Rapid Gas-Phase Reactions. Amines and Boron Trifluoride. II. Pressure Dependence of Rate Constant[1a]

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Abstract: Relative rate constants for reaction of monomethylamine and trimethylamine with boron trifluoride are reported for the pressure range 0.04–600 Torr. The limiting ratio at low pressure is about 0.06, and the extrapolated high-pressure ratio is of the order 4. The half-pressure for quasi-bimolecular behavior of the monomethylamine–boron trifluoride system is in the vicinity of 70 Torr. When the data are combined with those of Kistiakowsky, *et al.*, individual pressure-dependent rate constants can be estimated. The amine–BF_3 series has loose activated complexes and low energy for redistribution among internal modes, making it an unusual candidate for theoretical unimolecular study.

A considerable amount of reliable experimental data relating to quasi-unimolecular reaction rate theory has been published in recent years (*e.g.*, ref 2 and 3). Investigations have included several reaction series. Using a chemical activation method, Rabinovitch and coworkers[2b] measured unimolecular decomposition rate constants of the homologous series of radicals ethyl through 2-octyl. Setser and coworkers[3] employed both thermal and Rabinovitch chemical activation methods in their studies of the decomposition of some chloroethanes. Both groups found reasonable agreement with RRKM theory[4] and have given, thereby, additional support to an assumption that all internal degrees of freedom may be taken as active in intramolecular energy transfer.

These reaction series involved "rigid" activated complexes. Another reaction series, one which involves "loose" activated complexes, is explored in the present paper. Kistiakowsky and coworkers[5] showed that the association reactions of amines with boron trifluoride, the reverse of a unimolecular reaction, proceed with high collision efficiency and so involve relatively loose activated complexes.

That study was made with a diffusion flame method and was followed by studies[6] which measured relative rates using a competition method. The two methods are complementary: the former permits measurements of absolute rates at low pressures, though with some scatter, and the latter permits study of relative rates at low and high pressures, though with the possibility of competitive local depletion and, at low pressures, of wall effects.

Each of the preceding investigations[5,6] was made at relatively low pressure. The present work was undertaken to extend the measurements of ref 6a to higher ones, and so determine the pressure dependence and the high-pressure limiting value of k_m/k_t where m refers to monomethylamine (MMA) and t to trimethylamine (TMA). Particular attention was given to the possibility of local depletion and to improved precision. To this end, several modifications were made in the procedure and in the apparatus. A relative rate study of the association of BF_3 with ammonia, dimethylamine, and trimethylamine has also been made subsequently by one of us and will be described elsewhere.[7]

Experimental Section

Apparatus and Procedure. Although several changes have been made, the essential feature of the method[6a] has been retained: a flow system is used in which a mixture of two amines reacts with a less than stoichiometric quantity of boron trifluoride. Changes include (1) removal of the two-stage mercury diffusion pump from the flow system, leaving the pumping action to a liquid nitrogen trap; (2) provision of driving vessels of 6 and 70 l., depending upon the flow rates needed; (3) expansion of the reaction vessel to 9-cm diameter about the nozzle orifices, with a length of 35 cm (the BF_3 and amine nozzles were 21 and 15 cm, respectively, from the bottom of the vessel); (4) inclusion of two right angle traps I and II in series immediately downstream from the reaction vessel; (5) inclusion of a solid particle trap S at the exit tube from trap II (S consists of a glass wool plug), when the reactor pressure is 3–5 Torr, or a fine pore sintered glass disk 35 cm^2 in area, when the reactor pressure exceeds 5 Torr; (6) inclusion of a variable leak placed after S to regulate pressure in the reaction (a by-pass around the variable leak was provided for low-pressure runs (less than about 0.1 Torr)). The system terminates in two parallel U-tube collection traps (III and IV) identical in position and function with those described in ref 6a.

Two pairs of pinhole nozzles, all approximately 2 mm in length of the construction at the orifice, conducted the amine–ethane and BF_3–ethane mixtures into the reactor. The radii of the first pair, estimated roughly from flow rate and Poiseuille's equation, were 0.0031 and 0.0056 cm, and for the amine and BF_3 nozzles, respec-

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(2) (a) B. S. Rabinovitch and D. W. Setser, *Advan. Photochem.*, **3**, 1 (1964); (b) M. S. Pearson and B. S. Rabinovitch, *J. Chem. Phys.*, **42**, 1624 (1965); (c) F. H. Dorer and B. S. Rabinovitch, *J. Phys. Chem.*, **69**, 1952, 1973 (1965); (d) G. Z. Whitten and B. S. Rabinovitch, *ibid.*, **69**, 4348 (1965).

