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Kinetics of the Catalytic Vapor Phase Carbonylation of Methanol to Acetic Acid

K. K. ROBINSON, A. HERSHMAN, J. H. CRADDOCK,
AND J. F. ROTH

Corporate Research Department, Monsanto Company, St. Louis, Missouri 63166

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The reaction kinetics have been established for the low pressure vapor phase catalytic carbonylation of methanol to acetic acid using a solid supported rhodium complex catalyst. The catalyst is a heterogeneous analog of a previously developed homogeneous liquid phase catalyst system based upon a rhodium complex and an iodide promoter. Significantly, the reaction order dependencies are identical to those established for the liquid phase reaction (i.e., first order in iodide and independent of methanol and carbon monoxide concentrations). This suggests that in spite of the obvious physical differences between these heterogeneous and homogeneous catalysts, a similar chemical reaction mechanism is probably operative.

INTRODUCTION

A novel catalyst was reported recently (*1*, *2*) for the low pressure liquid phase synthesis of acetic acid from methanol and carbon monoxide. This homogeneous catalyst is comprised of a rhodium complex and an iodide promoter and represents a major improvement over prior art methanol carbonylation catalysts. Prior liquid phase technology for this reaction is based on a homogeneous cobalt catalyst which operates at very high pressure (about 7500 psig carbon monoxide pressure) with about a 90% molar selectivity to acetic acid (*3*). The new rhodium catalyst system performs efficiently at much milder conditions (as low as 1 atm carbon monoxide) and gives better than a 99% molar selectivity to acetic acid.

It was subsequently reported (*4*) that a heterogeneous catalyst could be formulated for carbonylating methanol to acetic acid by depositing various forms of rhodium on a support and feeding the iodide promoter generally as methyl iodide. Such solid supported catalysts are capable of carbonylating methanol to acetic acid at mild conditions similar to those employed with the homogeneous liquid phase rhodium catalyst (i.e., carbon monoxide partial pressure of 1 atm or less).

The purpose of the present investigation was to study the reaction kinetics for the heterogeneously catalyzed vapor phase carbonylation of methanol and to compare the results with those reported (*2*) for the same catalytic reaction carried out in the liquid phase. Previously there have been few, if any, direct comparisons of the reaction kinetics of a catalytic homogeneous liquid phase reaction with the kinetics of a similar vapor phase system (employing an analogous catalyst).

Various forms of the active catalyst can be prepared depending on the rhodium salt, catalyst support, and impregnation technique employed. A very effective carbonylation catalyst was prepared by depositing a "preformed" active catalyst solution containing the rhodium and iodide components (*2*) on a BPL carbon support. This form of the heterogeneous catalyst was employed in our studies because it represented a form highly analogous to the liquid phase catalyst system. During the liquid phase kinetic investigation, an investigation of the reaction order relative to all reactants as well as the rhodium complex was performed. However, it is difficult to establish well-defined variations in catalyst concentrations due to nonuniformities in the distribution of the active complex on the support, and hence only one low level rhodium concentration was employed (variation of all other reactants was included in the present kinetic study).

EXPERIMENTAL METHODS

Apparatus. Experiments were performed in an 18-in. stainless steel tubular reactor, 0.5 in. in diameter. The 18-in. long reactor holds a maximum catalyst charge (1% rhodium on BPL carbon) of 25 cm^3 and was positioned vertically in a heated fluidized sand bath. Reaction temperature was measured with an internal thermocouple located in the center of the catalyst bed and was regulated with a West time-proportioning temperature controller (Model JPY).

The reaction system is shown in Fig. 1. The gas stream (carbon monoxide) was metered with an automatic flow control system, consisting of an integral orifice differential pressure transmitter used in conjunction with a Foxboro flow controller and a Cash needle control valve. The liquid reaction mixture consisted of methanol, methyl iodide, and acetic acid and was fed to the reactor by means of a Lapp metering pump. To insure that all reactants are in the vapor phase before passing through the catalyst bed, the liquid feed was first passed through a small vaporizing tube submerged in the heated sand bath. After contacting the catalyst the gaseous reaction effluent exited from the bottom of the reactor where it was cooled in a 1-ft shell and tube water condenser. The gas was subsequently chilled to approximately 5°C in a product separator to remove all volatile reaction products by condensation. Both the liquid reaction mixture and effluent gases were continuously withdrawn from the product separator for analysis. The gas flow was measured with a dry gas meter while the liquid was collected in a glass flask.

