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Podand Solvents for Organic Reactions

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Three tris(oxaalkyl)phenylsilanes and two tris(oxaalkyl) phosphates were used as podand solvents in kinetic studies of proton transfer reactions between C-acids: dimethyl (4-nitrophenyl)malonate or phenyl-4-nitrophenylcyanomethane and the strong base: 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD). The acceptor numbers were measured for all new podand solvents. The kinetic parameters for studied reactions were obtained, discussed and compared with those of acetonitrile and OP(OEt)$_3$ as non-podand solvents. This study demonstrated that the second order rate constants strongly decreased and the energy barrier increased for the proton transfer reaction in podand solvents.

Spectroscopic observations showed that ionic products were strongly stabilised and therefore their lifetime was relatively long. The podand solvents formed the ionic channels in which ionic products are strongly solvated.

Keywords: Podand solvents; Tris(oxaalkyl) phosphates; Tris(oxaalkyl)phenylsilanes; Proton transfer reaction

INTRODUCTION

One of the most important factors in the kinetic studies of reactions in solutions is the selection of an appropriate solvent. The solvents have a strong influence on the kinds of reaction, the form of the substrate and the structure of the product. The solvent should not be considered only as a macroscopic medium characterised by physical constants such as density, dielectric constant and index of refraction, but also as a medium that consists of individual, mutually interacting solvent molecules. The interaction between species in solvents is on the one hand too big for it to be treated by the laws of the kinetic theory of gases, but on the other hand, it is too small for it to be treated by the laws of solid state physics [1,2].

It is difficult to systematise the numerous organic and inorganic solvents. Solvents can be classified according to their physical and chemical properties like chemical construction, physical constants, semi-empirical parameters, solvent effect, polarity, acid–base behaviour, etc.

In previous papers [3–5], we described the synthesis of bis- and tris-(oxaalkyl) podands. In these papers, we demonstrated that this new type of podands formed stable complexes with excess protons, metal cations and SbCl$_5$ in different solvents (Scheme 1).

We also demonstrated that ligands with two or three polyoxaethylene chains including boron, sulphur or phosphorus atoms can form proton or cation channels, in which large proton or metal cation polarizability was observed due to the fast fluctuation of the cations (Scheme 2).

In our opinion, the pronounced increase of the stability of ionic arrangements observed for podand solvents is due to the formation of such cation channels.

In this paper, for the first time, we applied podands as solvents. The structures of these podand solvents are shown in Scheme 3.

These compounds are characterised by the different lengths of the polyoxaalkyl chains. The influence of these podand solvents was studied in the proton transfer reactions between C-acids such as phenyl(4-nitrophenyl)cyanomethane and dimethyl (4-nitrophenyl)malonate with a strong N-base: 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD) by kinetic methods. The formulas of the C-acids and the N-base are given in Scheme 4.

For comparison analogous studies were done for non-podand solvents such as OP(OEt)$_3$. It is interesting to note that the deprotonation reactions of C-acids by various N-bases in acetonitrile were previously studied by us and the mechanism of

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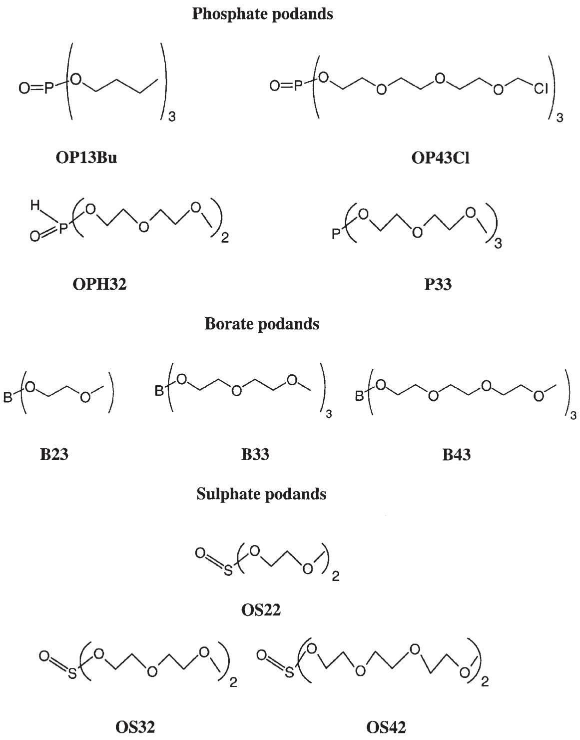


