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Electroreduction of Buta-1,2-diene on a Platinum Electrode in Sulphuric Acid Solution

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The electroreduction of buta-1,2-diene on a platinized platinum electrode in 0.5 mol dm^{-3} H_2SO_4 or D_2SO_4 solution has been studied at room temperature.

The reactant is reduced with a current efficiency of *ca.* 100% in a potential region of $220 > \phi/mV$ (RHE) $>$ *ca.* 100 and the main product is butane at $\phi <$ *ca.* 100 mV and *cis*-but-2-ene at $\phi >$ *ca.* 200 mV, respectively. The average deuterium atom number in butane decreases sharply from 6.3-6.6 to 3.9 when hydrogen starts to codeposit ($\phi <$ *ca.* 100 mV), while those of the butenes are 2-3 over the whole potential region studied, $0 < \phi/mV < 220$.

These results are interpreted by taking into account the different orientation of the orbitals of two adjacent π-bonds in buta-1,2-diene on the electrode surface.

We have studied the reduction of lower unsaturated hydrocarbons such as ethylene,[1] propylene,[2] butenes,[3,4] buta-1,3-diene[3,5] and but-2-yne[6] on platinum in acidic solution and we now report the following conclusions.

With respect to olefin reduction we have found the following: (*a*) the Horiuti–Polanyi mechanism *via* a half-hydrogenated intermediate takes place, where the first addition of a hydrogen atom to the adsorbed reactant is reversible but the second hydrogen-atom addition is irreversibly slow; (*b*) an isotopic study of H/D exchange shows that the first addition proceeds *via* two paths with different reaction rates.

In the case of buta-1,3-diene, its transoid and cissoid isomers undergo hydrogenation by keeping their geometrical configuration. In the H region, in which the diffusion of hydrogen through the solution is slower than that of the reactant, hydrogenation of both buta-1,3-diene (1,3-C_4'') and but-2-yne (2-C_4'') produces the three isomeric butenes but at different ratios, *i.e.* but-1-ene (1-C_4') $>$ *trans*-but-2-ene (*t*-2-C_4') $\approx$ *cis*-but-2-ene (*c*-2-C_4') for 1,3-C_4'' and *c*-2-C_4' $\gg$ *t*-2-C_4' $>$ 1-C_4' for 2-C_4''. Such a difference in ratio can be explained in relation to the orientation of the π-bond orbitals as follows. Both 1,3-C_4'' and 2-C_4'' have two π bonds but these are at a conjugate position for the former and at the same pair of the inner carbons for the latter. Hence the orientation of the orbitals of the two π bonds differs in these two reactants. Namely, all the orbitals are oriented in the same direction in 1,3-C_4'', whereas two sets of the pair of π-bond orbitals are oriented in orthogonal directions in 2-C_4''. These orientations play an important role in surface reactions. It has been concluded for the hydrogenation of 1,3-C_4'' that the geometrical configurations of the transoid and cissoid species are preserved on the metal surface as mentioned above and that the transoid isomer produces 1-C_4' and *t*-2-C_4' whereas the cissoid isomer produces *c*-2-C_4'. Preservation of configuration is what would be expected if all the π-bond orbitals were oriented in one direction, *i.e.* toward the surface. The ratio of the sum of 1-C_4' and *t*-2-C_4' to *c*-2-C_4' is almost the same as the thermodynamic ratio of transoid to cissoid isomers in the gas phase. On the other hand, 2-C_4'' is a linear molecule and will interact with the surface by using one of the two π bonds at the inner carbons. Thus direct addition of hydrogen to the interacting π bond will produce predominantly *c*-2-C_4', as is observed.

It is thus of interest to examine the behaviour of buta-1,2-diene (1,2-C_4''), which has two adjacent π bonds whose orbitals are perpendicular to each other. The present work is conducted to examine how the difference in geometrical configuration of the π-bond orbitals among 1,2-C_4'', 1,3-C_4'' and 2-C_4'' affects the product distribution and the isotopic H/D exchange, and to clarify the reaction mechanism.

EXPERIMENTAL

The cell used was a glass vessel consisting of three compartments for test, counter- and reference electrodes. The test electrode was a platinized platinum foil (apparent surface area 2.5 cm^2, roughness factor 770). The reference and counter-electrodes were a platinum wire and a platinized platinum foil, respectively. Potentials were referred to the reversible hydrogen electrode (RHE).

