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On the Mechanism of 1-Butene Isomerization on Supported Palladium

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The double-bond migration of 1-butene has been studied on supported palladium in the absence of hydrogen. The peculiarity of the reaction is its stereoselectivity towards *cis*-2-butene. The reaction has been kinetically followed both with the integral and differential reactor techniques in the range of temperatures 160°–240°C. The products distribution and the kinetic results suggest that the isomerization occurs through two mechanisms: the former involves two atomic centers and is stereospecific towards the *cis* isomer. The latter instead brings to an equilibrium the mixture of *trans*- and *cis*-2-butenes.

INTRODUCTION

The catalytic effect of palladium on the isomerization of olefins in the presence of hydrogen is well known (*1*, *2*). For instance, in 1-butene the double-bond migration occurs with formation of *trans*- and *cis*-2-butenes; the product distribution is dominated by the competitive processes:

$$(\text{2-olefin})_{\text{gas}} \leftarrow (\text{1-olefin})_{\text{ads}} \rightarrow (\text{paraffin})$$

The (trans/cis) ratio of the 2-olefin corresponds in that case to the thermodynamic equilibrium that favors the more stable 2-trans derivative (*1*).

In the present paper some kinetic results are given on the reaction of 1-butene on supported palladium, carried out in the absence of hydrogen. A peculiarity of the reaction under such conditions is the stereoselectivity towards the cis isomer. The experiments have been performed in a flow system at sufficiently small contact times so as to obtain a negligible conversion due to the alumina employed as support. Taking into account the behavior of the system both with and without hydrogen it has been possible to propose reaction mechanisms for the relevant processes.

EXPERIMENTAL

Material and analysis. The catalyst sample was an alumina-supported palladium obtained by hydrogenation of palladium chloride, the preparation of which has been described elsewhere (*3*). The percentage of dispersed palladium on the alumina surface amounts to 0.484%.

The 1-butene was a Phillips Petroleum Co. pure grade product. Its purity, tested by gas chromatography, was superior to 99.5%, the remaining being *n*-butane. Helium and hydrogen were gas chromatographically pure gases.

The analyses were performed by gas chromatography using an 8-m stainless steel column of benzyl cellosolve on Carbowax 60–80 mesh at 40°C. Helium was used as carrier gas. The 1-butene, *cis*-2-butene, and *trans*-2-butene were completely separated. Under constant gas flow condition the relative retention times were the following: 1-butene, 1; *cis*-2-butene, 1.36; *trans*-2-butene, 1.20.

Equipment and procedure. The differential reactor technique has been employed. Different mixtures of 1-butene and helium, after drying, were preheated (±0.1°C) and fed to a glass tubular reactor (177 mm high, 8-mm diameter) in which the catalytic bed was supported by glass wool.

The stream outgoing from the reactor was directly injected into a gas chromatograph for the analysis. The products present in the reaction mixture and analyzed

