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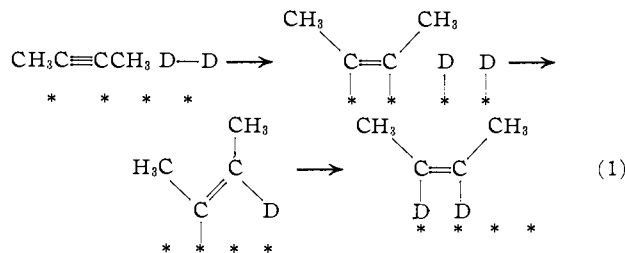
The Reaction between Deuterium and 1-Butyne, 1,2-Butadiene, and 1,3-Butadiene on Palladium-on-Alumina Catalyst

BY EDWIN F. MEYER AND ROBERT L. BURWELL, JR.

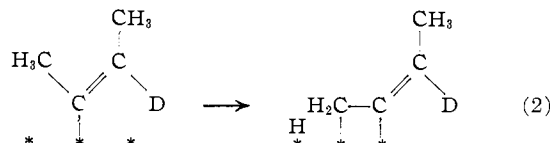
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Products of vapor phase reaction in the vicinity of room temperature were analyzed by gas chromatography, mass spectroscopy, and n.m.r. Little butane is formed until the reactant disappears. 1-Butyne gives 1-butene; 1,2-butadiene gives 0.40 1-butene, 0.53 *cis*-, and 0.07 *trans*-2-butene. The *cis/trans* ratio results from interaction between the methyl group and the surface in 1,2-diadsorbed 2-butene. 1,3-Butadiene gives 0.53 1-butene, 0.05 *cis*-, and 0.42 *trans*-2-butene. About 95% of 1,2-butadiene forms butenes by mere *cis* addition of two deuterium atoms, 1,2 or 2,3. The 1-butene is more exchanged than *cis*-2-butene. 1-Butyne forms 1-butene by 1,2-addition of two deuterium atoms accompanied by 16% equilibration of the original acetylenic hydrogen atoms. 1,3-Butadiene reacts by mere 1,2- or 1,4-addition plus, in 30% of the product, equilibration of some original hydrogen atoms. The isotopic distribution patterns of 1-butene and *trans*-2-butene are nearly the same. Unreacted 1,2-butadiene is unexchanged, but small amounts of exchanged 1-butyne and 1,3-butadiene appear in the vapor phase. Some isomerization of 1,2-butadiene to unexchanged 2-butyne was observed. In 1- and 2-butyne and 1,2-butadiene, we suggest that the major reaction path involves adsorption with the opening of one π -bond followed by successive reactions with H-* to give α -monoadsorbed butene and butene. The major reaction path in the hydrogenation of 1,3-butadiene involves none of the above intermediates but probably adsorption as a largely π -adsorbed *trans*-butadiene followed by reaction with H-* at carbon atom 4 to give an adsorbed allylic species which further reacts with H-* at carbon atoms 1 or 3.

As reported in the preceding paper¹ the addition of deuterium to 2-butyne on palladium-on-alumina catalyst in the vapor phase gives almost exclusively *cis*-2-butene-2,3-*d*₂. These results accord with the classical



mechanism. If this is the correct mechanism, the following reaction must have a nearly negligible rate since it would form more extensively exchanged *cis*-2-butene.



However, the species at the right is that which one would expect as an intermediate in the hydrogenation of the allene, 1,2-butadiene. Accordingly, we have investigated the reaction of deuterium with that compound.

The simple isotopic distribution pattern found in the addition of deuterium to 2-butyne contrasts with the extensively smeared pattern reported by Douglas and Rabinovitch for the addition of deuterium to acetylene on nickel catalysts even at -78° .² One may suspect that this contrast originates with the acetylenic hydrogen atoms present in acetylene but not in 2-butyne. Accordingly, we have investigated the reaction between 1-butyne and deuterium. Finally, for completeness, we have examined the addition of deuterium to the remaining open chain isomer of C₄H₆, 1,3-butadiene.

We also felt that examination of the reactions of these relatively hydrogen deficient species is important in any over-all understanding of possible surface intermediates in hydrocarbon reactions. Further, it might aid in the elucidation of the role of hydrogen deficient species, some of which appear to form rather slowly reacting species on metal surfaces.³

(1) E. F. Meyer and R. L. Burwell, Jr., *J. Am. Chem. Soc.*, **85**, 2877 (1963).

(2) J. E. Douglas and B. S. Rabinovitch, *ibid.*, **74**, 2486 (1952).

Experimental

Materials.—1,2-Butadiene, provided by K. and K. Industries, Inc., contained 0.2% *cis*-2-butene and 0.02% *trans*-2-butene. Since both of these are products, and we could correct for their presence, the butadiene was used without further purification.

1-Butyne obtained from Farchand Research Laboratories was less than 50% 1-butyne. After distillation *in vacuo* between two bulbs with rejection of the initial and final fractions, the material contained 3.7% propyne, 0.7% 2-butyne, and two unidentified components present at about 0.2% each. Since the presence of the major impurities could be allowed for, it was used in this form.

Matheson butadiene, Chemically Pure Grade, was used as such. It contained 0.85% of an impurity which was probably 1-butyne, 0.82% *trans*-2-butene, and 0.13% 1-butene. In allowing for the impurities, it was assumed that 1-butyne hydrogenates much faster than 1,3-butadiene.

The 0.03% palladium-on-alumina catalyst¹ was used throughout.

Apparatus.—Procedures were essentially as previously described¹ with allowance for the fact that the reactants are gaseous at room temperature rather than liquid. 1,3-Butadiene was fed directly from a tank. The other two hydrocarbons were contained in a glass ampoule to which was sealed a glass-Teflon needle valve. The ampoule was placed in a water bath at a slightly elevated temperature and the flow of gas controlled by the needle valve. The method was not entirely satisfactory since the liquid in the flask was apt to evaporate erratically giving somewhat erratic flow rates. However, for the aim of this investigation, this defect was not serious.

Gas chromatography was performed on a 10-ft. column of dimethylsulfolane on Chromosorb P. It gave good separation of all of the C₄ hydrocarbons with which we were concerned.

