

# Ion Selectivity of a Polypyrrole Coated Pt Electrode for Hydronium Ion

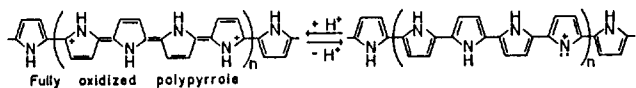
Jin-Doo Kim, Keun-Sun Lee, and Kang-Jin Kim\*

Department of Chemistry, Korea University, Seoul 136-701. Received October 17, 1988

Interests in polypyrrole (PPy) as an organic conducting polymer have been increasing rapidly because PPy can enhance the stability of photoelectrodes used in converting solar energy to electrical or chemical energy.<sup>1-5</sup> Relatively a few applications have employed the PPy modified electrode as potentiometric sensors.<sup>6</sup> However, the applications have been limited to anions, although there are some reports concerning the applications to cations using different polymers.<sup>7</sup>

This paper reports the first use of a PPy electrochemically modified Pt electrode as a potentiometric sensor for hydronium ion. Some electrochemical behaviors of the PPy coated Pt electrode are compared with those of a typical glass electrode.

Figure 1 compares a typical potentiometric response of the PPy coated Pt electrode with that of a representative glass electrode, Horiba model 6326, over a pH range of about 2 to 12. Under the condition both of the potentiometric responses to hydronium ion are nearly Nernstian with slopes of 59.9 and 58.7 mV, respectively, for the PPy modified Pt electrode and the glass electrode. The cause of the potential response is not clear at present, but it appears that a protonation-deprotonation equilibrium of the acidic proton in the oxidized PPy as illustrated in Scheme 1 may be responsible. Further investigation is needed to clarify the detailed mechanism.



Scheme 1.

The slope of potential response measured over the same pH range as above remained fairly constant with the increase of ionic strength from 0.010 M to 0.30 M as summarized in

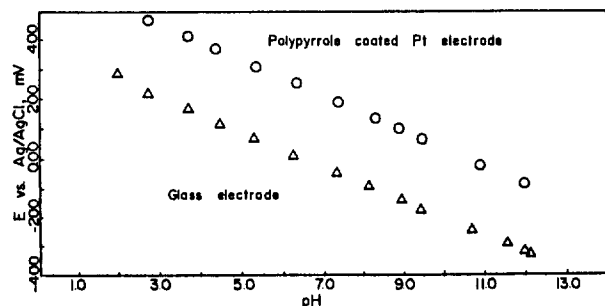


Figure 1. Hydronium ion response of electrodes vs. pH.

Table 1. Nernstian Slopes and Response Times for PPy Coated Pt Electrode at Various Ionic Strengths

Ionic strength, M	0.010	0.020	0.040	0.080	0.15	0.30
Nernstian slope, mV	-60.0	-60.0	-60.8	-60.2	-60.2	-60.5
Response time, sec	190	240	310	420	460	500

Table 2. Selectivity Coefficients of Li<sup>+</sup>, Na<sup>+</sup>, and K<sup>+</sup>

Cation	Li <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>
PPy coated Pt	6.3E-3	1.5E-5	9.3E-6
Glass electrode	1.0E-2	8.0E-5	1.4E-5

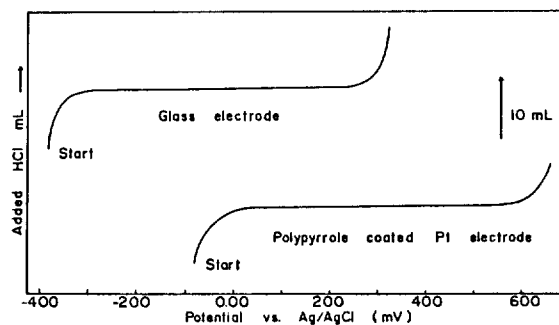


Figure 2. Titration curves for 10 ml of 0.10 M NaOH with 0.10 M HCl.

Table 1.

The increase of response time (Table 1) of the PPy modified electrode monitored at various pH with the increase of ionic strength suggests that the more ions are incorporated into the polymer film, the longer it takes to become equilibrated.

The stability of the PPy modified electrode was tested by measuring potential in a buffer solution of pH = 6.0. The electrode stored in distilled water was found to be stable at least for 14 days without change in potential within experimental error.

In addition to hydronium ion, the PPy coated Pt electrode responded to monovalent cations. The selectivity coefficients of some interfering cations against those of the glass electrode utilized here were measured over a range of concentration ratio of [Cation]/[H<sub>3</sub>O<sup>+</sup>] from about 3 × 10<sup>-2</sup> to about 8 × 10<sup>4</sup> and the results are listed in Table 2. It is noted that the selectivity coefficients of Li<sup>+</sup>, K<sup>+</sup>, and Na<sup>+</sup> for the PPy coated Pt electrode are only 0.63, 0.66, and 0.19, respectively, of those for the glass electrode.

