JOURNAL OF CATALYSIS 31, 127-135 (1973)

Study on the Pulse Reaction Technique

IV. Pulse Reaction Kinetics Coupled with a Strongly Adsorbed Reactant

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Received April 26, 1972

Sometimes, a catalyst surface is covered by the reactant and the reaction rate appears to be of the zeroth-order with respect to the gas-phase concentration. A theoretical analysis of the pulse reaction kinetics of such a reaction has been made on the basis of a hypothetical isotherm consisting of two straight lines. The conversion in the pulse technique is always larger than that in the flow technique. The deviation from the flow technique decreases with a decrease in the catalyst volume, and the conversion becomes identical to that in the flow technique at a sufficiently small catalyst volume. The effect of the reciprocal flow rate is different from that of the catalyst volume, that is, the conversion at a sufficiently large flow rate is entirely different from that in the flow technique. The conversion significantly depends on the pulse width. It increases with a decrease in the pulse width, and becomes identical to that in the first-order reaction at a sufficiently small pulse width. It is noteworthy that the conversion is essentially independent of the initial concentration at a sufficiently small pulse width, because, sometimes, the conversion independent of the pulse size is regarded as an evidence of the first-order reaction.

INTRODUCTION

Adsorption characteristics play a great role in the pulse reaction, as can be seen from its similarity to the gas chromatographic column. The Landmuir isotherm is the most famous and the most frequently used in the kinetic interpretations of the heterogeneous catalytic reaction. In the Langmuir–Hinshelwood mechanism, although the order of the reaction rate is unity in the concentration on the catalyst surface, it is generally less than unity in the gas-phase concentration. When the adsorption equilibrium constant is sufficiently large, the overall reaction rate appears to be the zeroth-order in the gas-phase concentration, because the catalyst surface is fully covered by the reactant even at a significantly low partial pressure. In such a reaction, a distinct difference can be expected between the results obtained with the pulse technique and those with the flow technique. However, the quantitative relationship between the two techniques have not been clarified. Some workers have made theoretical analyses of the *n*-th order reaction and have applied the results to the zeroth-order reaction (*1*, *2*). Their results, however, cannot be applied to all cases, because they assumed the Henry isotherm in spite of the zeroth-order reaction. The Henry isotherm is valid only when the surface coverage is low enough, while the zeroth-order kinetics may be valid in the opposite case.

Bett and Hall (*3*) made a comparison between the pulse and the flow techniques for the dehydration of 2-butanol over hydroxyapatite catalysts. The reaction order was revealed by the flow technique to be zero in 2-butanol, but the reaction seems to be a different type of the zeroth-order reaction from that treated in the present paper. In the latter, it was assumed that the adsorption equilibrium is established between the adsorbed species and the gas-phase molecules, while their results indicate that the surface adsorbed species may not be in equilibrium with the gas-phase molecules. Such a reaction will be treated in a later paper in this series.

The authors made theoretical analyses of the pulse reaction kinetics with the Henry isotherm (*4*) and with the Langmuir isotherm of not too large adsorption equilibrium constant (*5*). It is possible to analyze the pulse reaction kinetics with the Langmuir isotherm of much larger adsorption equilibrium constant by a similar method with the aid of an electronic computer. However, the results may include considerable error due to the replacement of derivatives with the simplest difference representation, and the error appears to increase with increasing adsorption equilibrium constant.

In the present paper, a theoretical analysis is made on the pulse reaction kinetics with the Langmuir isotherm of much greater adsorption equilibrium constant on the basis of several assumptions.