SCHEME 1

the proton transfer reaction has been described [6–8]. In this paper, the difference between acetonitrile as medium and podand solvents is discussed.

RESULTS AND DISCUSSION

As mentioned above, the group of podands form complexes with excess protons, metal cations and neutral molecules in different solvents.

For podand solvents donor and acceptor numbers were determined by calorimetric and ^{31}P NMR methods, using procedures described by Gutmann [10,11], respectively. The obtained donor and acceptor numbers are collected in Table I. For the sake of comparison the acceptor and donor numbers of phosphorane esters OP(OEt)$_3$ and OP(OBu)$_3$ as non-podand solvents are also given.

TABLE I Acceptor and donor numbers for studied solvents

Solvent	Acceptor number	Donor number* [9]
PhSi23	25.8	181
PhSi33	13.4	268
PhSi43	11.5	356
OP23	16.5	118
OP33	13.4	132
OP(OEt)$_3$	20.4	108

* Heats of interaction of macrocyclic compounds with $SbCl_5$ in CCl_4 solution (complex 1:1).

As the chain length increases, the acceptor number decreases, but the donor number increases. In the case of the phosphorus esters, the values of acceptor and donor number show insignificant changes.

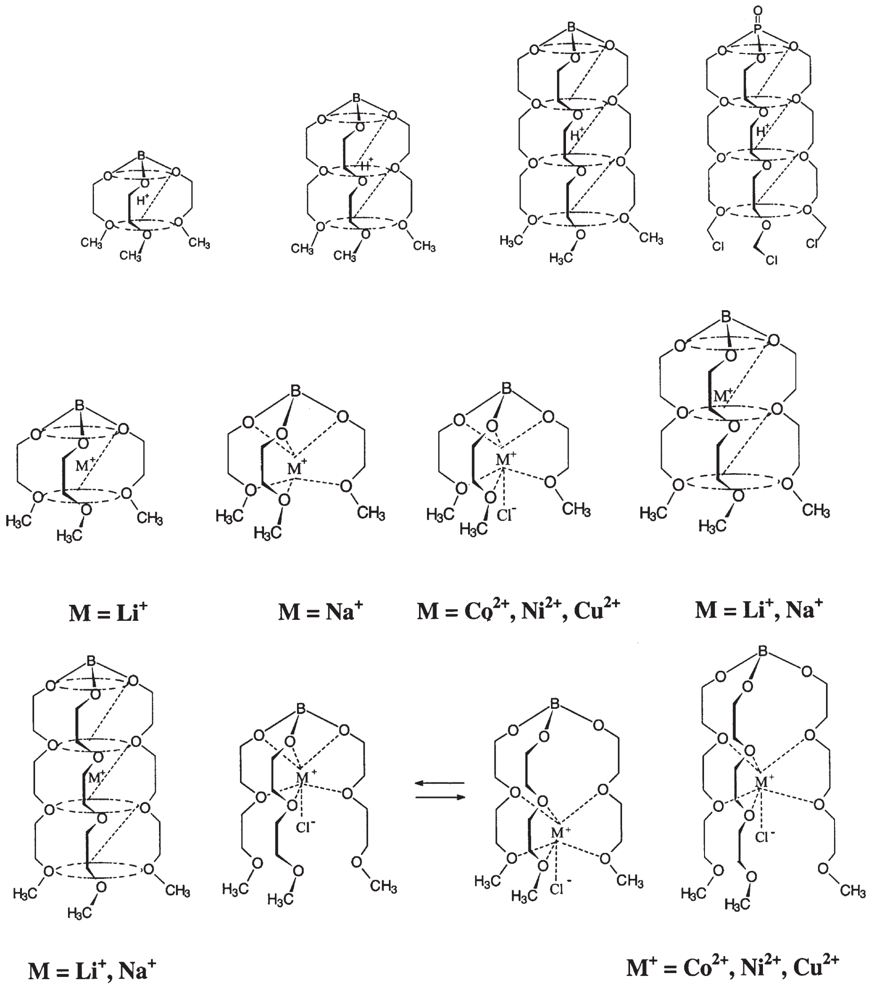
The Proton Transfer Reaction Between Dimethyl (4-Nitrophenyl)malonate and MTBD in Si-podand Solvents

