The Behavior of Isobutane in Concentrated Sulfuric Acid[1]

BY J. W. OTVOS, D. P. STEVENSON, C. D. WAGNER AND O. BEECK

The behavior of the butanes in sulfuric acid has been studied by circulating each of the four monodeuterobutanes through the acid under various conditions and analyzing the gaseous butane products mass spectrometrically. The only reactions occurring at a significant rate in concentrated sulfuric acid are hydrogen-exchange reactions involving isobutane molecules. n-Butane does not react, and no skeletal isomerization occurs with either of the butanes. The hydrogen-exchange reactions observed with isobutane are (1) the exchange of "primary" hydrogen atoms with the protons of the acid, and (2) intermolecular exchange of "tertiary" hydrogen atoms among isobutane molecules. It was found that isobutane molecules undergo both types of exchange if they react at all, and that all primary hydrogens in a molecule exchange with acid when any exchange. The behavior observed can be accounted for by an ionic chain mechanism, in which the chain carrying step is a transfer of a "tertiary" hydrogen with its electron pair from an isobutane molecule to an ion. Chains are initiated by oxidation of isobutane by sulfuric acid to form ions (and sulfur dioxide) and chains are terminated by reaction of ions to form non-reactive, non-volatile products. During the existence of a particular ion, its primary hydrogen atoms exchange very rapidly with acid protons, so that the regenerated hydrocarbon possesses a complete new set of primary hydrogen atoms.

As a part of a general investigation of the reactions of hydrocarbons in the presence of acidic catalysts,[2-5] there was undertaken a study of the hydrogen exchange reactions of paraffins in sulfuric acid.

By using sulfuric acid-d_2, Ingold, Raisin and Wilson[6] had established that hydrogen atoms of certain paraffins and naphthenes, particularly those possessing tertiary carbon atoms, exchange with the hydrogen atoms of sulfuric acid. Stewart and Harman[7] had shown, using sulfuric acid-d_2, that hydrogen exchange takes place between isobutane and sulfuric acid at a measurable rate at 10°. Therefore, as a beginning in an intensive study of such reactions, the hydrogen-exchange reactions of the butanes with sulfuric acid were studied in detail. In order to distinguish differences of behavior of the three types of carbon–hydrogen bonds (which was not possible in the studies reported in the references cited) most of the data were obtained using the four monodeuterobutanes and ordinary sulfuric acid. The vapor phase in each experiment was examined from time to time by direct mass spectrometric analysis.

Experimental

Materials.—n-Butane-1-d, n-butane-2-d, isobutane-1-d, and isobutane-2-d[8] were all of better than 98% isotopic purity and the olefin content was less than 0.02% in all cases. Details of their preparation via the Grignard reagents and their analyses by means of their mass and infrared spectra have been described previously.[9,10]

The isobutane-1-C^{13} was of 47.7% isotopic purity and contained <0.03% olefin. Details of the preparation and analysis have been described.[11]

Non-isotopic isobutane, isobutylene and cis-2-butene used were Phillips Research Grade hydrocarbons.

The sulfuric acid used was Baker and Adamson reagent grade, diluted with water to the required concentration. General Chemical Company's fuming sulfuric acid, 15%, reagent grade, was used to make up the acids of concentration above 96%.

Deuterosulfuric acid was prepared by addition of sulfur trioxide to deuterium oxide. Fuming sulfuric acid (15%) was heated until most of its excess sulfur trioxide had distilled into an H-shaped receiver, equipped with a Drierite tube at its exit. The required amount of D_2O (obtained from Stuart Oxygen Company under allocation from the Atomic Energy Commission, said to be 99.8+% isotopically pure) was placed in the other arm, and the sulfur trioxide was slowly distilled into it with cooling. The reagent so prepared was diluted to the required concentration with more D_2O. Its isotopic purity with reference to deuterium atoms and hydrogen atoms was determined to be 99.5+% by a special method, to be described in a subsequent publication,[12] involving hydrogen exchange with 2,3-dimethylbutane.

Apparatus and Procedure.—The butanes with or without added olefin, were ordinarily used at 250–350 mm. pressure in a volume of ca. 70 ml. They were circulated through 8–10 ml. of sulfuric acid at 25° at a rate of approximately 600 ml./min. (rate was constant but not accurately determinable). Circulation of the gas was accomplished by means of a glass piston pump. The vertical glass piston encloses an iron rod, and is actuated by two solenoids placed around the pump and alternately energized with 60-volt alternating current. The period of oscillation is governed by a variable vibrator circuit and is ordinarily selected so that the pump is in resonance, which in these experiments corresponded to 160 cycles per minute. An all-glass valve system makes possible circulation of the gas by movement of the piston in either direction.

Gas phase samples amounting to 700 ml. mm., or $^1/_{30}$ of the amount of hydrocarbon used, were removed periodically for examination mass spectrometrically. Methods used in this analysis are given in a special section below.

