Rate Temperature Maxima for the Olefin Disproportionation Reaction

A. J. MOFFAT AND ALFRED CLARK

Phillips Petroleum Company, Bartlesville, Oklahoma

Olefin disproportionation on cobalt molybdate-alumina shows a rate-temperature maximum which is caused by the reversible deactivation of sites superimposed on the irreversible poisoning of sites. A Langmuir-Hinshelwood model applied to a heterogeneous surface can be used to describe both the general kinetics and the reversible rate-temperature maxima which are observed.

INTRODUCTION

Many heterogeneous catalytic reactions show a maximum in rate as a function of temperature. Among these reactions are: ethylene polymerization over chromium oxide-silica-alumina (*1, 2*), hydrogen-deuterium exchange and parahydrogen conversion on a variety of catalytic surfaces (*3, 4, 5*), and olefin disproportionation on molybdena-alumina and cobalt molybdate-alumina (*6, 7*). These rate-temperature maxima fall into two general categories. The most common class is the *irreversible* poisoning or deactivation of the catalyst surface which has been reported to account for the observed rate maxima in ethylene polymerization (*2*) and olefin disproportionation (*7*). The second type of rate maxima is the *reversible* deactivation of the catalyst surface with increasing temperature. Hydrogen-deuterium exchange and parahydrogen conversion are prime examples of reversible rate maxima which have been observed. These reversible rate maxima cannot always be attributed to changes in catalyst structure with increasing temperature, since these catalysts are generally stabilized at high temperature before use. The true explanation of this reversible behavior directly involves the mechanism or mechanisms of the reaction.

NOMENCLATURE

A	Arrhenius preexponential factor
(C_2)	Ethylene concentration
(C_3)	Propylene concentration
(C_4)	Butylene concentration
$(C_3)_0$	Initial propylene concentration
C_j	Concentration of impurities
E	Arrhenius activation energy
E_i	Arrhenius activation energy of ith sites
K_3	Propylene adsorption coefficient
K_{eq}	Reaction equilibrium constant (a value of 0.12 was used)
K_i	Propylene adsorption coefficient of ith sites
K_j	Impurities adsorption coefficient
k_f	Forward rate constant
k_r	Reverse rate constant
P_3	Propylene pressure
ΔS	Differential entropy of adsorption excluding configurational entropy
t	Time
V	Volumetric flow rate
$V_c f$	Catalyst volume × void fraction
x	Fraction of propylene converted
θ_3	Fraction of sites covered by propylene

METHODS

An integral flow reactor was used in this study because of the broad temperature and activity ranges which were studied. A
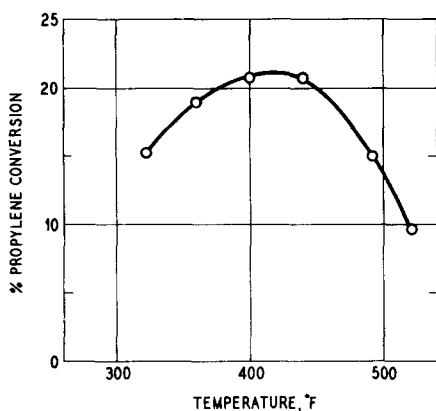
FIG. 1. The effect of temperature on the disproportionation of propylene on cobalt molybdate-alumina.

quartz reactor was used for most of the runs near atmospheric pressure. When conversions were measured as a function of pressure, a stainless steel reactor of similar design was used. In-line glc analyses were made using a Hewlett-Packard 5752B gas chromatograph. The relative response glc data of Messner et al. (8) were used in the treatment of data.

The catalyst used was cobalt molybdate on alumina (20–40 mesh). Each catalyst specimen was air activated at 1100°F for 12 hr followed by a 3.5 hr helium purge at 1100°F. The activated catalyst was cooled in a static helium atmosphere to the desired temperature of operation, at which point propylene or a propylene-helium reactant was introduced. Phillips research grade propylene was passed through activated magnesium oxide and a Linde 10X Molecular sieve before use. Both the air and helium used in catalyst activation were passed through Molecular sieve columns to remove traces of water.