The kinetic parameters for the reaction between dimethyl (4-nitrophenyl)malonate and MTBD in Si-podand solvents are shown in Tables II–IV. In Table II, the values of the observed rate constants of these reactions are collected. On the basis of these values, the second order rate constants were calculated and are summarised in Table III. For comparison, the corresponding values in acetonitrile solvent are also given. The values of the second order rate constants at 25°C are about 2000 dm^3 mol^{-1} s^{-1} and are almost independent of the polyoxaalkyl length chain of the Si-podand solvents. Comparison of these values with that obtained in acetonitrile solvent demonstrates clearly a significant decrease in the reaction rate. The kinetic parameters of these reactions observed in acetonitrile are mostly comparable with the Si-podand solvent with the shortest polyoxaalkyl chain (PhSi23). It is understandable because this podand solvent is polar and its acceptor number is very similar.

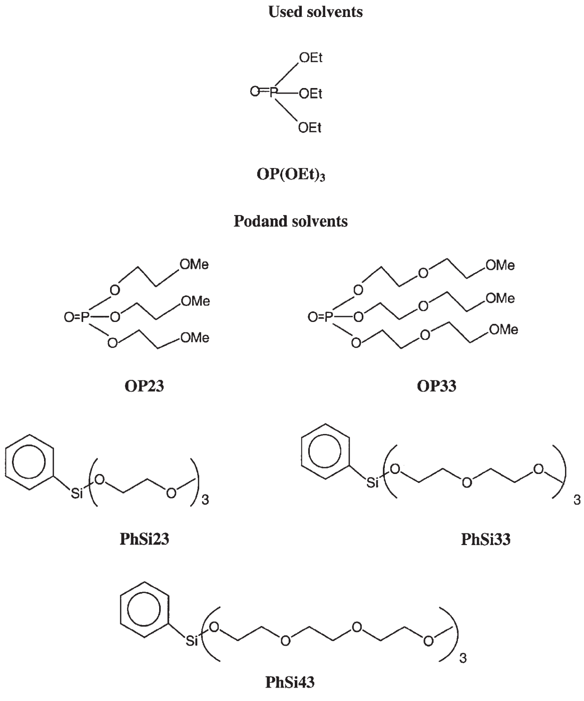
These second rate constants in Si-podand solvents are about 3-times smaller than those in classic solvents such as acetonitrile. However, the various dependencies of the second order rate constants on temperature are reflected in the values of the enthalpy of activation for the reactions in Si-podand solvents (Table IV).

As the polyoxaalkyl chain length increases the values of the activation parameters $(\Delta H^{\neq}, \Delta S^{\neq})$ strongly decrease. This dependence demonstrates that the energy barrier is determined by the number of O-atoms in the chains. Furthermore, the values of the $\Delta G^{\neq}$ parameters are independent of the Si-podand solvent chain length, indicating the comparable solvation process of the transition state for the reaction studied in Si-podand solvents.

