

The Mercury PhotoSensitized Hydrogenation of the Butenes and the Photolysis of Dinbutylmercury

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solutions of equal ionic strength are compared, the one with less perchlorate ion is appreciably more hydrolyzed. Rabinowitch and Stockmayer³ observed that some specific effect of perchlorate ion on this equilibrium must occur at constant ionic strength, and pointed out that Brønsted's principle of specific interaction of ions⁶ predicted deviations of this nature. The results of the present experiments, however, indicate that at a given perchloric acid concentration the concentration of perchlorate ions is the major factor concerned with the equilibrium.

The equilibrium $\text{Fe}^{+++} + \text{H}_2\text{O} \xrightleftharpoons[r_2]{r_1} \text{FeOH}^{++} + \text{H}^+$ is the

result of the equality of two opposing rates, neither of which formally involves a negative ion. The effect of adding perchlorate ion might be explained by assuming that such addition produces a greater decrease in the forward rate, r_1 , than in r_2 . This could come about if ferric ion formed a complex of sufficient stability and in

sufficient magnitude to account for the shift in equilibrium. If this were the case, we might have expected to find a marked difference between the two absorption spectra for ferric ion shown in Fig. 1. Of course, it is possible that the perchlorate complex has almost the same absorption as ferric ion throughout the whole range. An alternative explanation could be based on the kinetic experiments,⁷ in which it was shown that the large increase in the rate of a reaction between ions of the same sign depends almost entirely on the concentration and character of ions of opposite sign, and the further observation that the rate of the reaction between an ion and a neutral molecule shows only a small salt effect. Until reliable experimental evidence for the existence of a sufficient amount of a complex between ferric ion and perchlorate ion in dilute aqueous solution is presented, we incline to the belief that the shift in the equilibrium studied here is due almost entirely to the increase in r_2 caused by the specific effect of the negative ion.

⁶ J. N. Brønsted, J. Am. Chem. Soc. **44**, 877 (1922).

⁷ A. R. Olson and T. R. Simonson, J. Chem. Phys. **17**, 1167 (1949).

The Mercury Photo-Sensitized Hydrogenation of the Butenes and the Photolysis of Di-*n*-butylmercury

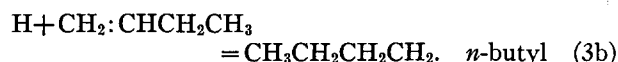
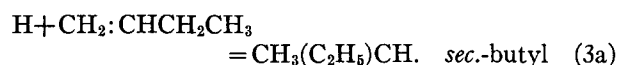
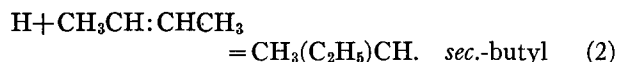
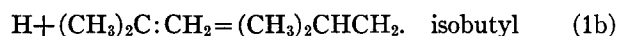
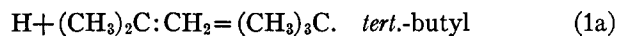
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The Hg-³P₁ photo-sensitized hydrogenations of isobutene, butene-1, and butene-2 have been studied from 24 to 300°C at an H₂:C₄H₈ ratio of 10:1. Mass spectrometer analyses of the products have led to the following conclusions: (1) When a H atom adds to isobutene, the tertiary butyl radical is formed. Any isobutyls decompose immediately into methyl and propene. (2) Addition of a H atom to butene-2 produces little *sec*.-butyl, mostly methyl plus propene. (3) Addition of a H atom to butene-1 produces considerable *sec*.-butyl. Any *n*-butyls decompose into ethyl and ethene. (4) The isomeric constitution of the octanes suggests that radicals add to olefinic double bonds at the carbon atom with highest electron density. Products from the photolysis of di-*n*-butylmercury at $\lambda = 2537\text{\AA}$ indicate that *n*-C₄H₉ = C₂H₅ + C₂H₄ has an activation energy of around 35 kcal.

THIS investigation was designed to study some of the elementary reactions of butyl radicals. It is an extension of earlier work with propylene.¹ Hydrogen atoms from the reaction of Hg-³P₁ with H₂ might be expected to add to the butenes as follows:



¹ W. J. Moore, J. Chem. Phys. **16**, 916 (1948).

Butyl radicals so produced might react by (a) combination, (b) disproportionation, (c) hydrogenation with H or H₂, (d) decomposition, (e) addition to butene (polymerization). Analysis of the final products should provide some information about the relative probabilities of these diverse reactions. The photolysis of di-*n*-butylmercury was also studied, to obtain further data on the products from *n*-butyl.

EXPERIMENTAL

The reaction vessel, a quartz tube 40 mm in diameter by 40 cm long, was mounted in a furnace provided with quartz windows. A Hanovia SC-2537 arc was used for the photo-sensitization experiments and a Hanovia type-L arc for the photolyses. The general experimental procedure has been described previously.^{1,2}

² W. J. Moore and H. S. Taylor, J. Chem. Phys. **8**, 396 (1940).