NOMENCLATURE

C	Concentration of reactant in gas phase (mol/cm^3 of bed)
C_s	Critical concentration defined by Fig. 1 (mol/cm^3 of bed)
C_0	Concentration of inlet pulse (mol/cm^3 of bed)
F	Flow rate of carrier gas (cm^3/sec)
k	Reaction rate constant (1/sec)
K	Adsorption equilibrium constant
L	Length of catalyst bed (cm)
M_A, M_B	Amount of A and B pulse (mol)
q	Concentration of adsorbed reactant (mol/cm^3 of bed)
q_s	Concentration of adsorbed reactant at full coverage (mol/cm^3 of bed)
t	Time since pulse is introduced (sec)
t_0	Pulse width of inlet pulse (sec)
t_d	Width of disappeared part of A pulse (sec)
t_f, t_b, t_e	Time when the front, the boundary, and the end of pulse arrive at z (sec)
u	Moving velocity of carrier gas (cm/sec)
u_f	Moving velocity of the front of the pulse (cm/sec)
V	Volume of catalyst (cm^3)
X	Conversion
z	Distance from the inlet (cm)
β	C_0/C_s
θ	z/u (sec)
Ω	Pulse size; FC_0t_0 (mol)

THEORETICAL ANALYSIS

Basic Equation

An analysis was made on the basis of the following assumptions: The first is that the substance in the gas phase moves as a plug flow of the linear velocity of u together with the carrier gas. The second is that the influence of the mass transfer onto the catalyst surface is negligible. The last assumption is that of a hypothetical isotherm. The concentration on the catalyst surface increases with the partial pressure, but in such a case as the langmuir isotherm, the surface is completely covered at a high pressure and the concentration on the surface does not increase anymore. By dividing the Langmuir isotherm into the increasing region and the saturated region, and by replacing each of them by a straight line, one gets the hypothetical isotherm shown in Fig. 1. The concentration on the surface linearly increases with the concentration in the gas-

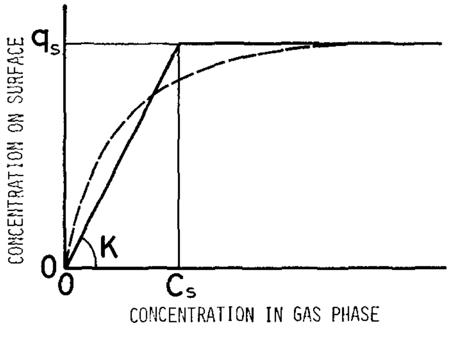

FIG. 1. Hypothetical isotherm.

phase, till the surface is completely covered. And it takes constant value independently of the gas-phase concentration at a larger concentration than the critical concentration. This assumption may result in some error, however, the tendency of the results may remain unchanged and the error may become small when the adsorption equilibrium constant is large enough.

The basic equation expressing the mass balance is given as follows:

$$\frac{\partial q}{\partial t} + \frac{\partial C}{\partial t} = -u\frac{\partial C}{\partial z} - kq, \quad (1)$$

$$q = q_s \quad \text{when} \quad C \geq C_s, \quad (2)$$

$$q = KC \quad \text{when} \quad C < C_s. \quad (3)$$

The initial condition is given as follows, because no substances are present before the introduction of the pulse.

$$C = q = 0 \quad \text{when} \quad t = 0. \quad (4)$$

When the reactant pulse is a rectangular one with the concentration of C_0 and the width of t_0, the boundary condition is given as follows:

$$C = C_0 \quad \text{when} \quad 0 \leq t \leq t_0, \quad (5)$$

$$\text{and} \quad C = 0 \quad \text{when} \quad t > t_0. \quad (6)$$

Chromatogram without Reaction

First of all, an analysis was made on the chromatographic column where no chemical reactions take place, that is, $k = 0$ in Eq. (1). According to the isotherm in Fig. 1, after the front of the pulse passes, the surface is completely covered, or, in other words, Eq. (2) holds. By substituting Eq. (2) into Eq. (1), the following equation is obtained, because $\partial q/\partial t = 0$:

$$\frac{\partial C}{\partial t} = -u\frac{\partial C}{\partial z}. \quad (7)$$

Equation (7) indicates that the pulse moves through the column with the moving velocity of u, and that the shape of the pulse does not change except at both ends of the pulse. After the main pulse termed "A" in Fig. 2 passes through, the adsorbed molecules desorb to form the tailing part termed "B." In the tailing part, Eq. (3) holds, and therefore the concentration in the gas-phase is C_s which is in equilibrium with q_s. Equation (1) is reduced to the following equation by substituting Eq. (3) into Eq. (1):

