# EQUILIBRIUM CH-ACIDITY OF CARBAMOYLMETHYLPHOSPHORYL COMPOUNDS IN DIMETHYL SULFOXIDE

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Carbamoylmethylphosphoryl compounds (CMP) $R_2P(O)CH_2C(O)NR_2'$ are used for the extraction of transplutonium and rare earth elements [1-4]. It was found that mercury cations form complexes not with the neutral CMP molecules, but with their anions [3]. The capability of the H atom of the methylene group in the CMP to be substituted by a metal is also taken advantage of in the synthesis [2, 4]. However, no quantitative data are available on the CH-acidity of CMP. It is known only that in benzene, the dialkyl (N,N-diethylcarbamoylmethyl)-phosphonates are much weaker acids than acetylacetone [3].

In the present work, we used the indicator method [5] to study the equilibrium CH-acidity of the CMP series $RR'P(O)CH_2C(O)NEt_2$ in DMSO (Table 1). The determination of pK is based on the spectrophotometric measurement of the equilibrium constant of the proton transition reaction involving the (HA) studied and an indicator ($HA_0$) acid. The position of the equilibrium (1) may depend, in particular, on the degree of association of the anions $A^-$ and $A_0^-$ with the metal cation $M^+$ (in the present work, the $K^+$ cation was used) with the formation of ion pairs [6, 7]

$$HA + A_0^- \overset{K_{eq}}{\rightleftharpoons} A^- + HA_0 \qquad (1)$$

$$pK_{HA} = pK_{HA_0} - \lg K_{eq} \qquad (2)$$

$$A_0^- + M^+ \overset{K_{as}}{\rightleftharpoons} M^+A_0^- \qquad (3)$$

$$A^- + M^+ \overset{K'_{as}}{\rightleftharpoons} M^+A^- . \qquad (4)$$

Ionic association in dilute solutions in DMSO is usually neglected, since DMSO readily solvates the alkali metal cations. It is known that at concentrations of $10^{-2}$-$10^{-5}$ mole/liter in DMSO, the K salts of substituted fluorenes that we used as indicators $HA_0$ are completely dissociated into ions [8], so that equilibrium (3) need not be taken into account. Equilibrium (4), at which a chelate coordination of cation $K^+$ with the CMP anion is possible, requires further investigation.

During ionic association [equilibrium (4)], the measured equilibrium constant of the proton transition $K_{meas}$ is related to the $K_{eq}$ value by the relationship

$$K_{meas} = K_{eq} \quad \{([A^-] + [A_0^-]) K_{as}' + 1\} . \qquad (5)$$

The true value of pK [corresponding to equilibrium (1)] is lower than the measured one by the amount ΔpK

$$\Delta pK = \lg \{([A^-] + [A_0^-]) K_{as}' + 1\} .$$

In experiments to determine the pK of CMP, the sum of concentrations ($[A^-]$ + $[A_0^-]$) did not exceed $1 \cdot 10^{-3}$ mole/liter, and therefore the ΔpK value could exceed the limits of experimental error (±0.1 log. units) only at values of $K_{as} > 300$ liters/mole. A conductimetric investigation of certain CMP salt solutions in DMSO (Table 2) showed that they are weakly associated ($K_{as} \le 300$ liters/mole), so that equilibrium (4) also need not be taken into account.

Finally the pK value of CMP in DMSO can also be influenced by the coordination of cation $K^+$ with the neutral CMP molecule

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TABLE 1. Equilibrium CH-Acidity of $RR'P(O)CH_2C(O)NEt_2$ in DMSO Relative to 9-Phenylfluorene (pK 18.5 [5]), Counterion $K^+$, 298 K

