BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 39 2057—2062 (1966)

The Effect of Substituents on the Half-Wave Potential of the Polarographic Reduction of Pyridine *N*-Oxide Derivatives[1]

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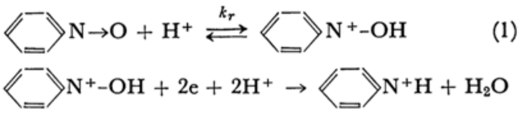
(Received March 23, 1965)

Polarograms of twenty-three pyridine *N*-oxide derivatives substituted at γ- and β-positions were extensively measured at various pH's. The half-wave reduction potential, $E_{1/2}$, was expressed by the form $-E_{1/2}=a\,[\mathrm{pH}]+b$. The wave height due to the reduction of the $\rangle\mathrm{N}\rightarrow\mathrm{O}$ group decreased with an increase in the pH in a pH region over $\sim$6. This phenomenon was common to all the compounds studied here; it was thought to be useful in identifying an aromatic *N*-oxide group by the polarographic method. The $E_{1/2}$ plot against Hammett's σ value of the substituent satisfied a linear relation well, and the slope of Hammett's ρ value was positive. This indicates that the reduction process is nucleophilic. The linear relation was explained qualitatively on the basis of the MO theory by applying the second-order perturbation method.

In a previous paper[2] concerning the pH dependence of the polarographic reduction wave of pyridine *N*-oxide, we showed that the reduction wave is actually due to the 2-electron reduction of the protonated *N*-oxide; we also determined the rate constant, k_r; in the proton addition process (1) using the equation derived by Koutecky[3] and by Matsuda[4]:



(1)

In the present study, polarographic measurements will be extended to twenty-two substituted pyridine *N*-oxides, and the relationship between their half-wave potential values ($E_{1/2}$) and Hammett's substituent constants (σ) will be discussed in terms of the lowest vacant MO energy of the substituted pyridine *N*-oxides and their protonated species predicted by the second-order perturbation method.

Experimental

Measurements.—The polarograms were recorded with two Yanagimoto polarographs, Model PA-102 and PB-4. The pH values were determined with a Beckman pH meter, Model G. The capillaries used for the dropping mercury electrode had the following values of m and t at an open circuit: (A) $m=1.23$ mg./sec. and $t=4.35$ sec. at $h=65$ cm., and (B) $m=0.879$ mg./sec. and $t=4.48$ sec. at $h=70$ cm. Capillary A was used in measurements with compounds I, IV, V, VI, and VII, and capillary B, with the other eighteen compounds. All the polarographic measurements were made at 25±0.1°C in a suitable buffer solution after bubbling purified nitrogen in for about 10 min. in order to remove the oxygen dissolved in the solution. The buffer solutions were the same as those employed in the previous report.[2] The ionic strength of the sample solution was adjusted to 0.45 by the addition of an appropriate amount of sodium chloride. A saturated calomel electrode was used as the external reference electrode. 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 were averaged.

Materials.—The compounds investigated in the present study are listed in Table I. Compounds II, VIII, XII, XIV, and XXIII were kindly supplied by Dr. Sadazi Kaziwara of our laboratory, and III, by Professor Yutaka Mori of Osaka Gakugei University. Compounds IV, V, IX, and X were synthesized by respective substitution reactions[5] from γ-nitropyridine *N*-oxide (XIII), which had been prepared by the nitration of pyridine *N*-oxide.[5] Compounds I, VI, VII, XI, XV, XVI, XVII, XVIII, XIX, XX, XXI, and XXII were prepared from the corresponding substituted pyridines by hydrogen peroxide oxidation in acetic acid. β-Fluoro-,[6] β-chloro,[7] and β-bromo[7] pyridines were prepared according to the literature, while β-methoxypyridine was prepared by the decomposition of diazotized β-aminopyridine in the presence of methanol.*1 The other substituted pyridines used for the above-mentioned *N*-oxide preparations were commercial products and were purified by a conventional method. All the compounds used for polarographic measurements were purified by at least three recrystallizations, and their purities were checked

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[1] The Polarographic Study of Aromatic *N*-Oxides. Part II. Presented at the meeting of "The Symposium on Polarography" held by the Chemical Society of Japan, Kyoto, October 1962.