Results

1-Butyne.—The addition of deuterium to 1-butyne was investigated at 35° with deuterium/1-butyne ratios of 2 to 6. The product of the reaction for *H* (moles deuterium added per mole of 1-butyne) between 0.09 and 0.73 was 99.1% 1-butene, 0.2% each of *cis*- and *trans*-2-butene, and 0.5% butane. The mass spectrographic analyses at *H* = 0.21 are given in Table I.

TABLE I
REACTION BETWEEN 1-BUTYNE AND DEUTERIUM

| | <i>d</i> ₀ | <i>d</i> ₁ | <i>d</i> ₂ | <i>d</i> ₃ | <i>d</i> ₄ | <i>d</i> _{NV} |
|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|------------------------|
| 1-Butene | 0.018 | 0.141 | 0.722 | 0.119 | 0.000 | 1.94 |
| Computed ^a | .008 | .149 | .725 | 0.119 | 0.000 | |
| 1-Butyne | .984 | .016 | .000 | | | |

^a The computed values assume *a/b* = 9.5 and *N*₂ = 0.84, *N*₃ = 0.16 for 1-butene. For butyne, it follows that *N*₀ = 0.982, *N*₁ = 0.018.

(3) A. K. Galwey and C. Kemball, *Trans. Faraday Soc.*, **55**, 1959 (1959); "Actes du Deuxième Congrès International de Catalyse." Éditions Technip, Paris, 1961, p. 1063.

In view of the marked drop in abundance between 1-butene- d_3 and 1-butene- d_4 , one and only one of the original hydrogen atoms is subject to isotopic exchange. This must be the initially acetylenic hydrogen atom at carbon atom 1. The 1-butyne- d_3 is, then, 1-butene-1,1,2- d_3 .

Consider the hydrogen-deuterium balance on the surface of the catalyst. Deuterium adsorbs from the gas phase. Isotopic exchange between hydrogen atoms of the hydrocarbon and deuterium removes deuterium from and transfers hydrogen to the surface. Hydrogen and deuterium are removed from the surface by formation of alkane. Since d_{av} for 1-butene is close to 2, little if any HD desorbs. The relative rates of the various reactions will determine the steady-state surface ratio, $*-D/*-H$ which we designate a/b .

The two atoms which add to form 1-butene must have been equilibrated with the surface D/H pool and, in some molecules, the original acetylenic hydrogen atom will also have been equilibrated. The equilibration may not be a thermodynamic one since addition of hydrogen and deuterium atoms will involve a kinetic isotope effect. Thus, a/b represents an effective concentration ratio and not necessarily the true ratio. Let N_i represent the fraction of 1-butene molecules in which i positions have been equilibrated, *i.e.*, the fraction of 1-butene- $(h,d)_i$. Given a/b , one can compute the fractions of 1-butene- $(h,d)_i$ which appear as 1-butene- d_0 , 1-butene- d_1 , . . . 1-butene- d_i by the standard binomial formula⁴

$$d_m(n) = \frac{(a/b)^m n!}{(1 + a/b)^n m!(n - m)!}$$

where $d_m(n)$ is the fraction of molecules in which of n equilibrated atoms m are deuterium. Finally, given N_0, N_1, N_2, N_3 , etc., and a/b , the complete isotopic distribution of a product can be determined.

For 1-butene, N_0 and N_1 are necessarily zero and we assume that N_4, N_5 , etc., are zero since only one hydrogen atom appears to undergo isotopic exchange. In Table I we present the values of a/b and N_2 (and $N_3 = 1 - N_2$) which best reproduce the experimental data. The real test of the choice is the agreement between d_1 observed and computed.

From n.m.r. there was no deuterium in the C_2H_5 -group of 1-butene; the signal from the $-CH=$ proton was essentially eliminated, and that from the $=CH_2$ protons was halved.

1,2-Butadiene.—The reaction between this compound and deuterium was investigated at 8–40°. 2-Butyne appeared at about 0.1 of total olefin but the actual ratio was variable. We have no explanation for the variability unless it was related to the erratic flow of butadiene. We were also able to detect 1,3-butadiene, roughly 0.003 that of olefin, and traces of 1-butyne. The olefinic product was 0.53 *cis*-2-butene, 0.07 *trans*-2-butene, and 0.40 1-butene. The proportions were constant to within 10% and changed little over the temperature range investigated. Butane was detected at about 0.01 of olefin.

Table II gives the results of mass spectrographic analysis of two samples. The isotopic distributions, corrected for the initial content of 0.2% *cis*-2-butene- d_0 , were nearly independent of conversion. 1-Butene was always somewhat more extensively exchanged than *cis*-2-butene.

The computed values in Table II were obtained in the same way as in Table I. The wider isotopic distribution pattern necessitates the assignment of finite values to N_4 and N_5 . The large value of a/b , 15.7, reflects the small degree of isotopic exchange.

(4) See G. V. Smith and R. L. Burwell, Jr., *J. Am. Chem. Soc.*, **84**, 925 (1962), for further details of this procedure.

TABLE II
MASS SPECTROGRAPHIC ANALYSES OF OLEFINIC PRODUCT OF
ADDITION OF DEUTERIUM TO 1,2-BUTADIENE

| | d_0 | d_1 | d_2 | d_3 | d_4 | d_5 | d_{av} |
|----------------------------|-------|-------|-------|-------|-------|-------|----------|
| Run 77 at 8°, $H = 0.38$ | | | | | | | |
| <i>cis</i> -2-Butene | 0.022 | 0.097 | 0.852 | 0.024 | 0.005 | 0.000 | 1.89 |
| Computed ^a | .004 | .109 | .857 | .024 | .005 | .000 | |
| 1-Butene | .011 | .090 | .854 | .030 | .010 | .005 | 1.95 |
| Computed ^b | .004 | .107 | .846 | .030 | .010 | .005 | |
| Run 67a at 40°, $H = 0.62$ | | | | | | | |
| <i>cis</i> -2-Butene | 0.020 | 0.125 | 0.818 | 0.028 | 0.006 | 0.003 | 1.88 |
| 1-Butene | 0.010 | 0.113 | 0.806 | 0.049 | 0.017 | 0.005 | 1.96 |

^a Assuming $a/b = 15.7$, $N_2 = 0.966$, $N_3 = 0.028$, and $N_4 = 0.006$. ^b Assuming $a/b = 15.7$, $N_2 = 0.949$, $N_3 = 0.034$, $N_4 = 0.010$, and $N_5 = 0.007$.

