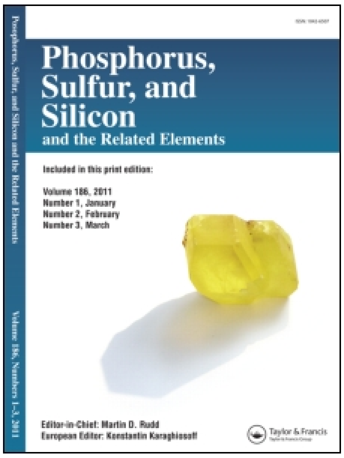

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ON THE TRANSESTERIFICATION OF DIALKYL ESTERS OF 2,3-DIALKOXY-CARBONYL-PROPANEPHOSPHONIC ACID WITH GLYCOLS

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The ability for transesterification of alkoxyphosphoryl and alkoxy-carbonyl groups has been investigated, using dialkyl esters of 2,3-dialkoxycarbonyl-propanephosphonic acid as a model. Their interaction with ethylene glycol, diethylene glycol, and n-octanol in the presence of a catalyst ($MnAc_2$ or Na glycolate) has been studied using GC, GPC, and ^{1}H-NMR. It has been established that the transesterification of the alkoxy groups at the phosphorus atom is difficult, while the alkoxy groups at the carbonyl carbon atom are nearly always 100% trans-esterified.

Key words: Transesterification; dialkyl esters; 2,3-dialkoxycarbonyl-propanephosphonic acid; glycols; alkoxy groups; catalyst.

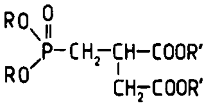
INTRODUCTION

The addition of dialkyl phosphites to activated double bonds[1] is one of the established methods for preparation of phosphonic acid esters. The transesterification of phosphonic acid esters was studied by many investigators[2,3] and it is a suitable method for the synthesis of phosphorus-containing oligomers.

The phosphonic acids, prepared by the addition of dialkyl phosphites to esters of unsaturated carboxylic acids, possess two kinds of groups, capable of transesterification—alkoxyphosphoryl and alkoxycarbonyl. There are no published comparative data on the ability for transesterification of these competitive groups. It is of some interest to examine the transesterification of compounds possessing both alkoxyphosphoryl and alkoxycarbonyl groups.

The dialkyl esters of 2,3-dialkoxycarbonyl-propanephosphonic acid (**I**), synthesized by us,[4] represent phosphorus-containing poly-functional compounds and can be utilized for the synthesis of phosphorus containing polymers and oligomers, which can further be used as polymer modifiers. Scheme I.

The aim of the present work is to examine the transesterification of dialkyl esters of 2,3-dialkoxycarbonyl-propanephosphonic acid with n-octanol, ethylene glycol, and diethylene glycol, in the presence of a catalyst ($MnAc_2$ or Na glycolate), and to compare the reactivity of the alkoxygroups at the phosphorus atom with that of the alkoxy-groups at the carbonyl carbon atom.



I

MPEI - ($R=CH_3$, $R'=C_2H_5$)

MIEP - ($R=C_2H_5$, $R'=CH_3$)

SCHEME I

RESULTS AND DISCUSSION

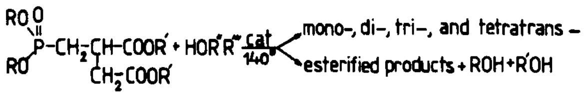
The transesterification of dicarboxylic acids esters with diols is an equilibrium process which proceeds in the presence of either basic or acidic catalysts.[5] The transesterification of phosphorus acids esters with different mono-, di-, and polyfunctional alcohols are catalyzed similarly.[6,7,8] For example, L. Maier[3] carry out transesterification of tris(diethylphosphonylmethyl)phosphonine oxide with 2,2-dimethyl-1,3-propanediol in the presence of sodium and tetraethyl titanate as catalysts, and cyclic tris(phosphonyl)phosphine oxide is obtained.

MPEI and MIEP are mixed esters of dicarboxylic and phosphonic acid and it is possible to obtain different products by transesterification of one, two, three or four alkoxygroups: Scheme II.

The results of the gas-chromatographic analyses of the alcohols formed in the reaction (Table I) show that the transesterification of the carbonyl alkoxygroups reaches almost 100% in almost every case while the alkoxy groups at the phosphorus atom are from 10 to 65% transesterified.

The reaction products are analysed by Gel-Permeation Chromatography (GPC). The degrees of completion of reaction, calculated on the basis of the peak areas of these products, are listed in Table I. The calculations are made with the simplifying assumption that the area of the chromatographic peak is proportional to the weight part of the product in the mixture. The molecular mass of the products is taken into account in order to calculate the molar ratio of the reaction products from the weight percents.