Results and Discussion

Preliminary Experiments.—Each of the two monodeutero-n-butanes was circulated through 10 ml. of 96.2% sulfuric acid (reagent grade) for three hours. Circulation was stopped for 18 hours, then resumed for a few minutes before the final samples were taken. There were no changes in the mass spectra (see below). Likewise, there was no detectable change in the mass spectrum of isobutane-2-d after five hours' circulation through 96.2% acid. However, isobutane-1-d was converted into ordinary isobutane (designated isobutane-d_0). After an induction period of 10–20 minutes the rate was first order in isobutane-1-d concentration (in the gas phase) and half-conversion was attained in three hours. There was no observable loss of hydrocarbon in these experiments and no formation of polydeuterated butanes.

From these experiments it is concluded that: (1) No skeletal isomerizations of either n-butane or

(1) Material contained herein presented at A. C. S. Meeting. San Francisco, Calif., April. 1949.

(2) D. P. Stevenson and O. Beeck. THIS JOURNAL. 70, 2890 (1948).

(3) O. Beeck. J. W. Otvos. D. P. Stevenson and C. D. Wagner. J. Chem. Phys., 16, 255 (1948); ibid.. 17, 418 (1949).

(4) J. W. Otvos. D. P. Stevenson. C. D. Wagner and O. Beeck. ibid.. 16, 745 (1948).

(5) C. D. Wagner. O. Beeck. J. W. Otvos and D. P. Stevenson. ibid.. 17, 419 (1949).

(6) C. K. Ingold. C. G. Raisin and C. L. Wilson. J. Chem. Soc.. 1643 (1936).

(7) T. D. Stewart and D. Harman. THIS JOURNAL. 68. 1135 (1946).

(8) For clarity in presentation the names isobutane-1-d, isobutane-2-d, n-butane-1-d and n-butane-2-d are used here in place of the more correct I. U. C. names. methylpropane-1-d. methylpropane-2-d. butane-1-d and butane-2-d.

(9) C. D. Wagner and D. P. Stevenson. THIS JOURNAL. 72, 5785 (1950).

(10) D. P. Stevenson and C. D. Wagner. ibid., 72, 5612 (1950).

(11) C. D. Wagner. D. P. Stevenson and J. W. Otvos. ibid.. 72, 5786 (1950).

(12) D. P. Stevenson, C. D. Wagner. O. Beeck and J. W. Otvos, ibid., in press.

isobutane take place in sulfuric acid at a measurable rate.

(2) No hydrogen exchange takes place between molecules of n-butane (intermolecular) or between the primary and secondary carbon atoms of single n-butane molecules (intramolecular). Whether the possible intramolecular exchanges among primary positions or among secondary positions occurs could not be determined, but such reactions are assumed to be very unlikely in the absence of exchanges of other types.
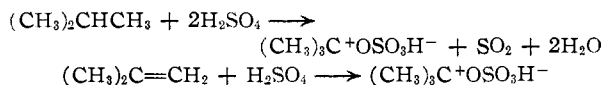
(3) The tertiary hydrogen atom[13] of isobutane does not exchange with acid protons, but the primary hydrogen atoms do exchange at a reasonable rate. This is evidently the exchange observed by Stewart and Harman.[7] There is no exchange between primary and tertiary hydrogen atoms, either intramolecular or intermolecular, and also no intermolecular exchange of primary hydrogen atoms among isobutane molecules. Whether the possible intramolecular exchange of primary hydrogen atoms or the intermolecular exchange of tertiary hydrogens occurs could not be determined in these preliminary experiments.

(4) The first order rate of exchange of isobutane-1-d with acid protons indicates that the reaction is proceeding in a steady state.[14] It reaches the steady state after an initial period of increasing specific reaction rate.

In order to obviate the possibility that the differences in behavior of isobutane-1-d and isobutane-2-d might be due to slight traces of olefin in the former, similar experiments were performed with samples containing 0.1% isobutylene. There was still no evident change in behavior of isobutane-2-d, but the rate of the isobutane-1-d reaction increased about 50% and the initial period of increasing rate was eliminated.

On the basis of this behavior of isobutane, a mechanism of reaction was developed which is similar in many respects to parts of the proposed chain mechanism of alkylation.[15] While this work was in progress, Burwell and Gordon[16] reported similar conclusions, made as a result of studies of the relation between hydrogen exchange and racemization of certain higher molecular weight optically active hydrocarbons in sulfuric acid.

Reaction Mechanism.—The basic mechanism that fits these observations and that is also consistent with the observations of Burwell and Gordon is the following: (1) Carbonium ion chains are started by the formation of carbonium ions[17] from isobutane or from traces of contaminating olefin[15]

$$(CH_3)_2CHCH_3 + 2H_2SO_4 \longrightarrow$$
$$(CH_3)_3C^+OSO_3H^- + SO_2 + 2H_2O$$
$$(CH_3)_2C{=}CH_2 + H_2SO_4 \longrightarrow (CH_3)_3C^+OSO_3H^-$$

(13) The term "tertiary hydrogen" is used for simplicity, referring to a hydrogen atom attached to a tertiary carbon atom. "Primary hydrogens" and "secondary hydrogens" are defined similarly.

(14) H. A. C. McKay, Nature, **142**, 997 (1938).

(15) L. Schmerling, This Journal, **66**, 1422 (1944); P. D. Bartlett, F. E. Condon and A. Schneider, ibid., **66**, 1531 (1944).

(16) R. L. Burwell, Jr., and G. S. Gordon, III, ibid., **70**, 3128 (1948); **71**, 2355 (1949).