(3) (a) J. C. Hassler and D. W. Setser, *J. Chem. Phys.*, **45**, 3246 (1966); (b) R. L. Johnson and D. W. Setser, *J. Phys. Chem.*, **71**, 4366 (1967).

(4) R. A. Marcus and O. K. Rice, *J. Phys. Colloid Chem.*, **55**, 894 (1951); R. A. Marcus, *J. Chem. Phys.*, **20**, 359 (1952); **43**, 2658 (1965); O. K. Rice, *J. Phys. Chem.*, **65**, 1588 (1961).

(5) (a) D. Garvin and G. B. Kistiakowsky, *J. Chem. Phys.*, **20**, 105 (1952); (b) G. B. Kistiakowsky and R. Williams, *ibid.*, **23**, 334 (1955); (c) D. Garvin, V. P. Guinn, and G. B. Kistiakowsky, *Discussions Faraday Soc.*, 17, 32 (1954).

(6) (a) Part I: J. Daen and R. A. Marcus, *J. Chem. Phys.*, **26**, 162 (1957); (b) S. H. Bauer, I. V. Martinez, D. Price, and W. D. Jones, Advances in Chemistry Series, No. 42, American Chemical Society, Washington, D. C., 1964, p 35.

(7) S. Glicker, to be submitted for publication.

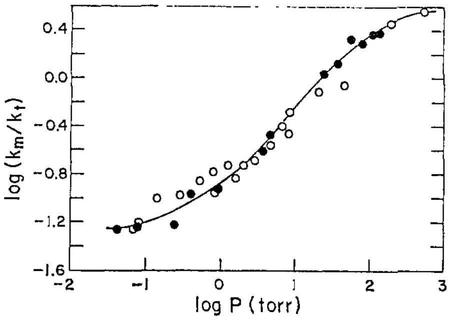

Figure 1. k_m/k_t *vs.* pressure: closed circles are data of Table I; open circles are data of Table II.

tively; those of the second pair were estimated as 0.0045 and 0.0085 cm, respectively. The first pair was used for reaction pressures below 1 Torr and the second pair for experiments above this pressure.

The procedure differed from that described in ref 6a for those experiments below 0.1 Torr where only trap II (single trap method) was used in place of alternate traps III and IV (alternate trap method). A significant addition to the procedure was the collection and analysis of all the solid products. The products, typically 5×10^{-5} mole, were collected from the walls of the reaction vessel, trap I, trap II, and trap S (when present) with approximately 15 ml of acetone, which was then removed from the products by a bulb-to-bulb distillation between −40 (acetonitrile slurry) and −196°. The product residue was dissolved in acetonitrile (typically 0.2 ml) prior to infrared analysis. A second additional step was the separation of ethane from the two methylamines prior to analysis of the latter, using a bulb-to-bulb distillation from −130 (*n*-pentane slurry) to −196°.

Table I. Experimental Data for the Reaction of MMA and TMA with BF_3[a]

p, Torr	k_m/k_t	R_m	R_t	R_{mb}	R_{tb}	R_e[b]	R_e[c]
0.043	0.056	1.79	0.36	0.110	0.397	0.56	6.77
0.066	0.059	3.28	0.74	0.177	0.684	2.07	9.77
0.25	0.062	1.84	0.25	0.469	1.03	2.47	13.3
0.40	0.11	8.10	3.65	0.183	0.785	9.97	43.5
0.93	0.12	9.57	7.60	0.117	0.795	17.6	37.8
3.6	0.26	7.95	5.65	0.441	1.19	21.5	66.4
4.5	0.35	9.64	7.22	0.108	0.231	18.3	41.6
24	1.1	12.3	15.8	0.131	0.144	195	273
37	1.4	20.5	27.7	0.382	0.373	247	663
59	2.2	32.6	47.0	0.752	0.491	297	1200
77	2.0	18.4	53.5	0.920	1.27	539	1570
115	2.4	36.7	51.5	2.16	1.25	509	2760
120	2.4	17.7	24.6	6.42	3.71	503	2680

[a] p is the total reaction pressure. R is the rate of flow of the indicated material in Torr/min into a standard volume of 54.2 cc. The subscripts m, t, mb, tb, and e refer to MMA, TMA, MMA adduct, TMA adduct, and ethane, respectively ($R_t + R_{tb}$ denotes, therefore, the initial flow rate R_t^0). [b] Flow through amine nozzle. [c] Flow through BF_3 nozzle.

