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# The Modeling of the Kinetics of Deactivation of a Commercial Hydrocracking Catalyst in the Reaction of Cumene Disproportionation

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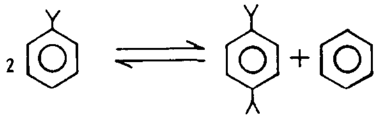
The mechanism of coke formation on a commercial hydrocracking catalyst is studied. The data by R. P. L. Absil, J. B. Butt, and J. B. Dranoff (*J. Catal.* **85**, 415, 1984) for cumene disproportionation have been analyzed using the theory and developments of J. Corella and J. M. Asua (*Ind. Eng. Chem. Process Des. Dev.* **21**, 55, 1982). Several coke formation mechanisms are presented and their Langmuir–Hinshelwood kinetic equations are deduced. Only the mechanisms with two active sites in the controlling step or with deactivation order 1.5 fit the data. The chemical mechanism of coke formation in this process is presented and a reasonable mechanistic explanation for the empirical deactivation kinetic equations given previously is presented. © 1986 Academic Press, Inc.

## INTRODUCTION

Langmuir–Hinshelwood-type kinetic equations for investigation of the reaction mechanisms of catalyst deactivation by coke formation have not been extensively used. Some authors who have made experimental use of this type of mechanistic equation of deactivation are Chu (*1*), Corella *et al.* (*2*), Forzatti and Buzzi-Ferraris (*3*, *4*), Lee and Butt (*5*), Dumez and Froment (*6*), Do and Weiland (*7*), Levy and DeGroot (*8*), and Srivastava and Guha (*9*), In this work we present a more extensive study of this approach for a given chemical process.

Recently Absil *et al.* (*10*) have presented a kinetic study of cumene disproportionation over a commercial hydrocracking catalyst. Their catalyst has a typical commercial formulation with the Co–Mo function supported on a crystalline aluminosilicate (zeolite) suspended or embedded in an amorphous $SiO_2/Al_2O_3$ matrix. This matrix has rather large pores to permit access of the large molecules involved in hydrocracking to the zeolite particles. They carried out experiments in a differential fixed bed reactor at different partial pressures of the reactants, with a total pressure near 8 atm in a temperature interval of 428–455 K. In this process the catalyst deactivates by coke formation, giving progressive diminution of the conversion. The weight percentage of coke on the deactivated catalyst ranged from zero up to about 5%. The overall main reaction is


(1)

to which we refer in the following as

$$2\,C \rightleftharpoons D + B \qquad (2)$$

In the proposed mechanism for this reaction the number of active sites involved in the controlling step (*m*) is 2, an important datum for the modeling of the kinetics of deactivation, as will be seen later on. Applying a balance of active sites at zero time of reaction and at time *t* and using well-known procedures, it is deduced that the rate of the main reaction at zero time is given by

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$$r_B(0) = \frac{kK_1^2\, L^2(P_C^2/P_H - P_BP_D/P_H)}{\left\{1 + \frac{K_1P_C}{P_H} + \left(\frac{1}{K_1} + \frac{1}{K_{II}}\right)\frac{P_BP_D}{P_H} + \frac{P_D}{K_5P_H}\right\}^2} \tag{3}$$

and at time $t$:

$$r_B(t) = \frac{kK_1^2(L - 2C_{PI_2})^2(P_C^2/\mathrm{P_H} - P_BP_D/\mathrm{KP_H})}{\left\{1 + \frac{K_1P_C}{P_H} + \left(\frac{1}{K_I} + \frac{1}{K_{II}}\right)\frac{P_BP_D}{P_H} + \frac{P_D}{K_5P_H}\right\}^2} \tag{4}$$

where $C_{PI_2}$ is the concentration of active sites lost at time $t$ by site coverage (Mechanism I below) or by pore blockage if the latter occurs. From Eq. (3), with conditions of partial pressure of hydrogen ($P_H$) constant, and for a differential reactor without feed B or D ($P_B = P_D \simeq 0$), and with the notation

$$K_1/P_H = K^2$$

and (5)

$$kL^2P_H = k'$$

it is deduced that

$$r_B(0) = \frac{k'K^2P_C^2}{(1 + KP_C)^2}. \tag{6}$$

This is the equation which Absil *et al.* (*10*) found experimentally and which is seen to be a simplification of Eq. (3).

