to follow the Hammett acidity function, h_0,[5] as indicated by the equations

$$K = \frac{a_\pi}{a_o a_{H^+}} = \left(\frac{c_\pi}{c_o}\right)\left(\frac{\gamma_\pi}{\gamma_o}\right)\left(\frac{\gamma_B}{\gamma_{HB^+}}\right)\left(\frac{1}{h_o}\right) = \left(\frac{c_\pi}{c_o}\right)\left(\frac{1}{h_o}\right)$$

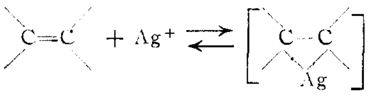
and

$$\Delta F^\circ = -2.303RT\,[\log\,(c_\pi/c_o) + H_o]$$

where a's refer to activities, c to concentrations, and γ to activity coefficients. The subscripts π and o refer to π-complex and olefin, respectively.

The fact that no measurable conversion of olefin to π-complex is detected by the solubility measurements over the range of acidities studied indicates that (c_π/c_o) probably can be no greater than 10^{-2} in 65% $HClO_4$. From this and the H_o value of about −6 for 65% $HClO_4$, one obtains the estimate that ΔF° for reaction 1 must exceed 11 kcal. This figure may also be used as an estimate for the minimum enthalpy change for reaction 1, since ΔS° for reaction 1 is expected to be near zero.[5]

Hepner, Trueblood and Lucas[6] have found rather small structural effects on the formation constants for the silver ion complexes of ordinary aliphatic olefins



By analogy, it seems likely that the estimate of a minimum figure of 11 kcal. obtained for ethylene and propylene for the ΔH^0 of reaction 1 applies as well to the more reactive olefins such as isobutylene. The activation energy for the hydration of isobutylene in one molar acid is about 22 kcal.[7] Therefore, the activation energy for conversion of the π-complex of isobutylene to t-butyl alcohol may be crudely estimated to be less than 11 kcal.

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[6] F. R. Hepner, K. N. Trueblood and H. J. Lucas, THIS JOURNAL, **74**, 1333 (1952).

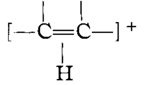
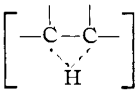
[7] *Cf.* E. L. Purlee, R. W. Taft, Jr., and A. DeFazio, THIS JOURNAL, **77**, 837 (1955), and references cited therein.

[CONTRIBUTION FROM THE COLLEGE OF CHEMISTRY AND PHYSICS, THE PENNSYLVANIA STATE UNIVERSITY]

The Reaction of Isobutylamine with Nitrous Acid. π-Complex and the Bridged-Protonium Ion[1a]

BY LAWRENCE G. CANNELL[1b] AND ROBERT W. TAFT, JR.

RECEIVED MAY 22, 1956

The reaction of isobutylamine and nitrous acid in aqueous solution has been carried out under controlled conditions of acidity and temperature. Seven products have been identified: *t*-butyl alcohol, *sec*-butyl alcohol, isobutyl alcohol, isobutylene, 1-butene, *trans*-2-butene and *cis*-2-butene. No detectable exchange of hydrogen is found in the hydrogen migration to give *t*-butyl alcohol when the reaction is carried out in D_2O, showing that the *t*-butyl cation intermediate does not undergo direct H–D exchange. Further, in view of Purlee and Taft's kinetic data on olefin hydration, the present results exclude the π-complex (of Taft's olefin hydration mechanism) as an intermediate in the hydrogen migration reaction. The present results are interpreted on the basis that the structures represented by I and II are distinct and different entities:  $[-\overset{|}{C}=\overset{|}{C}-]^+$ with H below, π-complex (I) and  $\left[-\overset{|}{C}-\overset{|}{C}-\right]^+$ bridged to H, bridged protonium ion (II). The activation energy for hydrogen migration is about 2.5 kcal. lower than that for methyl migration, but the entropy of activation favors the latter by about 5 cal./deg.

