

(e) *o*-Methoxyphenolate and catecholate mono anion (19a) were not substrates for the dioxygen transfer reaction from 4a-FIEtOO<sup>-</sup>. It's still our goal to determine the extent to which the reaction may be extended and to elucidated the mechanism of dioxygen transfer from 4a-FIEtOO<sup>-</sup>.

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## Solvolyse of *t*-Butyl Halides in Binary Mixtures of Methanol with 1,2-Dimethoxyethane, 1,2-Dichloroethane and Pyridine

Yeol Sakong, Shi Choon Kim, Jin Sung Kim, and Ikchoon Lee<sup>†</sup>

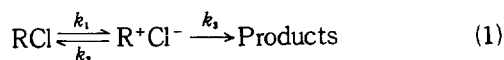
Department of Chemistry, Hanyang University, Seoul 133-791

<sup>†</sup>Department of Chemistry, Inha University, Incheon 402-751. Received September 28, 1989

The Gutmann acceptor number (AN), solvatochromic parameters ( $\alpha$ ,  $\beta$  and  $\pi^*$ ) and hydrogen bonding equilibrium constants ( $K_{HB}$ ) were determined for three binary systems of methanol with 1,2-dimethoxyethane (DME), 1,2-dichloroethane (DCE) and pyridine (PYD). The solvolysis rate constants of *t*-butyl chloride, bromide and iodide were also determined in the three binary systems. Solvent properties and solvolysis rates have been discussed in the light of various solvent parameters. Solvolysis of *t*-butyl halides are most conveniently explained by the two-stage mechanism involving ion-pair intermediate with the ion-pair formation for chloride and ion pair dissociation for iodide as rate limiting.

### Introduction

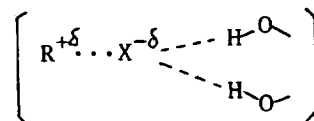
The solvolysis of *t*-butyl halides has been a subject of numerous investigations in view of its importance as a typical  $S_N1$  process. It has been well established that a two-stage mechanism for the solvolysis of *t*-butyl chloride applies in aqueous solutions<sup>1</sup> eq. 1.



where 
$$k_1^{obs} = \frac{k_1 k_3}{k_2 + k_3} \quad (2)$$

Blandamer *et al.*<sup>2</sup> suggested that in the case of *t*-butyl chlo-

ride the first stage requires the formation of a di-hydrogen bonded species, (II), as the intermediate ion-pair, (I), in eq. 1.



(II)

This emphasizes the importance of electrophilic hydrogen bonding assistance of the protic solvent in the ion-pair formation step for *t*-butyl chloride so that eq. 3 applies,

$$k_1^{obs} = k_1 \quad (3)$$

**Table 1.** The AN Scales Determined for MeOH-DME, MeOH-DCE, and MeOH-PYD Binaries

MeOH v/v%	MeOH-DME	MeOH-DCE	MeOH-PYD
100	38.2	38.2	38.2
90	37.4	37.7	37.1
80	36.5	37.1	36.2
70	35.8	36.9	34.4
60	34.8	36.4	—
50	33.5	35.7	31.9
30	30.4	34.1	27.1
0	8.9	13.8	11.0

since  $k_2 \ll k_3$  in eq. 2. If, however, the ion-pair formation proceeds reversibly, *i.e.*,  $k_2 \gg k_3$ , the rate determining step will become the second stage,  $k_3$ , eq. 4.

$$k_1^{obs} = \frac{k_1}{k_2} \cdot k_3 = K_{12} \cdot k_3 \quad (4)$$

In case of  $k_2 \cong k_3$ , the first stage is again rate-limiting, eq. 5.

$$k_1^{obs} = 1/2 k_1 \quad (5)$$

In order to investigate the various possibilities of change in the rate determining step within the framework of the two stage mechanism, (1), we have carried out solvolytic studies of methanol with 1,2-dimethoxyethane (DME), 1,2-dichloroethane (DCE) and pyridine (PYD). These three organic cosolvents have a common property of negligible hydrogen bond donor acidity,  $\alpha$ , with varying strength of hydrogen bond acceptor basicity,  $\beta$ , and polarity-polarizability,  $\pi^*$ , scale of the solvatochromic parameters advocated by Taft and coworkers, eq. 6.<sup>3</sup>