Reactor operating procedure. The same catalyst charge was used for all of the reaction kinetic experiments discussed. The reaction system was normally started up by adjusting and maintaining the reactor to the desired set of conditions of temperature, carbon monoxide pressure, and flow rate for 1 hr. The methanol feed mixture was then introduced to the reactor by pumping the liquid into a vaporizing tube submerged in the heated sand bath and

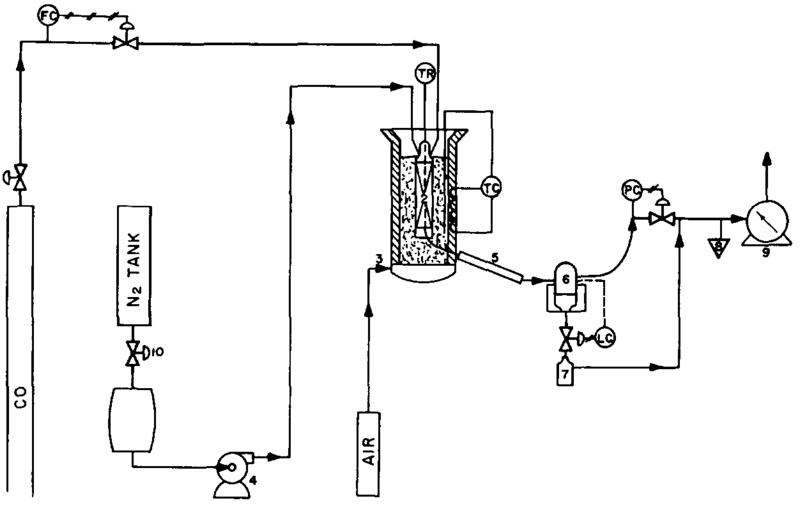


FIG. 1. Reactor system: (1) high pressure regulator; (2) fixed bed reactor; (3) fluidized sand bath; (4) metering pump; (5) water-cooled condenser; (6) product separator; (7) product collector; (8) sampling point; (9) wet test meter; and (10) low pressure regulator.

then into the top of the reactor. To obtain representative samples of the reaction mixture from the product separator, the liquid contents were dumped twice before taking an analytical sample. Reaction variables were then changed and 1 hr was allowed for the system to reach the new "steady-state" conditions.

Analysis. A quantitative analysis of the reaction products was carried out on a Wilkens Aerograph 204B gas chromatograph using a flame ionization detector and a 10-ft × 1/8 in. stainless steel column packed with Porapak Q. After injection of the sample, the column was programmed from 50° to 175°C at 4°C/min. Calibration curves based upon weight percent were made from solutions of known concentrations using the internal standard method (internal standard 3-pentanone). Samples of synthetic reaction mixtures were prepared by syringing the different components through a septum into a clean dry tared vial. These were then weighed to give an accurate measurement for each component present. Peak areas were determined by an Infotronics electronic integrator (Model CRS-10HB) with automatic base line drift corrector.

Materials. The rhodium salt used to prepare the active catalyst solution, $RhCl_3 \cdot 3H_2O$ (40% rhodium content by assay), was obtained from Engelhard Industries, Newark, NJ. Methyl iodide, hydrogen iodide, methanol, and acetic acid were obtained from Mallinkrodt Co. and were used as received. CP grade carbon monoxide from Matheson Co. was used in the carbonylation reaction. The carbon support was BPL grade activated carbon (12 × 30 mesh rescreened to 20 × 30 mesh), Lot 171 obtained from Pittsburgh Activated Carbon Co., Pittsburgh, PA.

Catalyst and reagent preparation. The solid catalyst system was prepared by impregnating the support with a "preformed" catalyst solution normally employed in the liquid phase carbonylation system.

Preparation of "preformed" liquid phase catalyst solution. A stock solution was prepared in the following manner. To a solution containing 240 ml distilled water and 152 ml glacial acetic acid, 3.6 g of $RhCl_3 \cdot 3H_2O$ was added. Prior to and during addition and dissolution of the rhodium salt, a constant carbon monoxide purge was maintained by bubbling the gas through the solution while the ingredients were stirred with a magnetic stirring bar.