The reactions between aliphatic amines and nitrous acid give extensive rearrangements. Whitmore and co-workers[2] accounted for the variety of products obtained from the diazotization of ethylamine, *n*-propylamine and *n*-butylamine, on the basis of a carbonium ion intermediate. Roberts and Yancey[3] found that ethylamine-1-C^{14} gives ethylene and ethanol, the latter containing 1.5% of the rearranged product, ethanol-2-C^{14}. This result indicates that the ethyl cation formed by the decomposition of the diazonium ion cannot be a bridged ethyleneprotonium ion since such an ion would give equal amounts of the two labeled alcohols. Roberts and Halmann[4] also applied the use of tracers to the study of the rearrangement of 1-propylamine-1-C^{14} and found that of the 1-propanol produced in the reaction, 8.5% had rearranged. The above authors have concluded that the reaction of aliphatic amines and nitrous acid provides as "free" a carbonium ion in aqueous solution as any known reaction.[3–5]

Evidence indicating that relatively free isobutyl, *sec*-butyl, and *t*-butyl cations are formed in the isobutylamine–nitrous acid reaction has been presented.[6]

The study reported in this paper was made for the purpose of finding whether a distinction must be made between the π-complex (obtained as an intermediate proceeding the rate-determining step in the hydration of ordinary branched aliphatic ole-

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[1] (a) The work reported herein was supported in part by Project NR055-295 between the Office of Naval Research and The Pennsylvania State University. Reproduction in whole or in part permitted for any purpose of the United States Government; (b) Union Carbide and Carbon Corp. Fellow for 1954–1955; (c) taken in part from the Ph.D. Thesis of Lawrence G. Cannell, The Pennsylvania State University, Jan., 1956.

[2] F. C. Whitmore and D. P. Langlois, THIS JOURNAL, **54**, 3441 (1932); F. C. Whitmore and R. S. Thorpe, *ibid.*, **63**, 1118 (1941).

[3] J. D. Roberts and J. A. Yancey, *ibid.*, **74**, 5943 (1952).

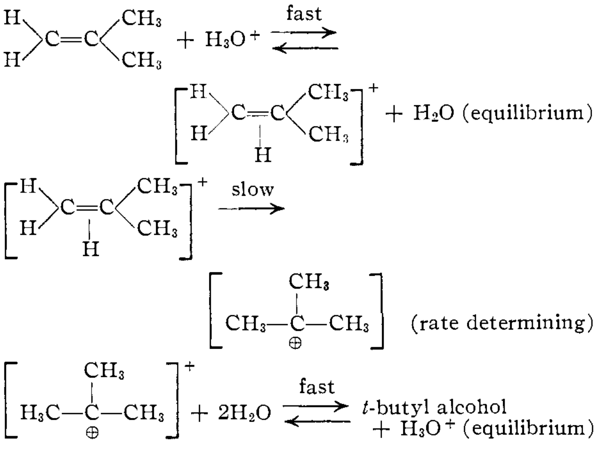
[4] J. D. Roberts and M. Halmann, *ibid.*, **75**, 5759 (1953).

[5] A. W. Fort and J. D. Roberts, *ibid.*, **78**, 587 (1956).

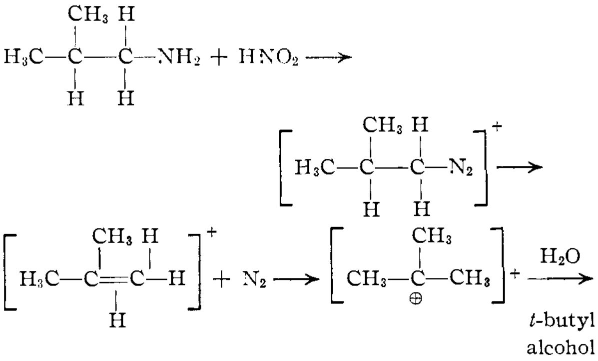
[6] L. G. Cannell and R. W. Taft, Jr., Abstracts of Papers presented at American Chemical Society Meeting, Dallas, Texas, April, 1956, p. 46N.

fins) and the bridged protonium ion (obtained either as a transition state or an intermediate in intramolecular hydrogen transfer reactions).

Taft and co-workers have obtained extensive evidence for the following mechanism of hydration of isobutylene by aqueous acids.[7]



It is readily apparent from the scheme below that the formation of *t*-butyl alcohol as the principle product from the diazotization of isobutylamine (previously studied by Linnemann[8] and by Henry[9]) could proceed through the same π-complex as proposed for the hydration of isobutylene.