Analysis. Analyses were made with a Perkin-Elmer Model 421 double-beam recording infrared spectrophotometer. Beer's law calibrations were made for MMA and TMA gases and for their BF_3 adducts in acetonitrile solution. The maximum experimental errors in the binary gas mixture and in the product mixture were estimated as 1.9 and 1.7%, respectively. Several additional synthetic product mixtures were dissolved in 10 ml of acetone, to conform to the experimental procedure, and then recovered from the acetone by a bulb-to-bulb distillation between an acetonitrile slurry (−40°) and −196°, yielding an experimental error identical with that obtained for the adducts not treated with acetone.

The stability of association products in both acetone and acetonitrile was examined by infrared analysis. There were no detectable spectral changes for at least several hours, a time considerably longer than that needed for completion of the analytical procedure. In addition, there was no detectable interference in these analyses by sorbed methylamines (see also ref 6b).

Reagents. Certified grade acetone and acetonitrile (Fisher Scientific) were stored over molecular sieves and used without further purification. Research grade ethane, MMA, TMA, and BF_3 (Matheson) were purified by repeated freeze (−196°)-pump-expand cycles to remove noncondensables, and then by bulb-to-bulb distillation from −78 to −196°. Mass spectrometric analyses for the experiments in Table I and for the closed circle experiments in Figure 1 indicated a maximum contamination of 0.4 mole % in the methylamine by other methylamines.

Equation

The conditions used in ref 6a to determine the relative bimolecular rate constant entailed the measurement of the rates of flow of amines into the reaction chamber and of the excess amines leaving the chamber. This method put a lower limit on the conversion of about 60% in order to maintain a reasonable precision. In the present work, the products were determined directly, permitting one to use much lower conversions. The expression used in ref 6a to determine the relative rate constants can be rewritten in terms of the product formed, as in Appendix I, to yield

$$k_m/k_t = (R_{mb}/R_{tb})/(R_m/R_t) \qquad (1)$$

where R_{mb}/R_{tb} and R_m/R_t are the ratio of formation of products and the ratio of excess amines, respectively.

The derivation of eq 1 assumes that there is negligible pumping selectivity of the amines and that there is no local depletion of either amine. Data on these approximations are given later.

Results

A material balance demonstrating a 1:1 stoichiometry was confirmed in experiments in which the change in amines was not a small difference between large numbers. Results are described in Appendix II.

The relative rate constants are given as a function of pressure in Table I and Figure 1 (closed circles) and in Table II and Figure 1 (open circles). The former were obtained at NASA, and the latter were obtained earlier at the Polytechnic Institute of Brooklyn. The analytical instrument and perhaps the technique were better in the closed-circled data, but the two sets of data are seen to agree reasonably well.

The four open-circle points in the 20-600-Torr range were performed under nonsteady-state conditions[8] and so should be viewed with some caution. Equation 1 remains valid under nonsteady-state conditions if the amine concentrations are uniform in the reaction region and if the per cent conversions are small enough that the ratio of ambient pressures is constant in time.

Experiments were made to test the two assumptions underlying eq 1. It is shown (Appendix III) that one of the conditions, negligible pumping selectivity of amines, is reasonably well fulfilled. The remaining condition, uniform amine concentration, has two aspects: no local depletion of total amine concentration and no local depletion of relative amine concentration (*i.e.*, one relative to the other). To investigate the latter, k_m/k_t was determined by eq 1 as a function of per cent conversion. (Relative depletion of one

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(8) For the series described in Table I steady-state conditions were maintained. However, the flow rates required to do so at pressures above 120 Torr were so large that appreciable amounts of products formed past the solid particle trap. No experiments in Table I series are therefore reported above 120 Torr.

