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BF_3-Catalyzed High Pressure Synthesis of Acetic Acid from Methanol and Carbon Monoxide

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Summary: *The reaction of acetic acid synthesis from methanol and carbon monoxide has been investigated kinetically in the presence of* BF_3+4H_2O *as catalyst at about 335° and 800 atm., varying operation variables such as temperature, pressure, and charge of methanol and catalyst.*

It has been found that almost all BF_3 *and water consist a liquid phase into which free methanol and dimethyl ether, in dehydration equilibrium, are dissolved, and there the reaction proceeds between methanol and dissolved carbon monoxide.*

A rate equation has been derived theoretically, which can explain the effects of the above-mentioned variables quantitatively; the fractional conversion rate is proportional to the fugacity of CO and to the reciprocal square root of the charged amount of methanol, and is expressed by a quadratic function of catalyst charge fraction.

The apparent activation heat is 34.1 kcal/mole, and of liquid phase reaction 22.7, and the rate constant is 2.37×10^{-5} *atm.*$^{-1}$ *min.*$^{-1}$ at *335°.*

Introduction

Several processes have been proposed to produce acetic acid from methanol and carbon monoxide under pressure. Among them, as to the method in which boron trifluoride and water are utilized so as to catalyze the reaction there have appeared only patent descriptions of Du Pont[1)].

We investigated this reaction kinetically some years ago for the case of the reactant mixture of $CH_3OH\cdot BF_3$ and $H_2O\cdot BF_3$, and found that at 200° in the liquid phase consisted of reactants and products the dehydration equilibrium $CH_3OH\cdot BF_3 \rightleftharpoons {}^1/_2CH_3OCH_3\cdot BF_3+{}^1/_2H_2O\cdot BF_3$ is established, and as the main reaction $CH_3OH\cdot BF_3+CO(\text{dissolved})\longrightarrow CH_3COOH\cdot BF_3$ goes on methanol is re-generated by reversal of the above equilibrium and finally nearly 100% of methanol is converted into acid[2)]. The rate is expressed by the equation

$$\frac{d(\text{AcOH})}{dt}=kf_{co}(\text{CH}_3\text{OH})_{equil},\ f=\text{fugacity, and}$$

this can explain the observed facts such as the effects of CO pressure and $MeOH/H_2O$ ratio and the rate change during the reaction, etc., quantitatively; $k=1.7\times10^{-5}$ atm.$^{-1}$ min.$^{-1}$ at 200° and the apparent activation energy=15 kcal, and the yield is, for example, 40% at 0.5 hr., 67% at 1 hr. and 90% at 2 hr., at 1,100 atm. for the initial molal composition of $CH_3OH\cdot BF_3/H_2O\cdot BF_3=1/1.5$.

Following the preliminary studies on the more diluted BF_3 catalyst[3)], the reason for the use of diluted one is given in ref. 3), a detailed investigation has been undertaken as regards the catalyst composed of BF_3 and $4H_2O$, which is to be dealt with here.

Results and Discussion

Experimental procedure and methods of analysis are the same as given before[1),2)].

Since the behavior of the system of BF_3 and H_2O is quite complicated[4)] and nothing is known about the mixture of $MeOH+H_2O+AcOH$ and BF_3 in which BF_3 is defficient to the former, especially at elevated temperature, e. g., 300°, some blank tests have been carried out as given below.

It can be seen from the table, that the most stable compound is the molecular complex $BF_3\cdot 2H_2O$ ($d_4^{20}=1.63$, m.p.$=6°$, b.p.$=59°$ at 1.2 mm)[5)] and when the excessive amounts of oxygenated compounds (H_2O, MeOH, AcOH and MeOMe) are present they remain all in free states and can be distilled out.