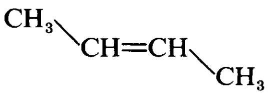
The electrolyte solution was an aqueous solution of 0.5 mol dm^{-3} H_2SO_4 prepared from special reagent-grade H_2SO_4 (Wako Pure Chemical Industries, Ltd) and triply distilled water. For the isotopic study, D_2SO_4 (96-98% D, Merck) and D_2O (99.75% D, Merck) were used. Reaction gas was a mixture of 1,2-C_4'' (12, 20 or 50 Torr)* and nitrogen to atmospheric pressure. The reactant 1,2-C_4'' was distilled *in vacuo* and fractionally collected using a gas chromatograph before use. Nitrogen was purified by passing through a train with silica gel and Ni/Cu net heated at *ca.* 770 K. The hydrogen supplied to the reference-electrode compartment was purified by a commerical purifier (Pd alloy membrane, type LW-06SC, Japan Pure Hydrogen Co).

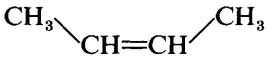
The experimental procedure was the same as described elsewhere.[1] In each run the test electrode was first anodized at 1.8 V (RHE) for 3 min and then aged for 1 min at the potential of the subsequent electroreduction. Electroreduction was initiated by circulating the reaction gas at a constant flow rate of *ca.* 200 cm^3 min^{-1} using a circulation pump (AP-TLC, Matsushita Electric Industrial Co). The electrode potential was controlled by a potentiostat (NP-1A, Nichia Keiki Co) over the range 0-220 mV (RHE). The reduction was carried out for 30 min except for the case of the isotopic study where the reduction was continued for 1-4 h. The reaction gas was occasionally sampled and analysed by a gas chromatograph (023, Hitachi Ltd) with a propylene carbonate column (3ϕ × 5 m) and by a mass spectrometer (M52, Hitachi Ltd). In the mass-spectrum analysis ionization potentials for butane and the butenes were 15.6 and 13.6 eV; corrections for the natural abundance of ^{13}C and for fragmentation were taken into account.

RESULTS

PRODUCT DISTRIBUTION AND KINETIC BEHAVIOUR

There are four possible products from 1,2-C_4'', as in the case of the reduction of 1,3-C_4''. They are


(*trans*-but-2-ene)


(*cis*-but-2-ene)

$CH_2{=}CH{-}CH_2{-}CH_3$ (but-1-ene)

$CH_3{-}CH_2{-}CH_2{-}CH_3$ (butane)

and will be denoted as *t*-2-C_4', *c*-2-C_4', 1-C_4' and C_4, respectively.

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* 1 Torr ≡ 101 325/760 Pa.

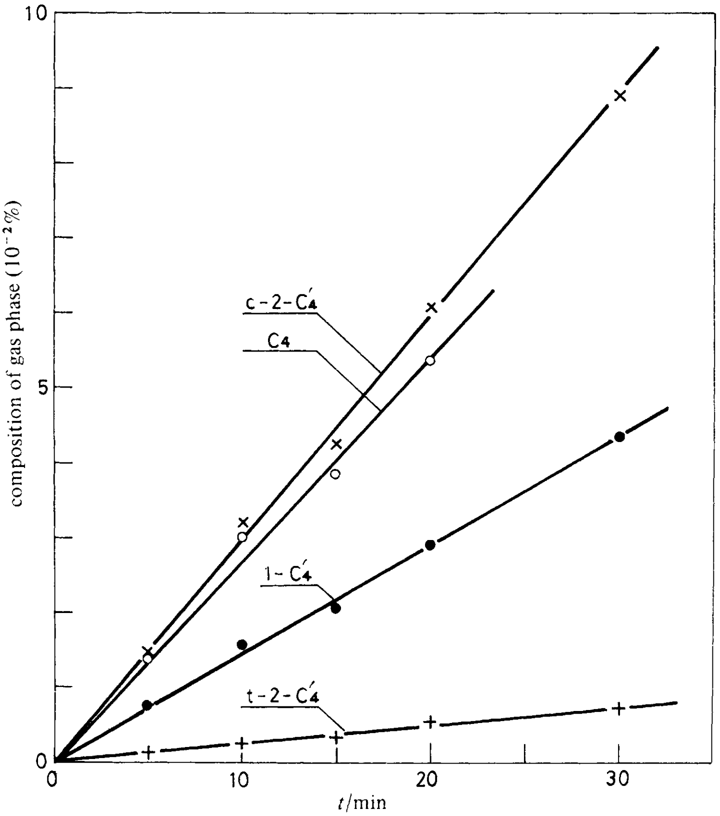

FIG. 1.—Variation of products with time at 211 mV and a buta-1-2-diene pressure of 20 Torr: ×, c-2-C_4'; ○, C_4; ●, 1-C_4'; +, t-2-C_4'.

Fig. 1 shows a typical distribution of the products obtained at different reaction times, where the intitial pressure of 1,2-C_4'' and the potential were 20 Torr and 211 mV (RHE), respectively. The amount of each product is proportional to the reaction time (conversion less than a few %) and the product ratio remains unchanged during the reaction. The catalytic activity of the electrode remains constant within the reaction time studied. We are able to estimate a reaction rate from the slope for the respective products.

