THE EFFECT OF A LIQUID CRYSTAL MEDIUM ON THE DECOMPOSITION OF *p*-NITROPHENYL DIMETHYLTHIOPHOSPHATE

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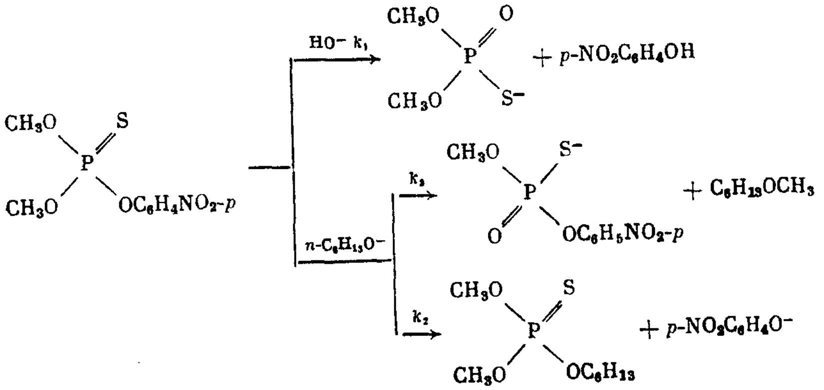
The lamellar liquid crystal meso phase formed in the cetyltrimethylammonium bromide—1-hexanol—water system assists the reaction of p-nitrophenyl dimethyl thiophosphate with a charged nucleophile (hexanolate anion) and uncharged nucleophile (ethylenediamine) with the loss of the p-nitrophenylmethylthiophosphate anion, i.e., the reaction at the carbon atom and not at the phosphorus atom.

There have recently been a number of communications on the effect of lyotropic liquid crystal meso phases on nucleophilic substitution reactions, indicating the possibility of control of their rates by altering the phase composition of the reaction medium [1-3].

We studied the decomposition of *p*-nitrophenyl dimethyl thiophosphate (Metaphos) in media containing cetyltrimethylammonium bromide (CTAB), 1-hexanol, water, and NaOH. A lamellar liquid crystal meso phase is formed in aqueous solution at a given ratio of CTAB and 1-hexanol. This meso phase also exists in the presence of NaOH at from 20 to 92°C as monitored using a polarizing microscope. The texture of the meso phase is fine confocal spheroliths arranged in a regular network.

The decomposition of Metaphos in the alkaline liquid crystal meso phase is possible by the pathways indicated in the scheme below:



(1)

(2)

(3)

The realization of these pathways was indicated by the decrease in the UV band for Metaphos at 273 nm and the appearance of two new bands. The maximum at 400 nm is related to the formation of the anion of *p*-nitrophenol (PNP) through pathways (1) and (3), while the appearance of the maximum at 292 nm is a result of the formation of the *p*-nitrophenylmethylthiophosphate anion through pathway (2). The anions of *p*-nitrophenylmethylphosphate (λ 288 nm [5]) and *p*-nitrophenylethylphosphate (λ 290 nm [6]) have analogous maxima in alkaline solution.

Evidence for parallel processes with different reaction sites is also found in the isolation of a nonequivalent amount of PNP per equivalent of Metaphos. The contributions of the alkylation and phosphorylation reactions to the total rate constant is determined relative to the fraction of *p*-nitrophenyl isolated at the end of the reaction, $\alpha = (k_1 + k_2)/(k_1 + k_2 + k_3) = D_{\infty}/D_{\text{calc}}$.

The data in Table 1 indicate that the yield of PNP is dependent on the time elapsed from the preparation of the solution until the onset of the reaction. This behavior is related to the rather prolonged establishment of phase equilibrium in this system. The achievement of equilibrium is accelerated with decreasing amount of water with retention of the

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TABLE 1. Rate Constants for the Decomposition of Metaphos in a Liquid Crystal Meso Phase (1-hexanol/CTAB = 0.55)

t*, h	Meso phase comp., wt. %			Yield of PNP, %	T, °C	$k_{ef}\cdot 10^4$**, sec^{-1}	$(k_1+k_2)\cdot 10^4$, sec^{-1}	$k_3\cdot 10^4$, sec^{-1}
	CTAB	1-hexanol	0,1 *N* NaOH					
24	10,71	6,08	83,21	83	46	6,29	5.24	1,05
84				70		5,80	4.08	1,72
144				66		5,27	3.50	1,77
168				5		5,52	0.248	5,27
24	19,05	10,48	70,47	73	46	3,31	2,41	0,90
48				11		2,48	0,311	2,17
24	28,61	15,64	55,75	4	46	1,80	0,07	1,73
				6	25	0,554	0,033	0,521
24***	7,36	6,0	86,64	82	46	9.22	7.59	1,63

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*Time from the preparation of the solution.

**$k_{ef} = k_1 + k_2 + k_3$.

***The 1-hexanol/CTAB ratio was 0.81.

CTAB/1-hexanol ratio equal to 0.55. The formation of the liquid crystal phase requires 24 h when the water content is 55%. Virtually only alkylation of the hexanolate anion occurs in the lamellar meso phase upon the establishment of phase equilibrium. The alkylation rate decreases with decreasing water content (Table 1). All the reaction pathways are realized during the formation of the meso phase. Change in temperature does not affect the ratio of the parallel reactions in the liquid crystal meso phase (Table 1). The activation energy for the alkylation reaction in the lamellar liquid crystal meso phase is approximately 44 kJ/mole.

