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BIS-QUATERNARY AMMONIUM SALTS AS PHASE TRANSFER CATALYSTS

Manfred Lissel*[b],David Feldman*[a], Malka Nir[a] and Mordecai Rabinovitz[a]
[a]Department of Organic Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel,
and [b]Fakultat fur Chemie, Universitat Bielefeld, Bielefeld, BRD.

Summary: Bis-quaternary ammonium salts are used for the extraction of polyanions and show better extractive abilities than common phase transfer catalysts.

Phase transfer catalysis (PTC) has now become a standard procedure in synthetic organic chemistry for reactions in which an anion reacts with the organic substrate [1]. The key factor in such PTC-processes is the catalyst. The most commonly used catalysts are quaternary ammonium- and phosphonium-salts (quats), crown-ethers, cryptates, open chain polyethers as well as arsonium- and triphenylsulfonium salts and polyamines.

The utilization of bis-quaternary ammonium salts (bis-quats) in reactions with inorganic or organic bis-anions had been raised in discussions [2]. Experiments with bis-pyridinium salts were reported recently [3] but no systematic study on ordinary bis-quats has been published. we decided to examine the applicability of bis-quaternary ammonium salts for the extraction of a variety of polyanions. An additional motivation is to overcome the difficulties involved in the extraction of polyanions under PTC-conditions. We report our results on the extraction of aqueous solutions of sodium dichromate, sodium chromate, sodium molybdate, potassium ferrocyanide, potassium ferricyanide, disodium terephthalate and disodium phthalate with bis-quats and its use as phase transfer catalysts in alkylation reactions.

Extractions with bis-quaternary ammonium salts

For the classification of the extractive properties of bis-quaternary ammonium salts we have estimated the loading of those and of common catalysts with each anion under PTC-conditions. In all cases studied equal volumes of a 10^{-3} M solution of the catalyst in dichloromethane and a 10^{-2} M aqueous solution of the inorganic or organic salt were equilibrated during 10 min at room temperature. The UV spectra of both phases were recorded. In addition atomic absorption estimations of the relevant metal present in the organic phase were performed. In the UV estimations, the remaining concentration of the anion in the aqueous phase served for calculation of the loading of the catalyst (mol anion/mol catalyst). The calculated values are presented in Table I. Most of the results reported in Table I were calculated from the atomic absorption analysis of the relevant metal present in the organic phase. In certain cases only the results of the UV-VIS spectrum are reported. From the data in Table I, one can see that four major groups of substrates were studied.

Chromate and dichromate: concentration measurements in the aqueous phase were made at 372 nm for chromate and at 353 nm for dichromate. The absorption maximum and the structure of the spectrum of the organic phase (Figure 1), shows that the same species is extracted from aqueous chromate and dichromate solutions, probably $HCrO_4^-$. The assignments were controversial in the literature [4] and go beyond the limits of the present research. The data presented in Table I afford the following conclusions regarding the extraction of chromate and dichromate:

1) The loading of the onium ion is independent on its lipophilicity but it does depend on the hydrophilicity of the catalyst's original counter anion [1,5].

2) In comparison with monovalent onium salts, the bis-quaternary ammonium salts carry double the amount of anions into the organic phase.

3) Loading values of more than one may be explained by the assumption that the extracted species is monovalent.

4) TEBA, PEG 400 and 18-crown-6 do not extract Cr(VI).

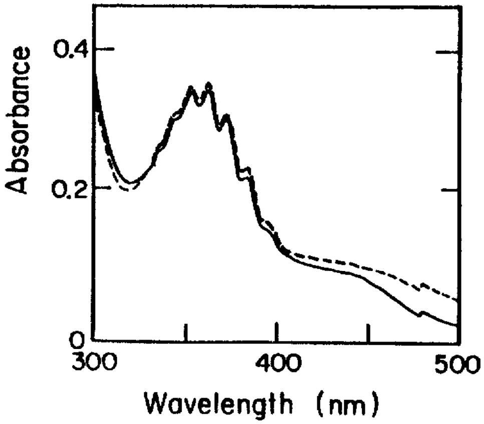

Figure 1: Superimposed UV-VIS spectra of the organic phase after 10 min equilibration with aqueous chromate (----), dichromate (——) and the PTC catalyst.

Table I. Loading of the catalyst with anions in mol anion[a]/mol catalyst[b]

Catalyst/cation	X	$Cr_2O_7^{2-}$	CrO_4^{2-}	MoO_4^{2-}	$Fe(CN)_6^{3-}$	$Fe(CN)_6^{4-}$	Terephthalate[c]	Phthalate[c]
$Bu_3N^+(CH_2)_4N^+Bu_3$	Br	0.88	<0.32		<0.1	<0.10	0.05	0.10
$Hex_3N^+(CH_2)_4N^+Hex_3$	Br	0.95	0.26		0.28	0.15	0.05	0.13
$Oct_3N^+(CH_2)_4N^+Oct_3$	Br	0.81	<0.24		0.14	<0.07	0.05	0.24
$Oct_3N^+(CH_2)_4N^+Oct_3$	HSO_4	1.30	1.73	0.73	0.16	0.15	0.57	0.95
Bu_4N^+	Br	0.47[c]	0.075	<0.20	0.04[c]		0.01	0.05
Bu_4N^+	HSO_4	0.59	0.94	0.58	<0.03	<0.06	0.02	0.08
Bu_4P^+	Br	0.48	0.20				0.02	
Bu_3MeN^+	HSO_4	0.28	<0.19		<0.06	<0.06		
Oct_3MeN^+	HSO_4	0.67	0.97		0.16	0.16		
Oct_3MeN^+ [c]	Cl	0.56	0.22		0.32	0.05	0.08	0.17
Hex_4N^+ [c]	Br	0.50	0.14		0.18			
Hex_4N^+ [c]	Cl	0.56	0.25		0.28		0.10	0.12
Ph_4P^+ [c]	Br	0.48	0.20					
$Et_3(C_6H_5CH_2)N^+$ [c]	Cl	0.01	0.02		0.02			
Polyethylene *glycol* 400[c]		0.02	0.02		0.01		0.01	
18-Crown-6[c]		0.01	0.02		0.02		0.01	

[a] Original anion of the inorganic salt.

[b] The loading calculations were based on atomic absorption estimations of the relevant metal present in the organic phase.

[c] The loading calculations were based on UV-VIS measurements.

Ferro- and ferricyanide: concentrtion measurements in the aqueous phase were made at 216 nm for ferrocyanide and at 302 nm for ferricyanide and in the organic layer by atomic absorption. From the data it can be seen that:

1) The more lipophilic ferrocyanide [6] is somewhat better extracted than ferricyanide.

2) the loading of the onium ion is dependent on its lipophilicity and not on the hydrophilicity of the counter anion.

Molybdate: (1) The loading of the onium ion is strongly dependent on the hydrophilicity of the catalyst's original counter anion.

(2) In comparison with the monovalent onium salts, the bis-quaternary ammonium salt carries 25% more of the anions into the organic phase.

Phthalate and terephthalate: concentration measurements in the aqueous phase were made for phthalate at 238 nm and for terephthalate at 239 nm. Both bis-anions were extracted from alkaline solution. $Oct_3N^+(CH_2)_4N^+Oct_3$ with hydrogensulphate as anion had extraordinary good extractive abilities.

Further studies on the bis-quaternary ammonium salts are under way.

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