After addition of the rhodium salt, the stirred reaction mixture was heated and maintained at 80°C using an electronic temperature controller. Stirring and heating were maintained overnight (~17 hr). The solution turned a bright lemon yellow color. The solution was cooled to room temperature and then 8 ml of 57 wt % aqueous HI was added dropwise (the flask was kept under a constant carbon monoxide atmosphere during the addition of HI) while stirring was maintained. Upon addition of the HI, the solution turned a reddish brown color. The "preformed" catalyst stock solution was divided into several portions for impregnation on various supports and testing.

Impregnation procedure. To 50 cm^3 of 20 × 30 mesh activated carbon (BPL) was added 35 ml of a catalyst solution prepared from the following:

40 ml acetic acid,
65 ml distilled water, and
65 ml "preformed" catalyst stock solution described above.

The mixture was swirled several minutes to insure good solid–liquid contacting and then the solvent was evaporated by a vacuum flash. A Rinco evaporator was employed to flash the solvent using a water aspirator vacuum and a water bath maintained at 70°C.

The resulting "dry" catalyst composition was placed in a vacuum oven (under "house" vacuum at 65°C) overnight to complete removal of volatile solvent components.

The calculated rhodium content of the solid catalyst was 1 wt % rhodium, and the atomic ratio of iodine/rhodium was 4.

RESULTS AND DISCUSSION

Preliminary investigations. Several potentially troublesome areas of data interpretation were investigated initially to insure that the rate data obtained would truly represent the reaction kinetics. These areas were (1) catalyst life, (2) control of reaction temperature, and (3) the question of mass transfer control.

The long term activity of the catalyst was determined by evaluating a set of base operating conditions and periodically reevaluating these conditions during the kinetic study. Any decline in catalyst activity could be detected by comparing the methanol conversion at any given time to the original conversion with fresh catalyst.

The following base operating conditions were selected for the kinetic study:

Catalyst	1 wt % rhodium on 20 to 30 mesh BPL carbon
Catalyst charge	25 cm^3
Temp	208°C
Total pressure	16 atm
Feed composition of:	
Carbon monoxide	80.6 mole %
Methanol	9.3 mole %
Methyl iodide	0.8 mole %
Acetic acid	9.3 mole %
Space time (cm^3 catalyst/cm^3 of feed/sec)	11.75 sec
Particle Reynolds no. ($\rho u D_p/\mu$)	3

where ρ is the gas density, u is the gas velocity, D_p is the particle diameter, and μ is the gas viscosity.

At the base conditions, methanol conversion was 64% for fresh catalyst. Conversion is defined as the number of moles of acetic acid formed (present as the acid and/or methyl acetate) per mole of methanol fed to the reactor. Base conditions were reproduced several times during the study. Methanol conversion remained constant for over 1000 hr, demonstrating no loss in catalyst activity. (The catalyst was under actual reaction conditions about one-third of this time.)

The methanol carbonylation reaction is an exothermic reaction. In order to minimize temperature variations in the reactor it was necessary to perform a number of experiments at different levels of methanol conversion to establish reactor conditions for isothermal operation.

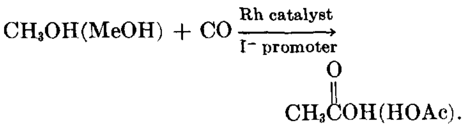
Experimentally, two typical temperature profiles along the catalyst bed at high and low levels of reaction heat generation were obtained, i.e., 16.4 and 4.8 kcal/hr, respectively. The results indicated that for the temperature control scheme employed (fluidized sand bath with electrical heating) isothermal conditions existed if the exothermic reaction heat was kept less than about 5 kcal/hr. To maintain a heat generation level of less than about 5 kcal/hr, the quantity of methanol converted was kept below 0.2 mole/hr by addition of acetic acid diluent in the feed and also by low rhodium catalyst loadings.

The dilution technique basically consisted of mixing equimolar quantities of methanol and acetic acid prior to addition of the iodine promoter as methyl iodide. After adding the desired amount of promoter, the feed mixture was introduced into the reactor in the normal manner.

