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Hydrogen-bonding Effects on the Electron Spin Resonance Spectra of the Anion Radicals of Several Aromatic Amine *N*-Oxides

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The hydrogen-bonding effects of ethanol, phenol, and water on the electron-spin-resonance spectra of the anion radicals of 4-nitro- and 4-cyano-pyridine *N*-oxides, pyrazine mono- and di-*N*-oxides, and 4-nitropyridine electrochemically generated in dimethylformamide have been studied quantitatively. The equilibrium constant, *K*, pertinent to the hydrogen-bonding systems was determined on the basis of analyses of the variation in the hyperfine coupling constant caused by the addition of a proton donor. The active site in a radical anion participating in the hydrogen-bonding interaction and the *K* values were then discussed on the basis of the theoretical calculation of the spin density and the coupling constant of the radicals in the hydrogen-bonding interaction. It has been pointed out that this sort of experiment in hydrogen bonding interaction is also useful for assigning the hyperfine coupling constant to a definite atom in a radical. Last, these *K* values are used to explain the mechanism of radical formation by the controlled potential electrolysis at different reduction potentials of pyrazine mono- and di-*N*-oxides in dimethylformamide-ethanol mixed solvents.

Since the first finding in 1962 by Deguchi,[1] Stone and Maki,[2] Piette *et al.*,[3] and other workers[4] regarding the quite large solvent dependence of the isotropic hyperfine coupling (hfc) constant of some organic free radicals, the study of the mechanism of solvent effects on electron spin resonance (ESR) spectra has attracted the attention of many workers. The theoretical considerations for explaining these solvent effects have been presented by Gendell, Freed, and Fraenkel (GFF),[5] who applied the mass-action-law, which describes the solvent dependence in terms of radical-solvent of molecular-complex formation, and who pointed out that the change in hfc constant arises from the redistribution of an unpaired electron due to the variation in the electronic state of free radicals with the complex formation. Later, this GFF theory was supported by experimental studies,[6,7] where mixed solvents consisting of water or alcohol and acetonitrile (AN) or dimethylformamide were frequently used. However, a successful quantitative examination of the GFF theory has been reported only by Stone and Maki.[8] In those studies, however, one component in the mixed solvents was a well-known proton donor, water, appearing in hydrogen-bonding complexes which seem to play an important role in the solvent effects.

Aside from the studies mentioned above, Deguchi *et al.*[1,9,10] also studied in detail the solvent effects on the ESR spectra of several organic free radicals; they showed that electrostatic interaction and charge transfer (CT) interaction, such as hydrogen bonding[9] or usual CT complex formation,[10,11] are the two main factors in the solvent effects. Including the studies mentioned above, a survey of the investigations reported thus far of solvent effects on the hfc constant or on the *g*-value of ESR spec-

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[1] Y. Deguchi, This Bulletin, **35**, 260 (1962).

[2] E. W. Stone and A. H. Maki, *J. Chem. Phys.*, **36**, 1944 (1962).

[3] L. H. Piette, P. Ludwig and R. N. Adams, *J. Amer. Chem. Soc.*, **84**, 4212 (1962).

[4] a) A. W. Iljasav, *Zh. Strukt. Khim.*, **3**, 95 (1962); b) F. W. Heineken, M. Bruin and F. Bruin, *J. Chem. Phys.*, **37**, 452 (1962); c) A. J. Tench and P. Coppens, *J. Phys. Chem.*, **67**, 1378 (1963); d) P. L. Kolker and W. A. Water, *Proc. Chem. Soc.*, **1963**, 55.

[5] J. Gendell, J. H. Freed and G. K. Fraenkel, *J. Chem. Phys.*, **37**, 2832 (1962).

[6] P. Ludwig, T. Layloff and R. N. Adams, *J. Amer. Chem. Soc.*, **86**, 4568 (1964).

[7] J. Pannell, *Mol. Phys.*, **7**, 317 (1964).

[8] E. W. Stone and A. H. Maki, *J. Amer. Chem. Soc.*, **87**, 454 (1965). See also Ref. 7.

[9] K. Mukai, H. Nishiguchi, K. Ishizu, Y. Deguchi and H. Takaki, This Bulletin, **40**, 2731 (1967).

[10] Y. Ōishi, K. Mukai, H. Nishiguchi, Y. Deguchi and H. Takaki, *Tetrahedron Lett.*, **46**, 4773 (1968). See also J. Yamauchi, H. Nishiguchi, K. Mukai, Y. Deguchi and H. Takaki, This Bulletin, **40**, 2512 (1967).

[11] S. Aono and M. Suhara, This Bulletin, **41**, 2553 (1968). Refer also to F. Gerson and W. B. Martin, Jr., *J. Amer. Chem. Soc.*, **91**, 1883 (1969); A. Ishitani and S. Nagakura, *Mol. Phys.*, **12**, 1 (1967).

tra[12),*1] clearly tells us that the hydrogen-bonding effect plays an important role in the case of solvents having O–H or N–H groups. However, only a few quantitative studies of the equilibrium system have been reported thus far.

In the foregoing paper[13)] we reported in detail on the ESR spectra the anion radicals of many heterocyclic amine *N*-oxides, and also on the polarographic behavior of these radicals. During our studies we found that the hfc constants (absolute value) due to the nitrogen atom $|a_N|$ or ring hydrogen $|a_H|$ show quite a large solvent dependence with the addition of a proton donor. In this paper quantitative data on the equilibrium constant, K, for the hydrogen-bonding systems composed of some heterocyclic amine *N*-oxide anion radicals and several proton donors will be reported on the basis of the different formulation in GFF's concept.[5)] These K values, as well as the change in the hfc constants with hydrogen-bonding interaction, are then discussed theoretically from the viewpoint of the electronic structures of these radical anions, and are also used to explain the mechanism of radical formation by controlled potential electrolysis at the different reduction potentials observed in non-aqueous polarograms of some amine *N*-oxides.

Experimental

Methods and Measurements. Anion radicals were generated electrochemically using the controlled-potential electrolysis cell reported in a previous paper.[13)] The potential for the electrolysis was determined by using the polarographic data. The electrolysis cell for nonaqueous polarography has also been previously reported in detail.[13)] The ESR spectra were measured under almost the same conditions as in the polarographic measurement. A 0.1 M solution of tetra-*n*-propylammonium perchlorate was employed as a supporting electrolyte throughout the experiments. It has been reported[14)] that this kind of bulky ammonium salt has almost no concentration effect on the hfc constants of free radicals. The instruments used for recording the ESR spectra were a Varian V-4502-15 X-band spectrometer with a 100 KHz magnetic field modulation, the magnetic field being monitored with a Varian F-8 nuclear fluxmeter and a Takeda Riken TR-5578 frequency counter. A Yanagimoto polarograph, Model PA-102, was used to record the DC and AC polarograms. The experimental conditions for operating these instruments and the cautions taken in obtaining the accurate observed values have already been described elsewhere.[13)] All the measurements were made at ~25°C.

