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DONOR—ACCEPTOR COMPLEXES OF HETEROAROMATIC N-OXIDES. A REVIEW

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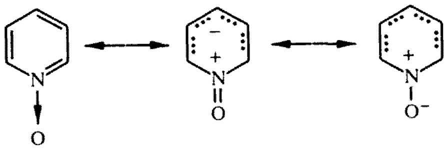
Tertiary amines and nitrogen heterocycles are known to undergo oxidation to give the corresponding N-oxides. These N-oxides, especially derivatives containing aromatic heterocycles, hold great interest. The value of these compounds as convenient intermediates in the synthesis of heteroaromatic compounds containing both electron-donor and electron-withdrawing substituents is well known. The unique nature of the properties of these compounds lies in the capacity of the N→O group to act as both a donor and acceptor of electrons depending on the structure of the N-oxide, solvent, and nature of interacting compound. This capacity arises as a consequence of the conjugation of the oxygen atom of the N-oxide group with the aromatic system, which may be described in the case of pyridine N-oxide by the following resonance structures:



The order of the N—O bond depends on the above-mentioned factors. The adjacent aromatic ring is included in conjugation in quinoline N-oxide. Such an electron density distribution in these compounds has led to their study in regard to intramolecular interactions such as tautomerism and resonance and intermolecular reactions.

The reactions of the N-oxide group include deoxidation, protonation, alkylation, and acylation [1, 2] as well as 1,3-dipolar cycloaddition proceeding with the involvement of both the N-oxide group and α-carbon atoms of the heterocycle [3]. Interest in these compounds has been found in regard to their potential biological activity such as antimicrobial and antidermatitis properties [4, 5] as well as the existence of natural N-oxides.

While the above-mentioned intramolecular processes [6] and chemical reactions involving heteroaromatic N-oxides have been described in detail, the intermolecular interactions leading to complexation have not been studied sufficiently. In the present review, an attempt has been made to systematize our knowledge in this area.

The classification of molecular complexes adopted in the literature taking account of several potential donor sites in aromatic N-oxides such as the π-system of the heterocycle, oxygen atom of the N-oxide group, or ring substituent includes three types of interaction with different acceptors (π, σ, and ν interactions) and, correspondingly, the following types of donor—acceptor complexes: 1) complexes with π-acceptors (*n*,π- and π,π-types), 2) complexes with σ-acceptors (*n*,σ- and π,σ-types), and 3) complexes with ν-acceptors (*n*,ν- and π,ν-types).

However, the formation of mixed complexes is not excluded. In such complexes, the acceptor molecule interacts simultaneously with the oxygen atom of the N-oxide group and the π-system or several acceptor molecules interact with different donor sites. This is especially likely in the case of heterocyclic compounds with fused rings, especially quinoline N-oxides. Such mixed complexes also include a third component such as acid anions or molecules of a solvent, in which complexation occurs.

The donor capacity of many compounds is characterized by their first ionization potential. However, the use of this term is not always possible for heterocyclic compounds, which have a system of π-bonds adjacent to the heteroatom. The

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TABLE 1. Electrochemical Oxidation Half-Wave Potentials of Pyridine and Quinoline N-Oxides

Substituent at $C_{(4)}$	Pyridine N-oxides, $E_{1/2}^{ox}$, V	Quinoline N-oxides, $E_{1/2}^{ox}$, V†	σ_n^+
NO_2	2,130	—	+0,790
Cl	1,795	1,630	+0,114
H	1,802	1,537	0
CH_3	1,606	—	-0,311
OCH_3	1,362	1,110	-0,778

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†Our data obtained at the Chernogolovka Branch of the Institute of Chemical Physics.

π-orbital is often the highest occupied molecular orbital of the donor though the molecule displays the properties of an n-donor and *vice versa* [7]. Thus, the electrochemical oxidation half-wave potential ($E_{1/2}^{ox}$), which is readily determined by polarography, is often taken to evaluate the donor capacity of N-oxides [8]. In all known cases, a linear relationship is found between these values and the σ^+ substituent constants in N-oxides. The presence of electron-donor substituents leads to a reduction in $E_{1/2}^{ox}$, which is less for polycyclic N-oxides than for monocyclic derivatives (Table 1).