Dewar in his discussion of the π-complex has not required that a distinction be drawn between the bridged state obtained in an intramolecular hydrogen transfer and the immediate state resulting from protonation of the C–C double bond.[10] That is, the two are implied to be identical. Winstein and Holness recently have generalized objections to the assumed identity.[11]

The isobutylamine–nitrous acid reaction has proved to be a suitable system for obtaining an answer to the point in question not only for the above reasons, but for the following as well: (a) the reaction may be studied under controlled conditions of temperature and acidity, comparable to those used for the studies of olefin hydration; (b) the rates of hydration of isobutylene and dehydration of *t*-butyl alcohol at the acidities used are known to be negligible[12]; (c) isobutyl alcohol does not rearrange to *t*-butyl alcohol under the reaction conditions; (d) the composition of the reaction product obtained when the reaction is carried out in D_2O provides conclusive evidence concerning whether or not the π-complex (of the Taft mechanism) is common to both this reaction and the hydration of isobutylene.

Experimental

Reagents.—The alcohols and isobutylamine were center cuts which fractionated with a constant boiling point and refractive index. Isobutylamine distilled at 65.8° (725 mm.) and $n^{20.0}D$ 1.3968.

Reaction of Isobutylamine with Nitrous Acid.—A 3-necked flask fitted with a water condenser, stirrer and dropping funnel was used. In some experiments the flask was placed on a mechanical shaker and the stirrer was eliminated. The evolved gases were passed through a series of three gas absorption towers and into a gas collection bottle. In consecutive order the towers contained aqueous base, liquid bromine and a basic permanganate solution. The reaction flask was set in a constant temperature bath (temp. control ±0.05°) for experiments at 38.0°. The experiments at 99° were run with the solution at its boiling point and the stirrer was not used. In a typical experiment 25 g. of sodium nitrite (U.S.P. grade) dissolved in 50 ml. of water, was added to a solution of the amine perchlorate prepared by neutralizing 21.0 g. of the amine dissolved in 130 ml. of water with *ca.* 48.6 g. of 60.3% perchloric acid. In order to ensure a slow rate of passage of gas through the traps, the nitrite solution was added a portion at a time over a 2 to 3 hr. period. After 2 to 3 liters of nitrogen had been evolved, 60% $HClO_4$ in amounts of 1 ml. or less was added in alternate portions with the nitrite solution until about 90% of the theoretical volume of gas was collected. In this manner the acidity of the solution was maintained at the minimum necessary for the reaction to occur. The maximum amount of acid added at 38.0° was 0.042 mole and at 99° 0.007 mole.

At 99° the volatile material was removed as the reaction proceeded by use of a reflux condenser with a take-off at the base. In experiments at 38.0° the reaction mixture was made basic (no gas is evolved under basic conditions) and the alcohol together with water and some unreacted amine was distilled off. The distillate was titrated with acid to determine the amount of recovered amine. With the distillate slightly acidic, the alcohols were salted out of solution with anhyd. KF. The alcohols were dried with anhyd. K_2CO_3 filtered and weighed (see Table I for yields).

The reaction in heavy water was carried out at 38.0° using ordinary 60.3% $HClO_4$ and 67.4% D_2O. The deuterium content of this solvent was 53.7% as determined by a density measurement on the recovered water.

The amount of olefin produced was calculated from the weight of the dibromide isolated from the excess bromine by treatment with ice-cold sodium bisulfite solution. When a second olefin trap (also having a fritted disk) was placed in series with the first, the amount of dibromide obtained was less than a gram. Infrared spectra showed that a small amount of the dibromides had undergone hydrolysis to give a carbonyl compound, indicating that the calculated yield of olefin may be somewhat too low.

Additional experiments (on a smaller scale) were made to obtain the gaseous olefins for infrared analysis. The gases were passed through aqueous alkali and then into absolute ethanol from which the olefins were obtained by fractionation. Infrared analysis showed that olefins obtained by this method were almost identical in composition with samples obtained by trapping the olefins in liquid nitrogen,

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(7) (a) R. W. Taft, Jr., E. L. Purlee, P. Riesz and C. A. DeFazio, THIS JOURNAL, **77**, 1584 (1955); (b) E. L. Purlee and R. W. Taft, Jr., *ibid.*, **78**, 5807 (1956); (c) P. Riesz, R. H. Boyd and R. W. Taft, Jr., in preparation.

(8) E. Linnemann, *Ann.*, **162**, 24 (1872).

(9) M. L. Henry, *Compt. rend.*, **145**, 899 (1907); Linnemann, ref. 8, reports only *t*-butyl alcohol as a product of the isobutylamine–nitrous acid reaction. Henry reports both isobutyl and *t*-butyl alcohol. The other products listed in Table I are reported herein for the first time.

