

**Table IV. Change in Gas Composition (Volume Percent) in the Pilot Plant**

composition	COG	after CO addition	after reaction	after PSA
H <sub>2</sub>	57.57	53.07	25.40	2.53
CO	6.45	9.65	0.00	0.00
CO <sub>2</sub>	2.56	3.40	2.74	0.16
CH <sub>4</sub>	26.60	26.00	45.60	85.53
C <sub>2</sub> -C <sub>4</sub>	3.62	3.55	5.13	10.23
N <sub>2</sub>	2.85	2.91	3.73	1.49

test was carried out using 20 wt % Co-20 wt % Mn<sub>2</sub>O<sub>3</sub>-0.1 wt % Ru/Al<sub>2</sub>O<sub>3</sub> catalyst prepared by the spray-drying method. The reduction conditions were set at SV of 1000 h<sup>-1</sup>, 260 °C, and 8 kg/cm<sup>2</sup>. A coke oven gas (H<sub>2</sub>/CO = 8.9) was arranged by addition of CO from a CO generating plant and provided as the reaction gas having a H<sub>2</sub>/CO volumetric ratio 5.5. As shown in Table IV, CO was converted completely, and after the unreacted H<sub>2</sub>, CO<sub>2</sub>, and N<sub>2</sub> were reduced by pressure-swing adsorption (PSA) plants, the content of C<sub>2</sub>-C<sub>4</sub> in the gas became 10.2%. The catalyst life was confirmed at least 3000 h without any deactivation. The scattering of catalyst from the reactor during the long-term reaction was 1%.

The product gas produced by this process generates 10 020 kcal/(N m<sup>3</sup>) of combustion heat and only 4 vol % LPG required to adjust the city gas calorific value (11 000 kcal/(N m<sup>3</sup>)), reducing the necessary amount by about one-third compared with the conventional methanation process.

**Registry No.** Co, 7440-48-4; Mn<sub>2</sub>O<sub>3</sub>, 1317-34-6; Ru, 7440-18-8; CO, 630-08-0; CH<sub>4</sub>, 74-82-8; C<sub>2</sub>, 74-84-0; C<sub>3</sub>, 74-98-6; C<sub>4</sub>, 106-97-8; CO<sub>2</sub>, 124-38-9.

### Literature Cited

- Bruce, L.; Hope, G.; Turney, T. W. Light Olefin Production from CO/H<sub>2</sub> over Silica Supported Fe/Mn/K Catalysts Derived from a Bimetallic Carbonyl Anion, [Fe<sub>2</sub>Mn(CO)<sub>12</sub>]<sup>-</sup>. *React. Kinet. Catal. Lett.* **1982**, *20*, 175-180.
- Buessenmeier, B.; Frohning, C. D.; Horn, G.; Kluy, W. (Ruhrchemie A.-G.) Ger. Offen. DE 2518964; *Chem. Abstr.* **1977a**, *86*, 124093c.
- Buessenmeier, B.; Frohning, C. D.; Horn, G.; Kluy, W. (Ruhrchemie A.-G.) Ger. Offen. DE 2536488; *Chem. Abstr.* **1977b**, *87*, 41705y.
- Dent, A. L.; Lin, M. Cobalt-based Catalysts for the Production of C<sub>2</sub>-C<sub>4</sub> hydrocarbons from Syngas. *Prepr. Pap—Am. Chem. Soc., Div. Fuel Chem.* **1978**, *23*, 502-512.

- Henrici-Olivé, G.; Olivé, S. The Fischer-Tropsch Synthesis: Molecular Weight distribution of Primary Products and Reaction Mechanism. *Angew. Chem.* **1976**, *88*, 144-150.
- Inagawa, H.; Yasumaru, J.; Usugi, Y.; Taki, K.; Ito, M.; Inui, T. COG to SNG by Co-Mn<sub>2</sub>O<sub>3</sub>-Ru/Al<sub>2</sub>O<sub>3</sub> Catalyst. *Proc., Regional Symp. Petrochem. Tech.* '87, Bangkok **1987**, CA-3-CA-11.
- Inui, T.; Funabiki, M. Methanation of Carbon Dioxide and Carbon Monoxide on Supported Ni-La<sub>2</sub>O<sub>3</sub>-Ru Catalyst. *Chem. Lett.* **1978**, 251-252.
- Inui, T.; Funabiki, M.; Suehiro, M.; Sezume, T. Methanation of CO<sub>2</sub> and CO on Supported Ni-based composite Catalysts. *J. Chem. Soc., Faraday Trans. 1* **1979a**, *75*, 787-802.
- Inui, T.; Funabiki, M.; Takegami, Y. Simultaneous Methanation on CO and CO<sub>2</sub> on Supported Ni-based composite Catalysts. *Ind. Eng. Chem. Prod. Res. Dev.* **1980**, *19*, 385-388.
- Inui, T.; Kuroda, T.; Takeguchi, T.; Miyamoto, A. Selective Conversion of Syngas to Olefins and Aromatic-rich Gasoline on Fe-Mn-Ru Containing Composite Catalysts. Submitted for publication in *Appl. Catal.*, 1989.
- Inui, T.; Sezume, M.; Miyaji, K.; Takegami, T. Pronounced Improvement of Methanation Activity by Modification of the Pore Structure of the Catalyst Support. *J. Chem. Soc., Chem. Commun.* **1979b**, 873-874.
- Inui, T.; Suehiro, M.; Saita, Y.; Miyake, Y.; Takegami, Y. Enhancement of Methanation Activity by Ammonia-water Vapor Treatment at the Stage of Catalyst-Salt Supported on a Carrier. *Appl. Catal.* **1982**, *2*, 389-398.
- Kokes, R. J.; Emmett, P. H. Chemisorption of CO, CO<sub>2</sub>, and N on Ni Catalysts. *J. Am. Chem. Soc.* **1960**, *82*, 1037-1041.
- Köbel, H.; Ralek, M.; Tillmetz, K. D. Feedstock for Chemical Industry by Selective Fischer-Tropsch Syntheses. Proceedings of the 13th Intersociety Energy Conversion Engineering Conference, San Diego, CA; Society of Automotive Engineer, Inc.: Warrendale, PA, 1978; Vol. 1, pp 482-486.
- Kugler, L. Synthesis of Light Olefins from CO and H<sub>2</sub>. *Prepr. Pap—Am. Chem. Soc., Div. Fuel Chem.* **1980**, *25*, 564-569.
- Mills, G. A.; Steffgen, F. W. Catalytic Methanation. *Catal. Rev.* **1973**, *8*, 159-210.
- Müller, K.; Deckwer, W. D.; Ralek, R. Fischer-Tropsch Synthesis on Polyfunctional Manganese/Iron-Pentasil Zeolite Catalysts. *Studies Surf. Sci. Catal.* **1982**, *12*, 267-274.
- Vielstich, W.; Kitzelmann, D. Japan Pat. Showa-56-25117; *Chem. Abstr.* **1981**, *94*, 86946p.
- Yang, C. H.; Oblad, A. G. Catalytic Synthesis of Light Olefinic Hydrocarbons from CO and H<sub>2</sub> over Some Iron Catalysts. *Prepr. Pap—Am. Chem. Soc., Div. Fuel Chem.* **1978**, *23*, 513-520.