The product of runs at 8°, $H_{av} = 0.25$, was examined by n.m.r. In the *cis*-2-butene, the proton signal from the $-CH_3$ groups was reduced by about $1/6$, the $=CH-$ signal was about halved. In the 1-butene, the $=CH-$ signal had vanished and the $-CH_2-$ signal was halved.

1,3-Butadiene.—The addition of hydrogen and of deuterium to 1,3-butadiene was investigated in a number of runs at 40°. No isomerization product of the butadiene was detected. The formation of butane was very small at $H < 0.9$, about 0.1% of total olefin. The proportions in the olefinic product were *cis*-2-butene 0.048, *trans*-2-butene 0.420, and 1-butene 0.532. The average deviation for the latter two compounds was less than ± 0.01 . The proportions were the same with hydrogen and deuterium and they were independent of the hydrogen/butadiene ratio.

For H between about 0.95 and 1.03, both butane and 1,3-butadiene were found in the products. However, we have no real test as to just how little butadiene will inhibit reaction of butenes. Very small quantities of butadiene might inhibit further reactions of butenes, yet both butadiene and butane would appear in the collector tube if the catalyst activity varied slightly during the collection period or if the flow rates varied slightly. Once butane appeared, the content in 1-butene fell rapidly, that in *cis*- and *trans*-2-butene rose. For example, for a sample with 4.2% butane and no butadiene, we give the observed per cent and, in parentheses, the per cent if no isomerization had occurred: *cis*-2-butene 17.1 (4.6), *trans*-2-butene 52.3 (40.2), and 1-butene 26.4 (51.0).

Results of two mass spectrographic runs are given in Table III. Corrections were made for initial content in impurities assuming that olefins would not react and that 1-butyne would form 1-butene with $N_2 = 0.84$ and $N_3 = 0.16$ as in Table I and with $a/b = 3.0$. This rather small value of a/b reflects the extensive isotopic exchange which accompanies the addition of deuterium to 1,3-butadiene.

From runs in which hydrogen was alternated with deuterium, the rate with hydrogen was about twice that with deuterium.

The *trans*-2-butene of run 79 of Table III was isolated by gas chromatography and examined by n.m.r. The spectrum corresponded to the introduction of 0.1 deuterium atom into each $=CH-$ position and 0.8 deuterium atom into each $-CH_3$.

Competitive Runs.—To gain some idea of the adsorptivities of the various unsaturated molecules which we studied, we have approximately measured their relative reactivities in mixtures of several pairs of these hydrocarbons. We computed the relative feed rates from the product analysis with the assumption that the product distribution of each diene or acetylene would be unaffected by the other component. Relative rates of reaction were then computed by relation 3.

TABLE III
MASS SPECTROGRAPHIC ANALYSIS OF PRODUCTS OF REACTION BETWEEN DEUTERIUM AND 1,3-BUTADIENE

| | d_0 | d_1 | d_2 | d_3 | d_4 | d_5 | d_6 | d_7 | d_{av} |
|------------------------|-------|-------|-------|-------|-------|-------|-------|-------|----------|
| Run 72b, $H = 0.20$ | | | | | | | | | |
| 1-Butene | 0.085 | 0.262 | 0.459 | 0.121 | 0.056 | 0.011 | 0.007 | 0.000 | 1.89 |
| <i>trans</i> -2-Butene | .080 | .272 | .457 | .116 | .056 | .014 | .005 | .000 | 1.86 |
| Computed ^a | .046 | .284 | .475 | .119 | .056 | .013 | .006 | .001 | |
| N_x^a | .000 | .000 | .691 | .131 | .134 | .017 | .020 | .007 | |
| 1,3-Butadiene | .976 | .016 | .005 | .002 | .001 | .000 | | | 0.036 |
| N_x^b | .970 | .019 | .005 | .003 | .003 | .000 | | | |
| Run 79, $H = 0.48$ | | | | | | | | | |
| 1-Butene | 0.158 | 0.301 | 0.323 | 0.130 | 0.063 | 0.019 | 0.006 | | 1.72 |
| <i>trans</i> -2-Butene | .164 | .283 | .308 | .135 | .073 | .027 | .010 | | 1.79 |
| <i>cis</i> -2-Butene | .234 | .351 | .287 | .086 | .031 | .011 | .000 | | 1.36 |
| 1,3-Butadiene | .830 | .121 | .041 | .009 | .000 | | | | 0.23 |

^a Computed for $a/b = 3.0$ and the values of N_x given in the table where x is the same as in d_x . ^b The observed butadiene pattern is reproduced by $a/b = 3.0$ and the listed values of N_x .

$$\text{selectivity} = (\log X_A/X_A^0)/(\log X_B/X_B^0) \quad (3)$$

In competition between 1,2-butadiene and 2-butyne, the former reacted faster by a factor of about 4. With 1,3-butadiene and 2-butyne, the ratio of the rates was very nearly unity. With 1-butyne and 1,2-butadiene, the former reacted faster by a factor of about 2.7.

Discussion

Selectivity and Products.—The hydrogenation of 1- and 2-butyne and of 1,2- and 1,3-butadiene on palladium is highly selective in the sense that very little butane appears as long as butyne or butadiene remains unreacted. This accords with previous experience with palladium.⁵⁻⁷ However, whereas each butyne gives one olefin each, the dienes give mixtures. The product distributions for 1,3-butadiene and 1,2-butadiene resemble those previously reported for palladium catalysts when subsequent isomerization was absent.^{7,8} A summary of product compositions for a temperature of about 35° is given in Table IV. The product composition is little affected by substituting deuterium for hydrogen, but this point was carefully examined only with 1,3-butadiene.

TABLE IV
HYDROGENATION OF BUTYNES AND BUTADIENE

| Reactant | Olefinic product | Butane as % of olefin | Isomerization of reactant |
|---------------|---------------------|-----------------------|--|
| 1-Butyne | 1-Butene | 0.5 | None |
| 2-Butyne | <i>cis</i> -2-ene | 1.0 | None |
| 1,2-Butadiene | 1-Butene | 0.40 | 2-Butyne + traces of 1-yne and 1,3-diene |
| | <i>cis</i> -2-ene | .53 | |
| | <i>trans</i> -2-ene | .07 | |
| 1,3-Butadiene | 1-Butene | .532 | None |
| | <i>cis</i> -2-ene | .048 | |
| | <i>trans</i> -2-ene | .420 | |

Deuteration.—Although we did not directly examine the effect of this series of hydrocarbons upon the hydrogen-deuterium exchange reaction, the rate of desorption of HD must be heavily inhibited by all three hydrocarbons since the ratio (moles of D-atoms incorporated)/(moles of -yne or -diene hydrogenated) is about 2.0 in all cases. For example, if we sum the deuterium content of 1-butene and 1-butyne in Table I,

(5) R. L. Burwell, Jr., *Chem. Rev.*, **57**, 895 (1957).

