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COMPLEXATION OF THE PYRIDINE BASES IN THE PRODUCTS FROM THE COKING OF COAL WITH ORGANIC SOLVENTS (REVIEW)

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Published data on the complexation of pyridine bases with organic substances of various chemical types are reviewed. Examples of the use of these data for the isolation of individual heterocycles are discussed.

Heterocyclic nitrogen compounds in the products from coke-chemical production are present in the form of the light pyridine bases (in coke gas, including pyridine and its methyl- and dimethyl-substituted derivatives, and also a certain amount of quinoline) and heavy bases (quinoline, isoquinoline, methylquinolines, acridine, and a certain amount of pyridines) contained in coal tar.

The light pyridine bases are extracted from the gas with sulfuric acid followed by treatment with ammonia to decompose the sulfates. The heavy bases, present in the tar, subsequently get into the various fractions of the tar during rectification. According to data in [1], the fractions containing the light pyridine bases contain 69% of pyridine, ≥7.5% of methylpyridines (picolines) and dimethylpyridines (lutidines), ≥0.6% of trimethylpyridines (collidines), and ~12% of quinoline. The coal tar contains [1] 0.2% each of quinoline, isoquinoline, and 2-methylquinoline (quinaldine) and also 0.6% of acridine; the content of pyridine and its methyl derivatives is 0.01-0.02% of each.

The bulk of the quinoline bases is concentrated in the naphthalene and absorber fractions of the tar, from which 20-25% is extracted by sulfuric acid and subsequent neutralization of the sulfate solution by a solution of alkali and by ammonia solution (or gaseous ammonia). According to data in [2], in the bases of the naphthalene fraction 61.5% constitutes quinoline, ~13% isoquinoline, and 7% quinaldine. In the bases of the absorber fraction the quinoline amounts to 28.4%, the isoquinoline to 13.5%, and the quinaldine to 9.54%. Most of the acridine is concentrated in the anthracene fraction (up to 7-8% of the fraction).

In industry [1, 3] during the treatment of light pyridine bases (after removal of the phenols with alkali and dehydration) fractions consisting of pure (up to 98%) pyridine (114-116°C) and pyridine-solvent (120-137°C) are isolated by rectification methods. The pyridine-solvent consists of a mixture of pyridine and methylpyridines. The fraction containing most of the α-picoline (≥74% of the potential amount)is collected in the range of 128-131°C, while the β-picoline fraction is collected in the range of 138-146°C [2]. (The latter contains 10% of α-picoline, 32% of β-picoline, 36% of γ-picoline, and ≥21% of 2,6-lutidine.) The fraction containing the lutidine bases is collected in the range of 158-167°C, and the collidine fraction is collected in the range of 168-171°C. The heavy pyridine bases (quinoline and its derivatives) are extracted from the tar fractions by washing with dilute sulfuric acid (15-17%) followed by decomposition of the sulfates with ammonia solution.

The individual light and heavy nitrogen bases are mainly isolated by chemical methods sometimes in conjunction with rectification [2-4]. The most laborious is the isolation of 2,6-lutidine from the mixture of β- and γ-picolines and subsequent separation of the latter as the highly pure isomers. The same applies to the separation of quinoline and isoquinoline [2-4].

Analysis of the ionization potentials (*I*) and pK_a values of the pyridine bases (Table 1), by means of which it is possible to assess the ability of these compounds to form complexes with one or the other organic solvent, shows that these constants differ quite substantially for isomeric heterocycles close in boiling and melting points. This fact makes it possible to suggest the possibility of isolating them from solutions in organic solvents as a result of the formation of molecular complexes with different stabilities (with a π—π^* bond or with a hydrogen bond) in these systems.

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TABLE 1. Physicochemical Properties of Some Nitrogen Bases Present in the Products from the Coking of Coal

Nitrogen base	bp, °C, at 760 mm Hg [5]	mp, °C [5]	Ionization potential, eV [6]	Basicity pK_a [8] (at 25°C)
Pyridine	115,4	-41,7	9,30	5,23†
2-Methylpyridine, α-picoline, (2-picoline)	129,4	-66,8	9,02	5,97
3-Methylpyridine, β-picoline (3-picoline)	144,0	-18,2	9,04	5,68
4-Methylpyridine, γ-picoline (4-picoline)	145,3	3,6	9,04	6,02
2,4-Dimethylpyridine (2,4-lutidine)	158,3	-64,0	8,85	6,63
2,6-Dimethylpyridine (2,6-lutidine)	144,0	-6,10	8,85	6,75
3,5-Dimethylpyridine (3,5-lutidine)	171,9	-6,54	8,85	6,15
2,4,6-Trimethylpyridine (2,4,6-collidine)	171...172	-43,0	8,94*	7,59†
Quinoline	237,6	-15...-16	8,62*	4,94†
Isoquinoline	243,2	26...28	8,54*	5,40†
2-Methylquinoline (quinaldine)	247,7	-1,0...-2,0	—	5,41
Acridine	346,0	107...110	7,78	5,60†

*According to published data [7].
†At 20°C.

It should be noted that in electron donors the stability of their complexes with an acceptor as a rule increases with decrease in the I value. An analogous effect is observed in cases where the electron affinity, usually characterized by the pK_a value, in the acceptors increases.

The energy of specific intermolecular interaction (ΔG_c) of such heterocycles with the organic solvent is determined by the following equation:

$$\Delta G_c = -RT \ln K_c = \Delta H_c - T \cdot \Delta S_c,$$

where K_c is the stability constant of the molecular complexes (liter/mole), ΔH_c is the enthalpy of complexation (kJ/mole), and ΔS_c is the entropy of complexation (J/mole·K).

The above-mentioned thermodynamic parameters are determined by familiar spectral methods or by GLC or calorimetry. This provides information not only on the energy values of specific intermolecular interaction but also on the mechanism and nature of this interaction.

Systematic investigations into the complexation of pyridines with organic compounds of various chemical types were conducted in the middle of the sixties. Thus, in [9] the problem of the H complexes formed by proton donors and acceptors containing π electrons and a heteroatom was discussed. The authors of this paper point out that heterocyclic proton acceptors have two independent proton-accepting centers, i.e., the heteroatom (Y) and the π-electron system are capable of forming H complexes of the X—H···Y (I) and X—H···π (II) types. Here the relative stability of the complexes (or their stability) is determined by the nature of the heterocyclic proton acceptor. In particular, for pyridine and its homologs the predominant form of complexation is form I.