Potential dependences of the rates thus obtained are shown in fig. 2, where the initial pressure of 1,2-C_4'' was kept constant at 20 Torr. All the reaction rates first increase with a decrease in the potential (ϕ), but those of the butenes (broken curves) reach a maximum at *ca.* 180 mV and then decrease on a further decrease in ϕ whereas the rate of C_4 formation gradually approaches a limiting value. Hence the product ratio differs depending on ϕ and one can note that (1) complete reduction to C_4 becomes predominant as ϕ decreases and (2) the product ratio among three isomeric butenes remains almost constant over the whole potential region studied in the following order: *c*-2-C_4' > 1-C_4' ≫ *t*-2-C_4'.

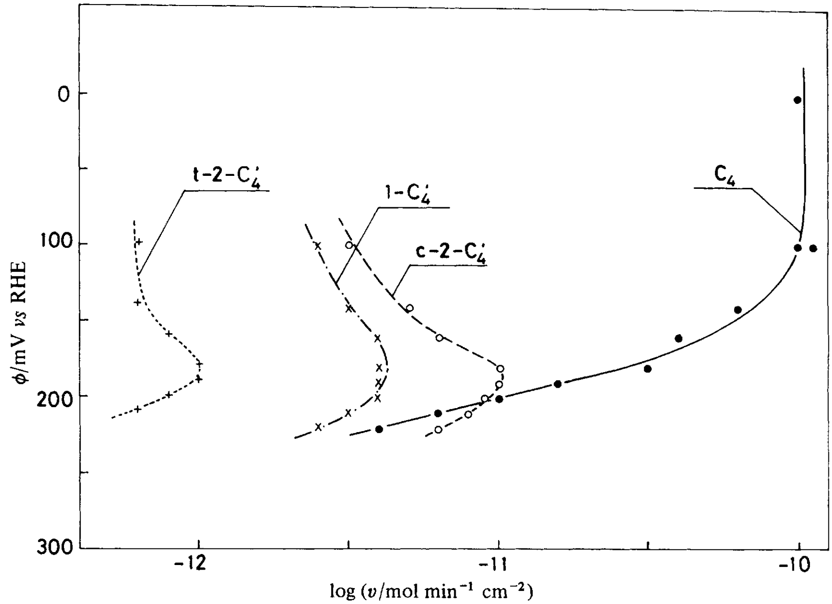

FIG. 2.—Potential dependences of the rates of formation of products at a buta-1,2-diene pressure of 20 Torr: +, t-2-C_4'; ×, 1-C_4'; ○, c-2-C_4'; ●, C_4.

At $\phi > 180$ mV a Tafel-like linear relation holds for the rate of C_4 formation, *i.e.*

$$\phi/\text{mV} = -316-47 \log (v/\text{mol min}^{-1} \text{ cm}^{-2}). \qquad (1)$$

For butenes the observed range at $\phi > 180$ mV is too short to deduce a linear relation with certainty. The slopes, however, are close to 60 mV, being larger than that for C_4 formation.

The total rate calculated by summing the respective rates in terms of current density is compared with the observed value in fig. 3. The current efficiency used for the reduction of 1,2-C_4'' is 100% at $\phi > 100$ mV. The Tafel line apparently holds at $\phi > 180$ mV with a slope of 70 mV, *i.e.*

$$\phi/\text{mV} = -87-70 \log (i/\text{mA cm}^{-2}). \qquad (2)$$

At $\phi < 100$ mV the hydrogen-evolution reaction occurs and the current efficiency decreases.

The effect of 1,2-C_4'' pressure [p(1,2-C_4'')] on the reaction rate is different at potentials above or below *ca.* 180 mV, as illustrated in fig. 4. The rate of C_4 formation increases in a linear manner with the pressure at $\phi = 100$ mV but becomes constant at p(1,2-C_4'') > 10 Torr at $\phi = 220$ mV. This fact is entirely the same as observed in the electroreduction of 1,3-C_4''.[5] Therefore, by analogy with the previous conclusion the reaction rate is taken to be controlled by diffusion of the reactant at $\phi < ca.$ 100 mV (termed the B region) and by the surface process at $\phi > ca.$ 100 mV (termed the H region).

