Reactions of Monoethylamine over Porous Copper in a Closed Recycling System

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REACTION SYSTEM

Reactions which can occur when monoethylamine reacts in an inert atmosphere are (*1* to *3*)

$$2\,C_2H_5NH_2 \rightleftarrows (C_2H_5)_2NH + NH_3 \qquad (1)$$

$$C_2H_5NH_2 + (C_2H_5)_2NH \rightleftarrows (C_2H_5)_3N + NH_3 \qquad (2)$$

$$2(C_2H_5)_2NH \rightleftarrows (C_2H_5)_3N + C_2H_5NH_2 \qquad (3)$$

$$(C_2H_5)_2NH \rightleftarrows C_2H_5NC_2H_4 + H_2 \qquad (4)$$

$$C_2H_5NH_2 \rightleftarrows CH_3CN + 2\,H_2 \qquad (5)$$

$$C_2H_5NH_2 + H_2 \rightleftarrows C_2H_6 + NH_3 \qquad (6)$$

$$C_2H_5NH_2 \rightleftarrows C_2H_4 + NH_3 \qquad (7)$$

In addition to the trans-ethylation reactions (1), (2), and (3), which are analogous to those found with methylamines (*1*), additional reactions can be present. Dehydrogenation to diethylimine by reaction (4) is analogous to the observed dehydrogenation of di-*n*-butylamine to di-*n*-butylimine over Raney nickel (*2*), and dehydrogenation to acetonitrile by reaction (5) has been suggested to occur over tungsten (*3*). The formation of ethane and/or ethylene according to reactions (6) and (7) is a distinct possibility. Thus ethane formation has been observed in a hydrogen-rich atmosphere over platinum, rhodium, and tungsten metal films but not over nickel, palladium, and gold films (*3*).

SCOPE

Conversion versus time data were observed at the following conditions. Feed: pure ethylamine/inerts, some runs conducted with varying amounts of initial hydrogen or ammonia; two runs made with diethylamine feed. Temperature: 205°, 231°, and 256°C. Initial partial pressure of ethylamine: 50 to 800 mm. Hg. Initial total pressure: 740 to 800 mm. Hg. Catalyst: porous copper with a B.E.T. surface area of 0.38 sq. m./g., and a pore volume of 1.4 cc./g.; catalyst activity was essentially constant. Run times: 50 to 200 min./run.

EXPERIMENT

Apparatus

The apparatus, which is similar in operation to that used in other studies (*4*, *5*), is shown in Figure 1. The reactor proper was constructed of 32 mm. Pyrex tubing. Gas flow was downward through a catalyst bed (⅛ × ⅛ porous copper pellets, 22.48 g., 1 in. high) supported on a perforated glass disc. Simultaneous measurement of temperatures at any two positions within the bed could be made.

A heated 3-mm. capillary manometer connected directly to the system. Glass lines, ports, and recycle pump were heated to 130°C. with flexible heating tape to prevent preferential sorption or condensation of reaction components. The gas was recycled using a Vanton Flexiliner Pump (Model XB-120).

Redistilled ethylamine (99.8 to 99.9% purity with balance diethylamine) was stored as a liquid under its own vapor pressure in a heated Pyrex feed cylinder fitted with a pressure stopcock and a sampling port. Reactant charge was made directly from the vapor space into the system proper. Pressures were related to moles injected in separate tests made without catalyst present.

Analysis

Product identification, calibration studies, and analysis were made using gas chromatography (*7*, *8*). Comparison of chromatograph traces was made for pure components, synthetic mixtures, and reactor off-gas samples using five different columns. Product analysis was made at 35°C. using a recommended (*6*) 2-½ m. glass column filled with Union Carbide Tergitol/E-35 (first ¼) and Carbowax 1500 (last ¾) coated on base-washed Chromosorb-W.