We should note that when there are strong electron-withdrawing ring substituents, heteroaromatic N-oxides may also act as acceptors. Examples are found in the complexes of 4-nitroquinoline N-oxide with polyhydric phenols [9] or desoxynucleotides. The carcinogenic and mutagenic properties of this compound have been attributed to the formation of the latter complexes [10, 11].

In the present review, information is given on the complexes of heteroaromatic N-oxides with π-, σ-, and ν-acceptors. Interaction with Bronsted acids, which may lead to the formation of salts with complete proton transfer or of a hydrogen bond, depending on the strength of the acid, is not considered. This question has been treated in sufficient detail by Ochiai [1] and Katritzky [2].

COMPLEXES WITH π-ACCEPTORS

The interaction of heteroaromatic N-oxides with π-acceptors has been described in a few studies and an attempt to derive conclusions concerning the structure of the complexes formed is made in only some of these investigations.

New charge transfer bands (CTB) often in the visible range arise in the electronic spectra of charge transfer complexes (CTC) of N-oxides with π-acceptors. The extinction coefficients of these bands, as a rule, are slight and these bands may be observed only in rather concentrated solutions. Sometimes these bands appear as shoulders or inflections on stronger long-wavelength absorption bands of N-oxides, for example, on intramolecular charge transfer (ICT) bands.

Both n,π- and π,π-complexes may be formed upon the interaction of heteroaromatic N-oxides and π-acceptors [12, 13]. The nature of these complexes is a function not only of the properties of the π-acceptor but also of the structure of the donor itself. Pyridine N-oxides have a greater tendency to form n,π-complexes, while quinoline and isoquinoline N-oxides have a greater tendency to form π,π-complexes.

The formation of CTC of different types, different stoichiometry, and different extent of charge transfer is possible for the same compounds. The solvent plays an important role in complexation and solvent molecules are even incorporated into the complex in some cases [14].

In our view, the examination of the interaction of heteroaromatic N-oxides with tetracyanoethylene deserves special attention. This compound is one of the strongest π-acceptors capable of complexing with both π- and n-donors. Furthermore, it lacks absorption bands in the visible range, which facilitates the observation of CTB. In the reaction of methylpyridine and imidazole N-oxides with tetracyanoethylene (TCE), n,π-complexes with new CTB in the visible range are initially formed [15]. After some time, the intensity of these bands is significantly diminished and new shorter-wavelength bands arise at λ 400-420 nm. The presence of electron-donor substituents accelerates the conversion process. This reaction is presumably a consequence of the slow conversion of the initially formed n,π-complexes into stable, "ionized" complexes with greater polarization:

$$\mathrm{P} + \mathrm{TCE} \rightleftharpoons \underset{n,\,\pi\text{-complex}}{\overset{\delta+}{\mathrm{D}} \cdots \overset{\delta-}{\mathrm{TCE}}} \rightleftharpoons \underset{\text{"ionized" complex}}{\overset{\dot{+}}{\mathrm{D}} + \overset{\dot{-}}{\mathrm{TCE}}}$$

However, complete electron transfer within the CTC is unlikely in this case since the properties of the diamagnetic "ionized" complexes obtained differ very considerably both from those of the tetracyanoethylene radical—anion (found, for example, in salts of tetracyanoethylene radical-anion with alkali metal cations) and N-oxide radical-cations. The tetracyanoethylene radical-anion is paramagnetic and has characteristic UV absorption with λ_{max} 445 nm [16]. N-Oxide radical-cations are very unstable, have strong oxidizing properties, and are formed in the one-electron oxidation of the corresponding N-oxides or catalytic decomposition of hydrogen peroxide in pyridines [17, 18].

Quinoline and isoquinoline N-oxides in dioxane or THF also react with tetracyanoethylene initially to give strongly colored 1:1 CTC, which exist only in solution. A change in color then occurs, accompanied by the precipitation of solid CTC. The composition of these N-oxide—tetracyanoethylene complexes ranges from 2:1 to 3:2 and even may be nonstoichiometric. The spectroscopic data indicate that the solid CTC are π,π-complexes. We have shown that there is a direct correlation between the complexation equilibrium constants and the λ_{max} values of the CTB of pyridine and quinoline N-oxides, on the one hand, and of the σ^+ Hammett constants of the substituent in the N-oxide and their $E_{1/2}{}^{ox}$ values, on the other [13, 19].