Samples and Solvent. 4-Nitropyridine *N*-oxide (4NPO), 4-cyanopyridine *N*-oxide (4CNPO), pyrazine mono- and di-*N*-oxides, and 4-nitropyridine (4NP) were adopted as the mother substances for producing the anion radicals. The methods of syntheses and purifications of these compounds, and also the ESR spectra, except for those of 4NP,[15)] in a dimethylformamide (DMF) solvent have been reported in previous papers.[13,16)] 4NP was yielded by the deoxygenation of the *N*-oxide-group oxygen atom of 4NPO by using the method reported by Hamana and Yoshimura,[15)] it being repeatedly recrystallized from petroleum ether (mp 47.0—47.2°C). As to the proton donors, ethyl alcohol, water, and phenol were used. On the other hand, ethyl ether was used as a reference substance. 99.5% special-grade ethyl alcohol and special-grade ethyl ether were, respectively, dried sufficiently with $CuSO_4 \cdot H_2O$ (alcohol) or a molecular sieve (ether), and then rectified carefully. Phenol of a special pure grade was distilled two times under reduced pressure. The solvent DMF and the supporting electrolyte, tetra-*n*-propylammonium perchlorate, were of the same quality as in a previous report.[13)]

Results

Behavior of ESR Spectra and Polarograms upon the Addition of Proton Donors. Since the polarographic reduction potential, $E_{1/2}$, of the

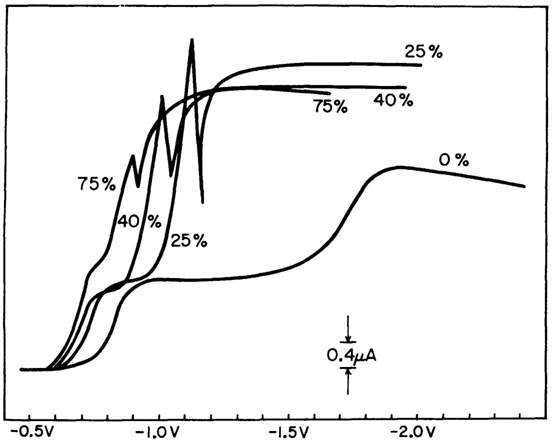

Fig. 1. Variation of the polarogram of 4-nitropyridine *N*-oxide (5.28×10^{-4} mol/*l*) in dimethylformamide with the addition of ethanol (vol%).

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12) T. Kawamura, S. Matsunami, T. Yonezawa and K. Fukui, This Bulletin, **40**, 1111 (1967); *ibid.*, **38**, 1935 (1965).

[*1] It was also reported that the visible spectrum of nitrobenzene anion radical in acetonitrile is blue shifted by the addition of proton donor (water). J. Q. Chambers and R. N. Adams, *Mol. Phys.*, **9**, 413 (1965).

13) T. Kubota, K. Nishikida, H. Miyazaki, K. Iwatani and Y. Ōishi, *J. Amer. Chem. Soc.*, **90**, 5080 (1968).

14) a) T. Kitagawa, *Rev. Polarog.* (Kyoto), **12**, 11 (1964); b) T. Kitagawa, T. Layoff and R. N. Adams, *Anal. Chem.*, **36**, 925 (1964); c) J. Burgess and M. C. R. Symons, *Quart. Rev.* (London), **22**, 276 (1968).

15) a) M. Hamana and H. Yoshimura, *J. Pharm. Soc. Japan*, **72**, 1051 (1952); b) K. Ezumi, H. Miyazaki and T. Kubota, *J. Phys. Chem.*, in press. See also K. Ezumi *et al.*, Preprints for the 21st Annual Meeting of the Chemical Society of Japan, Osaka (April 1968), No. 20114.

16) T. Kubota, H. Miyazaki and Y. Mori, *Rev. Polarog.* (Kyoto), **14**, 313 (1967). See also previous literature given in Refs. 13 and 15b.

compounds studied here moves toward a positive value (*i. e.*, these are a positive shift) upon the addition of proton donors into the DMF or acetonitrile solvent, the set potential for controlled potential electrolysis is also shifted to a positive potential. When the first and the second waves are obviously separated in the DMF solvent alone, just like the reduction wave of 4NPO,[13] as is shown in Fig. 1, the above-mentioned positive shift of $E_{1/2}$ is remarkable for the second wave. As a result, the coalescence of the first and the second waves occurs with an increase in the proton donor concentration, while the radical formed by the electrolysis simultaneously becomes unstable. Of

TABLE 1. SOLVENT EFFECTS ON HYPERFINE COUPLING CONSTANTS (ABSOLUTE VALUE) OF SOME AROMATIC AMINE OXIDE ANION RADICALS

[A] 4-Nitropyridine *N*-oxide[a]

Proton donor	Concentrtation		$a_{N(NO_2)}$	$a_{N(N\rightarrow O)}$	a_{3H}	a_{2H}
	mol/*l*	vol%				
Ethanol	0	0	6.040	4.730	3.320	1.260
	0.853	5	6.272	4.720	3.276	1.204
	1.705	10	6.492	4.703	3.324	1.196
	3.410	20	6.669	4.618	3.351	1.190
	5.115	30	6.913	—	—	—
	6.820	40	6.849	4.635	3.337	1.162
	10.230	60	7.326	4.577	3.337	1.143
	11.935	70	7.405	4.440	3.331	1.113
Water	2.770	5	6.495	4.716	3.309	1.187
	5.540	10	7.031	4.559	3.324	1.155
	8.310	15	7.404	4.491	3.332	1.153
	11.080	20	7.707	4.424	—	1.190
	13.850	25	7.955	4.514	3.305	1.116
	16.620	30	8.057	4.366	3.254	1.107
Phenol	1.306×10^{-2}	—	6.169	4.751	3.333	1.243
	3.094×10^{-2}	—	6.225	4.736	3.327	1.234
	5.092×10^{-2}	—	6.261	4.750	3.363	1.238
	5.834×10^{-2}	—	6.329	4.717	3.332	1.212
	$13.44\ \times10^{-2}$	—	6.489	4.713	3.324	1.220

[B] 4-Cyanopyridine *N*-oxide[a]

Proton donor	Concentration		$a_{N(N\rightarrow O)}$	$a_{N(C\equiv N)}$	a_{3H}	a_{2H}
	mol/*l*	vol%				
Ethanol	0	0	9.610	1.760	2.360	0.610
	0.171	1	9.512	1.787	2.144	0.912
	0.341	2	9.651	1.813	2.131	1.072
	0.682	4	9.642	1.824	2.059	1.143
	1.023	6	9.514	1.818	2.018	1.207
	1.705	10	9.620	1.830	1.999	1.255
	2.728	16	9.630	1.820	2.015	1.202

[C] Pyrazine mono-*N*-oxide[a]

Proton donor	Concentration		$a_{N(N\rightarrow O)}$	$a_{N(\rangle N)}$	a_{3H}	a_{2H}
	mol/*l*	vol%				
Ethanol	0	0	12.050	5.493	2.132	1.542
	0.017	0.1	12.134	5.589	2.122	1.640
	0.051	0.3	12.122	5.643	2.126	1.732
	0.102	0.6	12.121	5.742	2.135	1.796
	0.171	1.0	12.179	5.727	2.136	1.866
	0.341	2.0	12.184	5.804	2.141	1.844
	0.682	4.0	12.188	5.842	—	1.874

Table 1. (continued)

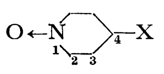
[D] 4-Nitropyridine[a)]

Proton donor	Concentration		$a_{\mathrm{N(NO_2)}}$	$a_{\mathrm{N}(>\mathrm{N})}$	$a_{3\mathrm{H}}$	$a_{2\mathrm{H}}$
	mol/*l*	vol%				
Ethanol	0	0	7.257	2.622	3.021	0.398
	0.341	2	7.538	2.590	3.037	0.434
	0.682	4	7.763	2.563	3.052	0.440
	0.853	5	7.830	2.577	3.064	0.443
	1.194	7	7.861	2.560	3.029	0.447
	1.705	10	8.016	2.550	3.052	0.454
	2.558	15	8.141	2.528	3.084	0.449
	3.410	20	8.344	2.496	3.023	0.453
	5.115	30	8.553	2.511	3.075	0.472
	6.820	40	8.818	2.469	3.082	0.484
	8.525	50	9.011	2.453	3.085	0.504
	10.230	60	9.189	2.442	3.078	0.508

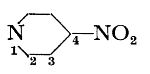
[E] Pyrazine di-*N*-oxide[a)]

Proton donor	Concentration		a_{H}	$a_{\mathrm{N(N\to O)}}$
	mol/*l*	vol%		
Ethanol	0	0	1.362	9.441
	0.341	2	1.496	9.775
	0.682	4	1.531	9.749
	1.023	6	1.546	9.727
	1.364	8	1.552	9.884
	1.705	10	1.565	—
	2.387	14	1.591	9.846
	3.069	18	1.616	—

a) Numbering of each ring atom in the radicalas is as follows:



and



course, the selection of the set-potential becomes difficult because of the above-mentioned coalescence of the first and the second reduction waves, the former being due to the anion-radical formation of mother compounds. Our hydrogen-bonding experiments were, thus, restricted within some limited concentrations of proton donors, as is shown in Table 1. Nevertheless, the anion radical of 4NPO was most stable, and it was possible to use some proton donors in making the hydrogen-bonding study. It should be now noted that even though ethyl ether of, for example, about 20% is added in a DMF solvent instead of ethyl alcohol, we observed almost no change in the polarogram of 4NPO or in the ESR spectrum of the 4NPO anion radical compared with those recorded in the DMF solvent alone, but that when ethyl alcohol is added the ESR spectra and polarograms undergo considerable change. These facts may support the evidence that the hydrogen-bonding effect is an important factor in bringing about the change in the ESR spectra and in the polarograms. As examples, the ESR spectral change in 4NPO and 4CNPO anion radicals arising from the addition of proton donors is shown in Figs. 2 and 3 respectively. Figures 4A and 4B show the variation in the hfc constants caused most predominantly by the addition of proton donors.