(17) The term "carbonium ion" is used to denote either the solvated ion, otherwise free in solution, R⁺(H₂SO₄), or the complexed, highly polarized ester, R⁺-OSO₄H⁻. The experiments do not differentiate between these structures.

The first reaction involves the oxidation of isobutane by sulfuric acid. It would be expected to be slow.

(2) The chains are carried by the shifts of hydride ions[18] between the carbonium ions and dissolved isobutane molecules or isobutane molecules at the interface

$$(CH_3)_3CH + {}^+C(CH_3)_3 \longrightarrow (CH_3)_3C^+ + HC(CH_3)_3$$
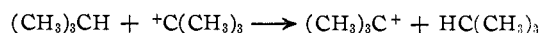
(3) During the existence of a carbonium ion any of its hydrogen atoms (all primary) may exchange with protons of the acid. We shall assume that this exchange occurs at a rate such that equilibrium between carbonium ion hydrogens and acid hydrogens is established during the life of each ion.

(4) Chains are terminated by some irreversible side reactions of carbonium ions leading to nonvolatile products. This picture would account for the lack of exchange between t-isobutane hydrogen atoms and sulfuric acid, since any molecule dissolving in acid, reacting and re-entering the vapor phase, would have received a new tertiary hydrogen from another isobutane molecule.

Tracer Tests of the Mechanism.—There are several ways of testing the mechanism. First, the exchange of tertiary hydrogen atoms from isobutane molecules to carbonium ions should occur in such a way that each molecule that (a) undergoes primary hydrogen–acid hydrogen exchange should also (b) acquire a new tertiary hydrogen. Although reaction (a) in terms of hydrogen atoms is very rapid, the number of isobutane molecules undergoing reaction (a) and reaction (b) should be equal. This equality was experimentally observed by comparing the rate of the isobutane-1-d–sulfuric acid reaction with that occurring in a system containing isobutane-2-d (99.5% isotopic purity) and isobutane-1-C¹³ (48.2% isotopic purity with reference to the isotopic species, isobutane-C¹³) in contact with sulfuric acid. In the latter system, the tertiary hydrogen transfer becomes in over-all effect the reaction

$$BD + B'H \rightleftharpoons B'D + BH$$
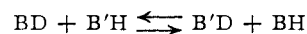
where B represents t-butyl and B' represents t-butyl containing a C¹³ atom. Mass spectrometric analysis is straight-forward, since B'D has a molecular weight of 60, while BD and B'H have molecular weights equal to 59. It can be shown that the mechanism requires, assuming no isotope effects on reaction rates, that the rate of the attainment of the above equilibrium and that of the attainment of the equilibrium

$$\text{Isobutane-1-}d + H_2SO_4 \rightleftharpoons \text{Isobutane-}d_0 + HDSO_4$$
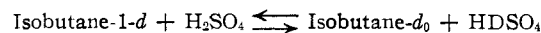
be identical. Analytically, the variation of $\ln\left(1 - \dfrac{\Delta y}{\Delta y_{eq.}}\right)$ with t should be the same for the two reactions, where Δy represents the change in isobutane-1-d or isobutane-1-C¹³-2-d mole fraction in the gas phase at time t and $\Delta y_{eq.}$ represents the similar change at equilibrium. In Fig. 1 is shown such a plot for the two reactions in both 93.5%

(18) The term "hydride ion" refers to a hydrogen nucleus with an electron pair, but in these systems it is assumed not to be an ion in the sense that it is free from the influence of the rest of the hydrocarbon molecule.

H_2SO_4 and 96.2% H_2SO_4. The slightly slower rate for the tertiary hydrogen-transfer reaction may be due to an isotope effect or may be due to the presence of differing amounts of traces (<0.01%) of olefin. Actually, the slopes, k, of the curves for the reactions in their steady-state phase differ by less than 20%. The addition of 0.1% isobutylene was found to have the same effect on the tertiary hydrogen transfer reaction as it has on the primary hydrogen–acid hydrogen exchange.

The question remains whether the same molecules are involved in both types of exchange, as is required by the mechanism. In order to test this point, an equimolar mixture of isobutane-1-d and isobutane-2-d was circulated through acid in the usual manner. No isobutane-1,2-d_2 (mass = 60) was produced, although the isobutane-1-d content decreased and isobutane-d_0 content increased proportionately at a rate expected for a mixture with that isobutane-1-d content. It is thus demonstrated that when a molecule is involved in tertiary-tertiary hydrogen exchange, it also exchanges all of its primary hydrogens for acid hydrogens. Since the numbers of molecules per unit time participating in both exchanges are equal, it follows that the converse is also true. A molecule undergoing any hydrogen exchange undergoes both types of exchange, in agreement with the mechanism.

An additional proof was obtained that all primary hydrogen atoms in a molecule exchange with acid if any exchange. Circulation of 1.5 millimoles of ordinary isobutane through 5.2 ml. of deutero-sulfuric acid (95% acid, >99.5 atom % D) gave, in the initial stages, isobutane-d_9 only, with the lone hydrogen atom attached to the tertiary carbon. After half the molecules had undergone exchange, an appreciable amount of isobutane-d_8 began to appear, because of isotopic dilution of the sulfuric acid-d_2.