TABLE I. Products from isobutene hydrogenation.

	23°C	300°C
2,2,3,3-tetramethylbutane	12.2	11.0
2,4,4-trimethylpentene-1	—	1.3
neopentane	11.7	5.5
isobutane	52.2	73.5
propane	2.2	—
propene	5.5	—
ethane	0.6	—
ethene	0.8	—
methane	15.2	9.0

The hydrocarbons used were Phillips Research Grade, and mass spectrometer analyses confirmed their purity as 98.5 percent or better. The dibutylmercury was Eastman (white label), redistilled in vacuum. The hydrogen was deoxygenated by passage through palladized asbestos, anhydrous calcium sulfate, and a silica gel trap at -195°C .

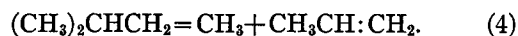
The hydrogenation runs were made with an olefine pressure of 20 to 30 mm and an 8 to 10 fold excess of hydrogen. A few runs with 20 to 30 fold excess of hydrogen showed little change in the product distribution. Assuming the quantum yield of the ethylene hydrogenation to be unity at 23°C , the light input to the reaction vessel could be calculated roughly to be of the order of 5×10^{-8} einsteins/sec. A few runs were made with about 10 times this intensity.

At the end of a run, gas non-condensable at -195°C was pumped off; the hydrogen was burned on cupric oxide and the residual gas recorded as methane. A second fraction was taken at -68° , and a third at room temperature. These were separately analyzed with a Consolidated mass spectrometer. For these analyses we are indebted to the Mass Spectrometer Section of the National Bureau of Standards.

RESULTS

A. Isobutene Hydrogenation

The products from runs at 23° and 300°C are shown in Table I. Except for a trace of 3,4-dimethylhexane the only C_8 product is 2,2,3,3-tetramethylbutane, the dimer of the tertiary butyl radical. The sole product of the addition of a hydrogen atom to isobutene appears to be tertiary butyl. Either the isobutyl radical is not formed at all owing to a higher activation energy of reaction (1b) compared with (1a) or it decomposes before reacting,



The considerable amounts of methane, propene, and neopentane (methyl-*tert*-butyl) are consistent with reaction (4). Reactions (1a) to (3b) are exothermic by 36 to 44 kcal./mole³ so that the radicals formed by

³ J. S. Roberts and H. A. Skinner, Trans. Faraday Soc. 40, 339 (1949).

TABLE II. Products from butene-2 hydrogenation.

	23°C	300°C
3,4-dimethylhexane	0.8	1.7
2,3-dimethylpentane	—	4.8
2,2-dimethylpentane	—	1.2
<i>n</i> -hexane	—	1.2
hexene	—	1.0
2,3-dimethylbutane	—	2.7
pentane (<i>n</i> -?)	4.7	7.0
pentene	—	2.3
<i>n</i> -butane	48.7	23.5
propane	2.1	6.0
propene	13.7	11.3
ethane	4.5	5.8
ethene	4.9	—
methane	18.8	31.4

binary collisions are "hot" to this extent. It is likely, therefore, that the activation energy of reaction (4) is less than 40 kcal. whereas that for decomposition of *tert*-butyl is considerably greater than 40 kcal.

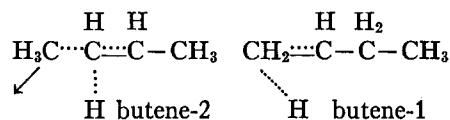
In addition to the volatile products there is considerable polymer.

B. Butene-2 Hydrogenation

The products are shown in Table II. Only the *sec*-butyl radical can be formed in this instance. Like the isobutyl, this can split without rearrangement into methyl and propene. Thus methane, propene, 2,3-dimethylpentane (isopropyl-*sec*-butyl) are found in the products. There is only a small amount of the dimer of *sec*-butyl, 3,4-dimethylhexane, but there is a large amount of unidentified higher polymer. The expected pentane would be isopentane (methyl-*sec*-butyl), but the analyses suggest *n*-pentane.

C. Butene-1 Hydrogenation

The products are given in Table III. Because of the complexity of the product distribution an analysis in terms of the exact isomers present was not always possible. The much higher percent of 3,4-dimethylhexane from butene-1 as compared with butene-2 is noteworthy, inasmuch as this octane is presumed to arise from the *sec*-butyl radical in both cases. This difference may arise from a distinction in the hydrogen atom addition:



When a H atom attacks butene-2, a CH_3 radical can be driven off by a simple replacement reaction on the C atom attacked. When a H atom adds to butene-1, however, the *sec*-butyl radical formed is less likely to decompose since the methyl broken off must come from the other end of the molecule.

TABLE III. Products from butene-1 hydrogenation.