Earlier researches on the complexation of pyridines were carried with phenols, which are the strongest proton donors. The intermolecular H bond of β-naphthol with pyridines (pK_a = 9.63†) in cyclohexane solution was studied in [10] by UV spectroscopy (Table 2). It was noticed that the formation energy of the hydrogen bond correlated with the shift of the π—π^*

†Here and subsequently the pK_a values are given in [8].

TABLE 2. Thermodynamic Parameters of the Complexes of β-Naphthol with Pyridines at 14-40°C [10]

Pyridine	$-\Delta H_c$, kJ/mole	$-\Delta G_c$, kJ/mole
Pyridine	10,42	24,28
2-Picoline	11,09	28,89
3-Picoline	10,89	26,59
4-Picoline	11,22	29,90

TABLE 3. Stability Constants of the Complexes of Certain Phenols with Pyridines at 25°C [11]

Phenol	K_s, liter/mole		
	pyrdine	4-picoline	3,4-lutidine
Phenol	53,0	77,0	82,0
3,4-Dimethylphenol	28,4	53,0	58,0
3,5-$(CF_3)_2$-Phenol	612,0	1178,0	1454,0
3-CF_3-4-Nitrophenol	1125,0	2352,0	2274,0
2,6-Dichloro-4-nitrophenol*	163,0	315,0	—

*According to [12].

band. Decrease in the ionization potential of the pyridine corresponds to an increase in the ΔH_c value. It should be noted for comparison that the ability of the same β-naphthol to form complexes with aromatic hydrocarbons is considerably weaker: with benzene $-\Delta H_c$ = 4.56 kJ/mole, $-\Delta G_c$ = 6.57 kJ/mole; with toluene, 3.56 and 8.20 kJ/mole.

The complexation constants of the phenols with pyridines were determined from the IR spectra of dilute solutions of the compounds in carbon tetrachloride [11, 12]. The most stable complexes are formed by phenols containing NO_2 and CF_3 groups as substituents. Some of these data are given in Table 3.

In [13] the H-complexation of 2,4,6-trimethylphenol and diphenylamine (pK_a = 0.9) with certain pyridines was studied for comparison. In particular, the dipole moments (μ_c), which differed significantly from the dipole moments of pyridines (μ_i), were determined. Thus, for 2,4,6-trimethylphenol with pyridine μ_c = 3.48 D and with 4-picoline μ_c = 3.82 D; for diphenylamine with pyridine μ_c = 4.01 D and with 4-picoline μ_c = 4.33 D. At the same time, for pure pyridine and 4-picoline μ_i = 2.32 and 2.66 D [14] respectively.

In addition to the dipole moments, the stability constants of the obtained complexes in these systems were determined [15]. They amounted to 4.61-6.44 liter/mole for 2,4,6-trimethylphenol and 1.35-1.76 liter/mole for diphenylamine. We note that in the investigated hydrogen complexes with diphenylamine the increase in K_s corresponds linearly to the decrease in the pK_a values of the pyridine bases. Such a correlation was not obtained for the complexes with 2,4,6-trimethylphenol. In the more recent paper [16], data in the range of $-\Delta H_c$ = 27.2-31.0 kJ/mole were obtained for the enthalpy of complexation of phenol with pyridines. It was established that there is no correlation between the ΔH_c and pK_a values for the majority of pyridine bases. A linear relation between ΔH_c and the proton affinity was established for all the investigated bases in the gas phase.

During a study of the complexation of pyridines with phenols with the general formula RC_6H_4OH (R = H, 3-Me, 4-Me, 3-NO_2, 4-NO_2) by IR spectroscopy in carbon tetrachloride solution at various temperatures, it was established [17] that acid—base interaction with the formation of O···H—N ion pairs is observed in these systems together with the formation of a hydrogen bond. It was noticed that ion pairs can appear on the condition that the enthalpy of the H bond between the neutral molecules is substantially lower than 46 kJ/mole. Thus, for phenol and nitrophenols (pK_a 7.15, 8.40) during the formation of complexes with pyridine, quinoline, and acridine with a OH···N bond the $-\Delta H_c$ value varies in the range of 18.4-33.1 kJ/mole. The complexation of phenol and 2,4,6-tribromophenol with quinoline was studied by IR spectroscopy [18].

In the eighties and nineties the discussion of the complexation of phenol with pyridines continued on the basis of more recent experimental data. Thus, in [19] the complexation of phenol with pyridines was studied in carbon tetrachloride: K_s = 51.9 liter/mole (at 25°C) and 31.9 liter/mole (at 40°C). The other thermodynamic parameters were: $-\Delta H_c$ = 25.1 kJ/mole, $-\Delta G_c$ = 9.6 kJ/mole, $-\Delta S_c$ = 51.1 J/mole·K. A comparative investigation of the intermolecular interaction of pyridine with

TABLE 4. Constants for the Complexation of Phenol with Pyridines at 20°C [21]

Pyridine base	K_s, liter/mole	Molecular refraction R_D	Pyridine base	K_s, liter/mole	Molecular refraction R_D
Pyridine	59,8	12,34	2,4,6-Collidine	137,1	43,73
2-Picoline	74,7	33,08	Quinoline	57,4	43,64
3-Picoline	73,1	33,04	Isoquinoline	61,4	43,13
4-Picoline	80,0	38,67	Acridine	67,2	76,16
2,6-Lutidine	95,2	38,32			

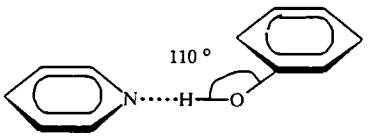

Fig. 1

phenol and ethyl alcohol (with an N···HO bond) in benzene at 30°C showed [20] that phenol (pH_a = 9.98) formed complexes with pyridine more readily than ethanol (pK_a = 15.9).

In one paper of recent years on the complexation of phenol with pyridines [21] the dipole moments of the complexes were measured (in carbon tetrachloride). The K_s values were calculated (Table 4), and it was shown that there was no linear correlation between the K_s and pK_a values of the pyridine bases. The reaction of the pyridines and of 2-methylpyridine, in particular, with phenol takes place according to the scheme presented in Fig. 1.

