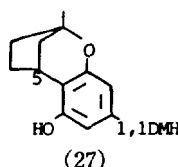


5.57 (1H, brs)  
4.49 (1H, br)  
6.33 (2H, s)

73



3.32 (1H, br)  
6.84 (1H, brs)  
6.99 (1H, d,  $J=6$  Hz)

91

\*Spectra were determined on a Bruker WH-60 spectrometer in deuteriochloroform. Values given in ppm relative to tetramethylsilane as internal standard. Numbers in parentheses determined by integration of areas. Letters in parentheses denote singlet (s); doublet (d); broad (br); and multiplet (m).

structural elucidation of new alkylation products.

The preparation and structural proof for the new compounds 8, 9, 10, 11, 14, 15, 17, 22, 23, 25, 26, 27 will be reported in a forthcoming paper.<sup>12</sup> The other substance 12, 13, 16, 18, 19, 20, 21, 24 were reported.<sup>13</sup>

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## Spectroelectrochemical Behavior of Polypyrrole Coated on SnO<sub>2</sub> in Aqueous Solutions

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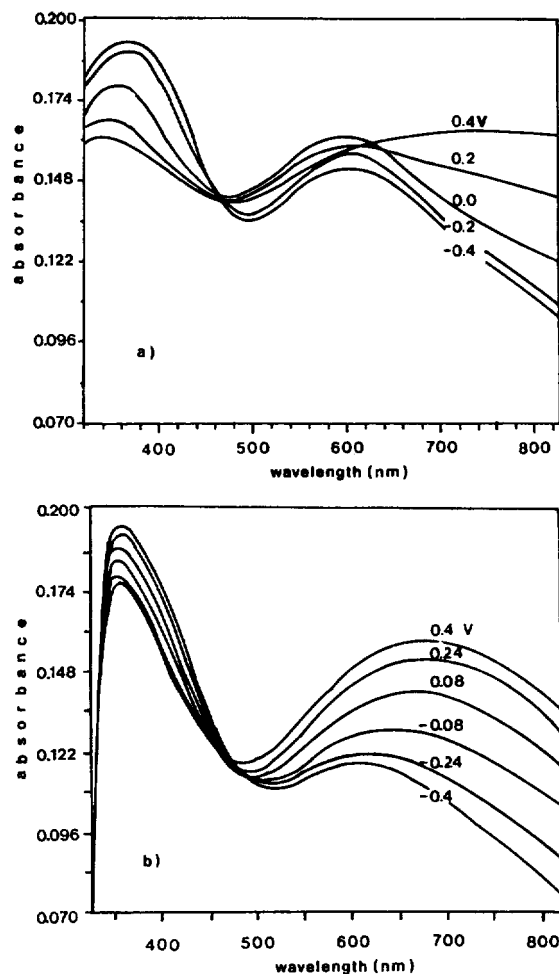
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Polypyrrole (PPy) has received a great deal of attention because of its good electrical conductivity, ability to enhance the stability of photoelectrodes, and interesting redox properties<sup>1-3</sup>. Modified electrodes with PPy have been applied as potentiometric sensors<sup>4</sup>. The response behavior of those sensors would be closely related to the chemical status of the pyrrolylium nitrogens, the nature of doping anions as well as the interaction between pyrrolylium nitrogen and doping anions<sup>5</sup>.

Accordingly, it is important to obtain a better understanding of the electrochemical nature of the PPy and its interaction with anions. In this connection, it is appropriate to compare the chemical structures corresponding to various oxidation states of PPy. In this paper we report the spectroelectrochemical studies on the formation of radical cations (or polarons) and dications (or bipolarons) in PPy for the first time as a function of potential cycling and the reaction of the cations with OH<sup>-</sup>.

