# Rate Constants of Elementary Steps by Pulse Technique

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Two methods for measuring the rate constants of the elementary steps by the pulse technique are proposed. The first gives the adsorption and the desorption rate constants from the retention time and the half width of the chromatographic peak, and was applied to the adsorption of benzene on HY and CaY zeolites. The second gives the surface reaction rate constant and the desorption rate constant of the reactant from the peak of the product which is not adsorbed on the catalyst surface. The method was applied to the cracking of cumene on HY and CaY.

ne application of the pulse reaction technique is One application of the pulse reasons the catalytic activity as an alternative for the continuous flow technique. Another and more important application is to obtain further information which cannot be obtained from the flow technique. It is well known that a catalytic reaction consists of several elementary steps, such as adsorption, surface reaction, and desorption. It must be noted that the term "elementary step" is not identical to the term "elenmentary reaction". Some elementary steps, such as surface reaction, may consist of several elementary reactions. The rate of an elementary reaction, or the rate of the elementary step may be useful for the quantitative understanding of catalytic activity. However, the reaction rate measured by the flow technique is an over-all reaction rate including the rates of several steps, and individual rates can hardly be distinguished by this technique.

The statistical moment technique provides a powerful approach to this problem. Kubin<sup>(1)</sup> and Kucera<sup>(2)</sup> have shown that the statistical moments are related to the rate parameters of axial dispersion, external diffusion, intraparticle diffusion, adsorption and desorption. The theory has been widely employed to calculate rate parameters, such as the chemissorption rate constant<sup>(3)</sup> and the intraparticle diffusivity<sup>(4,5)</sup>.

The statistical moments have been related to the reaction rate constant in systems which include the effect of intraparticle diffusion(6), the effects of axial dispersion and reversible adsorption(7), and the effects of axial dispersion, external diffusion, intraparticle diffusion, and reversible adsorption(8). Recently, the theory has been applied to the cracking of cumene on a silica-alumina cracking catalyst in order to calculate the rate constants of surface reaction, adsorption, and desorption(9), in the absence of mass transfer resistances. The major value of the moment technique is its theoretical exactness, i.e. even if the individual rate processes cannot be distinguished, a theoretical relationship can be obtained. It allows the measurement of rate parameters even if mass transfer resistances cannot be ignored. On the other hand, the calculation of the moments from the chromatographic peak is rather On propose deux méthodes pour mesurer, par la méthode d'impulsions, les constantes de vitesse des phases élémentaires. La première méthode fournit les constantes de vitesse d'adsorption, à partir du temps de rétention et de la demi-largeur du pic chromatographique; on l'a appliquée à l'adsorption du benzène sur les zéolites HY et CaY. La seconde méthode fournit la constante de vitesse des réactions superficielles et la constante de vitesse de désorption du réactif, à partir de la forme au pic du produit qui n'est pas adsorbé par la surface de catalyseur; on a appliqué ladite méthode au craquage du cumène sur les zéolites HY et CaY.

tedious, and the exact values of the moments can rarely be obtained experimentally  $^{(10)}$ .

Retention data is also useful for calculating the rate parameters. Roginskii and Rozental<sup>(11)</sup> have shown that the rate constants of adsorption, surface reaction, and desorption can be calculated from the conversion and the retention time. The method cannot be applied to a complicated system, e.g. when mass transfer resistances are also important, because the elution curve profile should be known as a function of time in order to relate the retention time to the rate parameters. However, the method does not require such a tedious calculation as that of the statistical moments.

In this paper, two methods for measuring the rate constants of the elementary steps are proposed. The first method gives the adsorption and the desorption rate constants of the linear and non-ideal chromatographic process, and the second method gives the surface reaction rate constant and the desorption rate constant of the reactant. The merit of both methods lies in the ease of the calculation and exactness of the theory is not stressed. The theoretical analysis is based on the assumption that the effects of mass transfer resistances are negligible. While this simplification may cause some errors, the method is simple and more inviting than a theoretically exact method accompanied by complicated calculations; the errors hereby introduced are not too large.