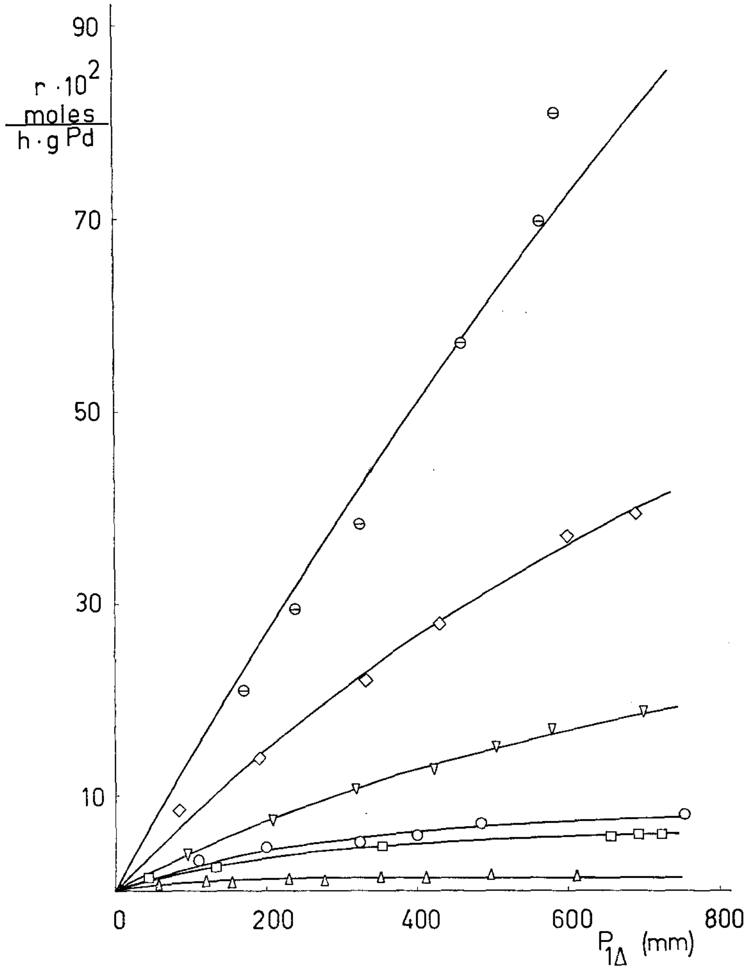

FIG. 1. Reaction rates (moles/ hr g Pd) to give *cis*-2-butene vs. partial pressure of 1-butene. Solid lines from Eq. (2); △, 160°; □, 180°; ○, 190°; ▽, 200°; ◇, 220°; ⊖, 240°.

were 1-butene, *cis*-2-butene, and *trans*-2-butene. Only traces of butane and butadiene were found. It was verified that products derived from a skeletal isomerization were not present.

The contact time t was kept sufficiently low in order to give small conversions ΔX (less than 1%) suitable for a direct evaluation of reaction rate through the ratio $\Delta X/t$.

Preliminary runs revealed that below 160°C it was difficult to obtain a precise determination of the reaction rate. The fresh catalyst samples were run with a reaction mixture for 4 hr at reaction temperature in order to eliminate completely the hydrogen adsorbed during the preparation. This procedure guaranteed good reproducibility of our kinetic data.

Blank runs were performed employing pure alumina as support and previously submitted to the same thermal treatment used for the preparation of the catalyst. It was verified that owing to our small contact time (HGSV^{-1} less than 0.01), the isomerization due to alumina was negligible except at 240°C.* At this temperature the

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* It is necessary to point out that also the absence of an effective thermal treatment of the nonactivated alumina employed kept low its isomerization activity [H. R. Gerberich and W. Keith Hall, J. Catalysis 5, 99 (1966)].

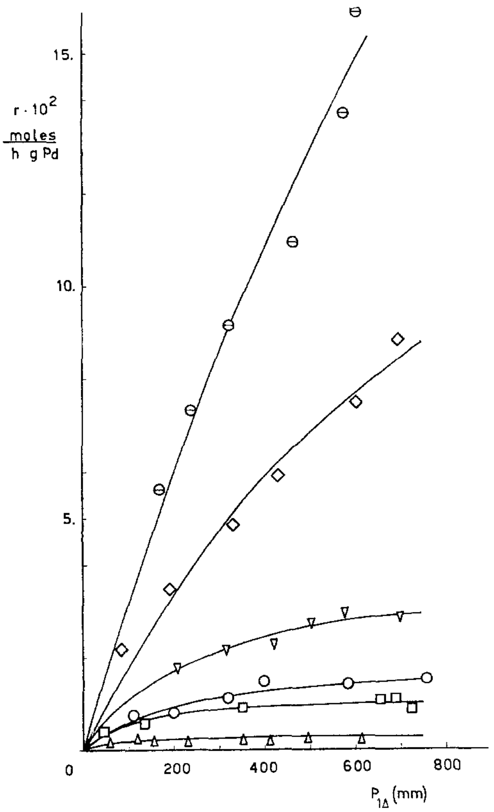


FIG. 2. Reaction rates (moles/ hr g Pd) to give *trans*-2-butene vs. partial pressure of 1-butene. Solid lines from Eq. (3); Symbols as in Fig. 1.

conversion due to alumina was evaluated as less that 6% of the total. The kinetic data at this temperature were so corrected.

