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Polarographic Studies on Substituted 2,2′-Bipyridyl *N*-Oxides[1]

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The polarographic behavior of 4-methoxy-2,2′-bipyridyl 1-oxide has been investigated in 20% dioxane-water solution. Two well defined reduction waves appear in the pH range 0.76—8.8, a third wave in pH 9.3—10.4, but only one wave in more alkaline solutions. The variation of $E_{1/2}$ with pH followed the relations $(E_{1/2})_1 = -0.37-0.10$ pH and $(E_{1/2})_2 = 0.84-0.065$ pH for waves 1 and 2, respectively. The diffusion current constant for the second wave decrease with increasing pH whereas for the first wave it remains constant upto pH 7.0 and decreases afterwards. Variation of diffusion current with temperature and reservoir height indicates the diffusion controlled nature. Wave 1 is produced by the 2 electron reduction of protonated *N*-oxide to 4-methoxy-2,2′-bipyridyl. This intermediate is further reduced, at more negative potentials, to 1,4′-dihydro-4-methoxy-2,2′-bipyridyl by consuming two more electrons and two hydrogen ions simultaneously. The third wave is presumably due to catalytic hydrogen evolution.

The polarographic behavior of pyridine *N*-oxides and purine *N*-oxides has been studied by several workers.[2–8] It has been found that these *N*-oxides give one or more reduction waves in buffered media. Pyridine *N*-oxide in various buffer solutions gives one wave[3,4,6] whose wave height decreases rapidly above pH 6, whereas adenine 1-*N*-oxide[2,7,9] gives a fundamental pattern of three polarographic waves over the pH range 1.4 to 5.6, the third wave being due to catalytic hydrogen evolution. It is also known that *N*-oxides such as nitrogen mustard *N*-oxide[10] and 2-azaadenine 1-*N*-oxide[7] are reduced polarographically to the corresponding amines. Alkaloid *N*-oxides such as narcotine *N*-oxide[3] have been reported to give three waves. It has been observed that the two-electron reduction waves of narcotine *N*-oxide are complicated by the adsorption at the electrode, the kinetic current of protonation and the reversible cleavage of lactone.

A detailed knowledge of the electrochemical behavior of *N*-oxides is of great interest in view of their biological importance, and the possible use of the electrolytic process of reduction for such *N*-oxides which give undesirable reduction products[11] when treated with conventional reductants like hydrogen and Raney nickel. Attempts have been made to correlate the herbicidal activity[12] of 2,2′- and 4,4′-bipyridyl salts to their redox potentials[13] as the herbicidal activity has been found to be dependent on the reversible reduction of the compound. Polarographic investigations on 2,2′-bipyridyl,[14,15] contain certain anomalies in that one report[14] states that it gives one wave while the other indicates that it gives three waves.[15] In view of the absence of polarographic data on substituted 2,2′-bipyridyl *N*-oxides and the existing anomalies in the data on 2,2′-bipyridyl it was considered desirable to investigate systematically the effect of concentration, pH, temperature and other factors on the polarographic reduction of substituted 2,2′-bipyridyl *N*-oxide.

Experimental

Apparatus. A sargent model XXI pen recording polarograph was used to record the current voltage curves. All the potentials were measured against saturated calomel reference electrode. An H-cell, one limb of which contained the calomel electrode and the other the test solution, served as the electrolytic cell. The capillary used had the following characteristics in 0.1 M KCl in open circuit:

$m = 1.507$ mg sec^{-1}, $t = 3.38$ sec, $h = 75$ cm of mercury.

The cell was water jacketed and all measurements were made at 25±0.1°C with the help of an external thermostat.

pH measurements were carried out with an Elico pH meter. Ultraviolet spectra were recorded with a Beckman model DU spectrophotometer using 1 cm quartz cells.

Chemicals. The substituted 2,2′-bipyridyl 1-oxides were prepared by the methods given in literature.[16] They were recrystallized several times and checked for their purity by elemental analysis and melting point data. Dioxane used was always freshly distilled before use. All the chemicals used for preparation of buffers were of analytical grade. Buffer systems used in the present study were as follows:

NaOAc+HCl (pH 0.65—1.24), $KOOC-C_6H_4-COOK$+HCl (pH 2.2—2.6), HOAc+NaOAc (pH 3.42—5.89), KH_2PO_4+NaOH (pH 6—8), KCl+H_3BO_3+NaOH (pH 8.5—10.0), Na_2HPO_4+NaOH (pH 11—13).

