BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 780—785(1972)

The Characterization of the Electronic Spectra of Heterocyclic Amine *N*-Oxides by Means of the Non-Aqueous Oxidation and Reduction Potentials and the Substituent Effects on Them

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(Received September 20, 1971)

The half-wave potentials of the voltammetric oxidation and the reduction of various heterocyclic amine *N*-oxides have been measured in CH_3CN by the technique of a rotating platinum electrode. The reversibility of the electrode process was particularly examined for the oxidation reaction by analyzing the oxidation wave and by recording the ESR spectra. Then, the mutual relationship between the electronic spectra of these *N*-oxides and the values of the oxidation-reduction potentials was discussed in detail; we found that this kind of treatment is very useful in assigning the spectra. Finally, a good linear relation between the oxidation potentials of substituted pyridine *N*-oxides and the Hammett σ^+ (Brown-Okamoto) constants was demonstrated and discussed.

It is well known that the polarographic reduction and the oxidation potentials of organic compounds are closely correlated with the molecular orbital energies or with the total energy difference between the starting molecule and the product (free radical) after electrolysis.[1-6] That is, the oxidation ($E^{\text{oxd}}_{1/2}$) and the reduction ($E^{\text{red}}_{1/2}$) potentials are in a linear relation to the highest occupied molecular orbital (HOMO) and the lowest vacant orbital (LVMO) energies respectively. In other words, the $E^{\text{oxd}}_{1/2}$ and the $E^{\text{red}}_{1/2}$ seem to be a good measure of the ionization potential and the electron affinity of solvated organic molecules.[7,8] Keeping in mind these facts it can easily be expected that the oxidation and the reduction potentials are correlated quite well with the ultraviolet (UV) absorption spectra of organic compounds if the effect of the configuration interaction is small, and that a singly-excited configuration from HOMO to LVMO contributes mainly to these UV spectra. Typical examples of this kind previously reported are the charge-transfer (CT) ab-

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[1] J. Koutecky, *Z. Phys. Chem. N. F.*, **52**, 8 (1967) and the other papers cited therein.

[2] M. J. S. Dewar, J. A. Hashmall, and N. Trinajstic, *J. Amer. Chem. Soc.*, **92**, 5555 (1970) and the other papers cited therein.

[3] K. B. Wiberg and T. P. Lewis, *ibid.*, **92**, 7154 (1970).

[4] T. Kubota, K. Nishikida, H. Miyazaki, K. Iwatani, and Y. Ōishi, *ibid.*, **90**, 5080 (1968).

[5] E. S. Pysh and N. C. Yang, *ibid.*, **85**, 2124 (1963).

[6] W. C. Neickam, G. R. Dimeler, and M. M. Desmond, *J. Electrochem. Soc.*, **111**, 1190 (1964).

[7] F. A. Matsen, *J. Chem. Phys.*, **24**, 602 (1956).

[8] B. Case, N. S. Hush, R. Parsons, and M. E. Peover, *J. Electroanal. Chem.*, **10**, 360 (1965), *etc.*

sorption bands of CT complexes,[9-11] which are in a good linearity with the half-wave potentials of the polarographic reduction and the voltammetric oxidation of the electron acceptor and the electron donor respectively.

We will in this paper be concerned with an examination of the mutual relation between the half-wave reduction and oxidation potentials and the UV spectra of heterocyclic amine *N*-oxides; it is believed that the results obtained here will be quite useful in characterizing the UV absorption bands of the *N*-oxides, which were extensively studied hitherto in our laboratory. In connection with these dicussions, we will also study what kind of substituent effect on the oxidation and reduction potentials can be expected.

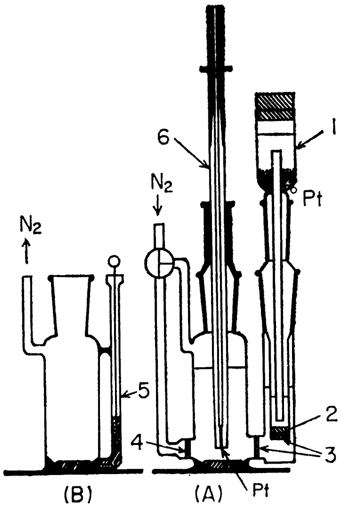

Fig. 1. Electrolysis cell used for recording DC and AC voltammograms. A and B show front and side views, respectively. (1) SCE. (2) salt bridge (see reference 4). (3, 4) fine (3) and coarse (4) glass filters. (5) terminal for ac measurement or three-electrode system. (6) rotating platinum electrode.

