Fig. 3 Adsorption from aqueous multi-solute system: *p*-cresol(1)-*p*-chlorophenol(2) at 25°C

Fig. 4 Adsorption from aqueous multi-solute system: *p*-cresol(1)-*p*-chlorophenol(2) at 25°C

$n_i^{\circ, \infty}$ = maximum moles of solute *i* adsorbed [mmol/g]
 n_T = total moles of solutes adsorbed [mmol/g]

n_T^{∞} = maximum total moles of solutes adsorbed [mmol/g]
 R = gas constant [J/mol·K]
 T = absolute temperature [K]
 x_i = mole fraction of component *i* in adsorbed phase ($=n_i/\sum_i n_i, i=1, 2, 3$) [—]
 z_i = mole fraction of solute *i* in water-free adsorbed phase ($=n_i/\sum_i n_i, i=1, 2$) [—]
 γ_i = activity coefficient of solute *i* in adsorbed phase [—]
 θ_i = fractional coverage of solute *i* [—]
 A_{ij}, A_{ji} = Wilson's parameters for interaction between *i* and *j* in adsorbed phase [—]
 π = spreading pressure [N/m]

<Superscripts>

° = single-solute system
 ∞ = value at maximum adsorption limit

<Subscripts>

i, j, k = component *i, j, k*
 T = total
1, 2 = adsorbates (organic solutes)
3 = water

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FORMATION OF HYDRAZINE BY PHOTOLYSIS OF AMMONIA IN A FLOW SYSTEM

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In industry, hydrazine (N_2H_4) has been manufactured from ammonia (NH_3) by a chlorine-oxidation process. However, it is the disadvantage of this process that a large amount of salt is also produced together with the N_2H_4 (in the ratio of 6 kg salt to 1 kg N_2H_4 hydrate). Considerable energy is then spent in the distillation separation of the product. Alternatives have been developed to overcome these shortcomings of the chlorine oxidation process. One is the ketazine process, which is based on an aerial oxidation²⁻⁴⁾ or

hydrogen peroxide oxidation⁷⁾ of NH_3 , the other is the direct process from NH_3 , e.g. the NH_3 -photolysis process, which is discussed in this note.

NH_3 decomposes into N_2H_4 by photolysis at the wavelengths 185–225 nm. The work of McDonald *et al.*⁶⁾, and Groth and Rommel¹⁾ involves this route. They obtained N_2H_4 selectively under reduced pressures in a closed recycling system, although the reaction rate was not measured. Mantell *et al.*⁵⁾ (Kellogg Co., Ltd.) have claimed that N_2H_4 is produced by photolysis of a mixture of nitrous oxide (N_2O) and NH_3 . This has been considered to activate N_2O rather than NH_3 . We have studied the rate of photolysis of NH_3

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in a flow system, under the conditions of atmospheric pressure and room temperature, with and without the presence of N_2O .

1. Experimental

Figure 1 shows a schematic diagram of the apparatus. The quartz spiral reactors ($3\text{ mm}\phi \times 0.5\text{ m}$ and 1.0 m) are irradiated with a low-pressure mercury lamp (LPML, Ushio, UL-1-70Q, 70W), a high-pressure mercury lamp (HPML, Toshiba, H-400P, 40W) and a xenone lamp (Toshiba, XL-500F, ozone-free) under nitrogen (N_2) circumstances. The absorption spectra of NH_3 and N_2O are measured with a double-beam spectrophotometer (Hitachi, Model-1200-20) in cylindrical quartz cells ($50\text{ mm} \times 20\text{ mm}$). A commercial NH_3 gas (99.991% of purity) is supplied to the reactors at a given flow rate. The effluent gas from the reactor enters a water-scrubber, and then the volume of insoluble gas (V) is measured. The molar ratio (R) of hydrogen (H_2) to N_2 in the insoluble gas is determined with a gas chromatograph (Hitachi, 063-TCD, Molecular-Sieve 5A). From the NH_3 feed rate (V_0) together with V and R , a one-pass conversion of NH_3 ($X_A = 2 \times 10^2 (R-3)(V/V_0)/(R+1)$) is determined. Changing the stopcock C_2 in **Fig. 1**, the effluent gas is washed with an ice-cooled 10% aqueous-acetone solution. This converts N_2H_4 to acetone azine quantitatively. The azine is then determined with a gas chromatograph (Hitachi, 163-FID, PEG-4000) and the selectivity to N_2H_4 (S_H) is estimated.