[2] T. Kubota and H. Miyazaki, This Bulletin, **35**, 1549 (1962).

[3] J. Koutecky, *Collection Czech. Chem. Commun.*, **18**, 183, 597 (1953); **19**, 857 (1954).

[4] H. Matsuda and Y. Ayabe, This Bulletin, **28**, 422 (1955).

*1 This is a modification of the method of Ref. 7.

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

[6] A. Roe and G. F. Hawkins, *J. Am. Chem. Soc.*, **69**, 2443 (1947).

[7] C. Räth, *Ann.*, **486**, 95 (1931).

TABLE I. SUBSTITUTED PYRIDINE *N*-OXIDES INVESTIGATED, WITH THEIR MELTING POINTS AND THEIR HALF-WAVE REDUCTION POTENTIALS AT pH 5.0

Compound No.	γ-Substituent	M. p., °C	$E_{1/2}$, V.
I	H	b. p. 138—140°C/15 mmHg	−1.281
II	NH_2	181—182 (HCl salt)	−1.465
III	NHOH	149—150 (decomp.) (HCl salt)	−1.434
IV	OCH_3	83	−1.416
V	OC_2H_5	119	−1.396
VI	CH_3	184—185	−1.357
VII	C_2H_5	108—109	−1.331
VIII	$NHCOCH_3$	266—267	−1.189
IX	Cl	163 (decomp.)	−1.174
X	Br	180 (decomp.)	−1.094
XI	$COOC_2H_5$	69	−0.862
XII	CN	225—226	−0.857
XIII	NO_2	163	−0.204 −1.436 *
	β-Substituent		
XIV	NH_2	153 (HCl salt)	−1.280
XV	OCH_3	115—116 (HCl salt)	−1.168
XVI	CH_3	149.5—150.5 (HCl salt)	−1.272
XVII	C_2H_5	84 (HCl salt)	−1.246
XVIII	$NHCOCH_3$	215	−1.129
XIX	F	143—144 (HCl salt)	−1.144
XX	Cl	164.5—165 (HCl salt)	−1.071
XXI	Br	187—188 (HCl salt)	−1.040
XXII	$COOC_2H_5$	103	−0.992
XXIII	CN	175—176	−0.943

* Two waves were observed: −0.204 V. and −1.436 V. attributed to reduction steps of NO_2 and $\geqslant N \rightarrow O$ groups, respectively.

by ultraviolet and infrared spectral methods and by elementary analyses.

Results and Discussion

The Polarographic Behavior of Substituted Pyridine *N*-Oxides.—First let us discuss the polarographic behavior of pyridine *N*-oxides substituted by NH_2, NHOH, OCH_3, OC_2H_5, CH_3, C_2H_5, and $NHCOCH_3$ at the γ-position and by NH_2, OCH_3, CH_3, C_2H_5, $NHCOCH_3$ and F at the β-position. A typical example of their polarograms is shown in Fig. 1 (b). All the compounds of this group showed a one-step reduction wave in the pH region studied (pH$>$1.0). The wave height corresponded to a 2-electron reduction in an acidic medium according to the Ilkovic equation, using the same constants as those used in the previous paper,²⁾ but the wave decreased rapidly with an increase in pH in the pH range over $\sim$6. These phenomena are just the same as those observed in the reduction of pyridine *N*-oxide (I),²⁾ whose polarogram is also shown in Fig. 1 (a). Thus the wave corresponds to the 2-electron reduction of the protonated N→O group, and the behavior observed in the pH region over $\sim$6 is probably due to the wave including the kinetic current arising from the proton addition to the N→O group in the molecules.²⁾ This type of pH dependence was also observed with all the other substituted pyridine *N*-oxides studied here and with some nitrone derivatives;⁸⁾ hence it may be thought to be characteristic of the reduction of aromatic *N*-oxides, and it would be very useful for the identification of an aromatic *N*→O group by the polarographic method. The variation in the half-wave potential, $E_{1/2}$, with pH can be expressed by Eq. 2 in the pH region from 1 to 8 with all the compounds of this group except for the two amino derivatives.*² The slopes, *a*, were almost all of the same order, as can be seen from Table II.

$$-E_{1/2} = a[\mathrm{pH}] + b \tag{2}$$

In the polarograms of γ-chloro- and γ-bromopyridine *N*-oxides, the maximum shown by the

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*² We obtained two straight lines, crossing at pH= 2.60 and 4.50 for II and XIV respectively. It should be noted that these values do not coincide with the pK_a's values (3.65 and 1.47 respectively).⁹⁾ At the present time, no satisfactory explanation for this fact can be given.