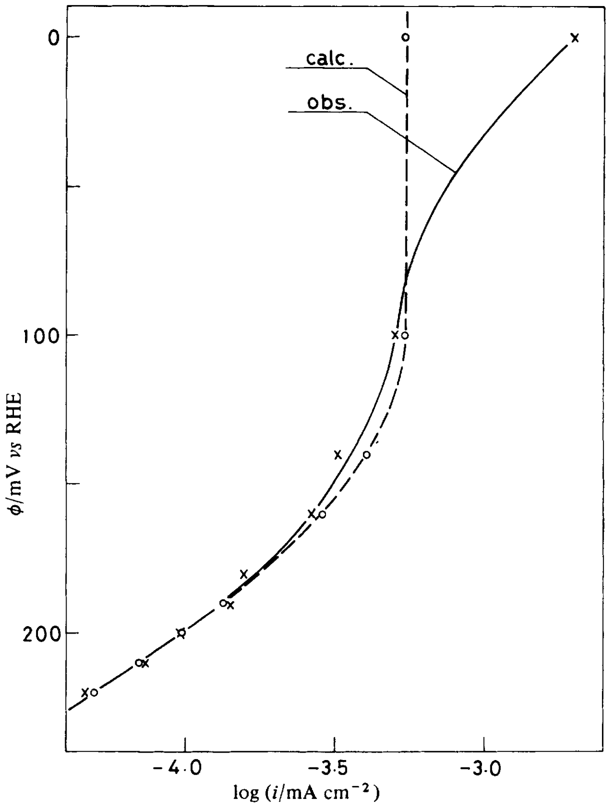

FIG. 3.—Comparison of the observed current with that calculated from the sum of the respective rates of formation of the products: ○, calculated; ×, observed.

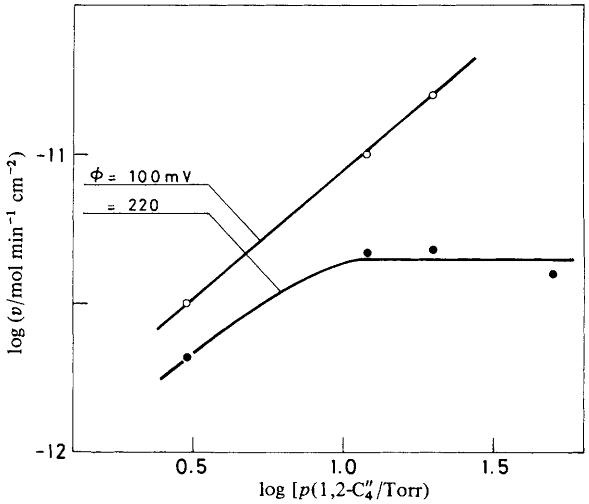

FIG. 4.—Pressure dependence of the rate of butane formation at ○, 100 and ●, 220 mV.

DISTRIBUTION OF DEUTEROSPECIES IN THE PRODUCTS

To obtain details of the surface process, electroreduction was carried out in 0.5 mol dm^{-3} D_2SO_4 instead of 0.5 mol dm^{-3} H_2SO_4 solution and deuterium distributions in the products were examined.

H REGION

Typical deuterium distributions obtained at $\phi = 190$ mV are shown in fig. 5, where d_n denotes the percentage of the deuterospecies containing n deuterium atoms.

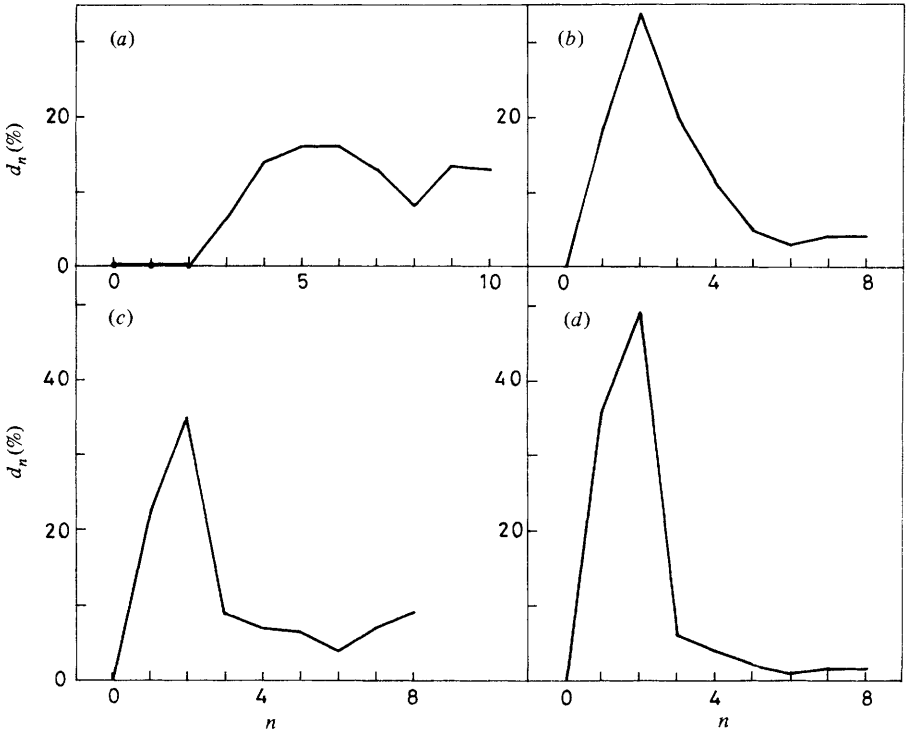

FIG. 5.—Distributions of deuterospecies in the products at $\phi = 190$ mV and $p(1,2\text{-}C_4'') = 20$ Torr: (a) C_4, (b) 1-C_4', (c) *t*-2-C_4' and (d) *c*-2-C_4'.