Evaluation of the Equilibrium Constant, *K*. According to the GFF concept, let us consider this hydrogen-bonding equilibrium:

$$\mathrm{RS} + \mathrm{D} \rightleftarrows \mathrm{RD} + \mathrm{S} \tag{1}$$

Here, RS, D, and RD stand for the assumed radical-solvent complex, the proton donor, and the radical-proton donor complex respectively. On the other hand, if no radical-solvent complex is assumed, the equilibrium may be written as:

$$\mathrm{R} + \mathrm{D} \rightleftarrows \mathrm{RD} \tag{2}$$

this sort of expression being usually employed for the equilibrium study of various charge-transfer (CT) complexes, including hydrogen-bonding complexes. If the equilibrium in Eqs. (1) and (2) is

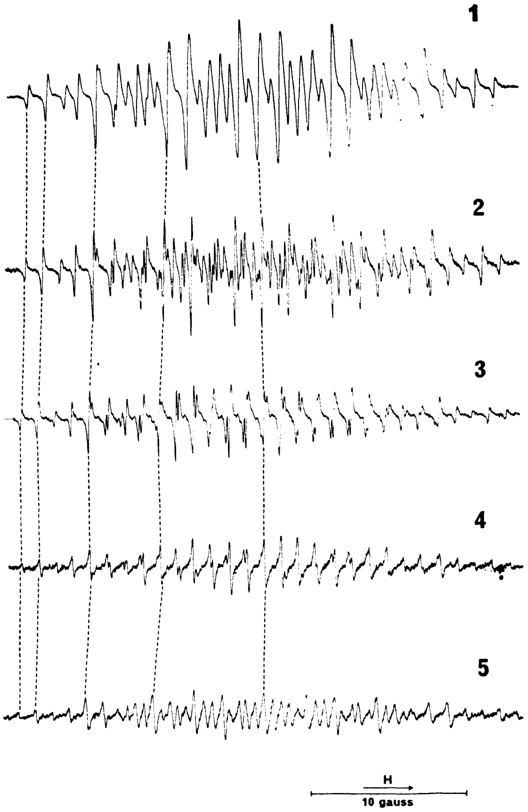


Fig. 2. ESR spectral change of 4-nitropyridine *N*-oxide anion radical in dimethylformamide with the addition of ethanol, the concentration of which is 0, 10, 30, 40 and 60 vol% for spectral No. 1, 2, 3, 4 and 5, respectively.

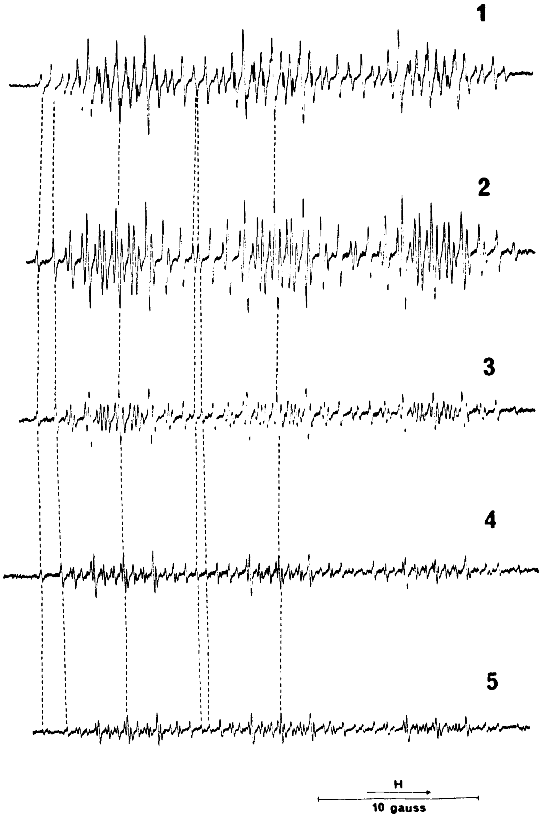


Fig. 3. ESR spectral change of 4-cyanopyridine *N*-oxide anion radical in dimethylformamide with the addition of ethanol, whose concentration is ~0, 2, 4, 10 and 16 vol% for spectral No. 1, 2, 3, 4 and 5, respectively.

very rapid,[*2] the observable hfc constant, $\bar{a}$, is easily given by $\bar{a}=P_{RS}a_{RS}$(or $P_{R}a_{R}$)$+P_{RD}a_{RD}$; for the case of hydrogen-bonding interaction, this expression for $\bar{a}$ would be correct because it is well known that the hydrogen-bonding equilibrium is very rapid.[*2] Using the definition of $K=(\mathrm{RD})\cdot(\mathrm{S})/(\mathrm{RS})(\mathrm{D})$ for Eq. (1), P_{RS} and P_{RD} are now written as $P_{RS}=1/(1+K\alpha)$, $P_{RD}=K\alpha/(1+K\alpha)$, and $P_{RS}+P_{RD}=1$. Here, $\alpha=(\mathrm{D})/(\mathrm{S})$. If Eq. (2) is applied, $K=(\mathrm{RD})/(\mathrm{R})(\mathrm{D})$, $P_{R}=1/(1+K(\mathrm{D}))$, and $P_{RD}=K(\mathrm{D})/(1+K(\mathrm{D}))$. Now, by combining those equations we can get:

$$\bar{a}=a_{RD}-(1/K)(\bar{a}-a_{RS})/\alpha \tag{3}$$

and

$$\bar{a}=a_{RD}-(1/K)(\bar{a}-a_{R})/(\mathrm{D}) \tag{4}$$

from Eqs. (1) and (2) respectively. The concentrations (D) and (S) in Eqs. (3) and (4) are those in the equilibrium state, but the radical concentration is very small ($<10^{-4}$ mol/*l*), so that, in good approximation, $(\mathrm{D})\approx(\mathrm{D})_0$ and $\alpha\approx(\mathrm{D})_0/(\mathrm{S})_0$. The zero subscript means the initial concentration. It can easily be understood that the plot of $\bar{a}$ against $(\bar{a}-a_{RS})/\alpha$ or $(\bar{a}-a_{R})/(\mathrm{D})$ should satisfy the linear relation if Eq. (1) or (2) holds. Thus, from the slope and the intersection at the ordinate the $1/K$ (then K) and a_{RD} values can be directly obtained.[*3]

For the equilibrium system where 1 (radical) : 2 (proton donor) complex formation, such as

$$\mathrm{SRD}+\mathrm{D} \rightleftarrows \mathrm{DRD}+\mathrm{S} \tag{5}$$

has to be taken into consideration in addition to the 1 : 1 form (Eq. (1)), Stone and Maki[8)] derived the equation:

[*2] The recombination rate process in usual hydrogen bonding or proton addition equilibriums was reported to be in the order of $\sim10^{10}$ (mol/*l*)$^{-1}$(sec)$^{-1}$. N. Mataga, Y. Torihashi and Y. Kaifu, *Z. Phys. Chem. N. F.*, **34**, 379 (1962); A. Weissberger (Editor), Technique of Organic Chemistry, Vol. 8, Part II, Chapters XV—XX "Very Rapid Reactions in Solution," p. 793, Interscience Publishers Inc., New York (1963).

