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# PROTONATION OF PHOSPHINYLMETHYLPYRIDINES AND THEIR N-OXIDES IN NITROMETHANE

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The protonation of phosphinylmethylpyridines with different structures and their N-oxides differing both in the nature and the number of functional groups (pyridine nitrogen, N → O, and P=O) was studied by potentiometric titration in nitromethane and IR spectroscopy. Regardless of the number of P=O groups, all the investigated phosphinylmethylpyridines were N bases, and their pK values changed in the range 10.4-4.7. In the case of N-oxides of phosphinylmethylpyridines, the oxygen atoms of N → O and P=O groups participated simultaneously in protonation, and the pK values were 6.7-5.0. The structure of the protonation products is discussed.

Phosphinylmethylpyridines and their N-oxides are interesting potential extractants. For a more detailed study of their acid–base properties, in the present paper we used potentiometric titration in nitromethane with perchloric acid and IR spectroscopy to study the protonation of phosphinylmethylpyridines differing in structure and their N-oxides differing both in the nature and in the number of functional groups (pyridine nitrogen, N → O, and P=O). The investigated compounds (I)-(XVI) and their pK values are given in Table 1.

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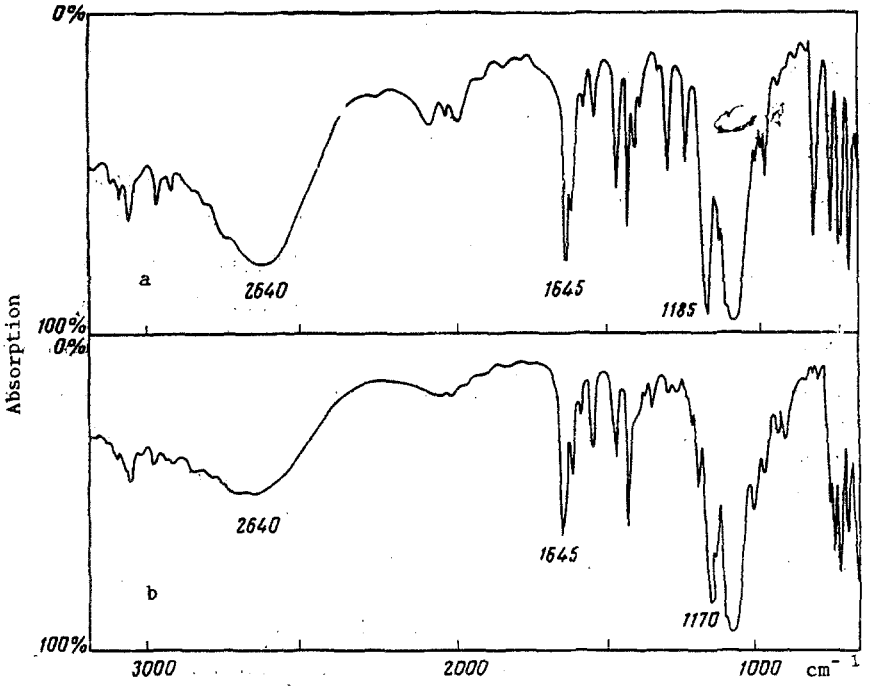



Fig. 1. IR spectra of protonated phosphorylmethylpyridines (KBr tablets): a) (I)·$HClO_4$; b) (IV)·$HClO_4$.

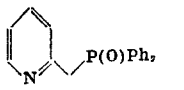
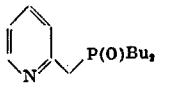
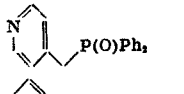
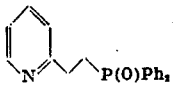
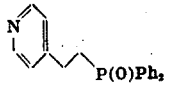
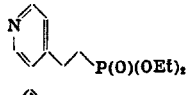
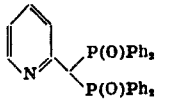
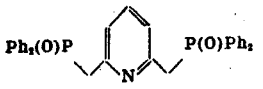
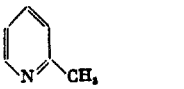
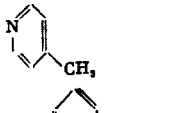
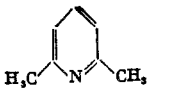
The synthesis of the phosphinylmethylpyridines and their N-oxides is described in [1]. The α- (IV) and the γ-[2-(diphenylphosphinyl)ethyl]pyridine (V) were prepared by the reaction of α- and γ-vinylpyridines with diphenylphosphine. The γ-[2-(diethoxyphosphinyl)ethyl]pyridine (VI) was prepared according to [2], and the picoline N-oxides were prepared according to [3].