8) T. Kubota, H. Miyazaki and Y. Mori, Part III, to be published.

9) H. H. Jaffé and G. O. Doak, *J. Am. Chem. Soc.*, **77**, 4441 (1955).

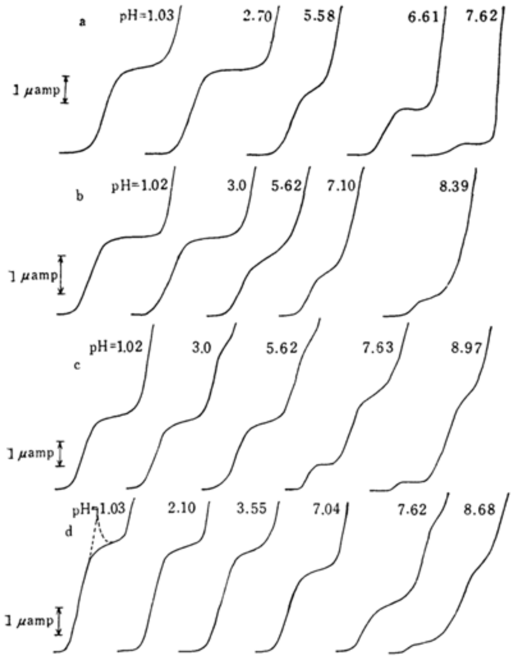

Fig. 1. Typical polarograms of some pyridine *N*-oxides in various pH solutions.
a : Pyridine *N*-oxide (I) (5.28×10^{-4} mol./l.)
b : β-NHCOCH$_3$ derivative (XVIII) (4.40×10^{-4} mol./l.)
c : β-Cl derivative (XX) (4.78×10^{-4} mol./l.)
d : γ-Br derivative (X) (5.19×10^{-4} mol./l., 0.005% gelatin added)
The dotted line in (d) represents the maximum wave which always appeared in reduction of γ-halogen derivatives in measurements without gelatin.

dotted line in Fig. 1 (d) was always observed over a wide pH range, although this maximum disappeared upon the addition of small amount (0.005%) of gelatin to the electrolytic solution. It should be noted, however, that the wave height of the γ-substituted halogen compounds was a little higher than that for the compounds discussed in the foregoing paragraph. On the other hand, no maximum was found with the β-chloro or the β-bromo derivatives. The polarograms of the former are shown in Fig. 1(c). The pH dependences of $E_{1/2}$ of the four halogen-substituted pyridine *N*-oxides also satisfied Eq. 2.

Cyano and carboethoxy derivatives (XI, XII, XXII and XXIII) exhibited somewhat different polarographic behavior. Thus, the polarograms of these compounds always showed two-step reduction waves.*[3] The pH dependence of the first wave height was similar to that for the common

TABLE II. THE VALUES OF a AND b in EQ. 2, $-E_{1/2}=a[\text{pH}]+b$, WHICH HOLDS IN THE pH REGION FROM 1.5 TO 7–8 EXCEPT WHERE INDICATED

Substituent	a	b
H	0.0865	0.849
γ-NH$_2$	0.074 0.1023	1.026 (pH 1—2.6) 0.953 (pH 2.6—7)
γ-NHOH	0.069	1.089
γ-OCH$_3$	0.094	0.946
γ-OC$_2$H$_5$	0.0963	0.914
γ-CH$_3$	0.0948	0.883
γ-C$_2$H$_5$	0.0933	0.864
γ-NHCOCH$_3$	0.0788	0.795
γ-Cl	0.087	0.739
γ-Br	0.0975	0.606
γ-COOC$_2$H$_5$	0.058	0.572
γ-CN	0.057	0.572 (pH 4—9)
γ-NO$_2$	0.04 0.096	0.004 (for the first wave) 0.956 (for the second wave)
β-NH$_2$	1.095 0.074	0.75 (pH 1—4.5) 0.91 (pH 4.5—8)
β-OCH$_3$	0.0785	0.775
β-CH$_3$	0.0816	0.864
β-C$_2$H$_5$	0.081	0.841
β-NHCOCH$_3$	0.072	0.769
β-F	0.0795	0.7465
β-Cl	0.0793	0.674
β-Br	0.0778	0.651
β-COOC$_2$H$_5$	0.0665	0.659
β-CN	0.0713	0.586

