Bis(tetramethylammonium), bis(tetrabutylammonium), and bis(tetraphenylarsonium) dihydrohexaoxoxenonates(VIII)

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Bis(tetramethylammonium), bis(tetrabutylammonium), and bis(tetraphenylarsonium) dihydrohexaoxoxenonates(VIII) were obtained in an aqueous solution and in acetonitrile. The rate constants of their decomposition were determined.

Key words: bis(tetramethylammonium) dihydrohexaoxoxenonate(VIII), bis(tetrabutylammonium) dihydrohexaoxoxenonate(VIII), bis(tetraphenylarsonium) dihydrohexaoxoxenonate(VIII), preparation; decomposition, rate constant.

Stable hexaoxoxenonates(VIII) of alkali and alkaline-earth metals, having an oxidizing potential 3.0 V in acid media (see Ref. 4), have been described.[1–3] This value is the highest among all chemical compounds known at this time. Organic derivatives of the compounds of this class have not been studied before.

For the first time we have obtained dihydrohexaoxoxenonate(VIII) solutions with onium cations Me_4N^+ (**1**), Bu_4N^+ (**2**), and Ph_4As^+ (**3**) that are relatively stable in H_2O and MeCN. These salts are formed in practically quantitative yields by the exchange reaction between Na^+ ions from an aqueous solution of sodium hexaoxoxenonate(VIII) and a corresponding onium cation pre-immobilized on an ion-exchange resin.

As a result, the residual amount of Na^+ in the solution does not exceed 2.7 % in the case of exchange for the Me_4N^+ ion and 0.3 % in the case of exchange for the Bu_4N^+ ion. The hexaoxoxenonate(VIII) anion remains unchanged in the course of the reaction, which was confirmed by the reverse synthesis of sodium hexaoxoxenonate(VIII) from the obtained compounds **1**—**3** in >80 % yield.

It was established that the hexaoxoxenonate(VIII) anion in the composition of salts **1**—**3** exists as $H_2XeO_6^{2-}$ in water ($5.2 < pH < 10.0$) and in MeCN. Thus, the molar extinction coefficients obtained by us at λ_{max} = 220 nm (ε 4800) and at λ_{max} = 270 nm (ε 2500) are typical and coincide with the UV spectroscopy data for a $H_2XeO_6^{2-}$ ion incorporated into inorganic hexaoxoxenonates.[5]

The decomposition curves of aqueous solutions of salts **1**—**3** are in the shape of an S, which attests to the radical nature of the decomposition processes. The rate constants of the initial stage of the reaction measured at pH 5.6 and 50 °C are $4.1 \cdot 10^{-5}$ and $6.5 \cdot 10^{-5}$ s^{-1} for $(Me_4N)_2H_2XeO_6$ and $(Bu_4N)_2H_2XeO_6$, respectively. The decomposition rate constants in MeCN at 50 °C are $2.4 \cdot 10^{-4}$ and $2.0 \cdot 10^{-4}$ s^{-1} for $(Me_4N)_2H_2XeO_6$ and $(Bu_4N)_2H_2XeO_6$, respectively.

All attempts to isolate the salts as individual compounds from the solutions failed because the salts decomposed.

Experimental

UV spectra were recorded on a Specord UV-VIS instrument, IR spectra (in pellets with KBr) were obtained on an IKS-29 spectrophotometer, and the pH of the solutions was controlled with a pH-340 device.

Bis(tetramethylammonium)dihydrohexaoxoxenonate(VIII) (1). A sodium hexaoxoxenonate(VIII) solution prepared from 81.6 mg (0.191 mmol) of $Na_4XeO_6 \cdot 6H_2O$ and an aqueous solution of tetramethylammonium hydroperoxide (pH 10.2) was passed at 0 °C through a glass column (*d* = 1 cm) containing the cationite KU-2-8 (20 cm^3) in the Me_4N^+ form. An aqueous solution of the $(Me_4N)_2H_2XeO_6$ salt (concentration $5.8 \cdot 10^{-3}$ mol L^{-1}) was obtained at the exit of the column, yield 97.0 %

Bis(tetrabutylammonium)dihydrohexaoxoxenonate(VIII) (2). This compound was obtained by analogy with salt **1**. The concentration of salt **2** in the aqueous solution was $6.0 \cdot 10^{-3}$ mol L^{-1}, yield 97.6 %.