1. Phosphinylmethylpyridines. All the investigated phosphinylmethylpyridines (I)-(VIII) and picolines (IX)-(XI) (see Table 1) have similar titration curves with one potential jump at the 100% neutralization point, which corresponds to the process $B + H^+ \rightleftarrows BH^+$ (1). These data, together with the results of an investigation of the IR spectra of protonated phosphinylmethylpyridines (see below) show that the protonation of phosphinylmethylpyridines in nitromethane occurs at the nitrogen atom of the pyridine ring. In all cases, the pK values of the phosphinylmethylpyridines are lower than those of the picolines (see Table 1). Such a decrease of the basicity of the phosphinylmethylpyridines is due to the acceptor nature of the diphenylphosphinyl group [4]. Thus, removal of the diphenylphosphinyl group from the reaction center leads to an increase of the basicity [cf. (II) and (IV)]. On the other hand, the addition of another diphenylphosphinyl group to the phosphinylmethylpyridine molecule leads to a decrease of the basicity, with this effect being greater if the two substituents are at the same carbon atom [cf. (I), (VII), and (VIII)]. Replacement of the diphenylphosphinyl group in (V) by a diethoxyphosphinyl group decreases the basicity of (VI) by 0.5 pK unit, which reflects the difference in the σ* constants of these groups, i.e., 0.58 and 0.73, respectively [4].

For determination of the structure of protonated phosphinylmethylpyridine salts, we prepared salts with perchloric acid (1:1) for (I) and (IV) and studied their IR spectra.

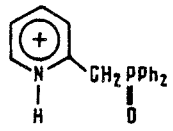
In the IR spectrum of (I), the intense band of the pyridine ring νPy = 1590 $cm^{-1}$ was shifted toward higher frequencies (to 1645 $cm^{-1}$) during the formation of the salt, which is characteristic of protonated nitrogen in the pyridine ring [5]. In addition, a wide intense band (ν = 2640 $cm^{-1}$) of the $N^+$–H group [6] and an intense band (ν = 1105 $cm^{-1}$) of the $ClO_4$ anion (Fig. 1a) appeared in the spectrum of the pyridinium salt. During the formation of the salt, the band of νP=O = 1185 $cm^{-1}$ shifted only insignificantly to lower frequencies (Δν = 5 $cm^{-1}$), with this ν remaining equal to 1180 $cm^{-1}$ in the spectrum of the solution of the salt in acetonitrile. Therefore, the P=O group in (I) does not participate in coordination with a mobile proton, which corresponds to the structure

TABLE 1. Basicity of Phosphinylmethylpyridines, Picolines, and Their N-Oxides in Nitromethane*

| Compound | | pK ($CH_3NO_2$) |
|---|---|---|
|  | (I), (XIII)* | 8,8 (7,8)* |
|  | (II) | 9,5 |
|  | (III), (XII)* | 9,2 (6,8)* |
|  | (IV) | 10,4 |
|  | (V) | 9,8 |
|  | (VI) | 9,3 |
|  | (VII), (XIV)* | 7,9 (5,1)* |
|  | (VIII) | 8,3 |
|  | (IX), (XV)* | 10,3 (6,3)* |
|  | (X), (XVI)* | 10,3 (6,8)* |
|  | (XI) | 10,8 |

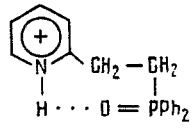
*The numbering and pK ($CH_3NO_2$) values of the corresponding N-oxides are given.

Scheme 1



Protonation of (IV) led to the same changes in the spectrum (Fig. 1b), but here the band $\nu P{=}O$ = 1180 $cm^{-1}$ was shifted somewhat more strongly toward lower frequencies (1170 $cm^{-1}$), with $\nu P{=}O$ = 1160 $cm^{-1}$ in the acetonitrile solution. This indicates intramolecular coordination of the P=O group with the mobile proton

Scheme 2



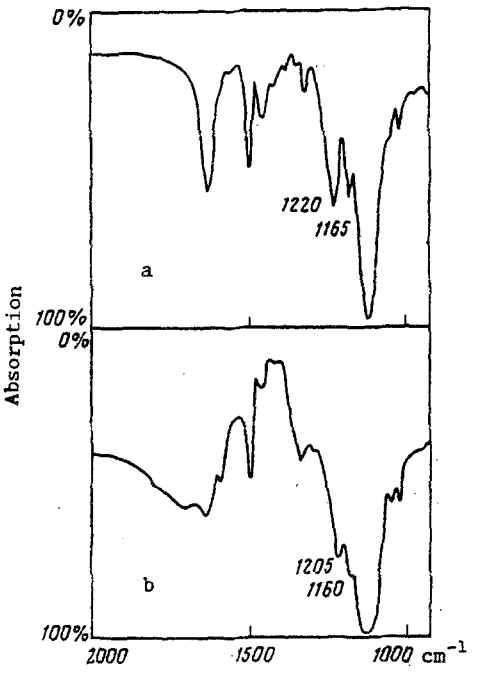



Fig. 2. IR spectra of N-oxides with perchloric acid (1:1), $CH_3CN$, 0.2 mole/liter: a) (XIII); b) (XIV).