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## Kinetics of Triaminoguanidine Nitrate Synthesis

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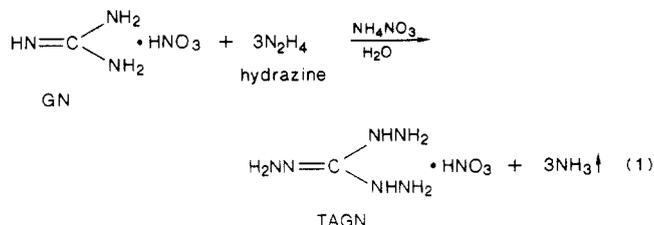
A kinetic study was performed on the synthesis of triaminoguanidine nitrate (TAGN) from guanidine nitrate, hydrazine, and ammonium nitrate in an aqueous solution. The reaction rate ( $-r_H$ ) was found to be equal to the sum of the rate of two independently occurring second-order irreversible reactions, namely, the main reaction between hydrazine and guanidine nitrate to form TAGN and the neutralization reaction between hydrazine and ammonium nitrate to form hydrazine nitrate. The parameters of the apparent kinetic model of these two reactions were derived from individual experiments following NH<sub>3</sub> off-gas evolution rate. A reaction mechanism was attempted to elucidate the apparent kinetic model of the main reaction. Moreover, the validity of this model for reactor design was proved by good agreement of conversion between continuous stirred tank reactor experiments and simulation predictions.

Triaminoguanidine nitrate (TAGN), one of the important propellant ingredients, has been used primarily as an oxidizer in cool-burning gun propellants for rapid fire weapon systems (Kaye, 1980a,b). It can be prepared by

the following methods: (a) dicyandiamide method (Satriana et al., 1966), (b) cyanamide method (Sauermilch, 1964, 1969), (c) calcium cyanamide method (Satriana et al., 1974), and (d) guanidine nitrate method (Morton et al., 1981; Frick and Hoffman, 1951; Sauermilch, 1964; Haury, 1976). Among the diversified chemical routes,

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synthesis of TAGN from guanidine nitrate (GN) and hydrazine in an aqueous solution was examined by Haury (1976) as the following reaction:



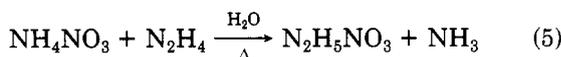
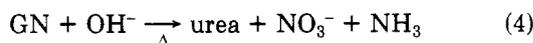
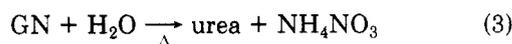
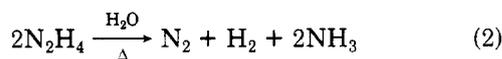
where ammonium nitrate (AN) was added as the stabilizer for reaction intermediates. Although the chemical recipe of this method was reported, no kinetic study has ever been undertaken to the knowledge of the authors. A kinetic model would be of great practical use in reactor design. Owing to the difficulty of quantitatively analyzing the species of eq 1—GN, TAGN, and the reaction intermediates monoaminoguanidine nitrate (MAGN), diaminoguanidine nitrate (DAGN), etc.—the reaction kinetics cannot be obtained directly by analyzing the above species. This paper attempts to study the reaction kinetics by monitoring  $\text{NH}_3$  off-gas evolution rate during reaction. The kinetic model is pursued and a mechanism is proposed, making it possible to obtain more insight into this reaction.

### Reaction Scheme

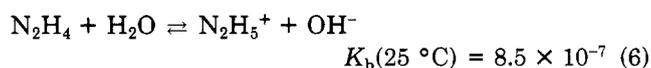
In order to study the kinetics of eq 1 by monitoring  $\text{NH}_3$  evolution rate, it is important to realize all possible reactions that might also generate  $\text{NH}_3$  during the course of reaction. Moreover, understanding of reaction scheme is the first step toward chemical kinetic study. In addition to the main reaction



the possible side reactions considered, from the chemical environment of this reaction system, are



Dissociation of  $\text{N}_2\text{H}_4$  in aqueous solution from eq 2 and hydrolysis of GN from eq 3 were found not to occur at the reaction temperature of 381 K. If eq 3 did occur, the product AN might further react with  $\text{N}_2\text{H}_4$  to produce  $\text{NH}_3$  according to eq 5. Our experimental study of eq 4, however, detected the formation of 0.12 mol of  $\text{NH}_3$  after heating 0.17 mol of GN in 180 mL of 0.8 N NaOH solution at 373 K for 1 h. Since no hydroxide was added to the reaction system, the only possible source of  $\text{OH}^-$  ion in eq 4 might come from hydrolysis of  $\text{N}_2\text{H}_4$  according to



Due to the small  $K_b$  value (Kirk and Othmer, 1980) of eq 6, the calculated  $[\text{OH}^-]$  only gives  $3.6 \times 10^{-3}$  M under the typical condition of  $[\text{N}_2\text{H}_4]_0 = 11.75$  M. Thus, the  $\text{NH}_3$  contributed from eq 4 may also reasonably be ignored.

This leaves only eq 5, the neutralization reaction between ammonium nitrate and hydrazine, as the only

possible side reaction that might be capable of generating  $\text{NH}_3$ . Our experiments do confirm the occurrence of the reaction. Therefore, ammonium nitrate plays not only as a stabilizer to stabilize the reaction intermediate, TAG (triaminoguanidine), as claimed by Haury (1976), but also chemically competes for hydrazine to generate  $\text{NH}_3$  according to eq 5. Since ammonium nitrate was added to the reaction mixture according to eq 1 under real condition, it is therefore important to discriminate the  $\text{NH}_3$  part contributed from main reaction 1a and the one from neutralization reaction 5. AN might change the activation energy and rate constant of main reaction 1a due to solvent effect, i.e., changing the energy level of reactants and transition states due to the presence of different solvents—water or AN aqueous solution. Parallel analysis might also apply to GN with respect to neutralization reaction 5. Therefore, we face the problem of whether the rate constants  $k_G$  and  $k_A$ , obtained respectively from the GN/ $\text{N}_2\text{H}_4$  and AN/ $\text{N}_2\text{H}_4$  systems from the following sections, are identical with those obtained from the GN/ $\text{N}_2\text{H}_4$ /AN system. In other words, will eq 1a and 5—both generate  $\text{NH}_3$ —occur independently or interrelatedly in the synthesis reaction 1?

The objective of this paper is to report measured kinetic data of both main reaction 1a and neutralization reaction 5 by monitoring  $\text{NH}_3$  off-gas evolution rate in the individual reaction. Subsequently, pursuit of the answer to the above question using these data will be performed, and finally the validity of kinetic model for design purpose will be verified with CSTR experiments.