Effects of Reaction Conditions.—The proposed mechanism accounts qualitatively and semi-quantitatively for the observed behavior of the isobutane hydrogen atoms as examined by tracer techniques. It was of interest also to examine the effects of reaction conditions on the over-all reaction rate.

Effect of Olefins.—It has been shown[14,19] that in any isotopic exchange reaction in which the concentrations of chemical species do not change and in which the exchange rate is constant, the rate of disappearance or appearance of isotope in one of the compounds must necessarily be first order, regardless of the mechanism of the exchange. Hence the rate of disappearance of isobutane-1-d in the exchange of isobutane-1-d with sulfuric acid must be first order when the rate of exchange becomes constant. Figure 1 shows that after an initial induction period the first order rate does become constant. It was found that the absolute value of the steady-state rate of exchange is dependent upon added olefin concentration. According to the proposed mechanism the observed
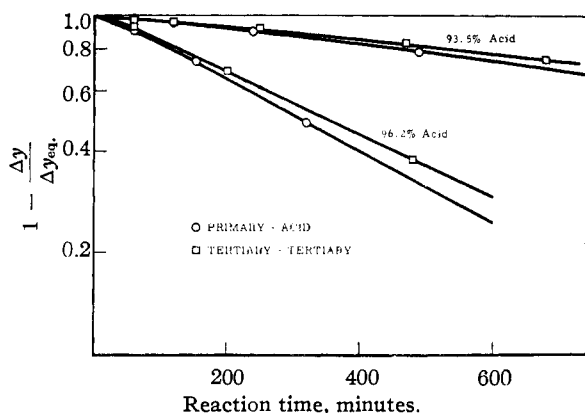
(19) J. N. Wilson and R. G. Dickinson. THIS JOURNAL, **59**, 1358 (1987).

Fig. 1.—Comparison of rates of the two hydrogen exchange reactions occurring in the system isobutane-sulfuric acid.
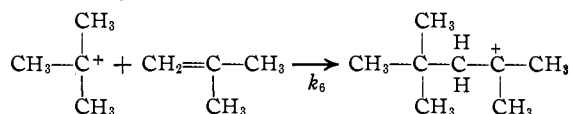
rate, R, of the reaction is the rate of the chain-carrying step

$$R = k_2BX$$

where B represents concentration of dissolved isobutane and X is the concentration of t-butyl carbonium ion. The addition of olefin would be expected to affect the rate only by affecting the carbonium ion concentration. It is generally assumed that dissolved olefin reacts to form carbonium ions

$$(CH_3)_2C\!\!=\!\!CH_2 \xrightarrow[k_5]{H_2SO_4} (CH_3)_3C^+OSO_3H^-$$
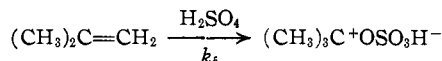
and that carbonium ions and olefin molecules may react in a polymerization reaction

$$CH_3\!\!-\!\!\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}{}^+ + CH_2\!\!=\!\!\underset{\underset{CH_3}{|}}{C}\!\!-\!\!CH_3 \xrightarrow{k_6} CH_3\!\!-\!\!\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}\!\!-\!\!\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}\!\!-\!\!\overset{+}{\underset{\underset{CH_3}{|}}{C}}\!\!-\!\!CH_3$$

If we let E and S represent the concentrations of dissolved olefin and unidentified non-volatile products, respectively, we can set up the following reaction scheme

$$B \xrightarrow{k_1} X \tag{1}$$

$$X \xrightarrow{k_4} S \tag{2}$$

$$E \xrightarrow{k_5} X \tag{3}$$

$$E + X \xrightarrow{k_6} S \tag{4}$$

where reactions (1) and (2) are part of the basic mechanism and reactions (3) and (4) are the reactions involving added olefins.

The differential equations associated with reactions (1)–(4) are

$$dX/dt = k_1B + k_5E - (k_4 + k_6E)X \tag{5}$$
$$dE/dt = -(k_5 + k_6X)E \tag{6}$$
$$dB/dt = -k_1B \tag{7}$$

Equation 7 is directly integrable and the solution, $B = B_0e^{-k_1t}$, may be substituted into equation 5. To solve equations (5) and (6) in closed form, however, we must make some simplifications that will render the equations linear. There are two extreme assumptions possible concerning E that yield linear equations. First, k_5t may be very large

at all times of interest so that all the olefin immediately forms carbonium ion. This would mean that $E = 0$ and $X_0 = E_0$, where the zero subscript denotes initial conditions. This assumption yields equation 8.

$$dX/dt = k_1 B_0 e^{-k_1 t} - k_4 X \quad X_0 = E_0 \quad (8)$$

Second, if $(k_5 + k_6 X)t$ is very small so that E remains essentially constant, $E = E_0$. This assumption yields equation 9.

$$dX/dt = k_1 B_0 e^{-k_1 t} + k_5 E_0 - (k_4 + k_6 E_0)X \quad X_0 = 0 \quad (9)$$

Both equations 8 and 9 can now be integrated. Since in none of the experiments on the effect of olefin was there any detectable decrease in butane pressure we may set $e^{-k_1 t} = 1$ and the resulting, simplified integrated equations become, respectively

$$X = \frac{k_1 B_0}{k_4}(1 - e^{-k_4 t}) + E_0 e^{-k_4 t} \quad (10)$$

$$X = \frac{k_1 B_0 + k_5 E_0}{k_4 + k_6 E_0}(1 - e^{-(k_4 + k_6 E_0)t}) \quad (11)$$