## TREATMENT

### *Kinetics of the Deactivation Reaction*

Together with the main reaction of cumene disproportionation simultaneous reactions of formation of coke are produced, resulting in deactivation of the catalyst. This in turn results in a continuous reduction of conversion at the outlet of the reactor. If this decrease of conversion is measured with precision in a differential reactor, without diffusional control (effectiveness factor = 1) and at different partial pressures of the reactants, $P_i$, one can obtain the chemical pathway of the deactivation, as has been previously demonstrated (*2c, 9, 11, 12*). It is well known how kinetic data obtained at zero time-on-stream, or without deactivation, can adjust to equations of the type of Eq. (3), from which one can infer, with caution, at least a kinetic network for the mechanism of the main reaction. In the same way, data on deactivation sometimes adjust to kinetic equations of the mechanistic type which, with all due precautions, can still give information about the reaction steps involved in deactivation.

The kinetic equation presented by Absil *et al.* (*10*) for the deactivation in cumene disproportionation

$$\frac{1}{[X(t)]^{0.5}} = \frac{1 + \delta t}{[X(0)]^{0.5}} \tag{7}$$

is most informative as to the processes involved. Let us see how this equation, empirical in principle and a particular case ($N = 2$) of Wojciechowski's equation (*13*), can be deduced in a rational way, starting off from the mechanistic considerations proposed by Corella and Asua (*11*). These authors have shown how, when there is only one cause of deactivation, many of the simplest mechanisms of deactivation for homogeneous surfaces (i.e., with all sites of the same strength) lead to equations of the following type:

$$-\frac{da}{dt} = \psi(P_i,T)\, a^d \tag{8}$$

in which

$$d = \frac{m + h - 1}{m} \tag{9}$$

where $m$ and $h$ are the number of active sites involved in the controlling step of the main and deactivation reactions, respectively. In the mechanism proposed for the main reaction by Absil *et al.* (*10*), one observes (in their Eq. (9)) that $m = 2$. Similarly, for the mechanism of deactivation (see page 422 of their paper) they give for $h$ a value of 2. Therefore:

$$d = \frac{2 + 2 - 1}{2} = 1.5 \qquad (10)$$

that is to say,

$$-\frac{da}{dt} = \psi(P_i,T)\, a^{1.5}. \qquad (11)$$

In an isothermal differential reactor $\psi(P_i,T)$ is a constant. Integration of Eq. (11) for $\psi(P_i,T)$ constant gives

$$\frac{1}{\sqrt{a}} = 1 + \frac{\psi(P_i,T)}{2}\, t. \qquad (12)$$

$\psi(P_i,T)$ is constant if the reactor is isothermal and differential as in this case (*10*) in which the cumene is highly diluted with nitrogen ($P_C = 0.076$ to $0.724$ atm, $P_{N_2} = 7.6$ atm) and the reactor is operated at conversions below 16%. Other situations in which $\psi(P_i,T)$ can be considered constant in the reactor have been studied previously (*14*, *15*). Likewise, for the differential reactor:

$$r_B(0) = \frac{X_B(0)}{W/F_{A_0}} \qquad (13)$$

$$r_B(t) = \frac{X_B(t)}{W/F_{A_0}} \qquad (14)$$

By the definition of activity:

$$a \equiv \left[\frac{r_B(t)}{r_B(0)}\right]_{T,P_i} = \frac{X_B(t)}{X_B(0)}. \qquad (15)$$

Substitution of Eq. (15) in Eq. (12) yields

$$\frac{1}{[X_B(t)]^{0.5}} = \frac{1 + [\psi(P_i,T)/2]t}{[X_B(0)]^{0.5}} \qquad (16)$$

which is equivalent to Eq. (7) used in the work of Absil *et al.* (*10*). Note, in addition, that the constant $\delta$ of that equation has the significance of $\psi(P_i,T)/2$.

### *Mechanisms of Deactivation*

In the following we present four mechanisms of deactivation and a comparison of fits to the experimental data.