### Experimental Section

A 3-neck 500-mL round-bottom flask with mechanical agitator and  $\text{N}_2$  bubbling inlet was employed for our kinetic study. Hydrazine hydrate, ammonium nitrate, and guanidine nitrate with purity greater than 98%, along with distilled water, were used as raw materials. The  $\text{NH}_3$  off-gas from reactor was absorbed by diluted  $\text{HNO}_3$  solution. The latter was sampled periodically (10–15 min) and the absorbed  $\text{NH}_3$  was determined by back-titration using a METROHM 636 titroprocessor. The experiments were conducted under atmospheric pressure. The raw materials were premixed by adding a suitable amount of GN to hydrazine hydrate and adjusting the amount of water to a total volume of 200 mL at room temperature. The flask was then introduced into the temperature-controlled oil bath. A reflux condenser was employed at the exit of the vapor phase so that near constant liquid volume can be maintained during reaction. The near concurrence of  $\text{NH}_3$  detection and the heat-up time to reach the desired reaction temperature indicates that the amount of  $\text{NH}_3$  evolved during heat-up period is negligible. This measure also ensures that isothermal kinetic data are collected.

$\text{N}_2$  bubbling (1.5 L/min) was applied all through the experiments in order to promote  $\text{NH}_3$  escaping from the reactor. This is especially important in measuring the reaction rate at temperatures lower than the boiling point of the reaction mixture, while the product  $\text{NH}_3$  does not so easily escape.  $[\text{NH}_3]_1$  of  $1.9 \times 10^{-4}$  and  $1.2 \times 10^{-3}$  M were measured at temperatures of 372 and 355 K, respectively, under steady-state conditions. These data are important for mechanism analysis as shown in the latter part of this study. In addition, application of  $\text{N}_2$  bubbling in TAGN synthesis was found to increase the yield by a few percent as compared with those without  $\text{N}_2$  bubbling (Ho and Wu, 1986).

For safety reasons, consult the relevant references for handling TAGN and hydrazine hydrate (Kaye, 1980a,b; Leng, 1985).

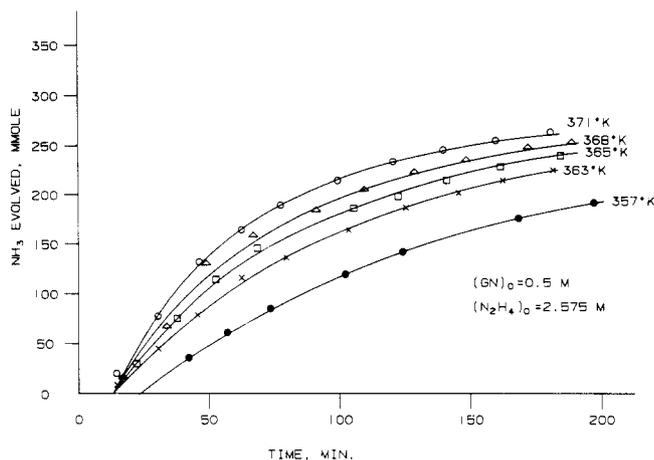


Figure 1. Experimental results for  $[GN]_0 = 0.5 \text{ M}$  and  $[N_2H_4]_0 = 2.575 \text{ M}$  under different reaction temperatures.

## Results and Discussion

**I. GN/ $N_2H_4$  System. A. Rate Equation Determination.** Figure 1 shows the kinetic measurements under a fixed  $[GN]_0$  and  $[N_2H_4]_0$  pair but different reaction temperatures.

Equation 1a may be considered as the sum of a consecutive-parallel reaction scheme comprising the following three reactions:



where intermediates MAGN and DAGN represent monoaminoguanidine nitrate and diaminoguanidine nitrate, respectively. Assume that reaction 1a is a second-order irreversible reaction governed by

$$-d[N_2H_4]/dt = k_G[GN][N_2H_4] \quad (10)$$

Integrating eq 10 with initial conditions and stoichiometric relationships gives

$$\ln \frac{[GN]_0([N_2H_4]_0 - [N_2H_4]^*)}{[N_2H_4]_0([GN]_0 - [N_2H_4]^*/3)} = \frac{[N_2H_4]_0/3 - [GN]_0}{k_G t} \quad (11)$$

where the subscript 0 denotes initial values and  $[N_2H_4]^*$  denotes the  $N_2H_4$  concentration consumed, which derived from the  $NH_3$  evolved.

Integral analysis of data in Figure 1 shows that, in order to conform to the rate law of the second-order irreversible reaction, a straight line must be obtained if the data in Figure 1 are plotted using the left-hand side of eq 11 against  $\{[N_2H_4]_0/3 - [GN]_0\}t$ . The slope of this line will then be equal to the rate constant. The test results are shown in Figure 2. It should be noted that time zero in Figure 2 is obtained as the time when  $NH_3$  was first detected in each experiment. The good linear relationship in Figure 2 indicates that the rate law of reaction 1a appears to be irreversible second order. However, the experimental results by variation of  $[N_2H_4]_0$  shown latter indicate that reaction 1a is not governed by a "simple" second-order irreversible rate law.

The temperature dependence of the rate constant can be derived from the Arrhenius equation. The Arrhenius plot for the  $[GN]_0 = 0.5 \text{ M}$  and  $[N_2H_4]_0 = 2.575 \text{ M}$  pair is shown as the A line of Figure 3. The activation energy

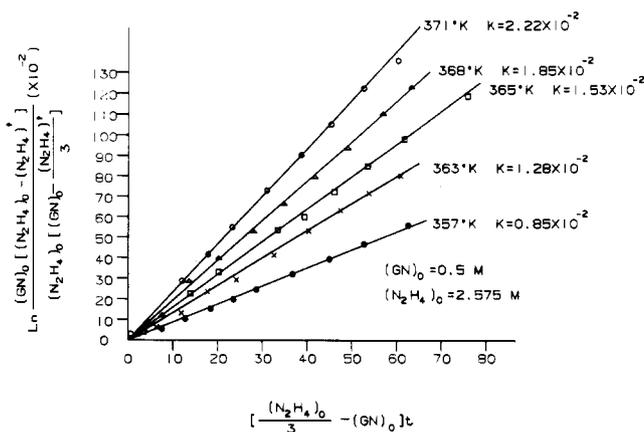


Figure 2. Integral analysis of experimental data in Figure 1 by second-order irreversible reaction scheme.