Several papers in these same years were devoted to the complexation of pyridines with pentachloro- and pentabromophenols. In one of them [22] the formation of H complexes of pentabromophenol with pyridines in various chlorine-containing solvents was investigated. It was established that higher K_s values were obtained in carbon tetrachloride and in chlorobenzene (Table 5), i.e., these solvents are more inert toward pyridines and phenols. In another paper [23] the complexation of pentachlorophenol with pyridines in carbon tetrachloride was studied. The IR and UV spectra were recorded, and the dipole moments of the complexes were determined (Table 6). A satisfactory correlation was established between the K_s and pK_a values of the investigated pyridine bases.

The hydrogen bond in the pentachlorophenol—pyridine base system (with high proton polarizability) was studied [24] on the basis of data on the conductivity of 0.1 N solutions of the compounds also in carbon tetrachloride. It was noticed that the K_s values increased in proportion to the pK_a values of the pyridine bases, due to the increase of the basicity in the series of pyridines. More recently, the solid complex of 4-picoline with deuterated pentachlorophenol was investigated [25]. The same solid complexes of pentachlorophenol with pyridine, quinoline and isoquinoline, and methyl- and dimethylpyridines, studied by high-resolution nuclear quadrupole resonance at 77 K, were discussed in [26]. Of particular interest were the results [27] from an investigation into the structure of the solid complex of 3-picoline with 2,6-dichloro-4-nitrophenol. This complex has one of the shortest hydrogen bonds (N···HO). According to data from x-ray, UV, and IR spectra, the distance from the N to the O is 2,544 Å.

In one of the earlier papers [28] complexes with a 1:1 molar composition were discovered by means of the PMR spectra in systems with quinoline and *o*-phenylphenol (pK_a = 9.97) in carbon disulfide solution. At 23-39°C the K_s constants amount to 3.7-4.4 liter/mole with $-\Delta H_c$ = 9.2 kJ/mole.

By measuring the dielectric constants of mixtures of quinoline with phenol in benzene [29] and determining the dipole moments of complexes with a OH···N bond, it was possible to establish that these complexes have the *trans* structure. In [30] the complexation of acridine with pentachlorophenol was proved by crystallography.

In addition to the above-mentioned paper [20], there are publications in which the complexation of pyridines with phenol and aliphatic alcohols is compared. The formation of 1:1 complexes of pyridines with phenol, benzyl alcohol, and isopropyl alcohol was studied by means of the IR spectra [31]. The spectra were recorded in toluene solution at −26-50°C. The data from the spectra were used to calculate the K_s values of the 1:1 complexes. In another paper [32] the ^{13}C NMR spectra of the complexes of phenol, methanol, and benzyl alcohol with pyridine and picolines were studied.

TABLE 5. Stability Constants of the Complexes of Pentabromophenol with Pyridines (1:1) at 25°C [22]

Pyridine base	K_s, liter/mole			
	CCl_4	$(CH_2)_2Cl_2$	C_6H_5Cl	$CHCl_3$
Pyridine	37,2	27,5	—	6,9
4-Picoline	69,6	24,7	—	12,2
2,4-Lutidine	48,8	42,3	62,2	11,8
2,4,6-Collidine	61,7	40,0	88,3	30,2
Quinoline	37,2	10,3	—	6,9

TABLE 6. Stability Constants of the Complexes of Pentachlorophenol with Pyridines (1:1) at 25°C [23]

Pyridine base	K_s, liter/mole	Pyridine base	K_s, liter/mole
Pyridine	71,0	2,4,6-Collidine	92,0
3-Picoline	85,3	Quinoline	52,5
4-Picoline	68,5	Isoquinoline	55,5

The excess enthalpies of mixing of binary systems of methanol (pK_a = 15.5) with pyridine, 2-picoline, and 2,6-lutidine at 25, 35, and 45°C were calculated from experimental data [33]. It was shown that complexes with a methanol—pyridine molar ratio of 1:2 are formed over a wide range of compositions. In [34] the IR spectra of the H complexes of *n*-propanol, *n*-butanol, *n*-amyl alcohol, and *tert*-butyl alcohol with pyridine and picolines were studied. The $-\Delta H_c$ values were calculated from the data on the integral intensity of the bands (ν_{OH}) (Table 7). As seen from these data, the complexes of 2-picoline with *n*-propanol have the highest enthalpy (17.5 kJ/mole). Investigation of the effect of various solvents on the formation of 1:1-molar complexes of *n*-propanol and 2-picoline by means of the IR spectra showed [35] that polar and aromatic solvents weaken the complexation.

The hydrogen bond of 2,6-lutidine with *tert*-butyl and isobutyl alcohol in binary systems and in hexane at 30-70°C was studied by PMR [36]. The strongest interaction with the formation of a hydrogen bond was observed in the 2,6-lutidine—isobutyl alcohol system ($-\Delta H_c$ = 19.26 kJ/mole). In the system with *tert*-butyl alcohol this type of interaction is weaker on account of the substantial self-association of the alcohol molecules: $-\Delta H_c$ = 14.23 kJ/mole. The absence of π complexes in these systems was also noted.

The thermodynamic characteristics of binary mixtures of pyridine bases with aliphatic alcohols were examined in [37]. The excess enthalpy of mixing for 4-picoline with 2-propanol, 2-butanol, isobutyl alcohol, and *tert*-butyl alcohol over a wide range of concentrations was determined by means of the data from isothermal calorimetry (at 20 and 30°C). The significant departure of these solutions from ideality was stressed, and it was shown that 2-butanol has the strongest interaction.

The excess enthalpy of mixing of binary mixtures of pyridine, 2-picoline, and 2,6-lutidine with methanol was determined in [38]. From the dependence of the excess enthalpy of mixing on the concentration over a wide range of concentration it follows that complexes with a methanol—pyridine molar ratio of 2:1 are formed. The enthalpy of H-complexation of methanol with pyridines was calculated from the data on the excess enthalpy of mixing on the calculation that only 1:1 complexes were formed (Table 8).

The excess enthalpy of mixing was also determined by calorimetry (at 30°C) in systems with pyridine bases (3- and 4-picolines) and 1-hexanol [40].