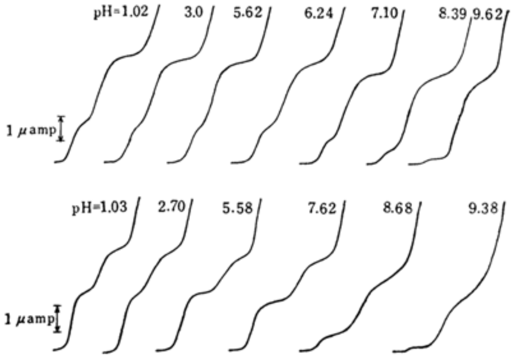

Fig. 2. Typical polarograms of some pyridine *N*-oxides showing 2-step reduction waves.
Upper: γ-CO$_2$C$_2$H$_5$ derivative (5.11×10^{-4} mol./l., 0.005% gelatin added)
Lower: β-CN derivative (5.26×10^{-4} mol./l.)

pyridine *N*-oxides discussed earlier, while the second wave height held almost unchanged over a wide pH range. Therefore, only one wave, which corresponds to the second one in the acidic solution measurements, was observed in measurements at a higher pH value. The situation may be demonstrated well by Fig. 2. It would be reasonable to identify the first wave as the reduction of the protonated cation ($\rangle$N$^+$–OH) on the basis of its

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*[3] Two waves also appeared in the polarographic reduction of halogen-substituted pyridine *N*-oxides, but the separation of the two was ambiguous.

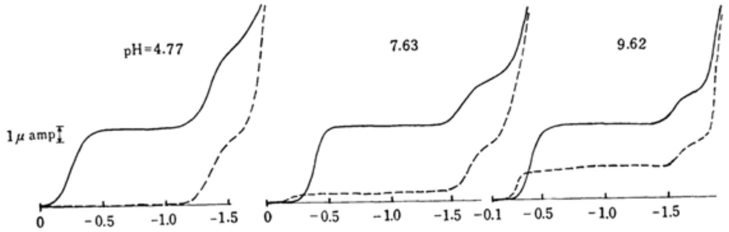

Fig. 3. Polarograms of γ-NO_2 (5.49×10^{-4} mol./l., 0.005% gelatin added, ——) and γ-NHOH (4.73×10^{-4} mol./l., ----) derivatives of pyridine *N*-oxide.

pH dependence and of the relation of its $E_{1/2}$ value to Hammett's σ, which will be discussed below. A plausible assignment of the second wave can not be attained at the present time. It was difficult to establish the relationship between $E_{1/2}$ and pH for XII in the lower pH region because of the ambiguous separation of the two waves, but a good linear plot was obtained in the 4—9 pH region, where the separation was clear.