| Compound | RR′ | pK | Indicator (pK)* | $K_{eq}$ † | $\sigma_{CH_2}^-(RR'P(O))$ | $\Sigma\sigma P$ |
|---|---|---|---|---|---|---|
| (I) | $(t\text{-}Bu)_2$ | 25,7 | 1,1,3,3-Tetraphenylpropene (26.2) | 3,39±0,10 | 0,44 ‡ | −3,10 |
| (I) | $(t\text{-}Bu)_2$ | 25,7 | 9-tert-Butylfluorene (24.6) | 0,08±0,01 | | |
| (II) | $(Et_2N)_2$ | 25,6 | 1,1,3,3-Tetraphenylpropene (26.2) | 4,28±0,08 | 0,46 | −3,08 |
| (III) | $Bu_2$ | 25,0 | 9-tert-Butylfluorene (24.6) | 0,46±0,11 | 0,45 | −2,44 |
| (III) | $Bu_2$ ** | 25,0 | » | 0,43±0,07 | | |
| (IV) | $(cyclo\text{-}Hex)_2$ | 25,0 | » | 0,38±0,04 | 0,46 ‡ | −2,38 |
| (V) | $Et_2$ | 25,0 | » | 0,35±0,03 | 0,47 | −2,20 |
| (VI) | PhBu | 23,6 | Fluorene (22.9) | 0,18±0,02 | 0,51 | −1,70 |
| (VII) | $(p\text{-}MeC_6H_4)_2$ | 22,7 | » | 1,4±0,2 | 0,55 | −1,44 |
| (VIII) | $Ph_2$ | 22,6 | » | 2,1±0,15 | 0,57 | −1,18 |
| (IX) | Ph(EtO) | 22,4 | 9-Benzylfluorene (21.8) | 0,25±0,03 | 0,56 ‡ | −0,69 |
| (X) | $(EtO)_2$ | 22,6 | » | 0,14±0,03 | 0,56 | −0,42 |
| (X) | $(EtO)_2$ ** | 22,6 | » | 0,14±0,05 | | |

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*The pK values of the indicators were taken from [5].

†Mean of the results of 4-6 measurements.

‡Calculated in the present work.

**Measurements with crown-ether.

$$HA + M^+ \xrightleftharpoons{K_{true}} HA \cdot M^+. \qquad (6)$$

It is known, for example, that the logarithms of the stability constants of the CMP complexes with the $K^+$ cation in THF are equal to 2.73-3.70 [9]. To evaluate this source of error in the determination of pK of CMP in DMSO, we measured the $K_{eq}$ values of certain CMP to which dibenzo-18-crown-6 has been added, which forms stable complexes with $K^+$ cations. It was found that the presence of the crown-ether does not change the pK value found [Table 1, compounds (III), (X)]. Thus, in the presence of CMP, the $K^+$ ions in DMSO either remain free, or form very unstable complexes. Hence, it follows that the changes in the pK values in Table 1 reflect the structural effects of the equilibrium CH-acidity of CMP.

## DISCUSSION

The data in Table 1 show that CMP are medium-strength CH-acids. If we compare the pK-values of the CMP studied in DMSO and those of the corresponding carbethoxyl derivatives $RR'P(O)CH_2COOEt$ [10], it can be seen that CMP are weaker acids than the latter by 3.5-4 pK units. Thus, the acidifying action of the carbamoyl group is much lower than that of the carbethoxyl group. This comparison can be expressed quantitatively by calculating from the data in Table 1 [compounds (II), (III), (V)-(VIII), (X), for which the $\sigma_{CH_2}^-$ values of the RR'P(O) groups are known [11]] the $\sigma_{CH_2}^-$ constant for the $C(O)NEt_2$ group. For this calculation the correlative equation was used, derived previously for compounds of type RR'P(O)CHXY [11]

$$pK = 49.98 - 23.919\Sigma\sigma_{CH_m}^- . \qquad (7)$$

A value of $\sigma_{CH_2}^-$ $(CONEt_2)$ = 0.58 ± 0.01 was obtained. Thus the position of the carbamoyl group is established in the known Issleib acidifying ability series of groups (the values of $\sigma_{CH_2}^-$ values are given in brackets): PhCO (0.98) > MeCO (0.88) > CN (0.80) > COOEt (0.725) > $CONEt_2$ (0.58) > RR'P(O) (0.44-0.57), etc.