# PART I

Adsorption and Desorption Rate Constants of Linear and Non-Ideal Chromatography

The first method yields the rate constants of adsorption and desorption in the linear and non-ideal chromatographic process from the retention time and the half width of the chromatographic peak.

## Theory

Although the chromatographic peak may be broadened by the mass transfer resistances as well as the finite rates of adsorption and desorption, the mass transfer resistances are assumed to be negligible in the present paper. Mass transfer resistances can be reduced by appropriate experimental conditions, and it is usually possible to ascertain experimentally the extent of the resistance effects. The mass balance equation in the linear and non-ideal chromatography, where no chemical reactions take place and the rates of adsorption and desorption are linear, is given as follows:

$$\epsilon \frac{\partial C}{\partial t} = -\epsilon u \frac{\partial C}{\partial z} - \epsilon k_{ad} C + (1 - \epsilon) k_{des} q \dots (1)$$

$$(1 - \epsilon) \frac{\partial q}{\partial t} = \epsilon k_{ad}C - (1 - \epsilon)k_{des} q....(2)$$

Since no molecules are present either in the gas phase or on the surface before the pulse is introduced, the initial conditions are

$$C = q = 0$$
, at  $t = 0$  and  $0 \le z \le L$ .....(3)

The inlet pulse must have a finite width; however, if the width of the inlet pulse is much less than that of the exit pulse, the inlet pulse may be regarded as an impulse or a delta-function:

$$C = C^{\circ}\delta(t)$$
, at  $z = 0$ .....(4)

The elution curve profile can be derived from Equations (1) - (4) and is given as

$$\frac{C}{C^{\circ}} = \delta(t) e^{-K_{ad}}$$

$$+ e^{-K_{ad}} \sqrt{\frac{K_{ad} K_{des}}{T}} e^{-K_{des}T} I_{1} \left(2\sqrt{K_{ad}K_{des}T}\right) \dots \dots (5)$$

The first term can be neglected, if the contact time is large enough, because it represents the molecules which pass through the bed without being absorbed on the surface. For a large value of its argument, the I, function can be approximated as

$$I_1(x) \simeq e^x/\sqrt{2\pi x}$$
;  $x > 25$ .....(6)

The minimum experimental values of  $k_{\rm ad}k_{\rm des}\tau$  is 36, and the error in using Equation (6) is about 3% which lies within the experimental error. Hence, Equation (5) can be reduced to the simpler form.

$$\frac{C}{C^{\circ}} = \frac{1}{2\sqrt{\pi}} \left( \frac{\kappa_{ad} \kappa_{des}}{\tau^3} \right)^{1/4} exp\left( -(\sqrt{\kappa_{ad}} - \sqrt{\kappa_{des} \tau})^2 \right) . (7)$$

One definition of the retention time is the time taken to achieve the maximum value of concentration. Therefore, the dimensionless retention time,  $\tau_R$ , can be obtained by substituting the concentration profile at the exit shown by Equation (7) into  $dC/d\tau=0$ :

$$\tau_R = \frac{\kappa_{ad}}{\kappa_{des}} \left\{ \frac{1}{2} \left( 1 + \sqrt{1 - \frac{3}{\kappa_{ad}}} \right) - \frac{3}{4\kappa_{ad}} \right\} \dots (8)$$

It is convenient to introduce a new variable, reduced time  $\rho$ , defined as

$$\rho = \kappa_{des} \tau \dots (9)$$

By substituting Equation (8) into Equation (9), the reduced retention time,  $\rho_R$ , is obtained.

$$\rho_R = \kappa_{det} \, \tau_R$$

$$= \kappa_{ad} \quad \left\{ \frac{1}{2} \left( 1 + \sqrt{1 - \frac{3}{\kappa_{ad}}} \right) - \frac{3}{4\kappa_{ad}} \right\}. (10)$$

One can also define a "reduced half width" pertaining to the reduced time,  $P_{\text{H}}$ , at which the concentration becomes one half of the maximum concentration.  $P_{\text{H}}$  is obtained from Equations (7) and (10):

$$\frac{1}{2} = \left(\frac{\rho_R}{\rho_H}\right)^{3/4} \exp \left\{ (\rho_H - \rho_R) \right\}$$

$$\left(2 - \frac{\sqrt{\rho_H} - \sqrt{\rho_R}}{\kappa_{ad}}\right) \qquad (11)$$

 $\rho_{\rm H}$  is a function of only  $k_{\rm ad}$ , because  $\rho_{\rm R}$  itself is a function of  $k_{\rm ad}$ , as can be seen in Equation (10).