The polarogram of γ-nitropyridine *N*-oxide (XIII) shown in Fig. 3 is of special interest. It was found that the compound shows two reduction waves, the first of which corresponds to an approximately four-electron reduction on the basis of the Ilkovic equation,²⁾ and that its wave height is almost independent of the pH value. On the other hand, the second wave height decreased as the pH increased. This two-step reduction can be reasonably explained as follows. At first the nitro group of the compound is reduced to NHOH by the first 4-electron reduction, and then the γ-hydroxyaminopyridine *N*-oxide (III) formed is subjected to $\rangle\mathrm{N}\rightarrow\mathrm{O}$-group reduction. This assumption is based on the facts that: (i) the second reduction wave of the nitro derivative (XIII) appeared at nearly the same $E_{1/2}$ value as that of the hydroxyamino derivative (III), and (ii) the pH dependence of its wave height was a typical one associated with the $\rangle\mathrm{N}\rightarrow\mathrm{O}$-group reduction discussed before. Moreover the $E_{1/2}$-σ plot falls right on the straight line in Fig. 4 if we plot the $E_{1/2}$ of the second wave of XIII against the σ value for γ-NHOH instead of that for NO_2, a fact suggesting that the second reduction wave of XIII is that of III to γ-hydroxyaminopyridine. However, an alternative possibility for the intermediate cannot be ruled out, for some other chemical evidence on pyridine *N*-oxide⁵⁾ would suggest that the intermediate produced by the first 4-electron reduction is 4, 4′-azopyridine 1, 1′-dioxide. However, the polarographic measurement of this azo compound, m. p. 246°C (decomp.); (5.09×10^{-4} mol./l., 0.005% gelatin added) showed two reduction waves. One was a wave of $E_{1/2}=-1.266$ V., and the limiting current was $i_l=3.79$ μamp. at pH=4.80, both $E_{1/2}$ and i_l being pH-dependent, and i_l decreased in the alkaline region. The other was a wave at about −0.01 V. at pH 4.80 continuing from an anodic wave. The former wave may be due to the reduction of an *N*-oxide group, but no further conclusive discussion can be made, since Hammett's σ values of the *p*-azo group are not known.[*4]

The Relationship between the Reduction Potentials of Substituted Pyridine *N*-Oxides and Hammett's σ Constants.—The plotting of $E_{1/2}$ versus Hemmett's σ constant of substituted pyridine *N*-oxides is of special interest in understanding the effect of substituents on $E_{1/2}$ and in elucidating the reduction mechanism.

As is apparent from Table II, the pH dependence of $E_{1/2}$ is nearly of the same order, and so we would expect straight lines with roughly equal slopes for the above plotting made at different pH's. Table I and Table III show the $E_{1/2}$ values observed at pH=5.0 and the selected σ values, cited mainly from Jaffé's review,¹⁰⁾ repectively. The plots of $E_{1/2}$ at pH=5.0 vs. σ are depicted in Fig. 4, where we can see that a good linear relation holds between them. The linear relation was also obtained for the values at different pH's, as had been expected. The slopes, that is, the ρ's of Hammett's equation, are: +0.457, 0.495 and 0.584 at pH values of 3.0, 4.0 and 5.0 respectively.

The plot for γ-NH_2 using the value of $\sigma=-0.66$ derived by Jaffé¹⁰⁾ deviated largely from the straight line in Fig. 4; the reduction actually took place at a more positive potential than that to be expected from the σ value. Zuman¹¹⁾ found a similar trend of the *p*-NH_2 value in the polarographic reduction of other systems, and he set σ as −0.13 in order to fit the polarographic reduction potential data. This σ value is better than Jaffé's, −0.66, for the present system, but it is not close enough

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[*4] In the meanwhile it would be worthwhile to point out that the γ-NHOH derivative (III) showed two waves in the alkaline region (see Fig. 3, the dotted curves). The first wave may be due to an azo-type compound formed from III in an alkaline solution.⁵⁾ In fact, the solution of III becomes more yellowish at a higher pH value.

10) H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953); *J. Org. Chem.*, **23**, 1790 (1958).

11) P. Zuman, *Collection Czech. Chem. Commn.*, **25**, 3225 (1960).

TABLE III. SELECTED SUBSTITUENT CONSTANTS

Substituent	σ[a]
γ-NH_2	−0.660 −0.13[b]
γ-NHOH	−0.339
γ-OCH_3	−0.268
γ-OC_2H_5	−0.250
γ-CH_3	−0.170
γ-C_2H_5	−0.151
$NHCOCH_3$	−0.015
γ-Cl	+0.227
γ-Br	+0.232
γ-$COOC_2H_5$	+0.678[c]
γ-CN	+0.660[d]
γ-NO_2	+0.778 +1.270[c]
β-NH_2	−0.161
β-OCH_3	+0.115
β-CH_3	−0.069
β-C_2H_5	−0.043
β-$NHCOCH_3$	+0.154[e]
β-F	+0.337
β-Cl	+0.373
β-Br	+0.391
β-$COOC_2H_5$	+0.398
β-CN	+0.56[d]

a) These σ-values were cited from Jaffé's review[10] unless otherwise noted.
b) See Ref. 11.
c) These are Jaffé's σ^* (σ^-) values.[10]
d) D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958).
e) See Ref. 9.