(6) W. M. Hamilton and R. L. Burwell, Jr., "Actes du Deuxième Congrès International du Catalyse," Éditions Technip, Paris, 1961, p. 987.

(7) G. C. Bond, "Catalysis by Metals," Academic Press, London, 1962, sections 12.4, 12.8.

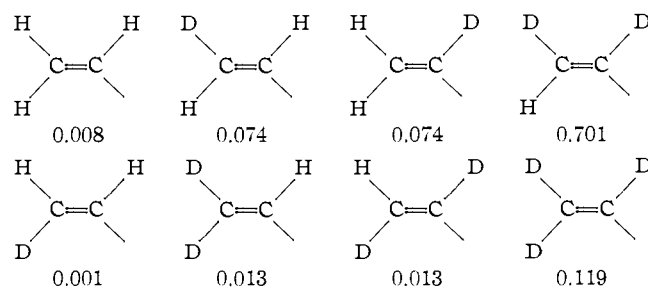
(8) A. Rieche, A. Grimm, and H. Albrecht, *Brennstoff Chem.*, **42**, 177 (1961). In liquid phase reaction in alcohol as solvent and on Pd-BaSO₄, 1,3-butadiene gives 63.6 1-butene, 30.8 *trans*-2-butene, and 5.6% *cis*-2-butene; 1,2-butadiene gives 44.5, 3.3, and 52.2%.

we obtain 0.421 g.-atom of deuterium per mole of reactant. This divided by the mole hydrogenated, (0.21, gives 2.00).

With all three hydrocarbons, the predominant products are the result of mere addition of two atoms from the surface D/H pool, that is, N_2 is large. Additional isotopic exchange occurs in all cases. With 1,2-butadiene, the additional exchange is small; $1 - N_2$ is 0.04-0.05 in run 77 of Table II. The degree of exchange is larger with 1-butyne. In the 1-butene of Table I, $N_3 = (1 - N_2)$ is 0.16. The extent of isotopic exchange is largest with 1,3-butadiene. As may be seen from Table III, $1 - N_2$ is about 0.30 in the initial olefinic product.

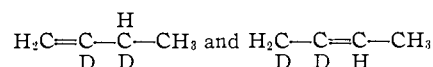
The rate of formation of isotopically exchanged reactant is negligible with 1,2-butadiene. Formation of 1-butyne in which the hydrogen atom at carbon atom 1 has been equilibrated occurs at a rate $1/12$ that of addition of deuterium. In run 72b of Table III, the rate of formation of isotopically exchanged 1,3-butadiene is $1/6.4$ that of the addition of deuterium.

The n.m.r. data are important in that they establish that the addition of two deuterium atoms to form the predominant products occurs directly and without any intramolecular rearrangements. In the addition of deuterium to 1-butyne, the isotopic distribution for 1-butene (Table I) is well reproduced by $a/b = 9.5$, $N_2 = 0.84$, and $N_3 = 0.16$. On this basis the product is



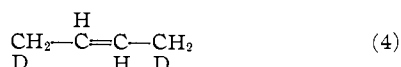
The =CH₂ group contains an average of 1.05 deuterium atoms and the —CH= group, 0.91. This accords with the n.m.r. results.

The combination of mass spectroscopy and n.m.r. establishes that the predominant products of the addition of deuterium to 1,2-butadiene are



Because of the rather extensive isotopic scrambling, the interpretation of the results of n.m.r. examination of the olefinic product of the addition of deuterium to 1,3-butadiene is less clear-cut. In the *trans*-2-butene

of run 79, Table III, deuterium was introduced at every position, but about 90% of the deuterium appeared at the terminal carbon atoms. Thus, formation of *trans*-2-butene involves actual 1,4-addition to give mainly



Mechanism, Butynes, and 1,2-Butadiene.—The classical mechanism, steps 1, 2, 3 of Fig. 1, accords with the nearly exclusive formation of *cis*-2-butene-2,3-*d*₂

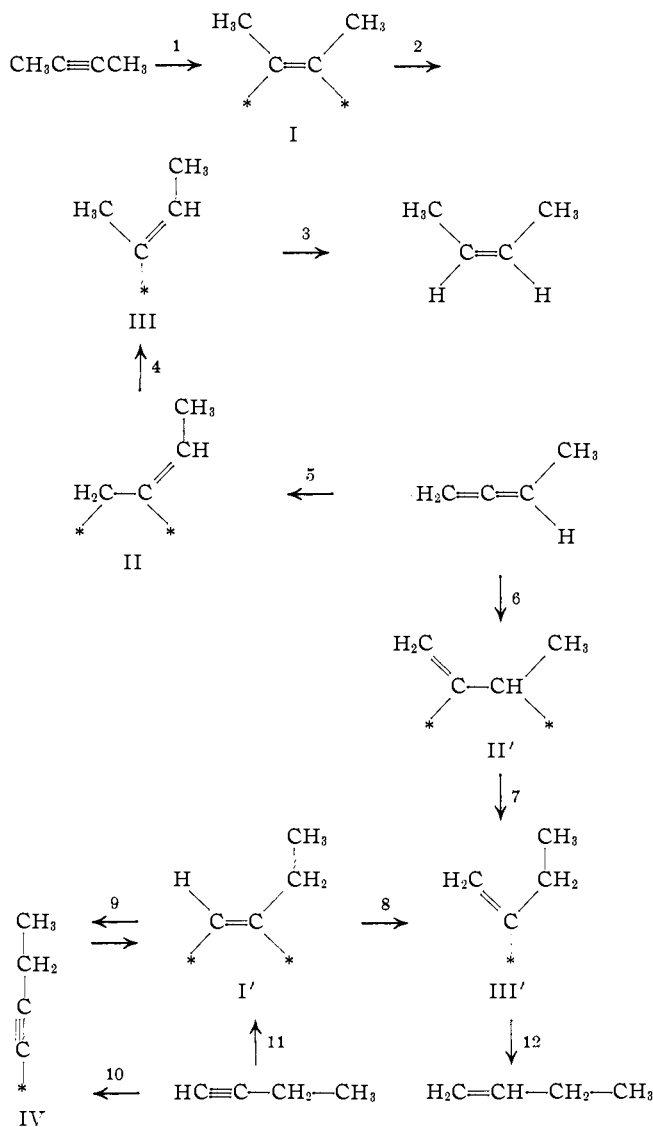
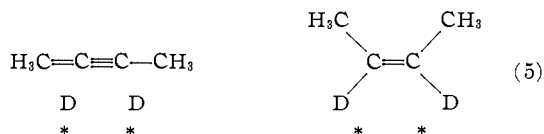