(10) (a) M. J. S. Dewar, *J. Chem. Soc.*, 406 (1946); *Bull. soc. chim. France*, C 75, C 86 (1951); (b) C. C. Price, "Mechanisms of Reactions at the Carbon–Carbon Double Bond," Interscience Publishers, Inc., New York, N. Y., 1946, p. 40.

(11) S. Winstein and N. J. Holness, THIS JOURNAL, **77**, 5572 (1955).

(12) (a) W. F. Eberz and H. J. Lucas, *ibid.*, **56**, 1230 (1934); (b) R. W. Taft, Jr., and P. Riesz, *ibid.*, **77**, 902 (1955).

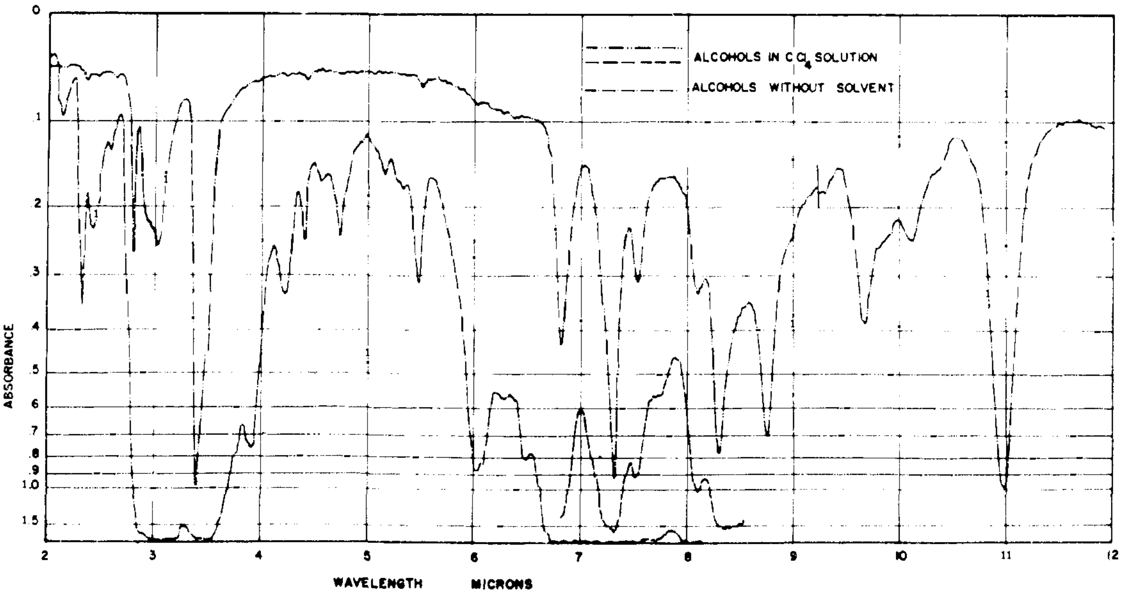

Fig. 1.—Alcohols produced from isobutylamine and nitrous acid at 38.0° with solvent 54% D_2O.

indicating that the samples were representative of the olefin produced in the reaction.

In preliminary experiments, which were conducted using 3 moles of nitrous acid to one of isobutylamine, it was found that the amount of olefin was about the same as in later runs (12%); however, the yield of alcohol was much less (16%). Isolation and infrared analysis of the products indicated that small amounts of acetone and ethyl methyl ketone were present. The amount of alcohol produced was reduced further if the time of reaction at 25.0° was increased and the mixture was heated while acidic. In confirmation of the analysis it was found that *t*-butyl alcohol when allowed to stand with a 5-fold excess of nitrous acid for 2 days at 5–25° gave considerable acetone. (For details of preliminary and related experiments and spectra of olefins *cf.* ref. 1c.) In the later experiments reported above, the reaction time and amount of nitrous acid were reduced with the result that no ketone was detectable and the material balance was increased to 96%.