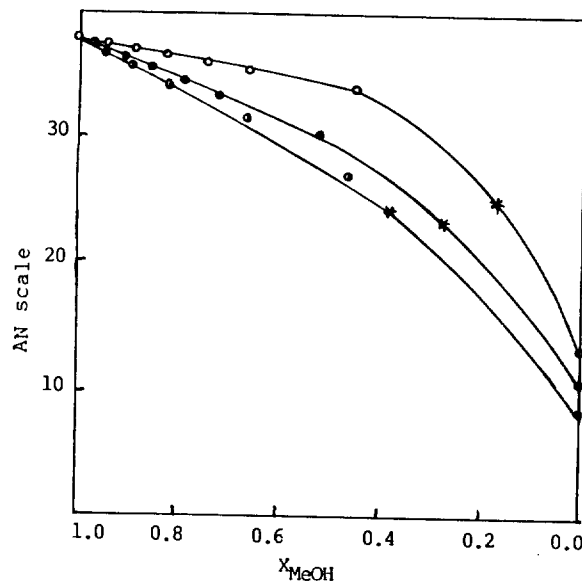
$$XYZ = a\alpha + b\beta + s\pi^* + \text{const} \quad (6)$$

where XYZ is any physicochemical properties correlated by the solvatochromic parameters,  $\alpha$ ,  $\beta$  and  $\pi^*$ , and  $a$ ,  $b$  and  $s$  are the sensitivities of XYZ to the three parameters, respectively. We have in addition determined the acceptor numbers (AN) of Gutmann<sup>4</sup> for the binary solvent mixtures and applied to the analysis of solvolysis rates of *t*-butyl halides.

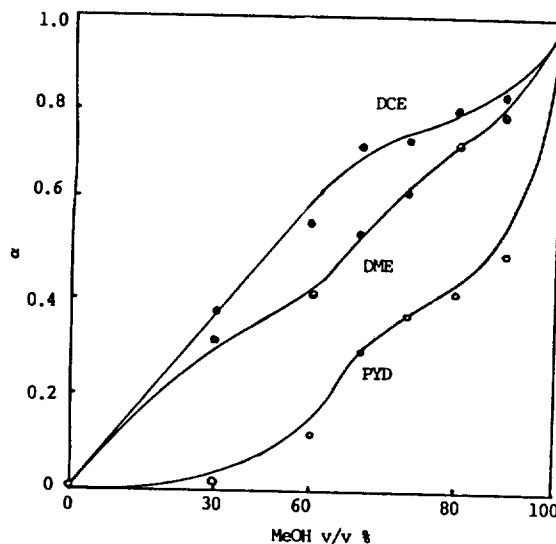
## Results and Discussion

**Solvent Parameters.** The AN scales determined for the three binary systems are shown in Table 1 and presented graphically in Figure 1. The isosolvation point ( $X_{\text{MeOH}}^{iso}$ )<sup>5</sup> at which both solvents of a binary mixture participate equally in the contact solvation shell were 0.17, 0.24 and 0.41 mole fraction methanol for MeOH-DCE, MeOH-DME and MeOH-PYD binaries, respectively. Thus the solvating ability of solvents increases in the order, DCE < DME < PYD < MeOH. Figure 1 reveals that AN decreases linearly in the dilute cosolvent region up to the cosolvent mole fraction of ca. 0.4.

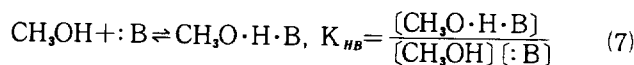
The hydrogen bonding equilibrium constants,  $K_{\text{HB}}$  in eq. 7, between methanol and cosolvents (:B) were 7.2 and 38.5  $\text{M}^{-1}$  for DME and PYD, respectively;



**Figure 1.** Variation of AN scale and isosolvation point (\*) for mole fraction of MeOH in MeOH-DME (●), MeOH-DCE (○) and MeOH-PYD (○) system, respectively.



