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On the Generation of H_2 from Formaldehyde in Basic Aqueous Solutions

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Abstract

The generation of H_2 from formaldehyde and glyoxalate in aqueous solutions at high concentrations of hydroxide has been studied in the temperature range 21-60 °C. The reaction is 1st order in formaldehyde and is of higher than 1st order in hydroxide concentration. Conversion ratio of the aldehyde to H_2 increases on increasing OH^- concentration and on raising the temperature. It decreases on increasing aldehyde concentration due to the competition by the Cannizzaro reaction which is 2nd order in the aldehyde. Effective rate constants and activation energies are provided.

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representation of the reactions involved. For the Cannizzaro reaction the rate constants have been determined⁹ at 40 °C. The conversion ratio to H₂ decreases on increasing [HCHO] because of the competition by the Cannizzaro reaction which is second order in the aldehyde. The higher than first order dependence of k_{obs} on [OH⁻] indicates that the hydrogen generation reaction, like the Cannizzaro reaction, occurs with an ionized species of the hydrate. The increase of the conversion ratio to H₂ on increasing [OH⁻] also results from a higher order reaction in hydroxide for the hydrogen generation reaction than for the Cannizzaro reaction.

Because nitrite, nitrate and aluminate are also present in waste solutions, their effect on H₂ generation was also measured. Addition of NaNO₃ (2.8M), NaNO₂ (2.2M) and NaAlO₂ (0.86M), all together, increased the rate by approximately a factor of 2 at 60 °C. The effective activation energy for production of H₂ in such solutions is 20 kcal mole⁻¹ for formaldehyde and 12 kcal mole⁻¹ for glyoxalate. In all of the systems that we have studied increasing the temperature increased the conversion to H₂, presumably at the expense of the Cannizzaro reaction. Although the detailed mechanism for H₂ generation is far from understood, it probably parallels the Cannizzaro reaction in that hydride transfer occurs here as well. Further experiments and computer modeling are underway to unravel the details of the mechanism of this reaction.

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Scheme I

Hydration and Acid-Base Cannizzaro Reaction Hydrogen Generation

Figure Captions

Figure 1: Dihydrogen generation from 5 mM formaldehyde solutions containing 1.0 M (triangles), 2.3 M (solid squares) or 4.0 M (open squares) NaOH at 60 °C.

Figure 2: The dependence of the initial rate of H₂ generation on [HCHO] (circles; at 2.3 M NaOH) and on [NaOH] (squares; at 5 mM HCHO).

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