BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 40 245—251 (1967)

The Polarography of Nitrones and the Effect of Substituents on Them[1]

Tanekazu KUBOTA and Hiroshi MIYAZAKI

Shionogi Research Laboratory, Shionogi & Co., Ltd., Fukushima-ku, Osaka

and Yutaka MORI

Laboratory of Organic Chemistry, Osaka Gakugei University, Tennoji-ku, Osaka

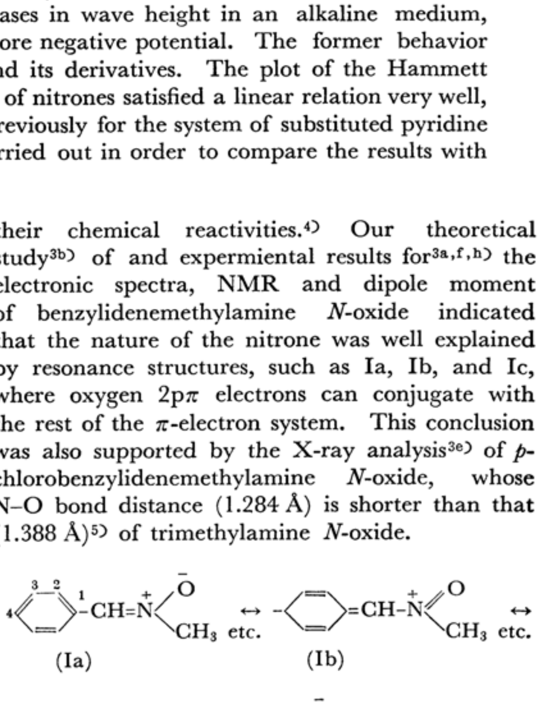
(Received June 12, 1965)

Polarograms and half-wave potentials ($E_{1/2}$'s) of sixteen substituted benzylidenementhylamine *N*-oxides were extensively measured in various pH solutions. The half-wave potential, $E_{1/2}$, was expressed in the form: $E_{1/2}=a\cdot\mathrm{pH}+b$. It was always observed that the four-electron wave due to the reduction of the $C=N\rightarrow O$ group decreases in wave height in an alkaline medium, and at the same time another wave appears in a more negative potential. The former behavior was similar to that found for pyridine *N*-oxide and its derivatives. The plot of the Hammett σ values of the substituents against the $E_{1/2}$ values of nitrones satisfied a linear relation very well, ρ being positive but smaller than that obtained previously for the system of substituted pyridine *N*-oxides. Controlled-potential electrolysis was carried out in order to compare the results with the polarographic results.

In the preceding papers[2] of this series, we reported that the polarographic reduction of pyridine *N*-oxide derivatives showed pH-dependent two-electron reduction waves, and that their half-wave potentials were in a good linear relation with the Hammett σ values of the substituents.

The present paper will describe the polarographic behavior of sixteen substituted benzylidenemethylamine *N*-oxides (nitrones). The aim of this study is to find out: (i) the difference in polarographic behavior between the two types of aromatic tertiary amine *N*-oxides, namely, pyridine *N*-oxides and nitrones, and (ii) the effects of substituents on the half-wave potentials of nitrones.

There has been much interest in the molecular and electronic structures[3] of nitrones as well as in their chemical reactivities.[4] Our theoretical study[3b] of and expermiental results for[3a,f,h] the electronic spectra, NMR and dipole moment of benzylidenemethylamine *N*-oxide indicated that the nature of the nitrone was well explained by resonance structures, such as Ia, Ib, and Ic, where oxygen 2pπ electrons can conjugate with the rest of the π-electron system. This conclusion was also supported by the X-ray analysis[3e] of *p*-chlorobenzylidenemethylamine *N*-oxide, whose N–O bond distance (1.284 Å) is shorter than that (1.388 Å)[5] of trimethylamine *N*-oxide.



(Ia) (Ib) (Ic)

The results of the present study will probably be useful in obtaining further evidence for resonance hybridization in nitrones.

Experimental

Polarographic Measurements. A Yanagimoto polarograph, Model PA-102, was used for recording

---

1) Polarographic Study of Aromatic *N*-Oxides. III. Presented at the 18th Annual Meeting of Chemical Society of Japan held at Osaka on April 3, 1965. After the presentation we learned of a completely independent paper (the proof for *Collection Czech. Chem. Commun.*, **30**, 1832 (1965) by P. Zuman and O. Exner) sent by Dr. Zuman, in which they also reported polarograms of nitrones. Although their point of view was somewhat different from ours, their findings were consistent with our results.