**Figure 2.** Variation of  $\alpha$  scale with MeOH content.



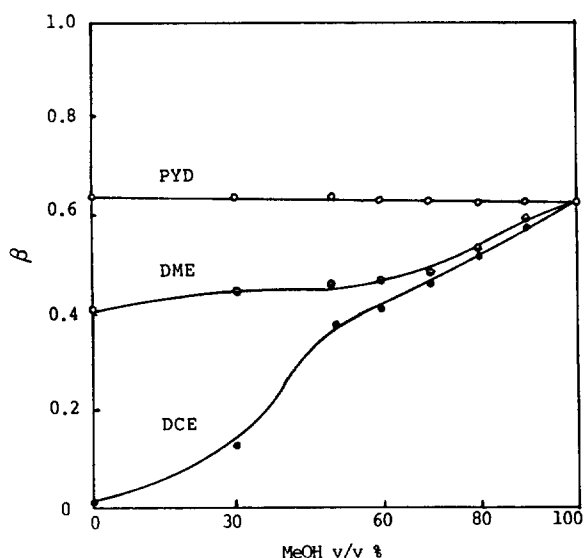
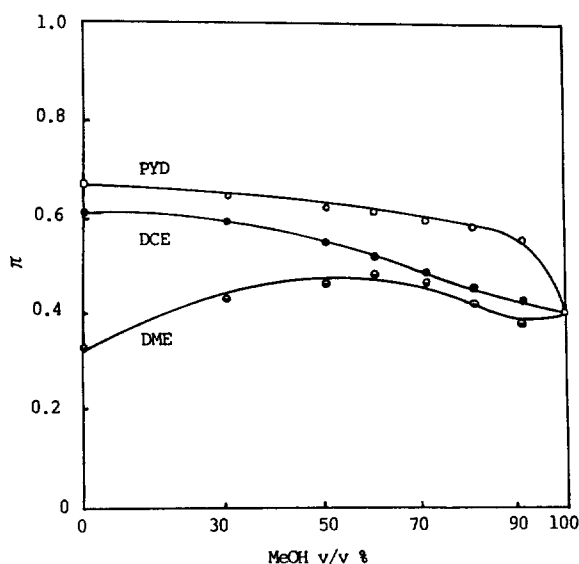
the  $K_{\text{HB}}$  value was negligible for DCE indicating that DCE acts merely as a diluent of methanol, as the very small isosolvation point (0.17) reflects. PYD is a strong hydrogen bond acceptor ( $K_{\text{HB}} = 38.5$ ) and solvating power is nearly the same as that of MeOH ( $X_{\text{MeOH}}^{iso} = 0.41$ ).

The three solvatochromic parameters,  $\alpha$ ,  $\beta$  and  $\pi^*$ , determined for the binary mixtures are summarized in Table 2, and presented graphically in Figures 2-4.

The  $\alpha$  values decrease in the order DCE > DME > PYD, indicating that scavenging of free HO-group (OH-free)<sup>6</sup> is quite effective in PYD but is negligible in DCE. The hydrogen bond donor acidity,  $\alpha$ , reflects the availability of free

**Table 2.** Solvatochromic Parameters Determined for MeOH-DME, MeOH-DCE, and MeOH-PYD Binaries

MeOH v/v%	$\alpha$			$\beta$			$\pi^*$		
	DME	DCE	PYD	DME	DCE	PYD	DME	DCE	PYD
100	0.98	0.98	0.98	0.62	0.62	0.62	0.60	0.60	0.60
90	0.79	0.83	0.50	0.59	0.57	0.62	0.59	0.63	0.76
80	0.73	0.80	0.42	0.52	0.52	0.62	0.63	0.65	0.78
70	0.62	0.74	0.37	0.48	0.46	0.63	0.68	0.69	0.80
60	0.54	0.72	0.29	0.46	0.41	0.63	0.68	0.71	0.81
50	0.41	0.56	0.12	0.46	0.38	0.63	0.66	0.75	0.82
30	0.31	0.38	0.01	0.45	0.12	0.63	0.64	0.79	0.85
0	0.00	0.00	0.00	0.41	0.00	0.64	0.53	0.81	0.87

**Figure 3.** Variation of  $\beta$  scale with MeOH content.**Figure 4.** Variation of  $\pi^*$  scale with MeOH content.

OH group in a binary mixture so that an added cosolvent, :B, reduces the OH-free concentration, and hence decreases  $\alpha$  scale, by hydrogen bonding to the free OH group of methanol, eq. 7. A strong base will scavenge more effectively the free OH group and the effectiveness will decrease with the decrease in the hydrogen bond acceptor basicity scale,  $\beta$  (Table 2), as well as with  $K_{HB}$  and  $X_{MeOH}^{iso}$ .

cosolvent:	PYD	>	DME	>	DCE
$\beta$	: 0.64		0.41		0.0
$K_{HB}$ :	38.5		7.2		0.0
$X_{MeOH}^{iso}$ :	0.41		0.24		0.17

which is exactly the reverse order of the  $\alpha$  scale. DCE is characterized by  $\alpha = \beta = 0$  so that the cosolvent DCE acts merely as a diluent of methanol. PYD being a strong base, the MeOH-PYD binary mixtures have nearly constant  $\beta$  values (Table 2 and Figure 3) in contrast to a steep decrease in  $\alpha$  scale with the PYD content.

The  $\pi^*$  scales of the DCE and PYD binaries increase with the cosolvent content, but the DME system has a sigmoid-shaped change of the  $\pi^*$  scale with an initial increase up to 40 (v/v)% addition of DME to MeOH.