The reaction of pure lower aliphatic alcohols (methanol, ethanol, butanol) with pyridines was examined in [41]. It was shown that complexation processes with alcohol—alcohol and pyridine—alcohol mixtures occur in these systems. Under normal conditions more than 95% of the alcohol molecules form self-associates with energies of 25 kJ/mole. In order to determine the enthalpy of the hydrogen bond in pyridine—alcohol systems, therefore, these systems are studied in the form of dilute solutions in carbon tetrachloride.

In [42] the formation of a hydrogen bond between quinoline and the OH group of alcohols (isopropyl, decyl, isoamyl) in hexane solution at 20°C is discussed on the basis of the data from the electronic spectra. The largest K_s value is observed for decyl alcohol (5.2-6.0 liter/mole), and the value for isoamyl alcohol is substantially smaller (1.7-1.9 liter/mole). In another paper [43] the energy of the hydrogen bond between quinoline and methanol was determined ($-\Delta H_c$ = 20.9 kJ/mole).

TABLE 7. Enthalpy of Complexation of Aliphatic Alcohols with Pyridine Bases [34]

Pyridine base	$-\Delta H_c$, kJ/mole			
	n-propanol	*n*-butanol	*n*-amyl alcohol	*tert*-butanol
Pyridine	15,3	14,0	16,7	6,9
2-Picoline	17,5	16,8	13,6	9,4
3-Picoline	17,0	16,7	16,3	13,1
4-Picoline	16,7	15,6	15,3	8,4

TABLE 8. Enthalpy of the H Bond in Systems with Methanol and Pyridines (1:1) [38]

Pyridine base	$-\Delta H_c$, kJ/mole	Remark
Pyridine	30,1	According to the IR spectra, the enthalpies of the H bond in these systems $-\Delta H_c$ are 13-18 kJ/mole [39]
2-Picoline	31,0	
2,6-Lutidine	32,0	

TABLE 9. Enthalpy of Complexation of Quinoline and Isoquinoline with Aliphatic Alcohols (according to GLC) [45]

Alcohol	Quinoline		Isoquinoline	
	K_s, liter/mole	$-\Delta H_c$, kJ/mole	K_s, liter/mole	$-\Delta H_c$, kJ/mole
Methanol	7,8	18,4	9,2	20,0
Ethanol	6,5	17,1	7,6	16,3
n-Propyl alcohol	4,2	12,5	6,5	15,8
tert-Butyl alcohol*	9,0	—	21,4	—

*Determined by the dielectric method at 25°C.

Proton transfer for the complexes of quinoline and isoquinoline with alcohol at low temperatures (77 K) was investigated by the luminescence method [44].

A comparison of the complexation of quinoline and isoquinoline with lower aliphatic alcohols (solutions in squalane) on the basis of thermodynamic parameters, calculated from GLC data, was made in [45] (Table 9).

The solvation of isoquinoline molecules with methanol was also studied in [46], and the systems containing isoquinoline and acetone were investigated by IR spectroscopy and by means of the Raman spectra (for comparison). During study of the dynamics of complexation and determination of the time for which the H complexes exist in solution (in nanoseconds), it was established that methanol reacts preferentially to acetone with isoquinoline. The time for which the complexes of isoquinoline with methanol exist (4.6 nsec) is almost twice as long as for the complexes with acetone (2.5 nsec).

The complexation of quinoline, isoquinoline, and 5,6-benzoquinoline with 1,1,1,3,3,3-hexafluoroisopropanol (as proton donor) in heptane solution was investigated by UV spectroscopy [47]. It was established that isoquinoline and 5,6-benzoquinoline form more stable 1:1 complexes than quinoline.

There is also a paper on the investigation of the solid complexes of 2,6-, 3,4-, and 3,5-lutidines with the general formula $HO-(Ph)_2C-(C\equiv C)_n-C(Ph)_2-OH$, where n = 2, 1, 0, by x-ray spectroscopy.

A series of investigations were devoted to the complexation of carboxylic acids with pyridine bases. In one of the earlier papers [49] the complexation of pyridine with several carboxylic acids was examined: butyric (pK_a = 4.82), methacrylic (4.4), benzoic (4.2), monochloroacetic (2.9), and monobutyl maleate (3.0). It was supposed that the weak acids (butyric, methacrylic, benzoic) form 1:1 H-complexes with pyridine (Fig. 2), while the strong acids form a 2:1 ionic complex (Fig. 3). The IR spectra of the solutions with the weak acids are characterized by a shift of a series of the absorption bands by 1-20

TABLE 10. Enthalpy of Mixing of Carboxylic Acids with Pyridines [54]

System	Composition of complexes	$-\Delta H_m$, kJ/mole
Acetic acid—4-picoline	2 : 1	6,20...6,55
Butyric acid—2,6-lutidine	1 : 1	6,36...6,76
Isobutyric acid—2,6-lutidine	1 : 1	4,90...4,95

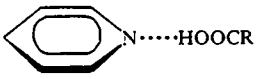

Fig. 2

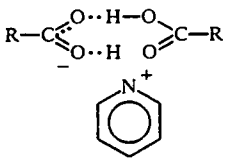

Fig. 3

cm^{-1} and by a change in their intensity. The complexes of quinoline with methacrylic acid (1:1) were investigated by IR spectroscopy; broad absorption bands with λ_{max} at 2500 and 1930 cm^{-1}, which correspond to the H bond, appear in the spectrum. Presumably, quinoline reacts like pyridine with weak acids.

Data on the conductivity of solutions of organic acids (at 40 and 70°C) and of formic (pK_a = 3.75), acetic (4.76), propionic (4.87), and butyric acids, in particular, with pyridine bases [50] and data from the IR spectra [51] show the presence of complexes in these systems.

Study of the IR spectra of complexes of nicotinic (pK_a = 4.73) and isonicotinic (4.89) acids with pyridine and 4-picoline [52] makes it possible to suppose that a strong H bond is formed in the solution. The hydrogen atom in this bond is closer to the oxygen atom. Another paper [53] is devoted to the complexation of monocarboxylic acids (concentration 0.1-1.0 N) with pyridine, 2- and 4-picolines, and 2,6-lutidine (concentration of bases 0.002-0.2 N) in benzene solutions. Base—acid H complexes (1:1 and 1:2) were formed, and their stability constants were calculated. The paper [54] was devoted to the determination of the enthalpy of mixing ($-\Delta H_m$) of 4-picoline and 2,6-lutidine with lower carboxylic acids in water and in cyclohexane at 25°C (Table 10).