Isotopic H/D exchange in C_4 proceeds to a significant extent in comparison with those in C_4'. The deuterium number, defined as

$$N_D \equiv \Sigma n d_n / 100 \qquad (3)$$

is 6.6 for C_4, and 3.0, 3.2 and 2.0 for 1-C_4', *t*-2-C_4' and *c*-2-C_4', respectively. Another contrast is that there are two definite maxima in the distribution of C_4, whereas there is a sharp peak at d_2 in the other distributions of C_4' although they fall off to the perdeuterospecies with $n = 8$. In the distribution of *t*-2-C_4' the fraction of higher deuterospecies seems to be larger but one must not pay too much attention to this because it is the smallest amount formed, as seen from fig. 2.

The distributions in fig. 5 are almost independent of potential in the H region.

B REGION

All the butenes show distributions similar to those in the H region with a large peak at $n = 2$. The deuterium numbers are 2.9-3.1 for 1-C_4' and t-2-C_4' and 2.1-2.5 for c-2-C_4'. These distributions are independent of potential. In contrast the distribution of C_4 clearly depends on the potential, as shown in fig. 6. The deuterium number decreases sharply from 6.6 to 3.9 on decreasing ϕ from 100 to 0 mV (table 1).

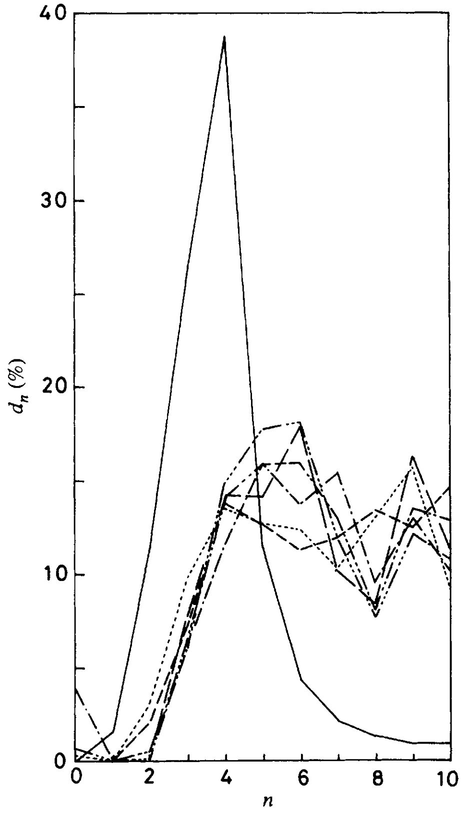

FIG. 6.—Potential dependence of the distributions of deuterospecies in butane at $p(1,2\text{-}C_4'') = 20$ Torr: ϕ = (——) 0, (– – –) 100, (-----) 141, (–·····–) 180, (–··––) 190, (–·–·) 200, (––) 210 mV.

TABLE 1.—DEUTERIUM NUMBER, N_D, OF BUTANE AND CURRENT EFFICIENCY (η) FOR THE REDUCTION OF BUTA-1,2-DIENE [$p(1,2\text{-}C_4'') = 20$ Torr]

ϕ/mV	N_D	η(%)	region
0	3.9	*ca.* 30	B
100	6.6	*ca.* 100	B or H
141	6.4	*ca.* 100	H
180	6.4	*ca.* 100	H
190	6.6	*ca.* 100	H
200	6.3	*ca.* 100	H
210	6.5	*ca.* 100	H

DISCUSSION

COMPARISON WITH THE ELECTOREDUCTION OF BUT-2-YNE

The present results are compared with those obtained for the electroreduction of but-2-yne (2-C_4'') in table 2.

The rate of C_4 formation at 180 mV is almost the same in both cases. Its potential dependence, namely the Tafel slope, is also the same within experimental error.

TABLE 2.— COMPARISON OF THE ELECTROREDUCTION OF BUTA-1,2-DIENE WITH THAT OF BUT-2-YNE (CRITICAL POTENTIAL 100 mV)

	buta-1,2-diene	but-2-yne
rate of C_4 formation at 180 mV/10^{-11} mol min^{-1} cm^{-2}	3.0	1.3
Tafel slope for C_4 formation/mV	47	43
v_{limit}/mol min^{-1} cm^{-2}	1.0×10^{-10}	1.9×10^{-9}
roughness factor	770	140
product ratio of butenes		
t-2-C_4'	1.00	1.00
c-2-C_4'	8.70	15.4
1-C_4'	3.55	trace

On the other hand, the limiting current in the electroreduction of 1,2-C_4'' is *ca.* 20 times smaller than that of 2-C_4''. The present limiting current is calculated for the true surface area estimated electrochemically from the amount of adsorbed hydrogen. Since the present roughness factor is 5.5 times larger than the previous one, the limiting current of 1,2-C_4'' for unit apparent surface area becomes *ca.* 4 times smaller than that of but-2-yne. This difference is attributed to a difference in the solubility of the respective reactants.