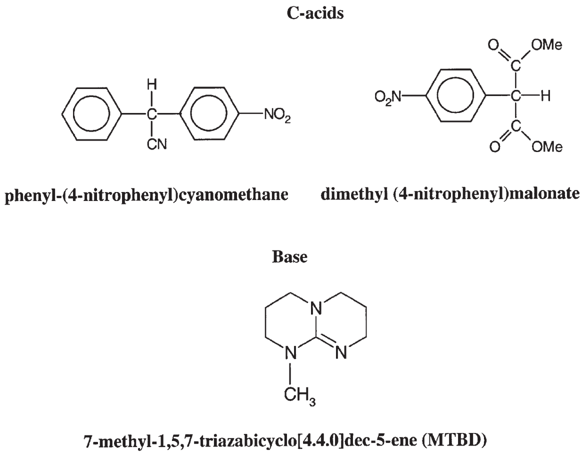
It is very interesting to note that the ionic product of the proton transfer reaction in acetonitrile solvent is very unstable and undergoes various further reactions. This means that the lifetime of such a product is very short (a few minutes). In contrast, in the case of Si-podand solvents the lifetime of the ionic product of the proton transfer reaction is very long (a few days). This observation is confirmed by UV–VIS spectra of the ionic product measured at various times.



SCHEME 2



SCHEME 3



SCHEME 4

TABLE II Observed rate constants (± standard deviation) for reaction between dimethyl (4-nitrophenyl)malonate MTBD in Si-podand solvents

Podand solvent	MTBD (M)	k_{obs} (s^{-1}) at 15°C	k_{obs} (s^{-1}) at 25°C	k_{obs} (s^{-1}) at 35°C	k_{obs} (s^{-1}) at 45°C
PhSi23	0.10	174 ± 3	341 ± 3	564 ± 4	831 ± 8
	0.15	229 ± 5	434 ± 6	690 ± 7	1010 ± 11
	0.20	301 ± 7	546 ± 8	825 ± 11	1210 ± 20
	0.25	360 ± 9	640 ± 12	980 ± 15	1422 ± 25
PhSi33	0.025	47 ± 1	118 ± 1	263 ± 1	433 ± 4
	0.10	160 ± 1	280 ± 2	530 ± 1	680 ± 5
	0.15	236 ± 1	400 ± 2	621 ± 7	870 ± 8
	0.20	338 ± 2	496 ± 3	760 ± 7	1054 ± 10
	0.25	409 ± 2	606 ± 8	889 ± 10	1196 ± 30
PhSi43	0.025	40 ± 1	100 ± 1	240 ± 3	360 ± 4
	0.10	160 ± 1	252 ± 2	400 ± 3	560 ± 5
	0.15	240 ± 1	348 ± 3	506 ± 2	685 ± 5
	0.20	327 ± 1	449 ± 3	617 ± 4	815 ± 6
	0.25	393 ± 1	528 ± 4	713 ± 6	910 ± 8

The Proton Transfer Reaction Between Phenyl (4-Nitrophenyl)cyanomethane and MTBD in Phosphate Solvents

We studied the kinetics of the proton transfer reaction between phenyl(4-nitrophenyl)cyanomethane and MTBD in two types of phosphate solvents, i.e. triethyl phosphate [$OP(OEt)_3$] and tris(oxaalkyl)phosphates: OP23 and OP33. The first one was used for comparison.

The kinetic parameters for the reaction of phenyl(4-nitrophenyl)cyanomethane and MTBD in two P-podand solvents are collected in Tables V–VII. The values of the observed rate constants of these reactions are given in Table V and the calculated second order rate constants are collected in Table VI. The second order rate constants for $OP(OEt)_3$ as solvent are much higher than those of the tris(oxaalkyl)phosphates (P-podand solvents).

