

those for the *p*-fluorines. This may be an indication that the unpaired electron density at the *o*-carbon is appreciably less than in normal triphenylmethyl. This could possibly explain the low value for the *o*-fluorine

hyperfine splitting observed in the completely fluorinated triphenylmethyl.

Acknowledgment. We wish to thank Professor J. A. Pople for his most helpful comments.

Electron Spin Resonance and Polarographic Studies of the Anion Radicals of Heterocyclic Amine N-Oxides¹

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Abstract: Polarograms of 30 heterocyclic amine N-oxides were recorded in dimethylformamide at about 25°. Electron spin resonance (esr) spectra of radical anions formed during controlled-potential electrolysis at the potential corresponding to the first reduction wave were observed for 16 of the oxides. The hydrogen (a_H) and nitrogen (a_N) hyperfine coupling constants were determined by the method of spectral simulation. With 4-cyano- and 4-nitropyridine N-oxide anion radicals, deuterium substitution was used to confirm the analysis. HMO calculations with the McLachlan modification, where the necessary parameters were chosen to give agreement with the a_H 's of pyrazine di-N-oxide, 4-cyanopyridine N-oxide, and pyrazine mono-N-oxide, yielded the following linear relations between calculated spin density, ρ , and experimental coupling constant for the compounds studied: $a_H = -25.7\rho_C$ and $a_N = 42.6\rho_N - 6.7(\rho_C + \rho_C') - 19.0\rho_O$. Also, using fewer parameters, a_N was satisfactorily expressed by $a_N = 41.9\rho_N - 2.1$. In addition, esr spectra of the anion radicals of pyridine N-oxide and its 2,6-dideuterio derivative were observed during electrolysis in liquid ammonia. The comparison of the a_H 's and a_N so observed with the calculated values using the equations given above was in a good agreement. Also the polarographic data were analyzed in terms of radical stability and were related to the esr results as follows. The peak height of the ac polarogram and the half-wave potential ($E_{1/2}$) of the first reduction wave are approximately linearly related to the radical stability. Moreover, the $E_{1/2}$ is in linear relation with the lowest vacant MO energy (ϵ_{LV}) and also with the Hammett σ value of a series of substituted pyridine N-oxides. Thus, $E_{1/2} = 2.75\epsilon_{LV} - 0.77$ and $-E_{1/2} = 1.08\sigma - 2.19$. The results are compared with those of related compounds reported in the literature.

The physicochemical nature and molecular interaction ability of heterocyclic amine N-oxides such as pyridine N-oxide, quinoline N-oxide, etc. have been studied from experimental and theoretical points of view.^{2,3} These studies, however, have been mainly limited to the neutral amine N-oxides with the exceptions of the anion radicals of pyridine N-oxide⁴ and 4-nitropyridine N-oxide⁵ and the neutral radical⁶ produced from 4-hydroxyaminoquinoline N-oxide, whose esr spectra were reported. There has been no systematic study of the nature of the anion radicals of the tertiary amine N-oxides.

In the course of the polarographic studies of heterocyclic amine N-oxides, it has been shown⁷ that anion

radicals may be produced by the reduction method of controlled-potential electrolysis in nonaqueous solvents. In the case of compounds such as 4-cyano- and 4-nitropyridine N-oxides, the produced anion radicals were relatively stable. As an extension of these studies, we report the esr spectra and their interpretations of the anion radicals of some heterocyclic amine N-oxides obtained by the above technique. Also the polarographic data recorded in dimethylformamide (DMF) are related to the esr results, and the half-wave reduction potential ($E_{1/2}$) is related linearly to the lowest vacant MO (LVMO) energy and also to the Hammett σ constant.

Previous Hückel MO (HMO) and antisymmetrized MO calculations of some basic heterocyclic amine N-oxides used to interpret the electronic spectra, dipole moments, etc. have suggested⁸ that the character of intramolecular charge transfer from the oxygen to the rest of the π system is determined by the LVMO, which may be occupied by an electron to produce an anion radical. This suggested that the above calculations would be very useful in analyzing the hyperfine coupling (hfc) constants of the esr spectra reported here, and, conversely, the information obtained during the present study would be a valuable check on the previous MO calculations.

(1) Presented at the 5th (Sendai, Sept 1966) and 6th (Kyoto, Oct 1967) Symposiums of Electron Spin Resonance, 13th (Osaka, Nov 1967) Symposium of Polarography, and the Symposium of Structure Chemistry and the Electronic State of Molecule (Sapporo, Oct 1967), these meetings being held by the Chemical Society of Japan.

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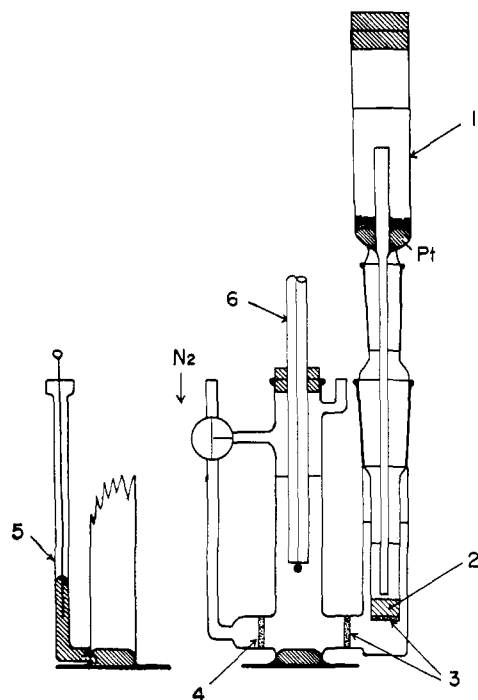


Figure 1. Polarographic cell used for recording dc and ac polarograms; (1) sce; (2) salt bridge which is composed of agar-agar (6%) and tetra-*n*-propylammonium perchlorate (6%) dissolved in aqueous DMF (water 30% and DMF 70%) and is solidified at room temperature; (3 and 4) fine (3) and coarse (4) glass filters; (5) terminal for ac polarographic measurement; (6) dropping Hg electrode.

Experimental Section

Polarographic Measurements. A Yanagimoto polarograph, Model PA-102, was used to record the dc and ac polarograms. The electrolysis cell shown in Figure 1 was used for recording the polarograms in dimethylformamide (DMF). A saturated calomel electrode (sce) was used as the external reference.⁹ The capillary used for the dropping mercury electrode had the following open circuit values of m and t in distilled water: $m = 0.855$ mg/sec and $t = 5.17$ sec at $h = 70$ cm. A 0.1 *M* solution of tetra-*n*-propylammonium perchlorate (TNPAP) was used as a supporting electrolyte throughout the present study. Polarographic measurements were made at $25 \pm 0.1^\circ$ and with *ca.* 5×10^{-4} *M* solution, containing an accurately weighed sample. Dissolved oxygen was removed by bubbling purified nitrogen gas through the sample solution. The correction of $E_{1/2}$ for the potential due to the so-called *IR*-drop term, which may be significant for nonaqueous solutions, was carried out by measuring the resistance of the cell circuit with a Wheatstone bridge equipped with a bulb voltmeter. The $E_{1/2}$ values obtained for nitrobenzene, 4-nitropyridine *N*-oxide, and pyrazine (*vs.* sce) are comparable to the literature values and are shown below. The first $E_{1/2}$'s were determined to be -1.093 (nitrobenzene), -0.768 (4-nitropyridine *N*-oxide), and -2.074 V (pyrazine). These should be compared with -1.09 (0.1 *M* $(C_2H_5)_4N^+ClO_4^-$ -DMF system),¹⁰ -1.13 (0.1 *M* $(C_2H_5)_4N^+ClO_4^-$ -DMF),¹¹ and -1.082 (0.1 *M* TNPAP-DMF)¹² for nitrobenzene, -0.78 (0.1 *M* $(C_2H_5)_4N^+ClO_4^-$ -DMF)¹¹ for 4-nitropyridine *N*-oxide, and -2.09 V (0.1 *M* $(C_2H_5)_4N^+ClO_4^-$ -DMF)¹¹ for pyrazine.

(9) There was a possibility of contaminating the DMF owing to water diffusing from the sce cell. This contamination was, however, small for the electrolysis cells shown in Figures 1 and 2. The titration with Karl Fischer reagents indicated that the water contaminated from the above diffusion was $\leq 0.13\%$ after 4 hr of operation. Since measurements were completed within ~ 1 -2 hr, it is certain that the water content remained less than 0.1%.

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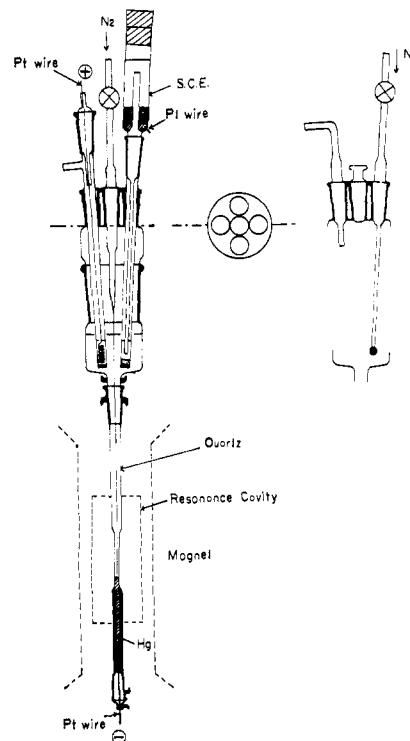


Figure 2. Controlled-potential electrolysis cell.