Table II. Experimental Data for the Reaction of MMA and TMA with BF_3[a]

p, Torr	k_m/k_t	R_m	R_t	R_{mb}	R_{tb}	R_e[d]	R_e[e]
0.064[b]	0.059	3.09	0.37	1.25	2.60		
0.070	0.076	1.93	0.93	0.018	0.115		16.7
0.083[b]	0.057	2.79	0.14	3.72	3.32		
0.14[b]	0.10	5.17	1.76	0.442	1.53		
0.30	0.11	2.62	0.39	0.408	0.559	7.9	8.05
0.53	0.13	4.37	1.60	0.027	0.073	14.7	33.0
0.79	0.17	4.85	1.27	0.018	0.028	18.4	17.0
0.84	0.11	3.69	1.26	0.060	0.178	8.95	7.05
1.1	0.19	3.80	1.61	0.113	0.258	16.6	13.0
1.6	0.15	4.82	1.85	0.223	0.571	21.3	26.1
1.9	0.19	3.54	1.50	0.265	0.589	19.8	31.0
2.8	0.22	4.42	2.04	0.350	0.760	7.31	39.0
3.7	0.24	4.14	1.85	0.482	0.908	11.3	42.0
4.5[b]	0.27	25.3	12.1	0.344	0.614		29.4
5.3	0.32	3.06	1.30	0.942	1.21	19.2	47.0
5.5	0.35	4.76	2.83	0.026	0.044	31.1	36.0
6.9	0.40	3.22	1.52	0.630	0.750	19.1	53.0
7.4	0.40	3.83	1.87	0.558	0.672	24.7	40.0
7.5	0.44	3.69	2.03	0.021	0.026	24.5	62.0
7.9	0.35	29.8	15.4	0.629	0.929		46.3
8.0	0.52	4.20	2.06	0.029	0.028	16.2	50.0
8.0	0.39	4.85	2.74	0.220	0.315	21.1	44.1
8.1	0.39	3.92	1.91	0.420	0.525	19.5	39.0
8.5	0.42	3.52	1.76	0.569	0.661	29.7	45.0
8.5	0.40	4.47	2.24	0.011	0.014	26.4	49.1
20.0[b,c]	(0.78)	8.03	7.79	0.373	0.472	27.7	54.0
45.1[c]	(0.90)	4.67	3.57	0.340	0.289	13.3	60.0
193[b,c]	(2.8)	6.82	6.38	1.12	0.380	64.0	58.6
600[b,c]	(3.5)	4.27	3.65	1.68	0.413	98.0	80.0

[a] See corresponding footnote in Table I. [b] These experiments appear in Table III, where $R_a^0(\text{run}) = R_m + R_t + R_{mb} + R_{tb}$. [c] Nonsteady-state conditions (see text). [d] Flow through amine nozzle. [e] Flow through BF_3 nozzle.

amine over the other would increase with increased conversion.) The results, in the neighborhood of 0.8 Torr, are given in Figure 2. They show no dependence of k_m/k_t on conversion. Investigation of effect of per cent conversion at high pressure was more difficult because of a clogging tendency, particularly at any significant conversion. However, the two highest pressure closed-circle experiments in Figure 1 have conversions differing by a factor of 5, yet the k_m/k_t's are similar. Further, any serious tendency to local relative depletion would cause the data in Figure 1 to approach unity, rather than permitting them to rise above unity.

To examine the possibility of local depletion of total amine concentration, Heller's criterion[9] was investigated, namely no depletion at a sufficiently high v/D ratio (v = linear velocity of gas energing from the nozzle; D = diffusion constant of emerging gas). His criterion is fulfilled, as described in Appendix IV.

Discussion

Since these reactions are the reverse of unimolecular dissociations (of amine–BF_3 adducts), they should show a quasi-unimolecular behavior, *i.e.*, a rate constant which is constant at high pressures but which decreases at low. This behavior is amply confirmed in Figure 1. The pressure at which the rate constant decreases to one-half its high-pressure value is termed below the quasi-bimolecular half-pressure, $p_{1/2}$.

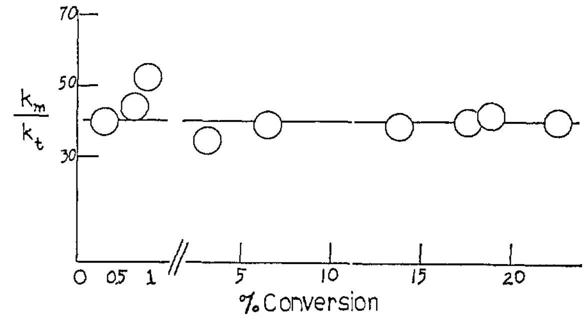

Figure 2. k_m/k_t *vs.* per cent conversion, using data in Table II between experiments using 6.9 and 8.5 Torr.

