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Transmethylation Reactions of Monomethyl and Dimethylamine over Montmorillonite in a Flow System

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In this work the transmethylation reactions of monomethylamine and dimethylamine were investigated under steady state conditions in a flow system. A differential reactor was employed with montmorillonite as the catalyst and the initial rates of these reactions were measured isothermally. Mass velocities through the reactor were sufficiently high to eliminate bulk stream diffusion to the catalyst interface as a possible rate-controlling step of the reaction process. Pore diffusion was checked experimentally and shown to impose no limit on reaction rates.

The controlling phenomena of the reactions were determined by applying the Freundlich and Langmuir adsorption isotherms to the experimental results in the form of initial reaction rate vs. average partial pressure of reactant at constant temperature. Velocity constants and Arrhenius equations for these controlling processes were also determined.

REACTION SYSTEM AND CATALYST

The transmethylation reactions among the methylamines are (*1, 2*):

$$2\,CH_3NH_2 \rightleftharpoons (CH_3)_2NH + NH_3 \qquad (1)$$

$$CH_3NH_2 + (CH_3)_2NH \rightleftharpoons (CH_3)_3N + NH_3 \qquad (2)$$

$$2\,(CH_3)_2NH \rightleftharpoons (CH_3)_3N + CH_3NH_2 \qquad (3)$$

Since experimental temperatures did not exceed 372°C., thermal decomposition of the methylamines presented no problems (*3* to *6*).

Considering the transmethylation process as being analogous to alcohol dehydration, catalysts such as silica-aluminas, clays, or phosphates are each suitable for the reactions listed above, and it is found that active metals may also be used (*7, 8*).

Montmorillonite K-106 from Girdler catalysts was selected as the catalyst for the investigation of reactions (1) and (3). The basic structure of montmorillonite consists of a three-layer silica—alumina with hydroxyl groups—silica lattice (*9, 10*). The nature of the acidic sites of silica-alumina has been studied for amine base adsorption using infrared absorption analysis (*18*), indicating that these sites are initially Lewis sites, becoming apparent Bronsted sites when there is proton transfer to the adsorbed substrate from a surface hydroxyl ion. This description of the catalyst function is in accordance with earlier postulations and reviews (*11*).

RANGE OF VARIABLES COVERED IN THIS STUDY

Total pressure, 1.22 to 3.75 atm. Reactor mass velocities, 20 to 260 g./(hr.$^{-1}$) (cm.$^{-2}$). Monomethylamine transmethylation reaction, Temperatures: 320°, 336°, 344°, 356°, and 371°C. Reactant partial pressure: 0.26 to 1.33 atm. Dimethylamine transmethylation reaction, Temperatures: 249°, 262°, 277°, and 293°C. Reactant partial pressure: 0.14 to 1.06 atm.

The monomethyl and dimethylamine reactants were standard items purchased from The Matheson Company, Inc., and were found to be 98.0 and 99.5% pure, respectively, with the impurities being traces of other methylamines.

EQUIPMENT AND PROCEDURE

Batches of reactant methylamine (gaseous at room temperature) were diluted with helium and fed to the flow reaction system from a pressurized reservoir tank (4-cu.-ft. capacity at S.T.P.) through an ammonia regulator. The regulator was used to establish the system pressure, and a ⅛ in. stainless Hoke needle valve at the reactor exit was employed for flow control. Beyond this valve, the remaining system operated at essentially atmospheric pressure, with the gas stream passing through a rotameter (with a range up to 6 cu.ft./hr.), thence to a water scrubber for removal of the amines and ammonia. The pressurized portion of the reactor system was constructed of ¼ in. stainless steel tubing and corresponding fittings.