Esr Measurements. ESR spectra were recorded with a Varian V-4502-15 X-band spectrometer with 100-kHz magnetic field modulation. Varian F-8 Nuclear Fluxmeter and Takeda Riken TR-5578 frequency counters were employed to monitor the magnetic field. Free radicals were generated in the microwave resonance cavity at $25 \pm 1^\circ$ by controlled-potential electrolysis¹³ using the apparatus shown in Figure 2.¹⁴ Pure dry N_2 gas was bubbled through the cathode solution and electrolyte reservoir to remove dissolved oxygen. The sample concentrations were almost the same as those used in the polarographic studies, and the potential for electrolysis was determined from the polarographic data.

Samples. Compounds used for experiments are the same as those used in our previous polarographic and spectroscopic studies¹⁵ unless otherwise stated. For convenience the compounds are numbered as follows: pyridine *N*-oxide (1), 4-methyl- (2), 4-ethyl- (3), 4-chloro- (4), 4-methoxy- (5), 4-ethoxy- (6), 4-carbethoxy- (7), 4-cyano- (8), 4-nitro- (9), 3-methoxy- (10), 3-carbethoxy- (11), and 3-cyano- (12) pyridine *N*-oxides, pyrazine mono- (13) and di- (14) *N*-oxides, pyridazine mono-*N*-oxide (15), pyrimidine mono-*N*-oxide (16), 3,5-lutidine *N*-oxide (17), quinoline *N*-oxide (18), isoquinoline *N*-oxide (19), phthalazine mono-*N*-oxide (20), quinoxaline mono- (21) and di- (22) *N*-oxides, acridine *N*-oxide (23), phenanthridine *N*-oxide (24), phenazine mono- (25) and di- (26) *N*-oxides, 4-nitropyridine-nitro-*N*¹⁵ *N*-oxide (27), quinoline *N*¹⁵-oxide (28), and 4-cyano-2,6-deuterio- (29) and 4-nitro-2,6-deuterio- (30) pyridine *N*-oxides. Compounds 20-22 and 24, 25 and 26, 15 and 16, 27, and 28 were supplied by Professor E. Hayashi at Shizuoka College of Pharmacy, Professor Y. Mori at Osaka University of Liberal Arts and Education, Dr. M. Ogata in our laboratory, Professor S. Nagakura at Tokyo University, and Dr. Y. Kawazoe at the National Cancer Center Research Institute, respectively.¹⁶ Compounds 29 and 30 were synthesized by the following methods. First 2,6-deuteriopyridine was prepared by the method used by Oae and Kozuka:¹⁷ bp 103-105°. The infrared (ir) spectra were

(13) Attempt to form these anion radicals by alkali metal reduction was not so successful, and decomposition occurred frequently.

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Table I. Various Heterocyclic Amine N-Oxides Investigated, with Their Numbering and Their Half-Wave Reduction Potentials, Lingane's Constants, Peak Height of Ac Polarograms, and the Set Potentials for ESR Measurement at the First Reduction Wave

No.	Compound	$E_{1/2}$, vs. sce	Lingane's constant, I^a	I_{ac} , $\mu\text{mhos/mmmole}$	Set potential, vs. sce ^b
1	Pyridine N-oxide	-2.297	4.94	106.2	-2.60 (no)
2	4-Methylpyridine N-oxide	-2.375	4.77	85.4	-2.65 (no)
3	4-Ethylpyridine N-oxide	-2.370	3.79	67.4	-2.58 (no)
4	4-Chloropyridine N-oxide	-1.889	4.24	57.6	-2.10 (no)
5	4-Methoxypyridine N-oxide	-2.402	3.51	66.5	-2.60 (no)
6	4-Ethoxypyridine N-oxide	-2.445	3.50	60.6	-2.65 (no)
7	4-Carbethoxypyridine N-oxide	-1.606	2.05	317	-1.85 (yes)
8	4-Cyanopyridine N-oxide	-1.557	1.99	307	-1.75 (yes)
9	4-Nitropyridine N-oxide	-0.768	2.04	403	-1.30 (yes)
10	3-Methoxypyridine N-oxide	-2.315	3.48	98.7	-2.52 (no)
11	3-Carbethoxypyridine N-oxide	-1.670	2.07	81.8	-1.90 (no)
12	3-Cyanopyridine N-oxide	-1.667	2.05	84.9	-1.90 (no)
13	Pyrazine mono-N-oxide	-1.809	2.85	325	-2.00 (yes)
14	Pyrazine di-N-oxide	-1.616	2.30	306	-1.78 (yes)
15	Pyridazine mono-N-oxide	-1.898	2.27	314	-2.15 (yes)
16	Pyrimidine mono-N-oxide	-1.949	1.69	79.5	-2.15 (no)
17	3,5-Lutidine N-oxide	-2.365	3.18	66.3	-2.56 (no)
18	Quinoline N-oxide	-1.809	2.59	317	-2.06 (yes)
19	Isoquinoline N-oxide	-1.946	2.34	231	-2.15 (no)
20	Phthalazine mono-N-oxide	-1.716	1.86	155	-1.90 (no)
21	Quinoxaline mono-N-oxide	-1.419	1.65	315	-1.60 (yes)
22	Quinoxaline di-N-oxide	-1.241	1.44	293	-1.40 (yes)
23	Acridine N-oxide	-1.30	1.87	180	-1.50 (yes)
24	Phenanthridine N-oxide	-1.774	1.29	174	-1.92 (no)
25	Phenazine mono-N-oxide	-0.972	1.91	348	-1.12 (yes)
26	Phenazine di-N-oxide	-0.833	1.47	306	-0.96 (yes)
27	4-Nitropyridine-nitro-N ¹⁵ N-oxide	-0.792	2.04	438	-1.30 (yes)
28	Quinoline N ¹⁵ -oxide	-1.805	2.64	344	-2.06 (yes)
29	4-Cyanopyridine 2,6-d ₂ -N-oxide	-1.595	2.13	347	-1.75 (yes)
30	4-Nitropyridine 2,6-d ₂ -N-oxide	-0.793	2.04	451	-1.10 (yes)

^a See text. ^b Here "yes" means the appearance of esr signal by the present technique, but no appearance for the sign "no."

identical with those reported in the literature,¹⁸ an obvious absorption due to ν_{CD} being found at 2251 cm^{-1} in CCl_4 . 2,6-Deuteriopyridine N-oxide and its 4-nitro derivative were then obtained by conventional methods: oxidation with H_2O_2 in glacial acetic acid² and then nitration with H_2SO_4 and KNO_3 .¹⁹ The ir (in CCl_4) and nmr (in CDCl_3) spectra of the former were identical with those obtained with a sample of 2,6-deuteriopyridine N-oxide kindly provided by Professor S. Oae.^{16,17} The 4-nitro-2,6-deuteriopyridine N-oxide yielded has mp 163°; ir = 1272, 1279, and 1288 cm^{-1} (Nujol mull) in the region of $\nu_{N\rightarrow O}$, and 1513 and 1337 cm^{-1} (Nujol mull) for NO_2 group. The 4-cyano-2,6-deuteriopyridine N-oxide was prepared from 2,6-deuteriopyridine N-oxide by the method reported by Okamoto and Tani²⁰ with the following change. The reaction of 1-methoxy-2,6-deuteriopyridinium iodide with KCN was carried out in D_2O -dioxane instead of H_2O -dioxane to obtain 4-cyano- and 2-cyanopyridines. Both of the products were easily isolated by utilizing the solubility difference of the picrates in ethanol. 4-Cyano-2,6-deuteriopyridine (mp 78°) thus obtained was oxidized with H_2O_2 in glacial acetic acid.² The melting point and ir data of purified 4-cyano-2,6-deuteriopyridine N-oxide were respectively: mp 228.5–229°, $\nu_{CD} = 2280$, $\nu_{C\equiv N} = 2223$, and $\nu_{N\rightarrow O} = 1277 \text{ cm}^{-1}$ by the Nujol mull method. It was evident from the esr spectra (see Figure 3) that deuterization was almost complete and simplified the accurate assignment of the proton hfc constants of the 4-nitro- and 4-cyano-2,6-deuteriopyridine N-oxides. All other compounds were purified by recrystallization or redistillation methods^{2,15} and then subjected to elemental analyses.

Calculation. The calculation of spin densities and the simulation of esr spectra were carried out using a Facom 270-20 computer, an IBM 1627-type plotter being employed for the spectral simulation. Eigenvalues and eigenvectors of each determinant were obtained by the Jacobi method. To carry out the simulation, a Lorentzian or a Gaussian waveform was selected, and the tail was extended to $8W$,²¹ where W is the assumed line width for all the

absorption bands. In this study, most of the compounds gave well-resolved esr spectra and were easy to analyze. Complicated spectra, however, were recorded for some compounds, such as acridine N-oxide, phenazine mono-N-oxide, pyridazine mono-N-oxide, etc. The hfc constants for these anion radicals were then determined by a trial-and-error comparison of simulated and experimental spectra.

Results

Esr Spectra of 4-Nitro- and 4-Cyanopyridine N-Oxides and Their Labeled Compounds with Isotopes.