Thus it follows that the ratio of the retention time to the half width is a function of only  $k_{ad}$ , because the ratio of the retention time to the half width is identical to the ratio of the reduced retention time to the reduced half width. In other words,  $k_{\rm ad}$ can be determined by the ratio of the retention time to the half width. Furthermore,  $\rho_R$  is a function of the ratio, because  $\rho_R$  is a function of  $k_{\rm ad}$  which in turn is a function of the ratio. Thus, the adsorption and the desorption rate constants can be obtained from the contact time, the retention time, and the half width, for  $k_{\rm ad}$  is the product of the adsorption rate constant and the contact time, and  $\rho_R$ is the product of the desorption rate constant and the retention time. These quantities were numerically calculated from Equations (10) and (11) by means of an electronic computer. The results are shown in Figure 1, where the ordinate represents  $k_{\rm ad}$  and  $k_{\rm des}$   $\tau_{\rm R}$ , or  $k_{ad}\theta$  and  $k_{des}t_R$ . It is convenient to use an apparent contact time, W/F, instead of  $\theta$ . In order to use W/F, the unit of the adsorption rate constant must be converted into the reciprocal of the unit of W/F. Hereafter, the adsorption rate constant with the converted unit is represented by  $k_{\rm ad}$ .

If the chromatographic peak is determined, the adsorption and the desorption rate constants can be easily obtained from Figure 1 in the following manner.

- 1) Measure the retention time and the half width from the chromatogram, and calculate the ratio of the retention time to the half width.
- 2) Read the values of  $k_{ad}'W/F$  and  $k_{des}t_R$  from the correlation diagram shown in Figure 1.
- 3) Divide  $k_{ad}W/F$  by W/F and  $k_{des}t_R$  by  $t_R$  and obtain the adsorption and desorption rate constants.

### Experimental

The method was applied to the adsorption of benzene on CaY and HY zeolites. CaY and HY were prepared by a conventional ion-exchange technique from NaY (SK-40 from Linde) with solutions of calcium chloride and ammonium chloride. The degree of ion-exchange was 74% for CaY and 80% for HY. The zeolites were pretreated for 2 hours in nitrogen stream at 550°C just before the adsorption measurement.

The apparatus was a conventional gas chromatograph with the flame ionization detector modified by replacing an analytical column with a small catalyst bed. The catalyst was held by small plugs of Pyrex glass wool in the Pyrex glass reactor with an inside diameter of 5 mm. The temperature was measured with a thermocouple adjacent to the packed section of the reactor. Nitrogen was used as the carrier gas and it was passed through a molecular sieve column installed before the sample inlet in order to remove moisture.

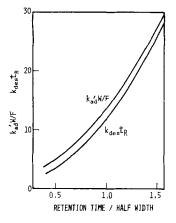


Figure 1 — A correlation diagram between the rate constants and the ratio of the retention time to the half width.

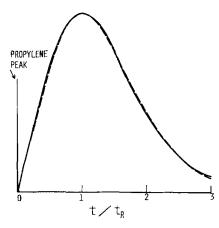


Figure 2 — Comparison between the theoretical peak (broken line) and the experimental peak (solid line) in the adsorption of benzene on CaY. Catalyst weight, 54.7 mg; N<sub>2</sub> flow rate, 50 ml/min.

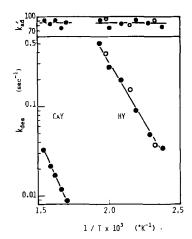


Figure 3 — Adsorption rate constant (cm<sup>3</sup>/g. sec) and desorption rate constant of benzene on CaY and HY. Empty circles were obtained with finely ground particle, and the solid circles, with a particle size of 28 - 48 mesh.