The Gel-permeation chromatographic data show that three types of products with different molecular mass are obtained as a result of the transesterification of



MPEI — R = Me, R' = Et

MIEP — R = Et, R' = Me

$R'' = CH_2CH_2$, $R''' = OH$

$R'' = CH_2CH_2OCH_2CH_2$, $R''' = OH$

$R'' = (CH_2)_7$, $R''' = CH_3$

SCHEME II

TABLE I

Degree of completion of the transesterification reaction of MPEI and MIEP with n-octanol, ethylene glycol and diethylene glycol, calculated on the basis of gas-chromatography and gel-permeation chromatography-data

Ester (Kt)	h-octanol				Ethylene glycol				Diethylene glycol			
	Gas-chromatography		Gel-permeation chromatography		Gas-chromatography		Gel-permeation chromatography		Gas-chromatography		Gel-permeation chromatography	
	P_m	P_e	P_m	P_e	P_m	P_e	P_m	P_e	P_m	P_e	P_m	P_e
MPEI ($MnAc_2$)	46	100	50.5	100	30	86	35	82	10	79	11.5	77
MIEP ($MnAc_2$)	98	60	100	57	100	45	100	51	97	50	100	55.7
MPEI (Na)	60	97.5	63	100	50	99	53	100	43	98	42	100
MIEP (Na)	98	65	100	71	95	50	100	56.5	94.8	60.4	100	60

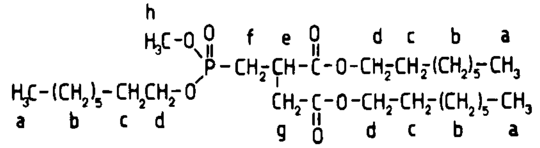
P_m = Degree of completion, calculated on the basis of substituted methoxy groups.
P_e = Degree of completion, calculated on the basis of substituted ethoxy groups.

TABLE II

Results of the GPC-experiments

Reaction mixture	Peak	Theor. M	Wt %	Mol %	Reaction mixture	Peak	Theor. M	Wt %	Mol. %
MPEI/octanol	E_2	463	5.5	7	MIEP/EG	M_2E_1	372	70.4	75
(MnAc$_2$)	E_2M_1	561	85.5	85	(MnAc$_2$)	$(M_2E_1)^k$	460	26.75	23
	E_2M_2	659	9	8	$(M_2E_2)^k$	$(M_2E_2)^k$	652	2.85	2
MPEI/octanol	E_2	463	10.5	11	MIEP/EG	M_2E_1	372	81.4	85.5
(Na)	E_2M_1	561	48.3	52	(Na)	$(M_2E_2)^k$	500	7.9	7.5
	E_2M_2	659	41.2	37		$(M_2E_2)^k$	652	10.7	7
MIEP/octanol	M_2E_1	576	84	86	MPEI/DEG	MPEI	296	16.85	23
(MnAc$_2$)	M_2E_2	660	16	14	(MnAc$_2$)	E_2	415	55.10	54
						E_2M_1	489	28	23
MIEP/octanol	M_2E_1	576	54.6	58	MPEI/DEG	E_2	415	18.4	21
(Na)	M_2E_2	660	45.5	42	(Na)	E_2M_1	489	74.29	74
						E_2M_2	563	7.32	5
MPEI/EG	MPEI	296	14.73	18	MIEP/DEG	M_2E_1	504	82.8	89
(MnAc$_2$)	E_2	327	32.7	37	(MnAc$_2$)	$(M_2E_2)^k$	828	17.2	11
	E_2M_1	357	19.5	20					
	$(E_2M_2)^k$	475	26.5	20.5					
	$(E_2M_2)^k$	650	7	4.5					
MPEI/EG	E_2M_1	357	9.5	64	MIEP/DEG	M_2E_1	504	70.9	80
(Na)	(E_2M_1)	490	35.4	30	(Na)	$(M_2E_2)^k$	828	29.1	20
	$(E_2M_1)^k$	740	55.4	6					

$E_{1(2)}$ = Mono- (di-) transesterified product by ethoxy groups.
$M_{1(2)}$ = Mono- (di-) transesterified product by methoxy groups.