As will be discussed later, these compounds revealed a typical one-electron reduction wave⁷ at the $E_{1/2}$ values where anion radicals were produced. Actually well-resolved esr spectra were obtained by controlled-potential electrolyses at the potentials (see Table I) which correspond to the limiting current of a one-electron reduction wave. The esr spectra of the compounds **8**, **9**, **27**, **29**, and **30** are shown in Figure 3, and the assignments of hfc constants are included in Table II. It was clear that the hfc constants (0.61 G for 4-cyanopyridine N-oxide and 1.26 G for 4-nitropyridine N-oxide) could be assigned to the protons at the 2 and 6 positions (see Figure 7 for numbering of each atom) of 4-cyano- and 4-nitropyridine N-oxides. We note that these are smaller than those of the 3 and 5 positions: $|a_{2H}| = |a_{6H}| < |a_{3H}| = |a_{5H}|$. Similarly a comparison of nitrogen hfc constants of 4-nitropyridine N-oxide and its N¹⁵-labeled compound for NO_2 group implied that $|a_{N(\text{NO}_2)}| > |a_{N(\text{N}\rightarrow\text{O})}|$. In Table I, we note that the ratio, $|a_{N(\text{N}^{15}\text{O}_2)}|/|a_{N(\text{NO}_2)}|$, is equal to 1.39 which compares favorably with the theoretical ratio, $|a_{N^{15}}|/|a_{N^{14}}| = 1.403$. With 4-cyanopyridine N-oxide two nitrogen

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Table II. Observed Hyperfine Coupling Constants of Various Anion Radicals of Heterocyclic Amine N-Oxides and Their Assignments^a

Anion radicals of	Hyperfine coupling constants, G (absolute value)			
Pyridine N-oxide	10.91 (1)	3.01 (2, 6)	0.44 (3, 5)	8.51 (4)
4-Carboxypyridine N-oxide	8.80 (1)	0.72 (2, 6)	2.83 (3, 5)	
4-Cyanopyridine N-oxide	9.61 (1)	0.61 (2, 6)	2.36 (3, 5)	1.76 (9)
4-Cyanopyridine 2,6- <i>d</i> ₂ -N-oxide	9.55 (1)		2.35 (3, 5)	1.75 (9)
4-Nitropyridine N-oxide	4.73 (1)	1.26 (2, 6)	3.32 (3, 5)	6.04 (8)
4-Nitropyridine-2,6- <i>d</i> ₂ -N-oxide	4.67 (1)		3.29 (3, 5)	6.09 (8)
4-Nitro pyridine-nitro-N ¹⁵ N-oxide	4.69 (1)	1.26 (2, 6)	3.35 (3, 5)	8.39 (8)
Pyrazine mono-N-oxide	12.09 (1)	5.55 (4)	2.13 (2H)	1.62 (2H)
Pyrazine di-N-oxide	9.49 (1, 4)	1.37 (2, 3, 5, 6)		
Pyridazine mono-N-oxide	10.03 (1)	5.26 (2)	0.42 (3 or 6)	1.41 (6 or 3)
	4.58 (4 or 5)	5.91 (5 or 4)		
Quinoline N-oxide	6.00 (1) ^b			
Quinoxaline di-N-oxide	6.72 (1, 4)	2.44 (5, 8)	1.81 (2H)	1.44 (2H)
Acridine N-oxide	6.82 (9)	5.34 (10)	2.89 (2H)	2.58 (2H)
	1.43 (2H)	0.49 (2H)		
Phenazine mono-N-oxide	7.58 (9)	3.60 (10)	1.80 (4H)	1.65 (2H)
	1.23 (2H)			
Phenazine di-N-oxide	5.91 (9, 10)	1.75 (4H)	1.36 (4H)	

^a The number written in parentheses designates the position (Figure 7) of each atom in the molecule, and the coupling constant is due to the assigned atom. The designations 2H and 4H imply that there are two and four protons, respectively, with the same hfc constant, but the assignment was not made directly from the spectra. ^b See text.

hfc constants were observed: $|a_N| = 9.61$ and 1.76 G. Since $|a_N|$ is typically 1–3 G in various nitrile anion radicals,²² it is reasonable to assign the 9.61 and 1.76

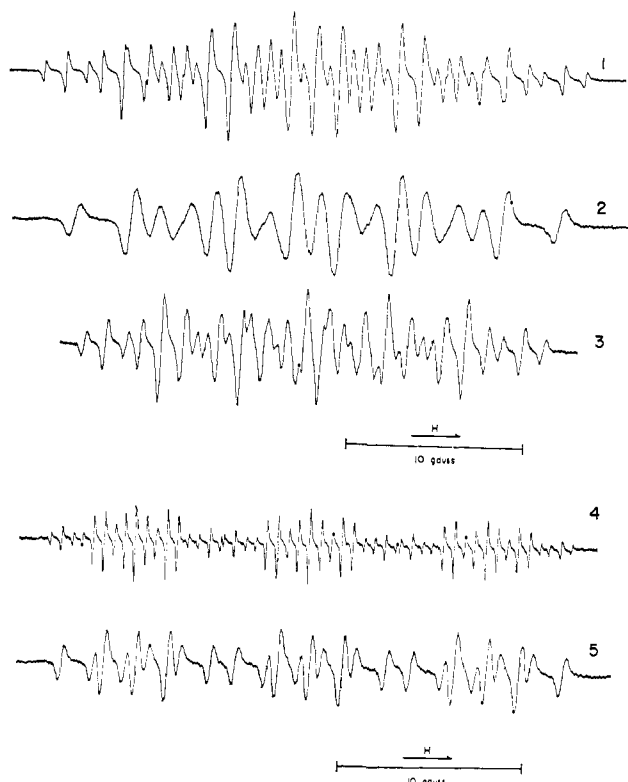


Figure 3. ESR spectra of the anion radicals of 4-nitropyridine N-oxide, 4-nitro-2,6-deuteriopyridine N-oxide, 4-nitropyridine N-oxide labeled with N¹⁵ for NO₂ group, 4-cyanopyridine N-oxide, and 4-cyano-2,6-deuteriopyridine N-oxide are shown by spectral number 1, 2, 3, 4, and 5, respectively.

hfc constants to the N atom of $\text{>N}\rightarrow\text{O}$ and $\text{C}\equiv\text{N}$ groups, respectively. Consequently all the hfc con-

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stants due to the protons and nitrogen atoms of 4-cyano- and 4-nitropyridine N-oxides were assigned as shown in Table II.

Esr Spectra of Pyrazine Mono- and Di-N-oxides.

The electrolyses at the one-electron reduction potentials, given in Table I, gave the well-resolved esr spectra shown in Figure 4. These spectra are easily under-

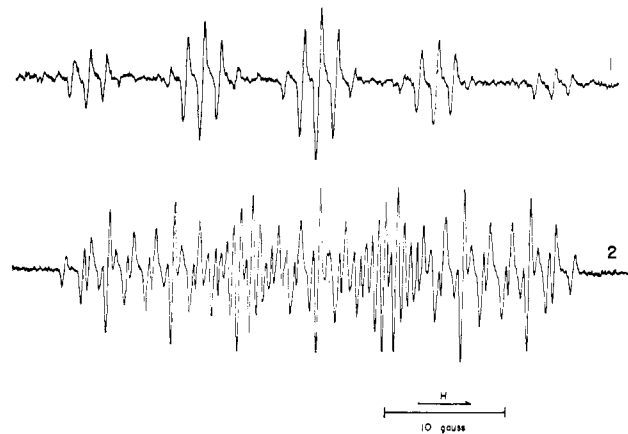


Figure 4. ESR spectra of the anion radicals of pyrazine di-N-oxide (1) and pyrazine mono-N-oxide (2).

stood from the molecular symmetry of the compounds and are analyzed straightforward. The results are included in Table II. Pyrazine di-N-oxide has only one proton hfc constant, $|a_H| = 1.37$ G, and this will be used later as the standard for the spin density calculations. The pyrazine mono-N-oxide anion radical gave two proton hfc constants, $|a_H| = 1.62$ and 2.13 G, which were assigned by means of the spin density calculation to the two *ortho* and the two *meta* protons, respectively (refer also to later discussion).

Esr Spectra of the Other N-Oxide Compounds.

Controlled-potential electrolyses of the other aromatic N-oxides at the potentials (Table I) corresponding to the first reduction wave usually gave well-resolved esr spectra (Figure 5). The assignments of the quinoxaline di-N-oxide and phenazine di-N-oxide anion