Other π-acceptors capable of forming CTC with polycyclic N-oxides are *p*-benzoquinone and its derivatives. Only changes in the electronic spectra, namely, slight bathochromic shifts of the $\pi \rightarrow \pi^*$ absorption bands of the N-oxides and $n \rightarrow \pi^*$ absorption bands of *p*-benzoquinone, indicate the existence of adducts of quinoline N-oxides with *p*-benzoquinone. These shifts correlate with the donor capacity of the substituents in the N-oxide. Such CTC have not been isolated in the solid state.

Brightly colored, nonstoichiometric, solid complexes of chloranil and bromanil with quinoline and isoquinoline N-oxides have been obtained. The spectroscopic data unequivocally indicate the formation of π,π-complexes (Table 2).

We should note that most active π-acceptors are also reactive dipolarophiles capable of giving products of 1,3-dipolar cycloaddition with heteroaromatic N-oxides [20].

COMPLEXES WITH σ-ACCEPTORS

A study of the structure and properties of molecular complexes of pyridine, diazine, and oxazole N-oxides [21-24] has shown that halogen molecules form a coordination bond with the oxygen atom of the N→O group to give 1:1 complexes. The UV and IR spectra were taken for these CTC and their stability constants were determined [21, 24, 25]. The stability constants were found to be higher than expected from a comparison of the basicities of the N-oxides and the corresponding heterocycles. This finding is readily explained in light of the semipolar nature of the $N^{\delta+} \rightarrow O^{\delta-}$ bond and increased steric access of the donor site, namely, the oxygen atom in the N-oxides (in comparison with the nitrogen atom in the corresponding heterocycles).

Indeed, the molecular complexes in the case of aliphatic compounds with extensive charge distribution in the oxide group have even higher stability constants [21].

Kulevsky and Severson [22] compared the IR spectra of the iodine complexes of pyridine, pyrimidine, pyrazine, and pyridazine N-oxides and found that the reaction with iodine leads to a diminution in the vibrational frequency of the N→O bond by 27-44 cm^{-1} [22]. These authors, in accord with the considerations discussed above, attribute this behavior to the formation of the donor—acceptor bond of the halogen molecule at the oxygen atom of the N-oxide group, which diminishes the order of the N→O bond.

The three-dimensional structure of complexes of N-oxides with σ-acceptors has not yet been adequately studied.

The large number of studies on the interaction of halogens with aromatic hydrocarbons to give π,σ-complexes and with amines, carbonyl compounds, and cyclic ethers to give n,π-complexes, i.e., complexes, in which either a π-system or heteroatom with an unshared electron pair exist separately, permit the relatively facile identification of the types of interaction and establish the molecular arrangement in these CTC [7].

On the other hand, a study of the complexes of iodine with nitrogen heterocyclic systems led to some unexpected observations. Thus, for example, the intensity of CTB for these complexes is much higher than for the complexes with aliphatic amines although the heats of formation of these complexes are similar. Furthermore, the CTB of the complexes of iodine with pyridine have an unusual shape with a slower descent in the low-frequency region [7]. Mulliken [26] attributed this anomaly

TABLE 2. Donor—Acceptor Complexes of Heteroaromatic N-Oxides

№	N-oxide (donor) D	Acceptor A	Complex type	D:A composition	Investigation methods	Reference
1	2	3	4	5	6	7
1	Pyridines and imidazole	TCE	n,π-"ionized" complex		UV spectroscopy, dielcometric titration, dipole moment methods	[12]
2	Pyridines, quinolines, and isoquinoline	TCE	π,π		IR and UV spectroscopy	[13]
3	Pyridine	2,4,6-Trinitrobenzene		1 : 1	UV spectroscopy	[14]
4	Pyridine, imidazole, oxazole	TCE	n,π-"ionized" complex		UV spectroscopy	[15]
5	Quinolines and pyridines	2,4,6-Trinitroanisole		1 : 1	UV and PMR spectroscopy	[19]
6	Pyridine	Phenyl isocyanate	Acceptor site) N═C bond		UV and NMR spectroscopy	[63]
7	Methylpyridines	N-Phenylmaleimide			UV and NMR spectroscopy	[64]
8	4-Chloropyridine, 4-chloroquinoline	TCE		1 : 1	UV and NMR spectroscopy	[65]
9	4-Methoxypyridine, quinoline, isoquinoline	TCE, dichlorodicyanobenzoquinone, chloranil, *tetracyanoquinodimethane*		1 : 1	UV and NMR spectroscopy	[68]
10	Quinolines	Bromanil, benzoquinone	π,π	Nonstoichiometric	IR and UV spectroscopy	[69]
11	Pyridine, trimethylamine, tribenzylamine	I_2	n,σ	1 : 1	UV spectroscopy	[21]
12	Pyridine, pyrimidines, pyrazine, pyridazine	I_2	n,σ	1 : 1	IR spectroscopy	[22]
13	Pyridines, oxazole	I_2, IBr	n,σ		UV spectroscopy, dielcometric titration, dipole moment methods	[24]
14	Pyridines	I_2	n,σ			[70]

