

EFFICIENT RECOVERY OF INTERMEDIATE HYDRAZINE IN GAS-PHASE PHOTOLYSIS OF AMMONIA BY ABSORPTION INTO FALLING FILM OF AQUEOUS AMMONIA

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The current technology for hydrazine synthesis based on chlorine oxidation such as Raschig synthesis and the Bayer process entails a sizable amount of chlorides,²⁾ and the new processes by-passing chlorine have received increasing attention in recent years.^{3,7,8)}

A photochemical approach to hydrazine synthesis directly from ammonia was made in the previous paper.⁶⁾ The predominant primary process at 185 nm is splitting off a hydrogen atom to give NH_2 radical, which affords hydrazine (NH_2NH_2) in the secondary processes. However, no hydrazine was detected in a static system by the subsequent decomposition into final products, nitrogen and hydrogen. Hydrazine should be immediately removed from the reactor employing a flow system with an extremely low residence time condition, which unfortunately resulted in a lower conversion of ammonia.

Thus attempts were focused in the present work on the efficient recovery of hydrazine from the irradiated zone without decreasing residence time capable of high conversion. A reactor device has been proposed for protecting hydrazine from irradiation in the gas-phase photolysis of ammonia by absorption into a liquid film of saturated aqueous ammonia falling and recycled near the irradiated zone.

1. Experimental

Apparatus and Procedure A schematic flow diagram of the apparatus is given in Fig. 1. A lamp 7 was inserted coaxially in a double-wall Pyrex tube. Aqueous ammonia was supplied through the outer annulus 10 from the bottom inlet, overflowed at the top of the inner tube to form a smooth liquid film 8 falling over the inner wall 9 without ripples, separated from gases by a gas-liquid separator 11, and then recycled by a circulation pump 4. Gaseous ammonia was supplied from a commercial cylinder 1 (99.99₁% purity) without further purification through a capillary 5, and irradiated in the gas-phase annular space between liquid film and lamp surface. Hydrazine thus

formed was absorbed by the liquid film of saturated aqueous ammonia and was analyzed by spectrophotometry (Hitachi double-beam spectrophotometer, Model 200-10, with 1 cm quartz cell) as *p*-dimethylaminobenzaldehyde azine¹⁾ at 456.5 nm. Gaseous products were collected in a microburette over a water-scrubber 12 and were analyzed for hydrogen and nitrogen by gas chromatography (Hitachi 163-TCD, Molecular Sieves 5A).

Reactor Specifications A low-pressure mercury lamp (0.9 cm o.d., effective length 12 cm) of PCQ-9G-1, Ultraviolet Products, Inc., Calif., was used as an ultraviolet source. The gas-phase temperature at 0.1 cm from the lamp surface was measured as 313 K. The circulation rate of aqueous ammonia (total volume 50 cm³) and the thickness of liquid film were 0.5 cm³/s and 0.03 cm, respectively. The spacing of the annular irradiated zone between liquid film and lamp surface was 0.14₅ cm. Thus the gas-phase reactor volumes with and without aqueous ammonia were 5.7 cm³ and 7.1 cm³, respectively. The Reynolds num-

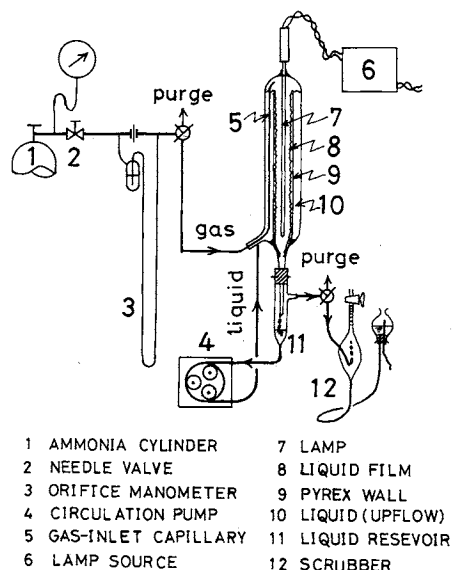


Fig. 1. Schematic flow diagram of apparatus for gas-phase photolysis of ammonia with recycling of aqueous ammonia.

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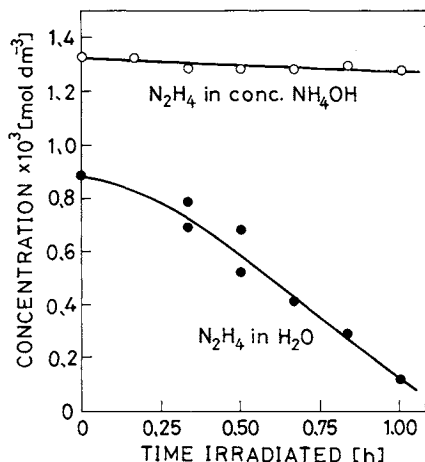


Fig. 2. Stability of hydrazine in concentrated aqueous ammonia against ultraviolet irradiation.

ber was less than 30, suggesting laminar flow for gaseous ammonia.

2. Results and Discussion

Figure 2 shows the stability of hydrazine in aqueous media for ultraviolet irradiation, where dilute solutions of hydrazine in water and in concentrated aqueous ammonia were irradiated by a low-pressure mercury lamp immersed in the solution. Hydrazine dissolved in concentrated aqueous ammonia was found to be quite stable for irradiation, while rapidly decomposed in water. The difference in the stability of hydrazine in aqueous media with and without ammonia was presumably due to absorption of light by ammonia. Formation of hydrazine from aqueous ammonia was observed under similar conditions, but the amounts were negligibly small, less than $4 \times 10^{-5} \text{ mol dm}^{-3}$ for 1 h irradiation as shown in Fig. 3. Radiations emitted from the low-pressure mercury lamp (185/254 nm) are transparent for water and available for the decomposition of hydrazine. In the presence of an excess of ammonia in water, the majority of light might be absorbed by ammonia and dissipated as thermal energy.