2) a) T. Kubota and H. Miyazaki, This Bulletin, **35**, 1549 (1962); b) T. Kubota and H. Miyazaki, *ibid.*, **39**, 2057 (1966).

3) a) T. Kubota, M. Yamakawa and Y. Mori, This Bulletin, **36**, 1549 (1963); b) T. Kubota and M. Yamakawa, *ibid.*, **36**, 1564 (1963), **35**, 555 (1962); c) J. Hamer and A. Macaluso, *Chem. Revs.*, **64**, 473 (1964); d) K. Shinzawa and I. Tanaka, *J. Phys. Chem.*, **68**, 1205 (1964); e) K. Folting, W. N. Lipscomb and B. Jerslev, *Acta Cryst.*, **16**, 1263 (1963); f) T. Kubota, *J. Am. Chem. Soc.*, **87**, 458 (1965); g) K. Koyano (née Shinzawa) and I. Tanaka, *J. Phys. Chem.*, **69**, 2545 (1965); h) K. Tori, M. Ohtsuru and T. Kubota, This Bulletin, **39**, 1089 (1966).

4) a) Y. Iwakura, M. Akiyama and S. Shiraishi, This Bulletin, **38**, 513 (1965); b) R. Huisgen, *Angew. Chem.* (International Edition), **2**, 633 (1963); c) E. Matsumura and Y. Mori, presented at the 18th Annual Meeting of Chemical Society of Japan, Osaka, April, 1965; d) *Memoirs of Osaka Gakugei University*, Series B, **15** (1966), in press.

5) A. Caron, G. J. Palenik, E. Goldish and J. Donohue, *Acta Cryst.*, **17**, 102 (1964).

the polarograms, while a Beckman pH meter, Model G, was used for measuring the pH values. The dropping mercury electrodes used had the following characteristics in distilled water under an open circuit: $m=0.855$ mg/sec, $h=70$ cm, and $t=5.17$ sec. A saturated calomel electrode was used as an external reference electrode. All the polarographic measurements were carried out at 25±0.1°C in a suitable buffer solution after pure nitrogen had been bubbled in to remove the dissolved oxygen. The buffer solutions were the same as those employed in previous papers.[2] The ionic strength of sample solutions was adjusted to 0.45 by adding an appropriate amount of sodium chloride. Measurements were made with about a 5×10^{-4} mol/l solution, containing an accurately-weighed sample, and the values obtained from three separate measurements with a single electrolytic solution were averaged. The polarograms of most nitrones recorded showed a maximum wave or a trough-shape wave, especially in a pH region where the decrease of wave height appeared. This maximum current was, however, suppressed by adding a small amount of gelatin to the electrolytic solution; the most suitable concentration was found to be 0.005%.

Controlled Potential Electrolysis. This electrolysis was carried out using a Yanagimoto Controlled Potential Electrolyzer, Model V-E3. The quantity of electricity was measured by (i) the graphic integration of a current-time curve, and (ii) the use of a copper coulometer. The current observed with an electrolytic solution containing no nitrone was then subtracted as being a base current due solely to buffer components.

Materials. The nitrones used in the present study are listed in Table 1. They were prepared by the condensation reaction of substituted benzaldehydes with methylhydroxylamine, as has been described before,[3a,4c,d] and purified by repeated recrystallizations. Their purities were checked by ultraviolet and infrared spectral methods and by elementary analyses.

Results and Discussion

Polarographic Behavior of the Nitrones Listed in Table 1. All the substances, I—XVI, were obviously reduced at the dropping mercury electrode. The half-wave potentials were generally pH-dependent, and are expressed by Eq. (1):

$$-E_{1/2} = a\,[\mathrm{pH}] + b \qquad (1)$$

The half-wave potential values observed at pH 5 and the a and b values in Eq. (1) are shown in Table 1 and Table 3 respectively.

In order to discuss the nature of the reduction waves of nitrones, we would like to pick up benzylidenemethylamine N-oxide, Compound I, as a typical example. Polarograms for the compound recorded at various pH's are shown in Fig. 1, while the pH-dependences of the limiting current, i_l, and the half-wave potential, $E_{1/2}$, are depicted in Fig. 2.