The CH-acidity of CMP is determined from the Hammet equation when the $\sigma_{CH_2}^-$ constants are used, previously derived in [11, 12]. Unfortunately, the $\sigma_{CH_2}^-$ constants for the $(t\text{-}Bu)_2P(O)$ and $(cyclo\text{-}Hex)_2P(O)$ groups are unknown. With regard to the Ph(EtO)P(O) group, the $\sigma_{CH_2}^-$ value was calculated from the data in [10, 13] and the correlative equations given in [12]. It was found (from four pK values in diglyme and DMSO) that for the Ph(EtO)P(O) group, $\sigma_{CH_2}^-$ = 0.56 ± 0.01. On the whole, from the data in Table 1, a general correlative equation (8) has been obtained, which encompasses the pK values of both CMP [excluding those

TABLE 2. Association Constants of CMP K-Salts in DMSO (298 K) and Spectral Characteristics of CMP Carbanions (THF, 298 K, Counterion $K^+$)

| Compound | $K_{as}$ | $\lambda_{max}$, nm | ε, liter/(mole·cm) |
|---|---|---|---|
| (III) | 300 | 245 | 9000 |
| (VIII) | 140 | – | – |
| (X) | Complete dissociation | 235 | 10400 |

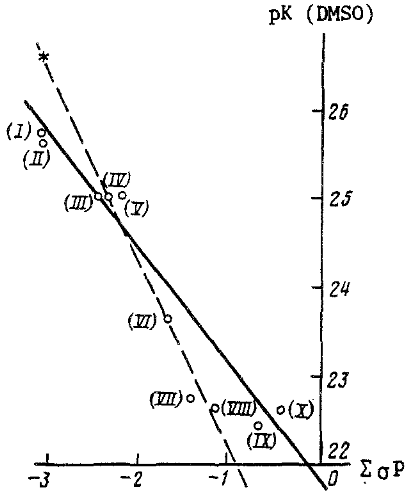

Fig. 1. Dependence of pK (DMSO) of CMP on $\Sigma\sigma^P$. The numeration of points corresponds to the numbers of the compounds shown in Table 1. The dashed line corresponds to equation (9), the continuous line to equation (10). * – pK value calculated for the $(t\text{-}Bu)_2P(O)$-derivative according to Eq. (9).

of compounds (I) and (IV)] and the four indicator CH-acids (for the $PhCH_2$ group, the value $\sigma^-_{CH} = 0.12$ was calculated from the data [14])

$$pK = 52.32 - 26.136\Sigma\sigma^-_{CH_m},\ n = 12,\ r = 0.998, \qquad (8)$$
$$S = 0.31,\ S_\rho = 1.85\ .$$

From (8), we calculated the $\sigma^-_{CH_2}$ constants for the $(t\text{-}Bu)_2P(O)$ and $(cyclo\text{-}Hex)_2P(O)$ groups: 0.44 and 0.46, respectively (of course, the accuracy of these values cannot be vouched for, since each was obtained from a single point). In general, CMP in DMSO behave as normal CH-acids.

Another, although not unexpected pattern is observed during the correlative analysis of the CH-acidity constants of CMP (pK) using the $\sigma^P$ constants. It should be noted that in a correlation of a Hammet CH-acidity of phosphinyl-substituted acetic esters $RR'P(O)CH_2COOEt$ [10] and benzylphosphoryl compounds $RR'P(O)CH_2Ph$ [13] with the substituent constants for the groups on the P atom, $\sigma^P$, a single correlative straight line could not be drawn. Only the corresponding phosphine oxides showed a linear dependence, while compounds with alkoxy groups attached to the phosphorus atom deviated in the direction of larger pK values, and those with dialkylamino groups, in the direction of smaller pK values. At that time, this phenomenon (apparent, as has now been clarified) could not be explained. Figure 1 shows the correlation between the pK of CMP and the $\sigma^P$ constants. The dashed line was drawn through points corresponding to phosphine oxides [point (I), which was obtained later, does not fall on this line]. In accordance with the data for phosphinylacetic esters and benzylphosphoryl compounds, points (IX) and (X) referring to compounds with ethoxy groups fall above this line, while point (II) for compound with diethylamino groups attached to the phosphorus atom falls below. The correlative equation is as follows:

$$pK = 19.87 - 2.175\Sigma\sigma^P,\ n = 6,\ r = 0.980, \qquad (9)$$
$$S = 0.23,\ S_\rho = 0.22\ \cdot$$

However, there is another possibility of correlation, with respect to all points, excluding only points (VII) and (VIII) relating to compounds with two aromatic substituents at the P atom (a continuous line on Fig. 1). In this case the points, relating to compounds with