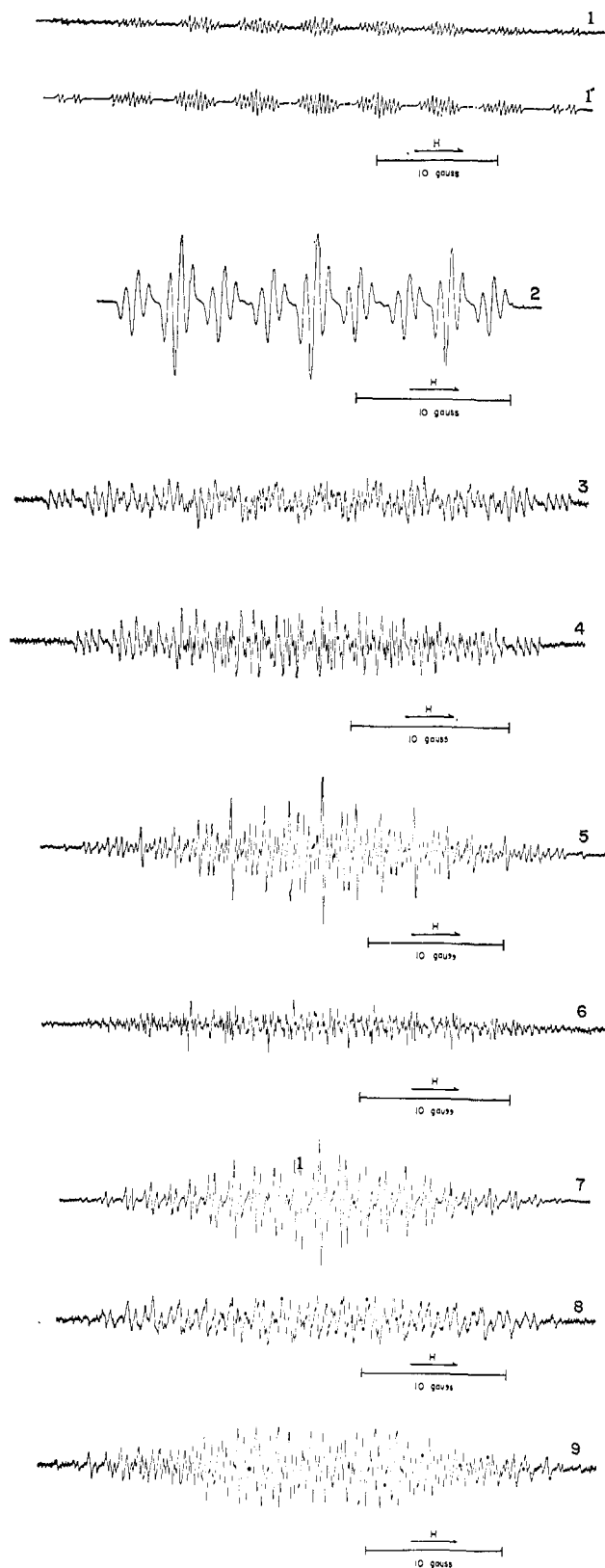


Figure 5. Observed (1) and simulated (1') esr spectra of pyridazine mono-N-oxide anion radical. Observed spectra of the anion radicals of 4-carbethoxy pyridine N-oxide (2), quinoline N-oxide (3), quinoline N-oxide labeled with N^{15} isotope (4), quinoxaline di-N-oxide (5), acridine N-oxide (6), phenazine di-N-oxide (7), phenazine mono-N-oxide (8), and quinoxaline mono-N-oxide (9).

radical spectra are easily deduced from the high symmetry of these molecules and the relative intensity

ratios of the hyperfine structures. In Figure 5, the spectral pattern of the 4-carbethoxy pyridine N-oxide anion radical resembles that which is expected for C_{2v} symmetry. The assignments, $|a_N| = 8.80$, $|a_{2H}| = |a_{6H}| = 0.72$, and $|a_{3H}| = |a_{5H}| = 2.83$, were deduced from a McLachlan HMO (MHMO) calculation discussed later. The above virtual C_{2v} symmetry nature of hfc constants of ester group was also reported on 4-carbethoxy pyridine, etc.²³ When the spectra were recorded with much smaller modulation, each line splits into a triplet with $|a_H| \approx 0.1$ G, presumably due to the two protons in carbethoxy group.

The hfc constants of the acridine N-oxide anion radical were determined by the method of spectral simulation. The $|a_H| = 6.82$ G (doublet) was assigned to the position 9 proton which is unique as a result of the C_{2v} molecular symmetry.²⁴ The esr spectrum of pyridazine mono-N-oxide (15) anion radical (Figure 5) had a poor S/N ratio as a result, probably, of the relative instability of this radical. The spectrum was slightly asymmetric and contained a few unidentifiable peaks. Again, spectral simulation with the aid of the MHMO calculations was used to determine the hfc constants. The finally obtained hfc constants are listed in Table II.

Although phenazine mono-N-oxide has the same molecular symmetry as that of acridine N-oxide, the splitting of the esr spectral lines of the anion radical is not so good because of the overlapping of each absorption line. Moreover, there is no obvious key lines. However, referring to the MHMO calculation results and repeating the spectral simulation after the manual construction of the spectra by the method of trial and error, the hfc constants were evaluated.²⁵ The esr spectra of the anion radicals of quinoline N-oxide and its N^{15} -labeled compound are also shown in Figure 5. As a result of the low symmetry of these molecules and the complexity of their spectra obtained, the analyses of hfc constants were incomplete. Only the $|a_{N^{14}}|$ value was estimated as follows. The total spectral band width change on substituting N^{15} for N^{14} may be expressed as $2|a_{N^{14}}| - |a_{N^{15}}| = 3.58$ G (observed value). We assume that the molecular electronic state does not change with isotope substitution. Then, using the relation $|a_{N^{15}}|/|a_{N^{14}}| = 1.403$ discussed above, we obtain $|a_{N^{14}}| = 6.0$ G.

Esr spectra of the N-oxides other than those discussed above could not be observed at $\sim 25^\circ$ during electrolysis at the potential corresponding to the first reduction wave.

Polarographic Data in DMF Solvent. Listed in Table I are $E_{1/2}$'s for the first reduction wave of the N-oxides, the Lingane constant, the peak height (i_{AC}) of ac polarogram, and the potential used for controlled-potential electrolysis with "yes" or "no" for the appearance of esr spectra. Lingane's constant,²⁶ I , was calculated by the equation $I = 607n\sqrt{D} = i_d/(cm^{2/3} \cdot t^{1/6})$, where i_d and c are wave height (μA) of diffusion

(23) M. Hirayama, *Bull. Chem. Soc. Japan*, 40, 1822 (1967).

(24) This is easily determined from the doublet hfc constant with the largest value (6.82), which is due to a proton assigned necessarily to position 9.

(25) It is noted that the hfc constants with small values are still a little uncertain, because the simulated spectra are quite sensitive to the selection of each hfc constant.

(26) I. M. Kolthoff and J. J. Lingane, "Polarography," Vol. 1, Interscience Publishers, New York, N. Y., 1952, p 70.

current and sample concentration (mM), respectively (see Experimental Section for m and t). In Figure 6 the polarograms of 4-cyano-, 4-nitro-, and 3-cyanopyridine N-oxides are illustrated as examples. Polarograms of the other compounds are similar. To determine the nature of the reduction waves, we examined the temperature and mercury height dependences of the first reduction wave of 4-nitropyridine N-oxide, a typical example. The results are: (i) mercury-height, h (in cm), dependence is very well expressed by $i_d = a\sqrt{h}$, where a is 0.189 with correction or 0.186 without correction for the reverse pressure of mercury; and (ii) the temperature dependence was calculated to be 1.24% by the compound interest method. This implies that the reduction wave may be due to the diffusion current.^{15a,27} Assuming that the Ilkovic equation may also be applied to the present system, and that the number of electrons participating in the reduction is clearly equal to one, we obtain the diffusion coefficient $D = 11.3 \times 10^{-6}$ cm²/sec at 25°, which appears to be slightly larger than that observed in aqueous solvents.^{15a,27,28} We assume that the nature of the first reduction wave of the other amine oxides listed in Table I is similar to that of 4-nitropyridine N-oxide.

Discussion

Calculation of Spin Density Distribution. The MO calculation of the spin density distribution in the heterocyclic N-oxide radicals was very useful in interpreting the esr spectra. The spin densities (ρ_r) were calculated by the equation²⁹

$$\rho_r = (C_{0r})^2 - \lambda \sum_s (\pi_{rs} C_{0s}^2) \quad (1)$$

which many workers have successfully used in the calculation of the spin density distribution of various organic free radicals. In eq 1 C_{0r} and C_{0s} are the coefficients at atoms r and s of the spin orbital ψ_0 occupied by the unpaired electron. π_{rs} is the atom-atom polarizability. As is generally done,^{22a,30} λ was set equal to 1.2. The HMO method was used to determine ψ_0 . The choice of the parameters for HMO calculation of heterocyclic N-oxides is important. First, the spin density, ρ_C , on the carbon atoms of pyrazine di-N-oxide was estimated using the McConnell equation,^{31a} $a_H = Q_{CH}^C \rho_C$, where $Q_{CH}^C = -22.5$ G^{31b,c} and a_H is the observed hfc constant, -1.37 G. McLachlan HMO (MHMO) calculations were then carried out so as to satisfy the experimentally derived $\rho_C = 0.0608$ and the boundary conditions discussed below.

The HMO Coulomb (k) and resonance (β) parameters describe the various physicochemical nature of compounds. For neutral heterocyclic amine N-oxides in nonpolar solvents, the following values have been recommended:^{3a} $k_{N\delta^+} = 1.6$, $\beta_{NO} = 1.0$, $k_O = 0.8$, and inductive effect = $(1/3)^n k_{N\delta^+}$. These values were derived

(27) (a) T. Kubota and H. Miyazaki, *Bull. Chem. Soc. Japan*, **35**, 1549 (1962); (b) T. Kubota, H. Miyazaki, and Y. Mori, *ibid.*, **40**, 245 (1967).

(28) It was reported that the D value of organic compounds dissolved in benzene, alcohol, etc. is larger than that in water: N. Riehl and G. Wirths, *Z. Physik. Chem. (Leipzig)*, **194**, 97 (1944).

(29) A. D. McLachlan, *Mol. Phys.*, **3**, 233 (1960).

(30) (a) P. H. Rieger and G. K. Fraenkel, *J. Chem. Phys.*, **39**, 609 (1963); (b) P. T. Cottrell and P. H. Rieger, *Mol. Phys.*, **12**, 149 (1967).

(31) (a) H. M. McConnell, *J. Chem. Phys.*, **24**, 633, 764 (1956), etc.; (b) J. V. M. Henning, *ibid.*, **44**, 2139 (1966); (c) L. D. Tuck and D. W. Schieser, *J. Phys. Chem.*, **66**, 937 (1962).