Procedure

Before each run a 15-min. hydrogen purge was made to recondition the catalyst. A run was begun by evacuating to 0.5 mm. Hg through valves *E* and *F*, and then with the recycle pump on, opening valve *A* until the desired ethylamine initial pressure was reached. The total pressure was then brought to near atmospheric by rapidly introducing inerts (nitrogen or helium) and/or reactive gases (ammonia or hydrogen) through

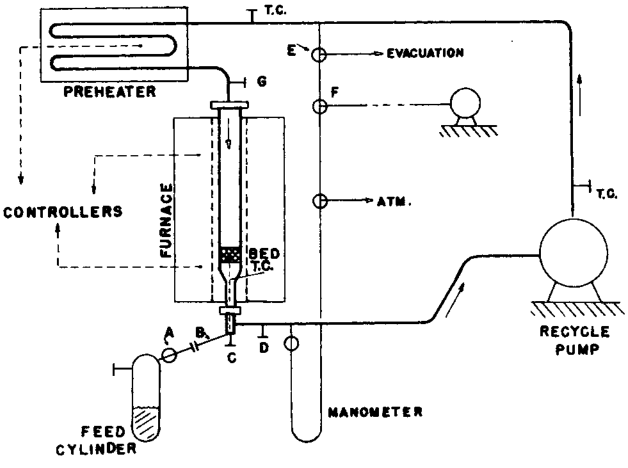

Fig. 1. Diagram of reactor system.

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TABLE 1. SAMPLE OF EXPERIMENTAL DATA

Run No. M-14
Feed composition: 99.8% EA, 0.2% DEA
Initial moles charged: 0.0244 g.-moles EA

Temperature: 256°C.
Initial pressures: 204 EA/N_2 to 60 mm. Hg.

		Molar composition, %						Material balance		
Time, min.	P, mm. Hg	NH_3	EA	DEI	DEA	TEA	AN	H_2*	H_2†	NH_3‡
0.9	760	1.35	95.83	1.17	0.48	—	—	1.17	0.00	1.45
4.5	—	3.74	89.11	2.82	1.17	0.04	0.10	3.02	—	3.87
8.2	—	5.57	84.29	3.85	1.65	0.08	0.24	4.32	—	5.46
12.0	768	6.85	79.51	4.74	1.92	0.18	0.69	6.11	3.77	6.82
16.0	—	8.32	75.85	5.61	2.35	0.33	0.64	6.90	—	8.42
20.0	—	9.54	70.97	6.30	2.97	0.41	1.17	8.64	—	9.89
30.0	774	12.58	63.88	7.46	4.04	0.50	1.36	10.18	6.42	12.30
40.0	—	13.39	61.52	7.31	5.19	0.58	1.57	10.44	—	13.46
50.0	777	14.95	56.92	7.69	6.34	0.93	1.83	11.34	7.69	15.69
60.3	—	14.61	54.94	7.28	7.33	1.08	2.49	12.27	—	16.57
80.0	780	11.76	51.93	6.39	9.99	1.39	4.05	14.49	8.93	18.96
100.0	—	14.68	45.69	5.73	11.38	1.73	5.02	15.77	—	20.37
120.0	782	14.30	44.73	5.08	12.52	1.98	5.44	15.95	9.73	21.36
148.9	783	14.25	40.43	4.78	13.87	2.40	6.50	17.77	10.13	23.25

* Calculated by Equation (8), (DEI) + 2 (AN).
† Calculated from total pressure rise.
‡ Calculated by Equation (9).

port *G*. Time zero was arbitrarily selected as the moment when all the amine had been introduced. Between runs the catalyst was stored under helium.

Samples were taken with heated gas-tight syringes at approximately 1, 5, 10, 15, and 20 min. total elapsed time, and then every 20 min. until the end of a run. Total sample withdrawal accounted for less than 0.6% of the system volume with an average of 0.3%.

Further details are given elsewhere (*8*).

PRELIMINARY OBSERVATIONS

Catalyst Properties and Behavior

The parent cupric oxide (Harshaw-Cu-0307-T-⅛, 99% pure) was reduced to pure copper at 200°C. using hydrogen. Surface areas and pore volumes of 5 sq. m./g., 0.26 cc./g. and 0.38 sq. m./g., 1.4 cc./g. were obtained, respectively, for the parent and reduced catalyst. For copper, surface area was obtained on fresh catalyst using Krypton B.E.T. adsorption (*9*). No micropore structure was detected (*9*).