Experimental

Measurements. A Yanagimoto polarograph, Model P8-AP, was used to record the DC and AC polarograms. This instrument uses the three-electrode system, so that the potential due to the so-called *IR* drop term arising from the resistance of the cell circuit is automatically corrected. In the case of polarographic reduction, the details of the experimental technique for obtaining the accurate values of reduction potential have already been reported elsewhere.[4] The capillary used for the dropping mercury electrode was: $m=0.855$ mg/sec and $t=5.17$ sec at $h=70$ cm in distilled water at an open circuit. On the other hand, the half-wave potential of the oxidation voltammogram has been measured using the rotating platinum electrode illustrated in Fig. 1. This electrode has a platinum rod 1 mm in diameter, which was sealed in a soft glass tube with a diameter of ~6.5 mm, as may be seen in Fig. 1. Just before the use of this electrode, we polished the plane head of the rotating platinum electrode with very fine emery paper in order to keep the platinum surface always fresh. This simple technique gave reproducible results.[12] To record the voltammogram, a combination of the above rotating platinum electrode (600 rpm) and a Yanagimoto polarograph, Model P8-AP, was employed, a saturated calomel electrode (SCE) being

Table 1. VARIOUS HETEROCYCLIC AMINE *N*-OXIDES INVESTIGATED, WITH THEIR NUMBERING, HALF-WAVE REDUCTION AND OXIDATION POTENTIALS (V *vs.* SCE), ELECTRON NUMBER (n) ENTERING IN THE ELECTRODE OXIDATION REACTION, SCF-MO ENERGIES (eV) AT LVMO AND HOMO, AND OBSERVED BAND POSITION (eV) AT ^1L_a (CT) AND ^1L_b BANDS[a)]

No.	Compound	Reduction $E_{1/2}^{\text{red}}$	Oxidation		SCF-MO		Observed band positions	
			$E_{1/2}^{\text{oxd}}$	n	E_{lv}	E_{ho}	^1L_a(CT)	^1L_b
1	Pyridine *N*-oxide	−2.302	1.802	1.0	−2.277	−9.564	4.40	3.81
2	Pyrazine mono-*N*-oxide	−1.836	2.312	1.07	−2.558	−9.923	4.53	
3	Pyrazine di-*N*-oxide	−1.615	1.741	1.32	−3.256	−9.679	3.87	3.4
4	Pyrimidine mono-*N*-oxide	−1.927	2.352	0.81	−2.413	−9.613	—	
5	Quinoline *N*-oxide	−1.840	1.537	0.82	−2.983	−9.223	3.54	3.54
6	Isoquinoline *N*-oxide	−1.948	1.600	0.66	−2.997	−9.372	3.95	3.20
7	Quinoxaline mono-*N*-oxide	−1.456	1.971	0.28[b)]	−3.220	−9.588	3.75	
8	Quinoxaline di-*N*-oxide	−1.247	1.598	1.03	−3.639	−9.305	3.02	
9	Phenanthridine *N*-oxide	−1.814	1.482	0.62	−3.061	−9.206	3.62	3.22
10	Acridine *N*-oxide	−1.358	1.280	0.91	−3.500	−8.740	2.73	3.22
11	Phenazine mono-*N*-oxide	−1.021	1.745	0.81	−3.752	−9.110	2.94	3.26
12	Phenazine di-*N*-oxide	−0.851	1.344	0.81	−4.022	−8.825	2.51	
	Tetramethyl-*p*-phenylenediamine	—	0.128	1.0	—	—	—	—

a) See text for detailed explanation.
b) The maximum wave appeared only for this oxidation wave, whose temperature dependence is large (6.34%) and concentration dependence is irregular, although $E_{1/2}^{\text{oxd}}$ value almost unchanged with the variation of concentration. Small n value for this case may be due to those irregular phenomena.

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[9] M. E. Peover, *Trans. Faraday Soc.*, **58**, 1656, 2370 (1962); **60**, 479 (1964).

[10] M. E. Peover and J. D. Davies, *ibid.*, **60**, 476 (1964).

[11] R. D. Holm, W. R. Carper, and J. A. Blancher, *J. Phys. Chem.*, **71**, 3960 (1967).

[12] Here, note that the oxidation voltammogram itself does not change whether or not the dissolved oxygen in solution is removed by bubbling pure nitrogen gas in the solution. Needless to say, however, the reduction voltammogram should be recorded under a pure nitrogen atmosphere.

