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Reaction Paths for Decyclization of Methylcyclopentane Over Pt/Al_2O_3 Catalyst

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It is shown that the decyclization of methylcyclopentane on dual-functional Pt/Al_2O_3 catalyst can proceed by an acid-dependent route in addition to an acid-independent platinum catalyzed mechanism. Evidence is based on data obtained using poisoning techniques, in which either the platinum function, or acid function, or both, were deactivated, and also by using the mixed catalyst technique. With only the monofunctional platinum mechanism operative, the distribution of decyclization products is nearly statistical; with only the acid-dependent route, the distribution suggests a carbonium ion mechanism. The observed hydrogen dependency of the acid-catalyzed reaction is consistent with simultaneous monofunctional acid and dual-functional modes of operation.

INTRODUCTION

Pt/Al_2O_3 catalysts have two distinct catalytic functions: hydrogenation–dehydrogenation activity and acid activity.

The Pt/Al_2O_3 catalyzed interconversion of cycloparaffins and paraffins (cyclization–decyclization) is a reaction of considerable commercial importance. There is a great deal of evidence for an acid independent cyclization–decyclization route catalyzed monofunctionally by platinum (*1–3*). On the other hand, Haensel (*4*) has suggested that the decyclization of methylcyclopentane is promoted by acid sites, while Iijima *et al.* (*5*) have presented evidence that this reaction takes place on two different kinds of sites. One type of site is platinum which, while highly active, is easily poisoned by low levels of either sulfur or coke. The other type of site, while less active, is also less affected by the poison and has been suggested by Iijima to be the acid sites of the alumina carrier. In this paper, we present further evidence for an acid dependent decyclization reaction on Pt/Al_2O_3 catalysts and provide some insight into the mechanism of this reaction.

EXPERIMENTAL

The results reported here were obtained in an all-glass, high-pressure reactor. The catalysts were ground to 100–200 mesh and dispersed in 100–200 mesh Pyrex to give a 4-cc bed. Unless noted otherwise, the catalyst was a Pt/Al_2O_3 reforming catalyst (RD 150.6, 0.61% Pt, and 0.67% Cl). The reaction conditions for all runs were: temperature = 900°F and hydrocarbon partial pressure = 1.13 atm. Except where noted, the hydrogen partial pressure was 33.9 atm. In regard to the data given in Tables 1, 2, and 4, and in Figs. 1 and 2, at any specified set of reaction conditions the level of conversion was varied by changing the contact time. These data were obtained using weight hourly space velocities in the range 24–1900.

A low-chlorine Pt/Al_2O_3 catalyst was prepared by the following procedure: The RD 150.6 catalyst was reduced for 2 hr at 450°F, after which it was heated to 950°F and cooled, all under flowing hydrogen. The catalyst was then subjected to four 30-min extractions with 1.5–2 volumes of 5 wt% aqueous ammonia at 150°F. After the fourth treatment, the extract tested free of chloride ion. Two more ammonia extractions were made, followed by four water extractions. The catalyst was then dried for 16 hr in air at 230°F and finished with two 2-hr hydrogen treats—the first at 450°F and the second at 900°F. The catalyst now analyzed 0.59 wt% Pt and 0.04 wt% Cl. Since the results from this catalyst were to be compared to those from a mixed catalyst, a portion was ball-milled to 5 μ size, pelleted, crushed, and sized to 100–200 mesh.

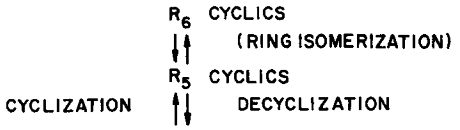
The alumina had been prepared by reaction of aluminum with water in the presence of mercuric acetate and had a surface area of 329 m^2/g.

Mixed catalysts were prepared using the technique of Weisz and Swegler (*6*). Each component was crushed, sized to 100 mesh, and ball-milled (~20 hr) until its particle diameter was 5 μ or less. About 3 g of composite catalyst was made up by mixing appropriate amounts of each of the components. The composite catalyst was then ball-milled an additional 2–3 hr, pelleted, crushed, and sized to 100–200 mesh.