SCHEME III

MPEI with n-octanol and $MnAc_2$ as catalyst; on the basis of Gas-chromatographic data, they are assigned to di- ($M = 463$), tri- ($M = 561$) and tetrasubstituted product ($M = 659$), respectively. The areas of these peaks are related as 5.5/85.5/9, meaning that the molar ratio of the products is 7/85/8, i.e. the mixture consists of 7 mol% di-, 85 mol% tri-, and 8 mol% tetrasubstituted product. The degree of substitution at the phosphorus atom is $85 \times 0.5 + 8 \times 1 = 50.5\%$. The molar ratio of the reaction products, and hence the degree of transesterification at the phosphorus atom, was determined similarly making use of the GPC-results (Table II). The results are summarized in Table I, and they are in good agreement with the GC-results. The GPC-data are also consistent with the results from the ^{1}H-NMR spectroscopic investigations of the products of transesterification with n-octanol.

It follows from the GPC data (Table II) that a mixture of di-, tri-, and tetrasubstituted products in molar ratio 11/52/37 is obtained in the transesterification of MPEI with n-octanol and Na octylate as catalyst. The ^{1}H-NMR spectrum of reaction products of the same system is given in Figure 1. Scheme III.

The integral intensity of the protons "a" is related to that of protons "e" just as the molar ratio of the products in the reaction mixture. The ratio of protons "a" and "e" in the disubstituted product is 6:1, in the trisubstituted product it is 9:1, and in the tetrasubstituted it is 12:1. Taking into account the molar composition of the reaction concerning the reaction products, one obtains $0.11 \times 6 + 0.52 \times 9 + 0.37 \times 12 = 9.78$. This quantity is in very good agreement with the ratio of the integral intensities I_a/I_e, determined from the NMR-spectrum, i.e. $24:2.5 = 9.6$. The GPC-data are consistent with the NMR-data for the other cases also.

	MPEI/n-octanol ($MnAc_2$)	MIEP/n-octanol ($MnAc_2$)	MIEP/n-octanol (Na)
from GPC	9.03	9.42	10.26
from NMR	9.33	9.33	10.33

Analysis of the data from Table I shows that the transesterification of the alkoxy groups at the phosphorus atom is more difficult, while the alkoxy groups at the carbonyl groups are nearly always 100% transesterified. This difference is expected because the two alkoxy groups are at two carbonyl groups, so allowing a simultaneous nucleophilic attack on the carbon atoms and consequently the transesterification is faster. The two alkoxy groups at the phosphorus atom cannot be attacked simultaneously so leading to slower transesterification. It is also probable that steric hindrance may develop in some cases after the transesterification of one of these groups.

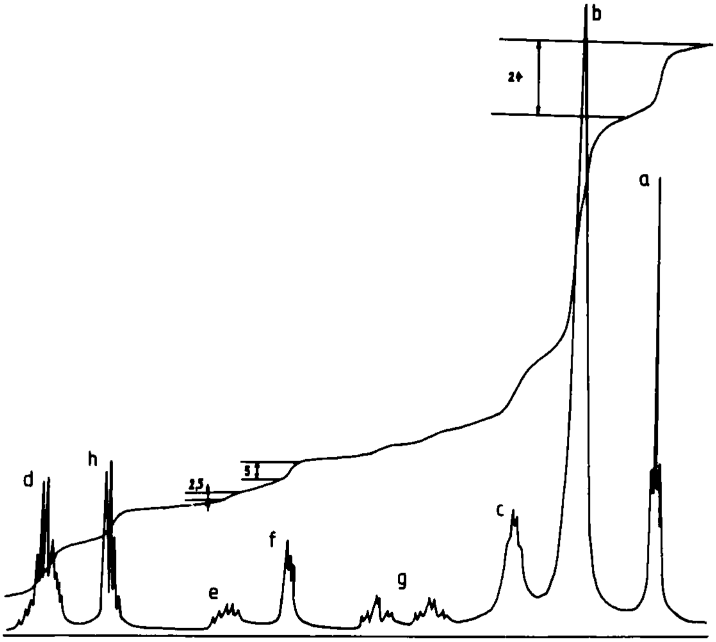
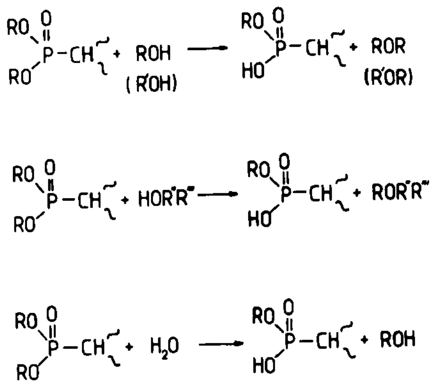


FIGURE 1 ^{1}H-NMR spectrum of the reaction product of the system MPEI/n-octanol (Na).

Our results indicate that the degree of transesterification at the phosphorus atom is higher when an ethoxy groups is present. Opinions about the specific behaviour of the methoxy group at the phosphoryl group due to hyperconjugation have been given[9] and our observations seem to confirm this effect.