RESULTS AND DISCUSSION

A. Irreversible and Reversible Site Deactivation

Figure 1 shows a plot of conversion vs. temperature for the disproportionation of propylene over Co-Mo-Al$_2$O$_3$ catalyst. The rate maximum noted could be caused by "an increasingly rapid rate of catalyst de-

cay as the temperature is raised" as was suggested by Bradshaw et al. (7). In this case, there would be an irreversible loss of catalyst activity. If this loss of activity with increasing temperature is reversible, then an increase in activity should be noted as the temperature is lowered to the temperature of maximum conversion (T_{max}). Figure 2 shows what happens to conversion (or reaction rate) when a given catalyst sample is subjected to three heating-cooling cycles at constant space velocity. In each cycle there was an irreversible loss of catalyst activity with no rate maxima noted on the cooling leg of the cycles. These results at first glance suggest that the principal cause of these rate maxima is the irreversible poisoning of catalyst sites, as was suggested by Bradshaw et al. (7).

Since poisoning could mask reversible deactivation, if it exists, the following procedure was used to test for reversible deactivation. Usually at temperatures above the rate maximum, the loss of catalyst activity was noted as a function of time at constant space velocity. After this time dependent decline in activity had assumed a predictable behavior, a rapid temperature change was introduced to cause a rate change
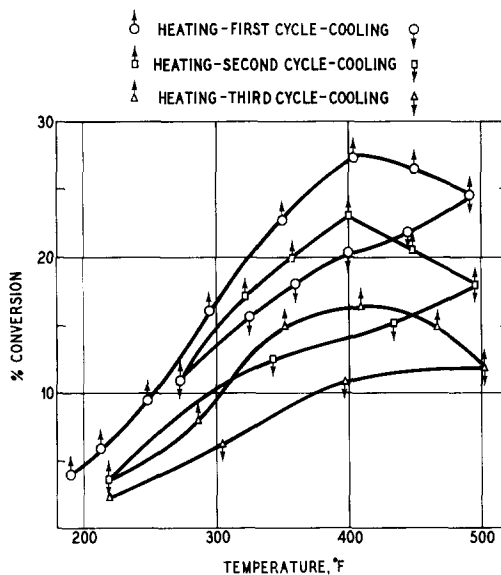

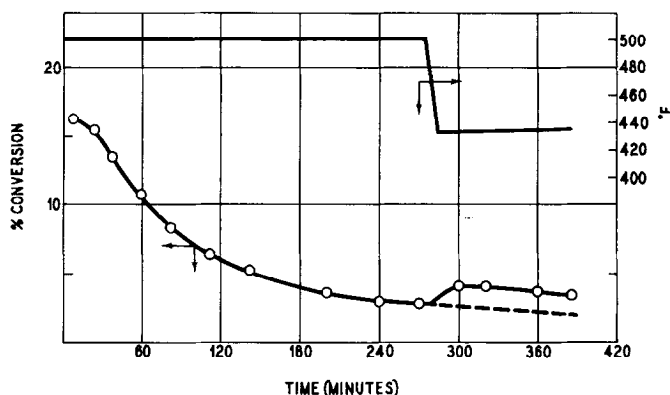FIG. 2. The effect of heating-cooling cycles on rate maxima.

FIG. 3. The effect of decreasing temperature on conversion above T_{max}.

which was superimposed upon the time dependent irreversible deactivation curve. In Fig. 3, for example, a drop in temperature from 500 to 433°F caused a 60 to 70% increase in conversion (rate). In Fig. 4, an increase in temperature from 430 to 500°F caused a disproportionate drop in rate that could not be accounted for by irreversible poisoning of catalyst sites. Also, a temperature drop from 500 back to 430–436°F in the same run resulted in a 40–50% increase in conversion. These two runs were typical of several which were made under similar conditions. Hence, it was concluded that there is a reversible deactivation of sites superimposed upon the irreversible poisoning of sites.

B. Basic Kinetics

It is suggested that perhaps these reversible rate-temperature maxima are a simple function of the surface reaction mechanism. Hence, an understanding of the basic reaction mechanism could help explain the observed rate maxima or vice versa.