At high temperature in a closed vessel almost all BF_3 and water remain in the liquid phase, viz., BF_3 can be regarded as being combined with $2H_2O$ and dissolved in excess water, and free methanol (above its critical temperature) is in dehydration equilibrium and each gaseous

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Charge $MeOH/BF_3/H_2O/AcOH$ mole ratio	Widmer column atmospheric distillation
0 : 1/4 : 1 : 0	H_2O is distilled out at 100°, and the residue is 0 : 1/2 : 1 : 0.
1 : 1/4 : 1 : 0	H_2O and MeOH are distilled out at 63–92°, and the residue is 0 : 1/2 : 1 : 0.
0 : 1/4 : 1 : 4/5	AcOH and H_2O are distilled out until 106°, and the residue is 0 : 1/2 : 1 : 1/10.
	Heating in an autoclave (335°)
0 : 1/4 : 1 : 0	Pressure 27 atm. (Vapor pressure of pure water 140 atm.)
1 : 1/4 : 1 : 0	Pressure 66 atm.; Material balance

	Hot liq. phase	Hot gas phase
MeOH	21.9%	7.8% (base, charged MeOH)
MeOMe	21.5%	48.3% (ditto)
BF_3	96 %	4.2% (base, charged BF_3)
H_2O	ca. 120%	ca. 23% (base, charged H_2O)

component (MeOH and MeOMe) is also in equilibrium with each dissolved in $BF_3 \cdot 2H_2O$ aq.

Therefore we can presume that the reaction must proceed in the liquid phase between the dissolved reactants, *i.e.*, $(MeOH)_{dissol.} + (CO)_{dissol.}$, and the independent factors contributing the reaction should be, other than temperature and CO pressure, charged amount of $BF_3 \cdot 4H_2O$ and MeOH, and the volume of autoclave, and not a mere $MeOH/H_2O/BF_3$ ratio.

Table 1 Effect of CO pressure (335°, M_0 1/2 mole, BF_3 1/8 mole)

Max. pr. (atm.)	React. time (hr.)	Material balance (Based on charged MeOH, %)				t'* (min.)
		AcOH	AcOMe	MeOH	loss+ MeOMe	
545	5	65.8	0.5	3.0	30.7	13.8
560	4	68.1	1.9	10.9	19.1	10.1
565	3	61.3	3.4	17.6	17.7	8.5
565	2	44.7	2.4	28.1	24.8	5.9
565	1	22.5	4.8	37.2	35.5	5.8
575	1/2	15.3	1.3	33.6	52.8	5.5
570	0	8.9	0.3	32.3	58.5	4.8
750	4	73.5	0.1	4.0	22.4	9.9
720	3	74.1	0.7	10.3	14.6	12.1
725	2	63.9	1.3	17.6	17.2	10.1
750	$1^1/_2$	60.8	1.3 MeOMe	20.0 observed	17.9 17.2	9.6
705	1	43.0	2.0	26.4	28.6	9.8
750	1/2	27.2	1.9	32.1	38.8	11.9
745	0	13.8	0.9	32.2	53.1	11.6
855	$2^7/_{12}$	83.8	0.3	11.0	4.9	15.6
860	2	80.0	1.0	13.5	5.5	10.0
860	$1^1/_2$	70.5	0.5	14.5	14.5	13.0
820	1	50.6	1.0	30.5	17.9	10.2
865	1/2	38.3	0.2 MeOMe	34.4 observed	27.1 21.8	10.9
820	0	8.2	6.1	28.7	57.0	9.9
1040	1/2	51.1	4.0	27.5	17.4	12.8
1025	1/6	28.7	3.0	33.8	34.5	12.4

* See the text.

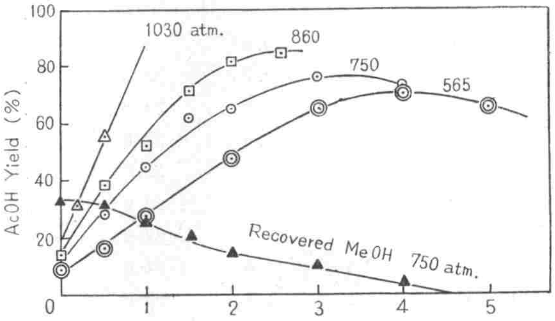

Fig. 1 Effect of CO Pressure (335°)

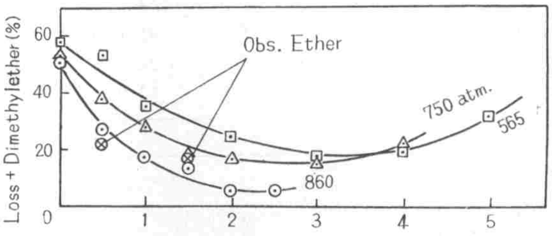

Fig. 2 Material Balance (335°)

The effect of CO pressure is reproduced in Table 1 and Figs. 1 and 2 under the condition: autoclave 133 cc, $(MeOH)_0$ 16 gr=1/2 mole, $BF_3 \cdot 4H_2O$ 17.5 gr=12.7 cc=1/8 mole as BF_3 at 335°.