Guaranteed-reagent benzene was used without further purification. The saturated vapour of benzene in nitrogen stream was taken with a syringe, and was injected into the carrier gas stream through a rubber septum of the sample inlet.

#### Confirmation of the model

As mentioned above, the model employed in the theoretical analysis is quite simple on account of several assumptions; the validity of the model is experimentally justified. The first assumption is that no chemical reaction takes place, which was checked by effluent analysis. The conventional apparatus for the pulse reaction technique was somewhat modified by the introduction of a cooled liquid nitrogen U-tube trap between the reactor and the analytical column. The effluents were condensed in the U-tube trap and were vaporized by heating with an oil bath and carried to the chromatographic column and to the detector. In all cases, only benzene peaks were detected and the assumption of no chemical reaction is acceptable.

The second assumption is linear chromatography, that is, the adsorption rate is first order with respect to the gas phase concentration, but is independent of the surface concentration, and the desorption rate is the first order with respect to the surface concentration. If the surface is uniform, the latter may be true. On the other hand, the former assumption is not always valid, because the adsorption rate decreases with an increase in the surface concentration. According to the concept of the Langmuir isotherm, the adsorption rate is proportional to the product of the gas phase concentration and the fraction of the bare surface, therefore, the second assumption can be satisfied if the size of the pulse is small enough to have a negligible effect on the shape of chromatographic peak. At first, liquid benzene was injected into the carrier gas stream by means of a micro-syringe, but the effect of the pulse size was remarkably large above 0.2 µl. Then saturated vapour of benzene in nitrogen stream was similarly injected. In this instance the pulse size could be reduced to a small enough value that the effect of the pulse size could be neglected. As shown in Table 1, the retention time and the half width were independent of the pulse size below 0.03  $\mu$ l in terms of liquid volume. All experiments thereafter were carried out with the pulse size of 0.01  $\mu$ l.

The third assumption is that the effect of the mass transfer resistance is negligible. The broadening of benzene pulse may be caused by mass transfer resistances as well as by the finite rates of adsorption and desorption, while an inert gas peak is broadened only by mass transfer resistances. It follows that the effect of mass transfer resistances relative to the effect of adsorption and desorption can be estimated from the comparison of the half width of the inert gas peak with that of the benzene peak. Here, propylene could be used as an inert gas, for the adsorption of propylene on HY and CaY had been found negligible (12). The results are shown in Figure 2. The half width of propylene peak was only a few seconds, which is far less than that of the benzene peak which was found to be several hundred seconds. Thus, the effect of mass transfer resistances can be neglected in comparison with the effects of adsorption and desorption. The relative unimportance of mass transfer resistance has been also reported by Zikanova(4) in pentane-zeolite 5A system. Furthermore, the effects of external diffusion and intraparticle diffusion can be estimated from the size of the particles. The empty circles in Figure 3 are results obtained with finely ground HY, and the solid circles pertain to a particle size of 28 ~ 48 mesh. As can be seen in Figure 3, the effect is indistinguishable within the range of external diffusion and intraparticle diffusion can be neglected. It should be noted that by "intraparticle diffusion" macropore diffusion and not diffusion through the zeolite cavity, is meant.

TABLE 1

THE EFFECT OF PULSE IN THE ADSORPTION OF BENZENE ON CaY at 316°C. CATALYST WEIGHT, 54.7 mg;  $N_2$  Flow Rate,  $50 \, ml/min$ .

Pulse Size (µl)* Retention Time (sec) Half Width (sec)	0.01	0.015	0.02	0.03
	617	612	621	619
	958	950	961	963
11011 (100)	500		301	200

<sup>\*</sup>in terms of liquid volume.

A further assumption is that the inlet pulse can be regarded as an impulse, and this can be confirmed by the comparison of the width of the inlet pulse and with the width of the exit pulse. The width of the inlet pulse was almost the same as that of the propylene peak shown in Figure 2, and was far less than the width of the exit pulse. This result indicates that the width of the inlet pulse is not zero but it is negligible in comparison with that of the exit pulse.