Evidence for a four-center mechanism in the disproportionation reaction is abundant (7, 9, 10). However, the way in which two olefins are brought together on the catalyst surface to form this complex is not too clear. Begley and Wilson (11) claim that a Rideal model fits their experimental data in the 300 to 900 psig pressure range on
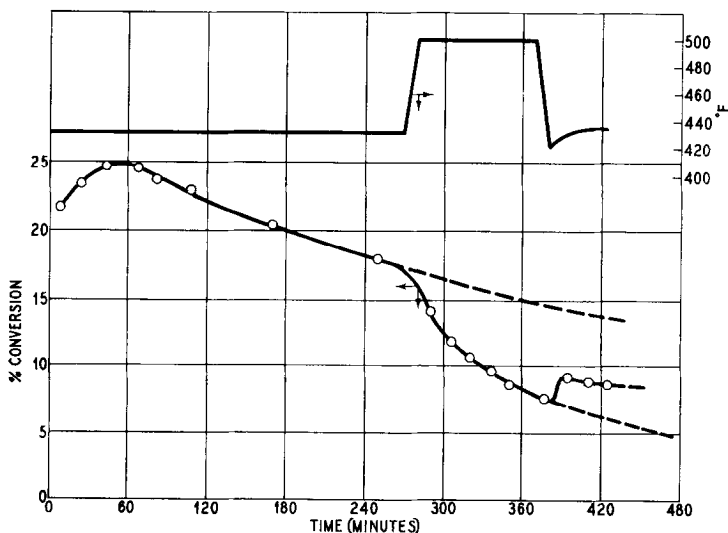

FIG. 4. The effect of temperature on conversion above T_{max}.

a tungsten-silica catalyst, while the data of Lewis (12) on Co-Mo-Al$_2$O$_3$ are best correlated by a Langmuir-Hinshelwood (L-H) model. The L-H model for propylene disproportionation leads to the following expression for the initial rate of the forward reaction:

$$-\frac{1}{2}\left(\frac{dC_3}{dt}\right)_0 = k_f\theta_3{}^2 = \frac{k_fK_3{}^2(C_3)_0{}^2}{[1 + K_3(C_3)_0]^2}. \quad (1)$$

Similarly, the initial forward reaction rate for the Rideal model is:

$$-\frac{1}{2}\left(\frac{dC_3}{dt}\right)_0 = k_f\theta_3(C_3)_0 = \frac{k_fK_3(C_3)_0{}^2}{1 + K_3(C_3)_0}. \quad (2)$$

Using the relationship (see appendix)

$$\left(\frac{dC_3}{dt}\right)_0 = -(C_3)_0\left(\frac{dx}{dt}\right)_0, \quad (3)$$

Eqs. (1) and (2) can be rearranged to give

$$\left[\frac{(C_3)_0}{(dx/dt)_0}\right]^{1/2} = \frac{1}{(2k_f)^{1/2}K_3} + \frac{(C_3)_0}{(2k_f)^{1/2}} \text{ (L-H)} \quad (4)$$

and

$$\left[\frac{(C_3)_0}{(dx/dt)_0}\right] = \frac{1}{2k_fK_3} + \frac{(C_3)_0}{2k_f} \text{ (Rideal).} \quad (5)$$

Hence a plot of the left hand side of Eqs. (4) and (5) vs. initial propylene pressure

TABLE 1

The Effect of Temperature and Pressure on Propylene Disproportionation over Co–Mo–Al$_2$O$_3$[a]

Run time (min)	Temperature (°F)	Pressure (atm)	Percent conversion	Contact time $(V_c f/V)$ (sec)[b]	$(dx/dt)_0$ (sec^{-1})
48	350	1.36	20.8	0.29	0.956
110	350	1.36	21.5	0.29	0.999
126	350	2.72	19.6	0.29	0.874
140	350	2.72	20.2	0.29	0.910
156	350	4.08	19.3	0.29	0.856
172	350	4.08	19.5	0.29	0.868
184	350	5.44	18.3	0.29	0.803
200	350	5.44	18.5	0.29	0.809
222	350	1.36	22.6	0.29	1.048
306	300	1.36	17.5	0.31	0.703
322	300	1.36	17.7	0.31	0.714
350	300	2.72	14.4	0.31	0.552
374	300	2.72	14.3	0.31	0.546
394	300	4.08	12.7	0.31	0.474
408	300	4.08	12.8	0.31	0.478
424	300	5.44	11.8	0.31	0.435
438	300	5.44	11.8	0.31	0.435
454	300	1.36	17.7	0.31	0.714
504	250	1.36	12.5	0.33	0.437
518	250	1.36	12.1	0.33	0.422
532	250	2.72	9.5	0.33	0.319
546	250	2.72	9.5	0.33	0.319
560	250	4.08	7.9	0.33	0.262
574	250	4.08	8.0	0.33	0.264
588	250	5.44	6.9	0.33	0.224
602	250	5.44	6.9	0.33	0.224
618	250	1.36	12.2	0.33	0.425
632	250	1.36	12.3	0.33	0.428

[a] A 0.40-g catalyst sample was used.