Strong interaction with the formation of H complexes was detected in solutions of pyridine bases with trifluoroacetic acid (pK_a = 0.23) in chloroform with the components at concentrations between $1 \cdot 10^{-2}$ and $5 \cdot 10^{-2}$ N [55]. The enthalpies of reaction were obtained from the results of thermometric titration at 25°C (Table 11). A linear correlation was established between the ΔH_c and pH_a values of the pyridine bases.

The complexes of isoquinoline with trifluoroacetic acid were also studied by IR spectroscopy in various media (hexane, octane, isooctane, carbon tetrachloride, toluene, butyl chloride, chloroform, and acetonitrile) [56]. It was established that the structure of the equimolar complex (1:1) depended on the interaction between the components of the complex and the solvent; in saturated hydrocarbons and carbon tetrachloride it is a complex with a hydrogen bond of the OH···N type; in polar acetonitrile it is an ion pair with proton transfer; in an aromatic solvent and in chlorobenzene the structure of the complex is intermediate. It was shown that the acid—isoquinoline complexes (2:1 or 3:1) are ionic (Table 12).

The NMR spectra of solutions of pyridine with acetic acid are discussed in [57]. It was noticed that complexes of the acetic acid monomer with pyridine are formed in these solutions. The enthalpy is $-\Delta H_c$ = 36 kJ/mole.

Complexation with N-containing derivatives of carboxylic acids and, in particular, with N,N-dimethylformamide, in which pK_a = −0.01 and I = 9.12 eV,* was studied in [58], and the K_s value was calculated from the data of the NMR spectra. It was established that weak complexes (1:1) with K_s = 0.31 liter/mole are formed in the pyridine—DMFA system.

The association and solvation of formamide (pK_a = −2.6) with pyridine and picolines were studied in [59]. A relation was obtained between the excess enthalpy of mixing and the concentration in binary systems with formamide and pyridine bases. The presence of 1:1 intermolecular complexes with a hydrogen bond was established in these systems (over a wide range of concentrations).

*Here and subsequently the I values were taken from [6].

TABLE 11. Enthalpy of the Hydrogen Bond in the Complexes (1:1) of Trifluoroacetic Acid with Pyridines [55]

Base	$-\Delta H_c$, kJ/mole	Base	$-\Delta H_c$, kJ/mole
Pyridine	50,2	3,5-Lutidine	58,5
3-Picoline	56,2	2,4,6-Collidine	66,6
4-Picoline	58,0	Quinoline	49,8
2,6-Lutidine	60,8	Isoquinoline	50,4

TABLE 12. Stability Constants of the Complexes of Isoquinoline with Trifluoroacetic Acid [56]

Solvent	Temperature, °C	K_s, liter/mole
Octane	34,0	3810 ± 20
Toluene	30,0	17930 ± 610
Acetonitrile	34,0	36500 ± 2100

TABLE 13. Complexes with a Hydrogen Bond in Pyridine Bases with Succinimide in Carbon Tetrachloride at 20°C [60]

Pyridine base	K_s, liter/mole	Pyridine base	K_s, liter/mole
Pyridine	14,0	2,4-Lutidine	19,0
4-Picoline	13,0	2,4,6-Collidine	7,0

The hydrogen bond in systems with succinimide (pK_a = 9.62) and pyridine bases was studied in [60]. The IR spectra of the binary mixtures were recorded in toluene (0.011 M) at 15°C and in carbon tetrachloride (0.003 M) at 20°C. It was shown that carbon tetrachloride (Table 13) has a smaller effect on complexation than toluene.

An investigation [61] was devoted to the complexation of pyridine with acetonitrile with the use of NMR spectroscopy.

Several papers are known on the investigation of the complexes of pyridine with aromatic nitro compounds. Thus, in [62] the crystalline compounds of pyridine bases with picric acid [2,4,6-trinitrophenol (TNP)] and amines and, in particular, pyridine—TNP—naphthylamine complexes (1:1:1) were studied. Analogous complexes are formed by 2- and 4-picolines and 2,6-lutidine. It was suggested in [63] that the stability of the complexes of TNP with acridine is determined by the forces arising during the displacement of the proton of the OH group toward the nitrogen atom of the heterocycle (a hydrogen bond of the O···H···N type) and also during the transfer of charge from the heterocycle to the vacant orbital of the nitro group in TNP. The K_s values calculated for 2,4,6-trinitrophenol, 1,3,5-trinitrobenzene, and 2,4,6-trinitroanisole from the IR spectra of solutions in chloroform are compared:

Electron donor	K_s, liter/mole		
	2,4,6-trinitrophenol	1,3,5-trinitrobenzene	2,4,6-trinitroanisole
Acridine	1461 ± 20	10,8 ± 0,2	12,2 ± 0,5

It is seen from the data in the table that K_s for the complexes with 2,4,6-trinitrophenol is significantly higher than with trinitroanisole and trinitrobenzene. These complexes are formed as a result not only of charge transfer but also of a hydrogen bond.

The formation of crystalline picrates with quinoline was also examined in [64]. It was noted that they are stabilized through ionic and hydrogen bonds.

In the nineties a series of papers were published on the complexation of pyridine bases with quinones and, in particular with benzoquinones and, chiefly, with halogenoanils. Thus, the 1:1 complexes formed during the reaction of 2-, 3-, and 4-picolines with chloranil were studied by conductometric titration [65]. The energetics of n—π^* and π—π^* complexes with charge transfer between the donor (pyridine) and the acceptor of π electrons (chloranil) were examined in another paper [66]. In a more recent paper by the same authors [67] the molecular complexes (also 1:1) of pyridine and picolines with halogeno-

TABLE 14. Complexation Constants of Chloroform with Pyridines (1:1 Complexes) [74]

System	K_s, liter/mole	System	K_s, liter/mole
$CHCl_3$ + pyridine	1,11	$CHCl_3$ + 3-picoline	1,42
$CHCl_3$ + 2-picoline	1,50	$CHCl_3$ + 4-picoline	1,31

Fig. 4

anils (chloro-, bromo-, and fluoroanils) were studied by conductometric titration. It was found that complexation takes place through the formation of an ion pair with the participation of the nitrogen atom of the pyridine ring.