Evidently the yield is over the stoichiometrical amount to BF_3, that is, the produced AcOH does not make BF_3 ineffective by combining tightly with it, as supposed from the above blank run.

As is seen in Fig. 2 in which the total of loss and ether is almost the same as the observed amount of ether in the early half of the reaction period, the material balance is satisfactory, but in the later period loss becomes noticeable and this, along with the decrease of AcOH yield (Fig. 1) and the observed formation of tarry matter, suggests the decomposition of product on prolonged operation.

The substantial yield at time zero is due to the reaction taking place during the warming-up period which is unavoidable in the present procedure, viz., the reactor containing all the reactants was heated under shaking and the time origin is given by the time when the temperature has reached just the specified value. Correction for this will be considered later, but the reaction during the cooling down can be neglected because of the rapidness of cooling.

Table 2 Effect of reaction temperature
(M_0 1/2 mole, BF_3 1/8 mole, total pr. 800-850 atm.)

React. temp. (°C)	React. time (min.)	Material balance (Based on charged MeOH, %)			
		AcOH	AcOMe	MeOH	loss+ MeOMe
320	60	33.8	0.8	34.6	30.8
320	30	18.2	0.6	34.1	47.1
320	10	9.5	0.7	35.3	54.5
330	60	36.5	2.6	34.8	26.1
330	30	25.7	1.6	33.6	39.1
330	10	11.0	1.4	33.6	54.0
335	60	52.8	1.4	25.9	19.9
335	30	32.8	1.3	37.6	28.3
335	10	19.1	1.8	31.6	47.5
340	60	58.2	1.7	27.6	12.5
340	30	37.2	2.1	32.8	27.9
340	5	15.7	2.0	34.2	48.1
350	60	67.6	0.9	14.7	16.8
350	30	53.1	1.6	31.7	13.6
350	5	26.6	1.7	32.7	39.0
360	30	68.1	1.4	14.2	16.3

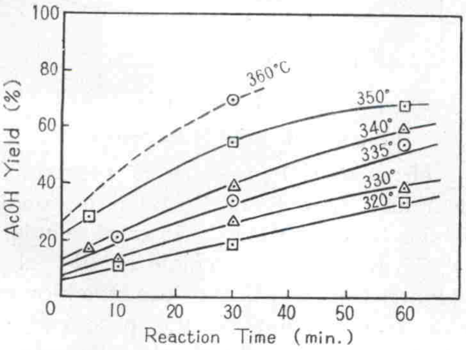

Fig. 3 Effect of Reaction Temperature (800～850 atm.)

The effect of reaction temperature is given in Table 2 and Fig. 3 where the condition is: autoclave 133 cc, MeOH 1/2 mole, $BF_3 \cdot 4H_2O$ 1/8 mole as BF_3, and total pressure at reaction temperature 800–850 atm. The effect of the amount of methanol charge and the charged fraction of $BF_3 \cdot 4H_2O$ relative to the reactor volume at 335° are reproduced in Table 3 and Fig. 4, and Table 4 and Fig. 5, respectively, the condition is the same as above except for variables, and the fraction β is defined by the percentage of the volume of the charged $BF_3 \cdot 4H_2O$ measured at reaction temperature (density=1.2) to the whole volume of the autoclave.

The analysis of the results has been performed on the initial reaction rate because the pressuse drop (isochore), decrease of methanol and some side reactions make the rate calculation during the course of the reaction quite difficult.

In order to correct the yield during the warming-up we adopt the following approximation.