TABLE 2. HALF-WAVE OXIDATION POTENTIALS (V *vs.* SCE) OF SUBSTITUTED PYRIDINE *N*-OXIDES RECORDED WITH ROTATING PLATINUM ELECTRODE, AND THE BROWN-OKAMOTO σ^+ VALUES OF THE SUBSTITUENTS

Substituent[a)]	$E^{\mathrm{oxd}}_{1/2}$	σ^+
H	1.802	0
4-CH_3	1.606	−0.311
4-C_2H_5	1.575	−0.295
4-OCH_3	1.362	−0.778
4-$NHCOCH_3$	1.315	−0.6
4-$N(CH_3)_2$	0.759	−1.7
4-Cl	1.795	0.114
4-$COOC_2H_5$	1.977	0.482
4-CN	2.27	0.659
4-NO_2	2.13	0.790
3-CH_3	1.793	−0.066
3-OCH_3	1.717	0.047
3-Cl	1.900	0.399
3-$COOC_2H_5$	1.918	0.366
3-CN	2.013	0.562

a) The positions 4 and 3 correspond respectively to para- and meta-positions against *N*-oxide group.

used as the reference electrode. Usually all the experiments were made at 25±0.1°C in a CH_3CN solvent containing 0.1 M tetra-*n*-propylammonium perchlorate (TNPAP) as the supporting electrolyte, the sample concentration being $\sim 5\times 10^{-4}$ mol/*l*. As typical examples, the oxidation voltammograms of 1,4-dimethoxybenzene and 9,10-diphenylanthracene have been recorded; they are compared with the values in the literature[13,14)] where the experimental conditions were the same as ours. The observed values of $E^{\mathrm{oxd}}_{1/2}$ (in volts) are 1.310 (1.34) for the former and 1.241 (1.22) for the latter; here, the values in parentheses are those reported in the literature.[13,14)] The agreement of the values seems to be good. Finally, the electron-spin-resonance measurements of the anion and the cation radicals of the compounds studied have been carried out by using a technique reported in a foregoing paper.[15)]

Samples and Solvents. The samples used are listed in Tables 1 and 2 along with the experimental results. The preparation, the purification, and the physical constants of these samples have been described in our previous papers.[4,16)] The supporting electrolyte, TNPAP, was synthesized in the usual manner[17)] and was recrystallized several times from a CH_3CN–H_2O mixture. Acetonitrile has been employed as the solvent throughout the present electrode reaction of oxidation and reduction. Spectrograde CH_3CN was rectified carefully after dehydration with CaH_2. Dimethylformamide (DMF) was also used for comparing the data with those in CH_3CN in the case of voltammetric or polarographic reduction, the quality of DMF being the same as has been described elsewhere.[4)]

Results and Discussion

Half-wave Potentials, $E_{1/2}$'s, of the Voltammetric Oxidation and Reduction. It is worthy of note that the electrode reactions of the aromatic amine *N*-oxides used are not all the same. An examination of the oxidation voltammograms shows that some compounds exhibit a reversible electrode reaction due to the cation-radical formation of a mother compound, while other compounds give an irreversible reaction. A typical example of the former is phenazine di-*N*-oxide, whose oxidation and reduction voltammograms are shown in Fig. 2. The high value of the first wave peak-height of alternating-current (ac) voltammograms should be noted; it indicates a reversible electrode reaction. In fact, the ESR spectra of the cation and of the anion radicals of phenazine di-*N*-oxide were observed by controlled potential electrolysis at the first wave of the oxidation and the reduction voltammograms respectively.[4,15,18)] The following oxidation voltammetric data on phenazine di-*N*-oxide also support the above interpretation: (i) the temperature dependence of the limiting current, i_l (μA), is 0.87%, as computed by the compound-interest method; (ii) the plotting of i_l *vs.* the concentration gave a good straight line through the point of origin, and (iii) the value of 0.063 V of the log-plot (the value of $\Delta E/\Delta \log\,[i/(i_l-i)]$ indicates a one-electron oxidation process.

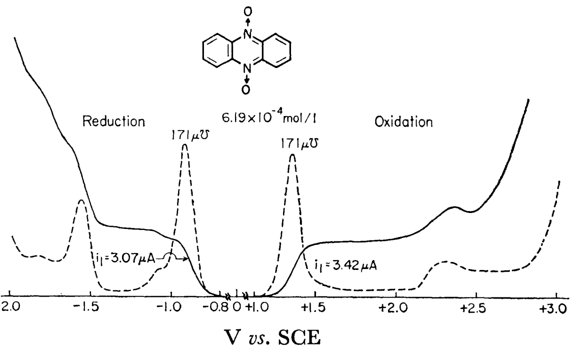

Fig. 2. DC (solid curve) and AC (dotted curve) voltammograms obtained by rotating platinum electrode for oxidation and reduction of phenazine di-*N*-oxide. The absolute value of current is taken at the ordinate for the convenience's sake.