Nitrogen used for removal of oxygen from solutions was purified by passing through gas washing bottles containing

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solutions of sodium salt of anthraquinone-2-sulphonic acid and $NaHSO_3$, alkaline pyrogallol, chromous sulphate in about 1N sulfuric acid, NaOH and distilled water in series.

Procedure. Stock solutions of *N*-oxides were prepared in pure dioxane. They were diluted with necessary amounts of water and buffer solutions so that the final volume of 10 m*l* of the test solution contained the desired concentration of *N*-oxide, 20% dioxane and 50% buffer. The final solution was thermostated till it attained a temperature of 25°C and during this time purified nitrogen was bubbled to remove the oxygen. The dropping mercury electrode was then introduced and the polarogram was recorded.

Results and Discussion

4-Methoxy-2,2′-bipyridyl 1-Oxide. 8.11×10^{-5}M solution of 4-methoxy-2,2′-bipyridyl 1-oxide was polarographed in 20% dioxane in various buffers over the pH range 0.85—13.0. A few typical polarograms in different buffers are shown in Fig. 1 and the other data are summarized in Table 1. From pH 0.76—8.8 two well defined and well separated waves were observed. At pH 9.3, 9.5, and 10.4 a third wave appeared which was clearly distinguishable from the second wave. However, in highly alkaline solutions (0.1N NaOH) only one wave was observed. The behavior of diffusion currents and half wave potentials with pH is shown in Figs. 2 and 3. It is of interest to note from Fig. 2 that $E_{1/2}$ becomes more and more negative with increase in pH of the solution. This indicates the participation of hydrogen ions in the electrode reaction. A similar variation of half wave potentials with

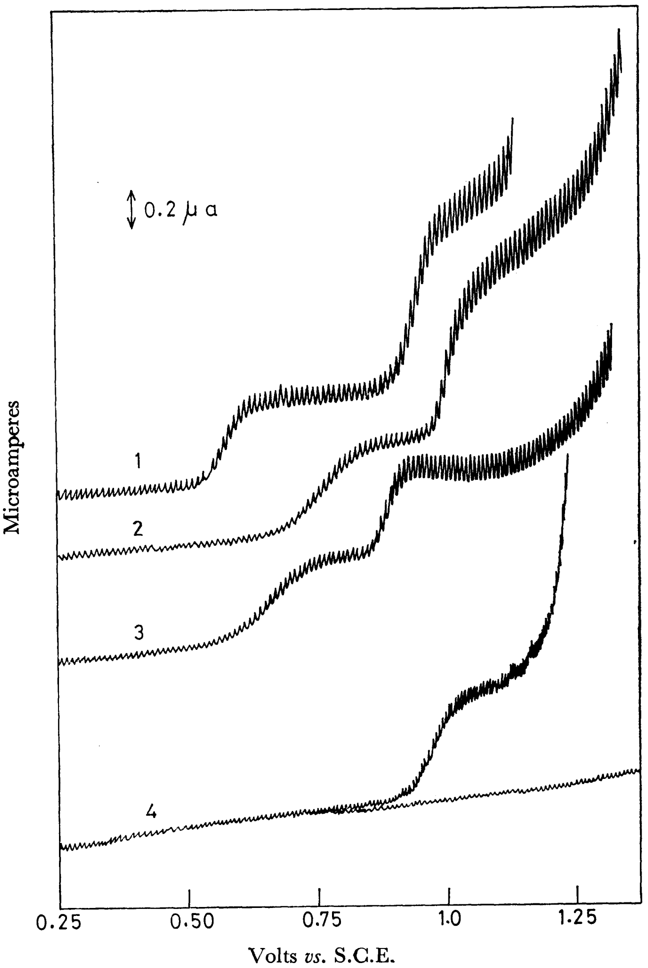

Fig. 1. Polarograms of 4-methoxy-2,2 -bipyridyl-1-oxide in various buffers. Curves 1, 2, 3, and 4 are at pH 2.45, 7.55, 8.80, and 0.1N NaOH, respectively. The scale for curves 3 and 4 has been shifted by 0.5 and 0.65 V, respectively, on the abscissa.