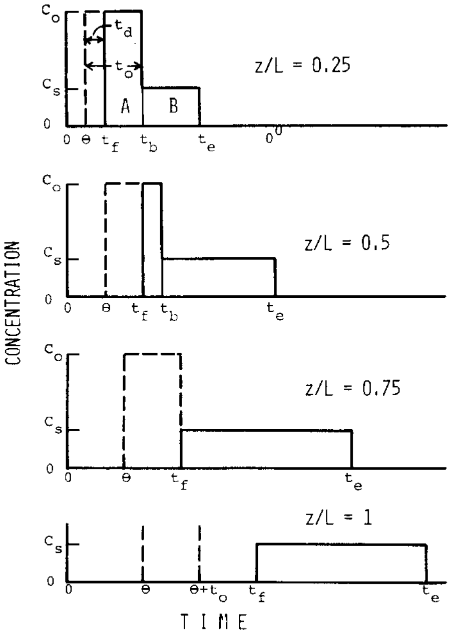

FIG. 2. Chromatogram without reaction. (--) The inlet pulse. $\beta = 3$, $t_0/K\theta = 0.25$.

$$\frac{\partial C}{\partial t} = -\frac{u}{1+K}\frac{\partial C}{\partial z}. \quad (8)$$

This equation also indicates that the shape of the pulse does not change, but the moving velocity is $u/(1 + K)$ and is less than that of the A pulse. Therefore the A pulse goes away from the B pulse which arises near the top of the catalyst bed, and in a space between them a new B pulse arises from the A pulse. In such a way, the width of the B pulse increases with the passage through the column, as shown in Fig. 2. The moving velocity of the boundary between the A pulse and the B pulse is identical to u. Therefore the time when the boundary reaches the position at distance z from the inlet is given as follows:

$$t_b = t_0 + \theta \quad (9)$$

The end of the pulse moves with the velocity of $u/(1 + K)$, therefore the time when the end reaches z is:

$$t_e = t_0 + (1 + K)\theta. \tag{10}$$

The movement of the front of the pulse is considerably complicated. According to the above-mentioned isotherm, the molecules which come in contact with the fresh surface are all adsorbed. Therefore, the molecules at the front of the pulse are all adsorbed, or, in other words, the width of the A pulse decreases with the passage through the column, as shown in Fig. 2. By defining dt_d as an increment of the width of the disappeared part necessary to cover the catalyst surface in an increment of the catalyst bed length, dz, the following equation is obtained:

$$q_s dz = uCdt_d. \tag{11}$$

The left side represents the amount of the adsorbed reactant and the right side represents the amount of the disappeared part of the pulse. The width of the disappeared part, t_d, is obtained by integrating Eq. (11).

$$t_d = \frac{q_s}{C_0}\theta. \tag{12}$$

This equation indicates that the width of the disappeared part increases with the passage through the column, or with an increase in z, as shown in Fig. 2. If the disappeared part is negligible, the front of the pulse reaches z at the time identical to the contact time, θ. Therefore in the present case, the front of the pulse reaches z at t_d after θ. Then the time when the front of the pulse reaches z is given as follows:

$$t_f = \left(1 + \frac{q_s}{C_0}\right)\theta. \tag{13}$$

In other words, the moving velocity of the front, u_f, is:

$$u_f = \frac{dz}{dt_f} = \frac{u}{1 + (q_s/C_0)}. \tag{14}$$

Equation (14) can be obtained also in the following way. The moving velocity of the molecules in the column is represented by the following equation (*6*):

$$u_i = \frac{u}{1 + (dq/dC)}, \tag{15}$$

and at the discontinuity of the concentration, the differentiation can be represented as follows (*6*):

$$\frac{dq}{dC} = \frac{q_+ - q_-}{C_+ - C_-}, \tag{16}$$

where subscripts + and − denote just before and just after the discontinuity. Just before the front of the pulse, the concentrations in the gas phase, C_+, and on the surface, q_+, are zero, and just after that, the concentrations, C_- and q_-, are C_0 and q_s, respectively. By substituting these relations into Eqs. (15) and (16), Eq. (14) can be obtained. The moving velocity of the boundary and the end can be derived also from Eqs. (15) and (16), and the results completely agree with those mentioned above.