Figure 1.

in the reaction between deuterium and 2-butyne. The following mechanism is equally concordant.⁶



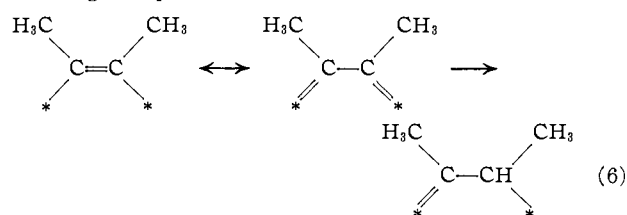
Here, 2-butyne is never adsorbed but reacts in a four-center reaction upon collision with appropriately spaced hydrogen atoms adsorbed on a surface largely covered with inert hydrocarbon residues.

However, a substantial fraction of the hydrogenation of 1-butyne must proceed *via* an extension of the classical mechanism. Exchanged 1-butyne appeared in the vapor phase and, if it reacted only by mechanism 5, the amount of 1-butene-(*h,d*)₃ would have been much too small. At $H = 0.21$ (21% conversion), N_1 for

1-butyne was only 0.018 whereas N_3 for 1-butene was 0.16 (Table I). Thus, 1-butene-(*h,d*)₃ must be formed very largely *via* an adsorbed species. In the addition of deuterium to acetylene, an even larger fraction must proceed through adsorbed species.² The principle of economy of hypothesis suggests that, for the present, we assume all of the reaction to occur by the classical mechanism.

On this basis the following intermediates are necessary: two types of diadsorbed butene, one substituted at both ethylenic positions to form the surface organometallic compounds I and I' of Fig. 1, and the other substituted at but one ethylenic position, II and II'; and α -monoadsorbed butenes, III and III'. Since N_2 is large for the olefinic product (Tables I, II, and III), the straight-through reactions are heavily predominant. For example, formation of *cis*-2-butene from 1,2-butadiene proceeds by the steps 5, 4, 3 with little reversal or side reactions.

Since species I may well be stabilized by resonance with a species involving d-p π -bonding with the surface one might expect it to react with *-H thus

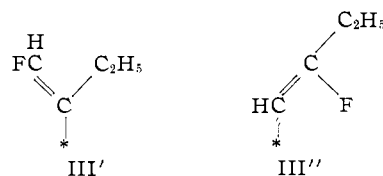


Clearly, however, either this reaction has a very small rate or the species at the right does not react further.

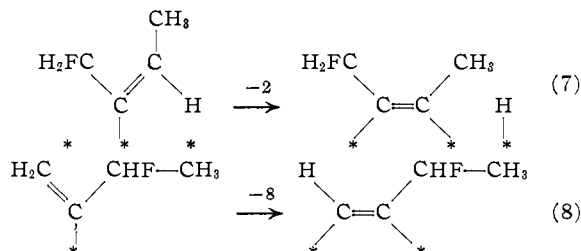
The product of steps 5, 4, 3 is *cis*-2-butene-1,2-(*h,d*)₂. At 8° (Table II), the *cis*-2-butene from 1,2-butadiene was 96.6% (*h,d*)₂. Step -3 would form (*h,d*)₃ by exchange at carbon atom 3. Thus, dissociative adsorption of butene is very slow, at least in the presence of the more highly unsaturated hydrocarbons. As we have already seen, the presence of the more highly unsaturated hydrocarbons almost completely inhibits adsorption of butenes as diadsorbed butanes and it greatly reduces the rate of desorption of HD.

The substantial amount of exchange at carbon atom 1 in the 1-butene formed from 1-butyne suggests 1-monoadsorbed 1-butyne (IV) as an additional surface organometallic intermediate. We do not see how to assess the relative rates of steps 10 and 11. Step 10 might proceed at a negligible rate but the reverse of one of them has a small, but finite rate since 1-butyne-1-*d* appears in the vapor phase (Table I).

Figure 1 shows but one of the two possible products of step 8. Here, the symbol F indicates an atom which has been equilibrated with the surface D/H pool.



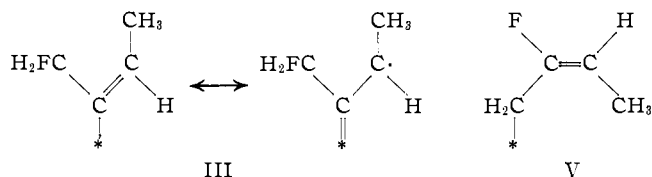
Reversal of step 8 has isotopic consequences in neither case. In particular, reversal from III' would not exchange the hydrogen atom at carbon atom 1 since it is away from the surface. However, when intermediate III or III' is formed from 1,2-butadiene, reversal of steps 2 or 8 would lead to isotopic exchange. Here the species at the left are formed *via* steps 5, 4 for eq. 7 and steps 6, 7 for eq. 8. A small rate for reactions -2 and -8 might account for the few per cent of multiply exchanged butenes from 1,2-butadiene. The species at the right of eq. 8 could further exchange the



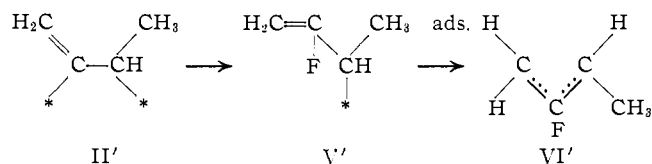
hydrogen atom at carbon atom 1 by formation of 1-monoadsorbed 1-butyne, step 9, and this might largely account for the greater degree of exchange in the 1-butene than in the 2-butene. In view of the small rates of reactions -10 and -11, these reactions would lead to but very small rates of isomerization of the allene to butynes.