First, the experimental equations are obtained

Table 3 Effect of methanol charge
(335°, 800-850 atm., BF_3 1/8 mole)

M_0 (mole)	React. time (min.)	Material balance (Based on charged MeOH, %)				t'* (min.)
		AcOH	AcOMe	MeOH	loss+ MeOMe	
0.25	10	44.4	0.6	30.6	24.4	7.0
0.25	30	69.4	1.5	15.3	13.8	9.1
0.25	60	97.1	0.1	3.2	−0.4	9.5
0.30	10	39.7	0.9	26.5	32.9	10.3
0.30	30	54.2	2.1	19.7	24.0	7.1
0.30	60	82.0	1.1	9.4	7.5	10.4
0.48	10	18.7	0.8	30.7	49.8	7.0
0.48	30	32.1	2.7	30.2	35.0	7.2
0.48	60	47.5	1.4	28.2	22.9	9.0
1.00	20	5.3	1.0	32.4	61.3	10.4
1.00	60	16.6	1.4	34.8	47.2	11.2
1.49	60	7.3	0.0	24.3	68.4	11.5

* See the text.

Table 4 Effect of $BF_3 \cdot 4H_2O$ charge
(335°, 800-850 atm., M_0 1/2 mole)

BF_3 (mole)	β	React. time (min.)	Material balance (Based on charged MeOH, %)				t'* (min.)
			AcOH	AcOMe	MeOH	loss+ MeOMe	
0.325	0.285	5	34.4	2.5	40.5	22.6	8.8
0.325	0.285	20	49.8	3.0	33.7	13.5	8.2
0.325	0.285	60	82.5	1.0	12.7	3.8	8.4
0.225	0.197	10	33.3	2.6	37.5	22.6	6.0
0.225	0.197	35	58.9	2.7	25.8	12.6	8.2
0.225	0.197	60	76.3	1.2	16.2	6.3	9.8
0.175	0.154	10	20.7	1.4	29.5	48.6	6.6
0.175	0.154	30	40.3	2.6	30.3	26.8	7.6
0.175	0.154	60	66.3	1.5	19.6	12.6	7.6
0.125	0.110	10	19.1	1.8	31.6	47.5	6.5
0.125	0.110	30	32.8	1.3	37.6	28.3	11.7
0.125	0.110	60	52.8	1.4	25.9	19.9	13.2
0.073	0.064	10	11.0	0.8	33.5	54.7	6.7
0.073	0.064	60	30.8	2.4	32.0	35.2	6.2

* See the text.

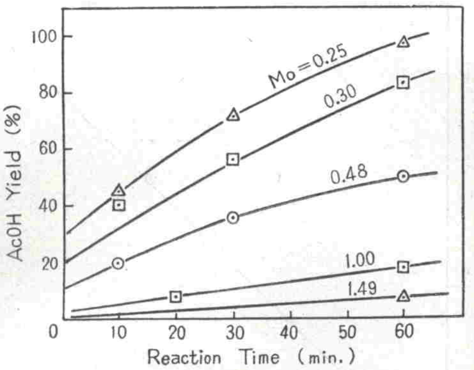

Fig. 4 Effect of Charged Methanol (335°, 800~850 atm.)

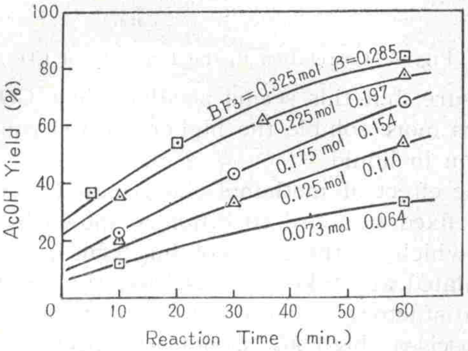

Fig. 5 Effect of BF$_3$·4H$_2$O Change (335°, 800~850 atm.)

to fit the observation in Fig. 3 (temperature effect) in the form

$$x = at^2 + bt + c \qquad (1),$$

and the tangents at $x=0$ are derived, where x is the fractional yield of total AcOH relative to the charged methanol $(M)_0$, and t is the apparent reaction time given in Figs. 1~5.

temp.	360°	350°	340°	335°	330°	320°
$-t_{(x=0)}$ (min.)	10.1	13.5	12.7	12.5	12.4	12.7
$(dx/dt)_0 \times 10^3$ (min.$^{-1}$)	26.2	17.3	10.6	8.2	6.4	4.4

The plot $\ln(dx/dt)_0$ versus $1/T$, which is fortunately linear, gives the apparent temperature coefficient of the reaction (Fig. 6) and apparent activation heat can be obtained to be 34.1 kcal/mol.