TABLE 2. (Continued)

№	N-oxide (donor) D	Acceptor A	Complex type	D:A composition	Investigation methods	Reference
1	2	3	4	5	6	7
15	Pyridines	$CuCl_2$, $CuBr_2$, CuClBr		1 : 1 dimer	NQR spectroscopy, IR spectroscopy, x-ray diffraction structural analysis	[32]
16	Pyridine	$Cu(NO_3)_2$	*n,v*	1 : 1 dimer	X-ray diffraction structural analysis	[71]
17	Pyridine	$Cu(ClO_4)_2$		2 : 1	X-ray diffraction structural analysis	[72]
18	Pyridine	$CuBr_2$		2 : 1 dimer	X-ray diffraction structural analysis	[73]
19	Pyridines	$HgCl_2$, $HgBr_2$		1 : 1 dimer	NQR spectroscopy, IR spectroscopy	[40–42]
20	Quinolines and isoquinoline	BF_3	*n,v*		UV and IR spectroscopy	[50]
21	Pyridines and quinolines	LnX_3	*n,v*	$LnD_mX_3 \cdot n\,H_2O$, X = NO_3, NCS, ClO_4, CF_3SO_3 D = N-oxide $m < 8$, $n = 0...4$	IR and UV spectroscopy	[74]
22	Pyridines	$AlCl_3$				[75]
23	Pyridine	$Sc(ClO_4)_3$				[76]
24	Pyridine	$InCl_3$			IR spectroscopy	[77]
25	Pyridine and quinoline	$U(SO_4)_2$		1 : 1	Spectrophotometry	[78]
26	Pyridines	TiF_4		2 : 1	IR spectroscopy	[54]
27	Pyridines	ZrF_4		2 : 1	IR spectroscopy	[55]
28	Heteroaromatic	SnF_4		2 : 1	^{19}F NMR spectroscopy	[58]
29	Pyridines (alkenes and styrenes)	$PtCl_2$		1 : 1 : 1	IR spectroscopy	[59–62]
30	Diethoxycarbonylpyridines	$HAuCl_4$	*n,v*	1 : 1	IR spectroscopy	[79]
31	Pyridines	$VOCl_2$, $VOBr_2$, $VO(NCS)_2$, $VOSO_4$, $VO(BF_4)_2$		2 : 1	IR spectroscopy	[80–82]
32	Pyridine	$SbCl_5$	*n,v*	1 : 1	IR spectroscopy	[83]
33	Pyridine	SO_3				[84]

to the circumstance that the pyridine molecule may function not only as an n-donor but also as a π-donor although the donor—acceptor bond in the iodine complex is achieved through the nitrogen bond. Two CTB are found in the spectrum of this complex. One CTB is related to transition of an n-electron to the antibonding orbital of iodine while the other is related to the transition of a π-electron. Similar behavior is noted for the complexes of iodine with other N-heterocycles [27, 28]. We should note that, in an examination of the interaction of iodine with N,N-dimethylaniline, Tsubomura [29] concluded that, despite the coordination site at the nitrogen atom, the unshared electron pair in the complex remains partially in the molecular π-orbital and the question whether this is a π,σ- or n,σ-complex remains open.

It is logical to assume that donor—acceptor interactions with mixed halogen atoms, leading to the formation of a nonplanar complex whose structure would be dependent on the nature of the acceptor, may arise in heterocyclic N-oxides.