*Mechanism I.* In this mechanism it is assumed that the deactivation is in series with the main reaction and also that the controlling step is the formation of coke precursor from two molecules of D adsorbed on the surface:

$$\mathrm{D} + \mathrm{l} \rightleftharpoons \mathrm{Dl} + \mathrm{H_2}; \quad K_5 = \frac{P_D C_l}{C_{Dl} P_H} \qquad (17)$$

$$2\,\mathrm{Dl} \xrightarrow{k_d} \mathrm{P_l l_2}\downarrow; \qquad dC_{Pl_2}/dt \qquad (18)$$

where l indicates an acidic active site. Note that in this mechanism $h = 2$; then by Eq. (9), $d = 1.5$. If the second step is the controlling one, the rate of coke formation will be given by

$$\frac{dC_{Pl_2}}{dt} = k_d C_{Dl}^2. \qquad (19)$$

Mann and co-workers (*16*, *17*), Beeckman and Froment (*18*, *19*), Langner (*20*), Haynes and Leung (*21*), and many others have shown how together with the site coverage there can be pore blockage. If this phenomenon occurs, it must be taken into account in the balance of active sites starting off from which the Langmuir–Hinshelwood-type kinetic equations of deactivation (*11*) are obtained. In this case, and as Corella and Monzón (*22*) show, in an isothermal and differential reactor the function of deactivation, $\psi(P_i,T)$, varies with the time-on-stream. Also, the classic representations ln $a$ (or ln $X_{B_s}$) vs $t$ (for $d = 1$), $1/a$ (or $1/X_{B_s}$) vs $t$ (for $d = 2$), or $1/\sqrt{a}$ (or $1/\sqrt{X_{B_s}}$) vs $t$ (for $d = 1.5$) do not provide straight lines but the slope ($\psi$) varies with the time. Since this does not occur with the data of Absil *et al.* (*10*), as the determinations of surface area and of coke content on the catalyst (*23*) do not indicate the existence of pore blockage and as the experimental data adjust well enough to a kinetic model without pore blockage, this is not going to be taken into account in the subsequent kinetic development. Therefore, carrying out a balance of acidic active sites at time $t$:

$$L = C_l + C_{Cl} + C_{I_1 l} + C_{I_2 l} + C_{Dl} + 2C_{Pl_2} \qquad (20)$$

where $I_1$l and $I_2$l are components of the main reaction and have the chemical struc-

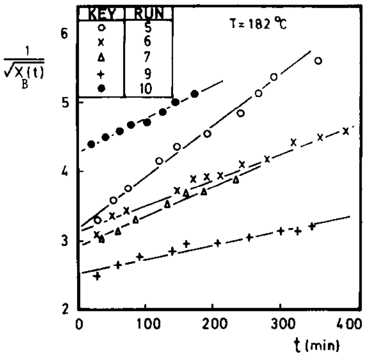


FIG. 1. Test of deactivation Mechanism I according to Eq. (29).

ture shown in the nomenclature. From this balance one deduces that

$$C_l = \frac{L - 2C_{Pl_2}}{\left\{1 + \frac{K_1P_C}{P_H} + \left(\frac{1}{K_I} + \frac{1}{K_{II}}\right)\frac{P_BP_D}{P_H} + \frac{P_D}{K_5P_H}\right\}^2} \tag{21}$$

From Eqs. (17), (19), and (21) one then can derive:

$$\frac{dC_{Pl_2}}{dt} = \frac{[k_d/(K_5P_H)^2]P_D^2(L - 2C_{Pl_2})^2}{\left\{1 + \frac{K_1P_C}{P_H} + \left(\frac{1}{K_I} + \frac{1}{K_{II}}\right)\frac{P_DP_B}{P_H} + \frac{P_D}{K_5P_H}\right\}^2} \tag{22}$$

which when integrated gives

$$\frac{L - 2C_{Pl_2}}{L} = \left[1 + \int_0^t \psi_l\, dt\right]^{-1} \tag{23}$$

where

$$\psi_l = \frac{2L[k_d/(K_5P_H)^2]P_D^2}{\left\{1 + \frac{K_1P_C}{P_H} + \left(\frac{1}{K_I} + \frac{1}{K_{II}}\right)\frac{P_BP_D}{P_H} + \frac{1}{K_5}\frac{P_D}{P_H}\right\}^2} \tag{24}$$

in which subscript 1 in $\psi_l$ refers to Mechanism I.