Table 1. Polarographic characteristic of 4-methoxy-2,2′-bipyridyl 1-oxide in various buffers at 25°C
Concentration of *N*-oxide = 8.11×10^{-5} M

	Wave 1			Wave 2		
pH	$(-E_{1/2})_1$ V vs. SCE	i_{d_1} μA	I_1	$(-E_{1/2})_2$ V vs. SCE	i_{d_2} μA	I_2
0.76	0.58	0.50	3.79	0.95	0.92	7.18
1.14	0.62	0.52	3.90	0.96	0.88	7.14
2.21	0.64	0.50	3.61	1.00	0.70	5.06
3.46	0.72	0.50	3.69	1.06	0.82	6.07
5.65	0.94	0.48	3.73	1.17	0.80	6.07
7.00	1.07	0.50	3.68	1.24	0.72	5.30
9.50	1.18	0.22	1.60	1.42	0.18	1.31
9.70	1.23	0.04	0.29	1.42	0.20	1.47

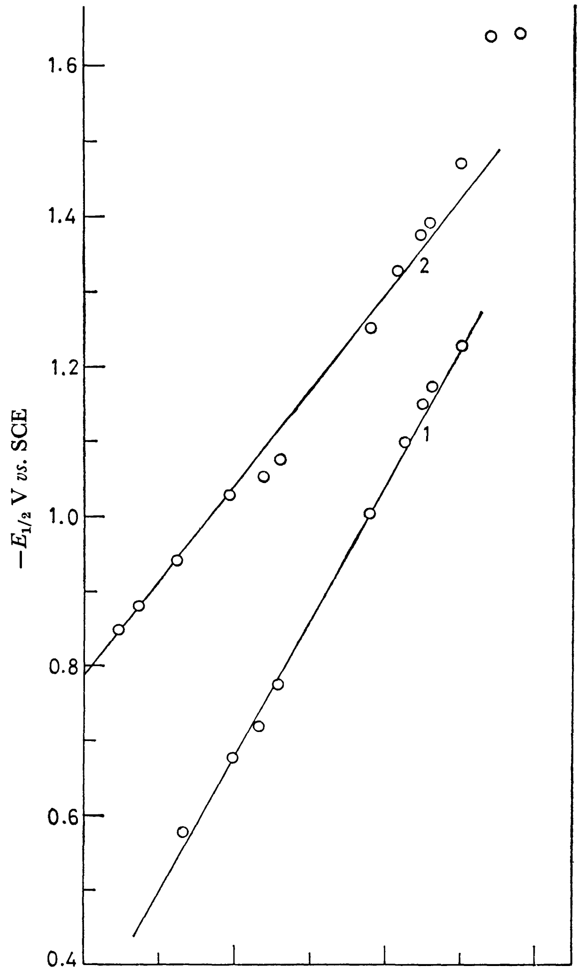

Fig. 2. Variation of half wave potentials of *N*-oxide with pH. 1. First wave; 2. Second wave.

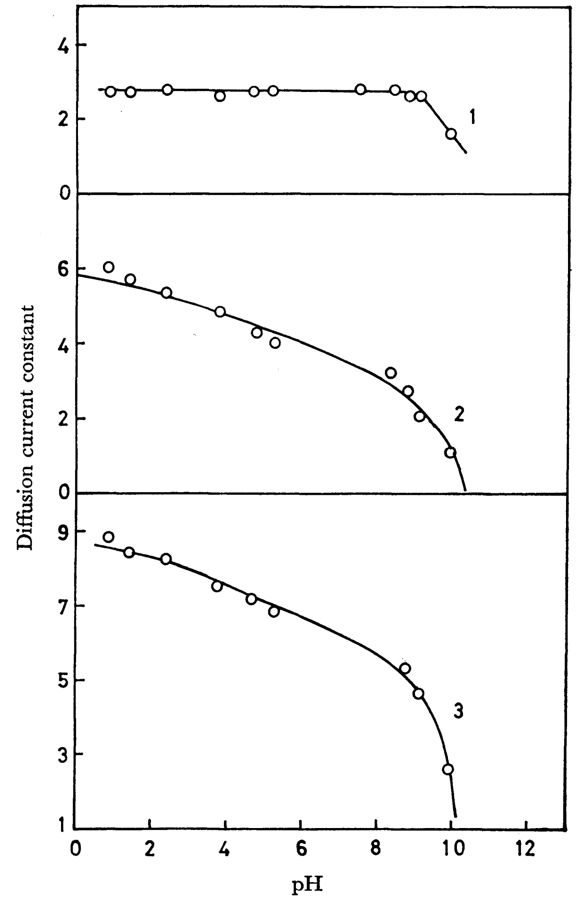

Fig. 3. Variation of diffusion current constant of *N*-oxide with pH. 1. First wave; 2. Second wave; 3. First and second waves.