In summary, all assumptions in the theoretical part have been experimentally satisfied. Figure 3 shows the comparison of the chromatographic peak obtained experimentally with that established theoretically. The latter was calculated as follows. First, the adsorption and the desorption rate constants were computed from the chromatographic peak obtained experimentally (the solid line); then the theoretical peak was calculated by substituting the rate constants hereby obtained into Equation è7î. The theoretical peak, shown by the broken line, closely agrees with the experimental peak, as shown in Figure 2.

# Adsorption and desorption rate constant

The adsorption and the desorption rate constants of benzene on CaY and HY are shown in Figure 3. The adsorption rate constant was found independent of temperature and of the species of the zeolite cation, which suggests that the adsorption is not an activated process. On the other hand, the desorption rate constant depends remarkably on temperature and on the cation. The activation energy of the desorption rate constant is computed to be 15.6 kcal/mol on CaY and 12.4 kcal/mol on HY. The difference in the activation energy between CaY and HY agrees well with the differences in the heat of adsorption of benzene between CaY and HY (18 kcal/mol on CaY and 15 kcal/mol on HY<sup>(12)</sup>, and 14 kcal/ mol on HY(18)). As the adsorption process appears to be a non-activated process, the activation energy of the desorption rate constant should be identical to the heat of adsorption. The difference between the activation energy in the present paper and published value of the heat of adsorption may be due to the experimental error. For instance, the heat of adsorption of benzene on 13X zeolite obtained by Boreskova, et al<sup>(12)</sup> (18 kcal/mol) is larger than that obtained by Eberly<sup>(14)</sup> (15.5 kcal/mol) and by MacDonald and Habgood<sup>(5)</sup> (15.7 kcal/mol), and the difference between them  $(2.3 \sim 2.5 \text{ kcal/mol})$  is almost identical to the difference between the value reported by Boreskova, et al(12) and by the present paper (2.4 kcal/mol on CaY and 2.6 kcal/mol on HY).

## PART II

Surface Reaction Rate Constant and Desorption Rate Constant

The second method yields the surface reaction rate constant and the desorption rate constant of the reactant from the shape of the peak obtained for the reaction product which is adsorbed only sparingly on the catalyst surface.

#### Theory

If the reaction product is not adsorbed on the catalyst surface, it is adsorption and desorption of the reactant and surface reaction that must be taken into consideration.

$$A \xrightarrow{k_{ad}} (A)_{ad} \xrightarrow{k} R. \tag{12}$$

The theoretical analysis was made on the basis of the assumptions in Part I: (1) The effect of mass transfer resistance can be neglected. (2) The inlet pulse can be regarded as an impulse. (3) The rates of all steps are linear. These assumptions lead to the following mass balance equation, the initial condition, and the boundary condition.

$$(1 - \epsilon) \frac{\partial q_A}{\partial t} = \epsilon k_{ad} C_A -$$

$$(1-\epsilon)k_{des} q_A - (1-\epsilon)k q_A \dots (14)$$

$$C_A = C_R = q_A = 0$$
, at  $t = 0$  and  $0 \le z \le L$ .....(16)

$$C_A = C_A \circ \delta(t)$$
 and  $C_R = 0$ , at  $z = 0$ .....(17)

The solution of Equations (13) - (17) gives the elution curve profile of the product:

Figure 4 shows the relation between the product concentration and the reduced time,  $k_{\text{des}T}$ . As shown in Figure 4, a plot of the logarithm of the product concentration against time gives essentially a straight line, and the slope of the line increases with a decrease in  $k_{\text{ad}}$ . The elution curve profiles in both extremes of  $k_{\text{ad}}$  are given as follows

When  $\kappa_{ad} \gg \kappa_{des} \tau$ , or  $k_{ad}$  'W/F  $\gg k_{des}t$ ,

$$\frac{C_R}{C_A^{\circ}} = \kappa \ e^{-\kappa \tau} \ . \tag{19}$$

When  $\kappa_{ad} \ll \kappa_{des} \tau$ , or  $k_{ad}$  'W/F  $\ll k_{des} t$ ,

$$\frac{C_R}{C_{A^{\circ}}} = \kappa \kappa_{ad} e^{-\kappa_{ad}} e^{-(\kappa + \kappa_{doe})\tau}....(20)$$

Therefore, the slope of the plot of  $\log C_R$  against  $\tau$  is k when  $k_{\rm ad}$  is large, and  $k+k_{\rm des}$  when  $k_{\rm ad}$  is small. In terms of real time, the slope of the plot of  $\log C_R$  against time is the surface reaction rate constant when the contact time is large enough, and the sum of the surface reaction rate constant and the desorption rate constant of reactant when the contact time is small enough.