Figure 2 shows the chromatogram at various position in the column obtained from Eqs. (9), (10), and (13). The width of the B pulse increases with the passage through the column, as mentioned above. On the other hand, the width of the A pulse decreases, because the moving velocity of the front given by Eq. (14) is less than that of the boundary, u. And, therefore, the A pulse disappears when $t_f = t_b$. After that, only the B pulse remains in the column, and it moves without any deformation of the shape of the pulse.

Derivation of Conversion

In the chromatographic reactor where the zeroth-order reaction takes place, the movement of the pulse is almost identical to that mentioned above except for the concentration change due to the reaction, as shown in Fig. 3. t_b and t_e, i.e., the time when the boundary and the end of the pulse reaches the position at distance z from the inlet of the catalyst bed, are the same as those given by Eqs. (9) and (10). On the other hand, t_f is different from that given by Eq. (13), because it depends on the concentration in the gas phase, as can be seen from Eq. (11).

The equation expressing the mass balance in the A pulse is obtained by substituting Eq. (2) into Eq. (1):

$$\frac{\partial C}{\partial t} = -u \cdot \frac{\partial C}{\partial z} - k \cdot q_s. \tag{17}$$

The solution of Eq. (17) indicates that the concentration decreases according to the same rate expression as in the flow technique.

$$C = C_0 - kq_s\theta. \tag{18}$$

In the pulse technique, Eq. (18) holds in the A pulse, that is, when $t_f \leq t \leq t_b$. By substituting Eq. (18) into Eq. (11), and by integrating the equation thus obtained, the equation for t_f can be obtained.

$$t_f = \theta + \frac{1}{k} \ln \frac{1}{1 - (kK\theta/\beta)}. \tag{19}$$

The total amount of the A pulse passing through z, M_A, is obtained by integrating the product of the concentration and the flow rate from t_f to t_b.

$$M_A = FC_0t_0\left(1 - \frac{kK\theta}{\beta}\right) \times \left(1 - \frac{1}{kt_0} \ln \frac{1}{1 - (kK\theta/\beta)}\right). \tag{20}$$

Just after the A pulse passes through, the B pulse arises from the A pulse. Now we consider the B pulse which arises at z_1. The time, t_1, when the B pulse reaches z is given as follows, because the boundary passes through z_1 at $t_0 + (z_1/u)$ and it takes $(z - z_1)(1 + K)/u$ for the B pulse to move from z_1 to z.

$$t_1 = t_0 + \frac{z_1}{u} + \frac{(1 + K)(z - z_1)}{u}. \tag{21}$$

The concentration of the B pulse at z_1 is C_s, and it decreases with the passage through the catalyst bed according to the first order kinetics, as can be seen from Eqs. (1) and (3). Therefore the concentration at z is given as follows:

$$C = C_s \exp\left(-kK\frac{z - z_1}{u}\right). \tag{22}$$

By substituting Eq. (21) into Eq. (22), and by integrating it from t_b to t_e, one gets the total amount of the B pulse, M_B.

$$M_B = \int_{t_b}^{t_e} FCdt_1 = F\frac{C_s}{k}(1 - e^{-kK\theta}). \tag{23}$$

The conversion is given as follows, because the total amount of the reactant passing through z is given by Eqs. (20) and (23), and because the amount of the inlet pulse is equal to FC_0t_0.

$$X = \frac{kK\theta}{\beta} + \frac{1}{kt_0}\left[\left(1 - \frac{kK\theta}{\beta}\right) \times \ln \frac{1}{1 - (kK\theta/\beta)} - \frac{1}{\beta}(1 - e^{-kK\theta})\right]. \tag{24}$$

It is noteworthy that this equation holds only when the A pulse still remains. The A pulse, where the reaction proceeds according to the zeroth-order reaction kinetics, disappears for two reasons: the disappearance of the pulse width because $t_f = t_b$, and the lowering concentration to less than C_s. Therefore Eq. (24) holds when $t_f < t_b$ and $C > C_s$, or, in other words, when $kK\theta < \beta(1 - e^{-kt_0})$ and $kK\theta < \beta - 1$.

