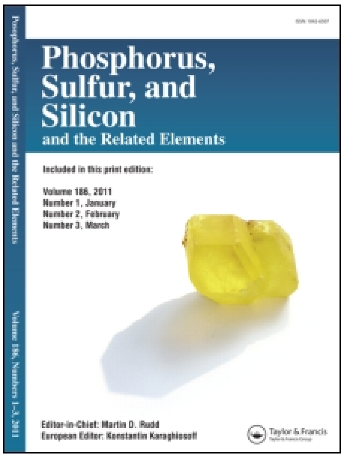

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Isotope Effect Evidence for Charge Localization in Phosphothioates

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ISOTOPE EFFECT EVIDENCE FOR CHARGE LOCALIZATION IN PHOSPHOTHIOATES

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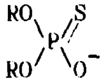
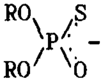
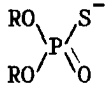
The problem of charge localization in phosphothioates got more attention since thioanaloges proved useful for stereochemical investigations of biochemical processes. On the basis of the existing evidence the structure 1c has been confirmed for aqueous solutions.


1a


1b


1c

We address here the problem of charge localization in phosphothioates in aprotic media using kinetic isotope effects. $S_N2(P)$ reaction of alkyl halides with the anion 1 gives thiolo ester as the only product:

$$\underline{1} + C_2H_5J \text{ ----> } (RO)_2P(O)SC_2H_5 + J^-$$

Extensive theoretical calculations of kinetic isotope effects, by means of BEBOVIB IV program, confirmed that the isotope effects of either oxygen or sulfur should allow us to indicate the most probable form of anion 1

Kinetic isotope effects

calculated			measured for oxygen			
isotope	1a	1c	f	R_f	R_0	α^a
^{18}O	0,9782	1,0000	0.5	1.3311	1.3472	0.9814
^{36}S	1,0082	0,9969	0.6	1.3347		0.9837
^{32}P	1,0020	0,9996	0.7	1.3392		0.9876
^{13}C	1,063	1,062	0.8	1.3366		0.9789
					mean^b:	0.983±0.002

[a] After correction for the natural abundance
[b] The error reported is standard deviation of the mean

The comparison of the theoretical predictions of oxygen kinetic isotope effect for two alternative mechanisms with the experimental value suggests that the reaction proceeds via upper path of the scheme. The actual form of the anion 1 in acetonitryle at 50°C is therefore 1a with negative charge localized on oxygen atom.