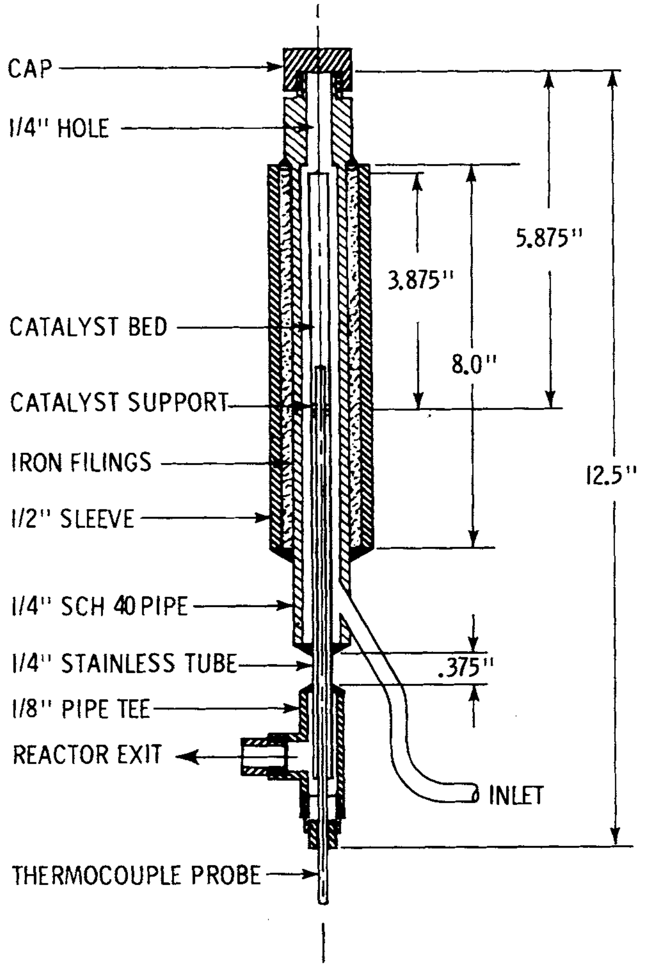

Fig. 1. Differential reactor cross section.

The vertically mounted down-flow reactor used is shown in Figure 1. The catalyst was charged and emptied through the top cap, the maximum catalyst capacity being 3½ g., although less than 1 g. was used for operation as a differential reactor (*15*). The reactor was heated by an 8 in. × 8 in. × 14 in. aluminum block (insulated with Fiberglas-asbestos sheets) with cartridge heaters in holes at each corner and with a central 1 in. hole to accommodate the reactor. The continuously heated and controlled furnace was suspended via pulleys and a counterweight and then simply lowered over the reactor prior to each run. This scheme eliminated lengthy heatup times. With the reactor operating in differential fashion, only low conversions were involved and no problem was encountered in maintaining isothermal operation.

Chromatographic analyses were made of gas samples of both feed and product streams to determine the extent of reaction under steady state conditions, given by the flow rate and the degree of conversion. Runs to determine controlling phenomena were made at constant temperature with reactant partial pressures varied by changing the total pressure at constant feed composition. Runs to determine the effect of bulk stream diffusion were conducted at constant temperature and pressure but with varying flow rates.

Desired feed mixtures were prepared by flashing amine from its storage cylinder through a molecular sieve packed tube into the system reservoir to a pressure up to the vapor pressure of the amine and then rapidly adding helium to a total pressure (usually 75 to 100 lb./sq. in. gauge), depending on the dilution desired. The mixture was allowed to stand overnight and no problems with inhomogeneity were encountered.

ANALYTICAL PROCEDURE

Prescribed analytical methods, based on titrations for the determination of one methylamine in the presence of others plus ammonia, are tedious and time consuming (*12*). However, mixtures of methylamines and ammonia may be detected conveniently by chromatographic analysis, and for this purpose a Burrell K-2 Kromotog chromatograph with a 2½ meter glass column was employed. Based upon the separation of the methylamines as reported by Sze (*13*), a stationary phase of 12½% diglycerol and 12½% tetrahydroxyethylethylene diamine (with 5% tetraethylene pentamine to neutralize the support) on —30, +60 mesh Celite was used, the column temperature being 95°C. and the helium carrier gas rate 75 ml./min. Under these conditions the analysis time was approximately 2 min.; thus samples from the flow system were analyzed immediately as they were produced.

With helium as the chromatographic carrier gas and also the diluent for the kinetic system, analyses were based on amine content of the gas stream. Relative amounts of the methylamines and ammonia were determined from the chromatographs using a weighted area technique with corrections for differences in thermal conductivities (*14*). The percent amine in the feed was determined by withdrawing gas samples in an evacuated flask, adding excess 0.1N hydrochloric acid, and back titrating with sodium hydroxide.