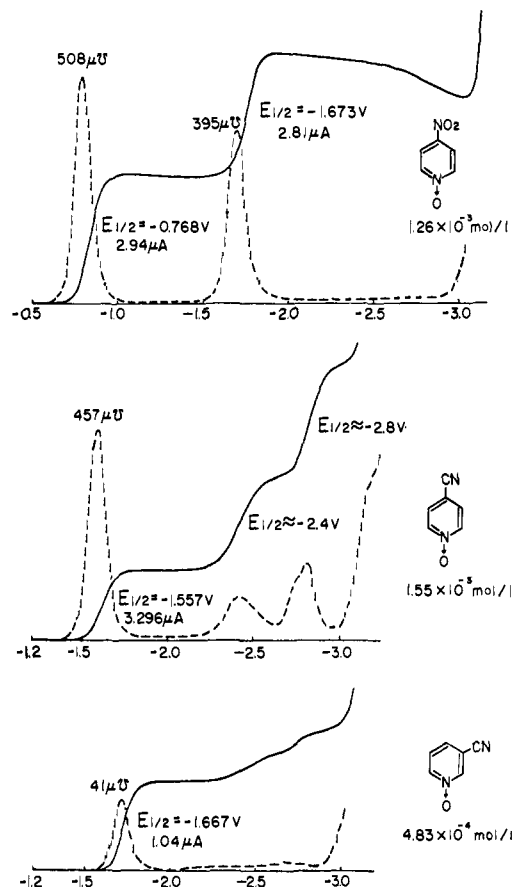


Figure 6. Typical dc and ac polarograms of the N-oxides shown in this figure.

from Jaffé's procedure^{32b,33} and also from the matrix elements for ASMO-Cl calculation of pyridine N-oxide by the method of composite system consisting of the O⁻ and pyridine residual part.^{8,34} These calculations suggested that the character of intramolecular charge transfer from the oxygen to the rest of the π system is determined mainly by the lowest vacant MO which is occupied by an electron during the formation of the anion radical. Especially, for basic heterocyclic N-oxides such as pyridine N-oxide etc., the unpaired electron density on the N atom of $\geq N \rightarrow O$ is quite large, and the N \rightarrow O bond becomes strongly antibonding in nature. In other words, the N \rightarrow O bond order is reduced in the anion free radicals. It is thus logical to predict that the HMO parameters which are applicable to the neutral amine oxides should be reduced in magnitude in the case of the present anion radicals. Thus, the boundary conditions for the parameterization of the $\geq N \rightarrow O$ bond were assumed to be: $k_{N\delta^+} < 1.6$, $k_O < 0.8$, $\beta_{NO} < 1$, and inductive effect = $0.1k_{N\delta^+}$. As will be discussed later, many MHMO calculations led to the conclusion that the best set of parameters was $k_{N\delta^+} = 1.0$ with inductive effect = 0.1, $k_O = 0.6$, and $\beta_{NO} = 0.8$. These satisfied the aforementioned $\rho_C = 0.0608$ in pyra-

(32) In the literature^{2,6} we found some other sets of parameters to explain a limited nature of tertiary amine N-oxides, but the above-mentioned values are in common range of the parameters.^{2,6} See also (a) N. Mataga, *Bull. Chem. Soc. Japan*, **36**, 1109 (1963); (b) H. H. Jaffé, *J. Am. Chem. Soc.*, **76**, 3527 (1954); (c) T. Kawamura, S. Matsunami, T. Yonezawa, and K. Fukui, *Bull. Chem. Soc. Japan*, **38**, 1935 (1965).

(33) H. H. Jaffé, *J. Chem. Phys.*, **20**, 279, 778, 1554 (1952).

(34) T. Kubota, *Nippon Kagaku Zasshi*, **80**, 578 (1959).

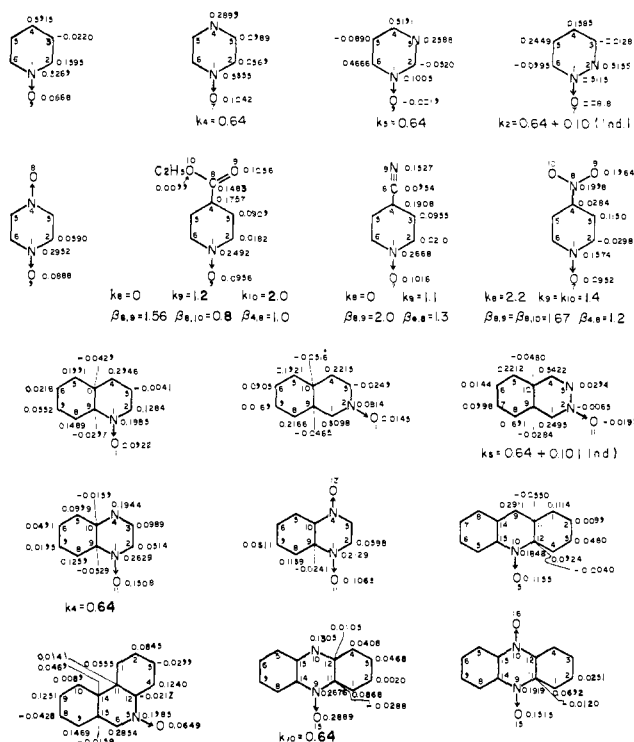


Figure 7. Calculated spin density distribution of the anion radicals of various heterocyclic N-oxides. The numberings of each atom and the calculation parameters are also given. See text for the parameters of the N-oxide group.

zine di-N-oxide. For pyridine-type C=N bonds, only the parameter k_N was changed to 0.64, so that the spin densities calculated by the MHMO method reproduced quite well those of 1,3,4,6-tetrazine, pyrazine, pyridazine, etc., which were obtained by Black and McDowell³⁵ by the methods of unrestricted SCF-MO and VESCF-MO calculations. In addition to that, $k_N = 0.64$ led to the best agreement between calculated $[\rho_3/\rho_2]$ and observed $|a_{3H}|/|a_{2H}|$ of pyrazine mono-N-oxide compared to any other parameter set within a reasonable k_N range: 0.5–1.0.

The spin densities distribution of 4-nitro-, 4-carboethoxy-, and 4-cyanopyridine N-oxides were calculated using the same MHMO parameters for the $\geq N \rightarrow O$ group and using the parameters given by Fraenkel, *et al.*,^{22a,30a,36} for the MHMO calculation ($\lambda = 1.2$ in eq 1) of NO_2 , $COOC_2H_5$, $C \equiv N$ groups, etc. The results are shown in Figure 7, where we see that the calculated spin densities of 4-nitro- and 4-cyanopyridine N-oxides satisfy the relation, $|a_{3C}| > |a_{2C}|$, determined experimentally. The spin density calculations of the other N-oxides studied here were also carried out using these conditions, and the results are also included in Figure 7.

(35) P. J. Black and C. A. McDowell, *Mol. Phys.*, **12**, 233 (1967).

(36) P. H. Rieger and G. K. Fraenkel, *J. Chem. Phys.*, **37**, 2811 (1962); P. Smith, J. T. Pearson, P. B. Wood, and T. C. Smith, *ibid.*, **43**, 1535 (1965).

(37) The parameter set, $k_{N\delta^+} = 1.5$ with inductive effect = 0.15, $k_O = 0.7$, and $\beta_{NO} = 0.9$, was also derived to satisfy the ρ_H in pyrazine di-N-oxide. However, with 4-cyanopyridine N-oxide, the calculation using the above and Fraenkel's^{22a} parameters yielded the result, $|a_{2H}| < |a_{3H}|$, which is opposite to that observed. Also, the agreement between experimental and theoretical hfc constants, derived on the other N-oxides listed in Table II, was not good in comparison with that yielded from the parameter set written in the text.

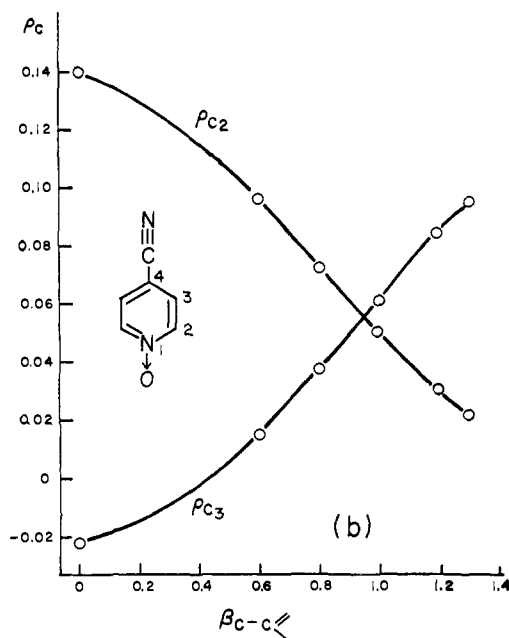
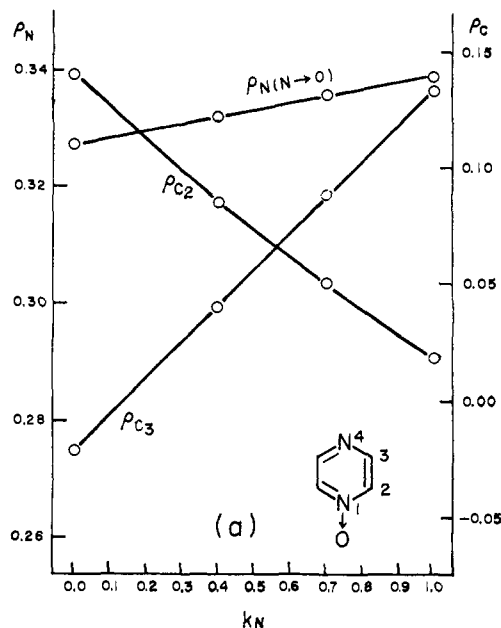


Figure 8. Variation of spin densities with parameter change of the Coulomb integral at the 4 position of pyrazine mono-N-oxide (a) and of the resonance integral of the bond connecting two carbon atoms of CN group and 4 position of 4-cyanopyridine N-oxide (b).