[*3] From this viewpoint Eq. (3) seems to be more convenient than the equation, $\bar{a}=(1/2)(a_{RS}+a_{RD})+(1/2)[(a_{RD}-a_{RS})\times(K\alpha-1)]/(K\alpha+1)$, given in the GFF paper.[5)]

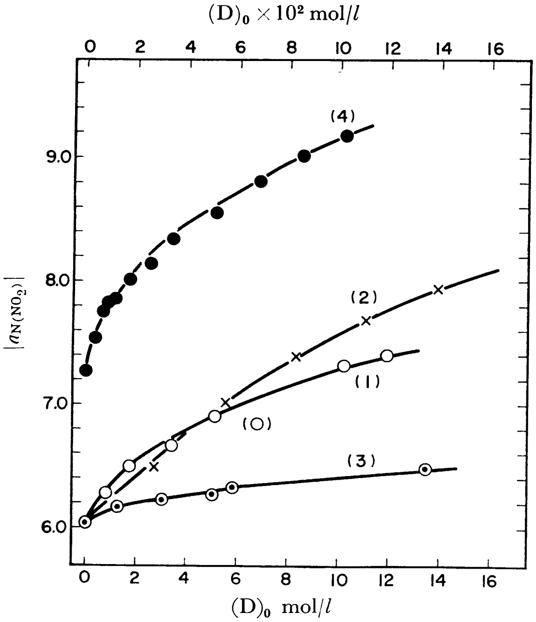


Fig. 4A. Variation of hfc constant due to the nitro group nitrogen atom of 4-nitropyridine *N*-oxide (curves 1, 2 and 3) and 4-nitropyridine (curve 4) with the addition of proton donor. Added proton donors are ethanol, water, and phenol for curves 1 and 4, 2, and 3, respectively. Upper abscissa should be referred only to curve 3. Here note that each curve is obtained theoretically by the method written in the text, but each point is the experimental value.

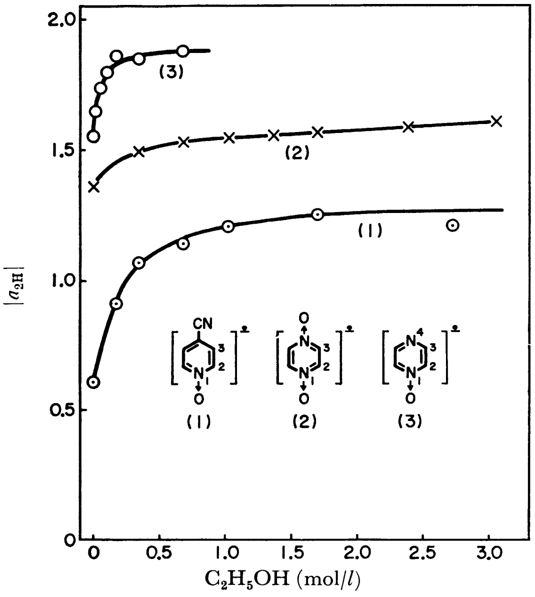


Fig. 4B. Variation of $|a_{2H}|$ of the anion radicals given in this figure with the addition of ethanol. Each curve is obtained theoretically (see text), but each point is the observed one.

$$\bar{a} = \frac{a_{SRS} + K\alpha a_{SRD} + KK'\alpha^2 a_{DRD}}{1 + K\alpha + KK'\alpha^2} \tag{6}$$

K' represents the equilibrium constant corresponding to Eq. (5), while a_{SRS}, a_{SRD}, and a_{DRD} are, respectively, the hfc constants pertinent to the SRS, SRD, and DRD complexes. Note that, in this case, the radical has two or more effective active sites in a molecule for hydrogen-bonding interaction. Usually $K' < K$, and K is not so large in the present experiment (see Table 2). In addition, if the experiment is made under the conditions where $\alpha \ll 1$, if, that is, the concentration of the proton donor (D) is much smaller than that (S) of the solvent, the $KK'\alpha^2$ and $KK'\alpha^2 a_{DRD}$ terms may be neglected in Eq. (6). Then, Eq. (6) is easily reduced to Eq. (3), from which the values of K and a_{SRD} are determined. Eq. (6) is now modified as follows:

$$\bar{a} = a_{DRD} - \frac{1}{K'}\left[\frac{(\bar{a}-a_{SRS}) + K\alpha(\bar{a}-a_{SRD})}{K\alpha^2}\right] \tag{7}$$

The plotting of $\bar{a}$ *vs.* "the quantity in the brackets" on the right-hand side of Eq. (7) makes it possible to evaluate the values of K' and a_{DRD} separately. Thus, we tried the above-mentioned linear plots using Eqs. (3), (4), and (7), and also using the

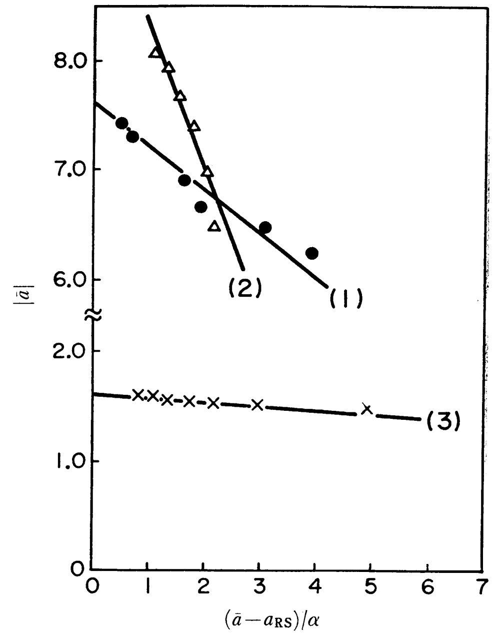


Fig. 5. Some examples of the linear relation of Eq. (3) (see text). The straight lines 1 and 2 are for the change of $|a_{N(NO_2)}|$ of 4-nitropyridine *N*-oxide anion radical with the addition of ethanol (line 1) and water (line 2), respectively. Line 3 is for the $|a_H|$ of the system: pyrazine di-*N*-oxide anion radical + ethanol. Solvent is dimethylformamide.

TABLE 2. EQUILIBRIUM CONSTANTS K'S AND HYPERFINE COUPLING CONSTANTS a's (absolute value) PERTINENT TO THE HYDROGEN BONDING SYSTEMS OF THE ANION RADICALS STUDIED HERE

Anion radical of	Proton donor	K (dimensionless) by Eq. (3)	a_{RD}* by Eq. (3)	K (l/mol) by Eq. (4)	a_{RD}* by Eq. (4)
4 NPO	Water	0.72 ± 0.16	$9.75\pm0.54^{a)}$	0.043 ± 0.016	$10.96\pm1.33^{a)}$
4 NPO	Ethanol	3.39 ± 0.59	$7.37\pm0.11^{a)}$	0.18 ± 0.04	$7.83\pm0.25^{a)}$
4 NPO	Phenol	—	—	25.95 ± 11.56	$6.51\pm0.11^{a)}$
4 CNPO	Ethanol	66.97 ± 10.18	$1.29\pm0.03^{b)}$	5.05 ± 0.82	$1.30\pm0.03^{b)}$
Pyrazine di-N-oxide	Ethanol	39.00 ± 7.02	$1.61\pm0.01^{c)}$	3.00 ± 0.58	$1.62\pm0.01^{c)}$
Pyrazine mono-N-oxide	Ethanol	301.57 ± 13.25	$1.89\pm0.01^{b)}$	23.25 ± 1.03	$1.89\pm0.01^{b)}$
4-Nitropyridine	Ethanol	$K=10.0\pm1.5$	$a_{SRD}=8.50\pm0.2^{a)}$	—	—
		$K'=0.49\pm0.02$	$a_{DRD}=10.00\pm0.05^{a)}$	—	—
		with Eqs. (5), (6) and (7).			