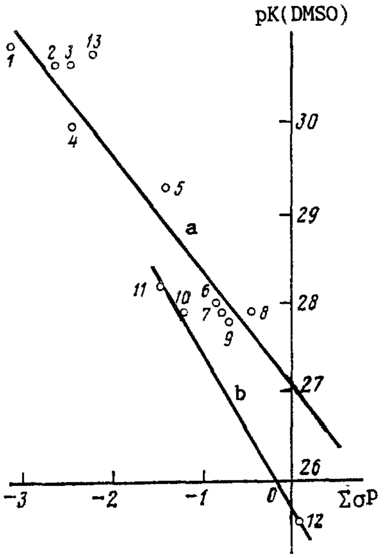

Fig. 2

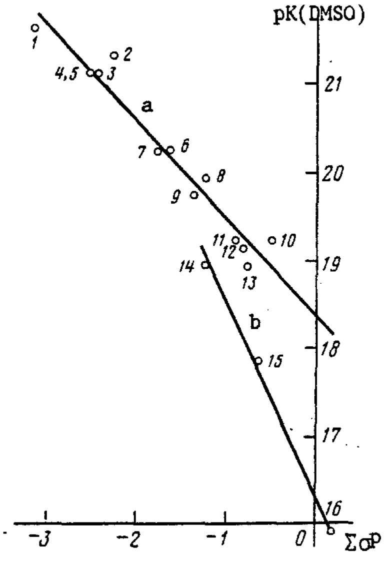

Fig. 3

Fig. 2. Dependence of pK (DMSO) of CH-acids $RR'P(O)CH_2Ph$ on $\Sigma\sigma^P$ according to [13]: a) compounds with aliphatic groups at the P atom (R, RO, $R_2N$) and compounds with one aryl; b) compounds with two aryls at the P atom. $RR'P(O)CH_2Ph$—R and R': 1) $(Et_2N)_2$; 2) $(i\text{-}Pr)_2$; 3) $Bu_2$; 4) $(Me_2N)_2$; 5) EtPh; 6) $(BuO)_2$; 7) $(EtO)_2$; 8) $(i\text{-}AmO)_2$; 9) Ph(EtO); 10) $Ph_2$; 11) p-$Tol_2$; 12) $(m\text{-}CF_3C_6H_4)_2$; 13) $Et_2$.

Fig. 3. Dependence of pK (DMSO) of phosphinylacetic esters $RR'P(O)CH_2COOEt$ on $\Sigma\sigma^P$ according to [10]: a) compounds with aliphatic groups at the P atom (R, RO, $R_2N$) and compounds with one aryl; b) compounds with two aryls at the P atom. $RR'P(O)CH_2COODEt$—R and R': 1) $(Et_2N)_2$; 2) $Et_2$; 3) $Pr_2$; 4) $Bu_2$; 5) $(Me_2N)_2$; 6) EtPh; 7) BuPh; 8) Me(EtO); 9) Et(EtO); 10) $(EtO)_2$; 11) $(BuO)_2$; 12) $(i\text{-}AmO)_2$; 13) Ph(EtO); 14) $Ph_2$; 15) $(p\text{-}ClC_6H_4)_2$; 16) $(m\text{-}NO_2C_6H_4)_2$.

alkoxy and diethylamino groups [(II), (IX) and (X)], naturally are included in the correlation.

$$pK = 21.78 - 1.297\Sigma\sigma^P;\ n = 7,\ r = 0.976,\ S = 0.31,\ S_\rho = 0.13\,. \tag{10}$$

To solve the problem as to which of the correlations corresponds to the actual relationships, we synthesized compound (I) $(t\text{-}Bu)_2P(O)CH_2C(O)NEt_2$. This is a phosphine oxide with a large negative value for the sum of $\sigma^P$ constants (−3.10). According to correlation (9) (the dashed line in Fig. 1), the pK of this CH-acid should be 26.6, while according to correlation (10) (the continuous line) it should be 25.8. Measurement showed a constant of 25.7, which confirms the adequacy of the second correlation. Taking into account point (I), the final equation obtained is:

$$pK = 21.80 - 1.281\Sigma\sigma^P;\ n = 8,\ r = 0.979,\ S = 0.29,\ S_\rho = 0.11\,. \tag{11}$$

Thus, the points corresponding to compounds with two aromatic substituents at the P atoms deviate from the general correlative dependence. This phenomenon is not new. The so-called "aryl effect" consisting in the deviation of the properties of the organophosphorus compounds carrying two aryl substituents at the P atom, from the uniformly changing properties of all the other organophosphorus compounds of this type, has been observed on more than one occasion. It was observed during the investigation of acid—base properties, complexation, extraction, in particular, with the use of CMP as extractants [2, 9].