Figure 1a and 1b show a series of absorption spectrum changes of the PPy film at various stage of oxidation on a working electrode immersed in a 1.0 cm×1.0 cm absorption cell at pH 2 and pH 12, respectively. The PPy coated working electrode was prepared on SnO<sub>2</sub> from an aqueous solution containing 50 mM pyrrole and 1.0 M HNO<sub>3</sub> using cyclic voltammetry as described previously<sup>3</sup>. During the absorbance measurements the potential was applied continuously in the range from -0.4 V to 0.4 V at 5 mV/sec with a Princeton Applied Research Model 273 potentiostat/galvanostat. All the potentials given here are referred to a Ag/AgCl electrode. The transparent SnO<sub>2</sub> on glass coated with PPy film was placed in a spectrochemical cell fixed in a rapid scan Hewlett Packard 8542A diode array spectrophotometer. The absorptrum of the PPy film was recorded instantaneously in the wavelength range from 300 nm to 800 nm at a certain applied potential.

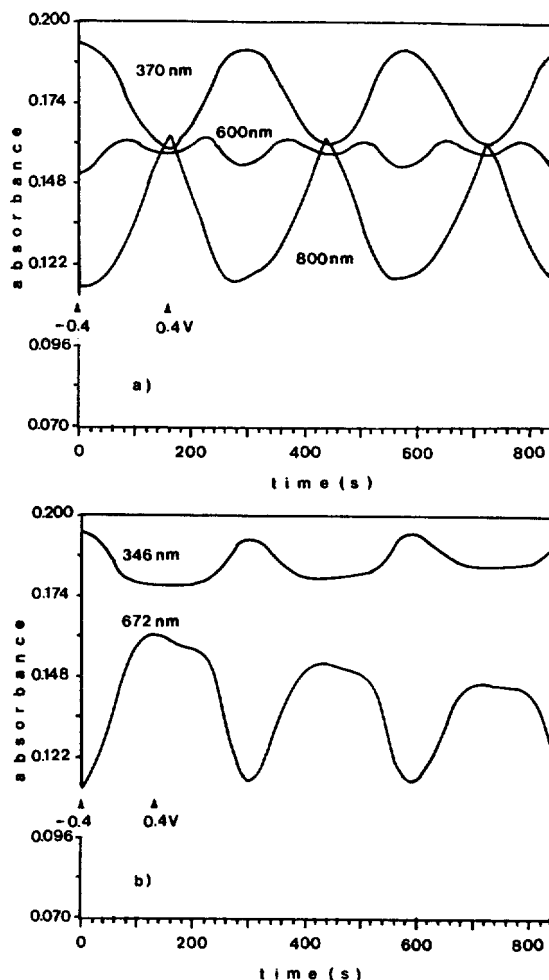
Similar spectral changes of PPy film as shown in Figure



**Figure 1.** A series of absorption spectra of PPy coated  $\text{SnO}_2$  electrode at various applied potentials vs Ag/AgCl in aqueous 1.0 M  $\text{KNO}_3$  adjusted to (a) pH 2 and (b) pH 12 with  $\text{HNO}_3$ , respectively.

1a under different conditions were obtained by Zotti and Schiavon<sup>5</sup>, Amemiya *et al.*<sup>7</sup>, and Genies and Pernaut<sup>8</sup>. At  $-0.4$  V, PPy exists as reduced form. As can be seen in Figure 1a, the reduced PPy displays a maximum absorption around 370 nm. This absorption was assigned to a  $\pi \rightarrow \pi^*$  transition from the valence band to the conduction band of PPy<sup>9</sup>. The band developed around 600 nm was assigned to a transition from valence band to higher polaron level, while fully oxidized form at 0.4 V shows a broad absorption around 800 nm which is mostly involved with the transition from valence band to bipolaron states<sup>6,9</sup>. The observed isosbestic points at about 460 nm and 630 nm are not very well defined, indicating that the oxidation and reduction in the PPy films cannot be represented by equilibrium reactions among neutral PPy's, polarons, and bipolarons<sup>7</sup>.

