Kinetics and the Mechanism of Isoamylene Alcohol Conversion in Acid Media Containing Formaldehyde

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Isoamylene alcohols (3-methyl-3-butene-3-ol, *I*; 3-methyl-1-butene-3-ol, *II*) in aqueous acid solutions (H_2SO_4, $HClO_4$) were subjected to reducible isomerization, hydration to 3-methyl-butane-1,3-diol (*III*) and dehydration to isopropene (C_5H_8). The kinetics and mechanism of these reactions were studied in detail [1, 2].

The unsaturated alcohols *I* and *II* and glycol *III* in acid solutions containing formaldehyde (CH_2O) are known to react with CH_2O to form multiple condensation products [3, 4]. We studied the kinetics of isopropene hydration (reaction *1*) to an equilibrium mixture of alcohols *I* and *II*, the hydration of alcohols *I* and *II* (*2*), and the condensation of compounds *I*, *II*, *III* with CH_2O (*3*) in various solutions of sulphuric and chloric acids, varying the content of CH_2O from 0 to 1.0 mole/l at 25 and 40 °C [5].

The observed rate constants of reactions (*1*), (*2*), (*3*) were found to depend on the acid concentration and at the given medium acidity on CH_2O concentration in the system.

The reaction mechanisms are discussed in terms of the kinetic regularities obtained.

The catalytic activity of formaldehyde is controlled by the medium acidity (h_o) and the concentration of nucleophiles (HSO_4^-, ClO_4^-).

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Ion Selective Extraction of Alkali and Alkaline Earth Metal Ions by New Crown Ether Reagents

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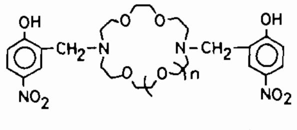
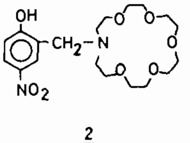
To understand the mechanism of solvent extraction of alkali and alkaline earth metal ions by crown ether-based reagents, [1–3], new chromogenic crown ethers 1 and 2 were synthesized, and their extraction behavior was studied.

1 is insoluble in water, and its 1,2-dichloroethane solution extracts selectively alkaline earth metal ions, especially calcium, according to the reaction (1). Potassium is partially extracted when present in high concentration. The reagent 2 extracts potassium selectively. The table summarizes the constants K_{ex}. The extraction ability of 1 or 2 is generally higher than the reagent 3 or 4 reported earlier. This probably reflects the difference in the mode of extraction. The extraction by the former reagent is based on the intramolecular ion-pair formation, while in the latter the adoption of chelate-type structure



1a (n=0), 1b (n=1)



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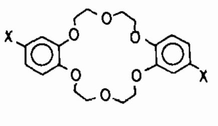

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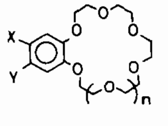

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X, Y = H, NO_2, Br, OH, picrylamino, chromophoric groups conjugated with dissociable protons.

TABLE. Extraction constants; 1,2-dichloroethane, 25 °C.

Mg	Ca	Sr	Ba
1a $< 1 \times 10^{-18}$	1.0×10^{-15}	6.3×10^{-18}	2.5×10^{-18}
1b $<< 1 \times 10^{-16}$	2.9×10^{-13}	3.1×10^{-14}	7.3×10^{-16}

with less charge separation within the extracted complex facilitates the transfer of the complex into the organic solution

$$(H_2L)_{org} + M^{2+} \rightleftharpoons (ML)_{org} + 2H^+$$

$$K_{ex} = [(ML)_{org}]\,[H^+]^2/[(H_2L)_{org}]\,[M^{2+}] \qquad (1)$$

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