The difference between these two types of solvents is due to the different solvation process of the substrates and the transition state. In the case of $OP(OEt)_3$, the solvation occurs through the oxygen atom of the O=P group, whereas in P-podand solvents oxygen atoms from polyoxaalkyl chains play a significant role in this process. This effect also explains the difference between the rates of proton transfer reactions for OP23 and OP33 solvents. For both types of phosphate solvent the values of activation parameters are different (Table VII).

In the case of $OP(OEt)_3$, the $\Delta H^{\neq}$ and $\Delta S^{\neq}$ are about four times lower than for the P-podand solvents and the value of $\Delta G^{\neq}$ for $OP(OEt)_3$ is also smaller than for the others. The values of the activation parameters of the reactions in P-podand solvents demonstrate that the energy barrier is much higher than in the case of $OP(OEt)_3$ as solvent. This observation is comparable to that for proton transfer reactions in Si-podand solvents as mentioned above.

The spectroscopic study of the stability of the ionic product of proton transfer reaction indicates the long lifetime of this product in P-podand solvents. Furthermore, this lifetime increases with an increasing of length of the polyoxaalkyl chain.

In conclusion, we state that the use of various podand solvents in studying the proton transfer reactions very strong determined the kinetic parameters as well as the stabilisation of products. This observation may play a very important role in studies of the transition states of organic reactions in which proton transfer occurs.

TABLE III Values of second order rate constants (± standard deviation) for reaction between dimethyl (4-nitrophenyl)malonate and MTBD in different solvents

	k ($dm^3\,mol^{-1}\,s^{-1}$)			
	Solvents			
Temp. (°C)	PhSi23	PhSi33	PhSi43	Acetonitrile [6]
15	1260 ± 44	1635 ± 52	1589 ± 32	4870 ± 30
25	2018 ± 52	2169 ± 34	1919 ± 45	6610 ± 40
35	2766 ± 93	2790 ± 35	2116 ± 23	9410 ± 25
45	3946 ± 105	3454 ± 84	2472 ± 79	13510 ± 55

TABLE IV Values of activation parameters (± standard deviation) for reaction between dimethyl (4-nitrophenyl)malonate and MTBD in different solvents

Solvent	$\Delta H^{\neq}$ ($kJ\,mol^{-1}$)	$\Delta S^{\neq}$ ($J\,mol^{-1}\,deg^{-1}$)	$\Delta G^{\neq}$ ($kJ\,mol^{-1}$)
PhSi23	26.1 ± 1.3	−95 ± 4	54.3 ± 1.3
PhSi33	16.5 ± 0.5	−126 ± 2	54.0 ± 0.5
PhSi43	8.4 ± 0.8	−154 ± 3	54.4 ± 0.8
Acetonitrile [6]	21.5 ± 1.3	−99 ± 3	51.1 ± 1.3

TABLE V Observed rate constants (± standard deviation) for reaction between phenyl(4-nitrophenyl)cyanomethane and MTBD in phosphate solvents

Podand solvent	MTBD (M)	k_{obs} (s^{-1}) at 15°C	k_{obs} (s^{-1}) at 25°C	k_{obs} (s^{-1}) at 35°C	k_{obs} (s^{-1}) at 45°C
$OP(OEt)_3$	0.005	23 ± 2	90 ± 5	177 ± 8	278 ± 10
	0.015	350 ± 3	530 ± 5	700 ± 10	930 ± 13
	0.020	540 ± 4	746 ± 5	971 ± 11	1250 ± 18
	0.025	710 ± 3	980 ± 6	1213 ± 14	1580 ± 20
OP23	0.005	5 ± 1	13 ± 2	31 ± 5	54 ± 3
	0.015	14 ± 1	32 ± 1	66 ± 6	119 ± 7
	0.020	19 ± 1	42 ± 1	86 ± 9	153 ± 9
	0.025	25 ± 1	51 ± 1	105 ± 9	190 ± 10
OP33	0.005	1.7 ± 0.1	4.5 ± 0.3	10.3 ± 0.3	17.5 ± 0.1
	0.015	4.9 ± 0.2	10.7 ± 0.2	21.8 ± 0.5	39.8 ± 0.5
	0.020	6.5 ± 0.2	13.8 ± 0.4	28.7 ± 0.5	50.9 ± 0.7
	0.025	8.5 ± 0.2	17.0 ± 0.5	34.9 ± 0.5	65.0 ± 0.8

