7. R. G. Gasanov and T. T. Vasil'eva, Izv. Akad. Nauk SSSR, Ser. Khim., No. 4, 800 (1989).
8. N. V. Blinova and R. G. Gasnaov, Metalloorg. Khim., 2, No. 373 (1989).
9. T. T. Vasil'eva, L. N. Goncharova, and R. Kh. Freidlina, Izv. Akad. Nauk SSSR, Ser. Khim., No. 5, 1182 (1977).
10. N. V. Blinova and R. G. Gasanov, Kinet. Katal., 31, No. 3 (1990).
11. J. K. Kochi, Advances Free-Radical Chem., 5, 189 (1975).
12. R. G. Gasanov, Doctor of Chemical Sciences Dissertation, Moscow (1981).
13. J. A. Hawari, S. Davis, P. S. Engel, et al., J. Am. Chem. Soc., 107, No. 16, 4721 (1985).
14. R. G. Gasanov, E. G. Sadykhov, and R. Kh. Freidlina, Izv. Akad. Nauk SSSR, Ser. Khim., No. 5, 1182 (1977).
15. G. K. Zhovnerko and V. E. Azabekov, Kinet. Katal., 28, No. 3, 531 (1987).

INTERPHASE ANALYSIS IN THE CHEMISTRY OF ALIPHATIC NITRO COMPOUNDS.

1. ALKYLATION OF ALKALI METAL SALTS OF TRINITROMETHANE UNDER INTERPHASE CATALYSIS CONDITIONS IN SOLID PHASE–LIQUID SYSTEMS

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Methylation of trinitromethane salts was studied under interphase catalysis conditions in a solid phase (a trinitromethane salt)—liquid (methyl iodide) system in the presence of interphase transfer catalysts — onium salts, cyclic and acyclic polyethers. The dependence of the yield of the methylation product — 1,1,1-trinitroethane — on the nature of the catalyst was also investigated, and based on this, catalysts were found, in whose presence the methylation process is realized more effectively than under homogeneous conditions.

A voluminous literature is available on the alkylation of aliphatic nitro compounds (see for example, [1]). However, the alkylation of nitroalkanes and their functional derivatives under interphase catalysis conditions (IPC) has practically not been investigated.

For mononitroalkanes, which are relatively strong CH-acids [2], there is no need to use the IPC both for the generation of carbanions and for the stimulation of alkylation. However, in the case of compounds with more than one nitro group at the primary carbon atom (polynitroalkanes), the corresponding polynitrocarbanions ($RC(NO_2)_2^-$) have a very low nucleophilicity (in particular, the trinitromethane anion) with respect to alkyl halides, which is reflected in low reaction rates in the medium of polar solvents [3].

One of the possible paths for the intensification of the nucleophilic substitution is to carry out the process under the IPC conditions. In this case the process can be carried out in low-polarity nonsolvating solvents or in the medium of the alkylating agent itself as result of transfer of the nucleophile into the organic phase under the influence of interphase transfer catalysts — the onium slats or polyethers [4].

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TABLE 1. $K^+C^-(NO_2)_2 + MeI \xrightarrow{\text{IPT cat.}} MeC(NO_2)_3 + KI$

Number of experiment	IPT catalyst, 0.1 mole/mole TNM	Yield of TNE, % after 1 day [a]
1	$Et_3N^+CH_2PhCl^-$ (TEBAC)	6,5
2	$Bu_3N^+CH_2PhCl^-$	64
3	$(C_{7-9}H_{15-19})_3N^+CH_2PhCl^-$ (TABAC)	40
4	$(C_{16}H_{33})Me_2N^+CH_2PhCl^-$	16
5	$Me_4N^+Cl^-$	1
6	$Et_4N^+Cl^-$	1
7	$Bu_4N^+I^-$	78(53)
8	$Bu_4N^+HSO_4^-$	45
9	$Oct_4N^+Br^-$	86
10	$C_{18}H_{37}N^+Me_3Cl^-$ (ATM-chloride)	18,5
11	$Bu_3P^+CH_2PhCl^-$	67
12	Benzo-12-crown-4	<1
13	15-Crown-5	95(79)
14	Benzo-15-crown-5	<1
15	18-Crown-6-MeCN	7,5
16	Dibenzo-18-crown-6	<1
17	Dicyclohexano-18-crown-6 (mixture of isomers)	88,5
18	PEG-400	69(47)
19	PEG-1000	95(79)
20	PEG-1500	82(74)
21	PEG-1500 [b]	94
22	PEG-6000 (0,05 mole/mole TNM)	73
23	PEG-15000 (0,01 mole/mole TNM)	95
24	PEG-20000 (0,1 mole/mole TNM)	48
25	PPG-250	6
26	PPG-425	35
27	PPG-1025	87(54)
28	PPG-2000	83
29	PEG-4000[c]	82
30	Laprol-503[d]	83
31	Laprol-564[e]	56
32	PEG-115 (0.05 mole/mole TNM)[f]	86
33	$MeO(CH_2CH_2O)_4Me$	8,5