The surface reaction rate constant and the desorption rate constant of reactant can be obtained as follows:

- 1) Measure the chromatographic peak of the reaction product at large enough contact time and at small enough contact time.
- 2) Plot the logarithm of peak height against time, and measure the slope.

Then the surface reaction rate constant can be obtained from the slope at large enough contact time. The desorption rate constant can be obtained from

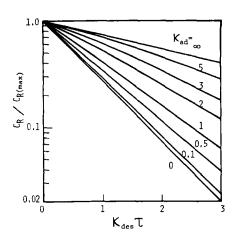


Figure 4 – Relation of the product concentration with the reduced time.  $k/k_{\text{des}} = 0.3.$ 

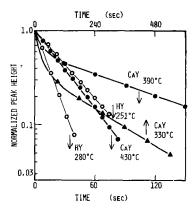


Figure 5 — Relation of peak height of propylene with time.

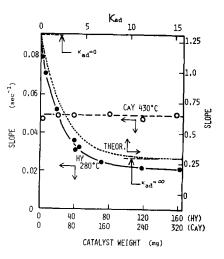


Figure 6 – Effect of the catalyst weight on the slope of the plot of log C<sub>R</sub> against time.

the difference in the slope of the curves obtained at a small contact time and at a large contact time.

# Experimental

The method was applied to the cracking of cumene on HY and CaY zeolites. The surface reaction rate constant and the desorption rate constant of cumene were measured from the chromatographic peak of propylene whose adsorption on zeolite catalyst appears to be negligible under the reaction condition.

The catalytic cracking of cumene to benzene and propylene is a well known catalytic reaction, and takes place with the formation of a minimum of byproducts. The basic mechanism of the reaction has been given by Prater and Lago<sup>(18)</sup>:

$$C + S \rightleftharpoons CS \rightarrow \text{Products}....(21)$$

where C is cumene, S is an active site, and CS is chemisorbed cumene on an active site. This kinetic scheme is completely identical to that in Equation (12). Recently, Campbell and Wojciechowski proposed the delta-mechanism which represents a more general case than the Prater-Lago mechanism. The delta-mechanism can be rewritten as follows:

where B and P are benzene and propylene, and BS and PS are chemisorbed species on an active site. Step (24) can be neglected, because, as mentioned above, appreciable adsorption of propylene has not been observed. The reverse direction of step (25) also can be neglected, because the reverse reaction is negligible under experimental circumstances. If the surface coverage of cumene and benzene is small enough, the effect of adsorbed benzene on the reaction rate can be neglected. It follows that, under the experimental condition in the present paper, the cracking of cumene can be represented by the Prater-Lago mechanism, hence Equation (12), and the herein presented theory can be applied to the cracking of cumene.

The apparatus and the procedure are the same as in Part I except that the degree of ion-exchange of CaY was 65% and that the chromatographic column was installed between the reactor and the detector. A 3 m by 4 mm column packed with PEG-1500 on Celite 545 was used at 70°C as the chromatographic column. Guaranteed-reagent cumene was used with further purification by percolation through a column packed with silica gel<sup>(15)</sup>.