As mentioned above, the moving velocity of the boundary between the A pulse and the B pulse is larger than that of the front of the pulse. Therefore, the

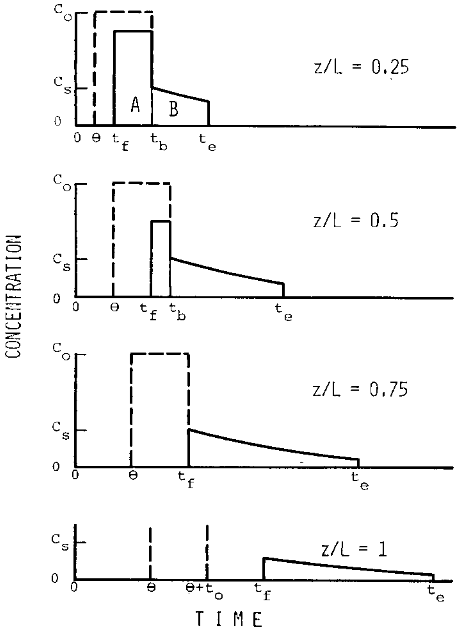

Fig. 3. Chromatogram with reaction. (- -) The inlet pulse. $\beta = 3$, $t_0/K\theta = 0.25$, $kK\theta = 2$.

width of the A pulse decreases as it passes through the catalyst bed, as can be seen from Fig. 3. If the catalyst bed is long enough, the width of the A pulse becomes zero somewhere. Terming that position z_2, one gets the following relation from Eqs. (9) and (19) because $t_f = t_b$.

$$kK\frac{z_2}{u} = \beta(1 - e^{-kt_0}). \tag{25}$$

The total amount of the B pulse passing through z_2 is obtained by substituting Eq. (25) into Eq. (23). After z_2, the concentration of the B pulse decreases according to the first-order kinetics. Therefore the conversion is given as follows:

$$X = 1 - \frac{e^{-kK\theta}}{kt_0\beta}[\exp\{\beta(1 - e^{-kt_0})\} - 1]. \tag{26}$$

This equation holds only when $t_b < t_f$ and $C_0 - kq_sz_2/u > C_s$, or when $kK\theta > \beta(1 - e^{-kt_0})$ and $\ln\beta > kt_0$.

With a decrease in the concentration, the reaction rate turns into the first-order one; this change corresponds to the transition of the isotherm in Fig. 1 from the saturated region to the proportional region. At that turning point, termed z_3, the following relations are given. From Eq. (18),

$$kK\frac{z_3}{u} = \beta - 1. \tag{27}$$

As the concentration of the A pulse at z_3 is equal to C_s, the amount of the A pulse is given as follows:

$$M_A = FC_st_0\left[1 - \frac{1}{kt_0}\ln\frac{\beta}{\beta - kK(z_3/u)}\right]. \tag{28}$$

The amount of the B pulse is obtained from Eq. (23):

$$M_B = F\frac{C_s}{k}[1 - \exp(-kKz_3/u)]. \tag{29}$$

After passing through z_3, the concentration of the A pulse and the B pulse decreases according to the first order kinetics. Therefore the conversion is given as follows:

$$X = 1 - \frac{e^{-(kK\theta+1-\beta)}}{kt_0\beta} \times (1 + kt_0 - \ln\beta - e^{1-\beta}). \tag{30}$$

This equation holds only when $C_0 - kq_s\theta < C_s$ and $t_b > t_f$ at z_3, or when $kK\theta > \beta - 1$ and $\ln\beta < kt_0$. Equation (30), however, is quite specious. Because, as mentioned above the present case corresponds to the transition from the saturated region to the proportional region in the hypothetical isotherm shown in Fig. 1, and it means that the initial concentration is only slightly larger than the critical concentration, C_s. Under such a condition, the hypothetical isotherm should not be used.