The results of MHMO calculations to study the effect on ρ_{2H} and ρ_{3H} by introducing a heteroatom or a substituent at the 4 position of pyridine N-oxide, as in pyrazine mono-N-oxide and 4-cyanopyridine N-oxide, are given in Figures 8a and b. In these figures spin densities corresponding to $k_N = 0$ (Figure 8a) or $\beta_{C-C} = 0$ (Figure 8b) are for the pyridine N-oxide anion radical itself. We deduce that in the pyridine N-oxide anion radical, $\rho_2 > \rho_3$, as was reported in the literature.^{2,4,8,38} The details will be discussed later. Note that increasing the k_N in pyrazine mono-N-oxide

(38) The McLachlan modification²⁹ ($\lambda = 1.2$) of the SCF-MO of neutral pyridine N-oxide calculated recently by S. Kobinata and S. Nagakura led to this same conclusion. The authors wish to thank Professor S. Nagakura for private communications.

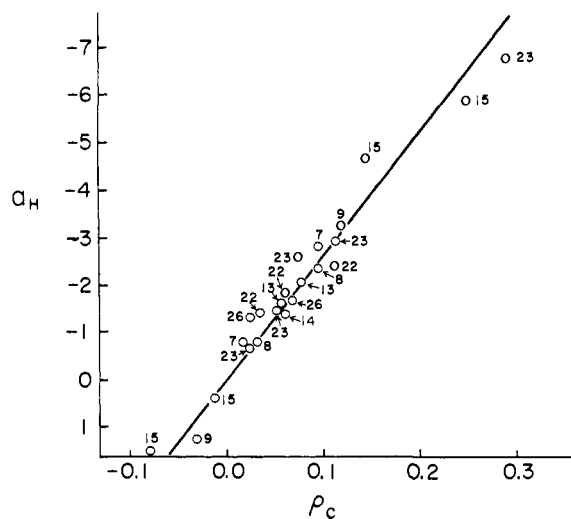


Figure 9. The correlation between ρ_C 's calculated and observed a_H 's. The straight line is a least-squares fit of the McConnell equation (eq 3).

or increasing the β_{C-C} in 4-cyanopyridine N-oxide decreases ρ_2 rapidly but increases ρ_3 , although $\rho_{N(N\rightarrow O)}$ is not very sensitive to these changes. This explains why, in the 4-cyano-, 4-nitro-, and 4-carboethoxypyridine N-oxides, the relation is $|a_{3H}| > |a_{2H}|$ although the opposite is expected for pyridine N-oxide. By using $k_N = 0.64$ and $a_N = -22.5\rho_C$,³¹ the result, $\rho_3 > \rho_2$, for the pyrazine mono-N-oxide radical is in good agreement with the observed $|a_{3H}|$ and $|a_{2H}|$. Since the difference between $|a_{3H}|$ and $|a_{2H}|$ (Table II) is small, the conclusion of $|a_{3H}| > |a_{2H}|$ may be ambiguous although we think this assignment to be preferable.³⁹ With 4-cyanopyridine N-oxide a better correlation between ρ_C 's and observed $|a_{CH}|$'s was obtained using $\beta_{C-C} = 1.3$ ⁴⁰ instead of the value 1.2 derived by Fraenkel, *et al.*^{22a}

Correlation of Spin Density Distribution with Observed Hfc Constants. We first discuss the correlation of proton hfc constants and calculated ρ_C 's on the various N-oxide anion radicals. As shown in Figure 9, there is, as expected, a linear relation between the calculated ρ_C and the observed $|a_{CH}|$. A least-squares fit of these data to the equations

$$a_H = Q_{CH}^C \rho_C + C \quad (2)$$

$$a_H = Q_{CH}^C \rho_C \quad (3)$$

gave the results: $Q_{CH}^C = -23.84$ G, $C = -0.29$ G, and a mean-square deviation $\sigma = \pm 0.39$ G for eq 2, and $Q_{CH}^C = -25.67$ G and $\sigma = \pm 0.44$ G for eq 3. The constant C in eq 2 may be interpreted as a deviation from McConnell's^{31a} eq^{31a} 3. However, $C = -0.29$ G is quite small and lies within the experimental error. The McConnell eq 3 appears to be well satisfied and the Q_{CH}^C value is reasonable in magnitude. The values $-22.5 \sim -30$ G⁴¹ have been reported for various organic compounds, although Q_{CH}^C depends on the kind

(39) If we use the parameter set written in footnote 37 with $k_N = 0.64$, then $\rho_2 > \rho_3$, $\rho_2 \approx |a_{2H}|/22.5$, and $(\rho_2/\rho_3) = (|a_{2H}|/|a_{3H}|)$ are found for pyrazine mono-N-oxide.

(40) It is noted that the bond order corresponding to this increases in magnitude during anion-radical formation relative to that of the neutral molecule, just like the central bond connecting the two benzene rings of biphenyl: H. Suzuki, *Bull. Chem. Soc. Japan*, **32**, 1340, 1350 (1959).

(41) A. Carrington, *Quart. Rev. (London)*, **17**, 67 (1963).

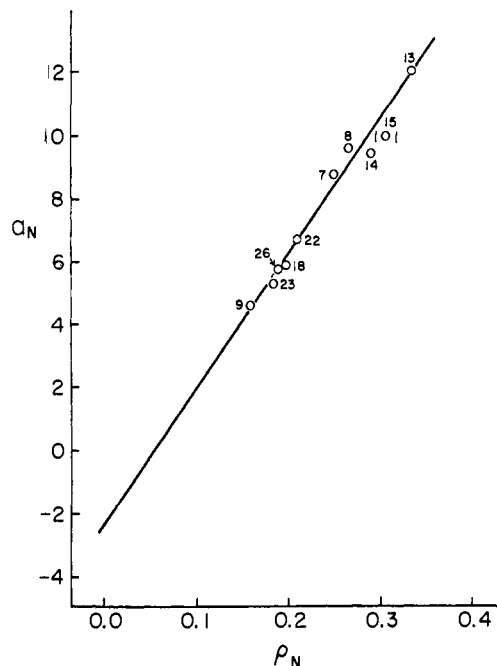


Figure 10. The correlation between calculated ρ_N 's and observed a_N 's for the N atom of N-oxide group of various N-oxide compounds. The straight line is a least-squares fit of eq 5. See footnote 45 in text for a discussion of pyridazine mono-N-oxide (indicated in parentheses).

and structure of the radical,⁴² such as anion or cation radical, bond angles, and steric factors. The fact that the McConnell equation is well fulfilled implies that the parameters chosen in these calculations may not be unreasonable.

Next we discuss the interrelation between the observed $|a_N|$'s and the spin densities on nitrogen and its neighboring atoms. According to the Karplus and Fraenkel theory,⁴³ we can write a_N as

$$a_N = (S_N + \sum_i Q_{NX_i^N})\rho_N + \sum_i Q_{X_i^N} \rho_{X_i} \quad (4)$$

and for the present case of the $CN(=C')\rightarrow O$ fragment

$$a_N = Q_N^N \rho_N + Q_{ON}^N \rho_O + Q_{CN}^N (\rho_C + \rho_{C'}) \quad (4')$$

where S_N , $Q_{NX_i^N}$, and $Q_{X_i^N}$ are the σ - π interaction parameters contributed from the N $1s^2$ inner-shell N- X_i and X_i -N σ bonds, respectively. If the contribution from the term $\sum_i Q_{X_i^N} \rho_{X_i}$ is small as suggested by Carrington and Santos-Veiga⁴⁴ for N-heterocyclic anion radicals, then eq 4 is simplified to

$$a_N = Q_N^N \rho_N \quad (5)$$

A plot of eq 5 is shown in Figure 10 for the compounds whose hfc constants were determined with some certainty. A nice linear relation was then yielded but the straight line does not intersect at the origin of the coordinates. The least-squares treatment using the eq

(42) T. M. McKinney and D. H. Geske, *J. Am. Chem. Soc.*, **89**, 2806 (1967); I. Bernal, P. H. Rieger, and G. K. Fraenkel, *J. Chem. Phys.*, **37**, 1489 (1962); D. H. Geske, J. L. Ragle, M. A. Bambenek, and A. L. Balch, *J. Am. Chem. Soc.*, **86**, 987 (1964); J. P. Colpa and J. R. Bolton, *Mol. Phys.*, **6**, 273 (1963).

(43) M. Karplus and G. K. Fraenkel, *J. Chem. Phys.*, **35**, 1312 (1961).

(44) A. Carrington and J. dos Santos-Veiga, *Mol. Phys.*, **5**, 21 (1962).

