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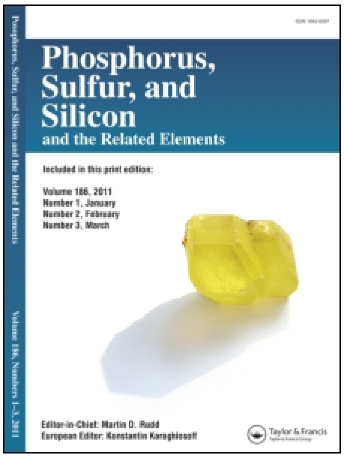

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ANALYSIS OF AMBIDENT REACTIVITY OF ALKALINE SALTS OF PHOSPHORUS MONOTHIOACIDS

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Abstract The ambident reactivity of alkaline salts of phosphorus monothioacids in alkylation reactions has been studied. The role of structure of ambident anions and ion pairs formation was established. The alkylation rate constants of the free anions and ion pairs are calculated. For the first time the complete quantitative analysis of the ambident reactivity in the alkylation of alkaline salts of phosphorus monothioacids is presented.

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The alkaline salts of phosphorus monothioacids are the typical ambident systems. The alkylation of these compounds by various alkylating agents in different solvents affords, as a rule, the S-esters. However, as early as in late 70-ties we have shown that the strong electrophilic agents (alkyl tosylates) in the aprotic highly dissociating solvents afford the considerable relative yield (occasionally predominating) of the O-esters[1].

$$\text{ABPSONa} + \text{RX} \longrightarrow \text{ABP(O)SR} + \text{ABP(S)OR} + \text{NaX}$$

It could be suggested that the invariable S-alkylation of the alkaline salts of phosphorus monothioacids is due to the shielding of the oxygen atom of the triad. The pathway to discard the shielding effect consists in using the aprotic dipolar solvents such as DMF and HMPA possessing the high dissociating strength (cf.[2-4]). In this case the alkylation is to affect the free anion of monothioacid, and the site of alkylation is determined not by the effect of the external factor (the shielding) but rather by the ambident reactivity inherent to the anion.

Accepting HMPA as the most appropriate solvent we have studied the effect of the substituents at the phosphorus atom in the salts of monothioacids on the relative yield (Q_S/Q_O) of the isomeric esters. The alkylating agents were propyl and iso-propyl tosylate. The Q_S/Q_O ratio was found to decrease in the order of thiophosphates > thiophosphonates > thiophosphinates. In the Hammett coordinates thiophosphates and phosphonates yielded the linear dependence, with the points corresponding to thiophosphinates deviating from this linear behavior.

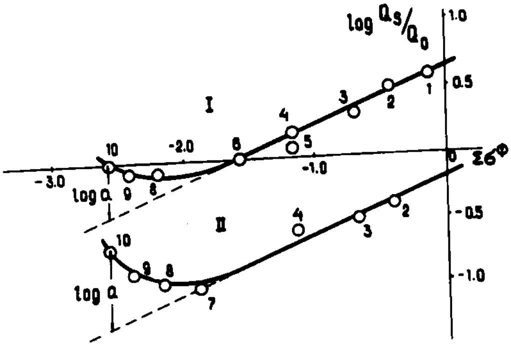

FIGURE 1 The Hammett correlation of log Q_S/Q_O by alkylation of sodium salts of phosphorus monothioacids: I - PrOTs, II - iso-PrOTs

For the linear region the Q_S/Q_O ratio was independent of the degree of conversion, and thus $Q_S/Q_O = k_s/k_o$, where k_s and k_o are the corresponding rate constants. In this region the Q_S/Q_O ratio was independent of the nature of counter ion too. From

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this it followed that the linear region is associated with the alkylation of the free ambident anions. This suggestion was confirmed by the linear dependence of $\log(Q_S/Q_O)$ on $\log(Q_{SH}/Q_{OH})$, where Q_{SH} and Q_{OH} are the relative contents of the SH- and OH-forms in the tautomeric equilibrium of phosphorus monothioacids, which has been studied by us previously[5].

Finally, the dissociation of salts in HMPA was studied by the conductance methods. Thiophosphates and phosphonates at concentrations about 10^{-2} mol/l in HMPA were found to dissociate by more than 60%, and thiophosphinates dissociate in small extent, occurring in solution mainly as the ion pairs.

There were good reasons to believe that in the region associated with the deviation from linear behavior together with the reactions of the free ions the competing reactions of the ion pairs begin to play the role, which by virtue of shielding can yield only S-ester. This accounts for the deviations resulting in the prevailing yield of the S-esters.

In order to look into this problem the kinetics of alkylation of these salts by propyl and iso-propyl tosylate was studied, and the rate constants k_{II} were measured. Taking into account the dissociation constants of salts, and assuming the concentration of the sodium ions to be constant during the alkylation, the equation was derived for the deviations from linear behavior:

$$a - 1 = \frac{k'_s}{k_s} \cdot \frac{[Na^+]_o}{K_d}$$

where log(a) is the deviation of the experimental point from the extrapolated linear dependence (Figu-

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re 1), and k'_s is the rate constant of S-alkylation of the ion pairs. Using k_{II} and (a) the partial constants k_s, k_o and k'_s were calculated. All three rate constants obeyed the Hammett equation (Figure 2).

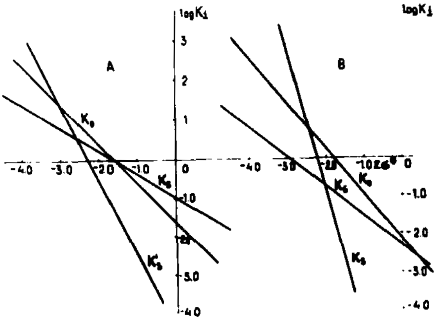

FIGURE 2 The dependences k_s, k_o and k'_s versus $\sum \sigma^{\Phi}$. A - PrOTs, B - iso-PrOTs.

To sum up, the following conclusions can be stated. The alkylation of thione-thiole phosphorus systems naturally obeys just the same general regularities, which were established for the other ambident systems. This refers in particular to the action of external factors.

However, the thione-thiole phosphorus systems allowed to get a deeper understanding of the character of internal factors action, and the results obtained are, perhaps, of a quite general nature.

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