Runs made after the catalyst was first charged (at 231°C.) were not repeatable, as indicated by lower ethylamine consumption rates and higher fractions of dehydrogenated products.

Homogenous Reaction and Materials of Construction

A test run made at 256°C. with no catalyst present showed no foreign chromatographic traces at shorter times. A similar test at 197°C., made to determine the sorptive effect of the construction materials, showed only a small drop in total pressure at longer times.

Reaction Components

Analysis for reaction components showed, even in a hydrogen-rich atmosphere, the absence of ethane, ethylene, and other light hydrocarbons, and the presence of all of the other compounds present in the reaction scheme. In addition no methylamines were detected. No extra chromatographic traces were observed with any of the columns. Thus reaction behavior is qualitatively described by Equations (1), (2), (3), (4), and (5), alone. A hydrogen balance gives

$$N_{H2} = \frac{N_0}{P_0}(P - P_0) = N_{DEI} + 2N_{AN} \qquad (8)$$

while a nitrogen material balance gives

$$N_{NH3} = N_{DEA} + N_{DEI} + 2N_{TEA} \qquad (9)$$

The nitrogen balance was found to be obeyed within limits of experimental error at conditions given by suitable combinations of high temperature, low ethylamine initial partial pressure, and short run times. At longer times the nitrogen balance gave evidence that ammonia was being removed from the gas stream by the catalyst, while the hydrogen balance gave evidence that ethylamine was being removed. In general the hydrogen balance was not as good as the nitrogen balance, partly because total pressure could not be measured as accurately as composition (see Table 1).

Isothermal Behavior

Except for the first minute after time zero, bulk temperatures in the center of the bed held constant to within ±0.5°C. for all runs with an average variation of ±0.3°C. During the first minute typical temperature fluctuations of ±1.0°C. were observed. The maximum variation in bulk temperature between any two points within the bed was about ±0.7°C.

Calculations (*10, 11*) showed for any observed reaction that the maximum temperature change was 0.1°C. between the bulk gas stream and the center of the pellet. The combined heat effect of all reactions occurring simultaneously would be no worse, since calculations (*12, 13*) showed that the dehydrogenations were endothermic, while the transethylations were mildly exothermic.

Diffusional Effects

Film diffusion effects were investigated by operating the recycle pump (calibrated against molar flow rate) at several speeds. Above 0.9 g.-moles/min. further increase in pump speed did not affect (within experimental error) either conversion in reaction (1) or values of the composition ratio of diethylamine to diethylimine. Regular runs were made at 1.1 g.-moles/min. Calculations for the major reaction according to the film theory model (*10*) showed that the pressure drop of ethylamine between the bulk stream and the pellet surface, ratioed to the total pressure, was always less than 0.01.

Pore diffusion would not be expected to control reaction rates because of the very large macropores (radius 74,000Å.) with negligible micropore structure, and because use of two different inerts (nitrogen and helium) with dissimilar diffusivities gave similar conversions. Substantiating calculations made according to the criterion of Weisz and Prater (*14*) gave isothermal Damkohler numbers less than 0.002, ensuring that pore diffusion did not limit rates.

DATA

Approximately 100 runs were made (*8*). Data of a sample run are given in Table 1. Included for comparison are the theoretical compositions of ammonia and hydrogen predicted by Equations (8) and (9), respectively. All runs but the last were conducted using the same catalyst batch (22.48 g.). The reaction scheme was studied at 205°, 231°, and 256°C. using initial ethylamine partial pressures from 50 to 790 mm. with constant, near atmospheric, total pressures. Run series were conducted at all three temperatures using a feed of ethylamine/inerts, and at 231°C. and 200 mm. Hg ethylamine initial pressure using feeds of ethylamine/hydrogen inerts and ethylamine/ammonia inerts. Hydrogen initial partial pressures varied between 16 and 552 mm. Hg, while those of ammonia varied between 8 and 548 mm. Two last exploratory runs were conducted using diethylamine feed.