RESULTS

Differential kinetic runs were performed at 160°, 180°, 190°, 200°, 220° and 240°C with partial pressures of 1-butene ranging from 40 to 725 mm. The resulting values of the reaction rates for the formation of *cis*-2-butene and *trans*-2-butene are graphically reported in Figs. 1 and 2.

A set of integral kinetic runs was made at 240°C. The same reactor has been employed by working with pure 1-butene; the contact times were increased by increasing the amount of catalyst and by reducing the flow rates. These values varied between 1.5 and 2.7 g of catalyst (alumina plus palladium) and 0.36–3.60 liter STP/hr, respectively. The reaction path is reported in Fig. 3.

Some experiments in the presence of hydrogen were made at 50° and 200°C; a comparison with the runs performed in the absence of hydrogen is given in Table 1. The contact time is conventionally expressed as (W/F), where W is the mass of palladium in the catalyst and F is the molar flow rate of 1-butene. Such an expression represents the true contact time (h) times the ratio of the catalyst density (g Pd/cc) over the 1-butene molar density (moles/cc) at STP. Taking into account the amount of palladium in the catalyst sample this ratio is equal to 119. The comparison between the relative rates of formation of the 2-butenes has to be referred to the conversion degree due to the high reaction rate in the presence of hydrogen.

REACTION MECHANISM AND KINETIC INTERPRETATION

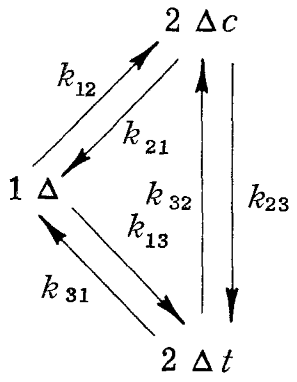
As can be seen in Table 1, in the absence of hydrogen the 1-butene isomerization reaction is quite a bit slower than the corresponding one in the presence of hydrogen. The latter reaction occurs at room temperature, while in the absence of hydrogen it is necessary to work with the same contact time, at 160°C to obtain appreciable conversions. Besides, the reaction is stereoselective in favor of the cis isomer, the ratio (*cis*-2-butene/*trans*-2-butene) being of the order of 5. These facts indicate that the reaction mechanisms are different.

TABLE 1

COMPARISON OF ISOMERIZATION CONVERSION OF 1-BUTENE WITH AND WITHOUT HYDROGEN

	With hydrogen	Without hydrogen
W/F hr g Pd/ (moles 1-butene)	1.96×10^{-3}	4.84×10^{-2}
$P_{1\Delta}$ (mm)	585	580
P_{H_2} (mm)	179	—
% Conversion to 2-butenes	56.8	0.96
trans/cis	1.63	0.174
Temperature (°C)	200°	200°

In the absence of hydrogen the general reaction pattern is the following:



(1)

where 1Δ represents 1-butene; $2\Delta_c$, *cis*-2-butene; and $2\Delta_t$, *trans*-2-butene. The experimental integral reactor data at 240°C have been employed for the analysis of the influence of the $2\Delta_c \leftrightarrows 2\Delta_t$ equilibrium on the reaction kinetics as studied with a differential reactor technique. At 240°C the application of a pseudo-first-order approximation is justified (see later). Therefore the kinetic equations for the scheme 1 are

$$dX_{1\Delta}/dt = -r_{1\Delta}$$
$$= -(k_{12} + k_{13})X_{1\Delta} + k_{21}X_{2\Delta c} + k_{31}X_{2\Delta t}$$
$$dX_{2\Delta c}/dt = r_{2\Delta c}$$
$$= k_{12}X_{.\Delta} - (k_{23} + k_{21})X_{2\Delta c} + k_{32}X_{2\Delta t}$$
$$dX_{2\Delta t}/dt = r_{2\Delta t}$$
$$= k_{13}X_{1\Delta} + k_{23}X_{2\Delta c} - (k_{32} + k_{31})X_{2\Delta t}$$

where X_i is the mole fraction of the *i*th component. The first order differential equation system has been integrated with a straightforward procedure (*4*); the calculated conversions fit well the experimental data (Fig. 3) with the following values of the rate constants:

$k_{12} = 0.657$ moles/hr g Pd
$k_{21} = 0.223$
$k_{23} = 0.500$
$k_{32} = 0.280$
$k_{13} = 0.152$
$k_{31} = 0.029$