Next, using this activation heat we can calculate the time, t', so that the amount of reaction between t' and the apparent time zero, assuming that the reaction proceeded at the specified reaction temperature from t', would be equivalent to the actual amount of reaction up to the apparent time zero, that is, the integral mean of the reaction of warming-up period, assuming that the rate is proportional to the fugacity of CO (given later), *i. e.*,

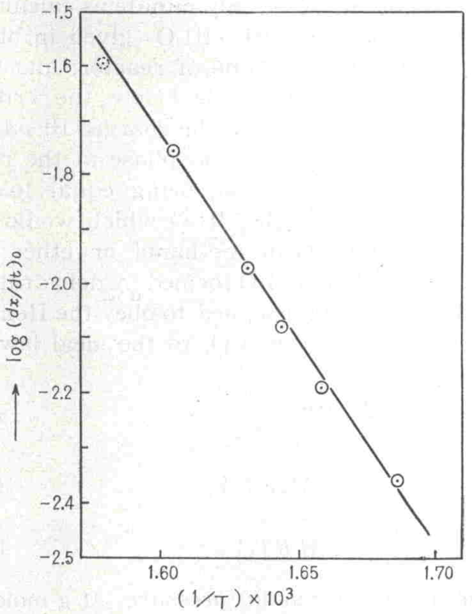

Fig. 6 Temperature Dependency of Initial Rate

$$t'f'_{co}e^{-E/RT'} = \int_{\text{start of warming-up}}^{\text{apparent time zero}} f_{co}e^{-E/RT}dt$$

where f' and T' are the specified reaction fugacity of CO and temperature, respectively, and f or T is the function of time in the warming-up, the T–t and f–t curves have been obtained for each run. The integration is performed graphically, the calculated t' being given in Tables 1, 3 and 4.

Then we add the respective time t' to the t of each run and draw again the curves like Figs. 1 and 3~5 with $(t+t')$ as abscissa, and expressing those curves by quadratic equations we get the corrected initial rates. The results are given in Table 5.

Table 5 Corrected initial rates

Total pr. (atm.)	565	750	860	1,030	
f_{CO} (atm.)	660	1,010	1,252	1,685	
$(dx/dt)_0 \times 10^3$ (min.$^{-1}$)	4.6	7.9	10.6	15.6	
M_0 (mole)	0.25	0.30	0.48	1.00	1.49
$(dx/dt)_0 \times 10^3$ (min.$^{-1}$)	23.5	19.0	12.0	2.5	1.0
charge BF$_3$·4H$_2$O (mole as BF$_3$)	0.073	0.125	0.175	0.225	0.325
V_l (cc)	8.5	14.6	20.5	26.2	38.0
β	0.064	0.110	0.154	0.197	0.285
$(dx/dt)_0 \times 10^3$ (min.$^{-1}$)	6.3	10.5	14.4	19.7	24.8

The rate equation has been constructed according to the following consideration together with rather broad assumptions:

1) Dehydration equilibrium is established quickly and each component is also in dissolution equilibrium, but, since the amount of H$_2$O

in the vapor phase is only minute as calculated from the pressure of $BF_3 \cdot 4H_2O$ (given in blank test) and the free volume of reactor, and that the reaction temperature is below the critical point of water, we regard the charged $BF_3 \cdot 4H_2O$ as the amount of the liquid phase at the reaction condition and p_{H_2O} as being equal to the vapor pressure of $BF_3 \cdot 4H_2O$ which would not vary by dissolution of methanol or ether gas and condensation of H_2O formed by dehydration. The dissolution is assumed to obey the Henry's law and gases, except CO, to the ideal law.

Then,

$$\frac{p^{1/2}{}_e \cdot p^{1/2}{}_{H_2O}}{p_m} = K \qquad (2),$$

$$\frac{M'_m}{V_l} = k'_m M_m RT/V_f \qquad (3),$$

$$\frac{M'_e}{V_l} = k'_e M_e RT/V_f \qquad (4),$$

where p denotes partial pressure, M g-mole, V volume, and K or k' equilibrium constant, and suffix e, m, l or f stands for dimethyl ether, methanol, liquid or gas space, respectively, and the prime on M refers to the dissolved state and bare M that in the gas phase.