INTERPRETATION OF DATA

Reaction Scheme

The general applicability of the nitrogen balance, coupled with the results of the detailed chromatographic analysis, are taken as substantive proof that (1), (2), (4), and (5) are the major reactions which occur when monoethylamine reacts over porous copper. In general the conversions of all species on the right-hand side of these reactions were found to increase with increasing temperature and decreasing initial partial pressure of ethylamine. In most runs for times longer than 30 min., conversions of ethylamine in reaction (1) were observed to rise linearly with time. Total percentage conversion of ethylamine ranged between 1 and 80% with an average of 20%. In the absence of initial hydrogen, conversions by transethylation at 205° and 231°C., via (1) and (2), were found to be an order of magnitude higher than conversions by dehydrogenation, via (4) and (5). However at 256°C., conversions by the two routes were of comparable magnitude. Such an increase in dehydrogenation with temperature is probably controlled by a thermodynamic effect, as previously suggested (3), since reaction (5) is an endothermic reaction with a temperature-sensitive equilibrium constant, while (1) and (2) have relatively temperature-insensitive equilibrium constants (*12*). Conversions in (4) were followed by observing changes in the composition ratio, diethylamine to diethylimine, defined as DEA/DEI. Although equilibrium constants were not calculated for (4), because of a lack of a firm material balance at long times, nevertheless equilibrium appeared to lie to the right, since in most runs diethylimine appeared immediately in the gas phase while diethylamine did not. Reaction (4) was strongly affected by the amount of hydrogen present, whether present initially as a result of catalyst pretreatment, added at the start of reaction, or generated by (5). As expected, increased amounts of hydrogen drove the reaction back to the left. Thus for many runs DEA/DEI versus time curves exhibited an early minimum. At longer times DEA/DEI rose nearly linearly with time for most runs. At 256°C. the fact that diethylimine exhibited a sharp early maximum in its composition-time profile (refer to Table 1) was attributable to the reversible effect of the large amount of hydrogen generated by (5). At 205° and 231°C. maxima were less broad.

Initial Rates

For a batch differential reactor operating in a chemically controlled region, initial reaction rates at various initial partial pressures of reactant provide the data from which the best form of the chemical rate equation can be deduced. In the present study initial reaction rates for reaction (1) were determined by drawing a smooth curve through conversion versus time data, and obtaining the slope at 4.5 min. This time was chosen because slopes could be found here with reasonable accuracy (±5%). Because of standard problems associated with startup, slopes at time zero were subject to greater error. In Figure

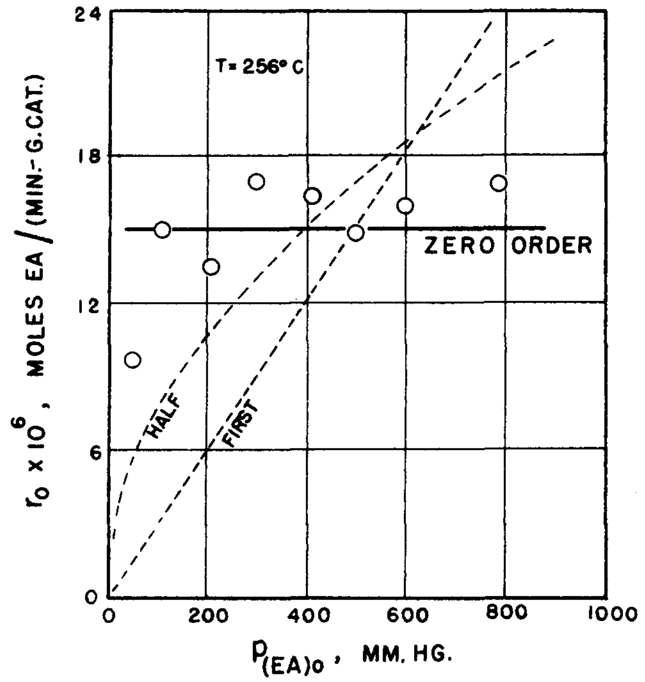

Fig. 2. Initial reaction (1) rate at 256°C versus initial partial pressure of ethylamine. Zero-order form preferred.