Infrared Spectra and Analysis.—Spectra were taken with a Perkin–Elmer model 21 double beam recording infrared spectrophotometer using a NaCl prism. Spectra of the alcohols in CCl_4 were taken in a NaCl cell of 0.55-mm. width over the range 2 to 12 μ, and cells of widths 0.109, 0.51 and 0.25 mm. were used for taking spectra of alcohols and dibromides without solvent over the range 2 to 15.5 μ. Comparison of the spectra of the alcohol mixture from the reaction with that of iso-, *sec*, *t*- and *n*-butyl alcohols and synthetic mixtures of the three indicated that all of the absorption peaks in the unknown were accounted for by the three alcohols. Further examination was made after most of the *t*-butyl alcohol was removed by water extraction. There was no evidence of the presence of *n*-butyl alcohol. The composition of the reaction mixture was determined quantitatively by using absorption peaks at 8.30, 9.65 and 10.10 μ for which the principal absorption was due to *t*-, iso- and *sec*-butyl alcohols, respectively. Comparison of spectra of both known and unknown mixtures showed that the analysis for each alcohol was corrected within about 1% of the total.

Spectra of the olefins were taken at pressures from 3.0 to 10.0 cm. using a 10-cm. gas cell with NaCl plates. Spectra of isobutylene, *cis*- and *trans*-2-butenes and 1-butene (all Philips Research Grade) were taken separately and extinction coefficients for the wave lengths given below were found to follow the Beer–Lambert law within experimental error. All reproducible peaks from the olefins from the amine–nitrous acid reaction could be accounted for by the spectra of the four olefins. *cis*-2-Butene and isobutylene were determined separately from the absorbance at 14.90 and 11.44 μ, respectively. With these two olefins determined, the amounts of *trans*-2-butene and 1-butene were determined from the absorbance at 10.30 and 10.95 μ, respectively. The quantitative analyses were checked by analyses at two different pressures and comparison of the calculated and actual total pressures. Comparison of the spectra of the dibromides from the olefin trap with spectra of dibromides obtained from the separate reaction of an excess of each of the olefins with bromine at 0° gave further confirmation of the reported composition of the olefinic mixture.

Results

Experiments were conducted at 38.0 and 99° with the minimum acidity for a convenient reaction rate ($pH > 3$). The work in the heavy water was carried out at 38.0°. The alcohols, *t*-butyl, *sec*-butyl and *iso*-butyl, and the olefins, 1-butene, *cis*- and *trans*-2-butenes and isobutylene, have been identified as reaction products.

The products were analyzed by infrared spectroscopy (*cf.* Experimental) with respect to the structure, yield and deuterium content. Table I summarizes the products found under the several reaction conditions. When the reaction was run in 54% deuterated water, analysis indicated that the amount of deuterium present in the *t*-butyl alcohol was too small to be detected.

Figure 1 shows the spectra of the alcohol mixture (after two washings with distilled water to remove OD) obtained from the isobutylamine-nitrous acid reaction in the heavy water. Figure 2 is the spectra of the alcohol mixtures obtained from the reaction in ordinary water.

To show that a small amount of CD could be detected by the method of analysis, *t*-butyl-*d* alcohol (about 25% in *t*-butyl alcohol) was prepared by the hydration of isobutylene in 27% deuterated 4.0 *M* HNO_3 at 21°. Under these conditions it has been shown that only one CD bond is formed by the hydration, and the CH to CD ratio in the new bond is approximately the same as the H/D ratio in the solvent.[7b] Figure 3 gives the spectra of a washed sample of the resulting alcohol. Peaks at 4.59 and 7.78 μ, which are common CD stretching and bending peaks are readily apparent.[13] From the inten-

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(13) *Cf.* for example J. D. Roberts, C. M. Regan and I. Allen, THIS JOURNAL, **74**, 3682 (1952); P. D. Bartlett and J. D. McCollum, *ibid.*, **78**, 1448 (1956); R. W. Taft, Jr., and E. L. Purlee, in preparation.