RESULTS AND DISCUSSION

Conversion vs Contact Time

Figure 4 shows the relation of the conversion to the contact time. In Fig. 4, the upper broken line represents the relation in the first-order reaction, and the lower one gives that in the zeroth-order reaction in the flow technique. The conversion in the pulse technique lies between the two broken lines. The conversion obtained with the large pulse width is close to that in the

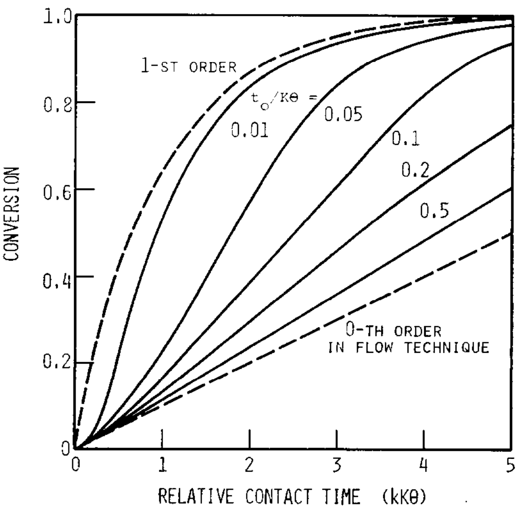

FIG. 4. Relation of the conversion to the contact time, when the contact time is varied by the catalyst volume. $\beta = 10$.

flow technique, and it increases with a decrease in the pulse width, but it can not exceed that of the first-order reaction by the upper broken line. Detailed examination of the figure indicates that the difference from the flow technique is small even at a sufficiently small pulse width when the contact time is sufficiently small. The difference in the results between the pulse and the flow techniques is caused by the following factors (*4*): the chromatographic separation between the components, the lowering of the concentration due to the broadening of the pulse, and the difference in the initial concentration. The last factor can be corrected easily (*2*, *4*), while the first and the second factors cannot be corrected easily. In the present case, the difference between the techniques is caused by the second factor. As mentioned above, the molecules at the front of the A pulse are all adsorbed. And after the A pulse passes through, the adsorbed molecules desorb to form the B pulse. The width of the B pulse is larger than that of the disappeared part of the A pulse. Therefore, the average concentration in the whole pulse is lower than that in the flow technique; this, roughly speaking, results in the larger conversion than that in the flow technique. It follows that the difference between the two techniques increases with the amount of the adsorbed molecules, or, in other words, with the adsorption capacity of the catalyst. If the amount of the catalyst is small enough, the difference between the techniques can be expected to be negligible.

In order to confirm the above expectation, the conversion at a sufficiently small contact time has been derived using the Taylor series:

$$X = X_0 + \theta\left(\frac{dX}{d\theta}\right)_0, \qquad (31)$$

where the subscript 0 denotes that $\theta = 0$. By substituting Eq. (24) into Eq. (31), one gets the equation for the conversion at a sufficiently small contact time.

$$X = \frac{kK\theta}{\beta}. \qquad (32)$$

This equation is exactly the same as that for the steady state flow technique. It follows that the reaction rate can be measured by the pulse technique, if only the amount of the catalyst is small enough.

One should note that the above-mentioned discussion holds when the initial concentration and the pulse width are independent of the contact time. The contact time can be varied not only by the catalyst volume but also by the flow rate of the carrier gas. In the latter, the initial concentration and the pulse width must depend on the flow rate, but in the former they are independent of the catalyst volume. It follows that the above-mentioned discussion is applicable when the contact time is varied by the catalyst volume at a constant flow rate of the carrier gas.