pH has been reported[15] in the case of other heterocycles, *viz.* 4,4′-, 2,4′-, and 2,2′-bipyridyls, 4-cyanopyridine,[17] alloxan, alloxantin and dialuric acid.[18] The variation of $E_{1/2}$ of both the waves of 4-methoxy-2,2′-bipyridyl-1-oxide with pH is linear almost over the whole pH range investigated. The data for both the waves could be fitted to the following relationships:

$$E_{1/2} = -0.37 - 0.10\,\text{pH} \quad \text{(for wave 1)}$$

$$E_{1/2} = -0.84 - 0.065\,\text{pH} \quad \text{(for wave 2).}$$

However, for the second wave the half wave potentials appear to become more negative than required by the above relationship beyond pH 9.3. This is presumably due to the third wave which appears at pH 9.3 and almost merges with the second wave at higher pH thus making the accurate calculation of half wave potentials difficult. It can be clearly seen from Fig. 3 that the height of the first wave remains constant up to pH 7 and starts decreasing beyond it. However, the second wave shows a slight decrease in the diffusion current with increasing pH from pH 0.76—5.65 and a larger decrease after pH 7.0. The decrease in wave height with increasing pH has also been reported for pyridine *N*-oxide, 4-methylpyridine *N*-oxide.[4] It is not due to any structural change in 4-methoxy-2,2′-bipyridyl 1-oxide in acid or alkali as indicated by UV spectra of the *N*-oxide in neutral, acid and alkaline media. The spectra of *N*-oxide at various pH are shown in Fig. 4.

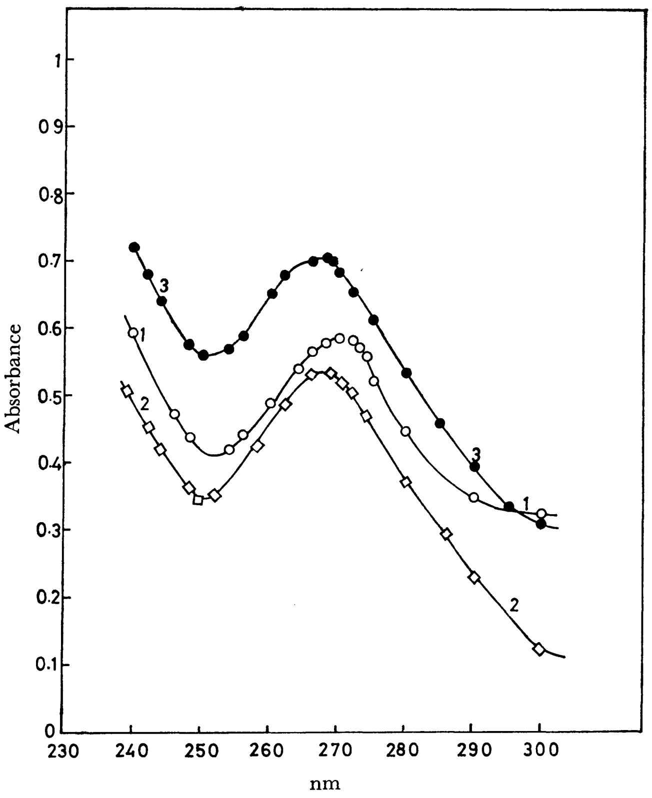

Fig. 4. UV spectra of *N*-oxide at different pH. Conc 3.901×10^{-5}M 1. 0.1N HCl; 2. 0.1N NaOH; 3. pH 7.