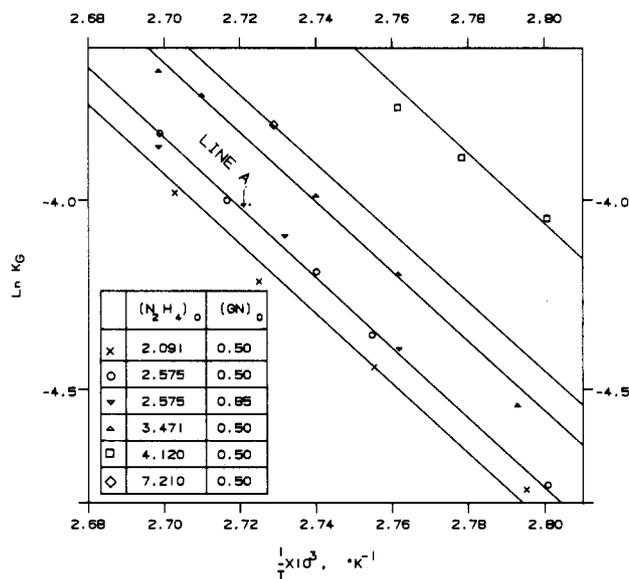


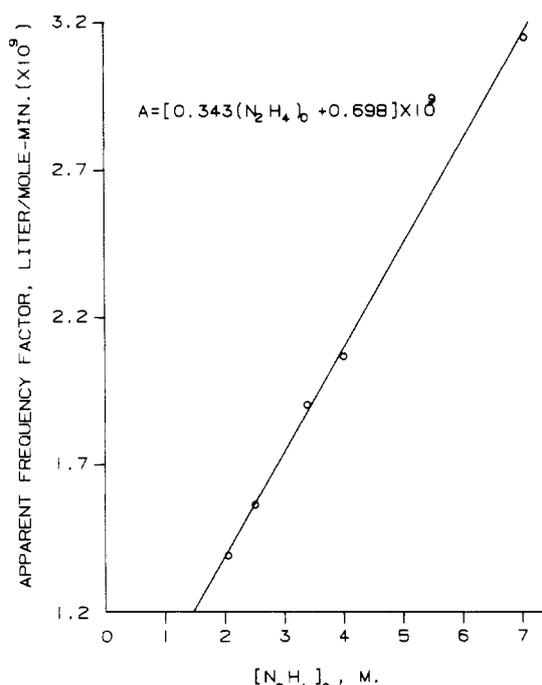
Figure 3. Arrhenius plot of experimental results under different initial concentrations and temperatures in the  $N_2H_4/GN$  system.

and frequency factor, derived respectively from the slope and intercept of line A, are 18.4 kcal/mol and  $1.57 \times 10^9 \text{ L}/(\text{mol}\cdot\text{min})$ , respectively.

Owing to the difficulty of maintaining a constant volume during reaction by using a high initial concentration and the difficulty of monitoring the fast  $NH_3$  evolution rate under such conditions, previous experiments of this study were carried out under initial concentrations much lower than those of practical interest. Nevertheless, in order to obtain a kinetic equation suitable for reactor design, the raw material initial concentrations were extended under carefully controlled conditions.  $[N_2H_4]_0$  concentrations ranging between 2.091 and 7.210 M were covered, although they were still lower than those for practical applications. Under the present experimental range, near constant reaction volume can be maintained (maximum deviation 6%). The details of each experiment and the corresponding data analysis are not reported here because they are respectively similar to those in Figures 1 and 2. The final results are shown in Table I and Figure 3. It is found from Figure 3 that changing  $[GN]_0$  under fixed  $[N_2H_4]_0$  reveals no significant effect of  $[GN]_0$  on  $k_G$  (o and v all fall on line A). Changing  $[N_2H_4]_0$ , however, gives a family of parallel lines, indicating that the observed rate constant possesses a  $[N_2H_4]_0$ -dependent frequency factor. In addition, the  $[N_2H_4]_0$ -dependent frequency factors are all related to the same activation energy of 18.4 kcal/mol, as

Table I. Experimental Results of the GN/N<sub>2</sub>H<sub>4</sub> System under Different Initial Concentrations and Temperatures

batch	[GN] <sub>0</sub> , M	[N <sub>2</sub> H <sub>4</sub> ] <sub>0</sub> , M	T, K	10 <sup>2</sup> k <sub>G</sub>	10 <sup>3</sup> (1/T), K <sup>-1</sup>	ln k <sub>G</sub>	R <sup>2</sup>
TK-51	0.5	2.575	357	0.86	2.801	-4.756	0.9994
TK-54	0.5	2.575	363	1.28	2.755	-4.358	0.999
TK-52	0.5	2.575	365	1.51	2.740	-4.193	0.9992
TK-55	0.5	2.575	368	1.83	2.717	-4.001	0.998
TK-56	0.5	2.575	370.5	2.18	2.699	-3.826	0.9992
TK-57	0.5	3.471	370.5	2.58	2.699	-3.657	0.9992
TK-63	0.5	3.471	369	2.42	2.710	-3.721	0.999
TK-60	0.5	3.471	365	1.86	2.740	-3.985	0.9996
TK-61	0.5	3.471	362	1.54	2.762	-4.193	0.992
TK-59	0.5	3.471	358	1.07	2.793	-4.538	0.992
TK-67	0.5	2.091	370	1.87	2.703	-3.979	0.998
TK-64	0.5	2.091	367	1.48	2.725	-4.213	0.999
TK-66	0.5	2.091	363	1.18	2.755	-4.440	0.999
TK-65	0.5	2.091	358	0.847	2.795	-4.768	0.998
TK-71	0.5	4.120	366.5	2.22	2.729	-3.808	0.996
TK-73	0.5	7.210	360	2.07	2.778	-3.878	0.999
TK-75	0.5	7.210	362	2.33	2.762	-3.759	0.9994
TK-76	0.5	7.210	357	1.73	2.801	-4.057	0.9994
TK-68	0.85	2.575	370.5	2.09	2.699	-3.868	0.999
TK-70	0.85	2.575	366	1.67	2.732	-4.092	0.998
TK-69	0.85	2.575	362	1.24	2.762	-4.390	0.992

Figure 4. [N<sub>2</sub>H<sub>4</sub>]<sub>0</sub> dependence of apparent frequency factor in the N<sub>2</sub>H<sub>4</sub>/GN system.

found earlier in this study. The dependence of the apparent frequency factor on [N<sub>2</sub>H<sub>4</sub>]<sub>0</sub> (Figure 4) can be correlated by

$$A = \{0.343[\text{N}_2\text{H}_4]_0 + 0.698\}10^9 \quad (12)$$

Summarizing the previous results of this study, an apparent kinetic model could therefore emerge

$$-r_H = -d[\text{N}_2\text{H}_4]/dt = k_G[\text{GN}][\text{N}_2\text{H}_4]$$

where  $k_G = \{0.343[\text{N}_2\text{H}_4]_0 + 0.698\}10^9 \exp(-E_a/RT)$  and  $E_a = 18.4$  kcal/mol under  $373 \text{ K} \geq T \geq 353 \text{ K}$ ,  $7.210 \text{ M} \geq [\text{N}_2\text{H}_4]_0 \geq 2.091 \text{ M}$ ,  $0.85 \text{ M} \geq [\text{GN}]_0 \geq 0.5 \text{ M}$ , and

$$0.5 \geq x_H (=1 - [\text{N}_2\text{H}_4]/[\text{N}_2\text{H}_4]_0) \geq 0.2 \quad (13)$$

Equation 13 shows that reaction 1a is obviously not governed by a simple second-order irreversible reaction. A more reasonable mechanism should be devoted to elucidate the experimental results summarized by eq 13.