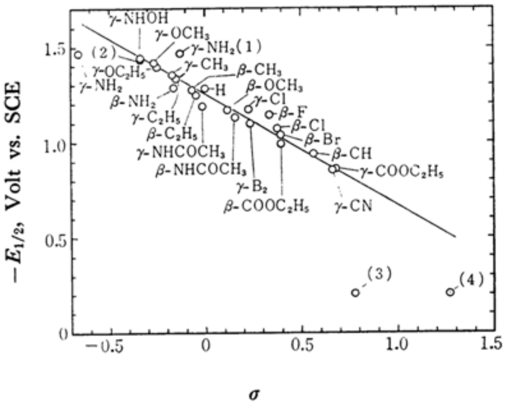

Fig. 4. The plot of $E_{1/2}$ against Hammett's σ. The points indicated by 1, 2, 3 and 4 represent, respectively, the plots of $E_{1/2}$ for II against Zuman's σ of γ-NH_2 (point 1), $E_{1/2}$ for the second wave of XIII against σ of γ-NHOH (point 2), and $E_{1/2}$ for the first wave of XIII against σ (point 3) and σ^- (point 4) of γ-NO_2 group.

to fit straight line, as do the other substituents.

Another exceptional case is that of an NO_2 group. We can see from Fig. 4 that the plots of $E_{1/2}$'s corresponding to the first and the second waves of γ-nitropyridine *N*-oxide deviate eminently from the straight line, regardless of the choice of convertional σ or σ^- values for the γ-NO_2 group. This situation has been explained above.

Now it should be noted that the ρ value is positive. This means that the more electron-releasing a substituent is, the more negative is the $E_{1/2}$ value. From this we can say that the first process which occurred on the cathode was an electron transfer from a dropping-mercury electrode to the active center of the molecule to be reduced ($\rangle N^+$-OH), in which process the electron on the dropping mercury electrode acted as a nucleophilic reagent. The same conclusion was also drawn by Zuman for other systems.[11]

A Consideration of the Relationship between $E_{1/2}$ and Hammett's σ in Terms of the Lowest Vacant MO Energy Qualitatively Predicted by the Second-Order Perturbation Method.—It would be noteworthy if we could point out that the MO theory gives some basis for the interpretation of the above-mentioned relationship between $E_{1/2}$ and Hammett's σ, as well as of the well-known relationship between $E_{1/2}$ and the lowest vacant orbital energy.

For the sake of convenience, a substitued pyridine oxide is divided into two composite systems, as is shown in Fig. 5, where R and S represent a pyridine oxide part and a substituent located at the β or γ position[*5] respectively. If we pick substituents having only one π-MO, such as CH_3, OCH_3, or NH_2, the lowest vacant orbital energy, E_{iR}, of pyridine oxide will change to E_{iR} according to Eq. 3, which was derived by the second-order perturbation mehtod;[12]

$$E_{\mathrm{iR}} = E^{\circ}_{\mathrm{iR}} + \frac{(C_{\mathrm{iR}})^2 \beta^2_{\mathrm{r-s}}}{E^{\circ}_{\mathrm{iR}} - E^{\circ}_{\mathrm{S}}} \qquad (3)$$

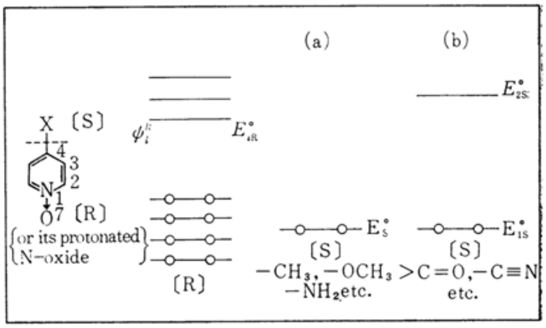

Fig. 5. Schematic diagram of MO for substituted pyridine *N*-oxides.

[*5] The atom at which the substituent is attached is designated as r.