On the other hand, substituting Eqs. (3) and (4) in the definition of activity, Eq. (15), one obtains

$$a \equiv \frac{r_B(t)}{r_B(0)} = \left[\frac{L - 2C_{Pl_2}}{L}\right]^2. \tag{25}$$

Substituting Eq. (25) in Eq. (23) one deduces that

$$a = \left[1 + \int_0^t \psi_l\, dt\right]^{-2}. \tag{26}$$

If $\psi_l$ is constant in the bed, i.e., in an isothermal and differential reactor such as the one used by Absil *et al.* (*10*), Eq. (26) simplifies to

$$a = (1 + \psi_l t)^{-2}. \tag{27}$$

From Eq. (27) one deduces:

(a) If Eq. (27) is written in differential form:

$$-\frac{da}{dt} = 2\psi_l a^{1.5} \tag{28}$$

where the observed order of deactivation is 1.5. This conclusion could also have been obtained by applying Eq. (9) directly to this mechanism.

(b) From differential reactor conversions the activity can be calculated as

$$a = \frac{X_B(t)}{X_B(0)}. \tag{15}$$

Substituting this into Eq. (27) one obtains

$$\frac{1}{[X_B(t)]^{0.5}} = \frac{[1 + \psi_l t]}{[X_B(0)]^{0.5}}. \tag{29}$$

On representing $[1/X_B(t)]^{0.5}$ vs $t$ (Fig. 1), Eq. (29) would seem to be confirmed. From the slopes of the lines of Fig. 2, one obtains the values of the function of deactivation, $\psi_l$, in each experiment. The partial pressures or experimental conditions with which each experiment at 182°C was carried out are shown in Table 1.

Let us now see if the experimental data confirm this mechanism. The function of deactivation for this mechanism (Eq. (24)) can be written as

$$\psi_l = \frac{\alpha P_D^2}{(\beta + \gamma P_C + \varepsilon P_BP_D + \pi P_D)^2} \tag{30}$$

TABLE I

Experiments at 182°C: Experimental Conditions

| Run | $P_{C_0}$ (mm Hg) | $P_{D_{S_0}} = \frac{1}{2}P_{C_0} \cdot X_B(0)$ (mm Hg) *a* | *b* | $P_{\text{Total}}$ (atm) | Space velocity $\left(\frac{\text{mol} \cdot \text{g} \cdot \text{cumene}}{\text{g} \cdot \text{cat} \cdot \text{min}}\right)$ |
|---|---|---|---|---|---|
| 5 | 104.4 | 4.80 | 5.10 | 7.60 | $6.51 \times 10^{-4}$ |
| 6 | 104.6 | 5.16 | 5.29 | 7.56 | $6.23 \times 10^{-4}$ |
| 7 | 109.9 | 6.26 | 6.39 | 8.21 | $6.16 \times 10^{-4}$ |
| 8 | 58.0 | 4.47 | 4.51 | 7.70 | $3.25 \times 10^{-4}$ |
| 9 | 62.6 | 3.26 | 3.28 | 7.82 | $5.41 \times 10^{-4}$ |
| 10 | 106.5 | 2.88 | 2.90 | 7.89 | $0.13 \times 10^{-4}$ |

[a] With $X_B(0)$ obtained by extrapolation with the equations of Mechanism III ($d = 1$).

[b] With $X_B(0)$ obtained by extrapolation with the equations of Mechanism I ($d = 1.5$).

Since, in the experiments carried out (*10*), $P_B = P_D$, Eq. (30) becomes

$$\psi_I = \frac{\alpha P_D^2}{(\beta + \gamma P_C + \varepsilon P_D^2 + \pi P_D)^2} \tag{31}$$

Equation (31) is a function that, for growing values of $P_D$, passes through a relative maximum, decreasing later. Figure 2, where $\psi_I$ vs $P_D$ is represented, shows good agreement of the experimental data which indicates that Mechanism I is consistent with this analysis of the experimental data.

It is necessary to make two comments regarding some details of Fig. 2 and of the similar ones shown afterward:

(a) The $P_D$ used in the abscissae is the nominal one at the outlet of the reactor at zero time $(P_{D_S})_0 = \frac{1}{2}(P_C)_0 (X_{BS})_0$. As the catalyst deactivates, the $P_D$ at the outlet decreases with time and the average $P_D$ in the bed will therefore vary in each experiment. One could take as reference an average $P_D$ in the bed throughout the time, and it would be more precise to use this average $P_D$, but in the present case the conclusions are unaltered.