TABLE 1. HALF-WAVE POTENTIALS OF SUBSTITUTED BENZYLIDENEMETHYLAMINE N-OXIDES

Material No.	Substituent	Mp, °C	$E_{1/2}$,* V
I	H	83.5—84	−0.881
II	4-CH_3	120.5	−0.892
III	4-Cl	127.5—128	−0.822
IV	4-Br	129—130	−0.799$_5$
V	4-OCH_3	183—184 (HCl salt, decomp.)	−0.935
VI	4-OH	223 (decomp.)	−0.961
VII	4-NH_2	207—208	−0.948
VIII	4-$N(CH_3)_2$	136—137	−0.951
IX	4-CN	187	−0.696
X	4-NO_2	206—207	−0.280** −0.934
XI	3-CH_3	163—164 (HCl salt)	−0.859$_5$
XII	3-Cl	166—167 (HCl salt)	−0.790
XIII	3-Br	168—169 (HCl salt, decomp.)	−0.776
XIV	3-OH	200—201 (decomp.)	−0.866
XV	3-CN	133—134	−0.758
XVI	3-NO_2	119.5—120	−0.350** −0.869

* Half-wave potentials associated with C=N→O group reduction at pH=5.0 are shown.

** Smaller $-E_{1/2}$ values are attributed to the reduction wave of NO_2 group.

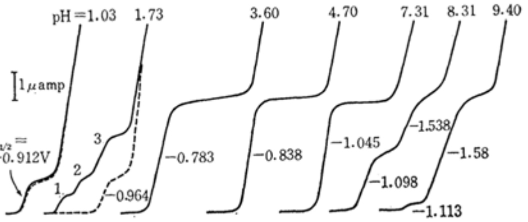


Fig. 1. Typical polarograms of (I) (5.26×10^{-4} mol/l) in various pH solutions containing 0.005% gelatin. Polarograms of benzaldehyde were also shown by dotted curves for comparison (5.22×10^{-4} mol/l).

The polarographic pattern varied remarkably with the pH. The wave height and the shape of the polarograms recorded at pH values less than 3.5 changed with the lapse of time. This change may be supposed to be due to the decomposition of the nitrone to benzaldehyde and methylhydroxylamine, since it is well known that the hydrolysis of usual nitrones occurs easily in such an acidic medium. Actually, this is clearly demonstrated by the fact that the polarogram at pH 1.03, where hydrolysis takes place quickly, is consistent with that of benzaldehyde. The wave that corresponds to benzaldehyde was also observed in the polarogram recorded at pH 1.73 (the third wave in Fig. 1), and its wave height increased with time. The fact indicates that the hydrolysis also occurred in such a pH region, although the rate is much smaller than that at pH 1.03.

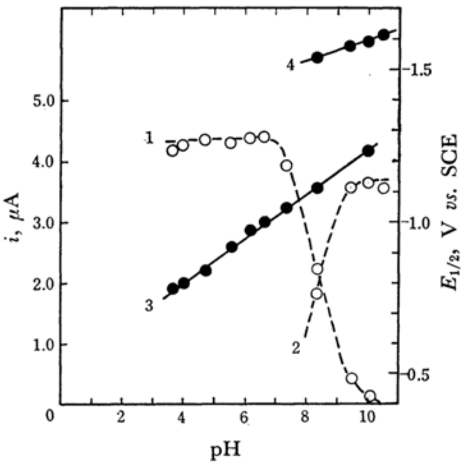
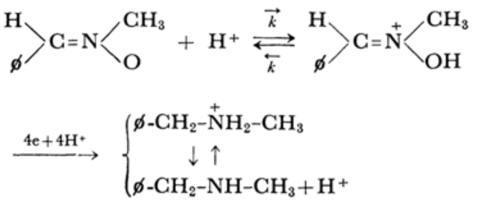


Fig. 2. The pH dependence of the limiting current, *i*, and half-wave potential, $E_{1/2}$, of I (5.26×10^{-4} mol/*l*). Curves 1 and 2 refer to the left scale, and 3 and 4 to the right scale. Curve 2 and straight line 4 are for the reduction wave that appears in an alkaline medium as a second wave (see Fig. 1).

In a pH region exceeding 3.5, the nitrone is stable; hence, the reduction wave showed no change with time. A typical one-step wave was obtained in measurements at pH values from 3.5 to 7.0. It was found to correspond to four-electron reduction6) from Ilkovic's equation, using $D=8.68\times10^{-6}$ cm^2/sec2a,b) (see also Fig. 2).