## Experimental results

The validity of the assumptions was verified essentially in the same manner as in Part I; comparison of the chromatographic peak of propylene introduced before the reactor with that of propylene produced by the reaction indicated that the effect of axial dispersion is negligible. The width of the former was only several seconds, and much smaller than that of the latter. These results also suggest that propylene is adsorbed only sparingly on the zeolite surface under reaction conditions. The broadening of propylene peak in the chromatographic column is also negligible. The effect of the particle size can also be neglected because the results obtained with a particle size range of 48 - 65 mesh was in good agreement with that obtained with fine particles. It follows that the effect of external diffusion and intra-particle diffusion can also be ignored. The width of the inlet pulse was measured by injecting a cumene pulse just before the detector, and was found to be of a duration of several seconds, and much smaller than that of propylene produced by the reaction. Therefore, the inlet pulse can be regarded as an impulse within the experimental error. The last assumption, that the rates of all the steps are linear, was verified by examining the effect of pulse size, which was found negligible in the reaction on HY, below 1.5 µmol. In the reaction on CaY, the effect of pulse size was also negligible except at extremely small pulse sizes. Again, the experimental conditions agree with the assumptions employed in the theory.

Figure 5 shows the relation between the logarithm of the peak height of propylene and time. The plot obtained with HY gives essentially a straight line, but the line obtained with CaY has a bend at the

beginning. As can be seen from the bold line in Figure 5, the bend is more noticeable at the lower temperature, which can be explained by the heterogenity of the active site. If there is some more active site other than the major one, the chromatogram of propylene may consist of two parts: one representing propylene produced on the more active site, and another, on the major site. At early times, the slope of the overall chromatogram is determined by the sum of both slopes. After the adsorbed cumene on the more active site has reacted, the overall slope is determined only by the slope of the line corresponding to the major site. With an increase in the temperature, both slopes, i.e., the surface reaction rate constants on both sites, increase. But an increase in the rate constants on the major site may be larger than that on the more active site, as the activation energy of the major site, i.e., the less active site, may be larger than that of another, in which case the difference between the slopes of the two sites decreases with an increase in the temperature.

Figure 6 shows the effects of the contact time on the slope of the plot of the logarithm of propylene peak height against time. The dotted line shows the relation of the slope of the line in Figure 4 to  $k_{ad}$ , i.e., the product of the adsorption rate constant and the contact time. The trend of the results obtained with HY agrees well with the theoretical results. The slope decreases with an increase in the contact time. and finally it became constant at considerably large contact time. Therefore, the slope at small enough contact times can be regarded as the sum of the surface reaction rate constant and the desorption rate constant of cumene, and that at large enough contact times, as the surface reaction rate constant. On the other hand, the slope obtained with CaY is independent of the contact time. This result was obtained in the following two cases:  $k_{ad}W/F >> k_{des}t$  or  $k_{ad}W/F <<$ k<sub>des</sub>t at all the experimental conditions. As mentioned above, the adsorption rate constant of benzene on CaY is almost equivalent to that on HY, but the desorption rate constant on CaY is much smaller than that on HY. These results obtained with benzene may hold true in the adsorption of cumene. If so, the present case corresponds to the former case, i.e.,  $k_{ad}W/F >> k_{des}t$ . Because  $k_{ad}W/F$  on CaY may be almost equal to that on HY, and  $k_{des}t$  on CaY may be much less than that on HY. Furthermore, in the reaction on HY, kad W/F was much larger than k<sub>des</sub>t at large contact time. The magnitude of conversion also suggests that kad'W/F >> kdest. In the latter case, unconverted cumene must be detected, because the adsorption rate is small and the desorption rate is large. In the reaction on CaY, unappreciable peak of unconverted cumene could not be observed. It follows that the present case corresponds to  $k_{ad}'W/F >> k_{des}t$  and the slope gives the surface reaction rate constant.

Figure 7 shows the Arrhenius plot of the rate constant thus obtained. The activation energy on HY is 27.7 kcal/mol, and is almost equal to that on CaY. These values of the activation energy are in good agreement with previously reported values for HY, alkaline earth Y, and impregnated silica-alumina, but they differ considerably from those for LaY and cogelled silica-alumina, as shown in Table 2. The surface reaction rate constant on HY was about a hundred times as large as that on CaY, as can be seen from Figure 7. This also compares with published values. Richardson<sup>(19)</sup> obtained the zeroth order rate constant with the continuous flow technique. The ratio of the rate constant on HY to that on 2% Cu-CaY was

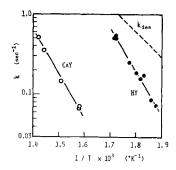


Figure 7 — Arrhenius plot of the surface reaction rate constant of the dealkylation of cumene on HY and CaY zeolite.

about a hundred. Boreskova, et al<sup>(12)</sup> obtained, using the pulse technique, the first order rate constant from the conversion and the adsorption equilibrium constant from the retention time, and calculated the surface reaction rate constant from the ratio of the former to the latter. The ratio of the surface reaction rate constant on HY to that on CaY was above ten.