Finally the PPy modified electrode was evaluated as an indicator electrode for a potentiometric titration of 10.0 ml of 0.10 M NaOH with 0.10 M HCl by a Mettler 610 autotitrator. Figure 2 demonstrates that the abruptness of the inflection near the equivalent point with the PPy coated electrode is essentially the same as that with the glass electrode.

It may be concluded that the PPy coated Pt electrode is almost comparable with a typical glass electrode in potentiometric response and has better selectivity coefficients for Li<sup>+</sup>, K<sup>+</sup>, and Na<sup>+</sup>.

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## References

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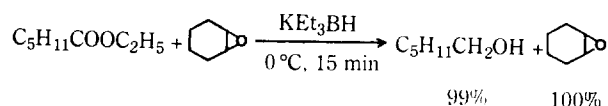
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## Chemoselective Reduction of Lactones with Potassium Tri-*s*-butylborohydride

Nung Min Yoon\*, Young Soo Hwang, and Ho Seok Yang

*Department of Chemistry, Sogang University Seoul 121-742. Received October 17, 1988*

Carboxylic acids esters are readily reduced to the corresponding alcohols with lithium aluminum hydride<sup>1</sup> (LiAlH<sub>4</sub>), diisobutylaluminum hydride<sup>2</sup> (DIBAH), and lithium triethylborohydride<sup>3</sup> (LiEt<sub>3</sub>BH). However these are so strong reducing agents that the chemoselectivity of ester function in the presence of other functionalities can not be expected. Recently we have found that potassium triethylborohydride (KEt<sub>3</sub>BH) is an excellent chemoselective reducing agent for esters<sup>4</sup> in the presence of epoxides, nitriles or amides.



These results intrigued us to explore the chemoselectivity of potassium tri-*s*-butylborohydride<sup>5</sup> (K*s*-Bu<sub>3</sub>BH), a bulkier borohydride, towards organic functionalities. We now wish to report such chemoselectivity of the reagent for lactones in the presence of other functional groups.

Chemoselective reduction of lactones with K*s*-Bu<sub>3</sub>BH was studied by competitive reaction. Thus an equimolar mixture of a lactone and other substrate containing more common functional groups such as ester, epoxide, amide etc. was reacted with 2.1 mole equivalents of K*s*-Bu<sub>3</sub>BH at 0°C for 5 min. The results are excellent as shown in Table 1.

**Table 1. Chemoselective Reduction of Lactones with K*s*-Bu<sub>3</sub>BH in Tetrahydrofuran at 0°C<sup>a</sup>**

entry	compounds	product	yield <sup>b</sup> (%)
1	γ-butyrolactone	1,4-butanediol	99
	ethyl caproate	ethyl caproate	96
2	γ-butyrolactone	1,4-butanediol	100
	ethyl benzoate	ethyl benzoate	95
3	γ-valerolactone	1-methyl-1,4-	93.2
	ethyl benzoate	butanediol	
4	α-methyl-γ-butyrolactone	ethyl benzoate	90
		2-methyl-1,4-	96
		butanediol	

	ethyl benzoate	ethyl benzoate	92
5	δ-valerolactone	1,5-pentanediol	96.3
	ethyl benzoate	ethyl benzoate	93.4
6	phthalide	phthalyl alcohol	100
	ethyl benzoate	ethyl benzoate	99
7 <sup>c</sup>	γ-butyrolactone	1,4-butanediol	88
	ethyl benzoate	ethyl benzoate	86
8 <sup>d</sup>	γ-butyrolactone	benzyl alcohol	10
		1,4-butanediol	30
	ethyl benzoate	ethyl benzoate	74
		benzaldehyde	10.3
9	γ-butyrolactone	1,4-butanediol	99
	styrene oxide	styrene oxide	100
10	γ-butyrolactone	1,4-butanediol	99
	cyclohexene oxide	cyclohexene oxide	99.8
11	γ-butyrolactone	1,4-butanediol	99
	N,N-dimethylcaproamide	N,N-dimethylcaproamide	99
12	γ-butyrolactone	1,4-butanediol	99
	capronitrile	capronitrile	99.8
13	γ-butyrolactone	1,4-butanediol	99
	1-chlorooctane	1-chlorooctane	99
14	γ-butyrolactone	1,4-butanediol	97
	decene	decene	100

<sup>a</sup> A mixture of one mmol each of lactone and other substrate was reacted with 2.1 mmol of K*s*-Bu<sub>3</sub>BH at 0°C for 5 min. <sup>b</sup> Yields were estimated by GLC. <sup>c</sup> Reaction with KEt<sub>3</sub>BH. <sup>d</sup> Reaction with DIBAH.

As shown in entry 1 and 2, γ-butyrolactone can be selectively reduced in the presence of either aliphatic ester (*i.e.* ethyl caproate) or aromatic ester (*i.e.* ethyl benzoate). And other representative lactones such as γ-valerolactone, α-methyl-γ-butyrolactone, δ-valerolactone and phthalide are also reduced with excellent chemoselectivity (entry 3-6). To the best of our knowledge, there have been no report of such selective reduction. We also undertook the competitive re-