Because of our results with 2-butyne, reactions of the type of -4 must be very slow although the traces of multiply exchanged *cis*-2-butene formed from 2-butyne might originate by step -4.

In Fig. 1 we have entered only one of the two conceivable products of step 4 (and also of step 7).

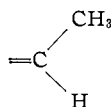


We have preferred species III to V on two grounds. It should be somewhat stabilized by resonance with a species involving d-p π -bonding with surface sites and it is a species required anyway for the hydrogenation of butynes. Species V has a geometry which would permit its conversion to an adsorbed allylic species but, of necessity, to the somewhat hindered *cis* form. The analogous species V', arising from step 7, 3-mono-adsorbed 1-butene, could form the more stable *trans*



form. It is unlikely that any large fraction of 1-butene from 1,2-butadiene could have passed through VI'. The addition of a hydrogen atom to VI' would be expected to generate a much larger ratio of *trans*-2-butene to 1-butene than is observed. However, formation of V and VI provides an alternative explanation for the origin of much of the small amount of multiple exchange observed in the products of the hydrogenation of 1,2-butadiene and of the greater degree of multiple exchange in the 1-butene.

The product distribution in the hydrogenation of 1,2-butadiene, 53% *cis*-2-butene, 7% *trans*-2-butene, and 40% 1-butene provides a striking case of the effect of steric interaction with the surface. As shown in Fig. 2, the plane of the group (in the plane of the paper) is



normal to that of the =CH₂ group (the plane is at right angles to the paper and only the hydrogen atom above the plane of the paper is shown). If adsorption is to occur at carbon atoms 1 and 2, the allene must approach the surface so that the plane of the =CH₂ group is parallel to that of the surface. Two such

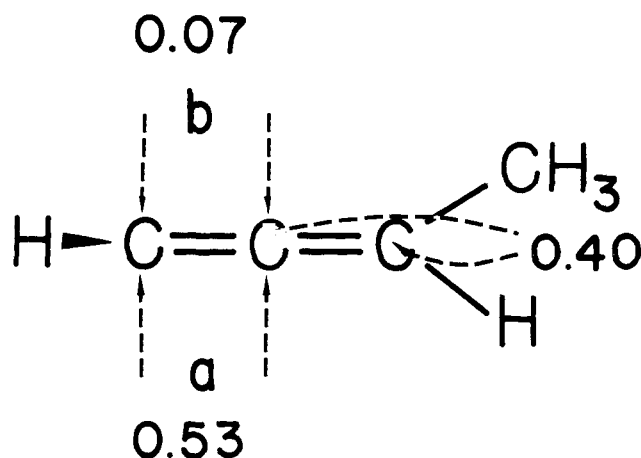
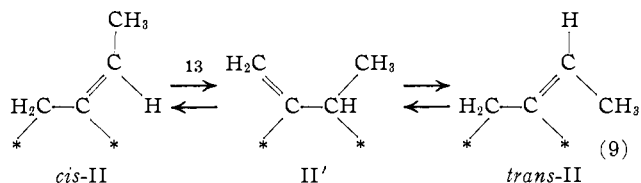


Fig. 2.—Hydrogenation of 1,2-butadiene.

approaches are possible, a and b. Approach b is hindered by the methyl group and accordingly is disfavored. Since approach a generates *cis*-2-butene and approach b, *trans*-2-butene, the thermodynamically less favored olefin, *cis*-2-butene, is formed with rather high selectivity.

In addition, the intermediates formed by approaches a and b, *cis*-II and *trans*-II, might equilibrate on the surface via isomerization to II'. Again steric interactions would make *cis*-II much the preferred form.



Our data provide no evidence bearing upon the rate of step 13.

Mechanism, 1,3-Butadiene.—It is generally considered that there should be a rough correlation between the heats of hydrogenation of unsaturated hydrocarbons, the strengths of binding to catalyst surfaces, and the relative rates of hydrogenation in competitive hydrogenations. Relevant thermochemical data are given in Table V for the C₄H₆ system.⁹

TABLE V

HEATS OF HYDROGENATION

| Reaction | −ΔH | Reaction | −ΔH |
|-------------------------------|------|----------------------------|------|
| 1-yne = 1-ene | 39.5 | 1,3-diene = 1-ene | 26.4 |
| 2-yne = <i>cis</i> -2-ene | 36.6 | 1,3-diene = butane | 56.5 |
| 1,2-diene = 1-ene | 38.8 | <i>cis</i> -2-ene = butane | 28.5 |
| 1,2-diene = <i>cis</i> -2-ene | 40.4 | | |

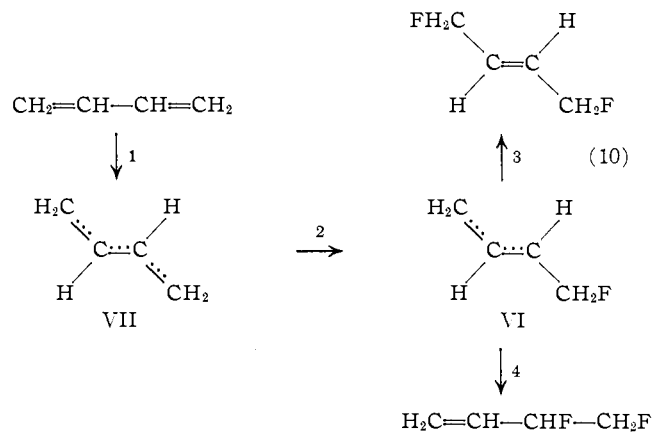
In competitive reactions between pairs, the relative reactivities are roughly 1,3-butadiene = 2-butyne = 1.0; 1,2-butadiene = 2.7; and 1-butyne = 11. These competitive rates and the enthalpies of hydrogenation match fairly well if one excludes 1,3-butadiene. In particular, the much lower enthalpies of hydrogenation of butenes provides a basis for understanding the suppression of their hydrogenation by the presence of butynes or 1,2-butadiene.