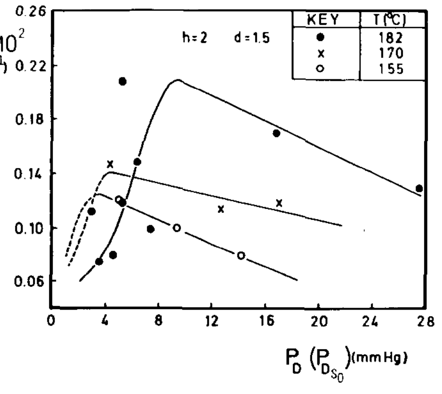


FIG. 2. Test of Mechanism I according to the deactivation function $\psi_I$, Eq. (31).

(b) It can be observed that the experiments at 182°C have been made in a zone of $P_D$ where $\psi_I$ shows a parametric sensitivity with respect to $P_D$ which is very pronounced; therefore, there appear two points at 182°C which adjust badly to all the mechanisms studied because there is considerable uncertainty for that sensitive range of $P_D$.

*Mechanism II.* This mechanism differs from the previous one in that the deactivation is taken to be produced by the reactant (C) and the product (D), i.e., deactivation of the series-parallel type. It is again assumed that the controlling step is the formation of coke percursor:

$$\text{C} + \text{l} \rightleftharpoons \text{Cl} + \text{H}_2; \quad K_1 = \frac{C_{\text{Cl}} P_H}{P_C C_l} \tag{32}$$

$$2\,\text{Cl} \xrightarrow{k_{dC}} \text{P}_2\text{l}_2 \downarrow; \quad dC_{\text{Pl}_2}/dt \tag{33}$$

$$\text{D} + \text{l} \rightleftharpoons \text{Dl} + \text{H}_2; \quad K_5 = \frac{P_D C_l}{C_{\text{Dl}} P_H} \tag{17}$$

$$2\,\text{Dl} \xrightarrow{k_{dD}} \text{P}_1\text{l}_2 \downarrow; \quad dC_{\text{Pl}_2}/dt. \tag{18}$$

In this mechanism the value of $h$ is also 2, so that, according to Eq. (9), $d = 1.5$. The chemical structures of $P_1l_2$ and $P_2l_2$ are shown in conclusions.

Carrying out the balance of active sites at time $t$ and in a similar way to the steps followed in Mechanism I, one arrives at

$$a = (1 + \psi_2 t)^{-2} \qquad (34)$$

where

$$\psi_2 = \frac{2L\left[\dfrac{k_{d_C}}{K_I^2}P_C^2 + \dfrac{k_{d_D}}{K_5^2}P_D^2\right]}{P_H^2\left\{1 + \dfrac{K_I P_C}{P_H} + \left(\dfrac{1}{K_I} + \dfrac{1}{K_{II}}\right)\dfrac{P_B P_D}{P_H} + \dfrac{P_D}{K_5 P_H}\right\}^2} \qquad (35)$$

or, in differential form:

$$-\frac{da}{dt} = 2\psi_2 a^{1.5}. \qquad (36)$$

Subscript 2 in $\psi_2$ refers to Mechanism II. Substituting in Eq. (34) the value of the activity, Eq. (15), one arrives at an expression similar to Eq. (29). From this expression one can calculate the value of $\psi_2$ at different $P_C$ or $P_D$. The function $\psi_2$, Eq. (35), is of the same type as $\psi_1$, Eq. (31). Therefore, Figs. 1 and 2 also serve to verify experimentally Mechanism II. Much more precise data of $\psi$ at different $P_C$, $P_D$, $P_H$, and $P_B$ would be necessary to discriminate between Eqs. (24) and (35) or to distinguish Mechanisms I and II.

*Mechanism III.* This mechanism is based directly on the sequence presented by Absil *et al.* (*10*) in their Fig. 7. In this it is assumed that the controlling step is the formation of the coke precursor. It is also assumed that the deactivation is in series with the main reaction as, according to Absil *et al.* (*10*), it is the product D which gives rise to the coke. Thus, for Mechanism III:

$$D + l \rightleftharpoons Dl + H_2;$$

$$K_5 = P_D C_l / C_{Dl} P_H \qquad (17)$$

$$Dl \rightleftharpoons E + l;$$

$$K_6 = C_{Dl} / P_E C_l \qquad (37)$$

$$E(g) + Dl \xrightarrow{k_d} P_3 l\downarrow;$$

$$dC_{Pl}/dt. \qquad (38)$$

Note that in this mechanism $h = 1$; then by Eq. (9), $d = 1$. Following the same procedure as before one arrives at