On the other hand, the oxidation voltammograms of quinoxaline mono-*N*-oxide, *etc.*, which have nitrogen lone-pair electrons in a molecule, are typical examples of an irreversible electrode reaction. The participation of the lone-pair electrons in the process of electrode oxidation is the main reason for these irreversible reactions, where the voltammograms change with repeated runs of the measurements unless the platinum electrode is kept on the fresh surface before each recording.

Tables 1 and 2 list the data on the oxidation voltammograms of all the samples used in this report. The *n* value shown in Table 1 stands for the electron number entering in the reaction; it was determined by comparing the wave height with that (standard) of tetramethyl-*p*-phenylenediamine recorded under the same condi-

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13) A. Zweig, W. G. Hodgson, and W. H. Jura, *J. Amer. Chem. Soc.*, **86**, 4124 (1964).

14) R. E. Visco and E. A. Chandross, *ibid.*, **86**, 5350 (1964).

15) K. Nishikida, T. Kubota, H. Miyazaki, and S. Sakata, *J. Mag. Resonance* (1972), in press.

16) T. Kubota and H. Miyazaki, This Bulletin, **39**, 2057 (1966).

17) D. H. Geske and A. H. Maki, *J. Amer. Chem. Soc.*, **82**, 2671 (1960).

18) The interpretation and the assignment of the hyperfine coupling constants of these radicals, and also the non-aqueous polarographic data on the electrode reduction, have already been reported in detail.[4,15)]

tions. The oxidation voltammogram of tetramethyl-*p*-phenylenediamine is typical of those due to the one-electron oxidation process.[19]

As was mentioned above, the reversibility of the electrode oxidation reaction is more or less different and depends on the compounds. Nevertheless, we have adopted the $E^{\rm oxd}_{1/2}$ values obtained here for the following discussions, since it may be assumed that the effect of the reversibility on the half-wave potential value is not severe. The circumstances as to the $E^{\rm red}_{1/2}$ values are somewhat similar to those presented above in the oxidation voltammogram. However, generally speaking, the reversibility in the electrode reduction process seems to be better than in the case of the oxidation process for many compounds. The polarographic behaviour of various aromatic *N*-oxides has already been reported in detail.[4,15,20] The results of the present reduction voltammetric study are quite similar to, and well reproduce those of the previous polarographic investigation,[4] so in this report we will not discuss these experimental results further. Since the values of $E^{\rm oxd}_{1/2}$ and $E^{\rm red}_{1/2}$ yielded under the same conditions are most reasonable for checking the theoretical treatment (*vide infra*), the $E^{\rm red}_{1/2}$ values observed by using the rotating platinum electrode in CH_3CN solvent are included in Table 1.

The Mutual Relation between UV Spectra and the Half-wave Oxidation and Reduction Potentials. It is well known that the HOMO and the LVMO are in a linear relation to the $E^{\rm oxd}_{1/2}$ and the $E^{\rm red}_{1/2}$ values respectively.[1-8,21,22] Also, the electronic spectra are intimately correlated with the energy difference between the electron-occupied orbitals and the vacant orbitals, so we can except a reciprocal correlation, which would be useful in the assignment of the electronic spectra, of the electronic spectra to the half-wave oxidation and reduction potentials.[23]

If we let ε_{ho} and ε_{lv} be the orbital energies for the highest occupied and the lowest vacant orbitals respectively, Eqs. (1) and (2) are satisfied:

$$E^{\rm red}_{1/2} = k_1\varepsilon_{lv} + k_2 \qquad (1)$$

$$E^{\rm oxd}_{1/2} = k_1\varepsilon_{ho} + k_3 \qquad (2),$$

where k_1, k_2, and k_3 are all constants. It is assumed here that the electrode reaction is a reversible one-electron process, such as ($R+e\rightleftharpoons R^{\dot{-}}$) or ($R-e\rightleftharpoons R^{\dot{+}}$), and that the difference in diffusion coefficients, activity coefficient, and entropy terms between R and $R^{\dot{-}}$ or $R^{\dot{+}}$ can be disregarded because the values[2] are similar. The left-hand-side terms of Eqs. (1) and (2) can now be expressed by $\Delta F/\mathscr{F}$, where ΔF is the free-energy change for the above electrode process in an non-aqueous solution and is related mainly to the electron affinity[24] for the formation of $R^{\dot{-}}$ or to the ionization potential[24] for the formation of $R^{\dot{+}}$, and also to the solvation-energy change ($\Delta F_{\rm solv}$) between R and $R^{\dot{-}}$ or $R^{\dot{+}}$.[2] Accordingly, the slope, k_1, in Eqs. (1) and (2) becomes $1/\mathscr{F}$. Because $\mathscr{F}$ in a Faraday constant (1 eV/1 V), $|k_1|$ is equal to 1 when an electron volt is taken as the energy unit. The $\Delta F_{\rm solv}$ term would be constant under the same experimental conditions in a series of similar compounds (see also later discussions), and would contribute greatly to the k_2 and k_3 terms in Eqs. (1) and (2). We can now write Eq. (3) by taking account of the difference between Eqs. (1) and (2) (here k_4 is a new constant):

$$(E^{\rm red}_{1/2}-E^{\rm oxd}_{1/2}) = k_1(\varepsilon_{lv}-\varepsilon_{ho}) + k_4 \qquad (3)$$

In turn, the singlet energy corresponding to a one-electron transition from HOMO to LVMO is given by[25]:

$${}^1E_{ho\to lv} = \varepsilon_{lv} - \varepsilon_{ho} + 2K_{ho\cdot lv} - J_{ho\cdot lv} \qquad (4)$$

The excited state pertinent to the transition energy, ${}^1E_{ho\to lv}$, may be mixed with the other excited states having the same symmetry, so that the ${}^1E_{ho\to lv}$ should be changed by the amount of the configuration interaction energy, ${}^1E_{\rm CI}$. The observed energy, ${}^1E^{\rm UV}_{ho\to lv}$, attributable mostly to the HOMO→LVMO transition, is thus written as ${}^1E^{\rm UV}_{ho\to lv}=\varepsilon_{lv}-\varepsilon_{ho}+2K_{ho\cdot lv}-J_{ho\cdot lv}+{}^1E_{\rm CI}$. $K_{ho\cdot lv}$ and $J_{ho\cdot lv}$ are, respectively, the well-known two-electron exchange and the Coulomb repulsion integrals[25] pertaining to the two MO's given in the suffixes. The combination of the above equations leads to Eq. (5):

$$(E^{\rm red}_{1/2}-E^{\rm oxd}_{1/2}) = k_1[{}^1E^{\rm UV}_{ho\to lv}+J_{ho\cdot lv}-2K_{ho\cdot lv}-{}^1E_{\rm CI}] + k_4 \qquad (5)$$

The linear relation between the experimental values of $(E^{\rm red}_{1/2}-E^{\rm oxd}_{1/2})$ and ${}^1E^{\rm UV}_{ho\to lv}$ may be obtained under the binding conditions that in a series of similar compounds, (i) the effect of ${}^1E_{\rm CI}$ on the ${}^1E_{ho\to lv}$ is small or is considered to be constant throughout the compounds, and (ii) the magnitude of the electron repulsion terms $(J_{ho\cdot lv}-2K_{ho\cdot lv})$ may be put constant in all the samples. In these cases, we can simply write Eq. (6):

$$(E^{\rm red}_{1/2}-E^{\rm oxd}_{1/2}) = k_1\cdot{}^1E^{\rm UV}_{ho\text{-}lv} + k_5 \qquad (6)$$

Previously we reported detailed Pariser-Parr-Pople (P.P.P.)-type SCF MO calculations of many aromatic tertiary amine *N*-oxides for use in interpreting the electronic spectra and the electronic structures.[26] These calculation results can be used to check Eqs. (3) and (6). For the compounds whose P.P.P. calculations have not yet been reported, the calculations have been newly carried out here using the same method as in

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[19] T. A. Gough and M. E. Peover, "Polarography," Vol. 2, ed. by G. J. Hills, Macmillan, London (1964), p. 1017.

[20] T. Kubota, H. Miyazaki, and Y. Mori, *Rev. Polarog.*, (Kyoto), **14**, 313 (1967).

[21] a) T. Tani and S. Kikuchi, Report of the Institute of Industrial Science, the University of Tokyo, **18**, No. 2 (1968), p. 51. b) T. Tani, K. Honda, and S. Kikuchi, *J. Electrochem. Soc. Japan*, **37**, 17 (1969), and the other papers cited in 21a and 21b.