The value of the ratio $(r_{2\Delta c}/r_{2\Delta t})$ obtained with the previously evaluated constants, was practically coincident with the value (k_{12}/k_{13}) in the range of conversions corresponding to the differential reactor runs. For instance, even at a conversion of 1.2% of 1-butene the ratios are, respectively,

$$(r_{2\Delta c}/r_{2\Delta t}) = 4.18 \qquad (k_{12}/k_{13}) = 4.32$$

Therefore the cis–trans isomerization and the reactions from 2-butenes to 1-butene can in first approximation be neglected. This fact justifies the employment of a scheme of two parallel irreversible reactions in the interpretation of the differential runs.

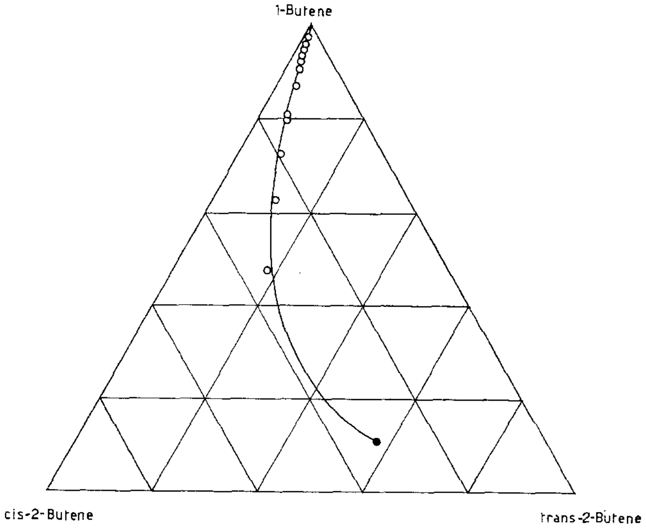


FIG. 3. Reaction path at 240° for 1-butene isomerization: ●, equilibrium point. Curve calculated for the reaction scheme (1) (see text).

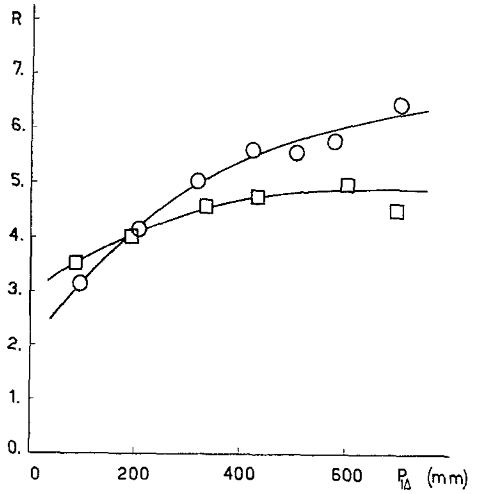


FIG. 4. $R = (cis/trans)$ 2-butene vs. partial pressure of 1-butene; ○, 200°, □, 220°.

As to the exact form of the rate laws for the 1-butene to 2-butenes isomerization it derives from Figs. 1 and 2 that the reaction kinetics can not be comprehensively justified by either the adsorption of 1-butene or desorption of the 2-butenes being the rate-determining step. In fact in the former case the initial reaction rate, that is, at negligible 2-butene concentration, should in every case be proportional to the partial pressure of 1-butene, and in the latter case should be independent of it. Surface reaction appears to be rate-limiting.

Besides by increasing the temperature the reaction rate becomes proportional with respect to $P_{1\Delta}$; this indicates that the reaction is monomolecular with respect to the reagent on the catalyst surface. Moreover the ratio (*cis*-2-butene/*trans*-2-butene) increases with the partial pressure of the reagent (Fig. 4). This could happen if *cis*-2-butene and *trans*-2-butene were formed by a single and a dual-site mechanism, respectively, after adsorption on identical active centers. However this is not our case because such a dependence is not if *cis*-2-butene and *trans*-2-butene were formed by a single and a dual-site mechanism, respectively, after adsorption on identical active centers. However this is not our case because such a dependence is not linear. On the contrary this can be explained with the intervention of two different adsorption types.