Bis(tetraphenylarsonium)dihydrohexaoxoxenonate(VIII) (3). This compound was obtained by analogy with salt **1**. The concentration of salt **3** in the aqueous solution was $6.7 \cdot 10^{-3}$ mol L^{-1}, yield 68.6 %.

The solutions of salts **1**—**3** in acetonitrile were prepared by mixing the initial aqueous solutions of the salts (0.5 mL) with MeCN (10 mL). The decomposition kinetics of aqueous and acetonitrile solutions of dihydrohexaoxoxenonate(VIII) salts were studied by observing the decrease in the optical density of the solution at λ = 220 nm.

Oxidant percentages were determined by the iodometric method, Na^+ ion concentration was determined by a flame photometry using a PFM-U4.1 photometer. Sodium hexaoxo-

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xenonate(VIII) obtained by reverse synthesis was identified by its IR spectrum, ν/cm^{-1}: 460, 690.

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A new insertion reaction of phenyl isocyanate

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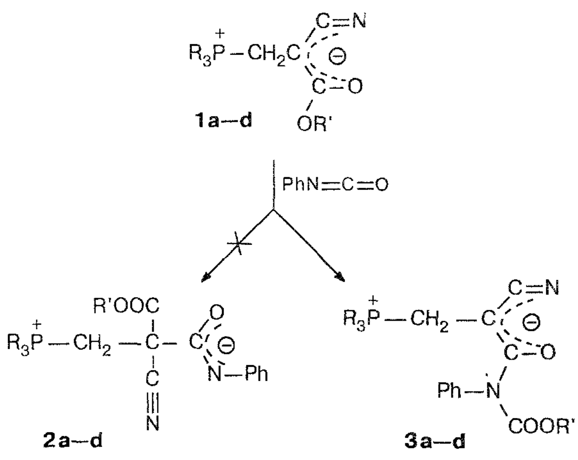
A new reaction of the insertion of phenyl isocyanate into the C—C bond of P-containing zwitterions based on 2-cyanoacrylates was found. A probable mechanism of this reaction has been discussed.

Key words: phenyl isocyanate, zwitterions, insertion reaction.

Reactions involving the insertion of phenyl isocyanate into M—X bonds, where M is C, Si, P, B, or Sn, and X is N, O, S, or Hal, are known.[1,2] We have discovered a new reaction of the insertion of phenyl isocyanate into the C—C bond of zwitterions **1**. We prepared the latter by the reaction of 2-cyanoacrylates with trialkylphosphines and hexaethyltriamide of phosphorous acid.[3] The interaction of phenyl isocyanate with zwitterions **1** resulted in high yields (60—80 %) of crystalline adducts, which turned out to be not the expected zwitterions **2**, but their isomers **3** (Scheme 1), as was unambiguously determined by X-ray diffraction analysis.*

This result may be accounted for by the nucleophilic attack by the N atom in the intermediate zwitterion **2** on the C atom of the carboxyl group, which is favored by the ionic interaction between the positively charged P atom and the carboxyl O atom. Decomposition of the unstable phosphorane **A** involves cleavage of the C—C

Scheme 1



a: R = Pr, R' = Me
b: R = Pr, R' = Et
c: R = Bu, R' = Et
d: R = Et$_2$N, R' = Et

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* The X-ray structural study of compound **3b** was carried out by Yu. T. Struchkov and O. V. Shishkin, and its results will be published separately.

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