Indeed, Troilina et al. [24] used the dipole moment method to show a nonplanar structure for the complexes of pyridine and oxazole N-oxides with I_2 and IBr. These authors propose formation of a donor—acceptor bond between the free atom in the halogen molecule and π-system of the aromatic ring in addition to the usual n,σ-interaction.

Kubota [21] compared the structures of the iodine complexes of pyridine, trimethylamine, and tribenzylamine N-oxides and came to the same conclusion for the iodine complex of pyridine N-oxide.

COMPLEXES WITH μ-ACCEPTORS

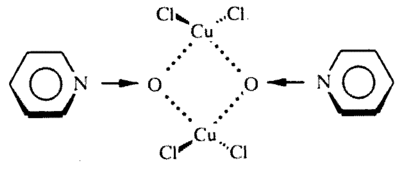
Most complexes of N-oxides with ν-acceptors have a very complex structure, especially those compounds, in which transition elements having vacant *d* or *f* orbitals act as the acceptors. Such complexes containing sometimes up to eight N-oxide molecules such as $Ln(4\text{-}CH_3C_5H_4NO)_8(ClO_4)_3$, for example, and a molecule of a third component, which are capable of forming dimers or even much more complex aggregates, were reviewed in detail by Garvey et al. [30].

Let us limit ourselves to an examination of the simplest such complexes usually containing not more than three or four subunits, for which information is found scattered in the literature.

Many coordination complexes of N-oxides with transition metal salts containing an anion of perchloric acid, which has very low basicity, have now been studied. In most cases, these complexes have a much more complex composition (in particular, they have a large number of N-oxide molecules) than the complexes containing salts with more basic Cl^- and Br^- anions. Such salts, which are Lewis acids, may form complexes with both π- and n-donor sites. The strength of the donor—acceptor bonds varies over a broad range from weak π-bond to a usual covalent bond. However, despite the potential variety of the complexes of N-oxides with metal acceptors, even the CTC with metal halides have not been studied extensively.

We have collated the information in the literature and related these data to the periodic group of the acceptor atom. Most of the complexes below belong to the n,ν type.

Watson [31] and Wootton [32] have produced the most interesting investigations of the interaction of heteroaromatic N-oxides with salts of Group I elements. These authors studied a large number of complexes with $CuCl_2$ and $CuBr_2$ and their structures. X-ray diffraction structural analysis and nuclear quadrupole resonance spectroscopy was used to show that these complexes are dimers. In the case of pyridine N-oxide, dimers $[(C_5H_5NO)CuCl_2]_2$ (I) may feature "chlorate" bridges.



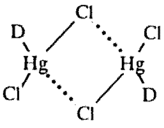
I

On the other hand, such bridges are unlikely for the dimeric complexes of 2,6-lutidine N-oxide $[(C_7H_9NO)CuCl_2]_2$ due to steric hindrance produced by the methyl groups.

Similar complexes with quinoline N-oxides have also been studied. Depending on the basicity of the ligand, the dimers or even polymers formed may be linked by either "chlorate" or "oxygen" bridges [33].

The data on the complexes of N-oxides with copper salts of other acids such as perchloric and nitric acids are given in Table 2. More complex adducts with copper ions have also been reported [34].

Several studies have been devoted to 1:1 complexes of HgX_2 (X is a halide ion) with pyridine N-oxide and its derivatives. The IR spectra of solid complexes were used to show the existence of dimers with bridging and terminal halogen atoms II [35, 36] or bridging donors III [37] such as the complexes of N-oxides with $CuCl_2$:



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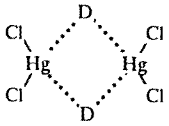


III

We should stress that the question of the coordination sites of the N-oxide molecules (*D*) to the mercury atoms was not considered. However, by analogy to the other complexes of N-oxides with transition metal salts such as $CuCl_2$ [31, 32], we may assume that the oxygen atom of the N-oxide group will be the coordination site.