12) K. Higashi and H. Baba, "Quantum Organic Chemistry," Asakura Publishing Co., Tokyo (1956), p. 164 (in Japanese).

Here C_{iR}, β_{r-s}, and E°_{S} represent, respectively, the coefficient on the atom r in MO ψ_i, the resonance integral between the atom r in a pyridine oxide part and the atom s in a substituent, and the energy of the highest-filled MO of the substituent. As β_{r-s} can be assumed to be a constant as the first approximation, the smaller the $|E^{\circ}_{S}|$ value or the larger the $|C_{ir}|$ value is, the smaller is the $|E_{iR}|$.[*6] If we use the naive MO's parameter, δ in our discussion,[*6] we can say that $E_{1/2}$ should move towards more negative values with a decrease in the δ of the substituent.[13] The order of estimated δ values appearing in the literature[14] is $CH_3 > OH—OR > NH_2—NR_2$; therefore, the order of $-E_{1/2}$ should be the reverse. This predicted order of $-E_{1/2}$, $NH_2 > OCH_3 > CH_3$ agrees with the order predicted from σ values using Fig. 4. However, for the case of halogen substituents, a similar teatment was not successful, probably because of their fairly large σ inductive effects, as well as because of intramolecular charge transfer from MO's of R to, for example, the 3-d atomic orbital of chlorine. These electron-withdrawing effects would be a reason why halogens have positive values of Hammett's σ's and why halogen-substituted pyridine oxides showed an easier reduction.

Let us now consider the term C_{ir}. Our previous MO calculations[15] on pyridine oxide and its proton addition compound always resulted in a larger coefficient on the 4-position than on the 3-position as to the lowest vacant MO (symmetry b_2); $|C_4| > |C_3|$. This suggests that the substituted pyridine oxide at the 4-position should have a larger $-E_{1/2}$ value than that at the 3-position for the same substituent. This prediction agreed with the observed $E_{1/2}$ data.

For a substituent having two or more π-MO's, like $>C{=}O$, $-C{\equiv}N$, etc., Eq. 3 is rewritten as:

$$E_{iR} = E^{\circ}_{iR} + \sum_{j=1}^{n} \frac{(C_{ir}\cdot C_{js})^2\cdot\beta^2_{rS}}{E^{\circ}_{iR}-E_{jS}} \qquad (4)$$

Generally speaking, however, the orbital (E°_{iR}) interacts more strongly with the vacant orbital of the substituent (E°_{2S} or higher) because of a smaller energy difference, as may be understood from Fig. 5; consequently, the level will be lowered. This stabilization results in an easier reduction (a smaller $-E_{1/2}$) of the substituted pyridine oxide compared with its mother compound. This also coincides with the tendency to be expected from Hammett's σ values.

In the case of nitropyridine *N*-oxide, the $-E_{1/2}$ value due to an NO_2 group reduction is much lower than that due to $\geqslant N \rightarrow O$-group reduction. This indicates that the lowest empty orbital of the compound originates from the nitro group.

The authors wish to express their deep thanks to Professor Emeritus Eiji Ochiai of The University of Tokyo and to Professor Shinzi Koide of Mukogawa Women's University in Nishinomiya for their valuable advice. Thanks are also due to Professor Mitsugi Senda of Kyoto University and Professor Saburo Nagakura of the Institute for Solid State Physics, The University of Tokyo, for their helpful discussions, and to Professor Yutaka Mori of Osaka Gakugei University and Dr. Sadazi Kaziwara of our laboratory for supplying some samples and for their discussions.

[*6] If we put $E^{\circ}_{S} = \alpha + \delta\beta$, δ is the parameter which is now being discussed. In addition, E, α, and β are negative values, and $-E^{\circ}_{iR} < -E^{\circ}_{S}$.

13) For the relationship between $E_{1/2}$ and the lowest vacant MO, see (a) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley & Sons, New York, N. Y. (1961), p. 173; (b) S. Koide, *J. Electrochem. Soc. Japan (Denki Kagaku)*, **23**, 485 (1955).

14) H. Baba, This Bulletin, **34**, 76 (1961); H. Baba and S. Suzuki, ibid., **34**, 82 (1961); Ref. 12, p. 150.

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