The transmethylation of monomethylamine was followed by measuring the increase in the relative area of the dimethylamine, ammonia chromatographic trace, while the trimethylamine chromatographic trace was used to follow the transmethylation of dimethylamine. A chromatographic check for methane as a possible reaction product was also performed using 10 X Linde molecular sieve and proved negative.

From the unbiased standard deviation for all the chromatographic analyses of the study, the maximum error in r_o, the initial rate of reaction due to analysis errors was approximately ±4% for 4% conversion of reactants.

DATA INTERPRETATIONS

A catalytic reaction may be controlled by a physical diffusion process, a chemical process such as chemisorption, or both. However, it may be possible to increase the rates of the physical steps by altering experimental con-

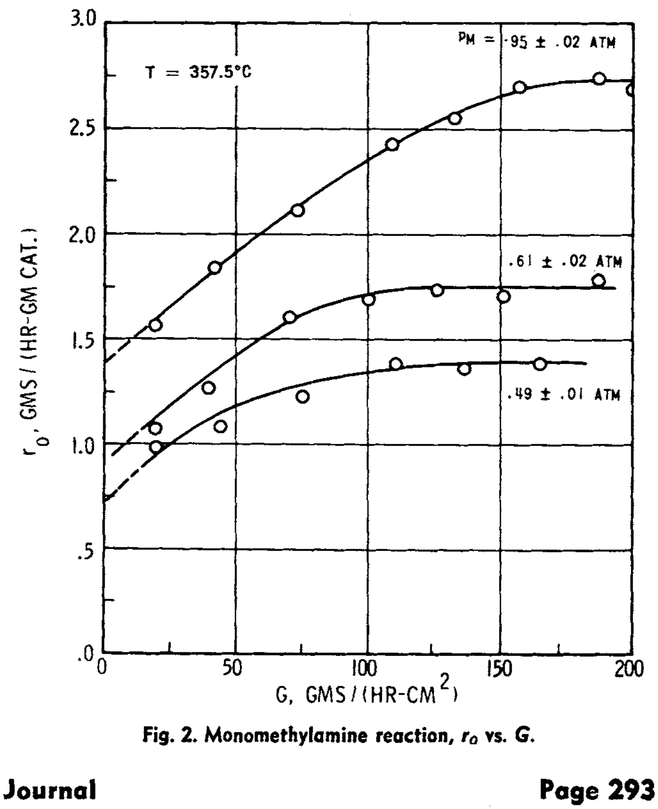

Fig. 2. Monomethylamine reaction, r_o vs. G.

ditions, in which case a chemical process then controls the reaction.

All rate data shown are for a catalyst size of −50, +60 mesh. This particle size presents a favorable surface area without an excessive pressure drop and also provides a ratio of particle size to inside diameter of the catalyst tube (0.18 in.) of 1:16.7, which is small enough to minimize channelling of flow through the catalyst bed.

BULK STREAM DIFFUSION

From the treatment of mass transfer in packed beds (*15*), the mass transfer coefficient may be written:

$$k_G = CT^a G^b / P^c \qquad (4)$$

where C is a constant and a, b, and c depend on the model chosen for the gas diffusivity and viscosity and are approximately 0.2, 0.5, and 1.0, respectively. Qualitatively, the rate of bulk stream mass transfer is inversely proportional to the total pressure and directly proportional to the square root of the mass velocity. This fact is important to this study since reactant partial pressure was changed by varying total pressure during each run.

To determine the mass velocities above which bulk stream diffusion does not limit the reaction process, the initial rates of both reactions were measured at constant temperature and pressure for varying mass velocities. The values at which r_o no longer increases with G are the minimum operating velocities for the system for obtaining true chemical process rates.

r_o vs. G results at constant temperature and several pressures for the transmethylation of monomethylamine and at constant pressure and several temperatures for the transmethylation of dimethylamine are shown in Figures 2 and 3. The latter shows that above 300°C. very high mass velocities are necessary to overcome bulk stream diffusion, and at this point diffusion becomes the controlling phenomena. For runs to determine the controlling chemical process of the reactions, velocities 25% higher than the established minimums were used.