Molecular mass determination showed that dimeric structures also exist in solution [35]. Ahuja [36] concluded that the coordination of the mercury atom must be tetrahedral in all complexes with pyridine N-oxides. However, we should note that x—ray diffraction structural analysis was used to show that the Cl—Hg—Cl bond angle is 173.5° in the adduct of 3,5-dibromopyridine N-oxide with $HgCl_2$ [38]. On the other hand, the Hg—Cl bond lengths in the complexes of pyridine N-oxides and γ-picoline is only 0.004-0.008 nm greater than in $HgCl_2$ itself (0.225 nm) [39]. An NQR study of the complexes of pyridine and 4-methylpyridine N-oxides with $HgCl_2$, $HgBr_2$, and HgI_2 showed that the signals for the chlorine atoms in the complexes with $HgCl_2$ are shifted toward lower frequencies by 1-3 MHz in comparison with pure $HgCl_2$, which appears to indicate a more or less linear structure of the $HgCl_2$ molecule in the complex [40]. In the case of tetrahedral configuration of the mercury complexes, the Hg—Cl bond lengths are equal to 0.25-0.25 nm and the chlorine resonance in this case should be 15 MHz less. These data and the finding that tetrahedral structure usually arises in the case of interaction with "soft" donor atoms such as sulfur, selenium, phosphorus, and arsenic [40] indicate that structure II is most probable for the 1:1 N-oxide—HgX_2 complexes.

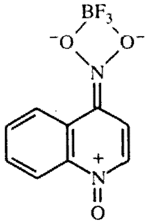
On the other hand, Scaife [41] noted that no signal was found, which could be attributed to chloride atom bridges in these complexes [39]. The existence of structure III similar to the dimers with $CuCl_2$ is again discussed in later NQR studies [42, 43]. The resolution of this question apparently requires further intensive study.

$ZnCl_2$ also forms $Zn(N\text{-oxide})_2Cl_2$ complexes [44, 45]. However, more complex aggregates such as $[Hg(C_5H_5NO)_6](ClO_4)_2$ [46] and $[Zn(C_5H_5NO)_6](ClO_4)_2$ [30] are formed with the anion of more strongly acidic perchloric acid. The complexes of pyridine N-oxides with halides [47] and cadmium thiocyanate [48] were also studied.

A characteristic feature of complexes with elements of the major subgroup of Group III is the formation of a strong covalent bond using the oxygen atom of the N-oxide component. This behavior, which is in contrast to the other adducts examined, is attributed primarily to the strong Lewis acid properties of these acceptors.

Kulevsky and Sveum [49] studied the 1:1 complexes of pyridine N-oxide with BF_3 and BCl_3 and used IR spectroscopy to show that the formation of the donor—acceptor bond between oxygen and boron greatly reduces the double bond nature of the N—O bond. For example, this band is found at 1127 cm^{-1} in the case of the BF_3 complex of 4-methylpyridine N-oxide, while it is found at 1213 cm^{-1} in 4-methylpyridine N-oxide itself.

UV and IR spectroscopy was used to show that a strong donor—acceptor bond is formed in the BF_3 complexes of isoquinoline and quinoline N-oxides with substituents at $C_{(2)}$ and $C_{(4)}$ between the oxygen atom of the N-oxide group, which is a "hard" donor site, and the boron atom. Thus, these are n,ν-complexes [50]. An exception is found for 4-nitroquinoline N-oxide with BF_3 (IV), in which the nitro group oxygen atoms are the donor sites:



IV

This finding, in our view, is not unexpected since the strong acceptor properties of the nitro group should lead to concentration of significant charge on this group and favor interaction with strong Lewis acids such as BF_3 [50]. Such complexes are formed between nitrobenzene and $AlCl_3$ [51], nitromethane and $AlCl_3$ [52], and N_2O_4 and BF_3 [53].

The remaining sparse data on the complexes of N-oxides with salts of Group III elements are given in Table 2.

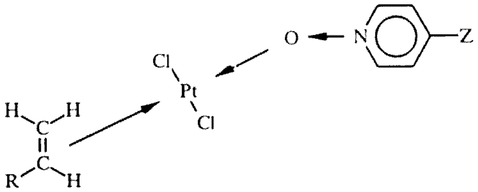
Dickson et al. [54, 55] have described complexes of pyridine N-oxides with TiF_4 and ZrF_4, in which the ratio of the ligand to the metal fluoride is 2:1. The IR spectra of these complexes showed that the vibrational frequencies of the N—O and O—M bonds correlate with the σ^+ constants of the substituents at $C_{(4)}$ of the pyridine ring. An increase in the donor properties of the group leads to a shift in the N→O band towards lower frequencies, while such an increase shifts the O—M band toward higher frequencies. This corresponds to a synchronous change in the strengths of these bonds. The positions of the N—O band in the complexes with TiF_4 and ZrF_4 are virtually the same, while the frequency for the O—Ti bonds is 30-40 cm^{-1} higher than for the O—Zr bonds. This behavior may be completely attributed to the difference in the atomic masses of these metals. The finding that the N—O band frequency for the complexes is found shifted to higher frequency by only 15-25 cm^{-1} in comparison with N-oxides (the shift is 45 cm^{-1} for the nitro derivative), in our view, indicates that there is only slight change in the double bond nature and that the O—M bond is weaker than the O—B bond in the BF_3 complexes.