**B. Mechanism.** Further endeavors are made in order to elucidate the experimental results summarized by eq

13. The mechanism outlined by eq 7-9 has only considered the forward reaction. The amount of dissolved NH<sub>3</sub> in the reaction solution, although small in quantity, could have comparable reactivity when compared with N<sub>2</sub>H<sub>4</sub> (Hendrickson et al., 1973). If this was taken into account, the mechanism depicted earlier in this study could be replaced by a reversible consecutive-parallel scheme as



Writing material balance equations for major species, we obtain

$$-d[\text{GN}]/dt = k_1[\text{GN}][\text{N}_2\text{H}_4] - k_{-1}[\text{MAGN}][\text{NH}_3]_1 \quad (17)$$

$$d[\text{MAGN}]/dt = k_1[\text{GN}][\text{N}_2\text{H}_4] - k_{-1}[\text{MAGN}][\text{NH}_3]_1 - k_2[\text{MAGN}][\text{N}_2\text{H}_4] + k_{-2}[\text{DAGN}][\text{NH}_3]_1 \quad (18)$$

$$d[\text{DAGN}]/dt = k_2[\text{MAGN}][\text{N}_2\text{H}_4] - k_{-2}[\text{DAGN}][\text{NH}_3]_1 - k_3[\text{DAGN}][\text{N}_2\text{H}_4] + k_{-3}[\text{TAGN}][\text{NH}_3]_1 \quad (19)$$

where [NH<sub>3</sub>]<sub>1</sub> denotes the NH<sub>3</sub> concentration in the reaction solution which, under a fixed temperature, quickly approaches the constant value given earlier in the Experimental Section. In order to derive the kinetic law from eq 14-16, the stationary-state treatment is applied to the reactive intermediates, which must be present in low concentrations. Equating eq 18 and 19 to zero leads to the following steady-state concentrations of intermediates:

$$[\text{MAGN}] = \{k_1[\text{GN}][\text{N}_2\text{H}_4] + k_{-2}[\text{DAGN}][\text{NH}_3]_1\} / \{k_{-1}[\text{NH}_3]_1 + k_2[\text{N}_2\text{H}_4]\} \quad (20)$$

$$[\text{DAGN}] = \{k_2[\text{MAGN}][\text{N}_2\text{H}_4] + k_{-3}[\text{TAGN}][\text{NH}_3]_1\} / \{k_{-2}[\text{NH}_3]_1 + k_3[\text{N}_2\text{H}_4]\} \quad (21)$$

Substituting eq 20 and 21 into eq 17, we find

$$-d[\text{GN}]/dt = \{(k_1^2 k_3 - k_1 k_{-1} k_3)[\text{GN}][\text{N}_2\text{H}_4]^2[\text{NH}_3]_1 + k_1 k_2 k_3 [\text{GN}][\text{N}_2\text{H}_4]^3 - k_{-1} k_2 k_3 [\text{TAGN}][\text{NH}_3]_1^3\} / \{k_{-1} k_{-2} [\text{NH}_3]_1^2 + k_1 k_3 [\text{NH}_3]_1 [\text{N}_2\text{H}_4] + k_2 k_3 [\text{N}_2\text{H}_4]^2\} \quad (22)$$

[NH<sub>3</sub>]<sub>1</sub><sup>2</sup> and [NH<sub>3</sub>]<sub>1</sub><sup>3</sup>, respectively of the order of 10<sup>-8</sup> and 10<sup>-12</sup> at 372 K, are so small that they may be neglected

**Table II. Experimental Results of the AN/N<sub>2</sub>H<sub>4</sub> System under Different Initial Concentrations and Temperatures**

batch	[AN] <sub>0</sub> , M	[N <sub>2</sub> H <sub>4</sub> ] <sub>0</sub> , M	T, K	10 <sup>2</sup> k <sub>A</sub>	10 <sup>3</sup> (1/T), K <sup>-1</sup>	ln k <sub>A</sub>	R <sup>2</sup>
TK-77	0.5	4.12	367	2.58	2.725	-3.657	0.998
TK-79	1.0	4.12	360	1.15	2.778	-4.465	0.9998
TK-86	1.0	4.12	362	1.43	2.762	-4.247	0.9992
TK-87	1.0	4.12	358	0.96	2.793	-4.646	0.997

when compared with the other terms. After rearranging, we have

$$-d[\text{GN}]/dt = \{(k_1^2 - k_1k_{-1})[\text{GN}][\text{N}_2\text{H}_4][\text{NH}_3]_1 + k_1k_2[\text{GN}][\text{N}_2\text{H}_4]^2\} / \{k_1[\text{NH}_3]_1 + k_2[\text{N}_2\text{H}_4]\} \quad (23)$$

Now let us consider the two terms in the denominator of eq 23. If

$$k_2 \rightarrow 0 \quad (24)$$

so that  $k_1[\text{NH}_3]_1 \gg k_2[\text{N}_2\text{H}_4]$  as the reaction is progressing, we could further neglect the smaller term to have

$$-d[\text{GN}]/dt = \{(k_1 - k_{-1}) + k_2[\text{N}_2\text{H}_4] / [\text{NH}_3]_1\} [\text{GN}][\text{N}_2\text{H}_4] = k_{\text{obs}}[\text{GN}][\text{N}_2\text{H}_4] = -r_G \quad (25)$$

where

$$k_{\text{obs}} = (k_1 - k_{-1}) + k_2[\text{N}_2\text{H}_4] / [\text{NH}_3]_1 \quad (26)$$

The linear dependence of the observed rate constant on hydrazine concentration is very evident from eq 26. Now consider the similar expression of  $k_G$  in the eq 13. Equation 13 is derived from experiments under lower N<sub>2</sub>H<sub>4</sub> conversion. The linear dependence of the observed rate constant on hydrazine initial concentration in eq 13, therefore, may be attributed to this reason. If so, then eq 26 can be employed to compare with eq 13 by equating the corresponding terms. First we introduce the

$$-r_H = -d[\text{N}_2\text{H}_4]/dt = -3r_G \quad (27)$$

relationship among eq 13, 25, and 26 to give

$$k_G = 3(k_1 - k_{-1}) + 3k_2[\text{N}_2\text{H}_4]_0 / [\text{NH}_3]_1 \quad (28)$$