RESULTS AND DISCUSSION

Poisoning Experiments with Sulfur

A series of experiments was carried out in which the initial segment of the reaction path for methylcyclopentane conversion was determined at various sulfur levels (as thiophene) in the hydrocarbon feed. The reaction system of interest is the three component network



(1)

where R_5 cyclics represent methylcyclopentane and methylcyclopentenes; R_6 cyclics are the total of cyclohexane, cyclohexene, and benzene; and paraffins are defined as hexane plus hexane converted to C_1–C_5 paraffins. The pertinent data are given in Table 1 and shown graphically in the trilinear diagram of Fig. 1. As can be seen, the reaction path is, at first, very sensitive to added sulfur; the direction of the reaction path indicates a rapid attenuation of the decyclization rate relative to the rate of ring isomerization. However, there appears to be no difference between the reaction path obtained with 300 ppm added S, and that obtained with 600 ppm added S, in spite of the fact that under these conditions there is still a significant decyclization rate. The question is whether this residual decyclization activity (i.e., with 300 or 600 ppm S)

TABLE 1
RESULTS OF SULFUR POISONING EXPERIMENTS

ppm S added as thiophene	Mole fraction in product		
	R_6 Cyclics	R_5 Cyclics	Paraffins
0	0.008	0.866	0.126
	0.015	0.808	0.177
	0.020	0.652	0.328
	0.027	0.637	0.336
	0.042	0.435	0.523
	0.046	0.353	0.601
	0.053	0.108	0.839
	0.046	0.031	0.923
	0.038	0.011	0.951
15	0.014	0.953	0.033
	0.027	0.914	0.059
	0.039	0.883	0.078
	0.050	0.839	0.111
	0.068	0.794	0.138
	0.096	0.704	0.200
100	0.035	0.924	0.041
	0.057	0.870	0.073
	0.062	0.861	0.077
	0.092	0.791	0.117
	0.106	0.770	0.124
	0.163	0.630	0.207
300	0.033	0.926	0.041
	0.059	0.876	0.065
	0.066	0.862	0.072
	0.089	0.819	0.092
	0.105	0.783	0.112
	0.138	0.712	0.150
600	0.035	0.926	0.039
	0.062	0.875	0.063
	0.065	0.861	0.074
	0.085	0.817	0.098
	0.100	0.785	0.115
	0.148	0.683	0.169

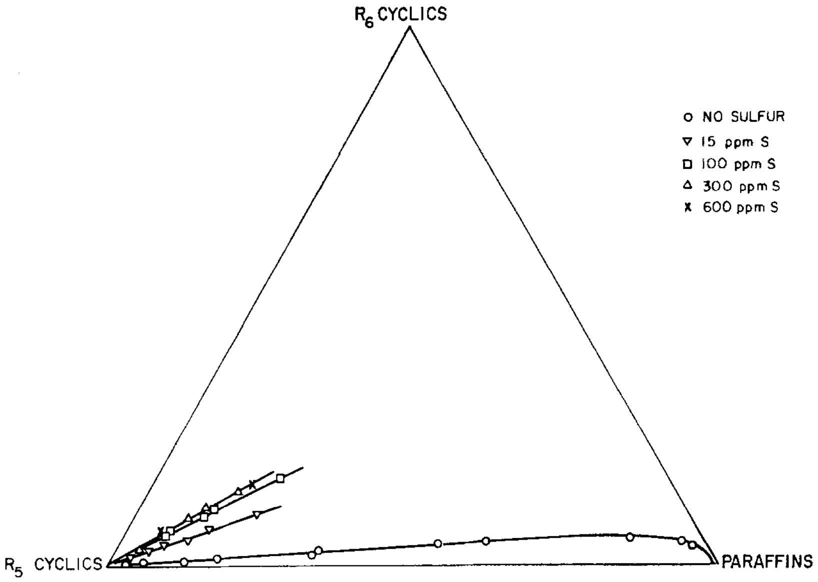


FIG. 1. Methylcyclopentane reaction paths at different sulfur levels.

proceeds by a route other than the monofunctional platinum one, or whether it is a manifestation of a sulfur-resistant platinum activity.

It is of some interest to note that the catalysts had a high hydrogenation–dehydrogenation activity even in our experiments with 600 ppm S. Thus, in all the runs of Table 1 the ratio of cyclohexane to benzene always appeared to be near equilibrium, and the ratio of methylcyclopentane to 1-methylcyclopentene was, within experimental error, found to be constant.