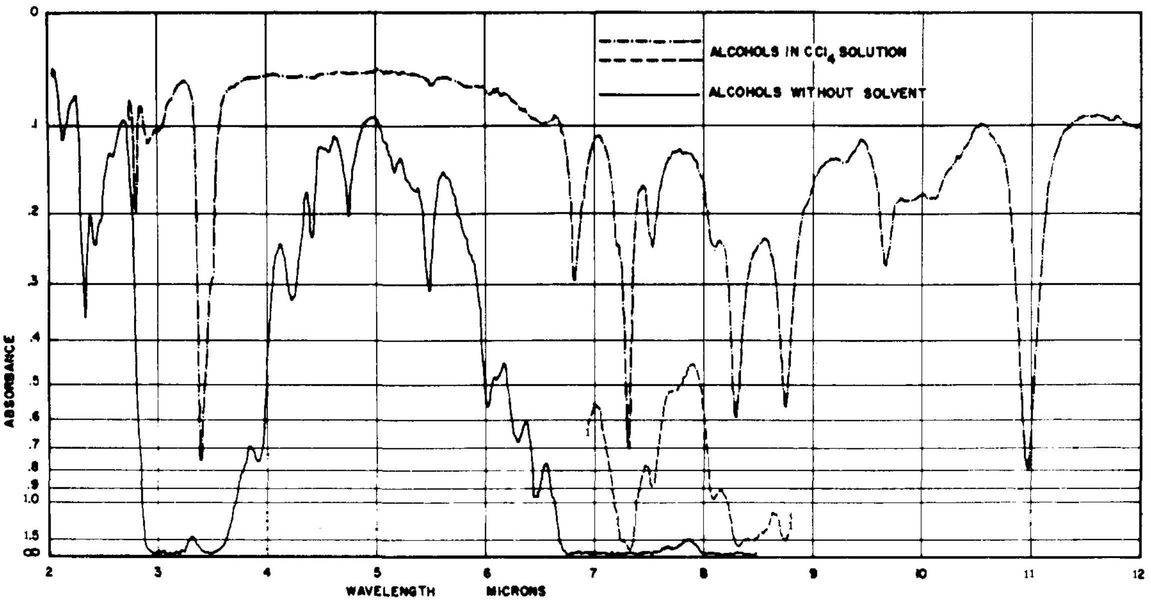


Fig. 2.—Alcohols produced from isobutylamine and nitrous acid at 38.0°.

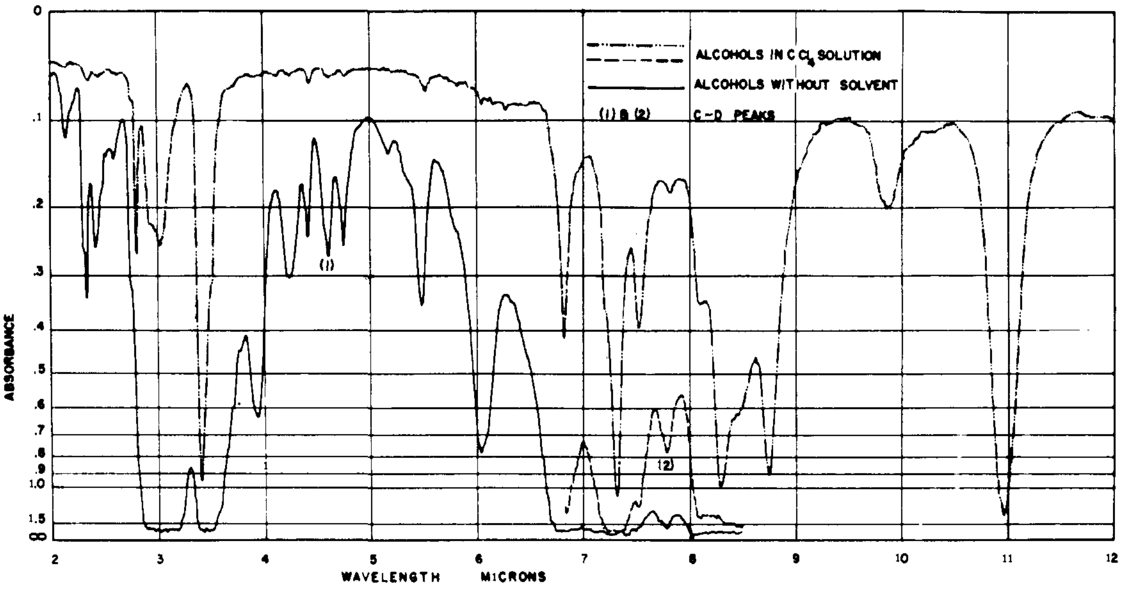


Fig. 3.—Mixture of 25% $(CH_3)_2C(OH)CH_2D$ and 75% $(CH_3)_3COH$.

sity of the CD peaks of this known sample it is estimated that no more that 2% *t*-butyl-*d* alcohol can be present in the mixture of alcohols obtained from the isobutylamine–nitrous acid reaction (Fig. 1). Since *t*-butyl alcohol constitutes 71% of the alcohols produced, it is clear that the hydrogen atom which becomes bonded to carbon at the cite of the original C–N bond must come very predominantly from the reactant molecule rather than the solvent.

Discussion

The variety and nature of the products which result from the isobutylamine–nitrous acid reaction are obviously characteristic of a carbonium ion reaction (the principal one being shown on p. 5816).