However, 1,3-butadiene competes on equal terms with 2-butyne although its enthalpy of hydrogenation is 10 kcal. less. This suggests that initial chemisorption of 1,3-butadiene involves more than the mere formation of 3,4-diadsorbed 1-butene. On the other hand, it is unlikely to involve complete conversion of both

(9) F. D. Rossini, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie University Press, Pittsburgh, Pa., 1953.

π -bonds to four σ -bonds since this should make butadiene much the most strongly adsorbed of the group. It may adsorb with retention of sp^2 hybridization. Such species were suggested by Rooney, Gault, and Kemball¹⁰ in another connection and by Moore in connection with the hydrogenation and isomerization of C_9 and C_{10} cyclic 1,2- and 1,3-dienes.¹¹

In the addition of deuterium to 1,3-butadiene, the isotopic distribution patterns of the two major products, 1-butene and *trans*-2-butene, are nearly identical (Table III) and 70% of the initial product is $CH_2FCH=CHCH_2F$ and $CH_2=CHCHFCH_2F$. Thus, none of the intermediates of Fig. 1 are involved to any major degree since N_2 must be zero for any process proceeding from 1,3-butadiene through I, II, III, or IV. We suggest the mechanism



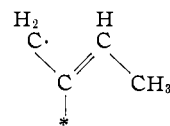
We avoid precisely specifying the nature of the binding of the adsorbed intermediates VII and VI, but we assume that the plane of the molecule is parallel to the surface of the catalyst. We showed above that intermediate VI cannot play any major role in the hydrogenation of the other hydrocarbons. In mechanism 10, it is the immediate precursor of both *trans*-2-butene and of 1-butene which accords with their identical distribution patterns.

Step 1 must be reversible since isotopically exchanged butadiene appears in the vapor phase (Table III). No very clear line of evidence indicates the nature of the exchange process. It seems simplest to assume that it occurs in part by reversal of step 2 of mechanism 10. This would have isotopic but no stereochemical consequences. If the surface geometry is such that addition to a particular one of the terminal carbon atoms is preferred, the large gap between N_3-N_4 and N_5-N_6 (Table III) could be understood. On this representation, *trans*-2-butene- $(h,d)_4$ would be mainly $CH_2F-CH=CH-CF_3$. Conversion of VI or VII to intermediates of the type of II and III might also be involved. This would put deuterium at the ethylenic positions. The n.m.r. data suggest that some deuterium is actually at these positions. However, although we consider that the n.m.r. data adequately establish that conversion of 1,3-butadiene to *trans*-2-butene principally involves 1,4-addition, we do not consider that the data are accurate enough for determination of detailed isotopic distributions.

cis-2-Butene is formed in small quantities ($\sim 5\%$) during the hydrogenation of 1,3-butadiene. In mechanism 10, *cis*-VII would be much less favored, as in butadiene itself, because of interactions between the terminal methylene groups. This accords with the results. Thus, *trans*- is favored over *cis*-2-butene be-

cause of steric interactions within the molecule whereas, in the hydrogenation of 1,2-butadiene, *cis*- is favored over *trans*-2-butene because of interactions with the surface of the catalyst.

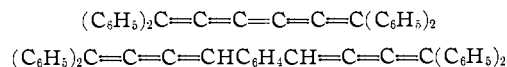
Isomerization of 1,2-Butadiene.—The mechanism of Fig. 1 provides the possibility of forming very small amounts of 1- and 2-butyne during hydrogenation of 1,2-butadiene. These would be isotopically exchanged. However, we observed the formation of rather large amounts of unexchanged 2-butyne (see the Experimental section). This would require an intramolecular shift of a hydrogen atom from carbon atom 3 to 1. Perhaps a species resembling the following might be formed on single sites. However, this isomerization re-



action needs further investigation before much speculation is warranted.

Hydrogen Deficient Species.—Galwey and Kemball³ have advanced evidence that hydrocarbons react with metallic surfaces to produce hydrogen deficient adsorbed species which react very slowly. The butynes and butadienes adsorb to form species equivalent to alkane minus four hydrogen atoms. In the presence of hydrogen and at least on some sections of the catalyst surface, these are not slowly reacting species. The species at the right of eq. 6 has the structure suggested by Galwey and Kemball for one of the inert species. It plays no important role in the hydrogenation of acetylenes. Of course, we have no knowledge as to the fraction of the surface which is catalytically active and relatively inert species may cover much of the surface during a hydrogenation.

It may be noted that even more highly hydrogen deficient species hydrogenate readily. Thus, molecules containing the $-C\equiv C-C\equiv C-$ grouping can be hydrogenated,¹² cumulenes of the following types can be hydrogenated¹³



and vinylacetylene is readily hydrogenated.⁸

The hydrogenation of vinylacetylene is of interest in connection with the results reported in this paper. In the presence of vinylacetylene, butadiene is inert. Nevertheless, under the conditions of the experiments (ethanol as solvent, Pd-BaSO₄ as catalyst), the initial products of the reaction were 69% 1,3-butadiene, 1% butane, and 30% butene which was 69% 1-butene, 17% *trans*-2-butene, and 15% *cis*-2-butene. Some butadiene must be diverted to butene without desorbing. It appears that a combination of the mechanism of Fig. 1 and of mechanism 10 is involved.