The Gutmann AN may be correlated with  $\alpha$  and  $\pi^*$  scales. The multiple linear regression of the AN values with  $\alpha$  and  $\pi^*$  gave the following relations.

$$AN(DME - MeOH) = 23.18\pi^* + 13.25\alpha + 111.70 \quad r = 0.998 \quad (8a)$$

$$AN(DCE - MeOH) = 2.82\pi^* + 8.28\alpha + 28.63 \quad r = 0.991 \quad (8b)$$

$$AN(PYD - MeOH) = 2.67\pi^* + 20.62\alpha + 172.90 \quad r = 0.989 \quad (8c)$$

The  $a/s$  values (eq. 6) calculated from eqs. (8) are 0.57, 2.94 and 7.72 for DME, DCE and PYD binaries, indicating that the electron pair accepting property of the binaries (AN scale) depends more on the hydrogen bond donor acidity ( $\alpha$ ) as the polarity-polarizability scale ( $\pi^*$ ) increases in the order, DME < DCE < PYD. Thus, the AN scale is more dependent on  $\pi^*$  than  $\alpha$  for the DME binaries while it is less dependent on  $\pi^*$  than  $\alpha$  for DCE and PYD binaries.

**Solvolyse of *t*-Butyl Halides.** The first-order rate constants,  $k_1^{obs}$ , for the solvolysis of *t*-butyl halides are summarized in Tables 3-5 together with the activation parameters,  $\Delta H^*$  and  $\Delta S^*$ . The rate changes with solvent compositions are presented graphically in Figures 5-7. In all solvent binaries, rates are fastest with *t*-butyl iodide and slowest with *t*-butyl chloride (Table 3). For chloride and bromide, the rates increase in the order of increasing  $\alpha$  and AN scales, i.e., PYD < DME < DCE, whereas for iodide the

**Table 3.** First Order Rate Constants ( $k_1, s^{-1}$ ) and Activation Parameters for Solvolysis of *tert*-Butyl Halides in MeOH-DME System

Substrate	Temp.	MeOH v/v %					
		100	90	80	70	60	50
<i>t</i> -BuCl ( $k_1 \times 10^6$ )	35 °C	4.24	2.95	2.71	2.44	2.22	1.68
	45 °C	13.8	11.6	10.1	8.79	6.64	4.96
	55 °C	43.4	35.5	30.1	26.9	23.6	16.6
	$\Delta H^*$ (kcal/mol)	22.7	24.3	23.6	23.4	23.1	22.4
	$-\Delta S^*$ (e.u.)	9.4	4.5	7.0	7.8	9.4	12.2
<i>t</i> -BuBr ( $k_1 \times 10^4$ )	35 °C	1.75	1.03	0.85	0.77	0.72	0.57
	45 °C	4.97	3.15	2.57	2.46	2.35	2.25
	55 °C	15.7	11.5	8.31	7.31	6.43	5.16
	$\Delta H^*$ (kcal/mol)	21.4	23.3	22.1	21.9	21.4	21.5
	$-\Delta S^*$ (e.u.)	6.3	0.9	5.2	5.9	7.8	7.8
<i>t</i> -BuI ( $k_1 \times 10^4$ )	35 °C	4.75	4.20	4.95	5.45	5.87	—
	45 °C	15.9	14.3	15.7	16.4	17.7	—
	55 °C	47.4	40.4	43.9	47.8	50.3	—
	$\Delta H^*$ (kcal/mol)	22.7	22.2	21.3	21.1	20.7	—
	$-\Delta S^*$ (e.u.)	0.2	1.8	4.3	4.8	5.8	—

**Table 4.** First Order Rate Constants ( $k_1, s^{-1}$ ) and Activation Parameters for Solvolysis of *tert*-Butyl Halides in MeOH-DCE System