The general relation of the conversion to the flow rate can hardly be obtained, because the effect of the flow rate on the initial concentration and the pulse width is not obvious. However, the relation can be obtained in the following case: the contact time is varied by the flow rate at a constant catalyst volume, and the reactant pulse is introduced into the carrier gas stream by the aid of a six-port valve. The reactant pulse in the sampling part of the six-port valve may be considered to be transported to the reactor without mixing with the carrier gas. Therefore the initial concentration at the inlet of the catalyst bed is identical to that in the sampling part, and so it can be regarded as constant. On the other hand, the pulse width can be regarded as in inverse proportion to the flow rate. Taking these relations into consideration, the relation of the conversion to the flow rate can be obtained from Eq. (24).

$$X = \frac{kK\theta}{\beta} + \frac{\beta}{kK\theta}\frac{q_s V}{\Omega}\left[\left(1 - \frac{kK\theta}{\beta}\right) \times \ln\frac{1}{1-(kK\theta/\beta)} - \frac{1}{\beta}\left(1 - e^{-kK\theta}\right)\right], \qquad (33)$$

where V is the volume of the catalyst bed, and the Ω is the pulse size and is equal to FC_0t_0. Equation (33) holds only in the following case.

$$\frac{\Omega}{q_sV} > \frac{\beta}{kK\theta}\ln\frac{1}{1-(kK\theta/\beta)}. \quad (34)$$

In the case where the inequality does not hold, i.e., where the A pulse disappears, the following equation holds.

$$X = 1 - \frac{e^{-kK\theta}}{kK\theta}\frac{q_sV}{\beta}\left[\exp\left\{\beta\left[1-\exp\left(-\frac{kK\theta}{\beta}\frac{\Omega}{q_sV}\right)\right]\right\}-1\right]. \quad (35)$$

Figure 5 represents the relation of the conversion to the contact time when the contact time is varied by the flow rate of the carrier gas and the pulse is introduced by the aid of the six-port valve. The relation is very similar to that in Fig. 4. The conversion lies between that in the first-order reaction and that in the flow technique, and it increases with a decrease in the pulse size. However, the relation at a sufficiently small contact time is quite different from that in Fig. 4. The difference from the flow technique is significant, and the conversion at a sufficiently small pulse size is close to that in the first-order reaction, even when the contact time is sufficiently small. The equation for the conversion at a sufficiently small contact time can be obtained by substituting Eq. (33) into Eq. (31).

$$X = kK\theta\left(\frac{1}{\beta} - \frac{q_sV}{2\beta\Omega} + \frac{\Omega}{2q_sV}\right). \quad (36)$$

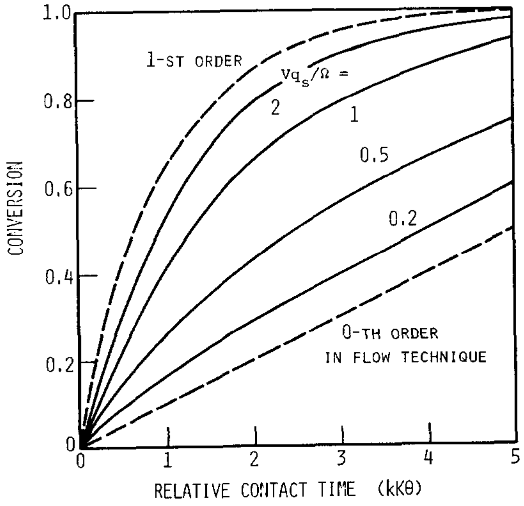

Fig. 5. Relation of the conversion to the contact time, when the contact time is varied by the flow rate of the carrier gas. $\beta = 10$.

And the equation for the small pulse size is obtained from Eq. (35).

$$X = kK\theta\left(1 + \frac{\Omega}{2q_sV\beta} - \frac{\Omega}{2q_sV}\right). \quad (37)$$

As can be seen from Eqs. (36) and (37), the conversion is quite different from that in the flow technique. As mentioned above, the difference from the flow technique increases with the adsorption capacity of the catalyst bed. The adsorption capacity in the present case is finite even at a sufficiently small contact time, because the contact time is reduced by increasing the flow rate at a finite catalyst volume. Therefore the difference can not be reduced by decreasing the contact time in the present case.