Taking the above facts into account, it was seen as necessary to reexamine the previously published correlative dependences of the pK of the CH-acids of the phosphinylacetic esters [10] and benzylphosphoryl compounds type [13]. It was here also necessary to combine into one correlative relationship all the CH-acids of one series studied, excluding from the correlation the points corresponding to compounds with two aromatic substituents. Correlative equations (12) and (13) were thus obtained. For $RR'P(O)CH_2Ph$ [13] (Fig. 2)

TABLE 3. Yields, Constants and Analysis Data for CMP

| Compound | Empirical formula | Yield, % | Mp, °C, bp, °C (p, mm Hg) | $n_D^{20}$ | Found/Calculated, % |  | $\delta^{31}P$, ppm (DMF) |
|---|---|---|---|---|---|---|---|
|  |  |  |  |  | P | N |  |
| (I) | $C_{14}H_{30}O_2NP$ | 70 | 86-87 (heptane-ether, 2:1) | – | 11,0/11,3 | 4,9/5,1 | 58,3 * |
| (II) | $C_{14}H_{32}O_2N_3P$ | 56 | 94–95(0,008) † | 1,4779 † | 10,0/10,1 | – | 28,2 * |
| (V) | $C_{10}H_{22}O_2NP$ | 65 | 144–145(0,5) | 1,4840 | 13,8/14,1 | 6,7/6,4 | 46,2 |
| (V) | $C_{10}H_{22}O_2NP$ | 74 | 145–146(0,5) | 1,4838 |  |  | 46,2 |
| (VII) | $C_{20}H_{26}O_2NP$ | 71 | 104-105 (benzene-ether, 2:1) | – | 9,1/9,0 | 4,3/4,1 | 25,7 |
| (IX) | $C_{14}H_{22}O_3NP$ | 49 | 171–172(2) | 1,5220 | 10,7/10,9 | 4,9/5,3 | 34,8 |
| (X) | $C_{10}H_{22}O_4NP$ | 50 | 142–143(1) | 1,4550 | 12,2/12,3 | 5,1/5,5 | 22,0 |

*Benzene.
†Cf. [15].

$$pK = 27.06 - 1.326\Sigma\sigma^{P};\ n = 9,\ r = 0.982,\ S = 0.27,\ S_\rho = 0.09 \tag{12}$$

[point (13) corresponding to compound $Et_2P(O)CH_2Ph$ clearly is excluded from the correlation]. For $RR'P(O)CH_2COOEt$ [10] (Fig. 3)

$$pK = 18.41 - 1.110\Sigma\sigma^{P},\ n = 13,\ r = 0.974,\ S = 0.22,\ S_\rho = 0.08. \tag{13}$$

The points corresponding to the compounds with aromatic substituents at the P atom form an individual straight line. Because of the small number of points (not more than three), it was not possible to calculate parameters, but from Figs. 2 and 3 it can readily be seen that these points lie on one line, passing below the main correlative line.

A similar pattern is also observed in diglyme solutions, but in this case, the quality of the correlations is lower. The possible reason for this is that in diglyme not the free-ionic acidity, but a certain effective acidity is measured, which is a combination of free-ionic and ion-pair acidities. The formation and nature of ion pairs strongly depend on the character of the groups attached to the phosphorus atom. This fact was taken into account in [11]. Thus, also with respect to the correlative analysis using the $\sigma^P$ constants, the CMP exhibit a typical behavior.