[a] Determined spectrophotometrically, the yield of the isolated TNE is shown in brackets (see the experimental part).

[b] On using a Cs salt of TNM.

[c] After 3 h.

[d] Technical grade poly(glyceropropylene oxide) ($\bar{M}$ = 500).

[e] Technical grade poly(propylene oxide), grafted to saccharose ($\bar{M}$ = 560).

[f] Technical grade poly(ethylene glycol) ($\bar{M}$ = 4000).

The present work is devoted to the investigation of the methylation of trinitromethane (TNM) salts, mainly the potassium salt, by methyl iodide under IPC conditions in a solid phase (the TNM salt) — liquid (MeI in an a amount of 1 ml per 1 mmole of the TNM salt) conditions, in the presence of interphase transfer (IPT) catalysts — quaternary onium salts (mainly the ammonium salts), cyclic and acyclic polyethers. The methylation of the TNM salt was carried out under standard conditions: the mixture was stirred for 8 h at 20°C, and then was allowed to stand without stirring for 16 h (altogether 24 h); the IPT catalyst was generally used in an amount of 10 mole % of the TNM salt used. The yield of 1,1,1-trinitroethane (TNE) formed was determined spectrophotometrically, and in some cases also by isolating the TNE (see Table 1 and the experimental part).

It should be noted that under homogeneous conditions (in acetone), the K salt of TNM reacts very slowly at 20°C with an excess of MeI: a high yield of the C-alkylation product*—TNE—was obtained only after 7 days [3]. From the data obtained in the present work (Table 1) it follows that under the PIC conditions, practically in all cases C-methylation of the TNM anion takes place and TNE is formed,† whereby its yield is strongly dependent on the struc-

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*The O-alkylation thus does not occur [3].

†In the absence of the IPT catalyst, the reaction does not proceed under these conditions.

structure of the catalyst; the use of IPC substantially facilitates the alkylation of the TNM salt, compared with the homogeneous variant: in the case of the best catalysts, a high yield (more than 70%) of TNE is obtained after 24 h instead of 7 days under homogeneous conditions (see above).

It must be stated that the dependence of the yield of TNE on the nature of the IPT catalyst obviously reflects the different overall rate of the process, since in all cases the amount of TNM which enters the reaction corresponds to the amount of the TNE formed (i.e., only C-alkylation of the ambidentate TNM anion takes place). In those cases where the yield of TNE is low, a further holding (stirring) of the mixture for more than one day leads to increase in the amount of TNE.

We shall now consider separately the influence of the various groups of catalysts. Among the quaternary ammonium salts (QAS), the catalysts with a medium chain length (C_4-C_8) have the highest activity — when they are used the yield of TNE is 50-80% (see Table 1, experiments 7-9). Trialkylphosphonium salt as a catalyst is not inferior to its ammonium analog (see experiments 11 and 2). Among the cyclic polyethers 15-crown-5 was found to be the best (the yield of TNE was 95%) (experiment 13). The benzo-crown ethers are ineffective due to their insufficient solubility in MeI.

However, the most interesting feature or this reaction is the possibility of the very effective use of alicyclic ethers in it: poly(ethylene glycols) (PEG) and poly(propylene glycols) (PPG), including the technical grade material (laprol, PEG), which in the case of the best catalysts are not inferior to crown ethers and QAS (experiments 19-23, 27-30, 32). The use of acyclic polyethers as IPT catalysts is more preferential than that of crown ethers and QAS, if we consider their availability and cheapness, and also the low toxicity [5]. Such a high effectiveness of the acyclic polyethers in a wide range of molecular weights is quite rarely encountered in IPC [4]. The best results were obtained on using polyglycols with molecular weight of $\bar{M} \geq 1000$, whereby the effectiveness of PEG and PPG with similar $\bar{M}$ is practically the same. An interesting feature of the high molecular weight poly(ethylene glycols) ($\bar{M} \geq 4000$) is the possibility of using them in smaller amounts as a catalyst (1 or 5 mole %) or shortening the reaction time to 3 h (experiments 22, 23, 29). The use of a counterion other than potassium, for example, the Cs^+ cation, somewhat increases the yield of TNE (see experiments 21 and 20).* It is important to note that in all cases, even in the presence of nonoptimal catalysts, TNE was recorded chromatographically as the main reaction product. Moreover, in most cases 1,1-dinitroethane (DNE) was detected in an amount of 1-3%,† which may be due to the possible denitration of TNE by potassium iodide separating out during the reaction [6].