However, this four-electron wave separated into two waves in the pH region over 7. With an increase in pH, the wave height of the first wave of the two decreased quickly and the second one increased, as can be seen from Fig. 1 and Fig. 2. On the other hand, since the ultraviolet absorption spectrum of I does not show any appreciable change in the pH region exceeding 3.5, it is believed that there exists only one molecular species, I, and that the proton addition to I does not take place in such a pH region; namely, pK_a is less than 3.3a,f) From these facts, the polarographic behavior observed in an alkaline medium seemed to be due, at least in part, to the kinetic current. The same conclusion was obtained from the temperature- and mercury pressure-dependences of the wave height for the first reduction wave, which are shown in Table 2. Thus, we can understand from the data in this table that, with an increase in pH, the temperature coefficient for the wave does increase quite evidently, and that at the same time the current that is independent of the mercury height contributes to the total wave.

It seems that the results hitherto described can be explained by considering the following reduction mechanism:7)



Accordingly, the second wave appearing in an alkaline medium may reasonably be assigned to the reduction wave for non-protonated molecules. The reduction process was irreversible, as is indicated by the reciprocal slope9) values, 56.3 mV and 72.3 mV (for the first wave) at pH 4.70 and 8.31 respectively. The reaction rate for the proton addition process, $\overrightarrow{k}$, has not been determined, as the exact pK_a of the nitrone could not be decided because of the instability of nitrones in acidic pH solutions.

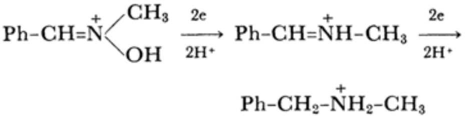
All the other nitrones except for the two nitro derivatives, X and XVI, showed quite a similar polarographic nature to I; all of them clearly showed a four-electron reduction wave in the 3.5—7 pH region, and the pH dependences of the waves were quite similar to those of I described above. Therefore, the reaction mechanism for their reduction seems to be the same as that described above. A good linear relation between $E_{1/2}$ and pH was found with all of them, and the slopes, *a* in Eq. 1, were about 65 mV, as may be seen in Table 3.

The Polarography of NO$_2$-substituted Nitrones. The two nitrones carrying a nitro group, X and XVI, showed a characteristic polarographic

---

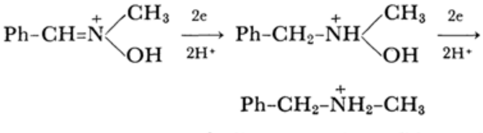
6) The value actually calculated of the electron number, *n*, participating in a polarographic reduction was 3.99 at pH 4.70.

7) At the present time we cannot determine which one of the following two routes is correct:



$$\mathrm{Ph\text{-}CH{=}\overset{+}{N}}{<}^{\mathrm{CH_3}}_{\mathrm{OH}} \xrightarrow[2\mathrm{H}^+]{2e} \mathrm{Ph\text{-}CH{=}\overset{+}{N}H\text{-}CH_3} \xrightarrow[2\mathrm{H}^+]{2e} \mathrm{Ph\text{-}CH_2\text{-}\overset{+}{N}H_2\text{-}CH_3}$$

(1)



$$\mathrm{Ph\text{-}CH{=}\overset{+}{N}}{<}^{\mathrm{CH_3}}_{\mathrm{OH}} \xrightarrow[2\mathrm{H}^+]{2e} \mathrm{Ph\text{-}CH_2\text{-}\overset{+}{N}H}{<}^{\mathrm{CH_3}}_{\mathrm{OH}} \xrightarrow[2\mathrm{H}^+]{2e} \mathrm{Ph\text{-}CH_2\text{-}\overset{+}{N}H_2\text{-}CH_3}$$

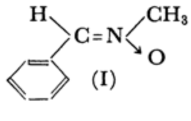
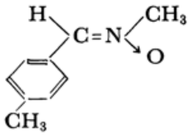
(2)

However, our recent findings8) on benzylideneaniline *N*-oxide and its related compounds indicated that the reduction of these *N*-aryl nitrones proceeds through route 1. See also H. Lund, *Acta Chem. Scand.*, **13**, 249 (1959); B. Z. Senkowski, M. S. Levin, J. R. Urbigkit and E. G. Wollish, *Anal. Chem.* **36**, 1991 (1964); S. Ono and M. Uehara, *Bulletin of the University of Osaka Prefecture*, Series A, **7**, 193 (1959).