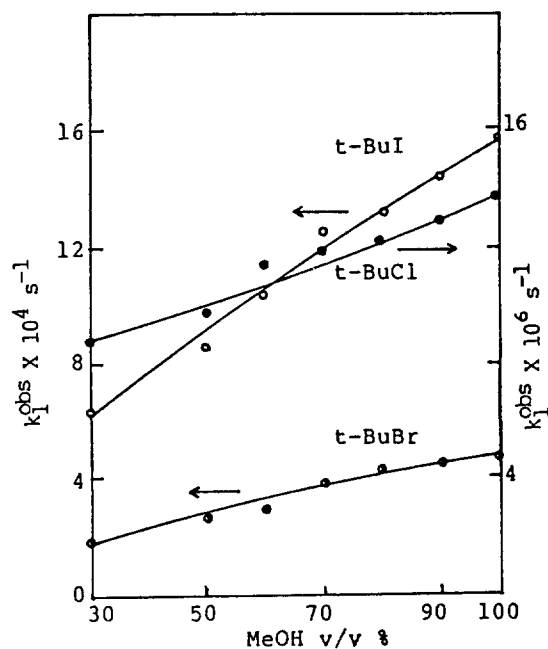
Substrate	Temp.	MeOH v/v %						
		100	90	80	70	60	50	30
<i>t</i> -BuCl ( $k_1 \times 10^6$ )	35 °C	4.24	3.96	3.89	3.78	3.64	2.95	2.72
	45 °C	13.8	12.9	12.3	11.9	11.5	9.79	8.86
	55 °C	43.4	39.3	36.9	34.5	33.6	30.2	26.8
	$\Delta H^*$ (kcal/mol)	22.7	22.4	22.0	21.6	21.7	22.7	22.3
	$-\Delta S^*$ (e.u.)	0.4	10.5	12.1	13.3	13.1	10.1	11.6
<i>t</i> -BuBr ( $k_1 \times 10^4$ )	35 °C	1.75	1.49	1.31	1.20	0.95	0.87	0.49
	45 °C	4.97	4.78	4.03	3.83	2.97	2.65	1.52
	55 °C	15.7	14.8	12.8	11.4	8.61	7.53	4.32
	$\Delta H^*$ (kcal/mol)	21.4	22.4	22.4	22.0	21.5	21.1	21.4
	$-\Delta S^*$ (e.u.)	6.3	3.3	4.2	5.1	7.1	8.8	8.7
<i>t</i> -BuI ( $k_1 \times 10^4$ )	25 °C	1.31	1.28	1.23	1.15	1.08	0.93	0.79
	35 °C	4.75	4.48	4.18	3.80	3.47	2.94	2.24
	45 °C	15.8	14.5	13.2	11.7	10.4	8.62	6.42
	$\Delta H^*$ (kcal/mol)	22.7	22.3	21.7	21.2	20.7	20.4	19.1
	$-\Delta S^*$ (e.u.)	0.2	1.6	3.5	5.3	7.3	8.6	13.2

rate order reverses for DME and DCE to DCE < DME, which is the order of the  $\beta$  scale. These suggest that for *t*-butyl-chloride and bromide, the first stage in eq. 1 ( $k_1$ ) is important whereas for iodide the second stage ( $k_2$ ) becomes more important in determining the rate since the ion-pair formation step is largely dependent on the electrophilic solvent assistance of the protic solvent toward the leaving group, halide, but the ion pair dissociation step requires nucleophilic assistance of solvent toward the *t*-butyl cation as well. However, Figures 5–7 reveal that the rates for the three halides in DCE-MeOH binaries increase slowly and almost linearly with the methanol content, whereas the rate increases in PYD-MeOH binaries are more steep and curved upward. These are in line with the nearly linear increases in  $\alpha$  and  $\beta$  scales in DCE-MeOH but a steep, curved increase in  $\alpha$  in PYD-MeOH with the near constant  $\beta$ .

The rates of *t*-butyl chloride and bromide solvolyses in DME-MeOH increase somewhat more steeply with the methanol content than in DCE-MeOH, which is again consistent with the major influence of  $\alpha$  on the rate (Figure 2). Strikingly, however, the rate of *t*-butyl iodide solvolysis in DME-MeOH decreases with the increase in the methanol content, closely following the increasing trend of  $\pi^*$  scale (up to 60% MeOH in Figure 4). This suggests that for *t*-butyl iodide the rate determining step changes to the second stage ( $k_2$ ), since the ion-pair stability will be dependent on the  $\pi^*$  scale so that the ion-pair association from the more stabilized ion-pair will lead to a greater  $k_2$  relative to  $k_3$ , satisfying the condition of eq. 4. In comparison with the DCE binaries, the DME binaries has lower  $\pi^*$  scale so that the stability of the ion-pair will be less in the latter mixtures and hence  $K_{12}(\text{DME}) < K_{12}(\text{DCE})$  but due to the greater stability of the

**Table 5.** First Order Rate Constants ( $k_1, s^{-1}$ ) and Activation Parameters for Solvolysis of *tert*-Butyl Halides in MeOH-PYD System