[22] R. Takahashi, "Reaction in Non-aqueous Solvents," Kagaku-zōkan 44, ed. by N. Ise, N. Tokura, and T. Fujinaga, (in Japanese) Kagaku-Dōjin (Kyoto) (1970), p. 147.

[23] a) A. T. Watson and F. A. Matsen, *J. Chem. Phys.*, **18**, 1305 (1950). b) I. Bergman, *Trans. Faraday Soc.*, **50**, 829 (1954); **52**, 690 (1956).

[24] Assuming that there is no change in the molecular geometry upon the $R^{\dot{-}}$ or $R^{\dot{+}}$ formation and no change in the electronic state compared to that of the ground state except for the one-electron addition to LVMO or the one-electron removal from HOMO, these values may be put equal to ε_{lv} or ε_{ho}.

[25] N. Mataga and T. Kubota, "Molecular Interactions and Electronic Spectra," Chapter 2, Marcel Dekker, New York (1970).

[26] M. Yamakawa, T. Kubota, and H. Akazawa, *Theoret. Chim. Acta* (Berl.), **15**, 244 (1969), and the other papers cited therein. See also C. Leibovici and J. Streith, *Tetrahedron Lett.*, **1971**, 387; J. C. D. Brand and K.-T. Tang, *J. Mol. Spectrosc.*, **39**, 171 (1971).

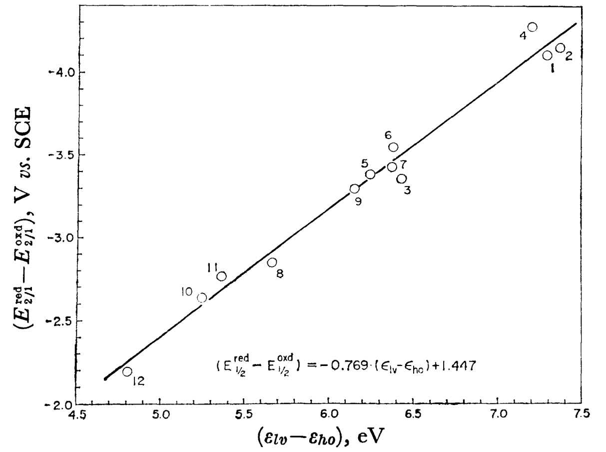

Fig. 3. The relationship between calculated values of $(\varepsilon_{lv}-\varepsilon_{ho})$ and observed values of $(E_{1/2}^{\rm red}-E_{1/2}^{\rm oxd})$ for heterocyclic amine *N*-oxides. See Table 1 for the numbering of each compound.

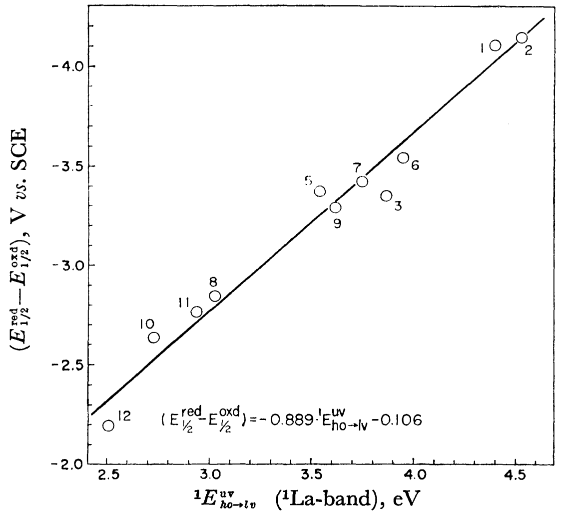

Fig. 4. The relationship between observed values of ${}^1L_a$ (${}^1E_{ho\to lv}^{\rm uv}$) band and $(E_{1/2}^{\rm red}-E_{1/2}^{\rm oxd})$ for heterocyclic amine *N*-oxides. See Table 1 for the numbering of each compound.

foregoing papers.[26,27] The calculation results are listed in Table 1.