The complexes of 2- and 4-picoline (donors) with 7,7,8,8-tetracyanoquinodimethane, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, *p*- and *o*-chloroanil, and also with 2,4,7-trinitro-9-fluorenone and 2,4,5,7-tetranitro-9-fluorenone (acceptors) were studied by IR, UV, and NMR spectroscopy [68]. In this paper it was stressed that complexation takes place through an ion pair with the participation of the nitrogen atom of the pyridine ring.

In one of the earlier papers on the complexation of quinolines with benzoquinones and chlorine-containing benzoquinones [69] the complexation of quinolines with π-electron acceptors (*p*-benzoquinone, tetrachloro-1,4-benzoquinone, and dichlorodicyano-1,4-benzoquinone) at 77 K was studied. It was established that quinoline, isoquinoline, and quinaldine were *p*-electron donors, whereas acridine and 8-hydroxyquinoline were π-electron donors. It was also noticed that the complexes of quinolines with dichlorodicyano-*p*-benzoquinone were ionic. More recently, data appeared on the complexation of acridine with tetracyanoquinodimethane (I = 9.42 eV) with the 1:2 molar composition [70, 71]. A development of these investigations was the paper [72], also published in the nineties. The 1:1 complexes of quinoline derivatives with π acceptors [2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDBQ), 2,3,5,6-tetrachloro-1,4-benzoquinone (chloroanil), and tetracyanoethylene (TCE) (I = 11.67 eV)] were studied by IR spectroscopy. The spectra were recorded for solutions of the compounds in dichloromethane. It was observed that quinoline formed solid 1:1 complexes with DDBQ (mp 206-208°C) and TCE (98-100°C); 6-methylquinoline also formed solid 1:1 complexes with DDBQ (160-162°C) and TCE (102-104°C).

A series of investigations have been devoted to the complexation of chlorine-substituted methane, ethane, and ethylene with pyridine bases. In [73] the results from a study of the complexation of chloroform in binary systems with pyridine and 2-, 3-, and 4-picolines by calorimetry and IR spectroscopy (at 35°C) are discussed. It was established that 1:1 complexes were formed. The strongest interaction was observed in the systems with chloroform and 2-picoline ($-\Delta H_c$ = 8.88 kJ/mole) and 3-picoline (8.51 kJ/mole); pyridine and 4-picoline showed weaker interaction (5.5 and 6.18 kJ/mole respectively). More recently [74], the same authors published the results of an investigation into complexation (1:1) in the same systems using PMR data. The complexation reaction is shown in Fig. 4, and the constants of the complexes are given in Table 14.

Another paper by these authors [75] gives the enthalpy of complexation of pyridine with chloroform ($-\Delta H_c$ = 16.16 kJ/mole), which is significantly larger than the parameter given in [73].

The reaction of pyridines with chloroform was studied [76] by dielectric polarization in cyclohexane at 25°C. Two types of bond were noticed, i.e., a bond formed through the free electron pair of the N atom of the pyridines (a *p* bond) and the typical H bond of chloroform with the π electrons of the heterocycle.

During investigation of the complexation of 3-picoline with various solvents (acceptors) [77] it was shown that cyclohexane was an inert solvent (see [76]), while chloroform formed complexes with picoline, and bonds of the two previously mentioned types were formed.

The complexation of 4-picoline and 2,4-lutidine with 1,1,2,2-tetrachloroethane and *trans*-dichloroethylene was studied [78] by dielectric polarization in cyclohexane. It was shown that 4-picoline formed more stable complexes (K_s = 0.38 and 0.9 liter/mole respectively).

There are papers on the complexation of pyridine bases with aromatic hydrocarbons. Thus, in [79] the density and viscosity of binary mixtures of 2,4- and 2,6-lutidines and 2,4,6-collidine with benzene (pK_a = 37, I = 9.25) and, for comparison, with cyclohexane were studied over a wide range of concentrations at 30-50°C. From the deviation of the viscosities from additivity it was established that 1:2 benzene—collidine complexes, in which the benzene acts as π-electron donor, were present. It was confirmed that cyclohexane is inert toward pyridines. In [80] the density, n_D values, and dielectric constants were studied in binary systems with 2-, 3-, and 4-picolines and benzene (and carbon tetrachloride for comparison). The excess molar volumes (V_m^E) and dipole moments (μ_k) of picolines in these systems were calculated over the whole range of concentrations at 20-50°C. It was found that 1:1 complexes were formed, and the stability of the complexes with carbon tetrachloride was higher than with benzene. The excess Gibbs energy of binary mixtures of pyridine with methyl-, ethyl-, *n*-propyl-, and *n*-butylbenzenes at 100°C was studied in [81], and very weak complexes were detected in these systems.

There is also a paper [82] indicating the presence of complexes of pyridine and its homologs with 2,4-dinitrostyrene and 2,4,6-trinitrostyrene. The complexation of pyridines and quinoline with trinitrotoluene at 25°C in benzene solutions with dielectric titration was the subject of an investigation in [83]. Here it was established that weak complexes due to π—π^* interaction of the molecules in parallel planes were formed. The simultaneous coexistence of pyridine—trinitrotoluene complexes (1:1 and 2:1, moles) was demonstrated. Somewhat later [84] it was established by means of the NMR spectra of these compounds in carbon tetrachloride at 25°C that the trinitrotoluene in these systems acts as π-electron acceptor. The stability constants are small, particularly in the systems with 2- and 3-picolines, on account of steric hindrances, and this confirms the results of the previous investigation. It was noticed that quinoline forms more stable complexes than pyridines with trinitrobenzene (K_s = 2.7 liter/mole). Considerably weaker complexes were detected in the quinoline—trinitrotoluene system (K_s = 1.1 liter/mole).

The excess free volumes ($V_m^E < 0$) in binary mixtures of quinoline with *m*- and *p*-cresol over the whole range of concentrations were calculated from the equilibrium data [85]. It was noted that the intermolecular interaction in these systems was characterized by the formation of hydrogen bonds, charge transfer, and a contribution from dipole—dipole interactions.