An arbitrary comparison was then made between the observed rate constant calculated from eq 13 at 372 K

$$k_G = (1.079 + 0.53[\text{N}_2\text{H}_4]_0)10^{-2} \quad (29)$$

and eq 28. After equating the corresponding terms, we obtain

$$k_1 - k_{-1} = 0.36 \times 10^{-2} \quad (30)$$

and

$$3k_2 / [\text{NH}_3]_1 = 0.53 \times 10^{-2} \quad (31)$$

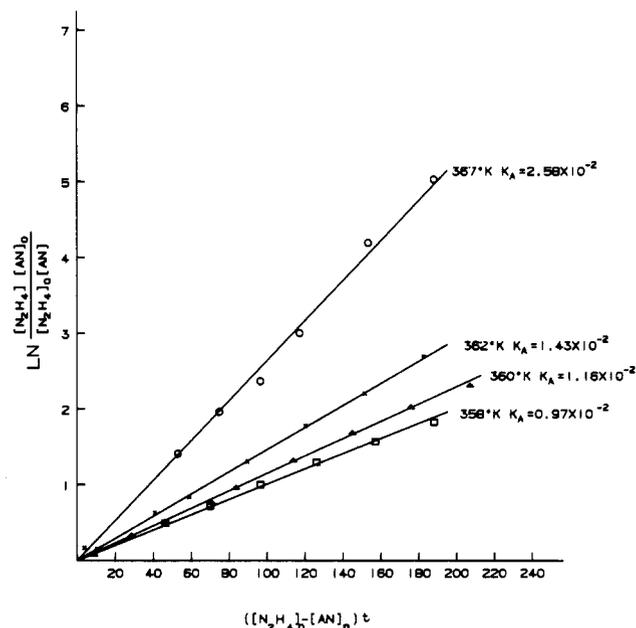
Substituting  $[\text{NH}_3]_1 = 1.9 \times 10^{-4}$  M at 372 K into eq 31, we have

$$k_2 = 3.36 \times 10^{-7}$$

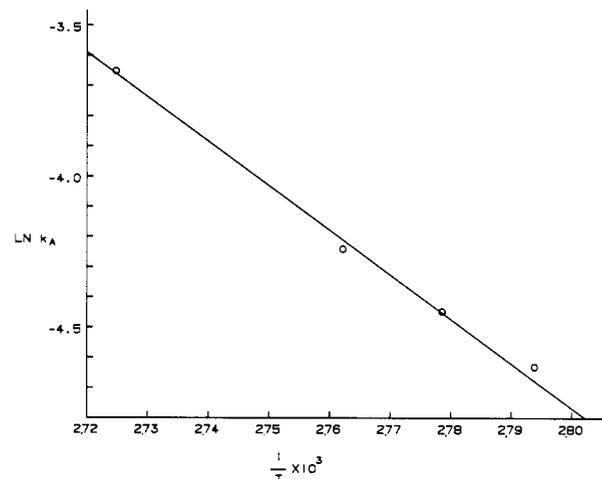
which is indeed very small to support the validity of the assumption eq 24 and, consequently, explain the linear dependence of the observed rate constant on hydrazine concentration shown in eq 13. Obviously, the mechanism outlined by eq 14–16 is more reasonable than the one depicted by eq 7–9. Equation 25 shows that reaction 1a should be a pseudo-second-order reaction.

**II. AN/N<sub>2</sub>H<sub>4</sub> System.** The neutralization reaction between N<sub>2</sub>H<sub>4</sub> and AN is somewhat simpler than the main reaction. We can obtain the kinetic measurements under a fixed [AN]<sub>0</sub> and [N<sub>2</sub>H<sub>4</sub>]<sub>0</sub> pair but with different reaction temperatures by the same method used in section I. Assuming the reaction rate follows a second-order rate law gives

$$-d[\text{N}_2\text{H}_4]/dt = k_A[\text{AN}][\text{N}_2\text{H}_4] \quad (32)$$



**Figure 5.** Integral analysis of N<sub>2</sub>H<sub>4</sub>/AN neutralization reaction rate data by second-order irreversible reaction scheme.



**Figure 6.** Arrhenius plot of experimental results under different initial concentrations and temperatures in the N<sub>2</sub>H<sub>4</sub>/AN system.

Integrating eq 32 with initial conditions and stoichiometric relationships gives

$$\ln \frac{[\text{AN}]_0([\text{N}_2\text{H}_4]_0 - [\text{N}_2\text{H}_4]^*)}{[\text{N}_2\text{H}_4]_0([\text{AN}]_0 - [\text{N}_2\text{H}_4]^*)} = ([\text{N}_2\text{H}_4]_0 - [\text{AN}]_0)k_A t \quad (33)$$

Following the typical integral method analysis of chemical reaction engineering, we present the testing results of eq 33 in Figure 5. The good linear relationship in Figure 5 indicates that the neutralization reaction conforms to a second-order irreversible rate law.

The temperature dependence of the rate constant can be derived from the Arrhenius equation. The experimental results are presented in Table II. Figure 6 shows the Arrhenius plot. The activation energy and frequency factor, derived respectively from the slope and intercept

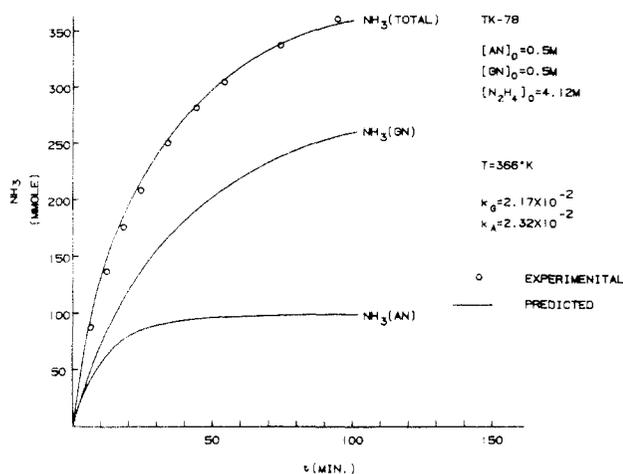


Figure 7. Comparison between the predicted total amount of evolved  $\text{NH}_3$  and the experimental amounts under  $[\text{AN}]_0 = 0.5 \text{ M}$ ,  $[\text{GN}]_0 = 0.5 \text{ M}$ ,  $[\text{N}_2\text{H}_4]_0 = 4.12 \text{ M}$ , and reaction temperature of 366 K.

of Figure 6, are 29.98 kcal/mol and  $1.86 \times 10^{16} \text{ L}/(\text{mol}\cdot\text{min})$ , respectively.

**III. GN/ $\text{N}_2\text{H}_4$ /AN System Simulation.** It is known from previous sections that there are two reactions that can evolve  $\text{NH}_3$  off-gas in the GN/ $\text{N}_2\text{H}_4$ /AN system:



If main reaction 1a and neutralization reaction 5a proceed independently in the GN/ $\text{N}_2\text{H}_4$ /AN system, then the additivity rule may be applied to the  $\text{NH}_3$  off-gas rate. In other words, we could predict the amount of  $\text{NH}_3$  evolved in the GN/ $\text{N}_2\text{H}_4$ /AN reaction system from the rate constants  $k_G$  and  $k_A$  measured respectively from the GN/ $\text{N}_2\text{H}_4$  and AN/ $\text{N}_2\text{H}_4$  systems in the previous sections.