PORE DIFFUSION

Should diffusion of the reactants from the surface to the porous interior of the catalyst be the controlling phenomenon, the true order of the reaction will not be determined (*16*). However, the effects of pore diffusion may be checked experimentally by measuring reaction rates for different catalyst particle sizes with all other parameters held constant. Larger particles present longer pores for diffusion, and if this process is the controlling step, the rate of reaction will increase as the particle size and pore depth are decreased. For the monomethylamine reaction, the measured rate was found to be constant for catalyst particle sizes from −100, +120 to −30, +40 mesh, a factor of 4 reduction in average particle diameter, thus indicating that pore diffusion imposes no limit on reaction rate.

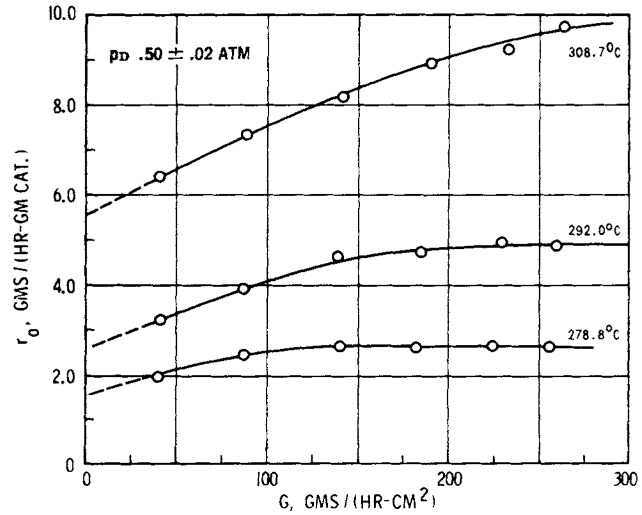

Fig. 3. Dimethylamine reaction, r_o vs. G.

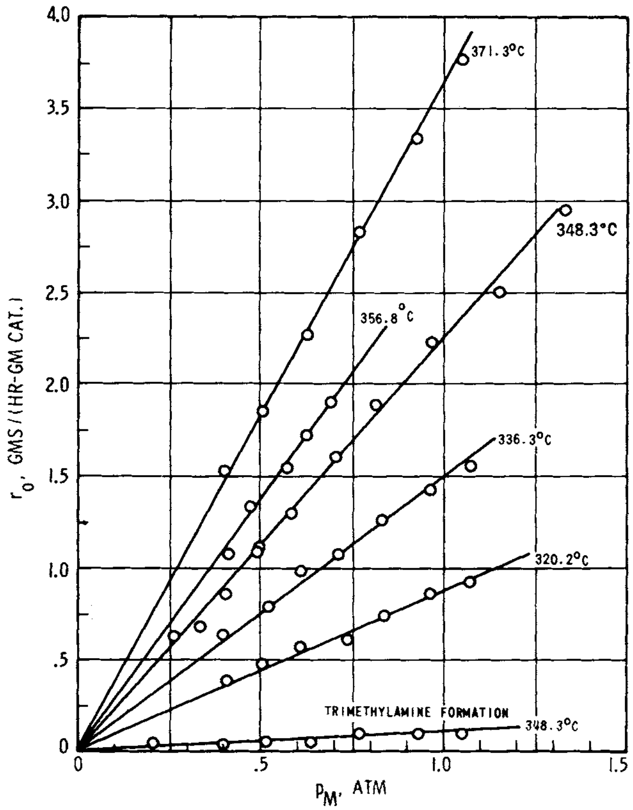

Fig. 4. Monomethylamine reaction, r_o vs. p_M.

RATE DATA AND INTERPRETATION

With experimental conditions such that a diffusional process does not limit the reaction, attention may be turned to the chemical processes of adsorption, desorption, or reaction on the catalyst surface as the controlling step.

The initial rates of reaction at sufficiently high mass velocities were determined vs. the average partial pressure of the reactant at several temperatures for both reactions under consideration. The results are shown in Figures 4 and 5. With low conversions, average partial pressures of reaction products are small compared with those of the reactant. Considering that the adsorption equilibrium coefficients are of similar magnitude (which is probable for the methylamines and ammonia), initial rate equations without product terms are applicable.