The activation energy of the desorption rate constant of cumene on HY is 14.3 kcal/mol. This is considerably smaller than the published values of the heat of adsorption (18 kcal/mol<sup>(13)</sup> and 21 kcal/mol<sup>(12)</sup>). The discrepancy may be due to the small weight of the catalyst (4 mg) or to the small catalyst volume.

#### **Conclusions**

Two simple methods for measuring the rate constant of elementary steps by the pulse technique have been presented. The first method was applied to the adsorption of benzene on HY and CaY zeolites, and the rate constants of adsorption and desorption were estimated. The adsorption process appears to be a non-activated process. The activation energy of desorption rate constants is 15.6 kcal/mol on CaY and 12.4 kcal/

Table 2

The Activation Energies of the Surface Reaction.

Catalyst	Activation Energy (kcal/mol)	Method	Kinetic Scheme	Refer- ence
Silica- Alumina " (cogelled)	40 23.4	Flow	Prater-Lago	(15) (17)
" (impregnated)  HY  CaY  NH4-Silica- Alumina	27 \sim 30 \\ 30 \\ 29 \\ 28.4	Pulse	First order	(12)
Ca-Silica- Alumina HY, 2% Cu-	27.7	,,	<b>,,</b>	(18)
CaY, and 2% $Cu$ -	28.2	Flow	Zero order	(19)
MgÝ LaY Silica-	19.5	Flow	△ mechanism	(18)
Alumina HY and CaY	23 27.7	Moment Pulse	Prater-Lago Prater-Lago	(9) Present Study

mol on HY; these values agree with published values of the heat of adsorption.

The second method was applied to the cracking of cumene on HY and CaY, and the surface reaction rate constant and the desorption rate constant of cumene were estimated from the peak shape of propylene. The surface reaction rate constant on HY is about a hundred times as large as that on CaY. The activation energy on both zeolite catalysts is 27.7 kcal/mol. These values agree well with published data. The activation energy of the desorption rate constant of cumene on HY is a few kcal/mol smaller than published values of the heat of adsorption.

#### Nomenclature

C,  $C_A$ ,  $C_R$  = concentration of adsorbate, reactant, and product in void of catalyst bed, mol/cm3 of void concentration of inlet pulse, mol/cm3 of void flow rate of carrier gas, ml/sec  $I_1(x)$ modified Bessel function of the first kind of order one surface reaction rate constant, 1/sec kad, kad' adsorption rate constant, 1/sec or cm3/g.sec  $k_{dee}$ desorption rate constant, 1/sec length of catalyst bed, cm concentration of adsorbed molecules, mol/cm³ of I. q, qsolid = time since pulse is introduced, sec  $t_R$ = retention time adjusted by subtracting dead volume, sec = linear velocity of carrier gas, cm/sec = weight of catalyst, g = axial distance along the bed, cm W  $\theta$ void fraction in catalyst bed. = contact time, L/u, sec

dimensionless surface reaction rate constant,  $k\theta$ dimensionless adsorption rate constant,  $k_{ad}\theta$  dimensionless desorption rate constant,  $k_{da}\theta$  dimensionless desorption rate constant,  $k_{da}\theta$  reduced time defined by Equation (9). reduced time when concentration becomes one half Kad K des ρ  $\rho_H$ of maximum concentration. = reduced retention time,  $\kappa_{det} \tau_R$ . = dimensionless time,  $(t - \theta)/\theta$ . = dimensionless retention time,  $t_R/\theta$ .  $\tau_R$ 

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