$$a = \exp(-\psi_3 t) \qquad (39)$$

or

$$\ln X_B(t) = \ln X_B(0) - \psi_3 t \qquad (40)$$

where

$$\psi_3 = \frac{2k_d K_6 P_D^2}{K_5^2 P_H^2\left\{1 + \dfrac{K_I P_C}{P_H} + \left(\dfrac{1}{K_I} + \dfrac{1}{K_{II}}\right)\dfrac{P_B P_D}{P_H} + \dfrac{P_D}{K_5 P_H}\right\}} \qquad (41)$$

or ($P_B = P_D$):

$$\psi_3 = \frac{\alpha P_D^2}{\beta + P_C + \varepsilon P_D^2 + \pi P_D}. \qquad (42)$$

Subscript 3 in $\psi_3$ refers to Mechanism III. On representing $\ln X_B(t)$ vs $t$ (Fig. 3), Eq. (40) would seem to be confirmed. From Fig. 3 one obtains the values of $\psi_3$ at different $P_D$. Equation (42) is a function that, for growing values of $P_D$, increases asymptotically towards a value of $\psi_1 = \alpha/\varepsilon$. This theoretical behavior is not experimentally found, however, as is shown in Fig. 4, which indicates that Mechanism III is not consistent with this analysis of the experimental data.

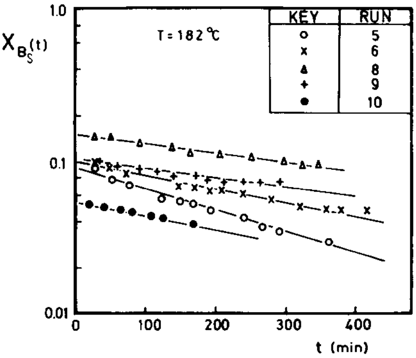


FIG. 3. Verification of Eq. (40), Mechanism III.

*Mechanism IV.* This mechanism differs from the above in that the reactant D is adsorbed in different ways in the main reaction and the deactivation reaction which, as has been shown before (*11*), can occur in some processes. In this mechanism the value of $h$ is also 1, so that, according to Eq. (9), $d = 1$. It is also assumed that the controlling step is the reaction of formation of coke precursor and the deactivation occurs in series with the main reaction since D is the species which gives rise to the coke. Hence:

$$D + I \rightleftharpoons DI^* + H_2; \quad K_5^* = \frac{P_D C_I}{C_{DI^*} P_H} \tag{43}$$

$$DI^* \rightleftharpoons E + I; \quad K_6^* = \frac{C_{DI^*}}{P_E C_I} \tag{44}$$

$$E(g) + DI^* \rightarrow P_2I \downarrow; \quad dC_{PI}/dt \tag{45}$$

where DI* indicates that D is adsorbed in a different way from that of D in DI.

The equations obtained for this mechanism are of the same type as those obtained with Mechanism III. Thus, for the same reason as Mechanism III, Mechanism IV does not adjust correctly to the experimental data.

*Other mechanisms.* One could envisage a number of other mechanisms for coke formation in a reaction as complex as this. For example, there might be bimolecular adsorption of both cumene and diisopropyl benzene, with intermediates produced from the decomposition of one or both involved in the formation of coke precursor, and so on. The mathematical solution of such mechanisms is quite complex and leads to deactivation equations of nonseparable variables. Such equations have not been studied very well up to now and could be a subject of research in themselves. Whether this would be fruitful is subject to question, since such results would be highly parameterized and perhaps no more informative than the plausible chemistry offered by Mechanisms I and II as shown below.

## CONCLUSIONS

The empirical kinetic equation which Absil *et al.* (*10*) propose for adjusting their data for deactivation in cuemene disproportionation can be deduced by mechanistic considerations, making use of the theory developed by Corella and Asua (*11*). The kinetics of deactivation are correlated by Eqs. (8) and (9) with $m = 2$, $h = 2$, or $d = 1.5$. The experimental data on the time variation of conversion are predicted by Eqs. (12) and (16), which are integrated forms of Eq. (8) with $d = 1.5$.

On the other hand, the sequences which best explain the deactivation, as they correspond to experimental data, are Mechanisms I and II. These differ from the approach proposed by Absil *et al.* (*10*) in that $h = 2$, rather than $h = 1$.