* The value of hyperfine coupling constant is that of $a_{N(NO_2)}$, a_{2H} and a_H for the superscript a, b and c, respectively.

experimental data listed in Tables 1A—1E. Assuming the 1 : 1 interaction model, quite a good linear relation for Eq. (3) or (4) was then yielded for each system except for the case of the 4NP anion radical plus ethanol, where the 1 : 2 model was much better (see below). In Fig. 5 these linear plottings for Eq. (3) are illustrated as examples.

The values of the equilibrium constant, K, and the hfc constants in the hydrogen-bonding state thus evaluated are shown in Table 2. Also, the solid curves given in Figs. 4A—4B were theoretically obtained using the values listed in Table 2. We see that there is quite a good agreement of the proton-donor dependence of $\bar{a}$ yielded experimentally with the corresponding curve obtained theoretically. The behaviour of the $|a_N|$ of the 4NP anion radical upon the addition of ethanol may be interpreted by assuming the 1 : 2 model. In small ethanol concentrations Eq. (3) or (4) is well satisfied, but the linear relation of Eq. (7) is again fulfilled in the region of relatively high ethanol concentrations. The values of K, K', a_{SRD}, and a_{DRD} were thus determined; they are included in Table 2. As may be seen in Fig. 4A, the experimental values of $\bar{a}$ were reproduced by the theoretical $\bar{a}$ curve drawn by employing the above-mentioned K and K' values.

Discussion

Active Site for Hydrogen-bonding Interaction. The compounds used in this study have, in a molecule, more active atoms than the one for hydrogen-bonding interaction. From the viewpoint of the electronic structures of the present anion radicals, it is important and interesting to examine which atom in a molecule enters into hydrogen-bond formation with proton donors. The studies reported thus far suggest that the intermolecular charge transfer of a lone-pair electron, belonging to the active-atom, non-bonding orbital which enters into hydrogen bonding to, for example, the O–H antibonding orbital of proton donors, is the most important mechanism in hydrogen-bond formation.[17] Of course, there is also electrostatic force. Now, note that the charge-transfer mechanism and the electrostatic interaction both bring about an increase in electronegativity at the atom in question. In other words, the Coulomb integral concerning the π-AO at the atom increases in magnitude in the HMO calculation, as was suggested by Frankel *et al.*[5] The change in the spin-density distribution arising from the perturbation due to hydrogen bonding can then be calculated. The parameter values in the HMO calculation, as modified by McLachlan's treatment (MHMO calculation),[18] have already been given for heterocyclic amine N-oxides and their derivatives, having NO_2, CN groups *etc.*, in order to interpret the hfc constants and, thus, the spin densities of these anion radicals in the free state.[13] The results agree well with the observed values.*4 Assuming some active sites,

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[17] S. Nagakura, *J. Chim. Phys.*, **61**, 217 (1964); K. Nukazawa, J. Tanaka and S. Nagakura, *J. Phys. Soc. Japan*, **8**, 792 (1953); R. S. Mulliken, *J. Chim. Phys.*, **61**, 20 (1964).

[18] A. D. McLachlan, *Mol. Phys.*, **3**, 233 (1960).

*4 Parameter values for the MHMO calculation of the anion radicals of N-oxide compounds are: $k_{N^{\delta+}}=1.0$ with inductive effect=0.1, $k_O=0.6$, and $\beta_{NO}=0.8$ for $\gt N^{\delta+}\rightarrow O^{\delta-}$ group. See Fig. 7 in Ref. 13 for the parameter sets and their literature on the substituents NO_2 and $C\equiv N$, and ring nitrogen atom ($\gt N:$). The hfc constants were theoretically calculated using the following equations[13] connecting spin density and σ-π interaction term: $a_{N(NO_2)}=99.0\rho_N-35.8(\rho_O+\rho_{O'})$; $a_{N(N\rightarrow O)}=42.57\rho_N-18.98\rho_O-6.66(\rho_C+\rho_{C'})$; $a_H=-25.67\rho_C$; $a_{N(C\equiv N)}=23.1\rho_N-6.8\rho_C$; $a_{N(\gt N:)}=27.3\rho_N-1.7(\rho_C+\rho_{C'})$.

the spin density and the hfc constant in the hydrogen-bonding state can be calculated using many parameter sets which are reasonably selected by referring to the ones in the free state, and the calculated values are compared with the behavior of the hfc constants observed upon the addition of proton donors (see Table 1 and Fig. 4). This comparison may lead to the acceptable conclusion as to which atom in an anion radical mainly participates in the hydrogen-bond formation.

First, let us discuss the 4NPO anion radical. This radical has two active groups in the molecule; one is the NO_2 group, while the other is the *N*-oxide group. If the lone-pair orbital of the *N*-oxide-group oxygen atom enters into hydrogen bonding, the Coulomb integral of the oxygen atom in the MHMO calculation becomes larger than the standard value, $\delta\alpha_0 = 0.6\beta$.[13),*4] The hfc constants[*4] obtained using the spin densities led from the calculation under the above boundary conditions are illustrated in Fig. 6. On the other hand, in Fig. 7 are shown the calculation results assuming that the nitro-group oxygen atom makes a hydrogen bond with the proton donors.[*5,19,20)] Since the ESR spectrum in the hydrogen-bonding interaction of the 4NPO anion radical can be well interpreted as the radical is in C_{2v} molecular symmetry, the hydrogen-bonded hydrogen atom of proton donors should be rapidly exchanged between two oxygen atoms in the NO_2 group (*vide infra*). The same circumstances would also hold in the 1 : 1 hydrogen bonding system, consisting of a proton donor and pyrazine di-*N*-oxide, as will be discussed later.

Now, when we compare the theoretical values shown in Figs. 6 and 7 with the experimental results seen in Table 1A and Fig. 2, it seems certain that the active center partaining to the hydrogen-bonding interaction of the 4NPO anion radical with proton donors is the nitro group in the molecule, since the experimental and theoretical results are in quite good agreement in this case. This conclusion is in agreement with the conclusion that the hydrogen-bonding or alkali metal-complexing center of the anion radicals of nitrobenzene and related nitro-compounds is in the nitro group,[6,14,21)]

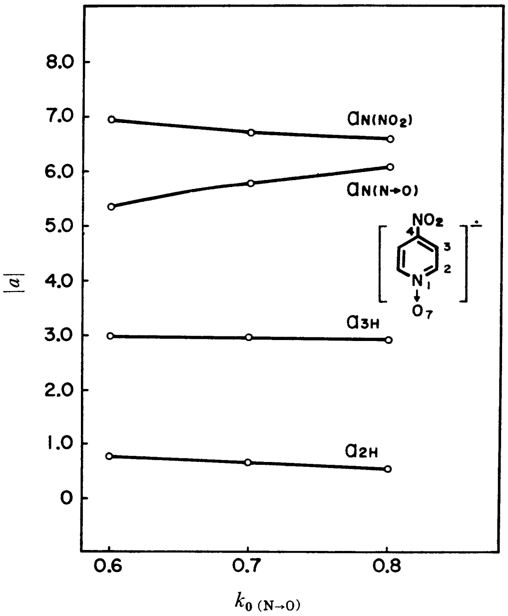

Fig. 6. The behavior of hfc constants theoretically estimated (see text for the method) assuming that the *N*-oxide oxygen atom of 4-nitropyridine *N*-oxide anion radical is the active site for hydrogen bonding interaction.