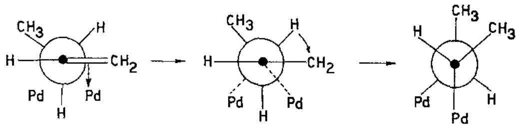


FIG. 5. Mechanism 1 of isomerization.

The preferential formation of the cis isomer can be explained through the participation of two-atom active centers. The suggested reaction mechanism is illustrated in Fig. 5 (Mechanism 1) by means of the Newman diagrams. A molecule of 1-butene is associatively π-adsorbed on a palladium atom; the reaction proceeds through the attack of another palladium atom on the carbonium atom adjacent to the double bond. This brings about an inversion of this carbon atom and an intramolecular shifting of one hydrogen atom. The final result is a 2-butene σ-bonded on two palladium atoms, that after desorption gives the *cis*-2-butene. Because each palladium atom can associatively adsorb one olefin molecule, the reaction should kinetically be described by a dual-site mechanism.

The adsorption on a single metal atom apt to give a double coordination by means of its *d* orbitals (*5*), can explain the formation of *trans*-2-butene. The cleavage of a C–H bond adjacent to the double bond of 1-butene can bring about the formation of a π-allyl complex, as illustrated in Fig. 6 (Mechanism 2). The last step is the shifting of the hydrogen to one end of the chain. A dissociation that leads to formation of the C_4H_7 surface species has been also pro-

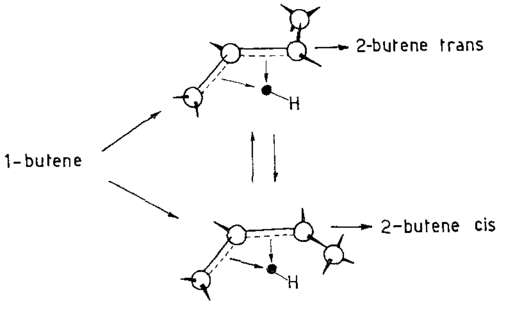


FIG. 6. Mechanism 2 of isomerization; ●, palladium atom.

posed for the interpretation of 1-butene isomerization on cobalt catalysts (*6*). Of course this mechanism is not stereoselective with respect to the trans isomer and a mixture of the *trans*- and *cis*- 2-butenes, probably close to the equilibrium composition, will be obtained by this route.

On the basis of the previously described mechanisms, in the Langmuir-Hinshelwood scheme, the following expressions for the reaction rates are derived:

$$r_{2\Delta c} = k_1 \frac{b_1 P_{1\Delta}}{(1 + b_1 P_{1\Delta})^2} + k_{2c} \frac{b_2 P_{1\Delta}}{(1 + b_2 P_{1\Delta})} \qquad (2)$$

$$r_{2\Delta t} = k_{2t} \frac{b_2 P_{1\Delta}}{(1 + b_2 P_{1\Delta})} \qquad (3)$$

where k_1 and k_{2c} are the rate constants for the formation of the cis derivative through Mechanisms 1 and 2, respectively; k_{2t} is the rate constant for the formation of a *trans*-2-butene by Mechanism 2; b_1 and b_2 are the corresponding equilibrium adsorption constants. The parameters k_1, k_{2c}, k_{2t}, b_1, b_2 were determined by a nonlinear least-square procedure (*3*). Such calculations were made by putting the ratio (k_{2t}/k_{2c}) equal to the equilibrium constant of the reaction $2\,\Delta_t \leftrightarrows 2\,\Delta_c$. The behavior of the reaction rate curves calculated employing such constants (solid lines) and drawn in Figs. 1 and 2 reveals a satisfactory agreement with the experimental data. In Table 2 are reported the kinetic and adsorption constants. Linear plots of log k_i and log b_i vs. $(1/T)$ are given in Figs. 7 and 8. From the slopes and the intercepts of the lines the standard heats and entropies of adsorption and the activation energies were calculated: the obtained values are collected in Table 3.