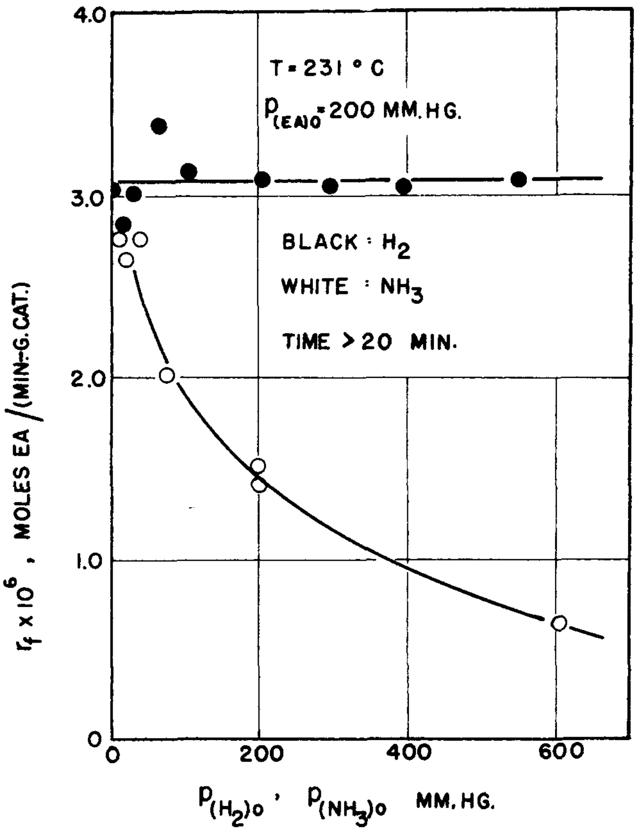

Fig. 3. Comparison of effects of hydrogen and ammonia on final reaction (1) rates.

2 rate data are presented for those runs made at 256°C. using a feed of only ethylamine and inerts.

RESULTS AND DISCUSSION

Rate Equation

According to the standard Hougen and Watson procedure (*15*), a number of alternative rate equations for (1) were tested using the initial rate data for those runs made with only ethylamine and inerts. At 256°C. a zero-order form of the rate equation

$$r_o = k \qquad (10)$$

was found to be statistically superior to half-, first-, and second-order forms (see Figure 2), while at 231°C. a number of additional rate equations were also tested with the same result. Comparisons were made by linearizing the appropriate equations and using the variance ratio test (*16*). At 205°C. data were insufficient to permit evaluation of the best form, although zero-order appeared likely. At 256°, 231°, and 205°C. the zero-order rate constants obtained were, respectively, $15.2 \pm 2.0 \times 10^{-6}$*, $6.0 \pm 1.0 \times 10^{-6}$, and 1.2×10^{-6} g.-moles/(g.-catalyst)(min.).

The reaction rate showed an approximate Arrhenius temperature dependence with an activation energy (based on the statistically sound rates at 231° and 256°) of 20 kcal./g.-mole. The frequency factor for k was near 10^8 g.-moles ethylamine/(g.-catalyst)(min.), or 10^{12} sec.$^{-1}$, which agreed with Topley's theoretical relation for zero-order kinetics (*17*).

As an additional test the Freundlich isotherm was applied to the data

$$r_o = k' P^n_{(EA)0} \qquad (11)$$

The best values of the rate constant k' and reaction order n were determined by a logarithmic least squares analysis. n was found to be 0.06 ± 0.23 and 0.16 ± 0.11 at 231° and 256°, respectively. The fact that the 95% confidence bands do not encompass half-integral or integral orders other than zero further substantiates the superiority of the zero-order form.