Poisoning Experiments with Nitrogen

In a second series of experiments, 100 ppm N (as *n*-propylamine) was added to the methylcyclopentane to poison the catalyst's acid activity. Because the formation of R_6 cyclics from methylcyclopentane requires acid activity, one would expect essentially no R_6 cyclics in the product if the acid activity were completely quenched. The experimental results are given in Table 2 and shown graphically in the trilinear diagram of Fig. 2. These results are as expected, the reaction path being essentially coincident with the R_5 cyclics–paraffins axis. In addition, the first two rows of Table 3 show that the amine poison appears to be reasonably selective for the acid function; the amount of platinum-catalyzed decyclization is nearly the same at similar contact times.

TABLE 2

RESULTS OF NITROGEN POISONING EXPERIMENTS[a]

Mole fraction in product		
R_6 Cyclics	R_5 Cyclics	Paraffins
0.001	0.736	0.263
0.002	0.574	0.424
0.002	0.333	0.665
0.003	0.177	0.820
0.005	0.105	0.890

[a] 100 ppm nitrogen as *n*-propylamine in methylcyclopentane feed.

TABLE 3

RESULTS FROM VARIOUS POISONING EXPERIMENTS

Poisons added	Relative contact time	Mole fraction in product		
		R_6 Cyclics	R_5 Cyclics	Paraffins
None	1.0	0.038	0.011	0.951
100 ppm N	0.8	0.005	0.105	0.890
600 ppm S	1.0	0.148	0.683	0.169
600 ppm S + 100 ppm N	1.0	0.008	0.974	0.018

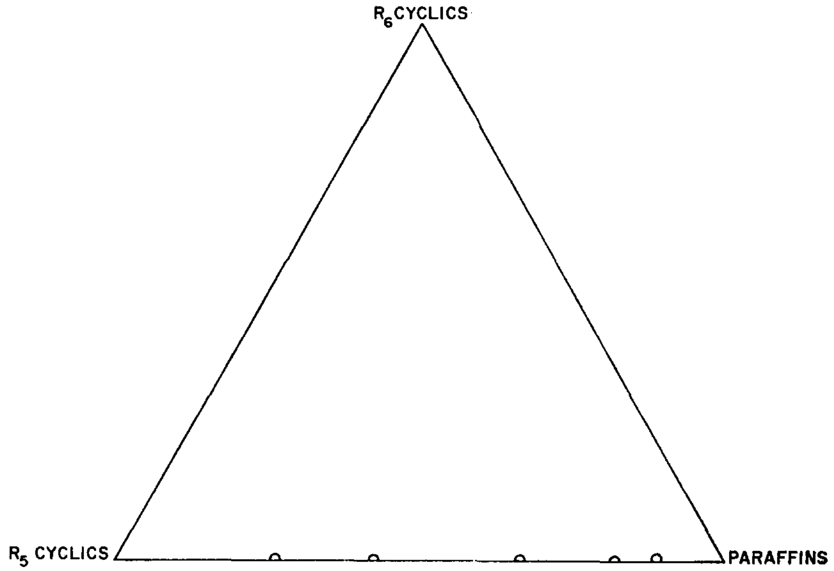


FIG. 2. Methylcyclopentane reaction path with 100 ppm N added as *n*-propylamine.

Double Poisoning Experiment

Because the *n*-propylamine functions as a suitable acid poison, an experiment which had been carried out with 600 ppm S was repeated at identical contact time with both 600 ppm S and 100 ppm N in the charge. If the residual decyclization activity were due to sulfur-resistant platinum, one would expect essentially the same amount of paraffins in the product. If the residual decyclization activity were acid dependent, one would expect essentially no reaction. The results are shown in the last two rows of Table 3. All the results in Table 3 are shown graphically in Fig. 3. It is seen that in the presence of both N and S, both the ring