The product ratio in butenes is independent of potential (fig. 2) and is listed in table 2 by referring to the amount of *t*-2-C_4'. Comparison with the results for the electroreduction of 2-C_4'' shows that 1-C_4' forms to a considerable extent in the present case, although *c*-2-C_4' is the main product in both cases.

ELECTROREDUCTION IN THE H REGION

BUTENE FORMATION

Buta-1,2-diene has two adjacent π bonds and their orbitals are located perpendicular to each other. The three double-bonded carbons are colinear. Thus 1,2-C_4'' may be adsorbed on a metal surface in three ways, as shown in fig. 7. Types A and A′ are formed by the terminal π bond directing the methyl group upward and downward, respectively, against the metal surface. On the other hand, type A″ is formed by the second π bond having the methyl group in the molecular plane parallel to the surface.

A, A′ and A″ undergo hydrogenation and all possible routes to the respective products of *c*-2-C_4', *t*-2-C_4' and 1-C_4' are illustrated in fig. 8, where the B are half-hydrogenated intermediates from 1,2-C_4'' to the butenes. These intermediates are formed by the addition of a hydrogen atom to either of the two carbons which provide π orbitals directed to the surface (the shaded orbitals of A, A′ and A″ in fig. 8). The looped arrows represent addition and subsequent rotation of the intermediates through a right angle so that another pair of the π-bond orbitals become perpendicular to the surface. As seen from fig. 8, the present scheme provides two routes for the

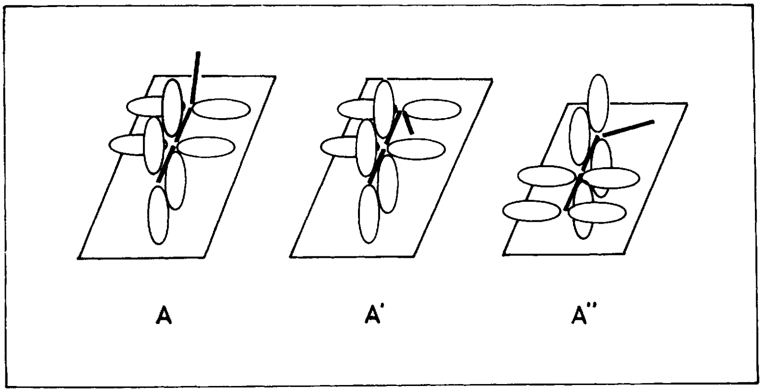

FIG. 7.—Geometrical orientations of buta-1,2-diene on the metal surface.