The exponential terms in both equations indicate the existence of an induction period. For large values of $k_4 t$ the exponentials vanish and the steady-state concentrations are, respectively

$$X_8 = \frac{k_1 B_0}{k_4} \quad (10a)$$

$$X_8 = \frac{k_1 B_0 + k_5 E_0}{k_4 + k_6 E_0} \quad (11a)$$

In order to permit a choice between the two extreme assumptions that were made regarding E the reaction of isobutane-1-d with acid was studied in the presence of small, known concentrations of isobutylene. The reaction rate curves in Fig. 2 show that there is no observable induction period in the presence of olefin and that the steady state rate is affected by the added olefin concentration. This effect of olefin is presumably on the steady state carbonium ion concentration. Clearly, then, equations 10 and 10a do not fit the facts since they predict that the steady state concentration of carbonium ion as well as the induction period should be independent of added olefin concentration. Equations 11 and 11a, on the other hand, do have the correct form. The added olefin increases X_8,
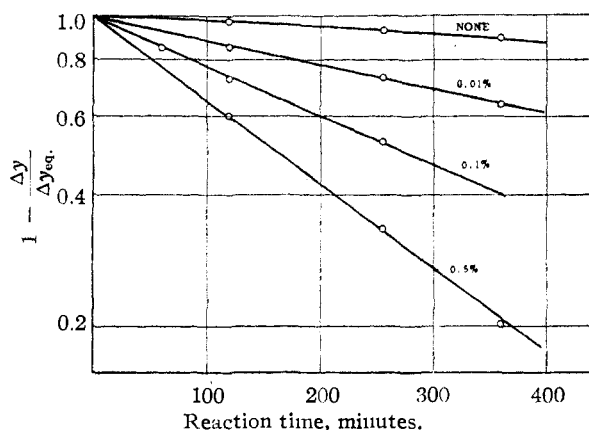

Fig. 2.—Effect of added isobutylene on the rate of the isobutane–sulfuric acid exchange reaction.

but not linearly. Figure 3 shows the experimentally determined relative steady-state rate $vs.$ added isobutylene concentration. The solid line is a plot of equation 11a with $k_1 B_0 / k_4 = 19$ in relative units where 100 represents the maximum possible rate at large olefin concentrations, $k_5 / k_1 B_0 = 32.5$ and $k_6 / k_4 = 6.2$ in reciprocal mole fraction. There are not enough experimental points to give a rigid test of equation 11a but it is clear that of the two assumptions that were made the latter is the one that fits the experimental results.
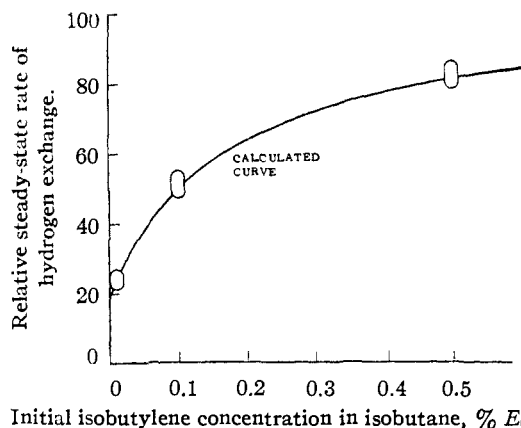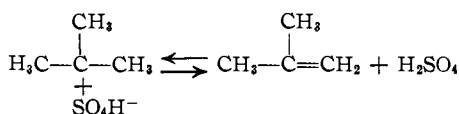

Fig. 3.—Relation between initial isobutylene concentration and the rate of hydrogen exchange.

Evidence has been obtained in other work to be reported[12] that secondary carbonium ions do not exist in this medium with a lifetime great enough to permit participation in chain propagating steps. Also, it should be noted that comparatively stable s-alkyl esters are formed by the action of sulfuric acid on olefins (the role of ester in the isobutylene reaction was ignored for simplicity; it can be included in the reaction scheme equally satisfactorily, but is not necessary) and the over-all rate of conversion of straight chain olefins to carbonium ions might be considerably different than with branched olefins. To explore these possibilities, similar experiments were performed with cis-2-butene as the "contaminant." This compound was found to be less efficient in eliminating the induction period and, at least in the reaction times studied, in increasing the steady-state rate. In the latter respect the 2-butene appeared to be roughly $^1/_5$ as effective as the isobutylene.

Recent results reported by Stewart and Calkins[20] make it appear very probable that this induction period noted with cis-2-butene is a period in which straight-chain olefins are being converted to branched, tertiary ions, perhaps by means of consecutive polymerization, isomerization of the polymer and depolymerization. They found that isobutane was essentially the only gaseous product obtained from the reaction of a variety of C_4-olefins and alcohols with concentrated sulfuric acid, and that with 2-butene but not with isobutylene there was an induction period preceding the evolution of the isobutane.

(20) T. D. Stewart and W. H. Calkins, This Journal, 71, 4144 (1949).