The CMP studied in the present work were synthesized by known methods: compounds (III), (IV), and (VIII) according to [2], and (VI) according to [9]. For the preparation of the remaining CMP, the following methods were used: A – reaction of the ethoxy derivative of trivalent phosphorus with N,N-diethylchloroacetamide (XI) according to A. E. Arbuzov

$$RR'P(OEt) + ClCH_2CONEt_2 \rightarrow RR'P(O)CH_2CONEt_2;$$

B – the same, but with the butoxy derivative; C – the Michaelis and Becker reaction of the K derivative of a partial ester of a trivalent P with (XI)

$$RR'P(O)H \xrightarrow{K} RR'POK \xrightarrow{ClCH_2CONEt_2} RR'P(O)CH_2CONEt_2.$$

The yields and constants of the compounds obtained are given in Table 3.

## EXPERIMENTAL

The $^{31}P$ NMR spectra were run on a Bruker HX-90 apparatus using 85% $H_3PO_4$ as external standard and the IR spectra were recorded on a UR-20 spectrophotometer. In the IR spectra of compounds (I), (II), (V), (VII), (IX), (X) intense bands were observed, characteristic of the P=O group (1195-1265 $cm^{-1}$) and the N–C=O groups (1640-1650 $cm^{-1}$).

Di(tert-butyl)(N,N-diethylcarbamoylmethyl)phosphine Oxide (I). A 3.6 g portion (0.018 mole) of O-ethyl (ditert-butyl)phosphinite was added at 150°C to 2.8 g (0.018 mole) of (XI), and the mixture was held for 1 h at 150°C. The mixture crystallized on cooling. Yield, 3.5 g (70%) of (I).

Bis(N,N-diethylamido)(N',N'-diethylcarbamoylmethyl) phosphonate (II) was obtained from 13.4 g (0.06 mole) of O-ethyl di(N,N-diethylamide)phosphinite and 9.1 g (0.06 mole) of (XI) in 30 ml of absolute toluene at 140-150°C (bath temperature). Yield, 10.3 g (56%) of II.

Diethyl(N,N-diethylcarbamoylmethyl)phosphine oxide (V) was obtained by methods B and C (see above). Method B: A 7.3-g portion (0.05 mole) of O-butyl diethylphosphinite was added at 160°C to 7.5 g (0.05 mole) of (XI), and the mixture was held for 1 h at 160°C. The mixture crystallized on cooling. Yield, 6.3 g (65%) of (V). The material was chromatographed on $Al_2O_3$ (grade II activity), $R_f$ 0.77 (benzene:alcohol, 2.5:1).

Method C. A mixture of 5.4 g (0.05 mole) of diethylphosphinous acid, 2 g (0.05 g·at) of potassium (dispersed according to Brul in 50 ml of absolute xylene), and 7.5 g (0.05 mole) of (XI) was held for 2 h at 100°C. Yield, 7.2 g (74%) of (V). The material was chromatographed on $Al_2O_3$ (grade II activity), $R_f$ 0.8 (benzene:alcohol, 2.5:1).

Di(p-tolyl)(N,N-diethylcarbamoylmethyl)phosphine oxide (VII) was obtained from 12.4 g (0.08 mole) of (XI) and 21.4 g (0.08 mole) of O-ethyl (p-tolyl)phosphinite under the same conditions as during the preparation of (V) by method B. Yield, 20.6 g (71%) of (VII).

O-Ethylphenyl (N,N-diethylcarbamoylmethyl)phosphinate (IX). A solution of 9.3 g (0.05 mole) of O-ethyl phenylphosphonite in 40 ml of ether was added to 2.1 g (0.05 g•at.) of potassium in 40 ml of ether. The mixture was boiled for 2 h, and then 7.4 g (0.05 mole) of (XI) were added. Yield, 7.6 g (49%) of (IX). The material was chromatographed on $Al_2O_3$ (grade II activity), $R_f$ 0.4 (benzene).

O-O-Diethyl (N,N-diethylcarbamoylmethyl)phosphonate (X) was obtained under the same conditions as in the preparation of (V) by method B. From 8.2 g (0.5 mole) of triethyl phosphite and 7.4 g (0.05 mole) of (XI), 6.1 g (50%) of (X) were obtained. The material was chromatographed on $Al_2O_3$ (grade II activity), $R_f$ 0.6 (benzene:alcohol, 2:1).