Weak specific intermolecular interactions were detected in systems containing quinoline with *n*-butylbenzene and *n*-decane [86]. The excess free volumes were also measured in this paper by the ebulliometric method, and the excess Gibbs energies were obtained.

The specific intermolecular interaction of pyridine, 1-picoline, and 2,6-lutidine with hexafluorobenzene was investigated in [87] from data on the viscosity of binary mixtures at 20-45°C. The values obtained for the excess enthalpy of viscous flow of these mixtures make it possible to suppose that the pyridines act as π donors. 2,6-Lutidine has the strongest donating activity.

A series of investigations were devoted the complexation of pyridine bases with heterocyclic compounds. In one of the earliest papers [88] on the results of spectroscopic investigations, the formation of complexes of pyridine with 2,5-diphenyloxazole in *n*-octane was discussed. The oxazole acts as electron acceptor ($-\Delta H_c$ = 18.42 kJ/mole, $-\Delta G_c$ = 6.24 kJ/mole, at 30°C K_s = 10.7 liter/mole). The complexes of pyridine, quinoline, and isoquinoline with pyrrole (pK_a = −0.27) [89, 90] and indole (pK_a = −2.7, I = 7.74 eV) [90] containing a hydrogen bond were investigated by dielectric polarization using data from the IR spectra. It was noted that 1:1 complexes were formed.

During investigation of the stereochemical structure of the complexes of pyridine, 2-, 3-, and 4-picolines, and 3,5-lutidine with pyrrole and indole using an electrooptical method (the Kerr effect) and the data from the IR spectra [91], it was established that the most probable structure is a structure where the N—H bond of the pyrrole or indole is perpendicular to the plane of the pyridine ring (Fig. 5). The relative content of this type of complex increases with decrease in the pK_a value of the base and with increase in its π system. The complexes of pyrrole with pyridine and quinoline were studied by means of the IR spectra (for solutions of these substances in hexane, toluene, and carbon tetrachloride) [94]. It was found that hexane was an inert solvent and that the stability constants in it were larger than in toluene and carbon tetrachloride (Table 15).

As a result of the study [93] of the complexes of pyridine and 2,6-lutidine with carbazole in cyclohexane, it was established that a fairly strong hydrogen bond (K_s = 12-13 liter/mole) is formed in these binary systems (Fig. 6).

In another paper [94] the complexes of pyridine with carbazole ($pK_a < -1.0$) and with isomers of carbazole in cyclohexane were investigated. The structure is presented in Fig. 7, and the calculated values are given in Table 16.

As seen from Table 16, the stability of the molecular complexes is significantly higher in the systems with dibenzocarbazole than in the systems with carbazole.

Several papers are known on the complexation of pyridines with the dinitro derivatives of pyridine, representing ketones or alcohols.

TABLE 15. Thermodynamic Parameters of the Complexes of Pyridines and Quinoline with Pyrrole at 30°C [92]

Pyridine base	K_s, liter/mole	$-\Delta H_c$, kJ/mole	$-\Delta S_c$, J/mole·K
Pyridine	5,5	23,0	62,0
2-Picoline	5,1	17,5	44,0
3-Picoline	6,7	18,4	44,0
4-Picoline	6,5	18,0	42,0
2,4-Lutidine	9,4	16,8	34,0
3,5-Lutidine	8,0	19,2	45,0
Quinoline	2,8	16,2	45,0

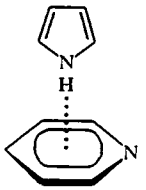

Fig. 5

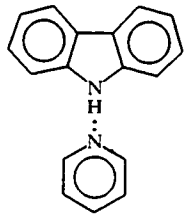

Fig. 6

The K_s values of the complexes of pyridine, 2-, 3-, and 4-picolines, 2,3-, 2,4-, and 2,6-lutidines, and 2,4,6-collidine with the ketones 1H-3,5-dinitropyridin-2-one and 1H-3,5-dinitropyridin-4-one and with the alcohol 2,6-dinitropyridin-3-ol were determined in aqueous solutions at 20-55°C [95]. It was noted that the complexes with the ketones were stabilized as a result of a hydrogen bond, while the complexes with the alcohol were stabilized ion pairs. In another paper [96] the results of a UV-spectroscopic investigation of the donor—acceptor complexes of pyridine bases with 2,4,6-trinitropyridine 1-oxide (Table 17), which are electron acceptors, were examined. As seen from the presented data, the complexes with 3- and 4-picolines are the most stable. In [97] the molecular complexes of pyridine bases with 3-hydroxy-2,4,6-trinitropyridine were studied by spectrophotometry in aqueous solution, and the thermodynamic parameters of complexation were determined.

An investigation into the complexes of pyridines with individual representatives of other chemical types is described in [98, 99]. This concerned the complexation (1:1) of pyridines with tetracyanoethylene (I = 11.67 eV), which is an electron acceptor (K_s = 15-20 liter/mole). The donor—acceptor complexes of quinoline and acridine with tetracyanobenzene were studied in [100].

There is a paper [101] on an investigation into the complexation of quinoline and isoquinoline with 9-(dicyanomethylene)-2,4,7-trinitrofluorene at 20°C using the electronic spectra. It was found that in the system with quinoline K_s = 0.9 liter/mole ($-\Delta H_c$ = 15.49 kJ/mole), while in the system with isoquinoline K_s = 0.54 liter/mole. Complexation in these systems takes place through the π electrons of the quinolines (donors). The optimum geometry of the complexes is a coplanar arrangement of the molecules of the donor and the acceptor with a distance of 3.3-3.4 Å between the planes of the molecules. It was established that strong complexation is observed when there is an amino group in the quinolines; in the 9-(dicyanomethylene)-2,4,7-trinitrofluorene—8-aminoquinoline system K_s = 5.94 liter/mole.

The complexation of quinoline and isoquinoline with α-cyclodextrin (cyclohexaamylose) was studied by spectrophotometry [102]. It was established that 1:1 and 1:2 complexes were formed. For quinoline K_s = 28.6 liter/mole (1:1 complexes) and 0.63 liter/mole (1:2); the values for isoquinoline were 22.7 and 10.8 liter/mole respectively.

A series of investigations are known on the formation of solid complexes, mainly of acridine, with a series of other compounds. Molecular solid complexes (1:1) of acridine and acridan at 77 K were studied by spectroscopy [103, 104]. In other papers [105-107] the characteristics of the crystalline complexes (1:1) of acridine with pyromellitic dianhydride and pyromellitic dithioanhydride were investigated.