If it is true that olefin is converted only slowly into carbonium ions, as indicated by the mechanism developed above, the exchange of primary hydrogen atoms with acid protons must not occur *via* the mechanism

$$H_3C\overset{\underset{|}{CH_3}}{\underset{\overset{+}{SO_4H^-}}{\overset{|}{C}}}CH_3 \rightleftharpoons CH_3-\overset{\underset{|}{CH_3}}{\overset{|}{C}}=CH_2 + H_2SO_4$$

Nevell, deSalas and Wilson[21] had observed that hydrogen exchange between camphene hydrochloride and hydrochloric acid could not be explained by a similar equilibrium in that system. It is possible that the reaction occurs directly between ion and acid, favored by distribution of the positive charge among the primary hydrogen atoms in the resonance structures

$$H_3\equiv C-C\overset{\overset{\displaystyle C\diagup\!\!\!\!\diagup H_3}{}}{\underset{\underset{\displaystyle \diagdown H_3}{}}{\diagdown C}}{}^+$$
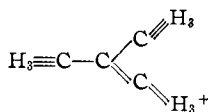
Effect of Acid Concentration.—Samples of isobutane-1-*d* were circulated through sulfuric acid of different concentrations, 92–100%. Reaction rate curves are shown in Fig. 4. It is clear that the rate of the reaction increases markedly with increased acid concentration. This may indicate that the more concentrated acid operates by (1) increasing the steady-state concentration of carbonium ions by increasing k_1 more than k_4, (2) increasing the solubility of isobutane (if the oxidation reaction and/or the chain-transfer reaction are homogeneous), (3) increasing the rate constant, k_2, for the reaction of isobutane with carbonium ion.

One experiment was performed using acid containing excess sulfur trioxide, corresponding to sulfuric acid with a hypothetical concentration of 101%. In this system it was noted for the first time that isobutane was consumed at a measurable rate; sulfur dioxide was produced at a more or less corresponding rate. (Traces of SO_2 were also noted in the gas phase after long contact times in experiments with 98% acid.) The usual exchange reaction also took place. The rate of the reaction, determined by the slope of the curve of the logarithm of the ratio of isobutane-1-*d* and total isobutane partial pressures *versus* time, decreased as isobutane was consumed, the slope being essentially proportional to the total isobutane pressure. The mechanism requires that the rate vary directly with isobutane concentration in acid.

Methods of Mass Spectrometric Analysis.—As indicated above, whether or not a monodeuterobutane reacted with sulfuric acid was determined by comparison of the mass spectrum of a "reaction product" with that of the "feed." The most reliable criterion of reaction in experiments with *n*-butane-1-*d*, *n*-butane-2-*d*, and isobutane-2-*d* is an increase in the ratio of the intensity of the ion of $m/q = 58$ to that of $m/q = 59$ in the mass spectrum[22] of the product over its value in the mass spectrum of the feed. Because of the peculiarities of the mass spectrum of isobutane-1-*d*, an increase in the ratio of the intensity of the ion of $m/q = 57$ to that of $m/q = 59$ is a more sensitive criterion of reaction for this compound. For exchange with the sulfuric acid in experiments involving *n*-butane-1-*d*, *n*-butane-2-*d* and isobutane-2-*d*, the increase in the 58/59 ratio is a direct measure of the extent of reaction, for small conversion, while for the reaction of isobutane-1-*d* the increase in the 57/59 ratio is equal to approximately six-tenths the extent of exchange. If we take ±0.3% as a reasonable measure of the reliability of measurements of the ratio of adjacent intensities in mass spectra on a single day, and if the mass spectrum of the product is compared with that of the feed measured on the same day, the limit of detection of exchange is 0.3% for the *n*-butane-*d*'s and isobutane-2-*d* and 0.5% for isobutane-1-*d*.

(21) T. P. Nevell, E. deSalas and C. L. Wilson. *J. Chem. Soc..* **1188** (1939).

(22) For the mass spectra of the various butanes see D. P. Stevenson and C. D. Wagner. *J. Chem. Phys..* **19**, 11 (1951).
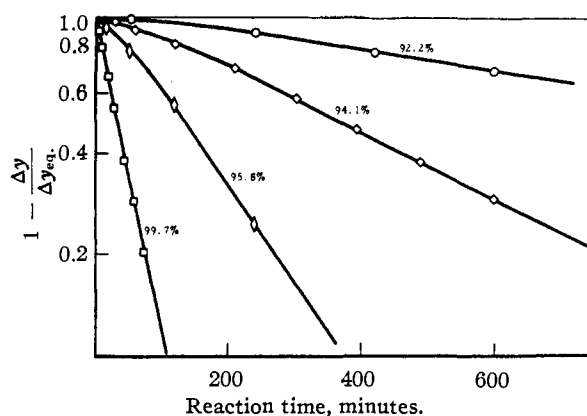
Fig. 4.—Effect of acid concentration on the rate of the isobutane–sulfuric acid hydrogen exchange reaction.