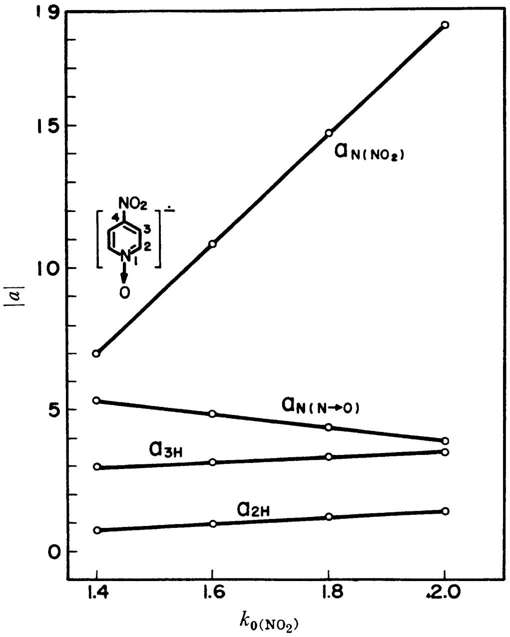

Fig. 7. The behavior of hfc constants theoretically estimated (see text for the method) assuming that the nitrogroup oxygen atom of 4-nitropyridine *N*-oxide anion radical is the active site for hydrogen bonding interaction.

[*5] It should be noted that the MO calculation[13,15,19)] leads to the conclusion that the $\rangle C{=\!=}NO_2$ bond order in the anion radicals of 4NPO, nitrobenzene, *etc.* becomes larger than in the corresponding neutral molecules. The possibility of the twisting around the C$=\!=$N bond due to the hydrogen bonding effect would be then rejected from the consideration unless bulky substituent at ortho position brings about the steric hidrance against the nitro group. This argument seems to be experimentally supported.[15b,6,20)]

19) a) D. H. Geske, J. L. Ragle, M. A. Bambenek and A. L. Balch, *J. Amer. Chem. Soc.*, **86**, 987 (1964); b) T. E. Peacock, *Proc. Phys. Soc.*, **78**, 460 (1961).

20) Y. Nakai, This Bulletin, **39**, 1372 (1966).

21) R. L. Ward, *J. Amer. Chem. Soc.*, **83**, 1296 (1961); C. Ling and J. Gendell, *J. Chem. Phys.*, **47**, 3475 (1967).

whose complexing ability is not so small in the anion radical. However, it should be recalled[22] that the protonation of the 4NPO neutral molecule in an aqueous solution occurs at the *N*-oxide group oxygen atom, and that the pK_a value is -1.7.[22] Therefore, we can say that the active center for the hydrogen-bonding or protoantion interaction of 4NPO is exactly reversed between the neutral molecule and the anion radical. There is much evidence supporting the idea that the intramolecular charge transfer (CT) from a *N*-oxide-group oxygen atom to a nitro group is an important factor in describing the nature of the ground state as well as the excited state of 4NPO, 4-nitroquinoline *N*-oxide, *etc.*[*6,22,23] For example, the p$K_a = -1.7$ of 4NPO is much smaller than the correspoding value, 0.78, of pyridine *N*-oxide.[22] The theoretical MO considerations[13,15,19] reported thus far on various aromatic nitro compounds including 4NPO suggest that the lowest vacant MO (LVMO) is mainly localized on the NO_2 group and that, thus, the unpaired π electron densitie on that group are very large. Also, an intramolecular CT absorption band pertinent to nitrobenzene, 4NPO, *etc.* may appear in the near ultraviolet region.[23,24] This result implies that the nitro-group oxygen lone-pair electrons become quite active for n-σ type intermolecular interaction when the species is in an anion radical or in an intramolecular CT excited state, although the above interaction is weak in the case of the neutral nitro compounds.[25] Our aforementioned conclusion on the active site of the 4NPO anion radical for hydrogen-bonding interaction seems, therefore, to be reasonable.

Next, let us discuss the hydrogen-bonding active site of the 4CNPO anion radical, which is of interest in comparison with that of the 4NPO anion radical discussed above. It is well known that the nitrile-group lone-pair electrons show a very weak n-σ-type intermolecular interaction ability,[26] so that the hydrogen-bonding power is also weak, and that the nitrogen hfc constant, $|a_N|$, due to the cyano group in the aromatic nitrile anion radicals is found only within 1—3 gauss.[13] In addition, the cyano group is a weak π substituent[27] and affects the near-UV spectra of aromatic substances weakly, and the intramolecular CT band partinent to benzonitrile has been reported not to be exhibited in the near-UV region.[27] In view of these facts, we may expect that the hydrogen-bonding ability of the nitrile group in π anion radicals is not large. In fact, MHMO spin-density calculations according to the procedure used in the case of 4NPO led to the finding that the stronger active site for the hydrogen-bond formation of the 4CNPO anion radical is the *N*-oxide group and not the cyano group, for, if we assume the latter case, the change in the calculated spin densities and hfc constants arising from hydrogen bonding does not reproduce the experimental results so well; however, the agreement between experiment and theory is good for the former case. Here, note that the hfc constant due to the hydrogen atom at the position 2, $|a_{2H}|$ (see Fig. 4B for numbering), increases in magnitude in the hydrogen-bonding complex, while $|a_{3H}|$ is relatively insensitive. These results are in good agreement with the calculation results. Conversely, this type of experiment on the solvent effect seems to be a useful technique for determining the assignment of the hfc constants.[13,16]

The calculation was next carried out on the anion radicals of pyrazine mono *N*-oxide and 4-nitropyridine. It was clearly concluded that, in the case of the former radical, the hydrogen-bonding interaction ability of the *N*-oxide group is stronger than that of the ring-nitrogen atom, but that the stronger active atom in the 4NP anion radical is, of course, the nitro-group oxygen atom, with the ring-nitrogen atom next. As may be understood from Table 1, the experimental values of $|a_{N(ring)}|$[13] and $|a_{2H}|$[13] for the case of the pyrazine mono-*N*-oxide anion radical are quite increased by the addition of ethanol, but the increase is small for the $|a_{N(N\to O)}|$ and $|a_{3H}|$ values. These results are satisfied by assuming the active site to be the *N*-oxide-group oxygen atom, and have confirmed the assignment of $|a_{3H}|>|a_{2H}|$ which was preferred in the previous paper.[13] In Fig. 8 are shown these calculated results. The calculation on the assumption that both the *N*-oxide-group oxygen atoms are the active centers of the hydrogen-bonding interaction for the pyrazine di-*N*-oxide anion radical

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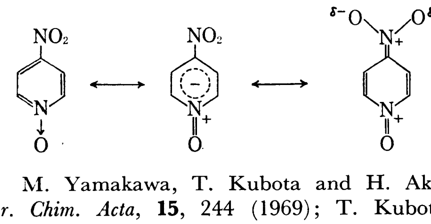
[22] See many experimental data given in the Chapter 4 of the book: E. Ochiai, "Aromatic Amine Oxides," Elsevier Publishing Co., Amsterdam (1967).

[*6] In resonance structures these circumstances will be written as follows:



[23] M. Yamakawa, T. Kubota and H. Akazawa, *Theor. Chim. Acta*, **15**, 244 (1969); T. Kubota and M. Yamakawa, This Bulletin, **35**, 555 (1962); S. Kobinata and S. Nagakura, *Theor. Chim. Acta*, **14**, 415 (1969).

[24] S. Nagakura and J. Tanaka, *J. Chem. Phys.*, **22**, 236 (1954); S. Nagakura, *ibid.*, **23**, 1441 (1955); J. Tanaka and S. Nagakura, *ibid.*, **24**, 1274 (1956), *etc.*

[25] S. Nagakura and M. Gouterman, *J. Chem. Phys.*, **26**, 881 (1957).

[26] N. Mataga and Y. Kaifu, *Mol. Phys.*, **7**, 137 (1963); T. Kubota, M. Yamakawa, M. Takasuka, K. Iwatani, H. Akazawa and I. Tanaka, *J. Phys. Chem.*, **71**, 3597 (1967) and other papers given therein.

[27] K. Kimura and S. Nagakura, *Theor. Chim. Acta*, **3**, 164 (1965); *Nippon Kagaku Zasshi*, **86**, 1 (1965).