8) T. Kubota, H. Miyazaki and Y. Mori, presented at the International Congress of Polarography, Kyoto, Japan, September, 1966.

9) "Reciprocal slope" means the slope of the plotting of *E* against $\log[i/(i_d-i)]$.

TABLE 2. THE TEMPERATURE- AND MERCURY PRESSURE-DEPENDENCE OF THE FIRST REDUCTION WAVE

Compound	Condition			Temp. dependence % deg$^{-1a)}$	Condition			Mercury pressure dependence
	pH	Concn. mol/l	Gelatin added %		pH	Concn. mol/l	Gelatin added %	
 (I)	4.70	5.23×10^{-4}	0.005	1.38	4.71	5.01×10^{-4}	0.005	$i=0.50\cdot\sqrt{h-h_b}$ b)
	8.31	5.23×10^{-4}	0.005	3.22	8.30	6.01×10^{-4}	0.005	$i=0.34\cdot\sqrt{h-h_b}+0.148$
	9.40	5.25×10^{-3}	d)	7.26	9.12 9.41	1.03×10^{-3} 5.09×10^{-3}	0.005 d)	$i=0.16\cdot\sqrt{h-h_b}+0.35$ c)
	4.72	5.26×10^{-4}	0.005	1.44	4.72	5.26×10^{-4}	0.005	$i=0.50\cdot\sqrt{h-h_b}$
	8.30	5.26×10^{-4}	0.005	2.68	8.30	5.26×10^{-4}	0.005	$i=0.32\cdot\sqrt{h-h_b}+0.505$
	9.52	5.27×10^{-3}	d)	11.16	9.12 9.52	1.04×10^{-3} 5.27×10^{-3}	0.005 d)	$i=0.325\cdot\sqrt{h-h_b}+0.705$ c)

a) Calculated by a compound interest method.

b) The symbols, i, h, and h_b, mean the limiting current (μA), the height (cm) of a mercury electrode, and the correction term for the reverse pressure (cm), respectively.

c) There is no good linear relation of i to $\sqrt{h-h_b}$.

d) A normal shape of the reduction wave was obtained without gelation.

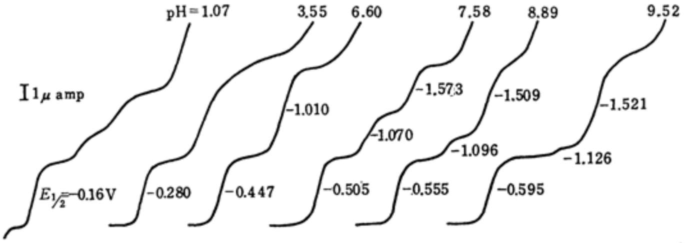


Fig. 3. The polarograms of 3-nitrobenzylidenemethylamine *N*-oxide (XVI) (5.11×10^{-4} mol/l) in various pH solutions containing 0.005% gelatin.

TABLE 3. THE VALUES OF a AND b IN THE EQUATION $-E_{1/2} = a[\text{pH}]+b$

Substituent	a	b	pH range
H	0.070	0.531	3.5—8.5
4-NH_2	0.069	0.60	3.5—9.0
4-$N(CH_3)_2$	0.071	0.598	3.0—9.0
4-OH	0.071	0.606	4.0—9.0
4-OCH_3	0.068	0.595	3.5—8.0
4-CH_3	0.065	0.567	3.5—8.5
4-Cl	0.066	0.492	3.0—9.0
4-Br	0.068	0.462	3.0—9.0
4-CN	0.063	0.383	2.5—7.5
4-NO_2*	0.074	0.566	3.5—8.0
3-OH	0.067	0.531	3.0—8.5
3-CH_3	0.067	0.527	3.0—9.0
3-Cl	0.069	0.445	3.0—8.5
3-Br	0.064	0.456	3.0—9.0
3-CN	0.071	0.405	3.5—7.5
3-NO_2*	0.088 0.044	0.429 0.719	3.5—6.6** 6.6—9.0

* The values a and b are applied to the half-wave potential due to C=N→O group in the molecule.