2. Results and Discussion

Figure 2 shows the absorption spectra of NH_3 and N_2O in the range of wavelengths from 185 to 225 nm. The extinction coefficient of N_2O was found to be one-60th that of NH_3 . Mantell *et al.*⁵⁾ recommended a molar ratio of N_2O to NH_3 less than one-fifth in feed gas. From the spectrophotometric aspect, however, N_2O is considered to contribute little to initiating the reaction.

LPML emits resonant light at the wavelengths of 185 and 254 nm. In a batch system, 70% of NH_3 is decomposed into a water-insoluble gas, containing $75.6 \pm 0.2\%$ of H_2 , in an hour. This shows the preferential decomposition to N_2 and H_2 . In a flow system, the cumulative volume of water-insoluble gas increases at a constant rate corresponding to various feed rates of NH_3 . This verifies the steady rates of photolysis of NH_3 . X_A and S_H are plotted against residence time (θ) for two reactors in **Fig. 3**. X_A is as low as 0.17%, even at $\theta = 12$ seconds. Because of the log-log plot, the difference in X_A between the two reactors (0.50 and 1.0 m) seems to be larger at shorter θ . However, it is not clear at present how significant this difference is. S_H increases with decreasing in θ and

Fig. 1 Apparatus used for Photolysis of NH_3

Fig. 2 Absorption spectra of NH_3 and N_2O

open symbol: X_A , closed symbol: S_H , circle: LPML 1.0 m, triangle: LPML 0.5 m, square: HPML 1.0 m

Fig. 3 Effect of Residence time on X_A and S_H

reaches to 68% at 0.53 seconds, and the curves for the two reactors agree with each other. The steep degradation in S_H suggests a consecutive decomposition of N_2H_4 . Ambient air suppresses both X_A and S_H , as shown in **Fig. 4**, with generation of ozone in ambient atmosphere. This is due to the fact that oxygen (O_2) and NH_3 absorb light at 185 nm, but transmit it at 254 nm, while N_2H_4 absorbs light at both wavelengths.

Fig. 4 Effect of ambient gas, air and nitrogen on X_A and S_H

Fig. 5 Effect of N_2O added to NH_3 on N_2H_4 STY and V

Fig. 6 Concentration of N_2H_4 in the effluent gas

Addition of 1.5–9.9% N_2O to NH_3 decreases space-time-yield (STY) of N_2H_4 , although V is kept unchanged, as illustrated in Fig. 5. The contribution of N_2O to the formation of N_2H_4 is still in question.

The xenon lamp does not decompose NH_3 without generation of ozone in an aerial ambient atmosphere.

HPML emits light in the range of wavelengths from 185 to 580 nm. The X_A for HPML is 10–20 times higher than that of LPML, but the S_H is as low as from one-tenth to one-twentieth that of LPML. This is illustrated in Fig. 3.

The concentrations of N_2H_4 in the effluent gas (C_H) from the reactor with either LPML or HPML are found to be almost the same, as shown in Fig. 6. C_H reaches a maximum at about 0.9 seconds, and then sharply decreases with time. A radical chain reaction is considered to take place in the photolysis of NH_3 . Between the irradiated zone and ice-cooled aqueous acetone solution there is a dark zone, where the photolyses of NH_3 and N_2H_4 stop but the consecutive decomposition of N_2H_4 by radicals does not. This is known as the photochemical after-effect. The results depicted in Fig. 6 can be interpreted on the basis of unsteady-state reaction kinetics.

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Nomenclature

C_H	= molar concentration of hydrazine in effluent gas	[mol/m ³]
R	= molar ratio of hydrogen to nitrogen in water-insoluble gas	[—]
S_H	= molar selectivity to hydrazine	[%]
STY	= space-time yield of hydrazine	[mol/(m ³ ·h)]
V	= issue rate of water-insoluble gas	[m ³ /(m ³ ·h)]
V_0	= feed rate of ammonia gas	[m ³ /(m ³ ·h)]
X_A	= conversion of ammonia in one pass	[%]
θ	= residence time in reactor	[s]

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