2) Reaction rate is assumed to be proportional to the concentration of methanol in solution and to that of dissolved CO, and we assume the latter is proportional to the activity of dissolved CO, accordingly, to the fugacity,

$$\left(\frac{dx}{dt}\right)_0 = kf\text{co} \cdot \frac{M'_m}{V_l} \cdot \frac{V_l}{M_0}. \qquad (5)$$

From (2)~(4) and the material balance $M_0 = M'_m + M_m + 2(M'_e + M_e)$ we get

$$M_m = (-m + \sqrt{m^2 + 8aeM_0})/4ae$$

and finally

$$\left(\frac{dx}{dt}\right)_0 = \frac{kf\text{co}k'_m RTV_l}{4aeV_f}\left\{\frac{-m}{M_0} + \sqrt{\frac{m^2}{M_0{}^2} + \frac{8ae}{M_0}}\right\} \qquad (6)$$

where

$a = K^2RT/p_{H_2O}V_f$, $\quad b = RTV_l/V_f$,

$m = 1 + k'_m b$, $\quad e = 1 + k'_e b$,

values to be introduced in the above equation are all known from the blank tests:

$K = 2.13$, $p_{H_2O} = 27$, $a = 9060/V_f$, $b = 49900/V_f$, $k'_m = 4.56 \times 10^{-4}$, $k'_e = 7.22 \times 10^{-5}$ (units are cc, atm., mole) at 335°.

From (6) we expect the initial rate should be proportional to the fugacity of CO (total pressure − 66 atm. given in the blank); this is shown in Fig. 7. The linearity is fair; that the line does not pass the zero point may be attributed to non-validity of the assumption of linear dependence between the concentration and the activity of CO in the entire range of pressure, but this seems peculiar since CO becomes more soluble the higher the CO concentration in liquid.

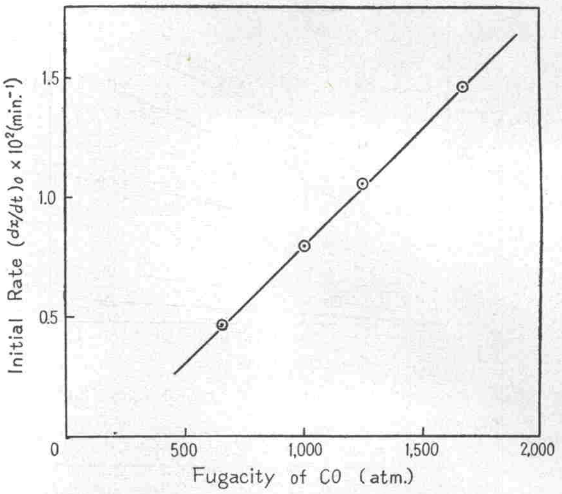

Fig. 7 Correlation to the Fugacity of CO

The effect of methanol charge under otherwise fixed standard condition is shown in Fig. 8 in which all the M_0-involving term in (6) are calculated and taken as abscissa; the linearity is satisfactory and the deviation at low value of abscissa (high M_0) is not unexpected since at high M_0 Henry's law will not be valid.

On numerical calculation the first term in the root sign of eq. (6) is less than 5% of the second, then neglecting the first we have

$$\left(\frac{dx}{dt}\right)_0 = \text{const.}\, f\text{co}\left(\frac{-m}{M_0} + \sqrt{\frac{8ae}{M_0}}\right),$$

further, since m/M_0 of this equation is at most 26% of $\sqrt{8ae/M_0}$ in the range of M_0 experimented we may drop the former and get