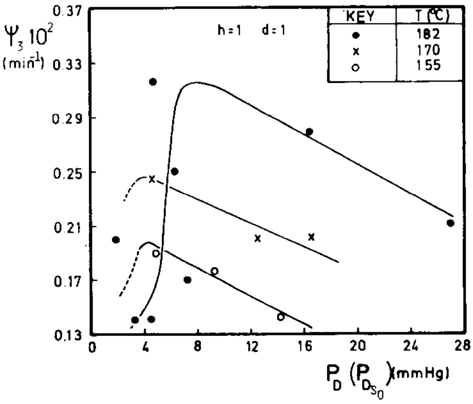
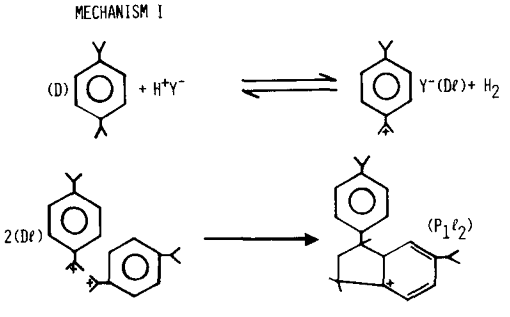
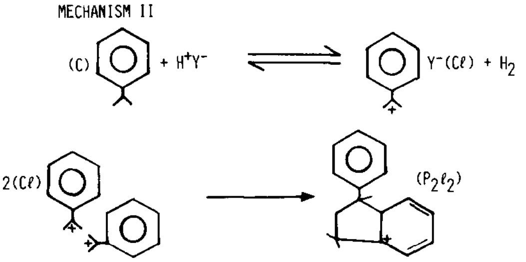


FIG. 4. Test of Mechanism III according to the deactivation function $\psi_3$, Eq. (42).

According to Mechanism I, Eqs. (17) and (18), the formation of the precursor of coke takes place due to the following chemical reactions:



By mechanism II, which also correlates the data, the coke precursor could also be formed starting from the cumene:

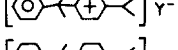
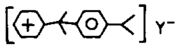


One notes the similarity of the carbenium ion intermediates, Cl and Dl, in the formation of coke precursor for both schemes, and it is doubtful that a clear distinction will be made between them in the rather complex overall reaction scheme. Indeed, it is entirely possible that both pathways are involved in coke formation here.

## NOMENCLATURE

| | |
|---|---|
| $a$ | activity at time-on-stream $t$, defined by Eq. (15) |
| $C_{il}$ | concentration of active sites covered by species $i$ |
| $C_l$ | concentration of vacant active sites |
| $C_{Pl}$ | concentration of active sites covered by coke or by coke precursor |
| $d$ | deactivation order |
| $h$ | number of active sites involved in the controlling step of the deactivation reaction |
| $k_i$ | kinetic constants |
| $k_d$ | deactivation kinetic constant |
| $K$ | equilibrium constant of cumene disproportionation |
| $K_i$ | adsorption equilibrium constants as defined in the reaction mechanisms |
| $K_2$ | $P_{I_1}C_l/C_{I_1l}$ |
| $K_3$ | $C_{I_2l}/P_{I_1}C_l$ |
| $K_4$ | $C_{Dl}P_B/C_{I_2l}$ |
| $K_I$ | $K_2K_3K_4K_5$ |
| $K_{II}$ | $K_4K_5$ |
| l | active site |
| $L$ | total concentration of active sites |
| $m$ | number of active sites involved in the controlling step of the main reaction |
| $P_i$ | partial pressures of species $i$ |
| $P_{i_0}$ | idem, at $t = 0$. |
| $P_1, P_2, \ldots, P_5$ | coke precursor species 1 . . . 5 |
| $r_B(t)$ | rate of benzene formation at time-on-stream $t$ |
| $W/F_{A_0}$ | ratio of catalyst weight to feed rate, Eqs. (13), (14) |
| $(X_{B_S})_t$ | conversion to benzene at time-on-stream $t$ |
| $\alpha,\beta,\gamma,\varepsilon,\pi$ | constants in Eqs. (30), (31), (42) |
| $\psi(P_i, t)$ | deactivation function, defined by Eq. (8) |

### *Chemical Species*

| | |
|---|---|
| B | benzene |
| D | *p*-diisopropylbenzene |
| E | intermediate formed by decomposition Dl or Dl* |
| H | hydrogen |
| $I_1l$ |  |
| $I_2l$ |  |
| l | $H^+Y^-$ |

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