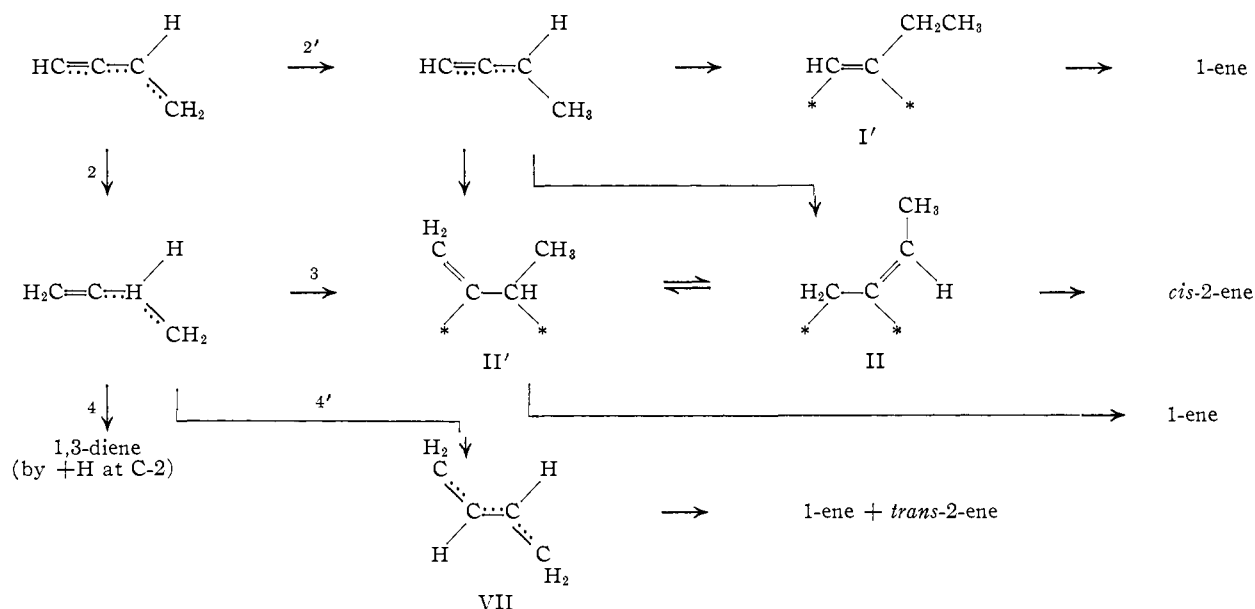
In mechanism 10, the addition of an atom of hydrogen to VI results almost exclusively in the liberation of butene rather than in the formation of diadsorbed butane or else that species rapidly desorbs. In step 3 of the mechanism on the next page, an allene would have to desorb. Rather, it remains as II' further to react. Step 4' does not result from desorption and readsorption of butadiene but from a nearly concerted reaction consequent to addition of a hydrogen atom to carbon atom 2. These proposals are related to that of Rieche,

(12) H. H. Inhoffen, F. Bohlmann, H.-J. Aldag, S. Bork, and G. Leibner, *Ann.*, **573**, 1 (1951).

(13) R. Kuhn and H. Fischer, *Chem. Ber.*, **92**, 1849 (1959); **93**, 2285 (1960).

(10) J. J. Rooney, F. G. Gault, and C. Kemball, *Proc. Chem. Soc.*, 407 (1960).

(11) W. R. Moore, *J. Am. Chem. Soc.*, **84**, 3788 (1962).



Grimm, and Albrecht,⁸ that 30% of the hydrogenation is diverted to adsorbed 1,3-butadiene, 1,2-butadiene, and 1-butyne.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF SOUTHERN CALIFORNIA, LOS ANGELES 7, CALIF.]

The Kinetics of Dehydrogenation of Isobutane by Iodine and the Heat of Formation of the *t*-Butyl Radical^{1a}

BY HIROSHI TERANISHI^{1b} AND SIDNEY W. BENSON

RECEIVED APRIL 8, 1963

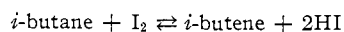
The kinetics of the gas phase thermal dehydrogenation of isobutane by I_2 to yield isobutene and HI was investigated in the temperature range from 250 to 310°. The reaction was found to proceed through an I atom and radical chain mechanism and the rate constants of the elementary steps were measured. The dissociation energy of the tertiary C-H bond in isobutane was found to be 90.9 kcal./mole at 25° and the heat of formation of *t*-butyl radical at 25° and 1 atm. was found to be 6.7 kcal./mole.

Introduction

A recent publication from this Laboratory has described the addition reaction of HI with isobutene.² The reaction above 200° proceeds homogeneously and quantitatively to yield isobutane and I_2 in accordance with the equation



and the rate-determining step, the addition of HI to isobutene, produces *t*-BuI. The equilibrium constant of the reaction



has also been studied in this Laboratory.³ It was of interest, therefore, to study the kinetics of dehydrogenation of isobutane by I_2 which might be expected to have *t*-BuI as an intermediate and for which the rate-determining step is $\text{I} + i\text{-C}_4\text{H}_{10} \rightarrow t\text{-Bu}\cdot + \text{HI}$.

From a kinetic study of the gas phase halogenation of a hydrocarbon and the accompanying inhibition of the reaction by HX, it is possible to determine the relevant C-H bond dissociation energy and also the enthalpy of formation of the corresponding radicals.⁴ However, there has been no other quantitative study on

the halogenation of isobutane except that of Eckstein, Scheraga, and Van Artsdalen.⁵ Their results on the photochemical and thermal bromination of isobutane have led to anomalous rate constants which raise doubts about the validity of the data.⁴

In the present study an effort was made to determine the reaction rate of the dehydrogenation of isobutane, to estimate the dissociation energy of the tertiary C-H bond which would be expected to dissociate at a much faster rate than the primary C-H bond and to calculate the heat of formation of the *t*-butyl radical.

Experimental

The materials and experimental apparatus used were the same as those described in the previous papers.^{3,6}

After evacuating the quartz glass cylindrical reaction vessel of 364-cc. capacity placed in an electric furnace, iodine vapor was admitted to the desired pressure by checking the absorption of light at 5000, 4900, 4800, 4600, or 4400 Å. by means of a spectrophotometer connected to an automatic recorder. Then isobutane was added and the total pressure was measured by a Bourdon spoon gage and a mercury manometer. Defining the instance of isobutane introduction as the 0-time of reaction, the absorption of I_2 thereafter was recorded continuously or at intervals, depending on the temperature at which the reaction was to be studied. The absorption of HI at 2700, 2600, and 2500 Å. was also recorded frequently throughout the reaction period.

After removing I_2 and HI, analysis of the reaction mixture by gas chromatography revealed the presence of isobutene as the

(1) (a) This work has been supported by Grants from the National Science Foundation and the U. S. Atomic Energy Commission; (b) on leave from the Department of Chemistry, Faculty of Science, Kyoto University, Kyoto, Japan.

(2) A. N. Bose and S. W. Benson, *J. Chem. Phys.*, **38**, 878 (1963).

(3) H. Teranishi and S. W. Benson, *J. Am. Chem. Soc.*, **85**, 2890 (1963).

(4) S. W. Benson and J. H. Buss, *J. Chem. Phys.*, **28**, 301 (1958).

(5) B. H. Eckstein, H. A. Scheraga, and E. R. Van Artsdalen, *ibid.*, **22**, 28 (1954).

(6) M. C. Flowers and S. W. Benson, *ibid.*, **38**, 882 (1963).