We should note that $SnBr_4$ [44] as well as SiF_4, $SiCl_4$, and $SiBr_4$ [56] also form complexes with heteroaromatic N-oxides with 2:1 ligand—halogen ratio. However, there is no correlation between the O—M band frequencies and σ constants for the TiF_4 and SnF_4 complexes with quinoline N-oxides substituted at $C_{(4)}$ [57]. The dependence of the ^{19}F NMR chemical shifts (in the *cis* and *trans* isomers) on the nature of the ligands was studied for these adducts [57, 58].

The literature data on the complexes of N-oxides with Group V-VII elements are rather sparse and have been discussed in a review by Garvey [30] (Table 2). Adducts with oxovanadium ions have been treated in greater detail. These adducts are divided into those with four or five N-oxide molecules and those with only two N-oxide molecules. In each case, complexes were obtained both containing water such as $VO[N\text{-oxide}]_nX_2 \cdot H_2O$ and lacking water depending on the method of isolation. A linear correlation is observed between the shift in the V—O band frequency in the IR spectra upon complexation with pyridine N-oxides substituted at $C_{(4)}$ and the σ constants.

Complexes with Group VIII elements (Fe, Co, Ni, Pt) have been described in detail by Garvey et al. [30]. On the other hand, we found it useful to shed further light on some CTC of N-oxides with $PtCl_2$, which differ strongly from those described above.

Dozens of complexes containing pyridine N-oxides, $PtCl_2$, and alkenes with general structure V have now been studied [59-62]:



V

Upon complexation, the N→O band in the IR spectra is shifted toward lower frequencies by 14-20 cm^{-1} for N-oxides with donor substituents Z and by 7-9 cm^{-1} for N-oxides with acceptor substituents Z.

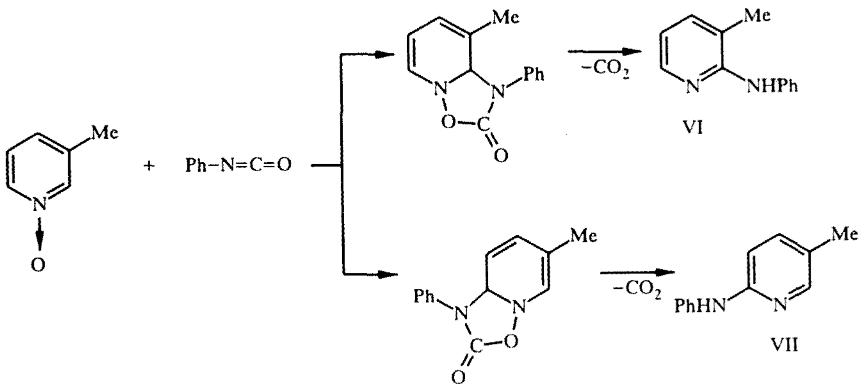
The effect of group Z on the position of the C=C band in the IR spectra holds interest. Complexation of N-oxides with $PtCl_2$ and alkenes (or styrene derivative) causes a shift to lower frequency by 78-133 cm^{-1}, whose magnitude depends linearly on the pK_a value of the ligand. An increase in the donor properties of the group at $C_{(4)}$ leads to a greater shift and, according to Shupack and Orchin [61], to an increase in the strength of the bond between the olefin and platinum along with weakening of the C═C bond (the shift of the double bond frequency toward lower frequencies in the CTC of alkenes with platinum salts by about 140 cm^{-1} is attributed to a weakening of this bond).