MATERIALS AND METHODS

The tris(oxaalkyl)phenylsilane: PhSi23, PhSi33, PhSi43, tris(oxaalkyl)phosphate: OP23, OP33 and alkylphosphate: $OP(OEt)_3$ ligands were prepared according to previously described procedures [3,9].

C-acids: dimethyl (4-nitrophenyl)malonate and phenyl(4-nitrophenyl)cyanomethane were prepared according to procedure described in Refs. [6–8].

N-base: MTBD as commercial product of Aldrich was used with any purification.

Kinetic Measurements

Kinetic measurements were made according to the procedure describing in ref. [6]. The kinetic runs were carried out using a stopped-flow spectrophotometer (Applied Photophysics) with the cell block thermostated to ± 0.1°C. The kinetic runs were completed under pseudo-first-order conditions with the base concentration in large excess. The observed rate constants were calculated from the traces of absorbance vs. time.

The observed rate constant k_{obs} depends on the base concentration and is given by the equation: $k_{obs} = k[B] + k_-[BH^+]K_d^{-1}$ for the two-step mechanism or $k_{obs} = k[B] + k_-[BH^+]$ for the single step of the proton transfer mechanism where k is the rate constant for the forward proton transfer reaction, k_- the rate constant for the reverse proton transfer reaction, $[B]$ the initial base concentration, $[BH^+]$ the concentration of the cation and K_d the dissociation constant of the ion pair. Rate constants for the forward (k) reaction were calculated by linear least-squares fit of the variation of k_{obs} vs. base concentration. The activation parameters were calculated by linear least-squares fit of $\ln k$ vs. $1/T$.

Spectroscopic Measurements

NMR spectra were recorded by using a Varian Gemini 300. All ^1H NMR measurements were carried out at an operating frequency spectral frequency (sfrq) = 300.075 MHz; pulse width (pw) = 45°; spectral width (sw) = 4500 Hz; acquisition time (at) = 2.0 s; $T = 293.0$ K and with TMS as the internal standard in CD_3OD.

^{13}C NMR spectra were recorded at an operating frequency sfrq = 75.454 MHz; pw = 60°; sw = 1900 Hz; at = 1.8 s; $T = 293.0$ K and with TMS as the internal standard.

For ^{31}P NMR the following parameters were used: frequency sfrq = 121.472 MHz; pw = 60°; sw = 50,000 Hz; at = 2.0 s; $T = 293.0$ K and with 85% H_3PO_4 as external standard.

TABLE VI Values of second order rate constants (± standard deviation) for reaction between phenyl(4-nitrophenyl)cyanomethane and MTBD in different solvents

Temp. (°C)	$OP(OEt)_3$	OP23	OP33
15	34500 ± 700	989 ± 47	336 ± 12
25	44300 ± 400	1909 ± 20	624 ± 3
35	52000 ± 600	3700 ± 78	1234 ± 32
45	65000 ± 200	6770 ± 140	2345 ± 89

TABLE VII Values of activation parameters (± standard deviation) for reaction between phenyl(4-nitrophenyl)cyanomethane and MTBD in different solvents

Solvent	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (J mol^{-1} deg^{-1})	$\Delta G^{\neq}$ (kJ mol^{-1})
$OP(OEt)_3$	13.2 ± 0.8	− 112 ± 1	46.6 ± 0.8
OP23	47.1 ± 1.4	− 33 ± 5	57.0 ± 1.4
OP33	46.6 ± 0.5	− 26 ± 2	54.3 ± 0.5

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