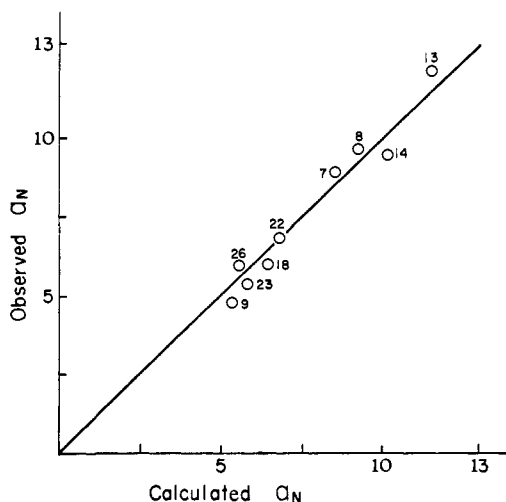


Figure 11. The correlation between the observed a_N 's due to the N-oxide group of various N-oxide compounds and a_N 's calculated using the eq 4' in text. See text for the values of σ - π interaction parameters.

6 yielded the values $Q_N^N = 41.87$ G, $C_N = -2.10$ G, and $\sigma = \pm 0.38$ G, with⁴⁵ the equation

$$a_N = Q_N^N \rho_N + C_N \quad (6)$$

The fact that C_N is not negligible suggests that the term $Q_{N,N}^N$ in eq 4 should be considered. A least-squares calculation of (4') with observed $|a_N|$ values yielded the σ - π interaction terms: $Q_N^N = 42.57$ G, $Q_{CN}^N = -6.66$, $Q_{ON}^N = -18.98$, and $\sigma = \pm 0.45$ G. The almost linear relationship between a_N values calculated by using these σ - π interaction parameters and the observed $|a_N|$ values is shown in Figure 11.

There are some difficulties in discussing the above Q values in detail, since a theoretical analysis of the Q values for $\geq N \rightarrow O$ fragment was not attempted. However, some conclusions can be made. The fact that the Q_N^N values derived from both the treatments (eq 4 and 6) are almost the same is reasonable. Recent detailed studies of the magnitude and the sign of Q_{CN}^N for a series of six-membered N-heterocyclic compounds showed that the value has a negative sign and is approximately ~ -1.5 G^{4,30b,44,46} except for a few reports where Q_{CN}^N is positive in sign.^{31b,47} Our Q_{CN}^N seems to be theoretically reasonable in sign, but a little large in magnitude. This may be attributed to a different kind of nitrogen-carbon bond from that of pyridine. Rieger and Fraenkel^{30a} derived σ - π interaction parameters for the nitrogen atom of the NO_2 group: $Q_N^N = 99$ and $Q_{ON}^N = -35.8$ G. In comparison to the values $Q_N^N = 42.57$ and $Q_{ON}^N = -18.98$

(45) Pyridazine mono-N-oxide was excluded from the present least-squares calculation because the bond frame i is different from the ii type.



Also excluded was phenazine mono-N-oxide where the a_H and a_N values deviated relatively from those theoretically expected.

(46) (a) N. M. Atherton, F. Gerson, and J. N. Murrell, *Mol. Phys.*, **5**, 509 (1962); (b) E. J. Stone and A. H. Maki, *J. Chem. Phys.*, **39**, 1635 (1963).

(47) R. L. Ward, *J. Am. Chem. Soc.*, **83**, 3623 (1961); **84**, 332 (1962).

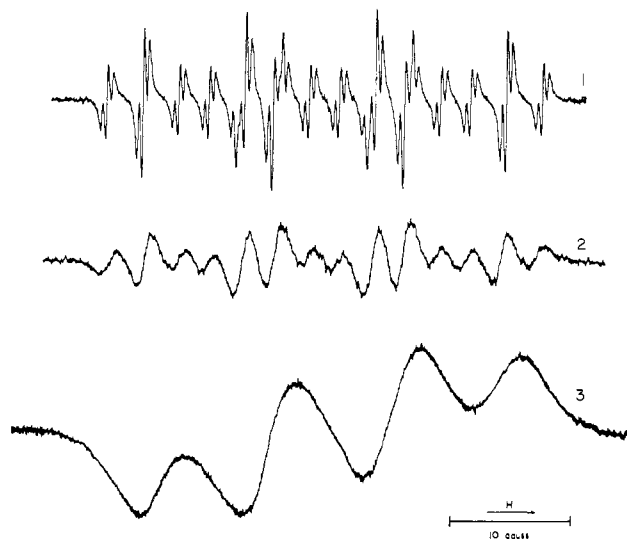
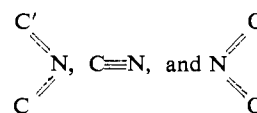


Figure 12. ESR spectra of anion radicals of pyridine N-oxide (1 and 2) and 2,6-deuteriopyridine N-oxide (3). These spectra were obtained by the method of electrolysis, not controlled-potential electrolysis, at about -50° in liquid ammonia solution with tetramethylammonium iodide ($\sim 10^{-3}$ M) as a supporting electrolyte. Spectrum 1 was recorded by very slowly increasing the electrolysis potential to 90 V over a 6-hr period. With more voltage the signals due to the solvated electron appeared. At lower voltage spectra with low resolution were observed. Spectrum 2, which was obtained at ~ 20 V, is shown as an example for this case. Spectrum 3 was measured under almost the same conditions as that of spectrum 2, and the hfc constant equal to 3.01 G apparently disappears.

G obtained here, note that the Q_N^N and Q_{ON}^N values for NO_2 group are about twice as large as those of the $\geq N \rightarrow O$ group. Perhaps this difference may be due to the fact that the NO_2 group has two $N \rightarrow O$ bonds, each of which contributes to nitrogen hfc constant.⁴

Now we discuss how the spin densities given in Figure 7 can reproduce the observed nitrogen hfc constants of the NO_2 , $C \equiv N$, and $\geq N$ groups in heterocyclic N-oxide compounds studied. Using the equations $a_N = 27.3\rho_N - 1.7(\rho_C + \rho_{C'})$,⁴ $a_N = 23.1\rho_N - 6.8\rho_{C'}$,^{22a} and $a_N = 99.0\rho_N - 35.8(\rho_O + \rho_{O'})$ ^{30a} for



respectively, we obtained the calculated a_N values (observed values are in parentheses): 7.63 (5.55), 2.56 (1.76), and 7.00 (6.04) G for N atoms in pyrazine mono-N-oxide, 4-cyanopyridine N-oxide, and 4-nitropyridine N-oxide, respectively. The agreement between calculated and observed values is not very good, but both the values are well coincident as the order of magnitude. There appears to be no misassignment for the a_N values discussed.

Hfc Constants Due to Nitrogen and Protons in Pyridine N-Oxide Anion Radical. Pyridine N-oxide is the most basic compound of the heterocyclic N-oxides studied and we discuss it separately. The spin density distribution (Figure 7) and the equations for a_H and $a_{N(N \rightarrow O)}$ given above predict the following coupling constants: $a_{2H} = -3.58$, $a_{3H} = 0.56$, and $a_{4H} = -9.53$ G, where $a_H = -25.67\rho_C$. However, $a_N = 10.78$ or 11.57 G was predicted by eq 4' or 6, respectively. The ESR spectrum of the pyridine N-oxide anion radical

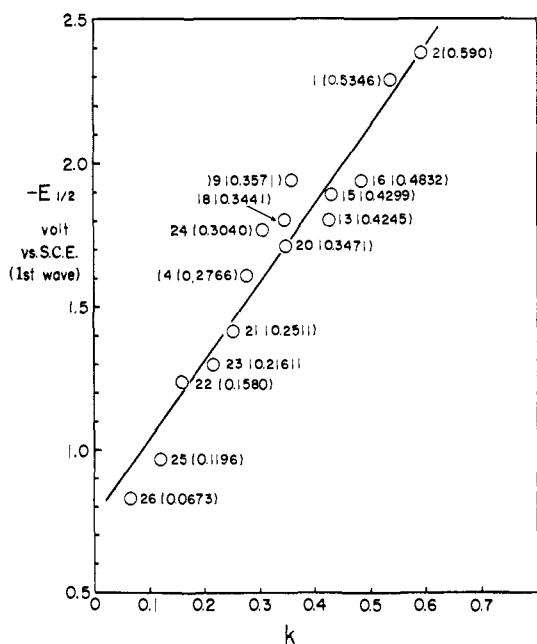


Figure 13. Relation between half-wave reduction potential of the first wave and the lowest vacant HMO energy of basic heterocyclic amine N-oxides. The latter value is expressed by $|k|$ in $\epsilon_{LV} = \alpha - k\beta$ and is indicated in parentheses in this figure.

was recently reported by Talcott and Myers⁴ who used electrolysis at -75° in a liquid ammonia solution saturated with tetramethylammonium iodide. Their results were checked and confirmed in this laboratory using an identical technique. However, our spectrum (Figure 12) shows no overlapped lines due to solvated electrons. When 2,6-deuteriopyridine N-oxide was used under the conditions of Figure 12(1), partial H-D exchange occurred. However, the experiment demonstrated that the $|a_{2H}|$ of pyridine N-oxide is much larger than $|a_{3H}|$. The esr spectra of usual and deuteriopyridine N-oxide anion radicals under almost the same conditions milder than in Figure 12(1) are shown in Figure 12(2,3). The hfc constants reported by Talcott and Myers and obtained here are comparable and are respectively (in gauss): $|a_{2H}| = 3.04, 3.01$; $|a_{3H}| = 0.47, 0.44$; $|a_{4H}| = 8.61, 8.51$; and $|a_N| = 10.82, 10.91$. These observed hfc constants agree well with the calculated ones. The above studies would thus tell us that the orbital charge density at the LVMO of pyridine N-oxide is large near *para* and *ortho* positions as well as on the nitrogen atom but is very small near the *meta* position. A strong 1A_1 absorption band of pyridine N-oxide appearing at $\sim 281 m\mu$ in *n*-heptane has been attributed to the band having the contribution from a configuration due to the charge transfer (CT) from the oxygen to the LVMO of the pyridine residue^{2,34} (see also the introductory section of this paper). The above intramolecular charge transfer causes the orbital charge density in the LVMO of pyridine N-oxide to be $4 > 2 > 3$ at carbon atoms. The above interpretation of the $\sim 281\text{-}m\mu$ band as a intramolecular CT band seems to be confirmed experimentally by the present esr study of the pyridine N-oxide anion radical.