A spectral investigation of the complexes of acridine with dimethylaniline at 77-293 K was undertaken in [108]. The complexation of acridine with naphthalene (pK_a = 0.15, I = 8.12 eV), phenanthrene, biphenyl (pK_a = 0.40, I = 8.27 eV),

TABLE 16. Stability Constants of the Complexes of Pyridines with Carbazoles at 20°C [94]

Pyridine base	K_s, liter/mole		
	carbazole	13-H-dibenzo[*a,i*]-carbazole	7-H-dibenzo[*c,g*] carbazole
Pyridine	12,0	27,0	27,0
2,6-Lutidine	13,0	62,0	42,0

TABLE 17. Stability Constants of the Complexes of Pyridines with 2,4,6-Trinitropyridine 1-Oxide [96]

Pyridine base (electron donors)	K_s, liter/mole	Pyridine base (electron donors)	K_s, liter/mole
Pyridine	9,88	2,3-Lutidine	2,34
2-Picoline	19,87	2,6-Lutidine	1,98
3-Picoline	23,39	2,4,6-Collidine	20,81
4-Picoline	25,60		

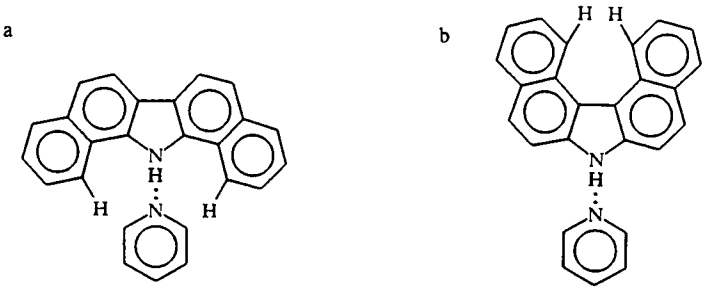

Fig. 7. Complexes: a) pyridine—13-dibenzo[*a,i*]carbazole; b) pyridine—7H-dibenzo[*c,g*]carbazole.

and 1,6-dimethylnaphthalene was studied in [109]. It was established that the K_s value was 0.5 liter/mole for the complexes with the first three compounds and 30 liter/mole for the last.

Complexation of acridine with α,β,γ-cyclodextrins (water-soluble complexes) was studied by fluorescent absorption [110]. The K_s value calculated from the spectral data was 413 liter/mole. In another paper [111] on the effect of alcohols on the complexation of β-cyclodextrin with acridine it was established that K_s = 287 liter/mole.

It is also necessary to mention the investigations of solid complexes of acridine with a series of different organic compounds (1:1) — 1,2,4,5-benzotetracarbonitrile [112] and N,N-dimethyl-1,4-dithiintetracarboxydiimide ($C_{10}H_6N_2O_4S_2$) [113].

Thus, by analyzing the ability of the individual components of pyridine bases to form complexes with various types of organic compounds (mostly in solutions), using the I and pK_a values and the thermodynamic parameters of complexation it is possible to plan possible ways of isolating the components from technical mixtures using modern methods of separation. Such methods involve the use of selective solvents, e.g., azeotropic and extractive rectification, liquid extraction with one or several solvents, and extractive crystallization. These methods have found increasing applications in industry. We will attempt to illustrate the latter using patent data of the achievements of individual firms.

A series of methods are known for isolating 2,6-lutidine from mixtures with picolines, based on their different capacities for complexation. In one of the recent publications [114] it was proposed to use compounds with the general formula HC(O)N(R)—R^1, e.g., N,N-dimethylformamide (pK_a = −0.01), as complexing agent in the presence of an acid halide or cobalt chloride at 30-120°C. Here, 2,6-lutidine forms a solid complex and is easily separated from picolines. Another familiar

method for the selective isolation of 2,6-lutidine is complexation with urea (pK_a = 0.1) in a molar ratio of 1:2 in an organic solvent (e.g., benzene [115]) in the absence of water. The purity of the obtained product is 99.1%.

Dissociative extractive crystallization was proposed for the separation of 3- and 4-picolines [116]. This is more effective than the previously described dissociative extraction [117] on account of the introduction of the extracting agent — piperazine (pK_a = 9.82), diazobicyclooctane, monoethanolamine (pK_a = 9.5), or *p*-toluenesulfonic acid. The last two agents were used in the form of aqueous solutions. In dissociative extractive crystallization a solid precipitate is formed, and this increases the separation factor (from 10 to 107).

The separation of 2-, 3-, and 4-picolines can be achieved by a combination of rectification and liquid extraction, e.g., in the benzene—water system [118]. The distribution coefficients of picolines in the two-phase system were calculated from data on the phase equilibria in the liquid—liquid system, and the selectivity of benzene to 3- and 4-picolines, which pass into the organic phase, was established.

It was found that there is an azeotropic point in mixtures of quinoline with *m*-cresol (an azeotrope with a maximum boiling point) with a low concentration of the azeotrope-forming agent (*m*-cresol) [119]. This creates prospects for the use of azeotropic rectification in the isolation of quinoline.

The formation of solid complexes (1:1) of quinoline and isoquinoline with hexafluorobenzene [120] was established from data on the liquid—solid phase equilibrium in binary systems. This fact is of undoubted interest to researchers in the selection of a method for the isolation of quinoline and isoquinoline. Industrial methods were developed for the isolation of quinoline and isoquinoline [121, 122], based on a combination of the sulfuric acid treatment of coal tar, followed by treatment with an organic solvent and precise rectification.

The results from a study of the complexation of quinoline and isoquinoline with α-cyclodextrin in aqueous solution [102] made it possible to propose the possible extractive separation of these isomers. A method for the concentration and isolation of quinaldine [123] was based on the complexation of quinaldine with α-cyclodextrin in aqueous solution.

According to the results in the previously mentioned papers [110, 111] and also data in [124], acridine can be isolated from coking products by an extraction method through complexation with β-cyclodextrin.

The presented examples show that the data from study of the complexation of nitrogen bases with various types of organic compounds can find practical application in the search for and selection of methods for the recovery and isolation of individual heterocyclic compounds from industrial mixtures.

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