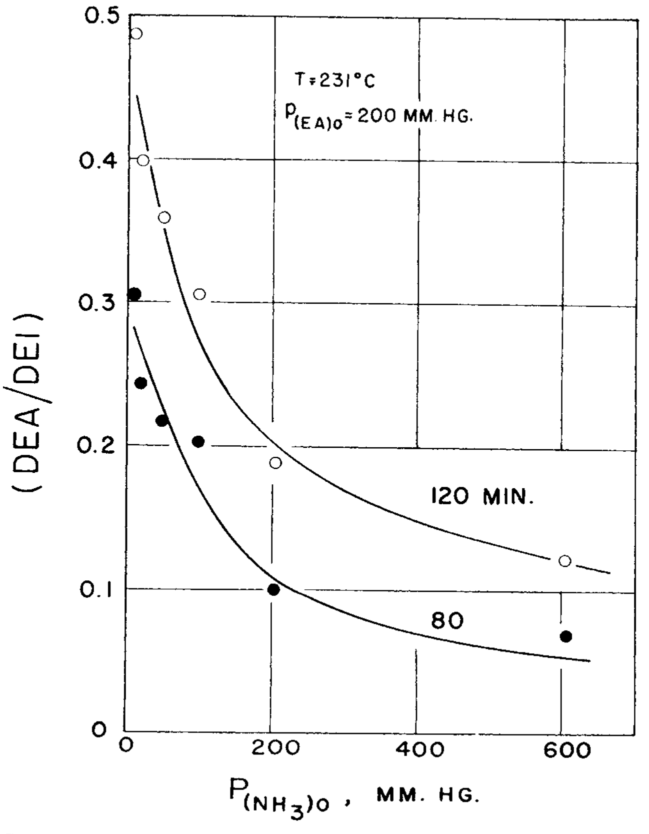

Fig. 4. Variation of diethylamine to diethylimine composition ratios with initial hydrogen partial pressure.

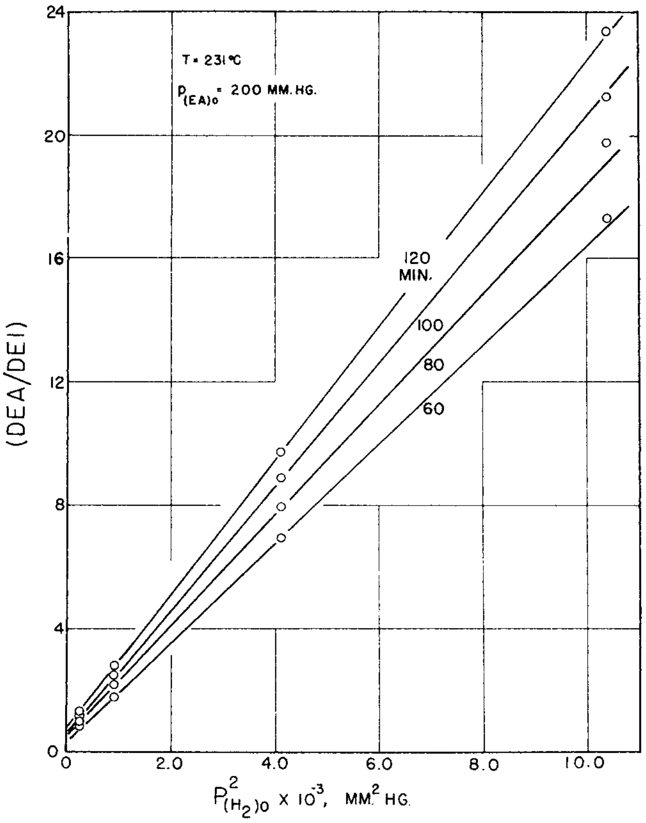

Fig. 5. Variation of diethylamine to diethylimine composition ratios with initial ammonia partial pressure.