** In this case two straight lines crossing at pH ≈6.6 were obtained.

nature which is quite different from the nature common to the other substituted benzylidenemethylamine *N*-oxides. Polarograms of 3-nitrobenzylidenemethylamine *N*-oxide, XVI, are shown in Fig. 3. The strange waves obtained at pH 1.07 are surely due to a partial decomposition (hydrolysis) of the nitrone. Normal waves, however, were recorded in the region of pH exceeding 3.5, where we can see that the height of the first four-electron (determined from Ilkovic's equation)[2)] wave was independent of pH; this behavior was quite different from that of the other nitrones. Polarograms similar to these were also observed in the case of NO_2-substituted pyridine *N*-oxides, and their first four-electron reduction waves were assigned to NO_2 group reduction.[2b)] In addition the half-wave potentials of the first waves for X and XVI showed a large derivation out of Hammett's σ-$E_{1/2}$ relationship, suggesting that the waves are not associated with C=N→O reduction (see discussions below). Now it seems quite reasonable to assign the first wave to NO_2 group reduction. The second wave may, accordingly, be thought to be due to the C=N→O group of benzylidenemethylamine *N*-oxide carrying a substituent that had been produced by the four-electron reduction of the NO_2 group, for example, NHOH.[10] This second wave separated into two waves in an alkaline medium; the height of the first wave decreased and that of the second increased with an increase in pH. This behavior was characteristic of the reduction of nitrones, as has been mentioned above.

The Effect of a Substituent on the $E_{1/2}$ of Benzylidenemethylamine *N*-Oxide. The plot of $E_{1/2}$ *versus* Hammett's σ constant of substituted nitrones is now of special interest in understanding the effect of a substituent on $E_{1/2}$ and in obtaining better knowledge of the reduction mechanism.

As has been mentioned above, the half-wave potentials are pH-dependent and may be expressed in the form of Eq. (1). Table 1 lists the $E_{1/2}$ values obtained for C=N→O reduction at pH 5. The plots of these values against σ constants of the substituents[11] are depicted in Fig. 4. It is obvious that a linear relation between $E_{1/2}$ and σ holds very well in the present system.

However, if we plot the σ values for the NO_2 group substituted at 3- and 4-positions against the $E_{1/2}$'s of the second wave (full circles in Fig. 4) or those of the first wave (not shown in Fig. 4) of X and XVI, there is always found a large deviation from the straight line that fits all other points. On the other hand, the plots of σ's for 3- and 4-NHOH, in lieu of those for NO_2, against the $E_{1/2}$ values of the second wave for X and XVI do fall right on the straight line drawn in Fig. 4. This led us to the conclusion that the first waves of X and XVI are due to the reduction of the NO_2 group, while the second wave is due to that of C=N→O in NHOH-substituted nitrones.

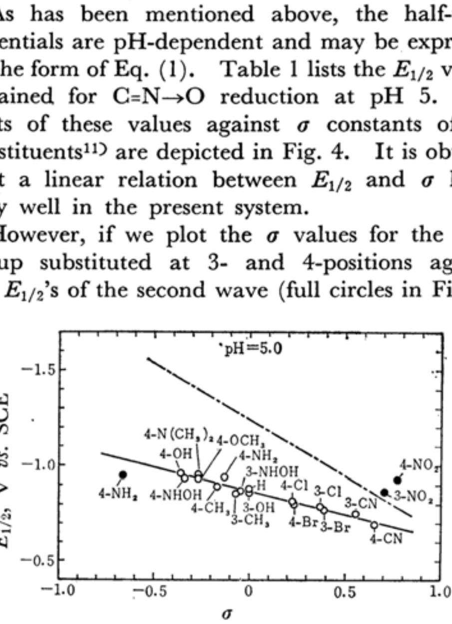
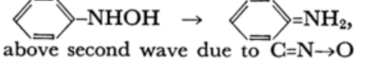


Fig. 4. The plot of $E_{1/2}$ at pH=5.0 against Hammett's σ. The broken line denotes the $E_{1/2}$-σ relationship with substituted pyridine *N*-oxides for comparison.