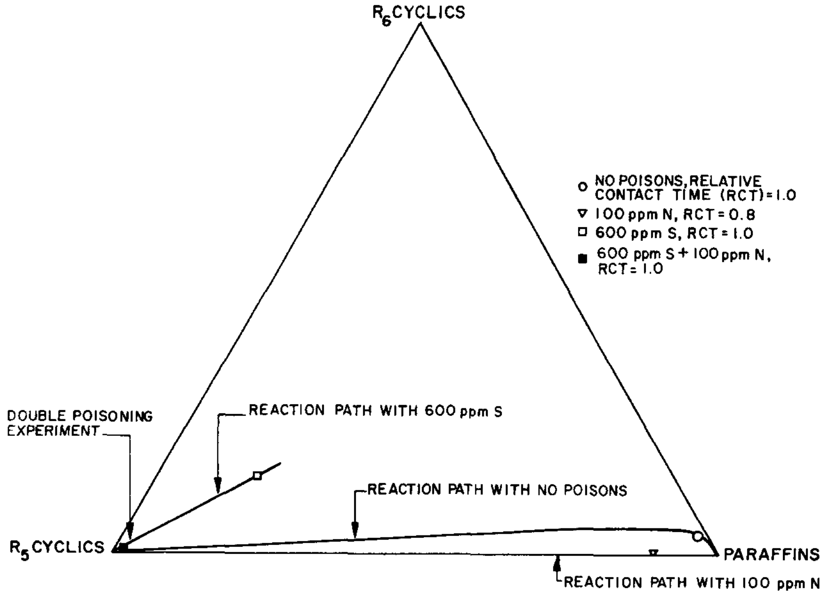


FIG. 3. Results of different poisoning experiments at similar contact times.

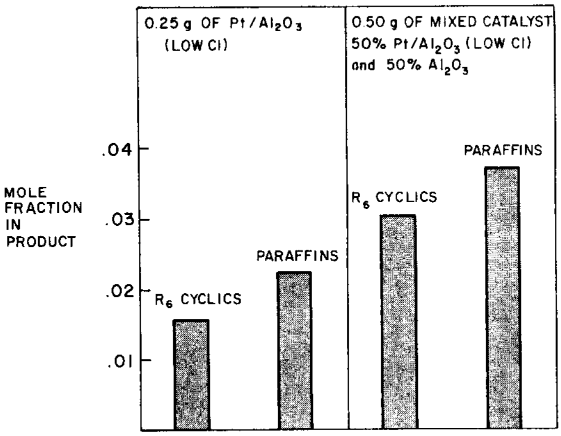


FIG. 4. Results of mixed catalyst experiment.

isomerization and the decyclization reactions are strongly quenched. This result seems to indicate that the residual decyclization activity (i.e., with 300 or 600 ppm S) is proceeding by a route other than the monofunctional platinum one, i.e., a route which is acid dependent.

Mixed Catalyst Experiment

To obtain further evidence for an acid-dependent decyclization route, a low Cl, Pt/Al_2O_3 catalyst was prepared and run with 300 ppm S in the methycyclopentane feed. A mixed catalyst (50% of the low Cl, Pt/Al_2O_3, and 50% Al_2O_3) was prepared and run under identical conditions. Twice as much of the mixed catalyst was used in order to maintain the same amount of Pt component. Thus, the contact time relative to the Pt component is the same, while that relative to the Al_2O_3 component is doubled. As can be seen in Fig. 4, R_6 cyclics and paraffin products increase proportionately when contact time relative to the Al_2O_3 component is increased while that relative to the Pt component is kept constant. This is what would be expected if the residual decyclization activity (i.e., with 300 ppm S) were acid dependent.

Difference in Hexane Distribution

It is of interest to compare product distribution obtained from the monofunctional

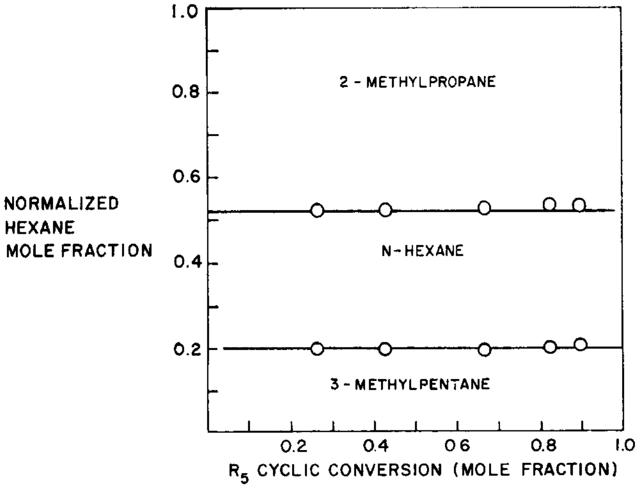


FIG. 5. Hexane distribution from methylcyclopentane decyclization with 100 ppm N as *n*-propylamine.