TABLE 2. POLAROGRAPHIC CHARACTERISTICS OF 4-METHOXY-2,2′-BIPYRIDYL-1-OXIDE IN NEUTRAL ELECTROLYTES
Temperature 25°±0.1°C

Electrolyte	Concentration $\times 10^5$	$(-E_{1/2})_1$	$(-E_{1/2})_2$ V *vs.* SCE	$(-E_{1/2})_3$	$(i_d)_1$	$(i_d)_2$ μA	$(i_d)_3$
0.1M KCl	4.38	1.17	1.41	1.62	0.06	0.04	0.20
	6.57	1.17	1.40	1.60	0.14	0.05	0.22
	8.76	1.20	1.43	1.60	0.24	0.06	0.30
0.1M LiCl	4.38	1.18	1.43	1.62	0.22	0.10	0.08
	6.57	1.17	1.42	1.63	0.28	0.16	0.10
	8.76	1.17	1.43	1.61	0.38	0.10	0.12

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It is clear from this figure that absorption maximum is at 266 nm in 0.1 N NaOH and pH 7.0. Wave 1, for reasons subsequently discussed could be assigned to the reduction of protonated *N*-oxide functional group. It is, therefore, expected that in a medium deficient in protons, wave height should decrease and this is what we observed in buffers of increasing pH. This is further substantiated by the polarographic behavior of *N*-oxide in unbuffered media *viz.* neutral supporting electrolytes. The data is presented in Table 2. It can be seen that *N*-oxide gives three waves in KCl, LiCl, and $N(CH_3)_4Cl$. The first two waves appear at a more negative potential than those found in buffered medium of pH 7.0, while the third wave appears at almost the same potential at which the third wave is found in buffered media of pH greater than 9.3. Thus for example $(E_{1/2})_1$, $(E_{1/2})_2$, and $(E_{1/2})_3$ in 0.1 M KCl corresponded to −1.17, −1.41, and −1.62 V *vs.* SCE whereas in buffer of pH 7.0 $(E_{1/2})_1$ and $(E_{1/2})_2$ corresponded to −1.07 and −1.24 V *vs.* SCE respectively. More negative half wave potentials in unbuffered solution further substantiate the observation that hydrogen ions are involved in the electrode process. It is instructive to find that the limiting currents for all the three waves in unbuffered media are very small compared to the values for the respective waves in buffer of pH 7.0. Even the total limiting current due to all the three waves in unbuffered media is substantially smaller than the total diffusion current of the two waves observed in buffer of pH 7.0. This observation strongly suggests that it is the protonated *N*-oxide which gets electroreduced, and in unbuffered media due to the paucity of hydrogen ions only a small fraction of *N*-oxide is electroreduced giving very low limiting currents.

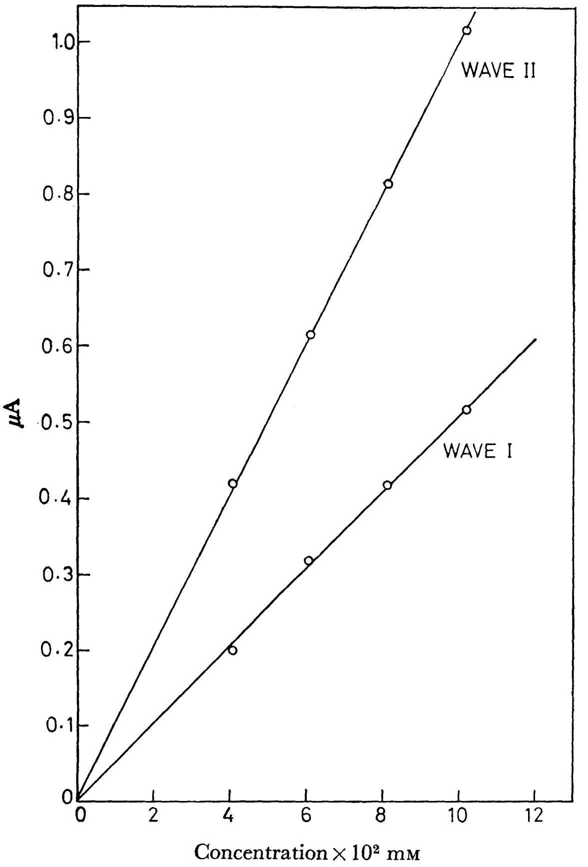


Fig. 5. Linear dependence of diffusion current of *N*-oxide on concentration at pH 0.85.