Let  $[\text{N}_2\text{H}_4]_T$  be the total  $\text{N}_2\text{H}_4$  concentration consumed by reactions 1a and 5a,  $[\text{N}_2\text{H}_4]_G$  be the  $\text{N}_2\text{H}_4$  concentration consumed by reaction 1a, and  $[\text{N}_2\text{H}_4]_A$  be the  $\text{N}_2\text{H}_4$  concentration consumed by reaction 5a; we then have

$$d[\text{N}_2\text{H}_4]_G/dt = k_G[\text{GN}][\text{N}_2\text{H}_4] \quad (34)$$

$$d[\text{N}_2\text{H}_4]_A/dt = k_A[\text{GN}][\text{N}_2\text{H}_4] \quad (35)$$

$$[\text{N}_2\text{H}_4]_T = [\text{N}_2\text{H}_4]_G + [\text{N}_2\text{H}_4]_A \quad (36)$$

Integrating eq 34 with initial conditions and stoichiometric relationships ( $[\text{N}_2\text{H}_4] = [\text{N}_2\text{H}_4]_0 - [\text{N}_2\text{H}_4]_G - [\text{N}_2\text{H}_4]_A$ ,  $[\text{GN}] = [\text{GN}]_0 - [\text{N}_2\text{H}_4]_G/3$ ) gives

$$-\left( \ln \left( \frac{3[\text{GN}]_0 - [\text{N}_2\text{H}_4]_G}{3[\text{GN}]_0} \frac{[\text{N}_2\text{H}_4]_0 - [\text{N}_2\text{H}_4]_A}{[\text{N}_2\text{H}_4]_0 - [\text{N}_2\text{H}_4]_T} \right) \right) = \left( \frac{[\text{N}_2\text{H}_4]_0 - [\text{N}_2\text{H}_4]_A - 3[\text{GN}]_0}{3} \right) k_G t \quad (37)$$

Similarly we have eq 38 from eq 35

$$-\left( \ln \left( \frac{[\text{AN}]_0 - [\text{N}_2\text{H}_4]_A}{3[\text{GN}]_0} \frac{[\text{N}_2\text{H}_4]_0 - [\text{N}_2\text{H}_4]_G}{[\text{N}_2\text{H}_4]_0 - [\text{N}_2\text{H}_4]_T} \right) \right) = \left( \frac{[\text{N}_2\text{H}_4]_0 - [\text{N}_2\text{H}_4]_G - [\text{AN}]_0}{3} \right) k_A t \quad (38)$$

Thus, given the values of  $[\text{N}_2\text{H}_4]_0$ ,  $[\text{GN}]_0$ ,  $[\text{AN}]_0$ ,  $k_G$ ,  $k_A$ , and  $t$ , we can calculate  $[\text{N}_2\text{H}_4]_A$ ,  $[\text{N}_2\text{H}_4]_G$ , and  $[\text{N}_2\text{H}_4]_T$  from eq 36–38.  $k_G$  and  $k_A$  are obtained from previous sections when the reaction temperature is specified. Figure 7 shows the results of the predicted individual and total amount of evolved  $\text{NH}_3$  under  $[\text{AN}]_0 = 0.5 \text{ M}$ ,  $[\text{GN}]_0 = 0.5$

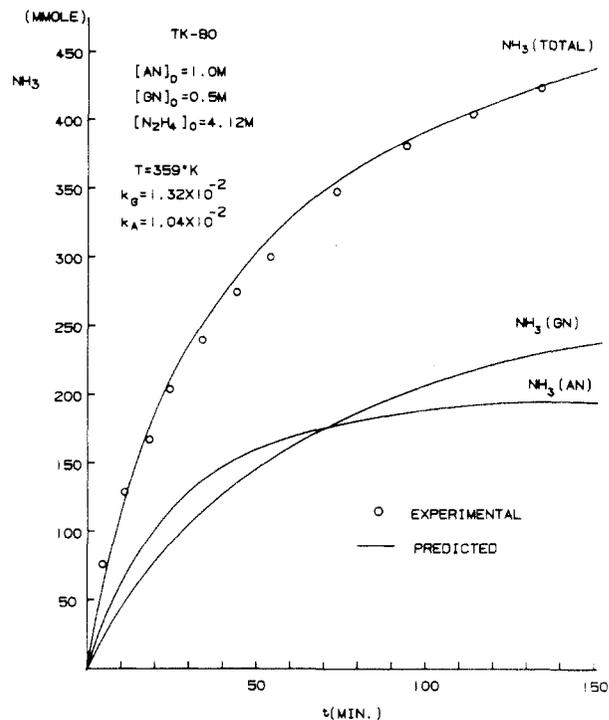


Figure 8. Comparison between the predicted total amount of evolved  $\text{NH}_3$  and the experimental amounts under  $[\text{AN}]_0 = 1.0 \text{ M}$ ,  $[\text{GN}]_0 = 0.5 \text{ M}$ ,  $[\text{N}_2\text{H}_4]_0 = 4.12 \text{ M}$ , and reaction temperature of 359 K.

M, and  $[\text{N}_2\text{H}_4]_0 = 4.12 \text{ M}$  at a reaction temperature of 366 K. The experimental totals were also given for comparison. The predicted total amount of  $\text{NH}_3$  evolved agreed satisfactorily with the experimentally measured data, suggesting that eq 1a and 5a proceed independently in the ternary reaction mixture GN/ $\text{N}_2\text{H}_4$ /AN. The results also answer the questions in the Reaction Scheme section that the presence of AN will not alter the reaction rate constant of eq 1a and presence of GN will also not alter the reaction rate constant of eq 5a. Similar evidence is presented in Figure 8 under different reaction conditions.

**IV. Continuous Flow Stirred Tank Reactor Simulation.** The design equation for the continuous flow stirred tank reactor is (Levenspiel, 1972)

$$\tau = [\text{GN}]_0 x_G / (-r_G) \quad (39)$$

where  $\tau$  denoted the average retention time in the reactor. Under typical conditions of  $[\text{GN}]_0 = [\text{AN}]_0 = 1.5 \text{ M}$ ,  $[\text{N}_2\text{H}_4]_0 = 11.6 \text{ M}$ , and a reaction temperature of  $T = 363 \text{ K}$ , the reaction rate expression can be derived from eq 13:

$$-r_G = 1.30 \times 10^{-2} [\text{GN}][\text{N}_2\text{H}_4] \quad (40)$$

where

$$[\text{N}_2\text{H}_4] = [\text{N}_2\text{H}_4]_0 - 3([\text{GN}]_0 - [\text{GN}]) - [\text{N}_2\text{H}_4]_A \quad (41)$$

In view of the fact that the maximum  $[\text{N}_2\text{H}_4]_A$  during reaction will only reach  $[\text{AN}]_0$  and  $[\text{N}_2\text{H}_4]_0 \gg [\text{AN}]_0$  under typical conditions, we attempt to neglect  $[\text{N}_2\text{H}_4]_A$  in the above equation to give

$$[\text{N}_2\text{H}_4] \approx [\text{N}_2\text{H}_4]_0 - 3([\text{GN}]_0 - [\text{GN}]) \quad (42)$$