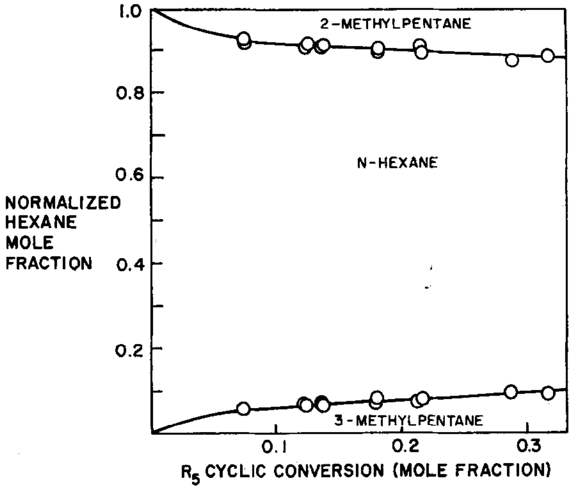
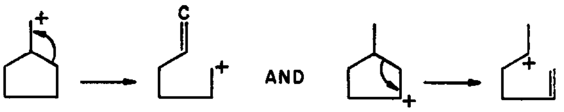


FIG. 6. Hexane distribution from methylcyclopentane decyclization with 300 or 600 ppm S as thiophene.

platinum-catalyzed decyclization with that obtained from the acid-dependent decyclization. In Fig. 5, results are shown for those runs in which the acid activity is poisoned with 100 ppm N and in which the decyclization is occurring only by the monofunctional Pt-catalyzed route. Here the initial distribution is 32% *n*-hexane, 48% 2-methylpentane, and 20% 3-methylpentane. This distribution is very nearly statistical; purely statistical cleavage of the methylcyclopentane ring gives 40% *n*-hexane, 40% 2-methylpentane, and 20% 3-methylpentane. In Fig. 6, the results are shown for those runs in which the Pt activity is depressed with 300 or 600 ppm S, and the decyclization is thought to occur by an acid-dependent route. Here the initial distribution is almost exclusively *n*-hexane, indicating very selective ring cleavage. It can be noted that the reactions are the only two possible carbonium ion transformations which do not involve isomerizing a tertiary or secondary ion to a primary one.



Influence of Hydrogen Partial Pressure on the Acid-Dependent Decyclization Route

In order to shed some light on the nature of the acid-dependent decyclization mechanism, a series of experiments was carried out to examine the effect of hydrogen partial pressure on the rate constant ratio (θ_D/θ_I) for decyclization vs ring isomerization. Data obtained at four different hydrogen partial pressures with 300 ppm S in the hydrocarbon feed are given in Table 4 along with the resultant rate constant ratios.

Also included in Table 4 is the observed ratio of methylcyclopentane to 1-methylcyclopentene. The average ratio at each hydrogen partial pressure is plotted vs hydrogen partial pressure (P_H) in Fig. 7. The relation

$$\frac{[\mathrm{MCP}]}{[1-\mathrm{MCP}^{=}]} = \frac{P_H}{K_P} \qquad (2)$$

for the dehydrogenation reaction is reasonably well-obeyed with a $K_P = 0.306$. These results indicate that, even with 300 ppm S in the feed, the platinum is still an active

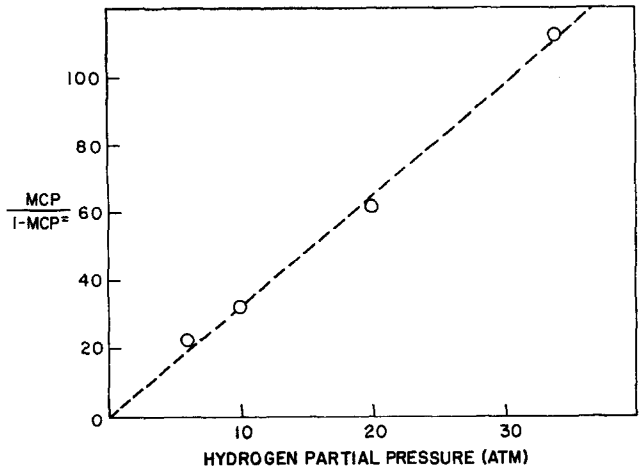


FIG. 7. Observed ratio of methylcyclopentane to 1-methylcyclopentene as a function of hydrogen partial pressure.