This is also related to the higher basicity of (IV) (pK 10.4) among the investigated phosphinylmethylpyridines, comparable with the basicity of picolines (see Table 1).

On the whole, during protonation in nitromethane, the investigated phosphinylmethylpyridines behaved as nitrogen bases regardless of the number and position of the P=O groups in the molecule.

2. Phosphinylmethylpyridine N-Oxides. The titration curves of the γ-substituted N-oxides [of phosphinylmethylpyridines (XII) and picoline (XVI)] had two potential jumps at the 50% and 100% neutralization points. This is characteristic of processes of protonation of oxygen bases [7] and corresponds to the scheme

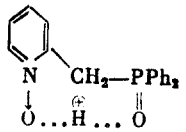
$$2B + H^+ \rightleftharpoons BHB^+ \quad (1)$$

$$BHB^+ + H^+ \rightleftharpoons 2BH^+ \quad (2)$$

It is remarkable that both compounds have identical basicity (Table 1); therefore, the protonation site here is the oxygen of the N → O group. Then the intermediate complex $BHB^+$ has the structure $\left[\diagdown N \longrightarrow O...H...O \longleftarrow N \diagup\right]^+$. The specifics of the effect of the phosphorus substituent is not manifested here.

Another situation was observed for the α-substituted N-oxide (XIII). Protonation here occurred in one step with one potential jump on the titration curve (scheme 1). On the other hand, the corresponding picoline N-oxide (XV) gave two potential jumps on the titration curve at the 50% and 100% neutralization points in accordance with scheme 2.

For establishment of the structure of the protonated N-oxide (XIII), we studied the IR spectrum of a mixture of (XIII) with perchloric acid (1:1) in acetonitrile (Fig. 2a). The spectrum contained intense bands of the functional groups P=O (1165 $cm^{-1}$) and N → O (1220 $cm^{-1}$), which were shifted 25 and 12 $cm^{-1}$, respectively, toward lower frequencies with respect to the spectrum of the starting base. This means that both groups (P=O and N → O) participate in proton bonding with formation of a chelate-type $(BHB')^+$-type complex [7]



The N-oxide (XIV) contains three functional groups, namely, one N → O and two P=O, able to participate in protonation. The titration here occurred in one step with one potential jump at the 100% neutralization point. We investigated the IR spectrum of a mixture of (XIV) with perchloric acid (1:1) in acetonitrile. The spectrum contained intense bands of the N → O (1205 $cm^{-1}$) and P=O (1160 $cm^{-1}$) groups, which were shifted 25 and 55 $cm^{-1}$, respectively, toward the low-frequency region with respect to the spectrum of the starting base (Fig. 2b); the spectrum contained no bands of free P=O groups (1215 $cm^{-1}$). Therefore, all three functional groups of (XIV) participate in protonation. An analysis of molecular models of asymmetric trioxide (XIV) showed that here a conformation with relatively close oxygen atoms is possible; such a conformation occurs during protonation of tris(diphenylphosphinylmethyl)benzenes [8]. The basicity of (XIV) (5.1) is higher than the basicity of the dioxide $Ph_2P(O)CH_2P(O)Ph_2$ (3.5)* and corresponds in strength to that of the substituted dioxide $Ph_2P(O)CH[CH_2CH_2P(O)Ph_2]P(O)Ph_2$ (5.1).* where the diphenylphosphinyl group of the substituent participates in protonation [9].

In conclusion, we should note that, unlike in the case of phosphinylmethylpyridines, the protonation process of phosphinylmethylpyridine N-oxides in nitromethane depends on the position of the substituent in the pyridine ring. Thus, the oxygen atoms of the N → O and P=O groups participate simultaneously in protonation in α-substituted N-oxides, and only the oxygen atom of the N → O group participates in protonation in γ-substituted N-oxides.

## EXPERIMENTAL

The basicity of the substances in nitromethane was determined by the method of [10] with a Radelkis OP-211/1 pH meter, and the electrodes were a Radiometer G 202C glass electrode and a calomel electrode with contact via a Radiometer K-401 porous ceramic.