Isomerization processes, including skeletal rearrangements and hydrogen shifts such as the interconversion of *n*-butane-1-*d* and -2-*d* are best detected through comparison of the ratio of the intensity of the ion $m/q = 44$ to that of $m/q = 59$. If ±1.0% is taken as the accuracy of measurement of the 44/59 ratio, the limit of detection of interconversion of *n*-butane-1-*d* and -2-*d* is 1.0%, that of interconversion of isobutane-1-*d* and -2-*d* is 0.8%, that of the conversion of *n*-butane to isobutane is 1.7%, and that of conversion of isobutane to *n*-butane is 0.3%. If both reactions take place simultaneously the limits of detection increase rapidly because a large number of simultaneous equations with relatively large off-diagonal terms must be solved.

In Table I there are shown typical examples of the data from which it was concluded that *n*-butane-1-*d*, *n*-butane-2-*d* and isobutane-2-*d* undergo neither exchange reactions with sulfuric acid nor isomerization reactions involving intermolecular hydrogen or carbon exchanges. There is included for comparison an example showing the existence of the exchange reaction of isobutane-1-*d* with sulfuric acid.

TABLE I

TYPICAL ANALYTICAL DATA ON THE PRODUCTS OF THE REACTIONS OF MONODEUTEROBUTANES WITH 96% SULFURIC ACID AT 25°

Substance	Contact time, hr.	58/59 Feed	58/59 Product	44/59 Feed	44/59 Product
n-Butane-1-*d*	3	0.1586	0.1587	2.42	2.40
	22[a]	.1586	.1580	2.42	2.45
n-Butane-2-*d*	2	.1387	.1380	4.30	4.33
	19[a]	.1387	.1365	4.30	4.41
Isobutane-2-*d*	5	.0816	.0869	...	...
	3[b]	.0846	.0942	19.37	19.18
Isobutane-1-*d*	2	.710	5.17	11.45	11.55

[a] See text for description of experiment. [b] 98% H_2SO_4.

For the actual determination of the conversion of isobutane-1-*d* into isobutane by the sulfuric acid the products were analyzed by solving simultaneous equations involving

TABLE II

RESULTS OF THE REACTION OF ISOBUTANE-1-*d* WITH 94.1% SULFURIC ACID

Time, min.	From ion ratios	Isobutane-1-*d*, mole per cent. — After normalization 59/57	44/43	30/29	Before normalization 59/57	44/43	30/29
30		93.5	93.0	93.8	91.6	92.0	92.7
60		89.7	89.6	89.2	89.4	88.5	87.4
120		81.2	81.3	81.3	79.3	79.6	80.6
210		69.2	68.8	69.2	68.2	68.1	68.6
303		57.2	56.9	57.4	57.1	57.0	57.5
392		47.6	48.0	47.8	46.8	47.0	47.1
488		38.4	38.9	38.9	37.8	38.4	38.2
602		30.9	30.6	31.6	30.5	30.1	30.1

TABLE III

CALCULATED UNCERTAINTIES OF ANALYSES OF MIXTURES OF ISOBUTANE-d_0 AND -1-d

| From ions | 59 and 58 | | 59 and 57 | | 44 and 43 | | 30 and 29 | |
	100% d_0	100% d_1	100% d_0	100% d_1	100% d_0	100% d_1	100% d_0	100% d_1
$\Delta(-d_0)$. %	±1.0	±0.9	±1.0	±0.23	±1.1	±0.9	±1.0	±0.8
$\Delta(-1-d_1)$. %	±0.06	±1.0	±0.12	±1.0	±0.10	±1.0	±0.10	±1.0

the intensities of the pairs of ions, 59 and 57, 44 and 43, and 30 and 29. The mass spectrometric data were obtained in the following order: isobutane, isobutane-1-d, the set of products from a given run, isobutane-1-d and isobutane. The averages of the isobutane and isobutane-1-d calibrations were employed to interpret the set of data in the products of the run. The values of the isobutane-1-d concentration estimated from each of the individual pairs of simultaneous equations were averaged after normalization. The results on a typical run, isobutane-1-d vs. 94.1% H_2SO_4, are shown in Table II.

If it is assumed that errors are random, and that the accuracy of specific intensity measurements is ±1.0%, it is possible to calculate the expected uncertainties of the analyses resulting from the solution of the various pairs of simultaneous equations.[23] The results of such calculations are shown in Table III. It will be noted that the accuracy for a given component varies with the composition of the mixture. This variation is essentially linear with composition.

In the cases of the reaction products resulting from the reaction of isobutane-2-d with isobutane-C^{13}, isobutane-C^{13}-2-d was directly determinable from the increase in intensity of the ion, m/q = 60. After correction of the observed intensities of the ions of m/q = 59, 58, 57 for contributions from isobutane-C^{13}-2-d (assumed to have a mass spectrum like that of isobutane-2-d) a set of simultaneous equations involving the corrected intensities of these three ions was solved for the concentrations of isobutane-d_0, -C^{13} and -2-d. A check on the accuracy of the analysis resulting from the solution of the set of simultaneous equations was made through the stoichiometry of the reacting system. Material balance requires

$$i\text{-}C_4H_{10} = (i\text{-}C_4H_{10})_{initial} + i\text{-}C_4H_{10}\text{-}C^{13}\text{-}2\text{-}d$$
$$i\text{-}C_4H_{10}\text{-}2\text{-}d = (i\text{-}C_4H_{10}\text{-}2\text{-}d)_{initial} - i\text{-}C_4H_{10}\text{-}C^{13}\text{-}2\text{-}d$$
$$i\text{-}C_4H_{10}\text{-}C^{13} = (i\text{-}C_4H_{10}\text{-}C^{13})_{initial} - i\text{-}C_4H_{10}\text{-}C^{13}\text{-}2\text{-}d$$

(23) Whitaker and Robinson, "Calculus of Observations," Blackie and Sons, London, 1929, p. 243.