Let us now focus attention on the intramolecular charge-transfer band (${}^1L_a$ band) of the amine *N*-oxides,[26] which is mainly due to an electron transition from HOMO to LVMO, where the effect of the configuration interaction is small except for the case of isoquinoline *N*-oxide (0.394 eV). On the basis of the calculation results made hitherto, we may say that the values of ${}^1E_{\rm CI}$ and $(2K_{ho\cdot lv}-J_{ho\cdot lv})$ are within the maximum variation of 0.11 ± 0.10 eV and -2.21 ± 0.80 eV respectively, and that, except for a few exceptional cases, these values may be seemed to be nearly constant. Therefore, the linear relation of Eqs. (3) and (6) can reasonably be expected to be as is given in Figs. 3 and 4. The mutual correlations are very good. That the slope of the straight line obtained in Figs. 3 and 4 is less than, but near, the $|1|$ should be noted. It can safely be said that the previous conclusion[26] that the ${}^1L_a$ (or CT) band of aromatic *N*-oxides arises mainly from a one-electron transition from HOMO to LVMO has been supported by the electrochemical study illustrated in Figs. 3 and 4. From the other standpoint, one can also discuss as follows. It may be remembered that, of the methods employed for analyzing the electronic spectra of a series of similar compounds, the so-called spectroscopic β method is a useful technique[28,29]; here the exchange integral, β, is taken to be a constant applied only to absorption bands which belong to electronic transitions similar in character (*i.e.*, for the ${}^1L_a$ and ${}^1L_b$ bands the β (${}^1L_a$) and $\beta({}^1L_b)$ values are separately assigned). In principle, the β value may be considered as a value including the electron repulsion terms pertinent to the electronic transitions in the same species; it is taken as a constant throughout the series of absorption bands in question, so that the assumptions used in deriving the present equation (6) (except for the discussion of the ${}^1E_{\rm CI}$ term) and in estimating the spectroscopic β value seem to be similar to each other. Thus, the experimental results shown in Figs. 3 and 4 confirm the usefulness of the above-mentioned spectroscopic β method.

Next, let us discuss the slope of the straight lines shown in Figs. 3 and 4, which is less than the theoretical value of $|1|$. In previous discussions, we assumed that there was no change in the solvation energy of a variety of cation or anion radicals. The *N*-oxides used, however, can be roughly grouped in three groups by size; *i.e.*, the substances range from monocyclic to tricyclic *N*-oxides, so that the effective ion radii of the cation or anion radicals fall in three groups. As may be understood from Born's equation,[30] these may turn out to be different solvation energies, which would more or less destroy our first assumption. In the present case, we may say, in general, that as the molecular size increases, the values of $|E_{1/2}^{\rm red}-E_{1/2}^{\rm oxd}|$, $(\varepsilon_{lv}-\varepsilon_{ho})$, ${}^1E_{ho\to lv}^{\rm UV}$, and *the solvation energy* of the anoin or cation radical ions, decrease, which may lead to the slope smaller than $|1|$ that is found for the data obtained *in vacuo*. The following experimental data can also account for the deviation from the ideal linear relationship of Eqs. (3) and (6). That is, the reversibility of the electrode process may be a little different between the reduction and oxidation voltammograms, since, in general, the heterocyclic compound producing the corresponding stable anion radical brings about a lesser stability in the corresponding cation radical, and *vice versa* (see also the first section of "Results and Discussion").

Finally, we would like to discuss the relationship between the ${}^1L_b$ bands of the *N*-oxides and the $(E_{1/2}^{\rm red}-E_{1/2}^{\rm oxd})$ values. Generally speaking, the ${}^1L_b$ band has a very different character from that of the ${}^1L_a$ (or CT) band; not only is the contribution from the HOMO→

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27) For the pyridine-type nitrogen atom the values of 14.51 eV and 1.20 eV were employed as the valence-state ionization potential and the electron affinity respectively. *Cf.* G. Pilcher and H.A. Skinner, *J. Inorg. Nucl. Chem.*, **24**, 937 (1962).

28) H. Baba, This Bulletin, **34**, 76 (1961); H. Baba and S. Suzuki, *ibid.*, **34**, 82 (1961); *J. Chem. Phys.*, **32**, 1706 (1960); L. Goodman and H. Shull, *ibid.*, **27**, 1388 (1957).

29) T. Kubota and M. Yamakawa, This Bulletin, **36**, 1564 (1963); M. Yamakawa, T. Kubota, H. Akazawa, and I. Tanaka, *ibid.*, **41**, 1046 (1968).

30) M. Born, *Z. Physik.*, **1**, 45 (1920); see also Ref. 25, p. 225.