The characterization of the nature of the electrode process has been done by studying the effect of concentration of *N*-oxide, height of mercury reservior and temperature on the limiting current. The polarograms obtained at varying concentrations of 4-methoxy-2,2′-bipyridyl 1-oxide in the range $4.05-10.13\times10^{-5}$M at pH 0.85 were well difined and well separated. Plot of i_d against concentration gave a straight line as shown in Fig. 5. This indicates the absence of adsorption or catalytic character in both the waves and suggests that both waves are diffusion controlled. Heterocyclic compounds, especially those containing nitrogen, are known to exhibit pronounced adsorption effects at the mercury drop. Even adenine 1-*N*-oxide[2] and Narcotine *N*-oxide are reported to give adsorption waves. In our data we found no evidence for any adsorption wave in the reduction of 4-methoxy 2,2′-bipyridyl-1-oxide at the dme. However, the third wave which appears beyond pH 9.3 does not follow Ilkovic equation and is probably a catalytic wave.

A study of the effect of varying heights of the mercury

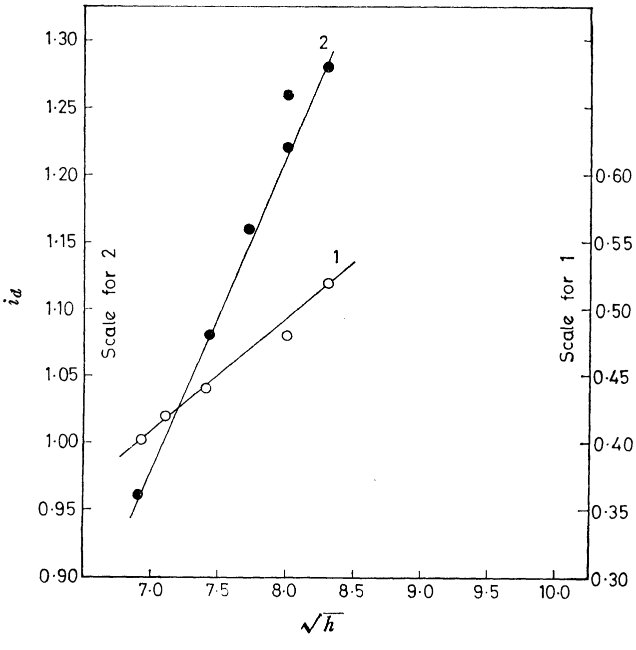


Fig. 6. Effect of mercury height on the diffusion current on *N*-oxide.

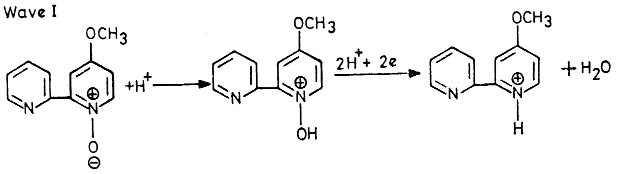
Table 3. Effect of temperature on the wave heights pH=3.3

T °K	i_{d_1}	i_{d_2}	Temperature coefficient Wave 1	Temperature coefficient Wave 2
303.5	0.40	0.78	—	—
308.5	0.50	0.98	4.6	4.7
312.5	0.58	1.12	3.0	3.6
316.5	0.64	1.20	2.3	1.7
322.5	0.76	1.32	2.9	1.6

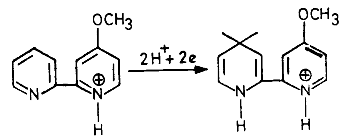
column on the diffusion currents as well as the determination of the temperature coefficient of both the waves indicates their diffusion controlled nature. The limiting currents are proportional to the square root of the mercury height as shown in Fig. 6, whereas the temperature coefficients are in the range 1.6—4.6% as summarized in Table 3. The diffusion controlled nature of the waves due to *N*-oxide function has also been reported for adenine 1-*N*-oxide by Elving.[2]

Mechanism of the Electrode Process. The observed polarographic behavior of 4-methoxy-2,2′-bipyridyl 1-oxide can be explained by the following reduction sequence:

Wave I



Wave II



Wave I is produced by the 2 electron reduction of protonated *N*-oxide to 4-methoxy-2,2′-bipyridyl. The *N*-oxide after reaching the electrode picks up two electrons and two protons simultaneously to form 4-methoxy-2,2′-bipyridyl, giving rise to the first two electron wave. 4-Methoxy-2,2′-bipyridyl thus formed as the intermediate is further reduced at more negative potentials to 1′,4′-dihydro-4-methoxy-2,2′-bipyridyl by consuming two more electrons and two hydrogen ions simultaneously, giving rise to the second two electron wave. The latter wave in addition to 4-methoxy-2,2′-bipyridyl reduction may have some contribution from a catalytic hydrogen reduction process. The evidence supporting the above mechanism is discussed below.