Metaphos is hydrolyzed in an alkaline aqueous medium to give *p*-nitrophenol in 100% yield; the rate constant $k_2 = 3.4\cdot 10^{-3}$ liter/mole·sec^{-1} at 25°C [8]. However, in alcohols containing sodium alcoholate, Metaphos undergoes transesterification with the loss of a *p*-nitrophenolate anion; in the presence of 1.0 mole/liter NaOAlk, $k_1 = 7.8\cdot 10^{-3}$ sec^{-1} at 46°C [7]. In both cases, nucleophilic attack proceeds at the phosphorus atom. Upon establishment of the phase equilibrium, alkylation of the hexanolate anion proceeds in 96% yield in the alkaline liquid crystal meso phase (28.61% CTAB, 15.54% 1-hexanol, and 55.75% 0.1 *N* NaOH) (see Table 1), i.e., a change in the reaction pathway is observed. A shift in the reaction mechanism was also found for the reaction of Metaphos with an uncharged nucleophile, namely, ethylenediamine (the liquid crystal properties are retained in the presence of this diamine). The reaction of Metaphos with ethylenediamine in an aqueous medium proceeds 70% through alkylation of the amine ($k_1 = 0.53\cdot 10^{-4}$ sec^{-1}, $c_{EDA} = 0.184$ mole/liter) and 30% by phosphorylation [8]. In the liquid crystal meso phase (28.39% CTAB, 15.37% 1-hexanol, 55.90% water, and 0.34% ethylenediamine), Metaphos alkylates ethylenediamine in 96% yield ($k_1 = 3.14\cdot 10^{-4}$ sec^{-1}, 25°C). It is interesting to note that the alkylation of ethylenediamine by Metaphos is inhibited in micellar solutions of CTAB in water and the phosphorylation of the amine is the predominant reaction pathway [8].

EXPERIMENTAL

A sample of CTAB supplied by Chemapol and Metaphos prepared according to Shroder [9] were used in this work. The reaction kinetics were studied spectrophotometrically on a Specord M-40 instrument relative to the increase in the intensity of the band at 400 nm and the loss in intensity of the band at 273 nm. The reaction was carried out in cells with l = 0.2 cm with $2.31\cdot 10^{-4}$ mole/liter Metaphos under pseudomonomolecular conditions. The solution of Metaphos was prepared in 1-hexanol. The rate constants were determined using an equation for first-order reaction kinetics. The validity of the Lambert—Beer law was checked for the PNP anion in these media (ε = 21,570). The liquid crystallinity and type of meso phase were determined using a polarizing microscope on a Boetius heating table with a Veb analytic PNMK 0.5 visual device.

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THE REACTION OF POTASSIUM CYANAMIDE WITH NORMAL ALKYL BROMIDES

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A study was carried out on the reaction of potassium cyanamide with normal alkyl bromides in 2-propanol, methanol, and dimethylformamide in order to obtain dialkylcyanamides. A virtually quantitative yield of dialkylcyanamides is achieved in dimethylformamide.

Dialkylcyanamides (DACA) have found use as wetting agents for fabrics, water-repellant materials [1], and additives to solid [2] and liquid diesel fuels [3].

Methods have been reported for the preparation of DACA from alkali and alkaline-earth metal cyanamides in protic media [4-5]. The yields of the desired product under these conditions did not exceed 50%.

In order to develop a preparative synthesis for DACA, we studied the reaction of potassium cyanamide (I) with normal 1-bromoalkanes (IIa)-(IId) in various solvents:

$$\underset{(I)}{K_2N{-}C{\equiv}N} + \underset{(IIa-d)}{RCH_2Br} \rightarrow \underset{(IIIa-d)}{(RCH_2)_2N{-}C{\equiv}N}$$

$$R = C_7H_{15}(a),\ C_{11}H_{23}(b),\ C_{14}H_{29}(c),\ C_{15}H_{31}(d).$$

This reaction does not proceed when the reagents are heated in dimethoxyethane, which is an aprotic solvent, at reflux, probably as a consequence of the poor solubility of salt (I).

We have found that the use of dimethylformamide as the solvent leads to a virtually quantitative yield of dialkylcyanamides (IIIa)-(IIId).

The addition of 2-propanol into the reaction mixture in dimethoxyethane leads to the appearance of significant amounts of *n*-alkyl isopropyl ether (IVa)-(IVd) as side-products in addition to (IIIa)-(IIId) as indicated by thin-layer chromatography.

Carrying out the reaction of potassium cyanamide with alkyl bromides (IIa)-(IId) in 2-propanol leads to the predominant formation of (IVa)-(IVd) (see Table 1).

Potassium cyanamide apparently acts as a nucleophile and base in this reaction.

$$2K_2N{-}CN + 4i\text{-}C_3H_7OH \rightarrow 4KOCH(CH_3)_2 + (NH_2CN)_2$$

$$KOCH(CH_3)_2 + \underset{(IIa-d)}{RCH_2Br} \rightarrow \underset{(IVa-d)}{RCH_2^{\alpha}{-}O{-}CH^{\beta}(CH_3^{\gamma})_2}$$

Heating salt (I) at reflux under comparable conditions in 2-propanol, decantation of the precipitation, and the addition of alkyl bromides (IIa)-(IId) to the mother liquor also leads to the formation of ethers (IVa)-(IVd).

Cyanamide dimer formed as a result of the alcoholysis of salt (I) was isolated from the reaction mixture, which supports the reaction scheme presented above.

Thus, DACA may be synthesized in high yield from alkyl bromides and potassium cyanamide in aprotic solvents, in which potassium cyanamide has satisfactory solubility. The reduction in the yield of DACA in protic solvents is related to the hydrolysis of (I), which proceeds by analogy to the hydrolysis of potassium cyanamide [6].

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