In the alkaline solution absorption behavior shows a few differences (Figure 1b). First of all, the absorption peak close to 346 nm, which can be identified as a  $\pi \rightarrow \pi^*$  transition<sup>9</sup>, shifted to higher energy. This shift may reflect a decrease in the length of conjugated electronic system in PPy<sup>10</sup>. Secondly, a decrease in the absorbance around 700 nm was accompanied by almost complete disappearance of the absor-



**Figure 2.** Absorbance vs potential (scan rate, 5 mV/sec) at PPy coated  $\text{SnO}_2$  electrode during the potential cycling between  $-0.4$  V to 0.4 V (initiated at  $-0.4$  V) in 1.0 M  $\text{KNO}_3$  adjusted to (a) pH 2 and (b) pH 12 with  $\text{HNO}_3$ , respectively.

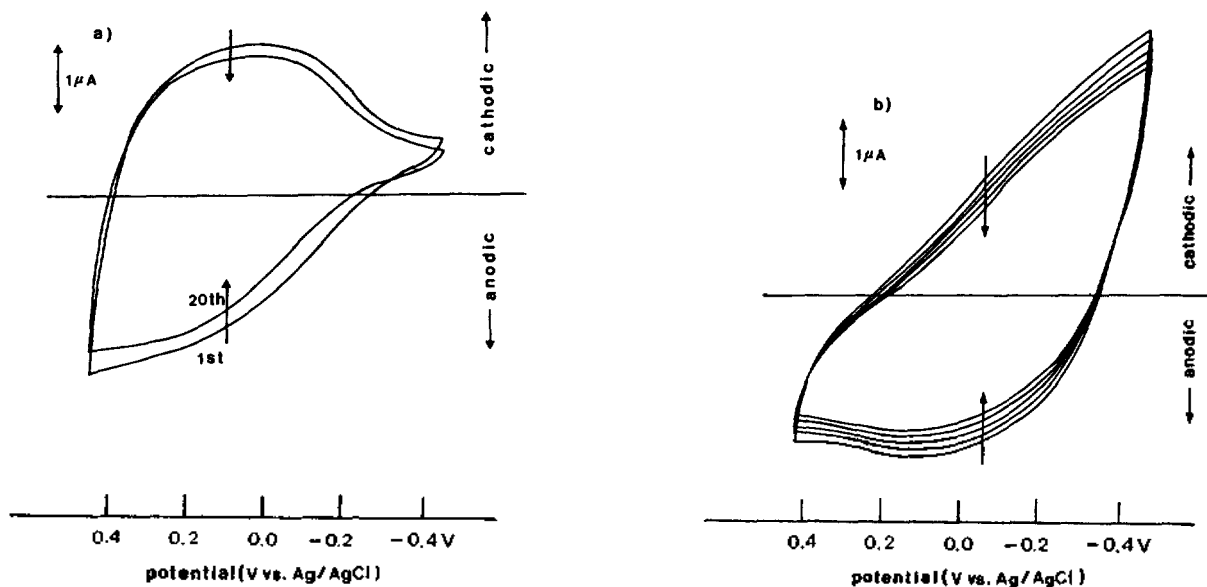
bance near 800 nm and a smaller increase of the 346 nm peak than those in pH 2 upon gradual reduction. And lastly, no isosbestic point was observed around 600 nm.

Figure 2a and 2b show the variation of absorbance on the cyclic voltage scan, where a ramp at 5 mV/sec was applied over the range from  $-0.4$  V to 0.4 V and then reversed to the initial voltage,  $-0.4$  V.

In Figure 2a the absorbance behaviors at three wavelengths were reproducible for several scans and little degradation was observed at pH 2. At  $-0.4$  V, the absorption of neutral PPy predominates. At 0.4 V, the oxidized PPy at 800 nm has the maximum. Inbetween these potential limits the absorbance at 600 nm, for example, exhibits two local band maxima. These periodic behaviors demonstrate that upon gradual application of potential anodically some neutral PPy first became radical cations (or polarons), and then dications (or bipolarons) as represented by<sup>8</sup>:



On the backward scan dications were quite reversibly re-

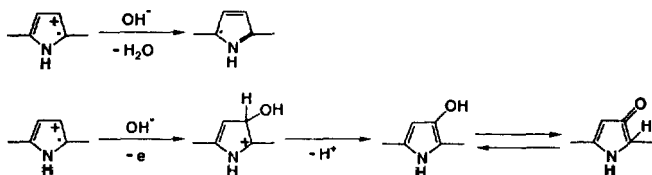


**Figure 3.** Repeated cyclic voltammograms of polypyrrole coated  $\text{SnO}_2$  in aqueous 1.0 M  $\text{KNO}_3$  adjusted to (a) pH 2 and (b) pH 12 with  $\text{HNO}_3$  respectively.

duced to neutral PPys *via* radical cations.

The absorbance behavior at pH 12 was, however, not entirely reproducible as typically shown in Figure 2b. The absorbance at 672 nm responsible for oxidized PPy near 0.4 V became broader in comparison with that in Figure 2a and decreased continuously, while the minimum at 346 nm became shallower as the potential cycle was repeated. The broadening is possibly due to the overlapping by the transitions of different species which were possibly formed by the reaction with  $\text{OH}^-$ . Hitherto two reactions with  $\text{OH}^-$  have been proposed. In alkaline solution,  $\text{OH}^-$  ions may react with radical cations as shown below, Eq. (3), and thus the production of diradical cations apparently remained minimal even at 0.4 V, because the remaining electron combines with a hole to result in a smaller number of charge carriers<sup>10</sup>. This is supported by the result that the conductivity of PPy can be decreased 3-4 orders of magnitude by the treatment with strong bases<sup>10</sup>. The loss of isosbestic point in Figure 1b can also be interpreted by the diminished formation of diradical cations under alkaline condition.

The other possibility is that  $\text{OH}^-$  ions directly combine with the radical cations to form pyrrolidinone end groups according to Eq. (4)<sup>11,12</sup>.



Thus some of cations seem disappeared irreversibly by the reaction with  $\text{OH}^-$ , which explains that the initial concentration of neutral PPy was not restored when the potential was brought back to  $-0.4$  V (Figure 2b). The present absorption study appears to support the latter possibility. However, further investigations should be necessary to clarify the subtle differences.

Finally, the different behavior of PPy in alkaline solution was further examined by the cyclic voltammograms shown Figure 3a and 3b. The currents decreased by 17% at pH 12 after 5 cycles compared with the decrease by only 8% at pH 2 even after 20 cycles. Furthermore, the cyclic voltammograms showed larger reduction currents at pH 12 (Figure 3b), indicating there possibly exist different reducible species. These voltammetric results possibly demonstrate that PPy in alkaline solutions were degraded faster due to the electrooxidation followed by the reaction with  $\text{OH}^-$  and the reaction products apparently contributed to the reduction currents of PPy as suggested above.

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## Reactivity and Mechanism of the Reactions Involving Carbonyl Ylide Intermediate

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The stereoselective reactions of highly substituted oxygen heterocycles, especially tetrahydrofuran complex and tetrahydropyran derivatives, have attracted considerable attention in recent years.<sup>1</sup> Conceptually tetrahydrofuran formation seems to be proceeded by the 1,3-dipolar cycloaddition of carbonyl ylides with  $\pi$ -bonds.<sup>2</sup> The carbonyl ylides are generated usually by the methods of thermolysis or photolysis of epoxides possessing electron-withdrawing substituents,<sup>3</sup> the thermal extrusion of nitrogen from 1,3,4-oxadiazolines,<sup>4</sup> and the loss of carbon dioxide from 1,3-dioxolan-4-ones.<sup>5</sup> One of the simplest routes for the generation of carbonyl ylides involves the addition of a carbene or carbenoid onto the oxygen atom of a carbonyl group. This can be readily achieved by the transition metal catalyzed decomposition of a diazo ketone in the presence of a carbonyl group (Scheme 1).