Figure 4 shows results for gas-phase photolysis of ammonia with and without recycling of aqueous ammonia. The values of space-time conversion of ammonia were essentially constant over a wide range of residence times (θ_G) for both series of runs, showing that the conversion of ammonia increased linearly with θ_G . The space-time yields of hydrazine with recycling of aqueous ammonia were again constant, while those for the vacant reactor rapidly decreased with increasing θ_G .

Evidence for steady-state photolysis of ammonia with recycling of aqueous ammonia is given in Fig. 5. Both the concentration of hydrazine in the recycling liquid (a) and the cumulative volume of gases in-

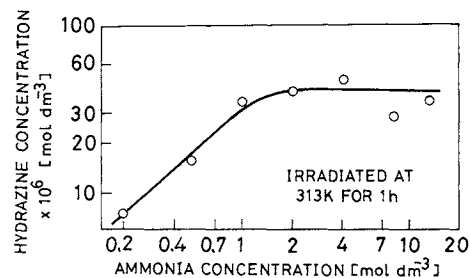


Fig. 3. Negligible formation of hydrazine in liquid-phase photolysis of aqueous ammonia.

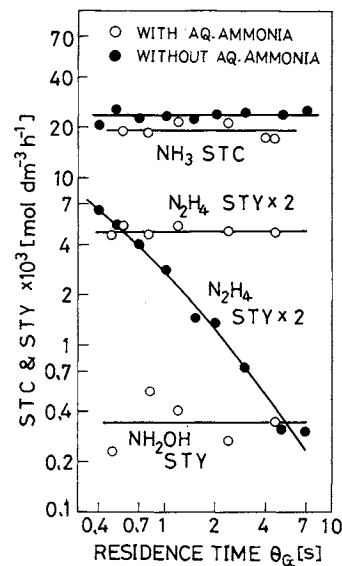


Fig. 4. Results for gas-phase photolysis of ammonia with and without recycling of aqueous ammonia.

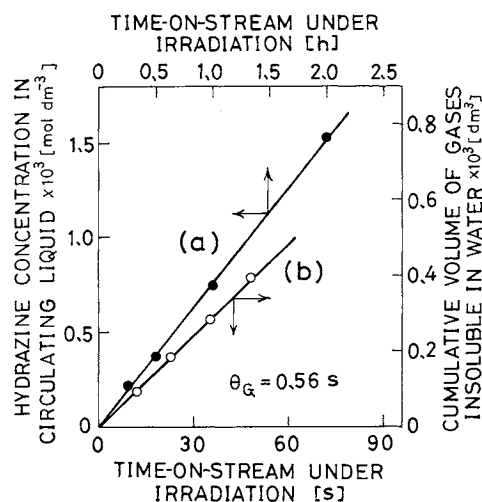


Fig. 5. Evidence for steady-state photolysis of ammonia with recycling of aqueous ammonia.

soluble in water (b) increased linearly with time-on-stream under irradiation.

Hydrazine formed in the gas-phase photolysis of ammonia in the vacant reactor travels through the long annular space and the subsequent irradiation would cause consecutive decomposition of hydrazine,

especially for longer residence time conditions. Since the quantum yield of ammonia photolysis at 185 nm approaches unity⁴⁾ at low pressure in the flow system with an extremely high linear velocity (~ 17.5 m/s; $\theta_G = 2.3 \times 10^{-3}$ s), the ultimate rate of formation of hydrazine is expected to be close to the rate of conversion of ammonia. The black circles in Fig. 4 suggest that N_2H_4 -STY approaches NH_3 -STC at low θ_G conditions.

In the presence of saturated aqueous ammonia near the lamp surface, hydrazine is absorbed into the liquid film and protected from irradiation as evidenced in Fig. 2. The observed STY values (white circles in Fig. 4) are the results of a dynamic balance for hydrazine among rates of formation, decomposition and absorption by aqueous ammonia. The absorption by the liquid film of aqueous ammonia was quite efficient and the amounts of hydrazine detected in the effluent gas (i.e., unabsorbed) were found to be only 0.15–0.35% as compared with those absorbed in the liquid film. The spacing between liquid-film and lamp surface in the present reactor was 0.14₅ cm, which is much less than the longitudinal length (12 cm) of the annular irradiated zone. Thus the selectivity to hydrazine would be constant regardless of the nominal residence time θ_G .

Another reducing substance besides hydrazine was detected in the aqueous ammonia by potentiometry. It seemed likely that hydroxylamine (NH_2OH) was formed through NH_2 radical and water as a possible cause for decreasing selectivity to hydrazine. Hy-

droxylamine could be determined separately from hydrazine by potentiometric titrations of the admixtures.⁵⁾ The amounts thus determined were 4.8–10.8% (N-basis) as compared with hydrazine, as shown in Fig. 4.

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Nomenclature

STC	=	space-time conversion of ammonia	[mol dm ⁻³ h ⁻¹]
STY	=	space-time yield of hydrazine	[mol dm ⁻³ h ⁻¹]
θ_G	=	nominal residence time of gaseous ammonia	[s]

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