TABLE 2
REACTION RATES AND ADSORPTION EQUILIBRIUM CONSTANTS

Temperature (°C)	$k_1 \times 10^2$ (moles hr^{-1} g Pd^{-1})	$k_{2t} \times 10^2$ (moles hr^{-1} g Pd^{-1})	$b_1 \times 10^4$ (mm^{-1})	$b_2 \times 10^3$ (mm^{-1})
160°	4.932	0.208	22.0	140.0
180°	21.87	1.139	10.0	10.0
190°	28.67	1.871	8.5	5.0
200°	114.96	3.919	3.1	4.0
220°	263.64	20.50	2.7	1.0
240°	932.0	66.99	1.3	0.48

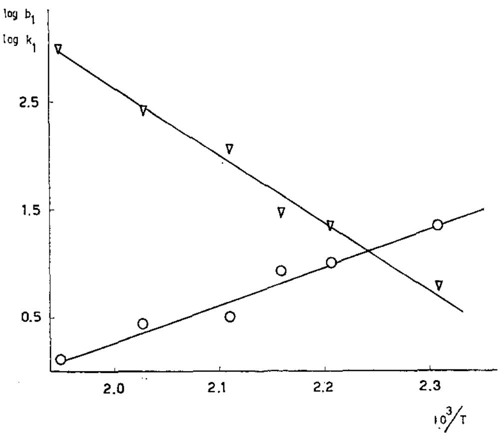


FIG. 7. log b_1, ○; log k_1, ▽ vs. $(1/T)$. Each plot has an arbitary zero for the ordinate.

TABLE 3
ADSORPTION AND KINETIC PARAMETERS

	Mechanism 1	Mechanism 2
$-\Delta H°_a$ (kcal/mole)	15.88 ± 1.81	29.90 ± 2.47
$-\Delta S°_a$ (e.u.)	48.82 ± 3.93	74.20 ± 4.94
$\Delta E^‡$ (kcal/mole)	28.84 ± 1.91	32.37 ± 0.71

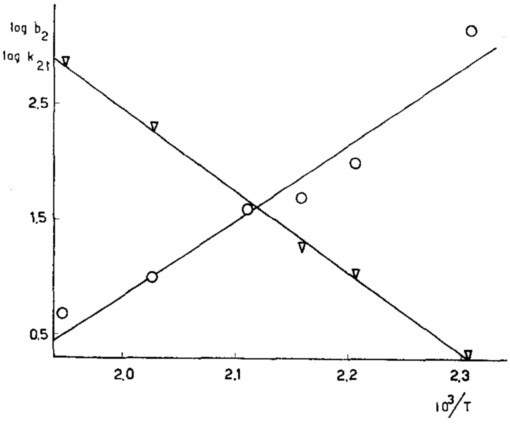


FIG. 8. log b_2, ○; log k_{2t}, ▽ vs. $(1/T)$. Each plot has an arbitary zero for the ordinate.

DISCUSSION

In the light of the values of $\Delta H°_a$ and $\Delta S°_a$ collected in Table 3 it is possible to speculate about the nature of chemisorption types connected with Mechanisms (1) and

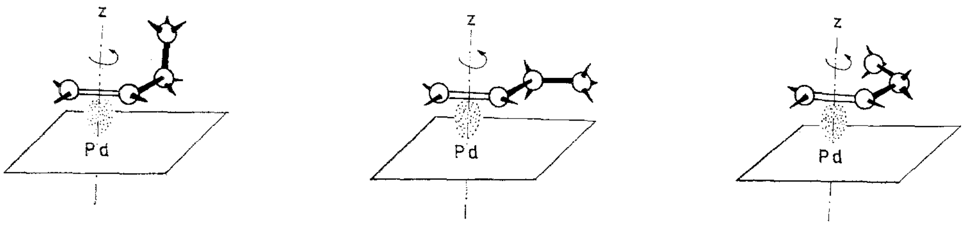


FIG. 9. Two-dimensional rotations of 1-butene-adsorbed molecule.

(2). Since our kinetic analysis shows that the chemisorption of the reactant can be considered an equilibrium process it is possible to perform a statistical thermodynamic analysis of these values.

The entropy of the gaseous 1-butene at 200°C (1 atm) is equal to 84.42 e.u. (*7*). Therefore the entropy of 1-butene adsorbed according to Mechanism (2) is given by $S^\circ_{a(2)} = 84.42 - 74.20 = 10.22$ e.u.