Introducing  $x_G = 1 - [\text{GN}]/[\text{GN}]_0$ ,  $\bar{M} = [\text{N}_2\text{H}_4]_0/[\text{GN}]_0$ , and eq 42 into eq 40 gives

$$-r_G = 1.30 \times 10^{-2} [\text{GN}]_0^2 (1 - x_G)(\bar{M} - 3x_G) \quad (43)$$

Substituting eq 43 into eq 39, we find

$$\tau = x_G / 1.95 \times 10^{-2} (1 - x_G)(7.73 - 3x_G) \quad (44)$$

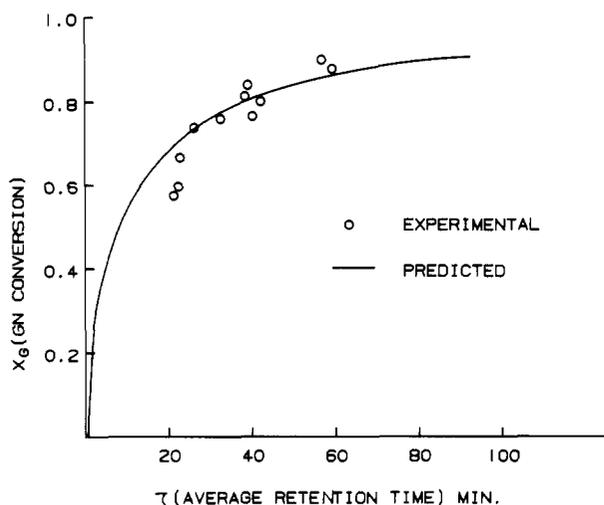


Figure 9. Comparison between the predicted GN conversion and the experimental conversions from a CSTR at steady state.

Figure 9 shows the comparison between predicted GN conversions and the experimental ones taken from a 1-L CSTR reactor under steady state. The predicted conversions agree satisfactorily with the experimentally measured data.

### Conclusions

The kinetic study of TAGN synthesis from GN/ $N_2H_4$ /AN mixtures has been carried out by monitoring  $NH_3$  off-gas evolution rate. The reaction scheme was proposed considering all possible side reactions that might generate  $NH_3$ . Two reactions, namely the one between GN and  $N_2H_4$  (eq 1a) and the one between AN and  $N_2H_4$  (eq 5a), are believed to proceed independently in the GN/ $N_2H_4$ /AN ternary mixture, and each contributed to the total observed rate in the ternary mixture in terms of the amount of  $NH_3$  evolution. Integral analysis of rate data suggests that both eq 1a and 5a conform to the second-order irreversible reaction rate law with activation energies of 18.4 and 29.98 kcal/mol, respectively.

An attempt to elucidate the main reaction rate expression eq 13 by a consecutive-parallel reversible mechanism and steady-state approximations appears to be successful. The validity of this rate expression for reactor design purposes is justified when experimental CSTR conversions are compared with the ones obtained from simulation predictions.

### Acknowledgment

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### Nomenclature

- $A$  = apparent frequency factor, L/(mol·min)  
 $E_a$  = activation energy, kcal/mol  
 $k_A$  = rate constant of AN/ $N_2H_4$  neutralization reaction, L/(mol·min)  
 $k_G$  = rate constant of GN/ $N_2H_4$  main reaction, L/(mol·min)  
 $k_{obs}$  = observed reaction rate constant, L/(mol·min)  
 $\bar{M}$  =  $[N_2H_4]_0/[GN]_0$   
 $R$  = ideal gas constant, 1.987 cal/(°C·mol)  
 $R^2$  = correlation coefficient  
 $T$  = reaction temperature, K  
 $t$  = reaction time started from first detection of  $NH_3$ , min  
 $x_G$  = conversion based on  $[GN]_0$   
 $x_H$  = conversion based on  $[N_2H_4]_0$   
 $[AN]_0$  = ammonium nitrate initial concentration, M  
 $[GN]_0$  = guanidine nitrate initial concentration, M  
 $[N_2H_4]_0$  = hydrazine initial concentration, M  
 $[N_2H_4]^*$  = hydrazine concentration consumed, derivable from  $NH_3$  evolved, M  
 $[N_2H_4]_A$  = hydrazine concentration consumed by neutralization reaction, M  
 $[N_2H_4]_G$  = hydrazine concentration consumed by main reaction, M  
 $[N_2H_4]_T$  = total hydrazine concentration consumed, derivable from  $NH_3$  evolved, M  
 $[NH_3]_1$  =  $NH_3$  dissolved in reaction solution, M

### Greek Symbol

$\tau$  = average retention time, min

**Registry No.** GN, 506-93-4; TAGN, 4000-16-2;  $N_2H_4$ , 302-01-2;  $NH_4NO_3$ , 6484-52-2;  $N_2H_5NO_3$ , 37836-27-4.

### Literature Cited

- Frick, D. H.; Hoffman, J. Chemical Engineering Report, University of Illinois, Urbana-Champaign, May 26, 1951.  
 Haury, V. E. U.S. Pat. 3,950,421, 1976.  
 Hendrickson, J. B.; Cram, D. J.; Hammond, G. B. *Organic Chemistry*, 3rd ed.; McGraw-Hill: New York, 1973; p 393.  
 Ho, C. Y.; Wu, W. H. Process Study of TAGN. CSIST internal report, 1986.  
 Kaye, S. M. *Encyclopedia of Explosives and Related Items*; US Army Armament Research and Development Command: Dover, NJ, 1980a; Vol. 9, PA-TR-2700, S-7.  
 Kaye, S. M. *Encyclopedia of Explosives and Related Items*; US Army Armament Research and Development Command: Dover, NJ, 1980b; Vol. 9, PA-TR-2700, T-28.  
 Kirk, R. E.; Othmer, D. F. *Encyclopedia of Chemical Technology*; Wiley: New York, 1980; Vol. 12, p 739.  
 Lenga, R. E. *The Sigma-Aldrich Library of Chemical Safety Data*, 1st ed.; Sigma-Aldrich Corporation: Milwaukee, WI, 1985; p 1045.  
 Levenspiel, O. *Chemical Reaction Engineering*, 2nd ed.; Wiley: New York, 1972; pp 99, 103.  
 Morton, J. W., et al. *Stability of TAGN Based Gun Propellants*; Chemical Propulsion Information Agency: Laurel, 1981; Vol. 2, CPIA-PUB-340, p 483.  
 Satriana, D. R., et al. U.S. Pat. 3,285,958, 1966.  
 Satriana, D. R., et al. U.S. Pat. 3,813,439, 1974.  
 Sauermilch, W. *Explosivstoffe* 1964, 12(9), 197.  
 Sauermilch, W. Ger. Pat. 1,518,197, 1969.

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