With monomethylamine as the reactant, the principal reaction is given by Equation (1), with Equation (2) becoming important at high conversions. As shown in Figure 4 for temperatures from 320° to 371°C., r_o is directly proportional to the amine partial pressure, thus indicating that adsorption of reactant monomethylamine on the catalyst surface is the controlling step. The rate equation is simply

$$r_o = k_M p_M \qquad (5)$$

which is the Langmuir-Hinshelwood initial rate equation

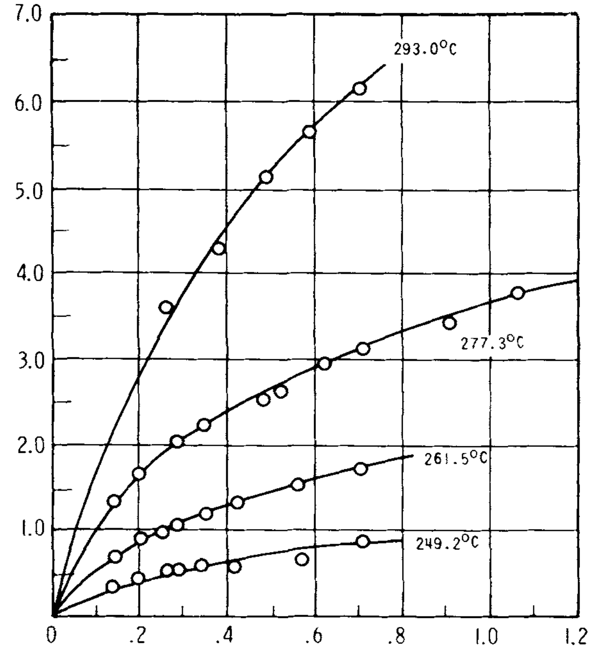

Fig. 5. Dimethylamine reaction, r_o vs. p_D.

for an adsorption controlling phenomenon (*17*). The rate of trimethylamine formation, reaction (2), is included for the run at 348°C. to show qualitatively the extent of secondary reaction (which is smaller at the other temperatures considered due to the lower levels of conversion).

The transmethylation of dimethylamine, reaction (3), occurs at rates comparable to those of reaction (1) at temperatures approximately 80°C. lower. The rate of reaction vs. partial pressure of dimethylamine, shown in Figure 5, is no longer linear. If the Freundlich isotherm is applied to the data

$$r_o = k_D{}^* p_D{}^{1/n}, \; n > 1 \tag{6}$$

The constants $k_D{}^*$ and n are readily determined from a ln r_o vs. ln p_D plot and the expression for r_o from the measured rates becomes

$$r_o = k_D{}^* p_D{}^{0.523} \tag{7}$$

The initial rate r_o varies approximately with the square root of the reactant partial pressure, indicating that a surface reaction step now controls the reaction process. Equation (7) fits the rate data to within ± 5% with the exception of several points at 249.2°C., where the data were taken at low conversions and were thus subject to larger analytical errors.

The Langmuir-Hinshelwood initial rate expression for a bimolecular surface reaction is

$$r_o = \frac{k_D K_D{}^2 p_D{}^2}{(1 + K_D p_D)^2} \tag{8}$$

with k_D and K_D given from the slope and intercept of plots of $1/\sqrt{r_o}$ vs. $1/p_D$. However, in describing the experimental data of Figure 5, Equation (8) yields much greater errors than the power form rate Equation (7), thus indicating that the reaction mechanism is more complicated than the simple form proposed by bimolecular surface reaction with ideal adsorption. Langmuir-Hinshelwood rate equations for other surface reaction phenomena were also considered, but did not describe the data with better accuracy than Equation (8).

The change in controlling step between the two reactions studied is attributed to the temperature difference involved. At lower temperatures, ion motion on the catalyst surface is slower and a surface reaction step thus limits the transmethylation of dimethylamine. For the monomethylamine reaction, the surface process is accelerated by the higher temperatures and activated adsorption becomes the controlling phenomenon.

Values for the velocity constants determined and the resulting Arrhenius equations are listed in Table 1. Values for K_D from expression (8) are also included and give the approximate heat of adsorption of dimethylamine on montmorillonite as —7.6 kcal./mole.

TABLE 1.