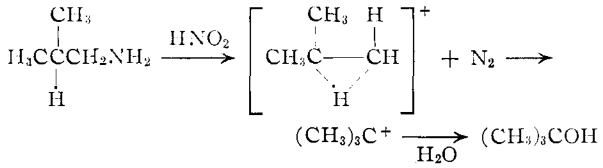
The bridged structure represents a state wherein the hydrogen is in transit along the reaction path

TABLE I

PERCENTAGE YIELDS OF PRODUCTS

Temperature, °C.	99	38.0
Olefins	21	11
1-Butene	17[a]	18[a]
cis-2-Butene	21	20
trans-2-Butene	32	28
Isobutylene	30	34
Alcohols	71	71
t-Butyl	60[a]	71[a]
sec-Butyl	30	19
Isobutyl	10	10
Amine recovered	. .	14
Material balance	92	96

[a] The percentage yields of alcohols or olefins are given on the basis of 100% for the total amount of alcohol or olefin isolated.



between carbon atoms and the interaction of the leaving nitrogen is small. The present results together with those of Purlee and Taft show that at no point in the migration does the hydrogen pass through a state which corresponds to the π-complex of the Taft olefin hydration mechanism.[7b]

The data of Purlee and Taft indicate that the conjugate acid of isobutylene which precedes the rate-determining step in the hydration, eliminates the added proton much more readily than it reacts to produce *t*-butyl alcohol. Thus at the acidity employed in the isobutylamine–nitrous acid reaction, such an intermediate would produce isobutylene with little or no *t*-butyl alcohol. Equilibration of the π-complex with deuterium in the solvent also is required so that any *t*-butyl alcohol formed from the π-complex would contain CD. Since neither result is realized, a π-complex intermediate common to both reactions is excluded.

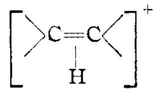
The present results are similar to those obtained by Doering, *et al.*, for the intramolecular hydrogen migration of phenylglyoxal to give mandelic acid under alkaline conditions.[14] Although the structure of reactants and the reaction conditions are markedly different for this reaction and the present one, no HD exchange with solvent has been detected during the hydrogen transfer in either reaction.

We find it convenient to rationalize the present results on a structural basis. The intermediate in the hydration of isobutene may be regarded as isomeric with the bridged hydrogen structure of the isobutylamine–nitrous acid reaction. Our present results do not provide an indication of whether the latter structure corresponds to an intermediate or a transition state, but the latter seems more likely.[15] In either event, both structures in question have the same carbon skeleton and one hydrogen which is not equivalent with the other eight. Both bear a substantial positive charge and both may react to give *t*-butyl alcohol. Nevertheless two distinct structures may be proposed to account for the different reactivities.

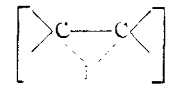
The π-complex structure I, as previously represented by Dewar and by Price,[10] may be assigned to the intermediate which precedes the rate-determining step in the olefin hydration. The bonding involves overlap of the orbital of hydrogen with π-orbital of the C–C double bond which extends above and below the plane defined by the directed sp^2 bonds of the system. Except for the embedded proton, the structure is that of an olefin with its trigonal coplanar structure about both C atoms. The bonding of the proton to the π-orbital is apparently quite weak.[7b]

The bridged protonium ion structure II, as previously represented by Winstein and Lucas[16a] and later by Cram,[16b] may be assigned to the ionic system undergoing intramolecular hydrogen transfer. The absence of exchange with solvent during the hydrogen migration indicates that the hydrogen atom is at all times firmly bonded by overlap between its 1s orbital and the sp^3 hybrid orbitals of one or both of the carbon atoms involved. This bonding can be described as a resonance hybrid of the valence bond structures[14]

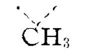
According to this description all bonds about the two carbon atoms are directed bonds which give rise to a non-coplanar structure similar to that of cyclopropane or ethylene oxide.



I, π-complex (directed bonds of structure coplanar)



II, bridged protonium ion (bonds of structure non-coplanar)

The present work implies that the bridged ion intermediates or transition states for general group migration reaction of cations (*e.g.*,  $\underset{CH_3}{>C-C<}$ for formation of the *s*-butyl products obtained in the present reaction) are not appropriately represented by the π-complex structure.