Since the composition of the isotopic preparations from which the feed was prepared by blending were accurately known and their mass spectra were well known as well, the synthetic composition could be checked mass spectrometrically by solving only the simultaneous equations involving the intensities of the ions of m/q = 58 and 57 in the mass spectrum of the feed. Thus the initial concentrations were known to better than ±0.5%.

The accuracy to be expected for the solution of the three simultaneous equations was calculated under the assumptions that the mass spectral intensities had a relative accuracy of ±1% and the composition of the product was the average of the observed range. The results of these calculations are shown in Table IV, where they are compared with the observed errors taken as the difference between the results of the direct mass spectrometric analyses and the values computed from the stoichiometry.

TABLE IV

ACCURACY OF ANALYSES OF TERNARY MIXTURES OF ISOTOPIC BUTANES

Component	Range of concentration, mole %	Calculated uncertainty, %	Measured error,[a] %
$i\text{-}C_4H_{10}\text{-}C^{13}$	25.0–15.0	±0.7	±0.5
$i\text{-}C_4H_{10}\text{-}2\text{-}d$	50.0–40.0	± .8	± .8
$i\text{-}C_4H_{10}$	25.0–35.0	± .4	± .8

[a] Fourteen analyses.

The agreement between calculated and observed error is satisfactory except in the case of isobutane. It is probable that errors in the determination of isobutane-C^{13}-2-d are all reflected in the determination of isobutane, rather than being distributed across all three components. No allowance for such error was made in the calculation.

Application of the 1,4-Addition of Grignard Reagents to α,β-Unsaturated Acid Derivatives. II. Preparation of 3,4-Diaryl-2-hexanones and 3,4-Diaryl-2-hexanols[1]

BY STANLEY WAWZONEK

3,4-Diaryl-2-hexanones and 3,4-diaryl-2-hexanols have been prepared from α-arylcinnamonitriles for testing as synthetic estrogens. The activity was found to be greatest for the 3,4-di-p-anisyl derivatives. The hexanols were found to be unsatisfactory starting materials for the preparation of stilbestrol dimethyl ether and related compounds.

The synthesis of 3,4-diaryl-2-hexanones and 3,4-diaryl-2-hexanols was undertaken to prepare variants of hexestrol and to determine the feasibility of using these compounds in a synthesis of stilbestrol. The ketones were prepared by the reactions devised by Kohler[2] for 3,4-diphenyl-2-hexanone and summarized below.

$$R_1C_6H_4CH\!=\!CC_6H_4R_2 \xrightarrow{C_2H_5MgBr}$$
$$\underset{I}{\overset{|}{CN}}$$

$$\left[\underset{\overset{|}{CN}}{R_1C_6H_4\overset{\overset{C_2H_5}{|}}{CH}C\!\!-\!\!C_6H_4R_2}\right]^- MgBr^+ \xrightarrow{H_2O}$$
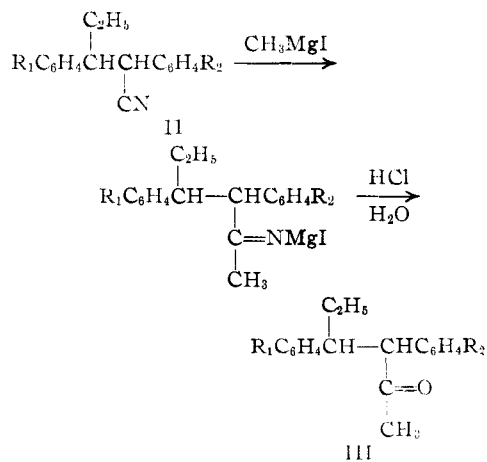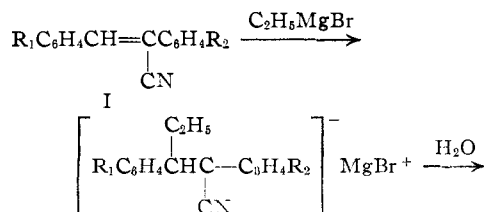
(1) Paper I, THIS JOURNAL, 68, 1157 (1946).
(2) E. P. Kohler, Am. Chem. J., 35, 386 (1906).

$$R_1C_6H_4\overset{\overset{C_2H_5}{|}}{CH}CHC_6H_4R_2 \xrightarrow{CH_3MgI}$$
$$\underset{II}{\overset{|}{CN}}$$

$$R_1C_6H_4\overset{\overset{C_2H_5}{|}}{CH}\!\!-\!\!\underset{\underset{CH_3}{|}}{\overset{\overset{CHC_6H_4R_2}{|}}{C\!=\!NMgI}} \xrightarrow[H_2O]{HCl}$$

$$R_1C_6H_4\overset{\overset{C_2H_5}{|}}{CH}\!\!-\!\!\underset{\underset{CH_3}{|}}{\overset{\overset{CHC_6H_4R_2}{|}}{C\!=\!O}}$$
$$III$$