TABLE 4

EFFECT OF HYDROGEN PARTIAL PRESSURE ON DECYCLIZATION–RING ISOMERIZATION RATE CONSTANT RATIO[a]

Hydrogen partial pressure	Mole fraction in product			θ_D/θ_I	$\left\{\frac{MCP}{1-MCP^{=}}\right\}$
	R_6 Cyclics	R_5 Cyclics	Paraffins		
33.88 atm	0.033	0.926	0.041	1.1	110.7
	0.060	0.876	0.064		111.0
	0.066	0.862	0.072		114.0
	0.089	0.819	0.092		110.0
	0.105	0.783	0.112		112.3
	0.138	0.712	0.150		113.4
Av					111.9
20 atm	0.058	0.905	0.037	0.68	64.0
	0.102	0.829	0.069		59.6
	0.148	0.747	0.105		60.9
Av					61.5
10 atm	0.051	0.928	0.021	0.43	31.9
	0.060	0.915	0.025		32.1
	0.060	0.913	0.027		32.2
	0.078	0.886	0.036		33.4
	0.100	0.859	0.041		34.2
	0.121	0.832	0.047		31.7
	0.098	0.854	0.048		32.2
Av					32.5
6 atm	0.063	0.917	0.020	0.32	22.0
	0.118	0.847	0.035		22.1
	0.176	0.766	0.058		23.3
Av					22.5

[a] 300 ppm S in methylcyclopentane feed.

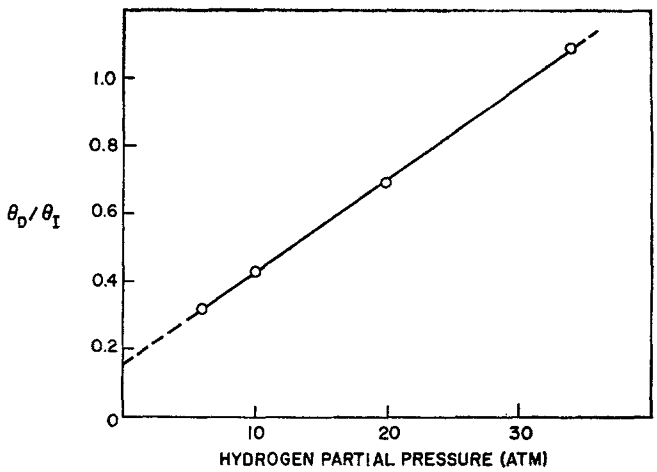


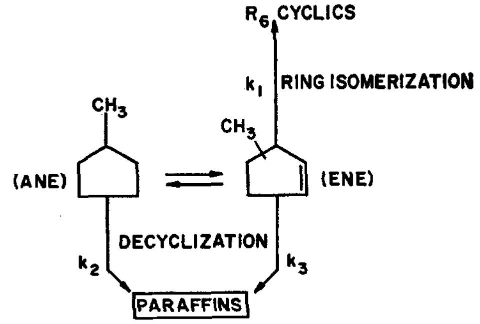
FIG. 8. Observed rate constant ratios for acid dependent decyclization vs ring isomerization as a function of hydrogen partial pressure.

enough hydrogenation catalyst to keep olefins in near equilibrium for dual-functional reactions.

The rate constant ratios (θ_D/θ_I) given in Table 4 are plotted vs hydrogen partial pressure in Fig. 8. The hydrogen dependency is of the form

$$\theta_D/\theta_I = a + b(P_H), \qquad (3)$$

and allows some speculation on the nature of the acid dependent decyclization. It is well-known that ring isomerization is dual-functional—the reaction proceeding via methylcyclopentene (*7*, *8*). The decyclization might (1) be dual-functional, (2) proceed directly from methylcyclopentane, or (3) involve a combination of these two possible schemes. The functional form of Eq. (3) is consistent with the combination route. For example, given the reaction system



initial conversion can be described by the equation

$$\frac{d[\text{Decyclization}]}{d[\text{Ring Isom}]} = \frac{\theta_D[\text{R}_5\text{ Cyclics}]}{\theta_I[\text{R}_5\text{ Cyclics}]} = \frac{k_3[\text{ene}] + k_2[\text{ane}]}{k_1[\text{ene}]} \qquad (5)$$

or

$$\frac{\theta_D}{\theta_I} = \frac{k_3}{k_1} + \frac{k_2[\text{ane}]}{k_1[\text{ene}]}.$$

However, from an equation analogous to (2)

$$\frac{[\text{ane}]}{[\text{ene}]} = \frac{P_H}{K'_p}$$

and

$$\theta_D/\theta_I = \left(\frac{k_3}{k_1}\right) + \left(\frac{k_2}{k_1K'_p}\right)P_H$$

which is of the same form as Eq. (3).

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