The degree of transesterification with n-octanol is higher than that of the glycols. The second hydroxyl group probably has an effect. The results show that Na glycolate (octylate) is a more effective catalyst than $MnAc_2$ for the described systems.

It was established that the transesterification is accompanied by release of some water, up to 0.054 mol with the glycols and up to 0.006 mol with octanol. We



SCHEME IV

TABLE III

The content of the hydroxyl groups in the transesterified products

Reaction mixture	OH (mass %)		Reaction mixture	OH (mass %)	
MPEI/EG ($MnAc_2$)	36.0	30.8	MPEI/DEG ($MnAc_2$)	22.5	23.0
MIEP/EG ($MnAc_2$)	33.3	28.2	MIEP/DEG ($MnAC_2$)	22.5	17.4
MPEI/EG (Na)	13.8	10.5	MPEI/DEG (Na)	21.3	18.8
MIEP/EG (Na)	15.7	10.0	MIEP/DEG (Na)	20.7	15.2

assume that some dehydratation of the hydroxyl-containing compounds occurred so explaining the presence of products with higher molecular weight (denoted as $M_iE_j^k$ in Table II). This reaction is possible in acidic media.[10]

The determination of the hydroxyl numbers of the reaction mixtures (hydroxyl number from 15 to 20 mg KOH/g) confirmed the observations of other authors[11,12] that side reactions occur during the transesterifications of dialkyl phosphites with hydroxyl-containing compounds so that acidic O═P—H group and dialkyl esters are formed: Scheme IV.

The values of the hydroxyl numbers, which are lower than those calculated on the basis of GC data, are listed in Table III. These results confirm that water has been formed as a result of esterification of hydroxyl groups.

In the present study of the transesterification of MPEI and MIEP with n-octanol and glycols, it has been established that the reaction rates of the various ester groups are different, the alkoxy groups at the carbonyl carbon atoms being substituted more quickly. These results can be utilized in the synthesis of phosphorus-containing polymers.

EXPERIMENTAL

Starting compounds. The diethyl esters of 2,3-dimethoxycarbonyl-propanephosphonic acid (MPEI), the dimethyl ester of 2,3-diethoxycarbonyl-propanephosphonic aicd (MIEP) were synthesized according to the literature;[4] ethylene- and diethylene glycol were obtained from SO "Neftochim"—Bourgas, and n-octanol from Fluka.

Experimental procedure. Transesterification—MPEI (or MIEP) 14.8 g (0.05 mol), DEG 42.4 g, (0.4 mol), dried over Na and freshly distilled (or EG, 28.4 g (0.4 mol), or n-octanol, 52.0 g (0.4 mol)) and 0.74 g catalyst ($MnAc_2$ or Na glycolate (octylate), which will be designated as Na in the tables) were mixed in a flask equipped with a stirrer, thermometer N_2 inlet, and a reflux condenser. The transesterification was carried out at 140° for 6 hours. The alcohols, formed in the process, were trapped in a cooled receiver. In the cases with n-octanol and MPEI/EG/Na, and MIEP/EG/Na, the excess n-octanol or EG was distilled off after completion of the transesterification at 85–90° and 10 mm Hg, and at 38–40° and 0.01–0.025 mm Hg, respectively.

Method for Analysis: 1. Gas chromatography (GC). The composition of the alcohols (distillates) released by the transesterification was determined by gas chromatography under the following conditions: glass capillary column (30 m/0.3 mm) with PEG 400 or PEG 20 M (for n-octanol) as stationary phase, column temperature 30° and 100°, carrier gas-N_2, CID, injector and detector temperature 220°, Perkin-Elmer Sigma-300 gas chromatograph with Shimadzu R-4c electronic calculator. The quantitative determinations were carried out by the absolute calibration method. The expected components in the distillates were identified by the retention times of model compounds.

2. Gel-Permeation Chromatography (GPC). The compositions of the reaction mixtures were found by gel-permeation chromatography on Water Associates apparatus with THF as eluent eluation rate 1 ml/min, 45°, styragel columns with pore sizes 1000, 500, 100, and 100 A, and the following compounds as markers: polyethylene glycol standards, MPEI, MIEP, n-octanol, EG, and DEG.

3. ^{1}H-NMR spectroscopy. ^{1}H-NMR spectra of the reaction products (in the cases with n-octanol) were recorded on Bruker WM 250 spectrometer at 250 MHz, at room temperature, with $CDCl_3$ as solvent.

4. Determination of the OH groups content. The content of the hydroxyl groups in the mixtures was determined by acetylation.

5. Determination of the water content. The water content of the reaction mixtures and the distillates was determined by the Karl Fisher method on meliotitrator DL-40 Mettler.

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