The value of diffusion current constant (*I*) is 3.7 for the first wave and is constant up to pH 7.0; its value is comparable with *I* value of 3.3 obtained for other *N*-oxide function by Warner and Elving.[2] The *I* value is also compatible with a two electron reduction process. In a macroscale electrolysis at the potential of the plateau of the first wave, 4-methoxy-2,2′-bipyridyl was detected in the solution.

The second wave is identical in behavior with that of the first wave of 2,2′-bipyridyl. The polarographic data for 2,2′-bipyridyl are summarized in Table 4. It is found that 2,2′-bipyridyl gives a single wave upto pH 3.4 and two waves in the pH range 3.6—10.5, the second wave becoming more and more drawn out in solutions of higher pH. The half wave potentials for the wave 1 of 2,2′-bipyridyl vary linearly with pH as shown in Fig. 7 and fit the relation

$$E_{1/2} = -0.81 - 0.066\,\text{pH}$$

which is similar to that obtained for the second wave of *N*-oxide *viz.* $E_{1/2} = -0.84 - 0.065$ pH. Slightly more negative values obtained for $E_{1/2}$ of wave II of 4-methoxy-2,2′-bipyridyl-1-oxide are due to the presence of *p*-methoxy group in 2,2′-bipyridyl which has a σ value of −0.27.[19] The diffusion current constant for the second wave of *N*-oxide is ~7 (Table 1) which is comparable to the *I* value (~7) for the first wave of 2,2′-bipyridyl (Table 4). The value of diffusion current constant obtained by Pfeifer[20] for the 2-electron reduction first wave of 2,2′-bipyridyl in the pH range 3.46—7.0 has been reported to be 5.6. This is also in excellent agreement with the *I* values we obtained in a similar pH range as shown in Table 4. It is thus proved that the electrode reaction producing the second wave is due to the reduction of 4-methoxy-2,2′-bipyridyl.

TABLE 4. INFLUENCE OF pH OF THE MEDIUM ON THE REDUCTION OF 2,2′-BIPYRIDYL

Concentration of 2,2′-bipyridyl$=5.7\times10^{-5}$M

	Wave 1			Wave 2	
pH	$(-E_{1/2})_1$ V *vs.* SCE	i_{d_1} μA	I_1	$(-E_{1/2})_2$[a] V *vs.* SCE	i_{d_2}[a] μA
0.76	0.88	0.68	7.33	no wave	no wave
1.14	0.91	0.70	7.49	no wave	no wave
2.21	0.95	0.68	6.98	no wave	no wave
3.46	1.01	0.54	5.68	1.20	0.7
5.65	1.17	0.52	5.61	1.34	0.7
7.00	1.25	0.59	5.40	1.41	0.7
10.30	1.45	0.20	2.09	1.79	0.7

a) The half wave potentials and diffusion currents are not accurate since the waves are drawn out.

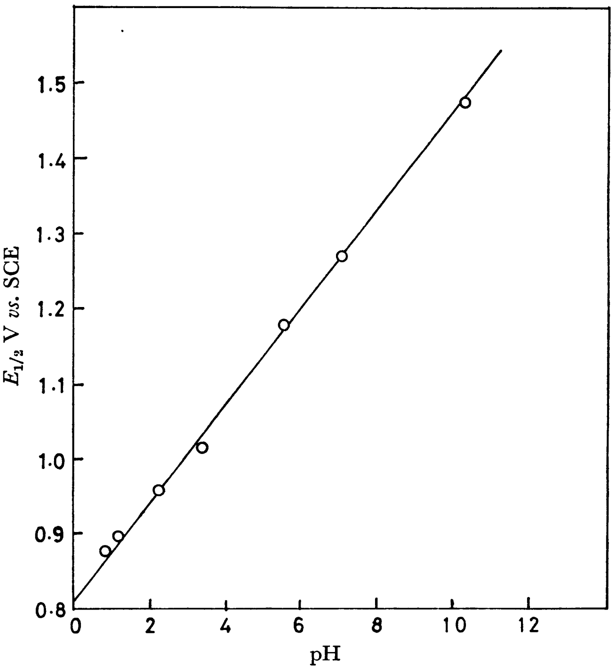


Fig. 7. Variation of $E_{1/2}$ of 2,2′-bipyridyl with pH.

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