The IR spectra were obtained with a UR-20 spectrometer, the tablets were KBr, and the solutions in acetonitrile had a concentration of 0.2 mole/liter and d = 0.063 ($CaF_2$).

α-[2-(Diphenylphosphinyl)ethyl]pyridine (IV). A mixture of 0.6 g (0.0057 mole) of α-vinylpyridine and 1.1 g (0.0054 mole) of diphenylphosphine oxide in 4 ml of benzene was heated for 3.5 h in a sealed ampul at 140°C. The crystals that precipitated during cooling and standing were filtered and recrystallized from a benzene–hexane mixture. We obtained 1.3 g (78%) of (IV) with mp 107-109°C [11].

γ-[2-(Diphenylphosphinyl)ethyl]pyridine (V). We obtained similarly 1.1 g (66%) of (V) with mp 115-117°C from 0.6 g (0.0057 mole) of γ-vinylpyridine and 1.1 g (0.0054 mole) of diphenylphosphine oxide. Found, %: N 4.75; P 10.1. $C_{19}H_{18}NOP$. Calculated, %: N 4.6; P 10.1.

Salt of α-[2-(Diphenylphosphinyl)ethyl]pyridine (IV) with $HClO_4 \cdot 2H_2O$. To a solution of 0.1 g (0.00033 mole) of (IV) in acetonitrile was added 0.045 g (0.000333 mole) of $HClO_4 \cdot 2H_2O$. The obtained solution was slowly evaporated at ~20°C. The resulting crystals were separated and recrystallized from acetonitrile. We obtained 0.11 g (76%) of (IV)·$HClO_4$. Found, %: C 56.0; H 5.0; Cl 8.3; N 3.7. $C_{19}H_{19}ClNO_5P$. Calculated, %: C 56.0; H 4.7; Cl 8.7; N 3.4.

Salt of α-[2-(Diphenylphosphinyl)methyl]pyridine (I) with $HClO_4 \cdot 2H_2O$. To a solution of 0.1 g (0.00034 mole) of (I) in nitromethane was added 0.034 g (0.00034 mole) of $HClO_4 \cdot 2H_2O$. The obtained solution was slowly evaporated at ~20°C. The resulting acicular crystals were separated, washed with ether, and dried. We obtained 0.11 g (82%) of (I)·$HClO_4$. Found, %: C 54.9; H 4.4; N 3.7. $C_{18}H_{17}NO_5PCl$. Calculated, %: C 54.9; H 4.4; N 3.6.

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# CHLORINE AND HYDROGEN TRANSFER BY METAL CARBONYL INTERMEDIATES

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The reduction of 1,1,1,5-tetrachloropentane by toluene in the presence of the $Fe(CO)_5$ or $M(CO)_6$ (M = Cr, Mo, W) in conjunction with triphenylphosphine was investigated. It was shown that the chlorine-containing metal carbonyl intermediates formed in the process take part in the transfer of the chlorine atom to the benzyl radicals. It was shown that $HMn(CO)_5$ is not the main intermediate responsible for the transfer of hydrogen by the chloroalkyl radicals, which are formed during the reduction of 1,3,3,5-tetrachloropentane by triethylsilane in the presence of $Mn_2(CO)_{10}$.

A distinguishing feature of systems based on transition-metal carbonyls (TMC) compared with the traditional initiators of radical processes in organic synthesis involving halogen-containing compounds is their selectivity. The selectivity of the transition-metal carbonyls can show up both at the initiation stages and at the stages of transfer of the halogen or hydrogen to the organic radicals [1].

It is known [2, 3] that the radical-cations of the metals are formed during the reaction of $Fe(CO)_5$ and $Cr(CO)_6$ with triphenylphosphine in a polyhaloalkane medium. The radical-cations contain $PPh_3$ in the ligand sphere of the metal and can abstract a halogen from the halogen-containing compound and then transfer it to the organic radicals [4-6]. On the basis of kinetic data on the addition of carbon tetrachloride to olefins in the presence of transition-metal carbonyls in [7, 8] it was shown that the chlorine-containing molybdenum and chromium carbonyl particles formed during the reaction can take part in the transfer of chlorine to the radical adducts.

In [9], the ability of $HMn(CO)_5$, like $HRe(CO)_5$, to transfer hydrogen to the chlorine-containing radicals formed during the reduction of 1,3,3,5-tetrachloropentane was studied.

The aim of the present work was to obtain evidence for the participation of the chlorine-containing metal carbonyl particles of iron, chromium, molybdenum, and tungsten in the

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