In recent years, a widespread application of carbonyl ylides to new synthetic transformation has occurred.<sup>2</sup> This research has been stimulated the chemists' interest in the use of carbenes and carbenoids as reactive intermediates for the gen-

eration of other types of ylides.<sup>6</sup> Even though many studies have been reported for the intermediates of carbonyl ylides in the reactions of carbenes with a carbonyl oxygens,<sup>7</sup> the reactions are limited to the discussion of the transition metal catalyzed decomposition of a diazo compounds in the presence of a carbonyl group.

In this paper we report the reactivity and mechanism of the reactions involving carbonyl ylide intermediate from the photolytic kinetic results of non-catalytic decompositions of diazomethane and diphenyldiazomethane in the presence of a carbonyl group.

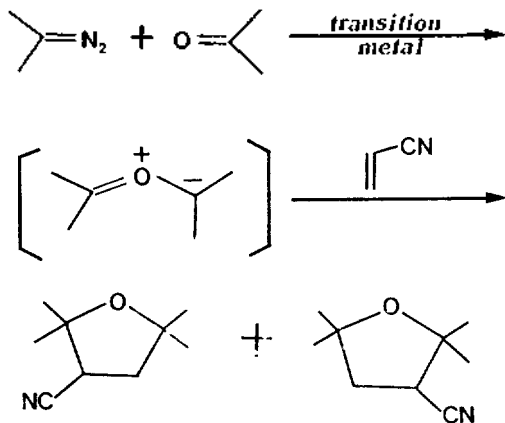
## Experimentals

**General Photolysis Conditions.** Diazomethane was generated by Aldrich MNNG Diazald apparatus as follows.<sup>8</sup> 1 mmol of 1-methyl-3-nitro-1-nitrosoguanidine (MNNG) is placed in the inside tube of the Diazald kit through its screw-cap opening along with 0.5 mL of water of dissipate any heat generated. 3 mL of diethyl ether is placed in the outside tube and the two parts are assembled with a butyl "O"-ring and held with a pinch-type clamp. The lower part is immersed in a liquid nitrogen bath and about 0.6 mL of 5 N sodium hydroxide is injected dropwise, very slowly to prevent frothing through the silicone rubber septum *via* a syringe with a narrow-gauge needle to prevent leakage around the shank. The flask was then filled to the mark with the appropriate solvent. The diazomethane was transferred to a 10 mm×10 mm×150 mm pyrex tubes which were degassed by three freeze-pump-thaw cycles. The samples were irradiated with a 450 W high pressure Hanovia mercury arc lamp filtered through a uranium glass absorption sleeve ( $\lambda > 340$  nm) for 6-10 hours which time the signal at 2160  $\text{cm}^{-1}$  corresponding to the diazo compound had disappeared fully. Ylides were determined by the following method. After removal of solvent, the residue was placed in a 2 mL volumetric flask, 5 mg of internal standard compound (fluorinated 1,4-dioxane and trifluorinated dioxolanes) was added and the mixture was diluted to the mark with the reaction solvent. Analysis by gas chromatography was performed using columns of a 530  $\mu\text{M}$ ×25 M 50% phenylmethyl silicone capillary and a 320  $\mu\text{M}$ ×30 M. Supelcowax 10 capillary by setting oven temperature programmed at 70-180°C with an initial time of 5 min, a ramp rate of 5°C/min and a final time of 15 min. Analytical samples were obtained by preparative gas chromatography at 125°C.

**Rate Measurements.** The photolytic reactions were carried out in a two-legged glass vessel (leg capacity *ca.* 1 mL each) which was connected to a 1 mm quartz UV cell and a tap for introducing reaction solutions and for degassing of nitrogen.

The solution of etherated diazomethane or diphenyldiazomethane was introduced to the quartz UV cell and fluorinated acetones or acetophenone was pipetted into separate legs of the reaction vessel and were degassed.

The solutions were equilibrated at desired temperature before being thoroughly mixed and transferred to the UV cell which was then placed in the cell holder of the spectrometer. The appearance of the coloured species in the reaction mixture was measured by the increase in optical density at suitable intervals on UV/vis spectrophotometer. The initial



Scheme 1