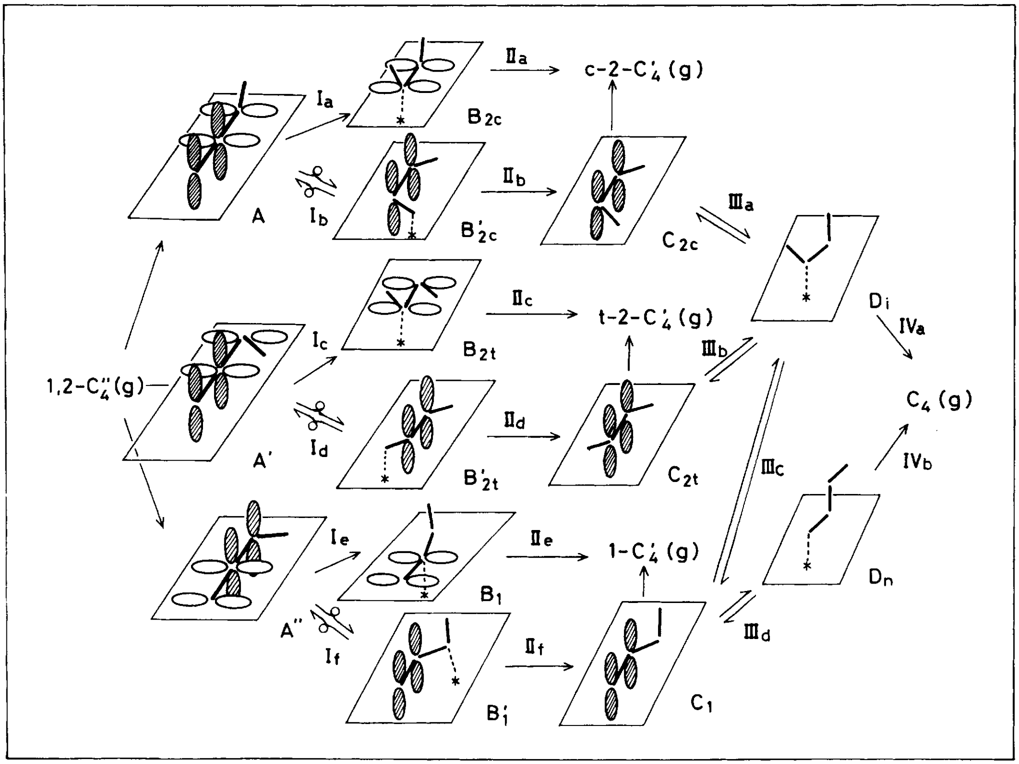

FIG. 8.—Reaction scheme for the electroreduction of buta-1,2-diene. Shaded orbitals interact with the surface.

formation of the respective butenes. For example, *c*-2-C_4' can be formed by either steps I_a and II_a or steps I_b, II_b and desorption of the adsorbed *c*-2-C_4'. A multi-route process has been discussed by Bond *et al.*[8] for the hydrogenation of propadiene on Group VIII metals in the gas phase and by Webb *et al.*[9] for the hydrogenation of acetylene on silica-supported Pd, Rh and Ir catalysts in the gas phase.

Of the two routes mentioned above, the direct, successive additions of two hydrogen atoms without rotation, *e.g.* steps I_a and II_a for *c*-2-C_4', are concluded to be the main route for the formation of each butene, based on the following four considerations. Each distribution of deuterospecies in the respective butenes (fig. 5) shows a sharp peak at $n = 2$, indicating successive additions of two hydrogen atoms in an irreversible manner. If either of the addition steps is reversible, isotopic H/D exchange must proceed to a considerable extent, as in the case of the hydrogenation of 1,3-C_4'' on Pt in D_2SO_4.[4] Secondly, the Tafel slope for each butene (fig. 2) is close to 60 mV and leads to a reaction order of unity with respect to the adsorbed hydrogen atom, H(a), provided that the step

$$H^+ + e^- \rightleftharpoons H(a)$$

is the equilibrium during electroreduction. This equilibrium has been confirmed in the electroreductions of 1,3-C_4'' under the same experimental conditions.[5a] This reaction order indicates that the first addition of H(a) is a rate-determining step. However, the deuterium distribution of 1-C_4' is broader, and hence some reversibility will be added to the addition steps. Thirdly, each deuterium distribution of the individual butenes shows the presence of highly exchanged deuterospecies although at low fractions, indicating the presence of another route for butene formation which accompanies rapid H/D exchange. The Tafel slope of 47 mV for C_4 formation, eqn (1), is equal to $2.303\boldsymbol{R}T/1.3\boldsymbol{F}$ and leads to a reaction order of 1.3 with respect to H(a). Hence the rate-determining step will be in the second or later stage of H(a) additions. If the first addition step is reversible, multiple H/D exchange becomes possible. Since the contribution of the highly exchanged deuterospecies is small, the half-hydrogenated intermediates and subsequent butenes will have a strong interaction with the surface. These butenes are more likely to be hydrogenated further to butane than to desorb because of the interaction. Fourthly, if the desorption step of the adsorbed butenes (C_{2c}, C_{2t} and C_1) is the route for the formation of each butene, the observed distributions of deuterospecies [fig. 5(*b*), (*c*) and (*d*)] will reflect those in C_{2c}, C_{2t} and C_1 and show that the deuterospecies with $n = 2$ is predominant in each adsorbed butene and hence that isotopic H/D exchange through the surface steps, *e.g.* I_b, II_b and III_a for *c*-2-C_4', does not take place to any considerable extent. Steps IV_a and IV_b are concluded to be irreversible from the hydrogenation of 1,3-C_4'' under the same experimental conditions.[5b] Thus it is expected that the deuterospecies with $n = 4$ will be predominant in C_4 after complete hydrogenation, which is not the case, as observed in fig. 5(*a*) or as shown by the N_D value of 6.3-6.6.

Next we discuss the distribution of the three butene isomers. The experimental results exhibit a marked preference for the formation of a thermodynamically less stable isomer of *c*-2-C_4'. The equilibrium ratio at a room temperature for *t*-2-C_4':*c*-2-C_4':1-C_4' is calculated as 1.00:0.31:0.04, whereas the observed value is 1.00:8.70:3.55 (table 2). Meyer *et al.*[10] have found a similar distribution in the palladium-catalysed hydrogenation of 1,2-C_4'' in the gas phase at room temperature and explained it by a steric effect caused by the methyl group of the reactant. As an extension of their discussion, it is expected that among A, A′ and A″ in fig. 8, the adsorption of A′ is sterically most hindered by the methyl group whereas that of A least; hence the thermodynamically less stable isomer of *c*-2-C_4' is produced with a high stereoselectivity. In the case of 2-C_4'' electroreduction, *c*-2-C_4' is formed exclusively (table 2) and the other butenes are formed only to a detectable extent. A geometrical consideration of the π-bond orbitals of 2-C_4'' suggests the preferential formation of the intermediate B_{2c} and hence the predominant formation of *c*-2-C_4'.