Now let us consider the slope of the straight line, which corresponds to ρ in Hammett's equation. As the pH-dependences of $E_{1/2}$ of various substituted nitrones are nearly all of the same order (see Table 3), we can expect that straight lines with roughly equal slopes will be obtained from plots using $E_{1/2}$ values at various pH's. Actually, the ρ values at pH 4, 5 and 6 were +0.220, +0.240 and +0.244 respectively. The straight line obtained for the pyridine *N*-oxide system[2b] under the same conditions is also shown in Fig. 4 for the sake of comparison. The ρ value for the present system is smaller than that ($\rho=+0.584$ at pH 5) for the pyridine *N*-oxide system. This suggests that the interaction ability between a substituent and an *N*-oxide group in a nitrone molecule is smaller than that in a substituted pyridine *N*-oxide molecule. In other words, we can say roughly that the *N*-atom of the N–O bond in pyridine *N*-oxide is a member of a six-π-electron ring system that interacts quite strongly with the oxygen atom, but that the C=N→O group in I is bound by a single bond with a benzene ring, in which a substituent is attached, so the resonance interaction at a ground state between a substituent and an N→O group may have few in nitrones compared with the system of pyridine *N*-oxide. This aspect is consistent with the conclusion, derived from the comparison of the molecular diagrams, that the N–O bond order is smaller in benzylidenemethylamine *N*-oxide[3b] than in pyridine *N*-oxide.[15,16]

The plus sign of the ρ value indicates that the reduction at a dropping mercury electrode is nucleophilic.[2b,13] Thus, the more electron-releasing the substituent, the more negative the $E_{1/2}$ value. Therefore, we believe that the method

---

10) This second wave, recorded at pH 4—6.6, was, however, larger than that expected for a four-electron reduction; therefore, there is a possibility that some other waves, such as  overlapped on the above second wave due to C=N→O group reduction.

11) The σ values used here are the same as those used in the case of substituted pyridine *N*-oxides. The problem of selecting the σ of a 4-NH_2 or NR_2 group was discussed in a previous paper;[2b] there it was concluded that the σ values cited by Jaffé[12] for 4-NH_2 or 4-$N(CH_3)_2$ do not fall so well on the straight line (shown by a full circle in Fig. 6) in the case of polarographic studies. The σ values of −0.13 (for 4-NH_2)[13] and −0.266 (for 4-$N(CH_3)_2$)[14] were also found to be better in the present case. The σ values for 3-NO_2 and 3-NHOH were adopted as +0.710 and −0.044 respectively,[12] these values were not used in our previous work.[2b]

12) H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

13) P. Zuman, *Collection Czech. Chem. Commun.*, **25**, 3225 (1960).

14) H. V. Bekkum, P. E. Verkade and B. M. Wepster, *Rec. Trav. Chim.*, **78**, 815 (1959).

15) T. Kubota and H. Watanabe, This Bulletin, **36**, 1093 (1963); T. Kubota, *ibid.*, **35**, 946 (1962); *Nippon Kagaku Zasshi (J. Chem. Soc., Japan, Pure Chem. Sect).*, **80**, 578 (1959).

16) The assigned N–O stretching bands appeared at ~1171 cm^{-1} for many nitrones[3c,17] and at 1265 cm^{-1} for pyridine *N*-oxide.[15,18] The above conclusion is believed to be in agreement with these spectral results on the assumption that the larger the N–O double bond character, the higher the N–O stretching frequency.

17) H. Shindo and B. Umezawa, *Chem. Pharm. Bull.*, **10**, 492 (1962).

18) a) H. Shindo, *Pharm. Bull. (Tokyo)*, **4**, 460 (1956); b) A. R. Katrizky, *J. Chem. Soc.*, **1960** 1519.

used to explain the substituent effects on $E_{1/2}$ of pyridine N-oxide[2b] may be successfully applied to the explanation of the nitrone system.

A Comparison of the Polarographic Behavior of Benzylidenemethylamine *N*-Oxide with That of Pyridine *N*-Oxide. It is now of special interest to find out the difference in polarographic behavior between I as a typical *N*-alkyl nitrone and pyridine *N*-oxide as a typical heterocyclic *N*-oxide. On the basis of the results mentioned above and those stated in the foregoing papers,[2a,2b] different characteristics are: (i) the former exhibits a four-electron reduction wave, but the latter, a two-electron wave, (ii) the former shows a smaller $-E_{1/2}$ (see Fig. 4) than that of the latter at the same pH value, and (iii) in a pH region where the wave height of the first wave decreases, the second wave does not appear in the case of pyridine *N*-oxide, while it does appear in the case of I. On the other hand, an analogous aspect of behavior between both the compounds is a pH dependence of the first wave which results from a kinetic current, and the $\mathrm{p}K_a$ values of both the compounds, as estimated from their polarographic behavior, are much larger than those obtained by spectroscopic or other methods

