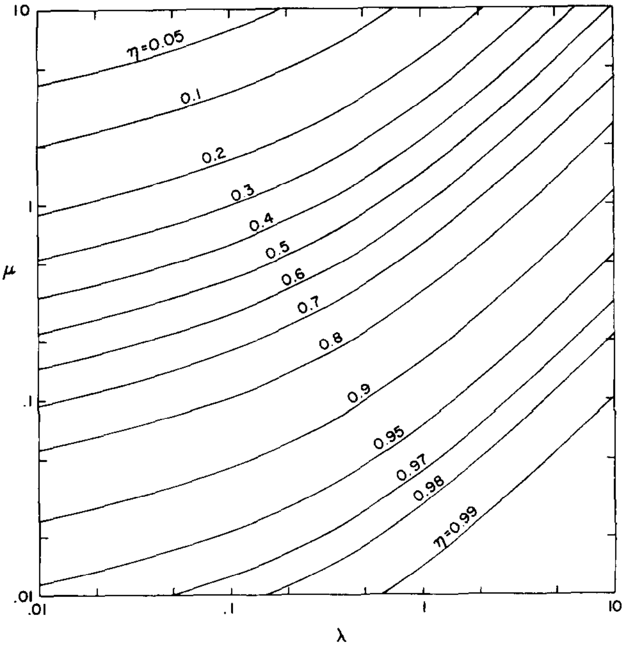

Fig. 1. Contours of constant effectiveness in the plane of the parameters λ and μ.

across whose boundary there is no diffusive flux in the surface. This analysis is being carried out in an ongoing program of research into the theory of diffusion and reaction. A hierarchy of problems involving interactions between adsorbed reactants, heterogeneous surfaces, etc. can easily be envisioned. A range of problems involving finite rates of adsorption and diffusion have been investigated by Amundson and Empie (*4*).

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The Unique Double-Bond Isomerization Properties of a Ruthenium Oxide–Silica Catalyst

An unique stereospecific double-bond isomerization activity has been observed for ruthenium oxide supported on silica gel. Results reported for other heterogeneous catalysts show that in the double-bond isomerization of 1-butene the initial product contains more *cis*-2-butene than *trans*-2-butene, although *trans*-2-butene is thermodynamically favored (*1–5*). Various explanations have been proposed but the reasons for the preference for the *cis*-isomer are not clear (*4*). In contrast to the preference for *cis*, we have observed that over a ruthenium oxide–silica catalyst the initial product contains about three to five times as much *trans*- as *cis*-2-butene (thermodynamic ratio is about two).

EXPERIMENTAL

Data illustrating this unique isomerization preference are presented in Table 1. The catalyst was prepared by impregnating a silica gel with an ethanol solution of $RuCl_3(OH)$ and treating with dry air at 538°C. The finished catalyst contained the equivalent of 4.9 wt % RuO_2 (the oxidation state of the ruthenium was not established). Residue chloride content was 0.03 wt %.

Phillips pure grade hydrocarbons were used. After drying over activated alumina the *trans*-2-butene feed charged to the reactor contained 0.7 wt % *cis*-2-butene while the *cis*-2-butene feed contained 1.5 wt % *trans*-2-butene. No measurable amount of 2-butene was detected in the 1-butene.

RESULTS AND DISCUSSION

The procedure of Haag and Pines (*1*) was used to calculate the relative isomerization rate constants for comparison with relative rates obtained with other heterogeneous catalysts. These calculations are based on the assumption that the reactions are first order in each of the three isomers. The rate constants (k_i) are defined in Fig. 1.

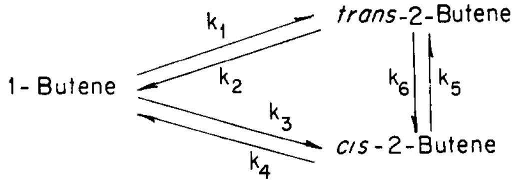

FIG. 1. Schematic representation of the six rate constants involved in the double-bond isomerization of the *n*-butenes.

A comparison of the relative rate constants for ruthenium oxide–silica catalyst along with those obtained by Haag and Pines for an alumina (*1*) and by Heckelsberg and Bailey for a nickel oxide–silica alumina catalyst (*3*) are given in Table 2.

The low values obtained over the ruthe-

TABLE 1

PRODUCT COMPOSITIONS OF FOUR DOUBLE-BOND ISOMERIZATION RUNS[a] USING FOUR DIFFERENT BUTENE FEEDS

Feed	Time (min)[b]	Product analyses (wt %) 1-Butene	*trans*-2-Butene	*cis*-2-Butene	*trans*/*cis*[c]
1-Butene	0	100	0	0	—
	15	78.1	18.4	3.5	5.3
	30	87.5	9.2	3.3	2.8
	45	91.8	6.4	1.8	3.6
	60	92.8	5.3	1.9	2.8
trans-2-Butene	0	0	99.3	0.7	—
	15	3.6	95.5	0.9	10.6
	45	4.5	94.6	0.9	10.5
	85	6.0	92.9	1.1	8.5
cis-2-Butene	0	0	1.5	98.5	—
	15	0.7	2.4	96.9	—
	40	0.3	2.5	97.2	—
Mixed-2-butenes	0	0	51.4	48.6	1.1
	15	3.8	47.8	48.4	1.0
	45	5.8	46.4	47.8	1.0

[a] Reaction conditions: 260°C, 100 psig, 1.5 g feed (g cat.)$^{-1}$ hr^{-1}.

[b] Flow system; time of snap sampling of product.

[c] Thermodynamic equilibrium of *trans*/*cis* at 260°C is 1.7.

TABLE 2
Relative Isomerization Rate Constants

Rate[a] constants	$RuO_2 \cdot SiO_2$ (260°C)	Al_2O_3 (230°C)	$NiO \cdot SiO_2 \cdot Al_2O_3$ (100°C)
k_1	2.7	3.8	8.0
k_2	1.0	1.0	1.0
k_3	0.02	9.1	10.0
k_4	0.01	4.6	1.8
k_5	0.01	2.4	1.5
k_6	0.03	4.6	4.0

[a] k_2 set equal to 1.0.

nium oxide–silica catalyst for the rate constants k_3 to k_6 indicate that *cis*-2-butene does not readily enter the double-bond isomerization reaction over this catalyst either as a reactant or as a product. This suggests the formation of a stable complex of the *cis*-isomer with the transition metal that does not readily react or desorb.

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