Determined velocity constants

$10^3/T$°K	$k_D{}^*$	K_D	$10^3/T$°K	k_M
1.767	7.40	6.06	1.552	3.61
1.817	3.79	7.53	1.588	2.73
1.871	2.05	8.76	1.609	2.26
1.915	1.03	10.62	1.641	1.46
			1.686	0.882

Arrhenius equations

$k_m = 1.00 \times 10^8 \quad \exp(-21{,}770/RT)$

$k_D{}^* = 9.39 \times 10^{10} \quad \exp(-26{,}060/RT)$

$K_D = 6.64 \times 10^{-3} \quad \exp(+7{,}640/RT)$

CONCLUSIONS

The initial rates of reaction for the transmethylation reactions of monomethyl and dimethylamine were measured over a tenfold range of reactant partial pressures at five and four temperatures, respectively. Initial rate data were taken with a flow system and a differential reactor using chromatographic analysis. Eleven initial rates were measured for an isotherm of each reaction to determine the controlling step.

For the transmethylation of monomethylamine, (T = 320° to 370°C.), the reaction rate is directly proportional to the average reactant partial pressure, indicating that the controlling phenomenon is adsorption of reactant on the catalyst. For the dimethylamine reaction, (T = 249° to 293°C.), a more complicated surface reaction controls and r_o is proportional to approximately the square root of the average reactant partial pressure. Above 300°C., high mass velocities are necessary to overcome bulk stream diffusion, and at this point, the transmethylation of dimethylamine becomes a diffusion controlled process.

These conclusions apply for the range of variables considered and may be quite different at other conditions.

NOTATION

G = mass velocity, g./(hr.$^{-1}$)(cm.$^{-2}$)
$k_D{}^*$ = effective reaction velocity constant for dimethylamine
k_i = reaction velocity constant for component i times concentration of vacant sites per gram catalyst
K_i = adsorption equilibrium constant of component i, atm.$^{-1}$
k_G = mass transfer coefficient
P = total pressure, atm.
p_i = partial pressure of component i, atm.
r_o = initial reaction rate, g./(hr.$^{-1}$)(g.-catalyst^{-1})
T = temperature, °C. or °K.
R = gas law constant

Subscripts

M = monomethylamine
D = dimethylamine

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Direct Contact Heat Transfer with Change of Phase:

Spray-Column Studies of a Three-Phase Heat Exchanger

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Transfer characteristics are presented for a perforated plate-spray column in which a volatile dispersed phase evaporates while rising in the continuous, counterflowing, immiscible phase. Optimal column heights, volumetric transfer coefficients, holdup, and foam heights are reported as functions of flow rate and temperature approach for a pentane-water system, A comparison with related studies is presented.

Recently multiphase exchangers where latent heat rather than sensible heat is transferred between immiscible fluids have been effectively used in water desalination by direct contact freezing. Some of the technical and economical aspects of utilizing these multiphase exchangers were reported by Umano (*1*), Wiegandt (2, 3), and others (*4*). Experimental direct freezing pilot plants (*5*) are presently in the process of accumulating valuable technical know-how.

Unlike the multiphase exchangers, where both the dispersed and the continuous fluids undergo change of phase, three-phase exchangers may be used for heat transfer at various temperature levels. The latter obviously depends on the choice of the transfer fluid. Stagewise operation of three-phase exchangers in a closed evaporation and condensation cycle was recently proposed by Harriott and Wiegandt (*6*) for simultaneous cooling and heating of sea water and desalined water streams in countercurrent flow. Some experimental data of condensation of methylene chloride in water flowing concurrently in a two-stage packed bed and a single-stage sieve-plate column were reported (*6*). Limited data were also reported on cocurrent flow evaporation of methylene chloride or pentane in water in a 2-in. diameter column. Wilke et al. (*7*) studied evaporation of water from sea water flowing concurrently in direct contact with hot Aroclor in an horizontal 3-in. pipe and steam condensation in direct contact with Aroclor in packed columns. Studies of condensation of steam in Aroclor in a simulated cocurrent spray column were also reported (*8*).

Despite increasing interest in technical information on direct contact heat transfer with change of phase, very little is known regarding the basic mechanism and heat transfer characteristics associated with evaporation of dispersions in immiscible liquids. Studies of single-drop evaporation in immiscible liquid media were recently reported by Sideman et al. (*9, 10*). These, however, may not be directly extended to population of drops, where the onset of nucleation is not simultaneous (and should be dependent on the vapor holdup and degree of turbu-