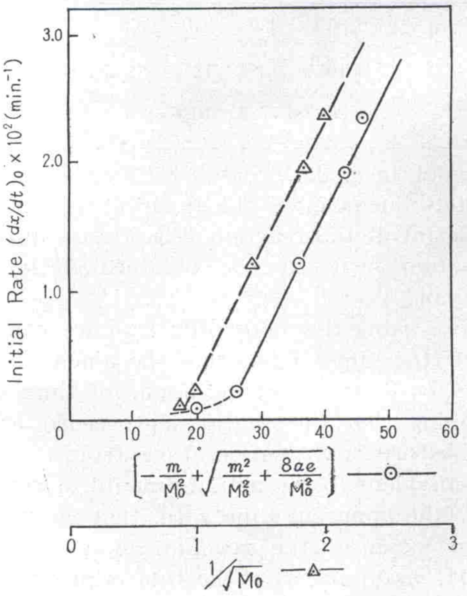

Fig. 8 Correlation to the Charged Methanol

$$\left(\frac{dx}{dt}\right)_0 = \text{const}\cdot f_{\text{CO}}/\sqrt{M_0} \qquad (7)$$

In Fig. 8 we can see this relation also to hold.

In order to see the correlation to the charge rate [$\beta \equiv$ (vol. of $BF_3 \cdot 4H_2O$ at 335°)/(vol. of reactor V_0) $= V_l/(V_l+V_f)$. Density of $BF_3 \cdot 4H_2O$ is assumed as 1.20 at 335°], the equation (6) is revised in the form involving β-containing terms separately,

$$\left(\frac{dx}{dt}\right)_0 = \frac{k f_{\text{CO}} k'_m RT}{4\boldsymbol{A}M_0}\left[\frac{\boldsymbol{M}}{\boldsymbol{E}}\left\{-1+\sqrt{1+\frac{8\boldsymbol{AE}M_0}{\boldsymbol{M}^2}}\right\}\beta\right], \qquad (8)$$

where $\boldsymbol{M} = 1+(k'_m RT-1)\beta = (1-\beta)m$,
$\boldsymbol{E} = 1+(k'_e RT-1)\beta = (1-\beta)e$ and
$\boldsymbol{A} = K^2 RT/p_{H_2O}V_0 = (1-\beta)a$,

and the linearity is checked as shown in Fig. 9. In this equation $8\boldsymbol{AE}\cdot M_0/\boldsymbol{M}^2$ lies between 10 and 56 under the experimented condition, hence dropping 1 in the root we get

$$\left(\frac{dx}{dt}\right)_0 \fallingdotseq \frac{k f_{\text{CO}} k'_m RT}{\sqrt{2\boldsymbol{A}M_0\boldsymbol{E}}}\left\{1-\boldsymbol{M}\sqrt{1/8\boldsymbol{AE}M_0}\right\}\beta .$$

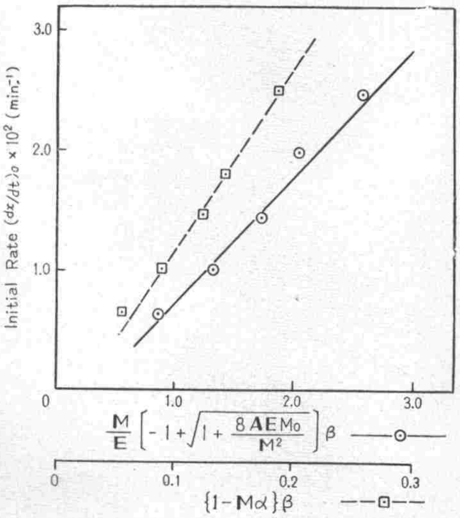

Fig. 9 Correlation to the Charged Fraction of $BF_3 \cdot 4H_2O$

Further, the change of $\sqrt{\boldsymbol{E}}$ is at most 25% against the four-fold change of β under experimental condition, so we regard the term $\sqrt{\boldsymbol{AE}M_0}$ as nearly constant and obtain an approximate formula,

$$\left(\frac{dx}{dt}\right)_0 \fallingdotseq \text{const}\cdot f_{\text{CO}}(1-\boldsymbol{M}\alpha)\beta = \text{const}\cdot f_{\text{CO}} \times[1-\{1+(k'_m RT-1)\beta\}\alpha]\beta ,$$

where

$$\alpha = 1/\sqrt{8\boldsymbol{AE}M_0} = \sqrt{\frac{p_{H_2O}V_0}{8K^2RT\{1+(k'_e RT-1)\beta\}M_0}} \fallingdotseq \text{const.},$$

viz., the initial rate is roughly expressed by a quadratic function of β, and this relation is seen to hold satisfactorily as given in Fig. 9.