The limiting high-pressure ratio of k_m/k_t extrapolated from the data in Figure 1 is about 4. The ratio falls to a value of about 2 at 70 Torr. Since the $p_{1/2}$'s of the two amine systems appear to be well separated, this 70 Torr represents the $p_{1/2}$ for k_m.

The center of gravity of points of Garvin and Kistiakowsky[5] indicates a k_m and k_t of about 5×10^{11} and 3×10^{12} cc/(mole sec), respectively, at 0.2 and 0.1 Torr. The resulting ratio[10] of k_m/k_t of *ca.* 0.08 at 0.1 Torr compares with a similar value in Figure 1. The results in Figure 1 are also consistent with a value of 0.08 for k_m/k_t obtained in an earlier study[6a] at 0.01–0.04 Torr and high conversions (60%).

A value of k_m^∞ and k_t^∞ can be estimated from Figure 1. It is seen there that k_m/k_t decreases by a factor of about (4/0.1) when the pressure is decreased from infinity to 0.2 Torr. Thus, k_m^∞ has a minimum value of $5 \times 10^{11} \times (4/0.1)$ or 2×10^{13} cc/(mole sec). If the half-pressure for k_t is in the neighborhood of 1 Torr, as one interpretation of the data in Figure 1 would indicate, the value of k_m^∞ is seen to be close to the kinetic theory value of 10^{14} cc/(mole sec). (The value of k_t^∞, seen from Figure 1 to be approximately $^1/_4 k_m^\infty$, is smaller than k_m^∞ perhaps for steric reasons.)

According to unimolecular theory, and hence for the reverse reaction of bimolecular association, the system having the larger number of degrees of freedom has the longer lifetime, other things being equal, and thus has a smaller quasi-bimolecular half-pressure. This behavior is evident in Figure 1, the k_m/k_t ratio decreasing rather than increasing with decreasing pressure.

At low pressures the possibility of wall effects enters. At 0.1 Torr the size of the reaction zone is typically in the neighborhood[5] of 1 cm (it depends on the system). Thus, on this basis, data in Figure 1 at 0.1 Torr and above are expected to describe homogeneous behavior. From the expression for the reaction zone,[11] a scaling indicates a reaction zone size of about 5 and 30 cm at 0.03 and 0.01 Torr, respectively, suggesting that surface effects could contribute below 0.03 Torr.

Appendix I. Derivation of Eq 1

If R^0 and R denote rate of flow of amine into and out of the reaction zone, respectively, mass balance

(9) W. Heller, *Trans. Faraday Soc.*, 33, 1566 (1937).

(10) k_m at 0.1 Torr was calculated from that at 0.2 Torr assuming a direct proportionality, since Figure 1 indicates MMA to be in the low-pressure region.

(11) The size of reaction zone is measured by the parameter c^{-1} in ref 5, where $c^2 = ka/D$, a being the amine pressure. In the low-pressure region k, a (at constant mole fraction) and $1/D$ are directly proportional to pressure p, so that c^{-1} is proportional to $p^{3/2}$.

yields

$$R^0 = R + \int kAB\,\mathrm{d}V \qquad \text{(A1)}$$

where A and B are the local amine and boron trifluoride concentrations, and V is the reaction volume. The ratio of reaction rates for MMA and TMA is

$$\frac{R_{\mathrm{m}}^0 - R_{\mathrm{m}}}{R_{\mathrm{t}}^0 - R_{\mathrm{t}}} = \frac{\int k_{\mathrm{m}}A_{\mathrm{m}}B\,\mathrm{d}V}{\int k_{\mathrm{t}}A_{\mathrm{t}}B\,\mathrm{d}V} \qquad \text{(A2)}$$

When the amine concentration is assumed to be constant throughout V, *i.e.*, when there is no local depletion of amine, and when the ratio of amines in the reaction zone taken equal to the ratio of excess amines, *i.e.*, when there is no pumping selectivity, eq 1 follows.

Appendix II. Material Balance

Material balance data are given in Table III where R_a^0(blank) is the rate flow of the amines into the reaction vessel in the absence of BF_3, and R_a^0(run) is the rate of flow of excess amines plus rate of product formation. The percentage difference represents possible loss of products and is given by the column % Error. The total flow rate of gases into the reaction vessel is denoted by R. The nature of the trap S is indicated in the final column. The last two experiments in Table III had extremely large R's, one having the largest R in Table I and the other having an R only 4% less than the largest in Table II. Because of these large R's the lack of product loss in the last two experiments was particularly encouraging.