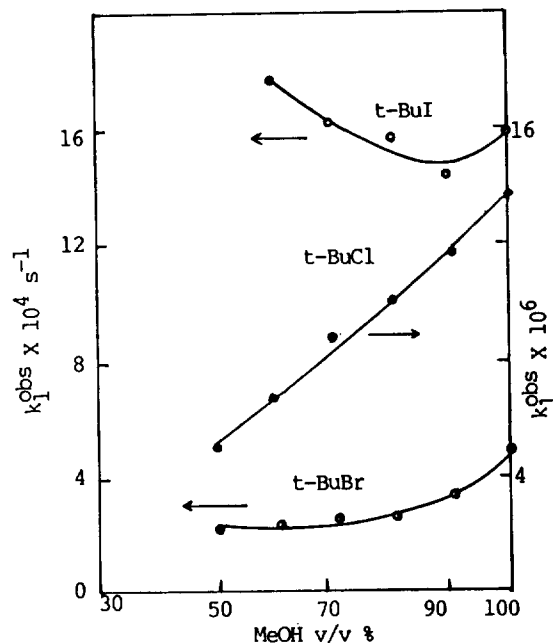
Substrate	Temp.	MeOH v/v %						
		100	90	80	70	60	50	30
<i>t</i> -BuCl ( $k_1 \times 10^6$ )	45 °C	13.8	8.25	6.18	3.69	2.88	—	—
	50 °C	27.1	16.9	11.2	6.82	4.72	—	—
	55 °C	43.4	28.9	18.9	11.6	8.65	—	—
	$\Delta H^*$ (kcal/mol)	22.7	25.4	22.6	23.2	22.2	—	—
<i>t</i> -BuBr ( $k_1 \times 10^4$ )	35 °C	1.75	1.01	0.76	0.52	0.39	0.29	0.13
	45 °C	4.97	3.36	2.41	1.75	1.28	0.86	0.44
	55 °C	15.7	10.5	7.44	5.71	3.94	2.73	1.22
	$\Delta H^*$ (kcal/mol)	21.4	22.9	22.3	23.4	22.5	20.7	22.0
<i>t</i> -BuI ( $k_1 \times 10^4$ )	35 °C	4.75	3.66	3.14	2.63	2.26	1.95	1.27
	45 °C	15.8	12.9	10.2	9.33	7.82	6.57	4.09
	55 °C	47.4	38.3	32.3	27.1	21.2	18.0	11.8
	$\Delta H^*$ (kcal/mol)	22.7	23.0	22.8	22.8	21.9	21.7	21.8
$-\Delta S^*$ (e.u.)	0.2	0.2	0.7	0.9	4.2	5.1	5.7	

**Figure 5.** Variation of  $k_1^{obs}$  with solvent composition at 45.0 °C in MeOH-DCE binaries.

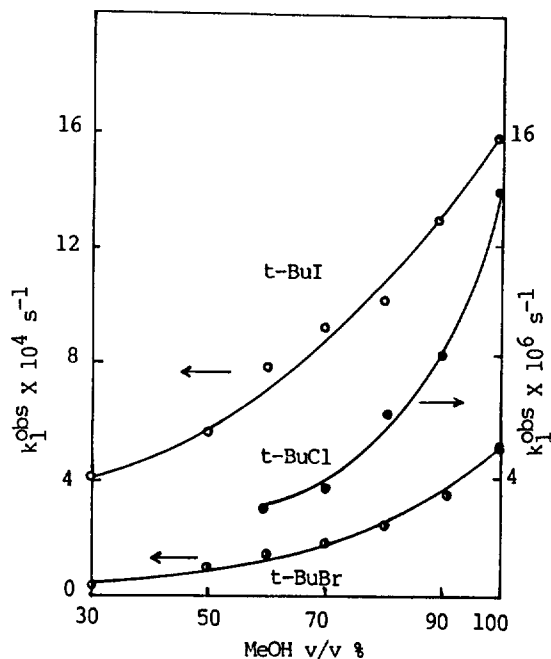
intermediate the barrier height of the second TS ( $k_2$ ) will become higher and hence  $k_3$  will be smaller, *i.e.*,  $k_3(\text{DME}) > k_3(\text{DCE})$ , as we observed ( $k_1^{obs}$ ) for the *t*-butyl iodide solvolysis in DME and DCE binaries (*vide supra*).

We have correlated  $\log k_1^{obs}$  with AN and the results are shown in Table 6.

The rate dependence on AN, *i.e.*, the coefficient  $\rho$ , indicates that the slower the rate the greater is the  $\rho$  value for *t*-butyl chloride and iodide in the three binaries; the  $\rho$  values are in the order, DCE < DME < PYD for chloride and DME < DCE < PYD for iodide, which are exactly the reverse order of  $k_1^{obs}$ . This is reasonable since the slower the rate is, the rate will be more dependent on the rate controlling factor which is

**Figure 6.** Variation of  $k_1^{obs}$  with solvent composition at 45.0 °C in MeOH-DME binaries.

the hydrogen bond donating ability ( $\alpha$ ) of solvent in the case of *t*-butyl chloride whereas it is the polarizing ability of solvent ( $\pi^*$ ), *i.e.*, stabilization of ion pair, (I), in the solvolysis of *t*-butyl iodide. The order DME < DCE < PYD is exactly the reverse order of the importance of  $\pi^*$  relative to  $\alpha$  in AN, which can be expressed as  $s/a$ ; the  $s/a$  values are 1.75, 0.34 and 0.13 for DME, DCE and PYD, respectively. These two halides constitute two extremes of the two stage mechanism, (1); for *t*-butyl chloride the first stage,  $k_1$ , is rate-limiting, whereas for iodide the second stage,  $k_3$ , is rate-limiting. The bromide provides an intermediate case, so that  $k_2 \approx k_3$  and the rate is also determined by the first step, with the half value of  $k_1$ .