[b] A void fraction of 0.4 was arbitrarily chosen. WHSV = 10.4 at 1.36 atm, 20.8 at 2.72 atm, 31.2 at 4.08 atm, and 41.6 at 5.44 atm.
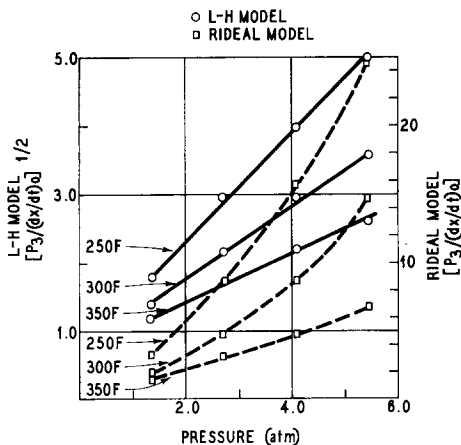
FIG. 5. A comparison of L-H and Rideal models.

should differentiate between the L-H and Rideal models.

Table 1 compares the effects of temperature and pressure on disproportionation kinetics. This comparison was made on an activated catalyst specimen at temperatures below T_{max}, at constant activity, and at approximately constant contact times. The values of $(dx/dt)_0$ were calculated from conversion data as shown in the appendix. Figure 5 shows that a linear plot is obtained for the L-H model (Eq. 4), which is in agreement with the conclusions of Lewis (12) that the data for this type of catalyst is best correlated by the L-H model.

C. Rate Temperature Maxima Criterion

The simplest and perhaps the most obvious explanation for this reversible rate maxima behavior can be derived from Eq. 1 for the L-H model. By making the substitutions

$$k_f = Ae^{-E/RT} \quad \text{and} \quad K_3 = e^{\Delta S/R}e^{-\Delta H/RT}$$

into Eq. 1, the initial rate expression becomes:

$$-\frac{1}{2}\left(\frac{dC_3}{dt}\right)_0 = r_0$$

$$= \frac{Ae^{-E/RT}e^{2\Delta S/R}e^{-2\Delta H/RT}(C_3)_0{}^2}{[1 + e^{\Delta S/R}e^{-\Delta H/RT}(C_3)_0]^2}. \quad (6)$$

By taking the derivative of the rate, r_0, with respect to temperature and setting the result equal to zero, one obtains

$$\frac{\Delta H}{RT_{max}} = \ln\left[-\left(\frac{E\beta}{E + 2\Delta H}\right)\right], \quad (7)$$

where $\beta = (C_3)_0 \, e^{\Delta S/R}$.

Assuming that ΔH is always negative (exothermic adsorption), the criterion for the existence of a rate maximum is:

$$|\Delta H| > \frac{E(\beta + 1)}{2} \quad (8)$$

or, since ΔS is negative and β is usually much less than unity,

$$|\Delta H| > \frac{E}{2}. \quad (9)$$

Hence, all that is necessary for the existence of a rate-temperature maximum is that the absolute magnitude of the heat of adsorption be greater than ½ of the Arrhenius activation energy. The above derivation assumes that ΔH, E, and ΔS do not change appreciably with temperature.

A rate-temperature maximum criterion similar to this was derived by Maatman et al. (13) for cumene cracking on silica-alumina. However, no rate maximum was observed, and it was assumed that the basic criterion was not met.

D. Rate Maxima Shifts

Equation 7 can be rewritten as

$$T_{max} = \frac{\Delta H}{R \ln\left\{-\left(\frac{E}{E + 2\Delta H}\right)\right\} + \Delta S + R \ln(C_3)_0}, \quad (10)$$

which indicates that a decrease in pressure should shift T_{max} to a lower temperature and thereby make it possible to separate the reversible and irreversible site deactivation effects. Several runs were made at various propylene pressures and the results are summarized in Table 2. There was a perceptible shift in T_{max}, but the shift was not enough to separate the reversible and irreversible effects completely.