Effect of Hydrogen and Ammonia

To assess the effects of these product gases on the reaction scheme, separate run series were made at 231°C. and atmospheric total pressure using one common initial partial pressure of ethylamine (200 mm. Hg) and varying amounts of hydrogen or ammonia. The effects of the two gases were widely different. Increasing the hydrogen partial pressure left final reaction (1) rates (obtained for times greater than 20 min.) unaffected but increased initial rates, whereas increasing the ammonia partial pressure left initial reaction rates relatively unaffected but decreased final rates. The effects on final rates are shown in Figure 3. In addition increasing hydrogen pressure greatly increased DEA/DEI, as shown in Figure 4 where this ratio is plotted against the square of the hydrogen partial pressure. The observed linearity suggests that higher hydrogen concentrations were much more effective in the hydrogenation of diethylimine to diethylamine. Reaction sites containing aminated unsaturates are evidently attacked much more rapidly when hydrogen concentrations are high, perhaps because of increased hydrogen atom surface diffusion under such conditions. On the other hand, with runs conducted using ammonia, increasing the ammonia partial pressure lowered this ratio (Figure 5). The ammonia evidently ties up some reaction sites which might otherwise act as hydrogenating-dehydrogenating centers.

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* The ± values represent twice the standard deviation.

As with regular runs, catalyst activity was conserved across the hydrogen run series. However, it dropped 50% across the ammonia run series because of the poisoning effect of ammonia. Thus when ammonia was present in the gas phase in concentrations above 10%, it was observed to disappear into the catalyst. Such an effect suggests that ammonia was strongly sorbed by the catalyst as reaction proceeded, and provides an explanation for the failure of the material balances in the regular runs to be obeyed under similar conditions. Quantitative interpretation was not possible since rates of sorption were not obtained independent of rates of reaction.

Although hydrogen is not chemisorbed on pure copper, it is known to be chemisorbed on copper formed by chemical reduction (*18*). The conserved activity of runs made with hydrogen added, and the constancy of the final rates, suggests that hydrogen was relatively weakly chemisorbed on the copper surface. Increased initial reaction rates suggest that hydrogen cleanses the catalyst surface, perhaps by removing residual adsorbed oxygen atoms (*18*). Indeed, one effect of subjecting the catalyst to large amounts of hydrogen was the improvement of the nitrogen material balance. This effect provided justification for the hydrogen conditioning step used prior to all runs. In runs made without hydrogen, conditioning appeared to leave a constant residual amount of hydrogen on the catalyst surface. In runs made with hydrogen, more than the residual amount of hydrogen appeared to be retained. This was indicated by the significantly higher initial value of (DEA/DEI observed in the first no-hydrogen run made after the hydrogen run series.

Diethylamine Runs

The two exploratory runs made with diethylamine feed gave the same reaction components as those runs made with monoethylamine feed, but material balances were not obeyed. Thus in one run made at 197°C. with fresh catalyst the major product at long times was acetonitrile (34% at 240 min.), which would have had to have been generated by (3) followed by (5). However this route is suspect, since no corresponding amount of triethylamine, an end product in (3), was detected. In addition, for this run, carbon was retained by the catalyst in an amount much greater, per mole of reactant converted, than was found using monoethylamine (0.81 versus 0.01). The specific form of the carbon was not determined.

Mechanisms

Because of the limitations of the Langmuir-Hinshelwood theory, and the number of alternative mechanisms which yield a zero-order form (depending upon the unknown magnitude of the ethylamine adsorption equilibrium coefficient), no claim could be made for the validity of a controlling mechanism for (1). Thus with dual-site surface reaction, a zero-order form implies that any one of either adsorption, desorption, or surface reaction can be rate controlling, while with single-site reaction, desorption of product can be rate controlling (*10*). In addition product inhibition is unlikely since the addition of moderate amounts of ammonia did not affect initial reaction (1) rates. Two of the more likely of these mechanisms are considered to be the desorption of ammonia (single-site) or the adsorption of ethylamine (dual-site). The desorption of ammonia is suggested since Topley's relation was obeyed and since extensive sorption of ammonia was observed. The adsorption of ethylamine is suggested since the hydrogen balance indicated that ethylamine was initially sorbed. In this case zero order would arise if $K_{EA} P_{(EA)0} << 1$. Since both K_{EA} and $P_{(EA)0}$ would be relatively large, their product would have a good chance of being significantly greater than unity.

The reactions over porous copper are similar to those obtained by Kemball and Moss (3) over nickel, palladium, and gold, where fission of the carbon-carbon bond did not control reaction rates, and unlike those over rhenium and platinum, where appreciable ethane via (6) was formed. It is interesting to note that at similar temperatures, similar products are obtained with reactions over gold and copper, metals with similar electron configurations and lattice structures. But reaction rates are much lower over the porous copper, both in terms of a lower frequency factor and a higher activation energy.