Finally we shall calculate the net activation heat, E_0, of the liquid phase reaction rate k. Several terms in equation (2) are by themselves temperature dependent; they are expressed as follows:

$k = Ae^{-E_0/RT}$, $\ln K = -\Delta F_d^0/RT$,
$\ln k_m = -\Delta F_m^0/RT$, $\ln k_e = -\Delta F_e^0/RT$,
$\ln p_{H_2O} = \boldsymbol{a} - \boldsymbol{b}/T$,

and $\Delta F^{0\prime}s$ and $\boldsymbol{a}$ can be evaluated from the blank, but $\boldsymbol{b}$ is taken as equal to that of pure water, i.e.,

$F_d^0 = -920$ cal/mol, $\Delta F_m^0 = 9296$ cal/mol, $\Delta F_e^0 = 11522$ cal/mol, all at 335°, and $\boldsymbol{a} = 11.0$, $\boldsymbol{b} = 4.74 \times 10^3$.

Eq. (6) is then transformed into

$$\left(\frac{dx}{dt}\right)_0 = \frac{A f_{\text{CO}} V_l \exp(\boldsymbol{a})}{4M_0} \times \exp\{-(E_0+\Delta F_m^0-2\Delta F_d^0+R\boldsymbol{b})/RT\} \times \left\{\frac{-m+\sqrt{m^2+\frac{8RM_0Te}{V_f\exp(\boldsymbol{a})}\exp\{-(\Delta F_d^0/RT)+\boldsymbol{b}/T\}}}{e}\right\},$$

or

$$= \frac{A f_{\text{CO}} V_l \boldsymbol{C} \exp(\boldsymbol{a})}{4M_0 e}\exp\{-(E_0+F)/RT\}$$

$$= \frac{\boldsymbol{C} f_{\text{CO}} V_l \exp(\boldsymbol{a})}{4M_0 e} k\exp(-F/RT),$$

where $e = 1+k'_e b$, $\boldsymbol{C} = -m+\sqrt{m^2+\cdots\cdots}$
and $F = \Delta F_m^0 - 2\Delta F_d^0 + R\boldsymbol{b}$.

We assume the variation of F with temperature is negligible as compared with the value of E_0+F in the experimented range of these high temperatures since the coefficients of the temperature dependent terms in F are the small differences of specific heats, and the variation of liquid density with temperature is also neglected, then k can be calculated at different temperatures from the known values of parameters appearing in this equation, for example:

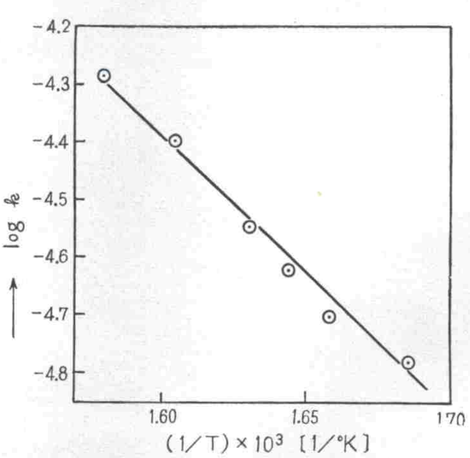

Fig. 10 Arrhenius Plot of Liquid Phase Reaction Rate

k(atm.$^{-1}$ min.$^{-1}$)$=3.97\times10^{-5}$ at 350°, 2.37×10^{-5} at 335°, 1.62×10^{-5} at 320.

The Arrhenius plot is given in Fig. 10 and $E_0=22.7$ kcal.

Thus, the higher value of the apparent activation heat obtained previously becomes to be due to the inclusion of temperature dependent terms in equilibria and *C*/*e*.

In the above treatment we have neglected the variation of k itself with the composition of BF_3/MeOH in the liquid, this might not happen when the dissolved amount of methanol is less than the stoiciometrical amount of BF_3 such as the most part of this investigation, because the reaction mechanism is supposed to be

$$CH_3OH+BF_3\longrightarrow(CH_3OH\cdot BF_3)\longrightarrow$$

$$CH_3^{+}+OHBF_3^{-}\xrightarrow{CO}CH_3CO^{+}+OHBF_3\longrightarrow$$

$$CH_3COOH+BF_3$$

and the rate determining step cannot be the first two.

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