The strong transition metal complex character given to the adsorption state suggests that such an entropy should be due essentially to the vibrations of the palladium–1-butene system plus the configurational entropy. The latter can be obtained by (*8*)

$$S^\circ_c = -R\{\ln \vartheta + [(1-\vartheta)/\vartheta]\ln(1-\vartheta)\}$$

ϑ being the coverage. Taking an average coverage $\vartheta = 0.5$ the value $S^\circ_c = 2.75$ e.u. is derived. The residual $(10.22 - 2.75) = 7.45$ e.u. is of the right order for the vibration of such a kind of system.

The entropy of 1-butene adsorbed according to Mechanism (1) is given by $S^\circ_{a(1)} = 84.42 - 48.82 = 35.60$ e.u. This value is rather high and suggests a high freedom of the adsorbed molecule. The adsorption being localized, consistently with the Langmuir isotherm, such an entropy could be essentially due to the rotation and to surface vibrations of the molecules. The two-dimensional rotation entropy of the adsorbed molecule can be calculated by means of the well-known formula (*8*)

$$S_{\mathrm{rot},2} = R\left\{\ln \frac{1}{\pi\sigma}\left[\left(\frac{8\pi^3 I}{h^2}\right)^{1/2}\right] + \frac{1}{2}\right\}$$

where I is the moment of inertia and σ, the symmetry number. The calculations were made for the three conformations given in Fig. 9; results were averaged, obtaining $S_{\mathrm{ro2,t}} = 9.0$ e.u. In addition, for that adsorption state it is reasonable to assume that the internal vibrations do not change appreciably by adsorption. A straightforward calculation with the standard method (*9*) of the vibrational entropy of 1-butene at 200°C gives $S^\circ_{v,i} = 7.70$ e.u. Taking into account also the configurational term one obtains

$$S_{v,e} = 35.60 - (7.70 + 9.0 + 2.75) = 16.15 \text{ e.u.}$$

that is, the entropy of surface vibrations of the molecule. This value is still high, but de Boer (*10*) has pointed out that also in the range of validity of the Langmuir equation, the molecule might not be strictly immobile because it could still have a translational freedom due to a hopping motion. For instance, an analysis (*11*) of localized adsorption of ammonia on silica-alumina brought to surface vibrational entropy values of the order of 25 e.u. at 300°C. It is interesting to point out that the rotational freedom of the π-adsorbed 1-butene, is consistent with a similar freedom revealed by NMR studies of π-coordinated ethylene in platinum complexes (*12*).

It is significant that also the adsorption energy of Mechanism 2 is quite a bit higher than that of Mechanism 1; this is consistent with previous considerations.

On the whole, it appears that in the isomerization of 1-butene on supported palladium both Mechanisms 1 and 2 are operative; the first one, which forms the cis isomer, prevails over the latter and justifies the stereoselective character of the process.

ACKNOWLEDGMENTS

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REFERENCES

1. BOND, G. C., AND WELLS, B. B., *Advan. Catalysis* **15**, 91 (1964).
2. BOND, G. C., AND RANK, J. S., *Proc. Intern. Congr. Catalysis, 3rd, Amsterdam* **2**, 1225. (North-Holland Publ. Co., Amsterdam, 1965).
3. CARRÁ, S., RAGAINI, V., AND GUELLA, F., *J. Catalysis* **8**, 261 (1967).
4. FROST, A. A., AND PEARSON, R. G., "Kinetics and Mechanism." Wiley, New York, 1962.
5. SIEGEL, S., *Advan. Catalysis* **16**, 123 (1966).
6. PHILLIPSON, J. J., AND WELLS, P. B., *Proc. Chem. Soc.*, p. 222 (1964).
7. "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons." American Petroleum Institute, 1953.
8. HAYWARD, D. O., AND TRAPNELL, B. M. W., "Chemisorption." Butterworth, London, 1964.
9. HOUGEN, O. A., AND WATSON, K. M., "Chemical Process Principles." Wiley, New York, 1957.
10. DE BOER, J. H., "The Dynamical Character of Adsorption." Oxford at the Clarendon Press, 1953.
11. CLARK, A., AND HOLM, V. C. F., *J. Catalysis* **2**, 21 (1963).
12. CRAMER, R., *J. Am. Chem. Soc.* **46**, 217 (1968).