

The rate of condensation increased exponentially with the increase in the catalyst concentration and, naturally, with temperature.

Alcoholic solvents had no appreciable influence upon the reaction rate in comparison with that of the homogeneous, solvent less, reaction. A retarding action of water was observed in the case of the methanol solvent but in butanol as solvent the effect was hardly observable.

The condensation product was analyzed by the hydrogenation in the presence of nickel catalyst at 120°C. under a hydrogen pressure of about 100 atm., followed by fractional distillation. It was found that the content of the higher condensates containing more than twelve carbon atoms in the molecule and the condensates of the cyclic nature in the product increased with the catalyst concentration, the mol ratio of the catalyst to the crotonaldehyde used, and the reaction temperature.

26. Studies on the Reaction between Ammonia and Carbon Disulfide at High Pressures. (I)

Influences of the Charging Quantity of NH_3 and CS_2 , and their Mol Ratio on the Formation of Ammonium Thiocyanate

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The reaction of ammonia with carbon disulfide giving NH_4SCN was studied in an autoclave at 110° C. changing the reaction times. After the autoclave was heated in an oil bath for a definite time, it was cooled quickly bringing into a bath cooled with running water and allowed to stand over night continuing to cool with water and then the pressure was released in cold state, the products were dissolved in methanol, and NH_4SCN in the products was determined with N/10 AgNO_3 solution.

In a case where the mol ratio of NH_3 to CS_2 is 2:1, the yield of NH_4SCN is decreased, as the charging density of NH_3 and CS_2 is increased. When the mol ratio of NH_3 to CS_2 is 4:1, the yield of NH_4SCN is independent on the charging density, and amounted to 90%. As the mol ratio of NH_3 to CS_2 is increased, the formation of NH_4SCN is increased. Released the pressure in the autoclave at a hot state immediately after the reaction has ended, a remarkable decrease in the yield of NH_4SCN is observed.

The results may be interpreted as follows. In the autoclave the following reactions exist in a state of an equilibrium.



As the gas in the autoclave is released, the following dissociations take place gradually :



so that when the pressure in the autoclave is released in a hot state, a decrease in the yield of NH_4SCN will be resulted, according to equation (3). Furthermore, the experimental result that by increasing charging density of NH_3 and CS_2 the formation of NH_4SCN is decreased can be explained quantitatively with a rate equation derived on above reaction schema from the stand point of chemical kinetics.

27. Preparation of Organo-mercurisulfides. (I)

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Merthiolate, *i. e.*, sodium ethylmercurithiosalicylate, which was synthesized by Kharasch *et. al.* in 1926, has strong sterilizing power.

But, the material mercuri-compound of this substance is expensive.

The authors, also with the same purpose, prepared the following compounds, using easily obtainable aromatic mercuri-compounds.

	dec. p.
p-Ethylmercaptomercuribenzoic acid.	179.5°-181°
p-(β-Hydroxyethylmercaptomercuri)-benzoic acid.	168°-170°
p-Carboxylphenylmercurithiosalicylic acid.	215.5°-216.5°
o-(β-Hydroxyethylmercaptomercuri)-benzoic acid.	142°-144°
4-(β-Hydroxyethylmercaptomercuri)-2-chloro-benzoic acid.	147°-149°
3-Chloro-4-carboxylphenylmercuri-thioalicylic acid.	204.5°-205.5°
2-Chloro-tolyl-4-mercurithiosalicylic acid.	153.5°-154.5°
2-Chloro-tolyl-4-mercuripseudothiourea chlorohydrate.	140°-150°