Equation (10) was derived for the idealized L-H model on a homogeneous surface. If the surface is homogeneous, then T_{max} should be completely independent of

TABLE 2

THE EFFECT OF PROPYLENE PRESSURE ON T_{max}

P_3 (atm)	T_{max} (°F)
1.00	450
0.16[a]	440
0.021[a]	400

[a] Helium as a diluent.

the level of catalyst activity. If, however, the surface is heterogeneous, T_{max} should shift markedly as catalytic activity is reduced by the preferential poisoning of the more energetic sites. In a variety of runs in which conversion was measured as a function of time, the irreversible decline in catalyst activity did not follow a first order relationship (see Figs. 3 and 4). It appeared that the surface was heterogeneous and that the more energetic sites were preferentially poisoned.

Three runs were made at three different levels of catalyst activity on the same catalyst specimen to see if T_{max} changed with catalyst activity. Before each run, the catalyst activity was lowered via irreversible poisoning or coking at 500°F. The temperature was first decreased rapidly to approximately 30–40°F above T_{max} after which the temperature was lowered slowly through and below the T_{max} region while glc analyses were being made. T_{max} could be observed to within ±20°F using this procedure. Table 3 shows that T_{max} is markedly dependent upon catalyst activity.

TABLE 3

THE EFFECT OF CATALYST ACTIVITY ON T_{max}

Approximate % of initial activity	T_{max} (°F)
45	~440
16	~400
4	~360

If the surface is heterogeneous as the data above indicate, then a rate maximum criterion could exist for each set of site energies:

$$\frac{\Delta H_i}{R(T_{max})_i} = \ln\left[-\left(\frac{E_i\beta_i}{E_i + 2\Delta H_i}\right)\right]. \quad (11)$$
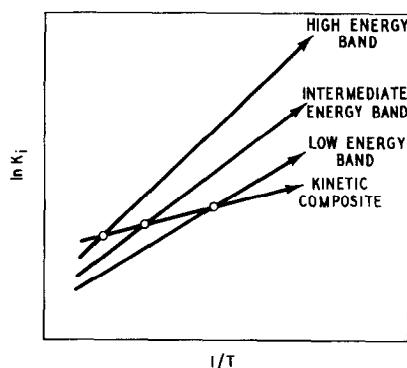

FIG. 6. ln K_i vs. $1/T$ for three different bands of sites compared to the kinetic composite of sites.

An increase in temperature could result in the reversible activation of high energy sites and deactivation of low energy sites. Hence, a different band of sites would be used at each temperature. Activation energies and heats of adsorption calculated using Eqs. (1) or (6) would have little theoretical meaning because one would be comparing the gross activity of different sets of sites at different temperatures. The number of sites in each set as well as the activity per site could and probably does vary considerably. As temperature increases, $|\Delta H_i|$ increases also;

$$\ln K_i = -\frac{\Delta H_i}{RT} + \text{const} \quad (12)$$

and the value of K_i could change or even remain constant depending on the distribution site energies. Figure 6 makes a comparison of how one might expect the adsorption coefficient, K_i, to vary with $1/T$ for three different bands of sites with the high energy band having the largest heat of adsorption, etc. The kinetic composite plot shows that the value of K_i may well be correct for each band of sites, but since comparisons are being made between different bands at different temperatures, the ΔH value from the kinetic plot would always be considerably less than the true heat of adsorption.

Equation 1 and the data in Table 1 were used to calculate the activation energy (8.2 kcal) and heat of adsorption (−2.8 kcal). This kinetically measured ΔH is much smaller than expected and may be as much

as an order of magnitude too small. A low ΔH value is consistent with a heterogeneous surface where sites are being activated and deactivated reversibly in compliance with the general criterion

$$|\Delta H_i| > \frac{E_i}{2}. \qquad (13)$$

It is concluded that a Langmuir-Hinshelwood model applied to a heterogeneous surface is consistent with (a) the observed kinetics below T_{max}, (b) the observed reversible rate-temperature maxima, (c) the shifts in T_{max} with decreasing propylene pressure, (d) the decrease in T_{max} with decreasing catalyst activity, and (e) the abnormally low apparent heat of adsorption.