**Figure 7.** Variation of  $k_1^{obs}$  with solvent composition at 45.0 °C in MeOH-PYD binaries.

**Table 6.** Correlation of Observed First Order Rate Constants,  $k_1^{obs}$ , with Acceptor Number, AN,  $\log k_1^{obs} = \rho AN + \delta$ , for solvolysis of *t*-butyl X in MeOH-Cosolvent binary mixtures

Cosolvent	X	$\rho$	$\delta$	(s/a)*	r(corr. coeff.)
DCE	Cl	0.50	72.90	0.34	0.967
	Br	1.33	88.45		0.994
	I	0.40	64.92		0.996
DME	Cl	0.76	83.33	1.75	0.965
	Br	0.95	74.86		0.958
	I	-0.28	22.71		0.954
PYD	Cl	1.49	105.91	0.13	0.993
	Br	0.98	75.12		0.985
	I	0.49	52.67		0.987

\*From eqs. (8). Reverse of  $a/s$ .

$$k_1^{obs} = \frac{1}{2} k_1$$

The solvatochromic correlations of  $\log k_1^{obs}$  vs.  $\alpha$ ,  $\beta$  and  $\pi^*$ , in eq. 6' were applied to the solvolysis data in the three binary systems (Table 7).

$$\log k_1^{obs} = a\alpha + b\beta + s\pi^* + \text{const} \quad (6')$$

For each binary system, only 5-6 solvent compositions are available, and as a result the correlations expressed as multiple linear correlation coefficient ( $r$ ) are only fair; we can not therefore attach much significance to the results obtained.

However in each binary system, the size of "a" is always the greatest with chloride indicating large electrophilic assistance by hydrogen bonding to the leaving group chloride at the TS. Strong scavenging of OH-free by PYD in PYD-MeOH binaries is reflected in large negative  $b$  values.

**Table 7.** Solvatochromic Correlations of  $\log k_1^{obs}$  vs.  $\alpha$ ,  $\beta$ , and  $\pi^*$  (eq. 6')

	X	Temp.	$a$	$b$	$s$	$r$
DME	Cl	35 °C	0.65	0.63	1.18	0.999
	Br	35 °C	0.23	3.48	3.47	0.994
	I	35 °C	0.17	-0.27	1.39	0.975
DCE	Cl	35 °C	0.40	-0.13	-0.20	0.978
	Br	35 °C	0.01	0.91	-0.49	0.997
	I	35 °C	0.12	0.33	-0.56	0.994
PYD	Cl	45 °C	-0.79	-59.9	-3.25	0.999
	Br	45 °C	0.77	-47.9	1.68	0.994
	I	45 °C	0.51	-22.5	1.09	0.979

## Experimental

**Instruments and Materials.** Bruker 300 MHz FT-NMR, FT-IR and Shimadzu UV/Vis spectrophotometer (Model 150), and Barnstead/Sybron conductivity bridge were used. Solvents, methanol (MeOH, Merk), 1,2-dimethoxyethane (DME, Fluka), 1,2-dichloroethane (DCE, Aldrich), hexane (Merk) and  $\text{CCl}_4$  (Merk) were GC grade, Triethylphosphine oxide ( $\text{Et}_3\text{PO}$ , Alpha), diphenylphosphinic chloride ( $(\text{C}_6\text{H}_5)_2\text{POCl}$ , Alpha) and methanol-*d* (MeOD, Fisher) were NMR grade. 1-ethyl-*p*-nitrobenzene (EPN), *N,N*-dimethyl-*p*-nitroaniline (DMPN), *p*-nitroanisole (PNA), and *p*-nitrophenol (PNP) were Wako GR grade. *t*-butyl halides (*t*-BuCl, *t*-BuBr, *t*-BuI) were Tokyo Kasei GR grade.