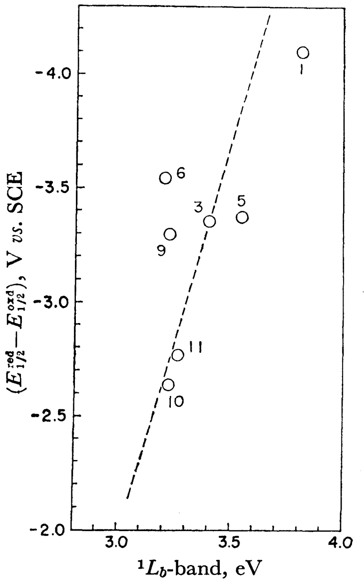

Fig. 5. Plot of the observed values of $(E^{red}_{1/2}-E^{oxd}_{1/2}$ against the observed ^1L_b band energies for heterocyclic amine N-oxides. See Table 1 for the numbering of each compound.

LVMO transition very small (if one considers the C_{2v} molecule, the contribution is zero), but also the effect of the configuration interaction on that band is quite large. Accordingly, we can not expect a linear relationship as in Eq. (6). For some N-oxides we plot (Fig. 5) the values of $(E^{red}_{1/2}-E^{oxd}_{1/2})$ against the ^1L_b band positions, whose assignment has already been reported.[26] It is now clear that there is no good linear relation and that, roughly speaking, the ^1L_b band position is quite independent of the values of $(E^{red}_{1/2}-E^{oxd}_{1/2})$, so the slope of the dotted line in Fig. 5 is very much larger than $|1|$ and is theoretically unreasonable. Conversely speaking, we can say that the bands employed in Fig. 5 can not be assigned to the ^1L_a (or CT) and that the experimental test of Eqs. (3) and (6) is quite usefull in confirming the band assignment.

Substituent Effect on the Oxidation Potentials of Pyridine N-Oxide Derivatives. In our previous papers, we have already reported a good linear correlation between the $E^{red}_{1/2}$ values and Hammett's σ constants on pyridine N-oxide derivatives[4,16] and discussed the physical meaning of this. Here, we have tested whether or not such a correlation holds in the case of the $E^{oxd}_{1/2}$ values, also. Fig. 6 shows the correlation of the $E^{oxd}_{1/2}$ values, which are listed in Table 2, with the Brown-Okamoto σ^+ constants.[31] A good linear relation, written as $E^{oxd}_{1/2}=0.565\ \sigma^+ +1.745$, with a root mean-square deviation equal to ± 0.066, is found to hold. It should be noted that, in the present case, if one adopts usual Hammett's σ or σ^- values[4,16] we can not find, in particular for the case of larger electron-donating substituents, a good linear relation such as is found in Fig. 6. The free-energy change due to the electrode oxidation reaction is, of course, electrophilic in nature and is just the reverse of that in the case of the electrode reduction process, where the use of σ^- and σ values was suitable[4,16] (the reaction is nucleophilic). Therefore, it is reasonable to say that the better description of the activated state of the oxidation reaction is made using the σ^+ values. Lastly, it is worthwhile to point out that the most important molecular orbital entering into the electrode oxidation is the HOMO, which is destabilized by introducing an electron-donating substituent such as NR_2 in the pyridine ring. This brings about the oxidation reaction more easily and makes the $|E^{oxd}_{1/2}|$ value smaller. These circumstances are just the reverse of those for the process of electrode reduction, where the $|E^{red}_{1/2}|$ value increases when the ring hydrogen atom is replaced with an electron-donating substituent.

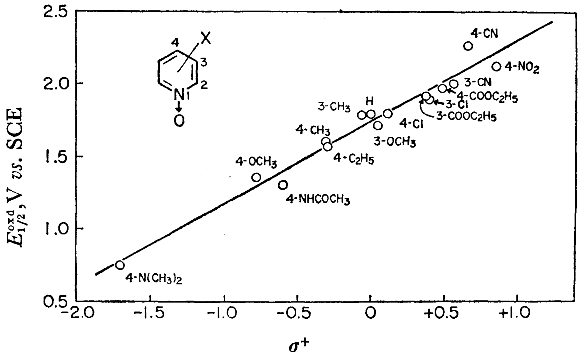

Fig. 6. Linear relation between Brown-Okamoto's σ^+ values and the half-wave oxidation potentials at the first wave of substituted pyridine N-oxides.

The authors wish to express their thanks to Professors Soichiro Musha and Makoto Munemori of the College of Engineering, University of Osaka Prefecture, and to Professor Saburo Nagakura of the Institute for Solid State Physics, the University of Tokyo, for their useful discussions.

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[31] H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, **80**, 4979 (1958).