the dosages used increases the product yield. The probable reasons are discussed to explain the effects of the additives on the radiolysis process. The authors suggest that the differences in the KNO_2 yields obtained in radiolysis of an identical KNO_3 feedstock might be tied-up with the effect of the impurities in the feedstock.

The Mechanism of Isocyanate Interaction with Alcohols

I. A. Proneena, Yu. L. Speereen,
A. A. Blagonravova, S. M. Ar'yef'yeva,
and A. P. Gantmakher

The State Scientific Research and Planning Institute for Paint Varnish Industry

The effects of temperature and of concentration of the reaction components on the rate of urethane formation were determined dilatometrically. The activation energies of the process were determined, using toluene and tetrahydrofuran as the solvent media. The results show that although the reaction is catalyzed by tertiary amines, tetrahydrofuran in small concentrations is catalytically inactive. In addition, the end product, urethane, also does not catalyze the reaction.

The reaction mechanism proposed includes the reactions of association of the alcohols and of formation of the isocyanate-alcohol complexes in hydrocarbon media and of the isocyanate-solvent complexes in polar media.

Kinetics of Catalyzed Hydrolysis of Allyl Chloride in Alkaline Media

Yu. A. Tr'yeg'yer, R. M. Fleed,
and N. A. Vorontzova

M. V. Lomonosov Institute of Fine Chemical Technology in the City of Moscow

The investigation of kinetics of hydrolysis of allyl chloride was carried out with and without promoting the reaction by different copper catalysts. Based on the overall rate, the process is of the first order with respect to both the allyl chloride and the alkali.

A generalized equation is proposed to describe kinetics of process. The equation takes into account the increasing retardation effect owing to accumulation of the product allyl alcohol due to the non-stationary character of the process. The activation energy and the heat of adsorption were calculated at the reaction conditions of this study. A relationship is shown to exist between the adsorption- and the complex-formation steps. Based on the kinetic data and X-ray analyses of the copper catalyst samples, certain assumptions are made to explain catalytic activity of the metallic copper, which is present as a separate phase in the oxides of copper.

Reactions of α-Oxides: Acid Catalyzed Reactions of Ethylene Oxide with Alcohols and with Other Oxygenated Compounds

N. N. L'yeb'yed'yev and V. M. Kozlov

D. I. M'yend'yel'yeyev Chemico-Technological Institute of the City of Moscow

Two reactions occur in acidic catalysis of ethylene oxide: with respect to the oxide, one of these reactions is of the first order and the other one is of the zero order. Depending on the strength of the acid catalyst, the rate of the first order reaction can be either independent of the alcohol concentration or it can vary linearly with the concentration, increasing or decreasing upon addition of a like ion. The latter reaction comprises an interaction of the protonated oxide with the reagent.

The initial step of the zero order reaction is formation of the glycol ester with the acid catalyst via addition of the acid to the ethylene oxide; in the subsequent step, the ester undergoes alcoholysis. The results show that the addition step is a reaction of the first order relative to both the oxide and the acid; on the other hand, the reactions of oxyethylation and alcoholysis are of the first order with respect to the ester and approximately of the second order with respect to the alcohol.

The Mechanism and Kinetics of Catalyzed Interaction of Isocyanates with Alcohols in the Presence of Organotin Compounds: Reaction Kinetics of *n*-Chlorophenylisocyanate in the Presence of Dibutyldilaurinate of Tin

S. G. Ent'yelees and O. V. N'yest'yerov

Institute of Chemical Physics of the Academy of Sciences of USSR

A spectrophotometric study was made of the reaction kinetics of *n*-chlorophenylisocyanate with methyl alcohol dissolved in *n*-heptane, in the presence of dibutyldilaurinate of tin. At the temperatures and concentrations of the reactants employed, the experimentally-determined rates show that the reaction is of the first order with respect to both the isocyanate and the catalyst. Formation of a complex between the catalyst and the alcohol was uncovered. The value of the equilibrium constant was determined spectrophotometrically and the values of ΔH and ΔS of the complex-formation were calculated.