The operating conditions were also checked to verify that the reaction was not controlled by external mass transfer. The standard diagnostic technique of doubling both the catalyst charge and total reactor feed rate was employed. By doing this the bulk stream velocity changes while space time (or catalyst contact time) remains constant. According to work by Petrovic and Thodos (*5*) the conversion should increase by about 12.3% relative when flow is doubled (exponent of Reynolds no. is −0.359) if the reaction is controlled by external mass transfer. Experimental data showed that by doubling the velocity (Reynolds no. increased from 2.95 to 5.90) while holding space time constant the methanol conversion remained constant at 34%. This result demonstrates that the carbonylation reaction was performed under kinetically controlled conditions. As further verification a calculational check was performed using the method of Hougen (*6*) which indicated that the reaction rate is slow enough to eliminate the possibility of external mass transfer resistance.

No studies were conducted experimentally to check on intraparticle diffusion. This would have involved screening several different particle sizes to determine the influence of catalyst pore diffusion on reaction rate. However, it is believed that at the slow reaction rates used to avoid "hot spots" and the small particle size of catalyst employed, intraparticle diffusion should not be significant.

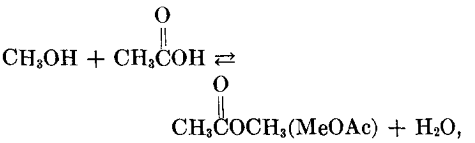
Determination of the reaction kinetics. The synthesis of acetic acid may be represented stoichiometrically by Eq. (1).



$$CH_3OH(MeOH) + CO \xrightarrow[I^- \text{ promoter}]{\text{Rh catalyst}} CH_3\overset{\overset{\large O}{\|}}{C}OH(HOAc). \quad (1)$$

However, at less than 100% methanol conversion to acetic acid, the synthesis reaction system is accompanied by several other known complex equilibrium reactions.

$$2CH_3OH \rightleftarrows CH_3OCH_3(DME) + H_2O, \quad (2)$$



$$CH_3OH + CH_3\overset{\overset{\large O}{\|}}{C}OH \rightleftarrows CH_3\overset{\overset{\large O}{\|}}{C}OCH_3(MeOAc) + H_2O, \quad (3)$$

$$CH_3OH + HI(aq) \rightleftarrows CH_3I(MeI) + H_2O. \quad (4)$$

It has been observed experimentally that the methyl iodide equilibrium reaction is extremely in favor of methyl iodide in the vapor phase reactions. At the methanol conversion levels studied, therefore, methyl iodide concentration should remain essentially constant in the reactor at the initial feed concentration. Although it was not possible to experimentally confirm whether the same amount of methyl iodide enters and leaves the reactor at any time (due to its high volatility) the assumption of constant methyl iodide pressure through the reactor is reasonable.

Since methyl iodide concentration in any run is assumed to be constant and no methyl acetate or dimethyl ether are in the reactor feed, reaction rate (or conversion) can be defined in terms of the number of moles of methanol feed converted to acetic acid or methyl acetate. The conversion data is based upon analysis of the reactor effluent. The reaction rate may be expressed in power law form. The relationship between the rate and concentration of reactants is given by Eq. (5).

$$r_A = k p_M{}^r p_{MI}{}^s p_{CO}{}^t, \quad (5)$$

where r_A	number of moles of methanol converted/sec cm^3 of catalyst,
k	reaction rate constant, (moles/atm)$^{r+s+t}$ sec cm^3 of catalyst,
p_i	partial pressure of species i (atm) and
r, s, t	reaction order for methanol, methyl iodide, and carbon monoxide, respectively.

Assuming that plug flow exists in the tubular reactor (i.e., with little or no backmixing of the flowing gas stream) the reaction rate expression can be combined with the flow "in" and "out" to yield a material balance equation on acetic acid across the tubular reactor (i.e., acid out − acid in = acid formed by reaction). This equation in integral form is as follows:

$$\Theta = C_{M_0} \int \frac{dx}{r_A} = C_{M_0} \int \frac{dx}{k p_M{}^r p_{MI}{}^s p_{CO}{}^t}, \quad (6)$$

where C_{M_0}	feed concentration of methanol, (moles/cm^3 of feed)
Θ	reactor space time (cm^3 catalyst/cm^3 of feed/sec) and
x	fractional conversion (moles methanol converted/moles methanol fed)

Note that reactor space time is not the actual time the reactants remain in the reactor but is directly proportional to catalyst contact time. Space time is a ratio of the volume of catalyst charged to the actual total feed rate and can be varied by changing either pressure or flow rate, or held constant by changing both simultaneously.