In a hydrogen-rich atmosphere over metal films, the reactions of ethylamine have also been interpreted by Kemball and Moss in terms of adsorbed molecular skeletal units such as C_2N_1, $(C_2)_2N_1$, N_1, and C_2; and the fission of the carbon-nitrogen bond in the C_2N_1 unit, rather than a Langmuir-Hinshelwood type mechanism, was suggested as the rate-controlling step in ethylamine trans-ethylation. Dehydrogenated amines were usually absent from the bulk stream, although two postulated intermediates (chemisorbed ethylimine and chemisorbed acetonitrile) may function in the present study as likely precursors for diethylimine and acetonitrile formation. Hydrogen transfer to such intermediates would occur rapidly.

CONCLUSIONS

A recycling differential reactor coupled with gas chromatographic analysis has been used to obtain kinetic data for the following system of simultaneous reactions which occur when monoethylamine reacts over porous copper:

$$2\, C_2H_5NH_2 \rightarrow (C_2H_5)_2NH + NH_3 \qquad (1)$$

$$C_2H_5NH_2 + (C_2H_5)_2NH \rightarrow (C_2H_5)_3N + NH_3 \qquad (2)$$

$$(C_2H_5)_2NH_2 \leftrightarrows C_2H_5NC_2H_4 + H_2 \qquad (4)$$

$$C_2H_5NH_2 \rightarrow CH_3CN + 2\, H_2 \qquad (5)$$

Using the methods of Hougen and Watson, we correlated data for reaction (1) with a zero-order form of the rate equation. Desorption of ammonia (single-site reaction) and adsorption of ethylamine (dual-site reaction) were plausible controlling mechanisms. Both the amount of hydrogen and the amount of ammonia present on and over the catalyst surface strongly influenced the reactivity and the product distribution of the reaction scheme. Concentration ratios of diethylamine to diethylimine were found to vary with the square of the initial hydrogen partial pressure, and inversely with initial ammonia partial pressure.

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NOTATION

k = zero-order reaction rate constant, g.-moles ethylamine/(g.-catalyst) (min.)
k' = Freundlich reaction rate constant
K_i = adsorption equilibrium constant of component i
n = reaction order

N_i = moles of component i formed by reaction
N_o = initial total moles
p_i = partial pressure of component i, mm. Hg
p_{io} = initial partial pressure of component i
P = total pressure, mm. Hg
P_o = initial total pressure
r = rate of reaction, g.-moles ethylamine/(g.-catalyst)(min.)
r_o, r_f = initial and final reaction rates

Subscripts

AN = acetonitrile
DEA = diethylamine
DEI = diethylimine
EA = monoethylamine
TEA = triethylamine

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Dynamics of a Multiple-Effect Evaporator System

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Presented is the development of a model for a system of evaporators at unsteady state operation, as well as a comparison of the dynamic behavior of the system predicted by the model with that observed in field tests. An objective of this project was to develop a suitable model of the process on the basis of the fundamentals of heat transfer, mass transfer, fluid flow, and the information commonly available from the design prints. The model predicts not only the dynamic behavior of the system to an upset in any of the operating variables but also the new steady state solution.

The field tests were made on the Freeport Demonstration Unit, located at Freeport, Texas. This plant was constructed under the direction of the Office of Saline Water, U. S. Department of the Interior. The details of the construction, operation, and successes achieved by this plant are well documented (*10, 12, 14, 26*).

The unit operation of evaporation is relatively old; yet many of the calculational procedures proposed by McCabe (*20*) in 1934 are still widely used. Principally, because of the need for fresh water, the evaporation process has enjoyed renewed interest in recent years (*1, 2, 9* to *12, 14* to *16, 18* to *21, 25* to *27*). Although numerous investigations on the dynamics of heat transfer and distillation processes have been reported (*7, 13, 17, 23, 24*), no study of the dynamics on a multiple-effect evaporator has been reported.

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