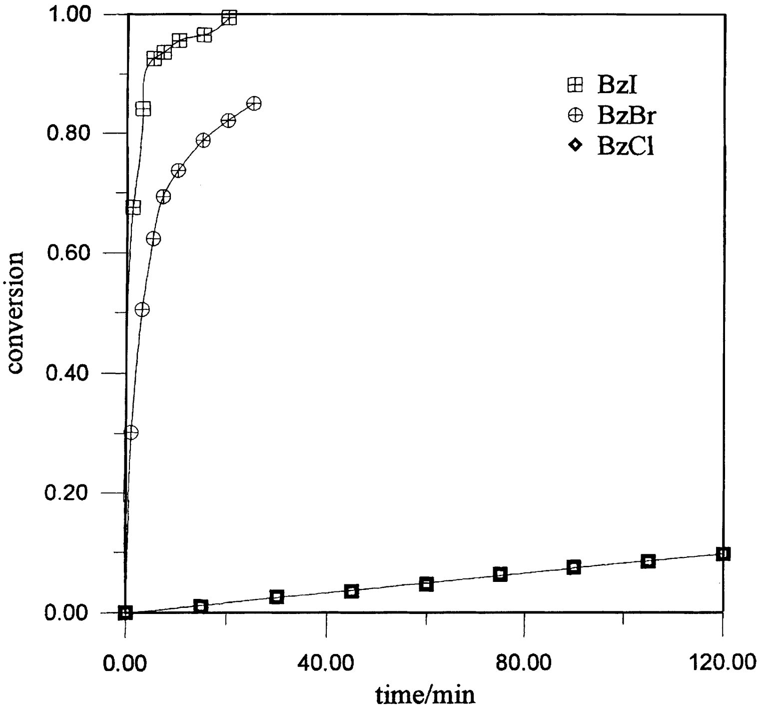

Fig. 9. The conversion of triethylamine vs. time in the reactions with the benzyl halides in acetonitrile at 30 °C. The initial mole ratio of Et_3N : RI : acetonitrile = 1:1:38, and the initial amount of Et_3N = 0.05 mol.

Table 4
The rate constant k and the relative reactivity k_{BzX}/k_{BzCl} of the reaction $Et_3N+BzX \rightarrow BzEt_3NX$ in acetonitrile at 30 °C. The initial mole ratio of Et_3N: BzX: acetonitrile = 1:1:38, and initial amount of $Et_3N = 0.05$ mol

BzX	k ($\times 10^5$ M^{-1} s^{-1})	k_{BzX}/k_{BzCl}
BzI	7391	2200
BzBr	817	243
BzCl	3.36	1

dissociation energy of Me–Cl, Me–Br, Me–I, Bz–Cl and Bz–Br. They are 81, 67, 53, 68, and 51 kcal/mol, respectively [33]. The differences between both the pairs (Me–Cl, and Me–Br) and (Me–Br, and Me–I) are 14 kcal/mol, and the difference between Bz–Cl and Bz–Br is 17 kcal/mol. Thus, we can predict that the difference between Bz–Br and Bz–I would be about 17 kcal/mol. Then the bond dissociation energy of Bz–I would be 34 kcal/mol. Comparing the rate constants shown in Tables 3 and 4, the relative reactivity of the halides is BzI > MeI > AllI > BzBr > EtI > PrI > HexI ≈ BuI ≈ BzCl.

5. Conclusion

The solvent effect on the quaternization of *tertiary* amines with halides can be summarized as: (i) for $\delta > 10$, the rate constant in aprotic solvent is larger than that in protic solvent, because the amine would form hydrogen bond with a protic solvent; (ii) $\ln k$ varies linearly with δ for each class of solvents possessing normal behaviors among solvent properties (dielectric constant, dipolar moment and solubility parameter); (iii) $\Delta S^{\neq}$ may play an important role in reactivity because the pre-exponential factor of the Arrhenius law is proportional to $\exp(1+(\Delta S^{\neq}/R))$. So, in selecting a solvent for the reaction, the solvent effect on both the activation energy and the activation entropy should be considered simultaneously. The solvent effect can also be simply evaluated from the activation Gibbs free energy. On the other hand, the substituent effect on the reactivity of RI is shown by the relative reactivity Bz (2193) > Me (1170) > allyl (522) > Et (5) ≈ Pr (1.3) ≈ Hex (1.1) ≈ Bu (1), where k_{BuI} in acetonitrile at 30 °C is 3.37×10^{-5} M^{-1} s^{-1}. So, the resonance effect of the substituents and the steric effect are the decisive factors in the reactivity of RI. The effect of the leaving group on the reactivity of BzX is obviously explained by the bond dissociation energy of Bz–X. They are 34, 51 and 68 kcal/mol for X = I, Br and Cl, respectively. The corresponding relative reactivities are 2200, 243 and 1, where $k(BzCl) = 3.36$ M^{-1} s^{-1} in acetonitrile at 30 °C.

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