Since a large excess of carbon monoxide was used in this study, flow rate changes with conversion can be neglected. The concentration of methanol in the reactor can be expressed in terms of the feed methanol concentration by $p_M = p_{M_0}(1 - x)$ and Eq. (6) becomes

$$\int_0^x \frac{dx}{(1-x)^r[1-(p_M/p_{CO})_0 x]^t} = k'\Theta\left(\frac{p_{MI}}{p_M}\right)_0^s\left(\frac{p_{CO}}{p_M}\right)_0^t p_{M_0}{}^{r+s+t-1}, \quad (7)$$

where $k' = kRT$.

This equation relates conversion (integral term) to space time and feed partial pressures of carbon monoxide, methyl iodide, and methanol. Experimentally the reaction orders r, s, and t were determined by making systematic variations of reaction parameters and observing the effect on methanol conversion. The reaction parameters with the approximate range of variations are listed below.

Reaction variable	Range
Pressure	6–25 atm
Temperature	200°C
Reactor space time	3–14 cm^3 cat./cm^3 feed/sec
CO/methanol in feed	1.5–5.0
MeI/methanol in feed	0.04–0.09
Particle Reynolds no. ($\rho u D_p/\mu$)	3–6

The general reactor balance expression [Eq. (7)] was simplified for data interpretation by assuming various integral reaction orders and then substituting numerical values for the powers r, s, and t. For example, if it is assumed that the overall reaction order is 1 ($r + s + t = 1$) then the reactor material balance equation becomes

$$\int_0^x \frac{dx}{(1-x)^r[1-(p_M/p_{CO})x]^t} = k'\Theta\left(\frac{p_{MI}}{p_M}\right)_0^s\left(\frac{p_{CO}}{p_M}\right)_0^t. \quad (8)$$

Similarly an overall reaction order of zero ($r = s = t = 0$) gives the following simplified form of Eq. (6).

$$x = \frac{k'\Theta}{p_{M_0}}. \quad (9)$$

At a fixed feed composition and reactor space time, conversion for a zero-order reaction [Eq. (9)] will be inversely proportional to the total pressure (or methanol partial pressure in the feed). However, for first-order kinetics [Eq. (8)] conversion will be independent of total pressure. Similarly for an overall reaction order greater than 1 ($r + s + t > 1$) the conversion increases as the total pressure is increased. Because reactor space time is a function of both pressure and flow rate, it can only be maintained constant at various pressures by making corresponding changes in the flow rate (i.e., 25% pressure increase would require a 25% increase in flow rate). Runs 1, 2, and 3 in Table 1 show the results of varying the pressure at a fixed feed composition and reactor space time. The conversion was unchanged for a 50% increase in reactor pressure (note corresponding 50% increase in flow rate to hold space time constant). The constant value of conversion for this pressure change indicates that the reaction is overall first order ($r + s + t = 1$). As further verification it can be seen from Eq. (7) that conversion should be directly proportional to reactor space time regardless of the pressure if the conversion is small (less than 30%) and/or the coefficient r (reactor order of methanol) is near zero. In Run 8 the space time is approximately 75% of that in Runs 1 and 3, and the conversion decreases by an exactly proportional amount. This was accomplished by increasing the flow rate at a fixed pressure. Similarly, in Runs 4 and 8 space time was varied by holding flow rate constant and changing pressure (pressure in Run 8 is doubled to give twice the space time as Run 4). As predicted by Eq. (8)

TABLE 1
SUMMARY OF EXPERIMENTS

Run no.	Conversion (mole %)	Space time (cm^3 cat./cm^3 feed/sec)	Flow rate (moles/hr)	Total pressure (atm)	p_{M_0} (atm)	$(p_{MI}/p_M)_0'$	$(p_{CO}/p_M)_0'$
1^a	64.0	11.8	2.92	16.6	1.49	.084	8.65
2^a	62.3	11.8	4.38	23.9	2.23	.084	8.65
3^a	64.0	11.8	2.92	16.6	1.49	.084	8.65
4^a	24.2	4.6	3.62	7.8	0.81	.084	7.60
5^a	19.9	3.1	5.42	7.8	0.81	.084	7.60
6	21.4	4.7	3.59	7.8	1.57	.084	3.96
7	14.5	3.1	5.38	7.8	1.57	.084	3.96
8	50.1	9.8	3.59	16.3	3.28	.084	3.96
9	26.0	10.0	3.57	16.7	3.36	.042	3.96
10	10.1	4.7	3.57	7.8	1.57	.042	3.96
11	34.5	14.5	3.57	24.2	4.86	.042	3.96
12	26.6	10.0	3.57	16.7	6.62	.042	1.49
13	9.4	5.1	3.57	8.5	3.36	.042	1.49

^{a} Acetic acid used as a diluent in the feed stream.

the conversion in Run 8 is essentially twice that of Run 4 (50.1% vs 24.2%).