After all, it is necessary to reduce the catalyst volume in order to obtain the same conversion as that in the flow technique.

Effect of Initial Concentration

Figure 6 shows the relation of the integrated reaction rate or, in other words, the amount of the converted reactant, βX, to the initial concentration, β. The lower broken line again represents the relation in the flow technique. The qualitative relation in the pulse technique is similar to that in the flow technique, but the quantitative relation in the two techniques is essentially different from one another. The integrated reaction rate increases with the initial concentration, and then it becomes constant. This tendency is quite similar to that of the flow technique, but the value of the reaction rate is entirely different from that of the flow technique. It follows that although the relation obtained with the pulse technique may coincide with a usual rate law, such as the linear relation of $1/r$ to $1/p$ for the Langmuir–Hinshelwood mechanism, the calculated value of the rate parameter may be entirely differ-

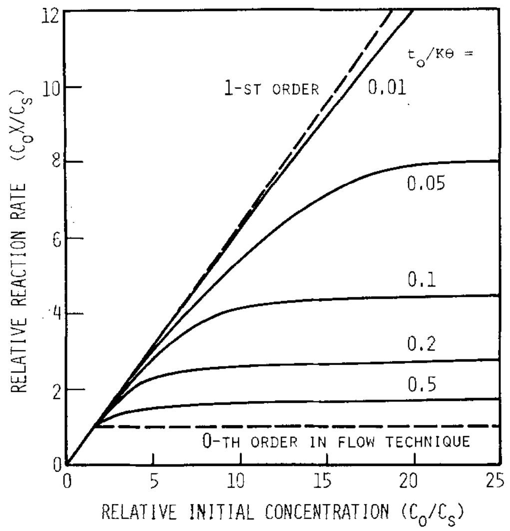

FIG. 6. Effect of the initial concentration on the reaction rate. $kK\theta = 1$.

ent from the true value. Blanton, Byers, and Merill (*7*) attempted to measure the rate parameters of the nonlinear reactions by the pulse technique. They avoided the above-mentioned problem by using significantly long pulse. As can be seen from Fig. 6, with an increase in the pulse width the results of the pulse technique get nearer to that in the flow technique, which suggests that their attempt is correct in principle. Generally speaking, it is necessary to confirm whether a much longer pulse affects the reaction rate or not.

Effect of Pulse Width

In most of the reactions studied in the present series, the effect of the pulse width is quite large. When the pulse width is large enough, the result obtained with the pulse technique is close to that obtained with the flow technique. With a decrease in the pulse width, it gets nearer to that in an extreme case. The extreme case in some reversible reactions is the irreversible reaction (*4*), and it in the reaction with the Langmuir isotherm is the first-order reaction (*5*). As can be seen from Figs. 4 and 6, the extreme case in the present case also is the first-order reaction. It is noteworthy that the result with a smaller pulse width is similar to that in the first-order reaction. Sometimes it has been regarded as an evidence of the first-order reaction that the conversion is independent of the pulse size. Figure 6 shows, however, that the conversion even in the zeroth-order reaction sometimes does not depend on the initial concentration. Such a result is caused by the disappearance of the A pulse at the top of the catalyst bed. The A pulse disappears when $t_f = t_b$, or when $C \leq C_s$, as mentioned above. Although the latter is quite specious, the former is peculiar to the pulse technique and indicates a typical difference between the pulse and the flow techniques. The width of the A pulse decreases as it passes through the bed, because, as mentioned above, the boundary between the A and B pulses moves faster than the front of the pulse. Therefore, if the catalyst bed is long enough, the width of the A pulse becomes zero somewhere. When the pulse width is small enough, the A pulse disappears near the top of the catalyst bed, and only the B pulse, where the reaction order is unity, stays in the catalyst bed. After that, the reaction proceeds in accordance with the first-order reaction kinetics. It follows that the result in the pulse technique may sometimes be quite similar to that in the first-order reaction.

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