Their analogous characters were attributed to the fact that both compounds have $\gtrdot N \rightarrow O$ groups which possess quite simlar natures, as has been shown by spectroscopic methods, X-ray analysis, and some other observations.[3a-h] The different points, however, seem to be attributable to the fact that the $C=N \rightarrow O$ group of the nitrone is more active in polarographic reduction. Accordingly, a wave due to the reduction of a free *N*-oxide group appeared also in an alkaline medium. Furthermore, it is well known that the *N*-oxide group in pyridine *N*-oxide shows a great resistance toward the reductive reactions[19] as a result of the large resonance effect between the $\gtrdot N \rightarrow O$ group and the pyridine ring.

Controlled-Potential Electrolysis. As has been mentioned above, the analyses of polarograms of most nitrones indicated that the reduction at a dropping mercury electrode is the four-electron reduction of the $-C=N \rightarrow O$ group of the compounds. As has been mentioned above, the limiting current observed in the polarographic reduction of most nitrones showed that the reduction involves a four-electron reduction. To obtain support on this point as well as additional information on the reaction scheme, we carried out a controlled-potential electrolysis of I under conditions similar to those of the polarographic study. A solution containing 2.03×10^{-4} mol of I dissolved in 100 cc of a buffer solution was used as a cathode solution, and the pH of the solution was kept constant (5.62) during the electrolysis. The electrolysis was carried out under a nitrogen atmosphere. The controlled reduction potential was -1.10 V, a value selected to meet the polarographic data. The average value of n[6] calculated from the observed quantities of electricity was 4.7 after subtracting the base current. This result does not conflict with the conclusion, derived from polarographic studies, that the reduction proceeds in a four-electron step, since the current efficiency does not seem to be unity in the present case.

This assumption was also confirmed by recording the change in the absorption spectra of the electrolytic solution with the lapse of reduction time. The results are depicted in Fig. 5. We can see there that the intensity of the initial spectrum (No. 1) decreases as the reduction proceeds, and that the final spectrum (No. 5) is almost completely identical to that of benzylmethylamine (C_6H_5-CH_2NHCH_3) in the same buffer solution, which is an expected final product of a four-electron reduction of I.

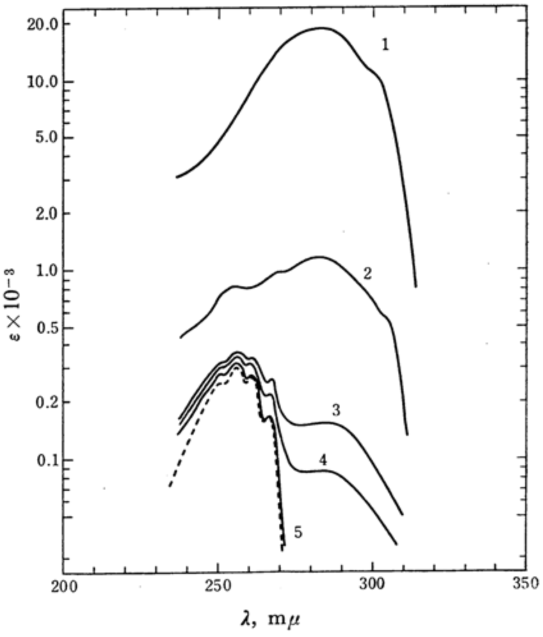


Fig. 5. The change of absorption spectra of I with the lapse of reduction time. Curve 1 is for the starting solution of an electrolysis, and curves 2, 3, 4, and 5 were respectively recorded after 360, 480, 600, and 840 minutes of the electrolysis. Dotted line stands for the spectrum of benzylmethylamine, whose concentration was the same as one calculated by assuming that all of I was completely converted into the benzylmethylamine. Vertical axis (ε) means apparent molecular absorption coefficient.

The authors wish to express their deep gratitude to Professor Emeritus Eiji Ochiai of the University of Tokyo for his valuable discussions. They are

---

[19] E. Ochiai, *J. Org. Chem.*, **18**, 534 (1953).

also grateful to Dr. P. Zuman of the Heyrovský Institute of Polarography, Czechoslovak Academy of Sciences, for sending us their results and for his discussion, and to Dr. Toshio Nakagawa of the Shionogi Research Laboratory and to Dr. Miyoshi Uehara, Department of Chemistry (College of Education), Osaka Prefecture University, for their helpful advice.