REFERENCES

1. AYSCOUGH, P. B., EDEN, C., AND STEINER, H., J. Catal. 4, 278 (1965).

2. ZAKHAROV, V. A., ERMAKOV, YU. I., et al., Kinet. Katal. 9, No. 3, 605 (1968).

3. HOLM, V. C. F., AND BLUE, R. W., Ind. Eng. Chem. 44, 107 (1952).

4. ASHMEAD, D. R., ELEY, D. D., AND RUDHAM, R., J. Catal. 3, 280 (1964).

5. HARRIS, J. R., AND ROSSINGTON, D. R., J. Amer. Ceram. Soc. 51, 511 (1968).

6. BANKS, R. L., AND BAILEY, G. C., Ind. Eng. Chem., Prod. Res. Develop. 3, 170 (1964).

7. BRADSHAW, C. P. C., HOWMAN, E. J., AND TURNER, L., J. Catal. 7, 269 (1967).

8. MESSNER, A. E., ROSIE, D. M., AND ARGABRIGHT, P. A., Anal. Chem. 31, 230 (1959).

9. CLARK, A., AND COOK, C. F., J. Catal. 15, 420–424 (1969).

10. MOL, J. C., MOULIJN, J. A., AND BOELHAUMER, C., Chem. Comm., 633 (1968).

11. BEGLEY, J. W., AND WILSON, R. T., J. Catal. 9, 375 (1967).

12. LEWIS, M. J., Dissertation, Virginia Polytechnic Institute, Blacksburg, Virginia, 1969.

13. MAATMAN, R. W., LEENSTRA, D. L., LEENSTRA, A., BLANKESPOOR, R. L., AND RUBINGH, D. N., J. Catal. 7, 1 (1967).

APPENDIX

Starting with an equation for the L-H model similar to one used by Begley and Wilson (11),

$$-\frac{\frac{1}{2}V\,d(C^{\xi})}{f\,dV_c} = \frac{k_f K_3{}^2(C_3{}^2) - k_r K_2 K_4(C_2)(C_4)}{[1 + K_2(C_2) + K_3(C_3) + K_4(C_4) + \Sigma K_j C_j]^2}, \qquad (14)$$

and assuming that $K_2 = K_3 = K_4$ and that $\Sigma\,K_j C_j$ is small, the rate equation reduces to

$$-\frac{\frac{1}{2}V\,d(C_3)}{f\,dV_c} = \frac{k_f K_3{}^2\left[(C_3)^2 - \dfrac{(C_2)(C_4)}{K_{eq}}\right]}{[1 + K_3(C_3)_0]^2}. \qquad (15)$$

Let x equal the mole fraction of propylene converted to products; then

$$(C_3) = (1 - x)(C_3)_0, \qquad (16)$$

$$(C_2) \approx (C_4) \approx \frac{x}{2}(C_3)_0, \qquad (17)$$

and

$$\frac{d(C_3)}{dt} = -(C_3)_0\frac{dx}{dt}. \qquad (18)$$

Equations (15) through (18) may be combined and rearranged to give

$$\frac{dx}{\left[(1-x)^2 - \dfrac{x^2}{4K_{eq}}\right]} = \frac{2k_f K_3{}^2(C_3)_0{}^2(dV_c/V)f}{(C_3)_0[1 + K_3(C_3)_0]^2}, \qquad (19)$$

which can be integrated to give

$$-2K_{eq}{}^{1/2}\left(\tanh^{-1}\left\{\left[2\left(1 - \frac{1}{K_{eq}}\right)x - 2\right]K_{eq}{}^{1/2}\right\} - \tanh^{-1}(-2K_{eq}{}^{1/2})\right)$$
$$= \frac{2k_f K_3{}^2(C_3)_0(V_c/V)f}{[1 + K_3(C_3)_0]^2} \qquad (20)$$

or

$$\left(\frac{dx}{dt}\right)_0 = [\text{lhs of Eq. 20}]\left(\frac{V}{V_c f}\right)$$
$$= \frac{2k_f K_3{}^2(C_3)_0}{[1 + K_3(C_3)_0]^2}. \qquad (21)$$

A similar treatment for the Rideal model leads to

$$\left(\frac{dx}{dt}\right)_0 = [\text{1hs of Eq. 20}]\left(\frac{V}{V_c f}\right)$$

$$= \frac{2k_f K_3(C_3)_0}{1 + K_3(C_3)_0}. \quad (22)$$

The Rideal model could also give a rate-

temperature maximum in which the basic criterion is

$$|\Delta H| > E(\beta + 1), \quad (23)$$

which differs from that for the L-H model.