Table III. Material Balance Results[a]

R_a^0(blank)	R_a^0(run)	Error, %	R	Trap S[b]
38.5	38.5	−0.3	69	None
8.5	8.9	+4.0	10.9	None
10.1	10.0	−1.0	17.0	None
7.5	7.3	−3	11.2	None
6.5	6.6	+2	11.2	None
16.4	16.7	+1.8	99	Wool
15.5	14.7	−5.2	138	Wool
9.8	10.0	+2	190	Wool
52.6	52.5	−0.2	3250	Disk

[a] All experiments but the last are taken from the Table II experiments in which $6.9 < p < 8.5$ Torr. The last is taken from the last experiment in Table I. [b] Wool = glass wool; disk = sintered glass disk.

Appendix III. Pumping Selectivity of Amines

The pumping selectivity is defined here as the ratio of amine pumping speeds to ratio of amine pressures in the vessel. The removal of a mercury diffusion pump from the reaction line decreased the pumping speed for the alternate trap method and decreased the pumping selectivity for both the single and alternate trap methods. The single-trap method, employed at pressures below 0.07 Torr, resulted in a faster pumping speed than before. The pumping selectivities of the amines at 0.02 and 0.1 Torr were 1.17 and 1.05, respectively, in the absence of ethane. The effect of a large quantity of ethane in the flow system reduced the pumping selectivity of the binary amine mixture further. In the last six experiments listed in Table I, the ratio of amines in the reaction vessel and in the collected sample was found to be equal. The pumping selectivity of ethane compared with total amine was also equal to unity within an experimental error of 1.5%. Similar tests were not made for the data in Table II.

Appendix IV. Local Depletion

In a sodium diffusion-flame study, Heller[9] found that a spherical reaction zone and a limited alkyl halide depletion of about 10% was obtained when the ratio of the linear velocity in the reagent nozzle (Na + He in his study) to the diffusion constant of sodium in the reaction vessel (*i.e.*, v/D cm^{-1}) was between 5 and 12 cm^{-1}. As the value of the ratio rose above 12 cm^{-1}, depletion within the reaction zone decreased,[9] and the decrease was attributed to whirl formation caused by the mixing of two streams of gases at much different speeds. Back diffusion occurred at v/D values less than 5 cm^{-1}. Kistiakowsky, *et al.*,[5] showed that the upper limit could be increased to 16 cm^{-1} in their BF_3–He–amine diffusion-flame studies.

The linear velocity through the orifice of the reagent nozzle ($BF_3 + C_2H_6$) in the present work was estimated roughly from the volumetric flow using the Poiseuille equation and the cross section of the orifice. The flow-rate dependence on pressure agreed satisfactorily with a Poiseuille-type behavior in the region of 0.05–1 Torr (3% at lower limit, 15% at higher one). A measure of the calibration error in v was obtained from the observed and calculated molar flows. The latter was in error by +10% at 0.25 Torr.

The mass diffusion coefficient D was calculated as in ref 5c. The multicomponent mixture was idealized as a binary mixture of BF_3 and an ambient gas whose molecular diameter and molecular weight were the mean of the amines and ethane present. Equation 10 of ref 5c was used.

In the first five experiments in Table I, the v/D was thus calculated to be *ca.* 3, 6, 30, 100, 200, and 100 cm^{-1}, respectively. The remaining experiments were at pressures above 1 Torr (where the Poiseuille formula would be considerably less accurate). However, the v/D ratio would be larger than those in the preceding experiments, for example, of the order of 10^5 cm^{-1} at the highest pressure. Thus, except for the experiments below 0.1 Torr, the v/D ratio was large enough to avoid depletion of total amine concentration. Even at the lowest presures, judging by the Heller criterion, the total depletion is expected to be minor.

In the three experiments (the first one in Table I and first two in Table II) in which v/D did not exceed 5 cm^{-1}, examination of the internal surface of the nozzles, particularly the BF_3 one, after each experiment gave no evidence of solid product formation that would indicate back diffusion of amines. However, several low-pressure experiments in the $v/D < 5$ cm^{-1} region were lost by clogging of the BF_3 nozzle. A greater nozzle flow rate greatly reduced the clogging problem.