Determination of Equilibrium CH-Acidity of CMP (I)-(X). Before the measurements, the compounds were dried in vacuo; DMSO was purified according to [5]. The transmetallation reactions were carried out in dilute DMSO solutions (concentration lower than $10^{-3}$ mole/liter), using an apparatus evacuated to $1\cdot10^{-4}$ mm Hg, and a freshly distilled solution of potassium dimsyl as the metallating agent. The pK values were calculated from spectrophotometric determinations of concentrational equilibrium constants $K_{eq}$ of the reactions of the CH-acids studied with K-salts of the CH-indicators by the method in [5]. The equilibrium constants of the reactions, the indicators used and their pK values are listed in Table 1. In most cases, the error in the determination of the equilibrium constants is such that the accuracy in the evaluation of pK is not lower than 0.1 log units. The spectral measurements were carried out in tightly sealed quartz cuvettes on a SF-26 spectrophotometer.

Determination of Equilibrium CH-Acidity in the Presence of Crown-ether. A sample of dibenzo-18-crown-6 (a double excess with respect to $K^+$) was introduced both before the beginning of the transmetallation reaction and after establishment of equilibrium. In both cases the position of the equilibrium did not change.

Electrical Conductivity of Solutions of CMP K Salts in DMSO was measured in the concentration range of 1 to $500\cdot10^{-5}$ mole/liter at a frequency of 1000 Hz in a cell with polished Pt electrodes (cell constant 0.036 $cm^{-1}$), using an R-5010 universal bridge. The dissociation constants were calculated by the Shidlovskii method. The solutions of the salts in DMSO were prepared in a tightly sealed vacuum apparatus using potasium dimsyl as the metallating agent, whose concentration was previously found spectrophotometrically relative to 9-phenylxanthene. The dilution of the solutions was carried out by recondensation of a given amount of DMSO into a volume connected to an electrical conductivity measuring cell.

The solutions of the CMP K salts in THF were prepared in an evacuated tightly sealed apparatus, using metallic potassium as metallating agent. The solution of CMP in THF of a given concentration was poured off onto a potassium mirror (the reaction proceeds quantitatively [3]) and then decanted.

## CONCLUSIONS

1. The equilibrium CH-acidity of carbamoylmethylphosphoryl compounds (CMP) relative to 9-phenylfluorene was determined by the indicator method in DMSO ($K^+$ counterion).

2. A linear correlation has been established between the pK values of CMP with the $\sigma_{\bar{C}H_2}$ constants of the substituents at the central C atom. The $\sigma_{\bar{C}H_2}$ constants were calculated for the $(t\text{-}Bu)_2P(O)$, $(cyclo\text{-}Hex)_2P(O)$, Ph(EtO)P(O) and $C(O)NEt_2$ groups.

3. Analysis of the dependences of the pK of CMP and other previously studied phosphoryl-substituted CH-acids on $\Sigma\sigma P$ of the substituents at the P atom shows that for all compounds, except for those containing an $Ar_2P(O)$ group, there is a single linear dependence. Compounds with two aryl groups at the P atom show a different dependence.

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# THERMODYNAMICS AND KINETICS OF THE COMPLEXING OF THALLIUM 3,6-DI-TERT-BUTYL-o-BENZOSEMIQUINOLATES WITH SOME COMPLEXING AGENTS

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Spectrophotometric and electrical-conductivity methods are currently the principal methods for the study of the complexing of amino-substituted phosphine oxides with transition and nontransition metals in the liquid phase. Their use has made it possible to evaluate the thermodynamic parameters of these processes and to obtain a comparative characterization of the complexing properties of organophosphorus ligands as a function of the structure [1-3]. In our opinion, the use of the EPR method may give additional information for the study of this process, since it makes it possible to evaluate not only the thermodynamics but also the kinetics of complexing in a number of cases.

o-Semiquinolate complexes of monovalent thallium, which are formed in the reaction of Tl metal with o-benzoquinones, were first detected in 1974 [4]. The EPR spectra of these particles are characterized by hyperfine coupling (HFC) of the unpaired electron with the nuclei of the paramagnetic $^{203}Tl$ and $^{205}Tl$ isotopes ($I = 1/2$) and the aromatic protons of the o-semiquinolate ligand. It was established that thallium complexes have high stability and that the HFC from Tl nuclei ($a_{Tl}$) is extremely sensitive to the nature of the solvent

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