After establishing that the overall reaction is first order, it was necessary to determine the reaction orders with respect to various reagents or, more specifically, the values of r, s, and t. This was achieved experimentally by varying the ratios of methyl iodide and carbon monoxide to methanol in the feed stream and observing the changes in methanol conversion [see Eq. (7)]. The data of Table 1 show the effect of variation of ratio $(p_{MI}/p_M)_0$ and $(p_{CO}/p_M)_0$. As the ratio $(p_{MI}/p_M)_0$ was halved while all other reaction parameters were held constant (Runs 8 and 9) the decrease in conversion (50.1% to 26.0%) was exactly proportional to the change of this

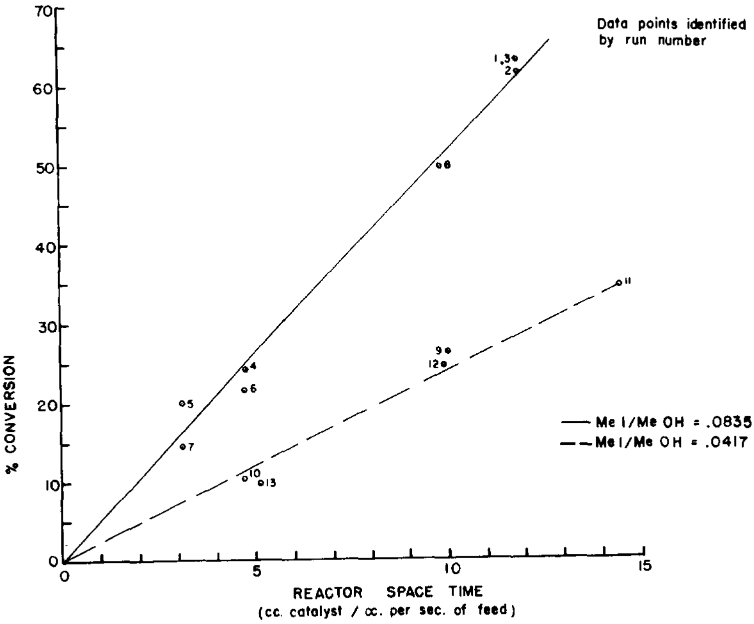


FIG. 2. Conversion as a function of reactor space time.

ratio. The carbon monoxide/methanol ratio $(p_{CO}/p_M)_0$ was almost tripled, with all other parameters held constant in Runs 9 and 12. No noticeable change in conversion occurred (26.0% vs 26.6%). These results demonstrate that reaction rate is directly proportional to methyl iodide concentration and independent of methanol and carbon monoxide (i.e., $s = 1$, $r = t = 0$). A plot of conversion versus reactor space time for the 13 runs listed in Table 1 can be correlated by two straight lines (Fig. 2).

The steeper line corresponding to the higher methyl iodide to methanol ratio $(p_{MI}/p_M)_0$ has exactly twice the slope of the line representing the lower methyl iodide to methanol ratio. The result again confirms the first-order dependence of reaction rate upon methyl iodide concentration.

Upon substituting the values for r, s, and t in the reaction rate expression [Eq. (5)] one obtains a similar kinetic expression to the one used previously to describe the reaction rate for the liquid phase rhodium-catalyzed reaction [i.e., the reaction is first order in iodide and is independent of methanol and carbon monoxide concentrations (*2*)]. This expression lacks only the term for dependence upon concentration of rhodium complex, [Rh], established during the liquid phase study.

$$r_A = kp_{MI}. \qquad (10)$$

The reactor material balance equation [Eq. (7)] simplifies to the form:

$$x = k'\Theta(p_{MI}/p_M)_0, \qquad (11)$$

where the fractional conversion of methanol is directly proportional to reactor space time and the ratio of methyl iodide to methanol in the feed. The value of the relative rate constant k' computed from the slope of the line in Fig. 2, is 0.59 (moles methanol converted/moles methanol fed) (cm^3 of feed/cm^3 of cat. sec).

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