BUTANE FORMATION

Further addition of hydrogen to the adsorbed butenes of C_{2c}, C_{2t} and C_1 undoubtedly follow the same route as that proposed for hydrogenation of the butenes.[4] This route is supplemented in fig. 8 as steps III and IV.

Steps III_a-III_d, which give either of the intermediates D_i or D_n, are taken to be reversible from information obtained in the reduction of butenes[3, 4] that isotopic H/D exchange and isomerization of the respective butenes occur to a considerable extent. Isotopic H/D exchange can take place by the forward and backward occurrence of steps III_a-III_d, and the isomerization between, *e.g.*, *c*-2-C_4' and *t*-2-C_4' can take place by the forward occurrence of step III_a and the backward occurrence of step III_b or *vice versa*.

The deuterium distribution of C_4 [fig. 5(*a*)] strikingly resembles that obtained in the hydrogenation of 1,3-C_4''.[4] Common aspects are that (i) the value of N_D is almost the same and (ii) there exist two peaks in the distribution, *i.e.* one at n = 5-6 and the other at n = 9-10. A mathematical analysis of the distribution is inevitably complex because C_4 is produced through steps III and IV from each adsorbed butene and the butene is formed through steps I_b and II_b, I_d and II_d or I_f and II_f. An attempt is now being made to explain the distributions and the appearance of the two maxima by using the reaction rates of each elementary step.

ELECTROREDUCTION IN THE B REGION

In the B region ($\phi < 100$ mV) the rate of C_4 formation reaches a limiting value, as shown in fig. 2, and the diffusion of 1,2-C_4'' to the electrode surface controls the overall reaction rate. The distribution of deuterospecies in C_4 at $\phi = 0$ mV differs completely from those observed at $\phi > 100$ mV (fig. 6). The distribution at 0 mV shows a sharp maximum at $n = 4$ and N_D decreases to 3.9 from 6.3-6.7 observed at ϕ = 100-220 mV.

Such a change is exactly the same as in the case of the electroreduction of ethylene.[1e] In the latter case, the coverage of the adsorbed species by ethylene decreases exponentially with a decrease in the electrode potential in the E region, where the diffusion of ethylene controls the overall reaction rate, and instead the coverage of adsorbed hydrogen approaches a saturation value.[1d]

Thus, in the present case 1,2-C_4'' arriving at the surface through a diffusion layer will immediately react with the deuterium atoms covering the surface at full coverage and become butane with the least probability of isotopic H/D exchange. In other words, the backward rates of steps I_b, I_d, I_f and III_a-III_d will be suppressed significantly by a predominant hydrogen adsorption on the free sites which are required for the backward occurrence of the above-mentioned steps.

CONCLUSIONS

(i) The electroreduction of 1,2-C_4'' in sulphuric acid solution on a platinized platinum electrode produces butane and three isomeric butenes with a current efficiency of *ca.* 100%. (ii) The potential and pressure dependences of the reaction rates for each product differ for $\phi > 100$ and $< ca.$ 100 mV (termed the H and B regions). (iii) In the H region butenes are the main products with a ratio of *t*-2-C_4':*c*-2-C_4':1-C_4' = 1.00:8.70:3.55. Butane is a minor product but has a large value of the deuterium atom number N_D, *i.e.* 6.3-6.6. (iv) In the B region butane is the main product (> 90%). The reaction rate is controlled by diffusion of the reactant to the electrode surface and is almost independent of potential. N_D for butane decreases to 3.9. (v) N_D values of the various butenes are 2-3 over the whole potential region.

(vi) These facts are reasonably explained by a reaction mechanism which takes into account the geometrical orientation of the reactant on the electrode surface.

[1] (*a*) K. Fujikawa, H. Kita and K. Miyahara, *J. Chem. Soc., Faraday Trans. 1*, 1973, **69**, 481; (*b*) K. Fujikawa, A. Katayama and H. Kita, *J. Chem. Soc., Faraday Trans. 1*, 1974, **70**, 1; (*c*) K. Fujikawa, H. Kita, K. Miyahara and S. Sato, *J. Chem. Soc., Faraday Trans. 1*, 1975, **71**, 1573; (*d*) K. Fujikawa and H. Kita, *J. Chem. Soc., Faraday Trans. 1*, 1979, **75**, 2638; (*e*) K. Fujikawa, H. Kita and S. Sato, *J. Chem. Soc., Faraday Trans. 1*, 1981, **77**, 3055.

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