	24°	24° (<i>t</i> × 10)	220°	300°
<i>n</i> -octane	0.4	0.4	0.2	—
3,4-dimethylhexane	30.0	16.6	9.6	1.5
2,2,3-trimethylpentane	—	—	—	1.0
octene-1	3.0	0.9	2.2	—
heptane+heptene	1.4	0.4	1.2	1.6
hexane+hexene	1.6	3.4	8.3	2.9
pentane+pentene	3.0	4.3	4.3	4.7
<i>n</i> -butane	45.7	53.5	38.3	16.9
propane	2.7	2.4	4.5	16.6
propene	5.4	6.9	11.2	14.8
ethane	1.9	4.0	2.9	14.1
ethene	4.3	—	6.2	2.1
methane	0.5	6.7	10.2	21.7

TABLE IV. Products from di-*n*-butylmercury photolysis.

	140°	220°	320°
<i>n</i> -octane	4.5	2.9	3.6
3,4-dimethylhexane	1.6	0.1	0.4
<i>n</i> -hexane	8.9	16.8	14.1
<i>n</i> -pentane	4.0	0.9	2.3
butene-1	—	4.2	1.9
<i>n</i> -butane	54.4	42.2	32.4
propane	—	1.6	4.1
propene	—	2.0	4.4
ethane	7.7	6.4	9.2
ethene	15.0	9.4	12.9
acetylene	0.4	1.0	2.3
methane	1.8	4.7	5.4
hydrogen	3.8	7.0	4.9

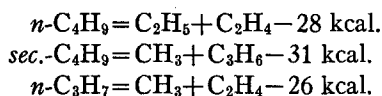
D. Di-*n*-Butyl Mercury Photolysis

The mercury dibutyl photolyses were run with a constant amount of alkyl, sufficient to yield a pressure of 20 mm in the reaction vessel at 120°C. The pressures were therefore greater in the high temperature runs but the vapor densities were about the same. The product analyses are given in Table IV.

The strength of the Hg—C bond has been estimated to be around 16 kcal.⁴ Hence butyl radicals formed by $\text{HgBu}_2 + h\nu(2537) = \text{Hg} + 2\text{Bu}$ would be "hot" to the extent of about 27 kcal. each (on the average). These butyls are therefore somewhat comparable with those from the atomic hydrogenation. The results in Table IV indicate that the preferred mode of decomposition of the radical is $\text{C}_4\text{H}_9 = \text{C}_2\text{H}_5 + \text{C}_2\text{H}_4$.

The occurrence of 2,3-dimethylbutane as the sole hexane product from propene was interpreted as the result of a preferential addition of the H atom to yield the *sec*-propyl radical.¹ It is also possible that, like *n*-butyl, *n*-propyl is so unstable that it immediately breaks into methyl and ethylene,⁵ but the small amounts of ethane and butane found in the propene hydrogenation lend some support to the view that little *n*-propyl is formed in the H atom addition.

The ΔH_{298} for the decomposition of the radicals can be estimated by combining the bond energies of Roberts and Skinner³ with the National Bureau of Standards heats of formation of hydrocarbons.⁶



⁴ N. V. Sidgwick and H. D. Springall, *Nature* **156**, 599 (1945).

⁵ See Rabinowitch, Davis, Winkler, *Can. J. Research* **B21**, 251 (1943).

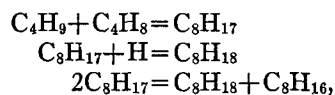
⁶ Nat. Bur. of Stand. Circular No. C-461 (U. S. Government Printing Office, Washington, D. C., November, 1947).

Since the reverse reactions probably have low activation energies,⁷ the activation energies for decomposition of these radicals into an olefin and a smaller radical would all appear to be around 35 kcal. Such values are in accord with the results of the present experiments.

E. Polymerization Reactions

In all of the above reactions a considerable fraction of the final product was a polymer of undetermined composition. The extent of polymerization varied from 45 to 65 percent of the total olefin consumption. In previous work with propene, about 40 percent of the olefin went to polymer. In contrast with these results is the slight polymerization of ethylene reported by LeRoy and Kahn⁸ under similar reaction conditions.

If any appreciable fraction of the octanes formed from the butene hydrogenations arises from chain breaking steps in a polymerization,



one must conclude that butyl radicals add to olefins at the position of highest electron density. The radical acts like an electron-deficient compound. The predominant radical addition is at the opposite end of the double bond from the predominant hydrogen atom addition.

ACKNOWLEDGMENT

A grant-in-aid of research from the Penrose Fund of the American Philosophical Society provided some of the equipment used in this investigation. We are indebted to Mr. Robert Reese, Miss Dorothy Thompson, and Miss Laura Williamson for the hydrocarbon analyses.

⁷ E. W. R. Steacie, *Atomic and Free Radical Reactions* (Reinhold Publishing Corporation, New York, 1946).

⁸ D. J. LeRoy and A. Kahn, *J. Chem. Phys.* **15**, 816 (1947).