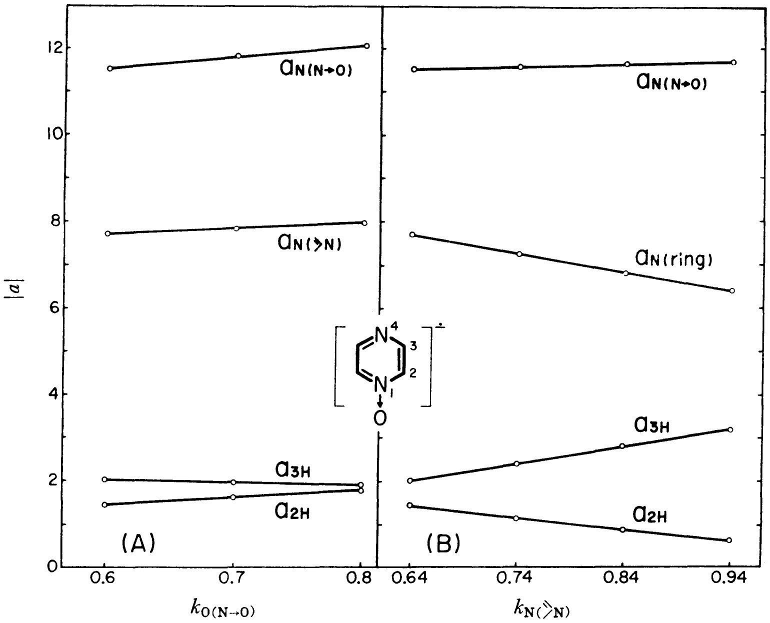


Fig. 8. The behavior of hfc constants theoretically estimated (see text) assuming that the active site entering into hydrogen bonding interaction is the *N*-oxide group oxygen atom (case A) or ring nitrogen atom (case B).

results in a good agreement with the experimental values listed in Table 1. Note also that the ESR spectrum observed in DMF-ethanol mixed solvents has a pattern corresponding to the V_h symmetry of the anion radical. This may be attributed to the rapid exchange of hydrogen-bonding interaction at the two oxygen atoms, just as in the case of the *p*-benzosemiquinone- 1-^{13}C molecule.[8]

Equilibrium Constants of Hydrogen Bond Formation. Let us first examine the values of the equilibrium constant, *K*, which are listed in Table 2. It is deemed that, except for pyrazine mono-*N*-oxide, the *K* values are not very large considering that the species are anion radicals; they are comparable to the corresponding *K* values of neutral pyridine *N*-oxide, quinoline *N*-oxide, *etc.*[28] However, it should be remembered that the compounds whose π-anion radicals are relatively stable are those which have electron-drawing substituents, like CN, COOR, NO_2, *etc.*, in a molecule and that these are conjugated with π-electron systems. In the present case, these substituents cause the decrease in the electron densities at the *N*-oxide oxygen atom, even in the anion radicals, as the calculation[13] of the spin densities shows. In turn, the nitro group in, for example, nitrobenzene is essentially a weak base. Pyrazine di-*N*-oxide may be also a weak base, as may be understood from the pK_a value (-1.62)[22] of phenazine di-*N*-oxide. This weak basicity of the above-mentioned functional groups might be one of reasons for the present, perhaps, small *K* values, except for the case of the pyrazine mono-*N*-oxide anion radical, which has rather large *K* value compared with those of the other radicals (see Table 2). The basicity of neutral pyrazine-mono-*N*-oxide may be not so different from, or only a little weaker than, that of pyridine *N*-oxide. This may be inferred from the fact[22] that the pK_a value (1.57) of acridine *N*-oxide is almost the same as that (1.32) of phena-

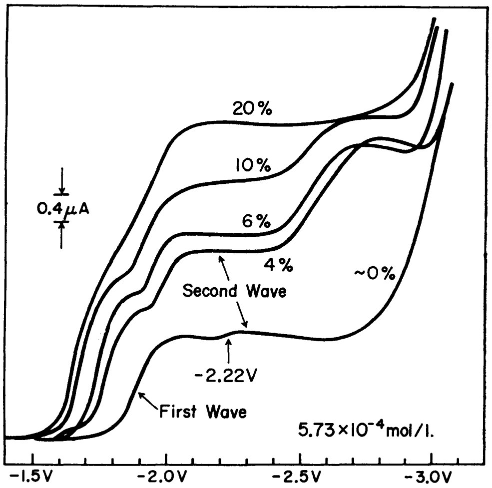


Fig. 9. Observed polarograms of pyrazine mono-*N*-oxide in the mixed solvents: dimethylformamide+ethanol (vol%).

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[28] T. Kubota, *J. Spectroscopical Soc. Japan*, **10**, 83 (1962).

TABLE 3. ANION RADICALS PRODUCED BY THE CONTROLLED POTENTIAL ELECTROLYSIS OF PYRAZINE MONO- AND DI-*N*-OXIDES AT DIFFERENT POLAROGRAPHIC REDUCTION WAVES AND UNDER DIFFERENT ETHANOL CONCENTRATIONS ADDED IN DMF SOLVENT

Mother compound	Ethanol concentration	Anion radical species[a] (observed ESR spectra) produced at		
		First wave	Second wave	Third wave
Pyrazine mono-	~0	PMNO	Pyrazine	—
N-oxide	0.1	PMNO	Pyrazine	—
(PMNO)	0.3	PMNO	PMNO	—
	1.0	PMNO	PMNO	—
	>2.0	PMNO	PMNO	—
Pyrazine di-	~0	PDNO	PMNO	Pyrazine
N-oxide	<0.5	PDNO	PMNO	Pyrazine
(PDNO)	1.0	PDNO	PMNO	PMNO
	>2.0	PDNO	PDNO	PDNO

a) ESR spectum observed at the second or third reduction wave is sometimes contaminated more or less by the other spectra, but the main spectrum is the one shown in this Table.

zine mono-*N*-oxide. Keeping in mind this fact, we may expect that the *K* value (the active site is the *N*-oxide group) of the pyrazine mono-*N*-oxide anion radical for the hydrogen bonding with alcohol is larger than that (~15 *l*/mol in *n*-heptane, ~6—7 in CCl_4) of the corresponding equilibrium in the pyridine *N*-oxide, quinoline *N*-oxide, and acridine *N*-oxide neutral molecules, because the former is the anion radical with an extra electron in the molecule. In fact, this is actually the case, the *K* value (23.3 *l*/mol) obtained here being larger than that just mentioned above for the neutral species.

Now let us consider the hydrogen-bonding equilibrium constant, *K*'s, formed between the 4NPO anion radical and water, ethanol, and phenol. As Table 2 indicates, the *K* values are increased in the following order of proton donors: water<ethanol<phenol. This order seems to be in agreement with that of the proton-donating power for 1:1 hydrogen-bond formation studied by infrared spectral measurements.[29] In relation to these results, it is thought that, for the same hydrogen-bonding systems as the above, the $|a_{\rm RD}^{\rm N}|$ value (see Eqs. (3) and (4), and Table 2) of the 4NPO anion radical is in an order just the reverse of that of the *K* value, namely, water>ethanol>phenol. Remember that the *K* value for the 4NPO anion radical-water system is quite small. Much water is necessary to bring about the change in the hfc constant $|a_{\rm N}|$, as may be seen in Table 1. In these mixed solvents with high values of $\alpha=({\rm D})/({\rm S})$ (see Eq. (3)), the nature of the mixed solvents is never the same as that of DMF itself in the present experiments. The dielectric constant of water is very large. The effect of electrostatic interaction, that is, the effect of the reaction field of the mixed solvent on the electronic state of radicals can not be ignored in these cases. In view of this, the thermodynamic and ESR data for the case of phenol as the proton donor might be attributed to the fact that the data are closer to hydrogen binding itself; since phenol is a strong donor, the phenol concentration added in the solvent system is small. The solvent character may be unchanged with the addition of such a small phenol concentration.[*7]