EXPERIMENTAL

Distilled MeI (bp 42-43°C) was used in the investigation. The K salt of TNM was prepared according to [8]. The spectrophotometric monitoring of the course of reaction was carried out on a "Specord UV-VIS" spectrophotometer, and TLC was carried out on Silufol plates.

Methylation of TNM Salt under the IPC Conditions. A calculated amount of an IPT catalyst (Table 1) was added to a suspension of a K salt of TNM in MeI (1 ml per mmole of K-TNM), the mixture was stirred for 8 h and allowed to stand overnight. To separate the TNE, the reaction mixture was filtered off, the filtrate was twice washed with a 5% solution of $Na_2S_2O_3$, and then 5-6 times with an equal amount of water, and dried over $MgSO_4$. After the removal of MeI, the residue was recrystallized from hexane, mp 57°C (cf. [9]).

Spectrophotometric Determination of the Yield of TNE. Three aliquot portions were withdrawn from the organic phase. The first aliquot was dissolved in a mixture of EtOH and a 0.1 N aqueous solution of H_2SO_4 (1:4, here and below the ratios are per volume), and the amount of the unreacted TNM was determined from the absorption region with λ_{max} 350 nm (ε 14500).

The second aliquot was dissolved in a mixture of EtOH and 0.1 N aqueous solution of $NaHCO_3$ (1:4), and the total absorption at λ 380 nm was measured, due to TNM and also DNE formed as result of reaction, from which by extraction of the absorption calculated during the analysis of the first aliquot, produced by TNM at this wavelength (ε 4200), the amount of DNE (λ_{max} 380 nm, ε 17000) formed in the reaction was calculated.

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*The high activity of the Cs salts compared with other alkali metal cations was shown in [7].

†During the separation of TNE, an additional amount of DNE is formed (10-15%), possibly, as a result of the reaction of TNE with $Na_2S_2O_3$ during the treatment of TNE for the removal of I_2. This is the reason for the decrease in the real yield of the separated TNE, in comparison with the yield determined spectrophotometrically.

In the third aliquot, the yield of TNE was determined by preliminarily subjecting it to denitration to DNE. The aliquot was dissolved in a small volume of a mixture of EtOH, 0.1 N solution of NaOH and 0.1 N aqueous solution of KI (2:1:1), the solution was allowed to stand for 30 min and was then diluted with a mixture of EtOH and 0.1 N solution of NaOH (1:4). The overall content of DNE was determined in the same way as in the case of the second aliquot, and then by the substraction from it of the amount of DNE which was obtained in the analysis of the second aliquot, gave the amount of DNE formed from TNE.

LITERATURE CITED

1. V. I. Erashko, S. A. Shevelev, and A. A. Fainzil'berg, Usp. Khim., **35**, 1740 (1966).
2. O. P. Beletskaya, O. A. Reutov, K. P. Butin, et al., CH-Acids [in Russian], Khimiya, Moscow (1980).
3. S. A. Shevelev, V. I. Erashko, and A. A. Fainzil'berg, Izv. Akad. Nauk SSSR, Ser. Khim., No. 12, 2725 (1976).
4. Z. Demlov and E. Demlov, Interphase Analysis [Russian translation], Mir, Moscow (1987).
5. A. P. Khmel'nitskii and E. G. Lubenets, Zh. Vses. Khim. O-va, **31**, No. 2, 203 (1986).
6. D. J. Glover and M. J. Kamlet, J. Org. Chem., **26**, 4734 (1961).
7. S. S. Yufit, I. A. Esikova, and O. I. Danilova, Dokl. Akad. Nauk SSSR, **295**, No. 3, 621 (1987).
8. F. Bogart, A. Seeler, and P. Noble, J. Org. Chem., **31**, 2806 (1966).
9. G. S. Hammond, W. D. Emmons, C. Parker, et al., Tetrahedron, **19**, Suppl. 1, 177 (1963).