**Measurement of  $^{31}\text{P}$  chemical shift and AN scale<sup>7</sup>.** External lock material was MeOD.  $(\text{C}_6\text{H}_5)_2\text{POCl}$  was used for reference peak. CPD program was used for protecting spin-spin coupling. Parameters for exact peak were 1 for line broadening, 15 for pulse width, and 10 for delay time.  $^{31}\text{P}$  chemical shift spectra were measured in three concentration of  $\text{Et}_3\text{PO}$  and AN scales were calculated by means of least square method.<sup>7</sup>

**Hydrogen bonding equilibrium constant<sup>7</sup>.** The molar absorptivity ( $\epsilon$ ) was calculated by the slope of plotting absorbances of free OH peak against four concentrations of MeOH, which were 0.75, 1.25, 1.86 and  $2.50 \times 10^{-2}$  M in  $\text{CCl}_4$ . And these were sampled in IR NaCl cell of which path length was 1 mm. When MeOH ( $[A_0] = 2.5 \times 10^{-2}$ ) formed hydrogen bonding complexes ( $[C] = [A_0] - [A]$ ) with DME, DCE and PYD which were diluted as 1.86, 2.50, 4.00, 4.50 and  $7.00 \times 10^{-2}$  M of  $[B_0]$ , the equilibrium constants  $K_{\text{HB}}$  were calculated by equation 9. The concentration  $[A]$  was obtained through multiplying molar absorptivity by the absorbance of free OH peak which did not form complex.

$$K_{\text{HB}} = \frac{[C]}{[A]([B_0] - ([A_0] - [A]))} \quad (9)$$

**Measurement of UV/Vis spectral data and solvatochromic parameters.<sup>7</sup>** The absorbances ( $\lambda_{\text{max}}$ ) for EPN of  $2 \sim 3 \times 10^{-3}$  M were converted in terms of  $\nu_{\text{max}}$ . Solvatochromic parameters for different contents of MeOH in MeOH-DME, MeOH-DCE and MeOH-PYD system were calculated by means of solvatochromic comparison

method<sup>8-10</sup> using EPN, DMPN, PNA and PNP.

$$\nu = \nu_0 + s\pi^* + a\alpha + b\beta \quad (10)$$

**Kinetic procedures**<sup>7</sup>. Rates of solvolysis for tert-butyl halides in these systems were measured at 35, 45 and 55 °C by conductivity method, and rate constants  $k_1^{obs}$  were determined by the Guggenheim equation.<sup>11</sup> Activation parameters were calculated as described in the previous report.<sup>12</sup>

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## Electrochemical and Spectrophotometric Studies on Polyaniline and its Degradation

Jung-Kyoon Chon\* and Byung-Hoon Min

Department of Chemistry Hankuk University of Foreign Studies, Seoul 130-791

Woon-Kie Paik

Department of Chemistry, Sogang University, Seoul 121-742. Received October 4, 1989

A spectroelectrochemical study on the redox chemistry of polyaniline (PANI) was carried out by using indium-thin oxide (ITO) transparent electrode in aqueous acidic solutions. Three different PANI-derived species were observed depending on the potential. The most highly oxidized species having alternating benzenoid-quinoid structures degraded through hydrolysis reaction. The degradation products were confirmed to be *p*-benzoquinone (BQ) and *p*-diaminobenzene (PDAB) by spectrophotometry and potentiostatic experiments. Finally, a degradation mechanism is deduced from the observed behaviour.

### Introduction

Recently interests in polyaniline (PANI) as a conducting polymer have been increasing rapidly.<sup>1-12</sup> Possible applications of PANI include use in electrochromic<sup>2</sup> and microelectronic devices,<sup>3</sup> in stabilizing photoelectrodes and protecting metals,<sup>4-6</sup> in ion exchange<sup>7</sup>, and in organic batteries.<sup>8,9</sup> However, there are few reports concerning the spectroscopic properties and the electrochemical degradation of PANI-film.<sup>10-12</sup>

Kobayashi *et al.*<sup>10</sup> reported that *p*-benzoquinone (BQ) is a degradation product on the basis of spectral data taken through PANI-film. They also suggested that two redox reactions were involved in the electrochromic reaction of

PANI.<sup>10</sup> Stilwell and Park<sup>11</sup> proposed a degradation scheme, based on their coulometric and spectrophotometric experiments. They suggested that the degradation process proceeds via hydrolysis of the oxidized species of PANI, pernigraniline, resulting in the production of *p*-benzoquinone. In another report<sup>12</sup> they assigned the spectra obtained from reduced PANI to  $\pi-\pi^*$  transition of the aromatic (benzene B band) structure, and those from oxidized PANI to the band of free electron carriers (delocalized radical cations).

In this paper spectroelectrochemical measurements using transparent indium-tin-oxide (ITO) electrode, and conventional cyclic voltammetric and spectrophotometric experiments are reported. The species of PANI appearing at various applied potentials were confirmed and the degrada-