ROLE OF CHARGE TRANSFER COMPLEXES IN SOME REACTIONS INVOLVING HETEROAROMATIC N-OXIDES

The formation of CTC is accompanied by redistribution of electron density in the donor and acceptor molecules. Three types of interaction are possible: 1) formation of a stable complex (see above), 2) more extensive intramolecular transformations leading to new compounds, and 3) intermolecular reactions of the CTC with other components.

1,3-Dipolar cycloaddition to heteroaromatic N-oxides and O-alkylation of the latter may proceed within CTC. For example, the reaction of pyridine and methylpyridine N-oxides with phenyl isocyanate and N-phenylmaleimide begins with formation of a CTC existing only in solution and detected by UV and NMR spectroscopy [63, 64]. The formation of CTC not only facilitates further reaction with the dipolarophile but also determines the stereochemistry of the cycloaddition products formed.

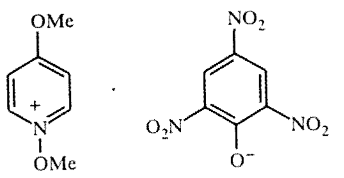
Isomers VI and VII were isolated in the reaction of 3-methylpyridine with phenyl isocyanate:

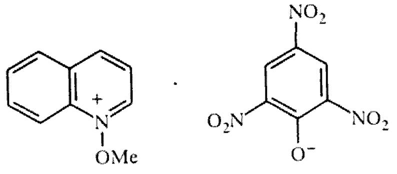


Although the formation of VII is sterically preferred, the major reaction product is VI. The authors attribute this finding to secondary orbital effects between the protons of the N-oxide methyl group and aromatic ring of phenyl isocyanate.

An analogous process is observed in the reaction of 3-methylpyridine N-oxide with N-phenylmaleimide [64].

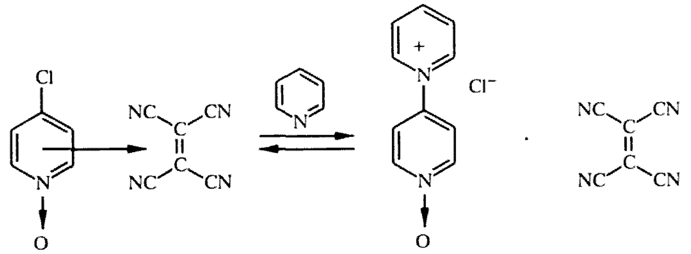
The reaction of 4-methoxypyridine and quinoline N-oxides with 2,4,6-trinitroanisole in dioxane has recently been shown to lead initially to give "weak" CTC. CTB arise in the visible region. A slight downfield shift is observed for the PMR signals of the donor protons, while a slight upfield shift is observed for the acceptor protons as a consequence of intermolecular interaction. The further, more extensive reaction involves migration of a methyl group from 2,4,6-trinitroanisole to the oxygen atom of the N-oxides and precipitation of 1,4-dimethoxypyridinium and 1-methoxyquinolinium picrates (VIII, IX) [19].


VIII


IX

The spectral data of these picrates differ significantly both from the spectra of the starting compounds and the "weak" CTC. Thus, O-alkylation of the N-oxides by 2,4,6-trinitroanisole within the CTC is observed in this case.

Reaction with nucleophiles is an intermolecular reaction of the CTC of heteroaromatic N-oxides with other components. This reaction is facilitated by the pronounced electron deficiency of the N-oxide molecules within the complex. Thus, for example, 4-chloropyridine N-oxide in its complex with tetracyanoethylene readily undergoes nucleophilic substitution with pyridine [65]:



When tetracyanoethylene is lacking, this reaction does not proceed even under vigorous conditions. The reactions of the CTC of 4-chloroquinoline N-oxide and bromanil with benzoic acid hydrazides or of the CTC of 4-nitroquinoline N-oxide and tetracyanoethylene with the chloride ion may serve as an example of such reactions [66].

Therefore, the above data indicate that heteroaromatic N-oxides hold interest for use in the formation of molecular complexes with various types of acceptors. These complexes hold importance in light of their use as intermediates in the synthesis of several heterocyclic compounds. Furthermore, they may have independent practical importance. Thus, for example, the CTC of quinoline N-oxides with tetracyanoethylene are dielectrics with properties similar to semiconductors [67].

Nevertheless, the properties and structures of most of the reported CTC of heteroaromatic N-oxides have not been adequately studied and require more extensive investigation.

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