Relation of Polarographic Data to Radical Stability, Lowest Vacant MO(LVMO), and Hammett's σ Value. On examining the Lingane constant (I) and peak height of the ac polarogram (i_{ac}) given in Table I, we found

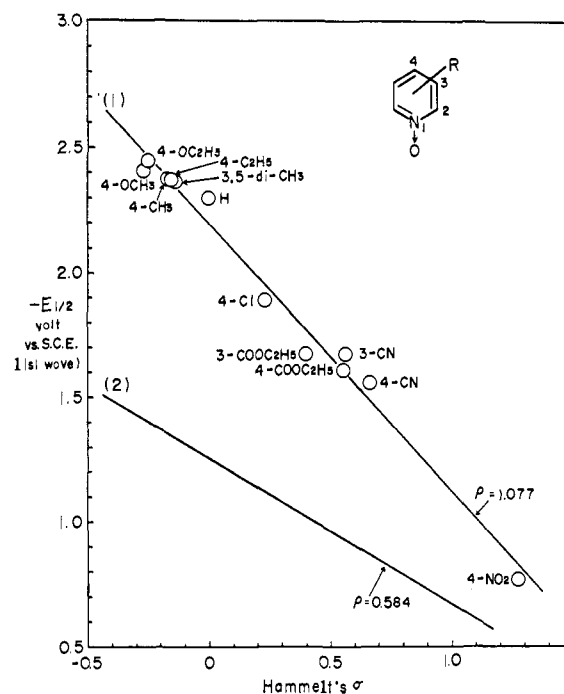


Figure 14. The correlation between Hammett's σ value and half-wave reduction potential of the first wave of substituted pyridine N-oxides. Straight line 2 is reproduced from our previous reports^{7,15a} and is derived from aqueous solvent experimental data.

that for most compounds, whose esr spectra were observed by the present technique, i_{ac} is very large (more than $180 \mu\text{mhos/mmole}$) but I is not so large (1.5–2.9) in comparison with those compounds which gave no esr signal. i_{ac} appears to be a good measure of radical stability; that is, the radical formation is reversible and the radicals thus produced are relatively stable. For compounds like pyridine N-oxide, the radical is not too stable at room temperature, and succeeding reactions after the radical formation occur at the first reduction wave. This is indicated by an increase in dc current, then an increase in I , but a decrease in i_{ac} . However, this difference of reversibility of the electrode reaction or of dc wave height has only a small effect on the determination of the half-wave reduction potential ($E_{1/2}$), which is now discussed below.

To date there are many reports that describe the linear relation of $E_{1/2}$ to LVMO energy.⁴⁸ The $E_{1/2}$ is also a good measure of the electron affinity of various organic compounds. We checked this relation for various basic heterocyclic N-oxides studied here, and the linear relation obtained is shown in Figure 13. In this figure the orbital energies of LVMO are shown in parentheses and were calculated using the parameters corresponding to neutral N-oxides (see section on "spin density distribution"). Here $E_{1/2}$ was assumed to be determined by the LVMO energy of the neutral molecules, not of the anion radical. A fairly good linear relation between the two quantities was obtained: $E_{1/2} = 2.747\epsilon_{LV} - 0.766$ with the deviation $\sigma = \pm 0.109$ for $E_{1/2}$. The slope of this equation, theoretically the resonance integral β in eV,⁴⁸ is reasonable in magnitude. Next, a comparison of the results in Table I and Figure 13 qualitatively implies that the smaller the $-E_{1/2}$,

(48) J. Koutecky, *Z. Physik. Chem. (Frankfurt)*, **52**, 8 (1967), and other papers given therein.

that is, the larger the electron affinity, the larger the stability of anion radicals produced, and the esr spectra are detected at room temperature by the present technique.

But there are some exceptional cases; for example, $E_{1/2}$'s and ϵ_{LV} 's of isoquinoline N-oxide, phenanthridine N-oxide, and phthalazine mono-N-oxide are almost the same magnitude as those of quinoline N-oxide, pyrazine mono-N-oxide, and pyridazine mono-N-oxide. The esr spectra of the former compounds, however, could not be observed, and this was attributed to the relative instability of any radicals formed. In addition we may suppose that these unstable radicals are very reactive as a result of their irregular spin density distribution (Figure 7). For example, the N \rightarrow O bond in isoquinoline N-oxide and phthalazine mono-N-oxide has a very small spin density compared with that of the other compounds. In the case of phenanthridine N-oxide the positions 11-14, which are in the same ring as the N \rightarrow O group, have very small spin density.

Last, a linear relation between $E_{1/2}$ and Hammett's σ value (Figure 14) was obtained: $-E_{1/2} = 1.08\sigma - 2.19$ with a root mean square deviation equal to ± 0.06 . Here Hammett's σ values used are the same as reported for the case⁴⁹ where the polarographic reduction mecha-

(49) The σ value for NO₂ group is the σ^* (+1.270) of Jaffé. For 3,5-dimethylpyridine N-oxide, the σ value is taken as twice the σ_m of the CH₃ group: H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

nisms and $E_{1/2}$ - σ relations were studied in aqueous solution for a series of substituted pyridine N-oxides.^{7,15a} The slope (Hammett's ρ value) obtained here in DMF solvent may be compared with that obtained from the aqueous solution study. From Figure 14 we deduce that the former ρ values are much larger than the latter. The main reason for this may be due to the following facts. In the present case there is no protonation effect on the reduction mechanism of N-oxide bond, but in aqueous solvent the protonation of the oxygen atom of N \rightarrow O bond plays an important role during the reduction.^{7,15a,27} It is now well known² that the mutual interaction between substituent and N-oxide group is larger in nonaqueous solvents than that of the hydrated or protonated species in aqueous solvents; thus the ρ value of the former case appears to be larger than in the latter case.

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Mass Spectrometric Study of the High-Temperature Equilibrium $C_2F_4 \rightleftharpoons 2CF_2$ and the Heat of Formation of the CF_2 Radical

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Abstract: A mass spectrometric study of the thermal decomposition of C_2F_4 in a graphite Knudsen cell showed that C_2F_4 can be maintained in thermal equilibrium with the CF_2 radical. The equilibrium reaction $C_2F_4 \rightleftharpoons 2CF_2$ was studied over the temperature interval 1127-1244°K, and, from the measured heat of reaction, $\Delta H_f^\circ = 76.3 \pm 3$ kcal mole⁻¹, the heat of formation of CF_2 was calculated to be -39.3 ± 3 kcal mole⁻¹.

There has been a continued interest over the past 15 years in the experimental determination of the heat of formation of the CF_2 radical. However, the values obtained by appearance potential measurements¹⁻⁴ or from predissociation in the spectra⁵ are widely scattered, varying from -17 to -45 kcal mole⁻¹. A value for $\Delta H_f^\circ(CF_2)$ of -43 ± 5 kcal mole⁻¹ was calculated⁶ on the basis of the measurements of Farlow,⁷ who prepared C_2F_4 by reaction of CF_4 with graphite.

- (1) J. R. Majer and C. R. Patrick, *Nature*, **192**, 866 (1962).
- (2) J. L. Margrave, *ibid.*, **197**, 376 (1963).
- (3) W. C. Steele, *J. Phys. Chem.*, **68**, 2359 (1964).
- (4) F. Gozzo and C. R. Patrick, *Nature*, **202**, 80 (1964).
- (5) B. A. Thrush and J. J. Zwolenik, *Trans. Faraday Soc.*, **59**, 582 (1963).
- (6) "JANAF Thermochemical Tables," D. R. Stull, Ed., Dow Chemical Co., Midland, Mich., 1964, No. PB-168-370.
- (7) M. W. Farlow, U. S. Patent 2,709,192 (May 24, 1955) (assigned to Du Pont).

Pottie⁸ recently calculated $\Delta H_f^\circ(CF_2) = -36.8 \pm 3.0$ kcal mole⁻¹ from the ionization potential of CF_2 (11.86 ± 0.1 eV) and the appearance potential of CF_2^+ from C_2F_4 (15.26 ± 0.05 eV) by using the value -152 kcal mole⁻¹⁹ for the heat of formation of C_2F_4 . With the value $\Delta H_f^\circ(C_2F_4) = -155.0 \pm 2.0$ kcal mole⁻¹ recommended in the JANAF Tables,⁶ one obtains $\Delta H_f^\circ(CF_2) = -38.3 \pm 3$ kcal mole⁻¹ from Pottie's data.

The most direct estimate of the heat of formation of CF_2 was made recently by Modica and LaGraff.¹⁰ From the shock-tube studies of the C_2F_4 - CF_2 thermal equilibrium, these authors obtained $\Delta H_f^\circ(CF_2) =$

- (8) R. F. Pottie, *J. Chem. Phys.*, **42**, 2607 (1965).
- (9) C. A. Neugebauer and J. L. Margrave, *J. Phys. Chem.*, **60**, 608 (1956).
- (10) A. P. Modica and J. E. LaGraff, *J. Chem. Phys.*, **43**, 3383 (1965).