Relation of Equilibrium Constant Data to the Radical Species Produced by Controlled Potential Electrolysis. In the course of this experimental study, we observed that the polarograms of pyrazine di- and mono-*N*-oxides in a DMF solvent exhibit a slight increase in wave height at about −1.98 and −2.24 V for the former and the latter respectively (abbreviated henceforth as "the second wave; see Fig. 9). This observation seems to be attributable to the presence of a slight quantity of water[13] introduced into the solvent during the process to remove the dissolved oxygen with N_2 gas. The result in the case of pyrazine mono-*N*-oxide is illustrated in Fig. 9 as an example. The second wave obviously increases in wave height with the addition of a proton donor, ethanol. When controlled-potential electrolysis is carried out at the first and the second reduction waves, the recorded ESR spectra, *i.e.*, the anion radicals produced, are different and depend on the concentration of the proton donor. At any rate, the second wave would be due to the electrode reaction of radical species produced at the first wave, and the reaction is dependent on the proton-donor concentration. These

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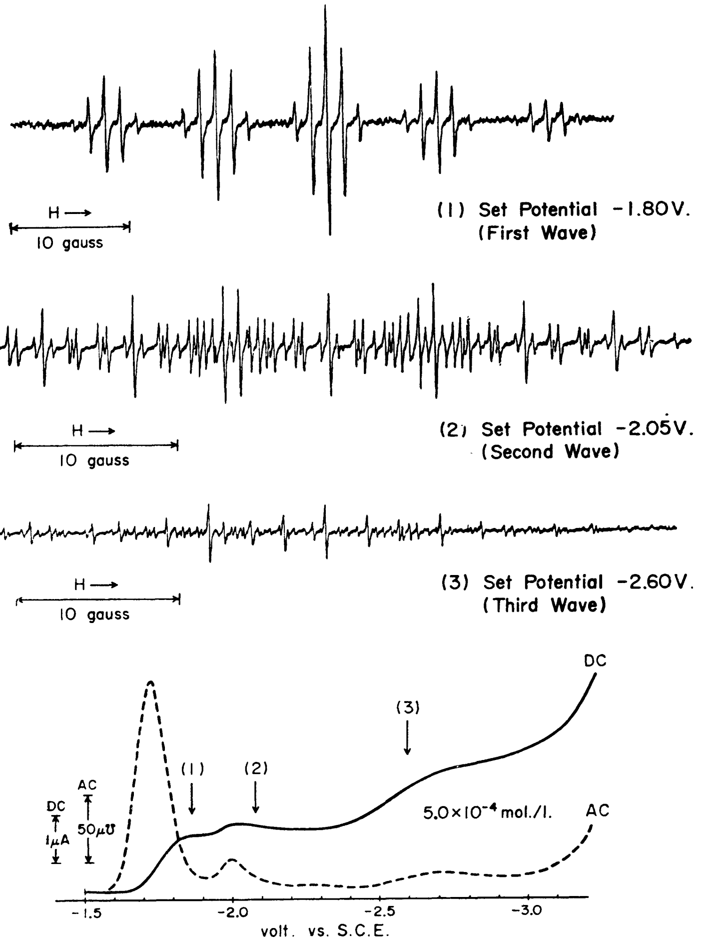
29) M. Tuboi, *Kagaku no Ryoiki* (in Japanese), **7** (No. 10), 611 (1953).

[*7] The presence of supporting electrolyte, tetra-*n*-propylammonium perchlorate 0.1 mol/*l*, would render the system somewhat complicated.



(4) Polarogram of Pyrazine di-N-oxide

Fig. 10. ESR spectra observed by the controlled potential electrolysis of pyrazine di-*N*-oxide at the three different potentials shown in the polarogram (4) in this figure. ESR spectra (1), (2) and (3) are easily identified to the anion radical of pyrazine di-*N*-oxide, pyrazine mono-*N*-oxide, and pyrazine, respectively, by comparing with the data given in our foregoing paper.[13] But, note that the spectrum (3) is contaminated to some extent by the spectrum (2) of pyrazine mono *N*-oxide anion radical (see footnote of Table 3).

experimental results have been summarized in Table 3, while the ESR spectra observed at three different potentials, corresponding to the first, second, and third reduction waves, are exhibited in Fig. 10 for the case of pyrazine di-*N*-oxide itself without any proton donor. The identification of these spectra is easy,[13] as may be understood from the figure caption. It is understood that incresing the ethanol concentration makes the deoxygenation process of the *N*-oxides more difficult, and that, when the quantity of ethanol added is more than a suitable critical concentration, the ESR spectrum of the pyrazine mono- or di-*N*-oxide anion radical occures even in electrolysis at a more negative potential than that of the first reduction wave. This relation is depicted in Fig. 11, in which the C ($\sim$0.3%) and C′ ($\sim$2.6%) points, respectively, correspond to the above-mentioned critical concentrations of pyrazine mono- and di-*N*-oxides. These concentrations are almost in agreement with those where hydrogen-bonded and free species exist in an equal molar ratio. In other words, there is an intimate correlation between the hydrogen-bonding equilibrium constant, *K*, and the experimental results shown in Table 3 and Fig. 11. We also note that when ethyl ether instead of ethanol is added to the DMF system, the phenomenon seen in Fig. 11 and Table 3 is not observed. This result

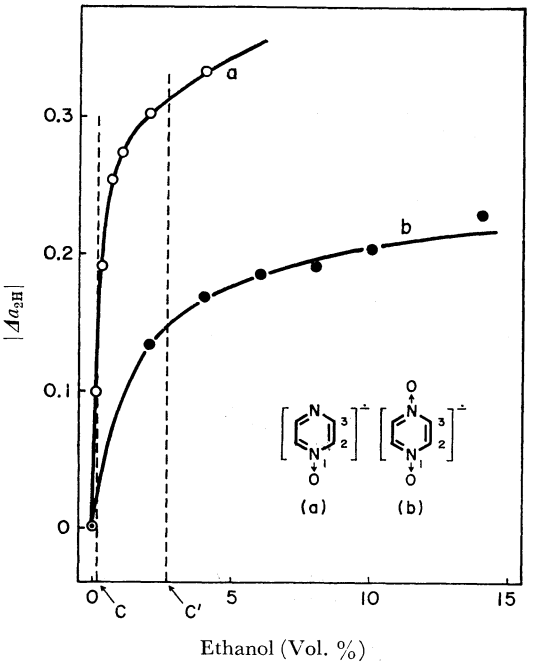


Fig. 11. Change (Δa_{2H}) in $|a_{2H}|$ of the anion radicals shown in this figure upon the addition of ethanol. See text for the meaning of the points C and C′. Solvent: dimethylformamide

suggests the importance of hydrogen-bonding interaction in relation to the experimental results presented above.

The reason for this phenomenon is not completely clear. One possibility is that the anion radical in hydrogen-bonding interaction is more stabilized than in the free radical itself, if no side chemical reaction occurs. Dianion or similar unstable chemical species of the mother compounds produced by the electrolysis at the second or third reduction waves*[8] easily bring about electron transfer to the neutral molecule. Thus, the anion radical stabilized by hydrogen bonding has been observed at all reduction waves. If the anion radical is not stabilized, the deoxygenation reaction of the mother compound occurs in the higher-potential electrolysis. The ESR spectra corresponding to that of the anion radical of deoxygenated species have thus been observed.

The authors wish to express their thanks to Professor Saburo Nagakura of the Institute for Solid State Physics, the University of Tokyo and to Professor Yasuo Deguchi of the Department of Chemistry, the University of Kyoto for useful discussions.

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*[8] In this connection it is noted that the ESR spectrum of 4NPO anion radical is always observed by the electrolysis at the second reduction wave as well as the first wave regardless of the addition of ethanol in DMF solvent. 4NPO anion radical is quite stable, so that the equilibrium such as $(4NPO)^{=} + (4NPO) \leftrightarrows (4NPO)^{\dot{-}}$ may occur easily whether or not the species is hydrogen bonded. That dianion $(4NPO)^{=}$ is formed at the second reduction wave was experimentally confirmed from the polarographic measurement of 4NPO anion radical itself.[30]

30) H. Miyazaki, K. Nishikida and T. Kubota, presented at the 14th Symposium of Polarography, Hiroshima, Oct. 7, 1968. Abstract No. 7.