The absence of C–D in the *t*-butyl alcohol obtained from the isobutylamine-nitrous acid reaction in D_2O shows conclusively that the *t*-butyl cation intermediate does not undergo a direct rapid H–D exchange with the aqueous media. Shull, Oakwood and Rank have reported an equivalent result.[17] The reaction of *t*-butyl alcohol-d_9 with concentrated HCl solution at room temperature gives *t*-butyl chloride-d_9 without measurable H–D exchange. Purlee and Taft have obtained kinetic evidence that the mechanism of H–D exchange between olefin or alcohol is that for the olefin–alcohol interconversion.[18] It is inferred that the results of Otvos, Stevenson, Wagner and Beeck[19] must be accounted for on the basis of the high rate of olefin-π-complex–carbonium ion interconversions in concentrated sulfuric acid, rather than any facile H–D exchange of the carbonium ion by an independent process.

Although previous work on product determination of the aliphatic amine–nitrous acid reaction has not been carried out under the controlled conditions of temperature employed in the present work, a comparison of the results affords at least a crude measure of the effect of β-methyl substitution on the ease of rearrangement. From the work of Roberts and Yancey[3] with ethylamine, Whitmore and Thorpe,[2] and Roberts and Hal-

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(14) W. E. Doering, T. I. Taylor and E. F. Schoenewalt, THIS JOURNAL, **70**, 455 (1948).

(15) *Cf.* for example, J. D. Roberts and J. A. Yancey, *ibid.*, **77**, 5561 (1955).

(16) (a) S. Winstein and H. J. Lucas, *ibid.*, **60**, 836 (1938); (b) D. J. Cram, *ibid.*, **74**, 2137 (1952).

(17) E. R. Shull, T. S. Oakwood and D. H. Rank, *J. Chem. Phys.*, **21**, 2024 (1953).

(18) E. L. Purlee and R. W. Taft, Jr., unpublished results.

(19) J. W. Otvos, D. P. Stevenson, C. D. Wagner and O. Beeck, THIS JOURNAL, **73**, 5741 (1951).

mann[4] with *n*-propylamine, and the present study with isobutylamine, the rounded-off figures given below are obtained for the alcohols:

Amine	Rearrangement, %	Migration of H relative to CH_3
Ethyl	2	. .
n-Propyl	80	25[a]
Isobutyl	90	5[b]
Neopentyl	~100[c]	. .

[a] Corrected by a statistical factor of 2 favoring H relative to CH_3 migration. [b] Corrected by a statistical factor of 2 favoring CH_3 relative to H migration. [c] Inferred from the results of M. Freund and F. Lenze, *Ber.*, **24**, 2150 (1891).

It is apparent that substitution of methyl for hydrogen on the β-carbon atom greatly facilitates rearrangement,[20] the effect being larger for methyl than hydrogen migration.

Since the products of the isobutylamine–nitrous acid reaction are rate controlled, the product ratios obtained (Table I) provide measures of the relative rates of migration. On this basis the data permit the estimate that the energy of activation for hydrogen migration is about 2.5 cal. lower than for methyl migration, but the entropy of activation favors the latter (based on the migration of one methyl) by about 5 cal./deg.

UNIVERSITY PARK, PENNSYLVANIA

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[20] Similar results have been obtained and discussed for anchimeric assistance in solvolysis reactions, *cf.* S. Winstein and E. Grunwald, THIS JOURNAL, **70**, 828 (1948).

[JOINT CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MARYLAND, AND FROM THE CHEMICAL CORPS, CHEMICAL WARFARE LABORATORIES, ARMY CHEMICAL CENTER, MARYLAND]

The Transesterification of Trialkyl Phosphites with Aliphatic Alcohols[1,2]

BY FRIEDRICH W. HOFFMANN,[3] RICHARD J. ESS AND ROBERT P. USINGER, JR.

RECEIVED JUNE 14, 1956

Trialkyl phosphites undergo an uncatalyzed alcohol exchange reaction when heated with aliphatic alcohols to yield mixtures of tertiary phosphites containing different alkyl groups. The scope of this reaction was investigated and a probable mechanism for the reaction postulated. The yields of the mono- and ditransesterified trialkyl phosphites were found to be dependent on the ratio of alcohol to phosphite employed. The results of this study indicate that the exchange reaction of a trialkyl phosphite with an alcohol having a larger alkyl group than the ester is a general reaction which can be applied to the preparation of mixed trialkyl phosphites.

While the transesterification with alcohols is a well-established procedure in the carboxylic ester series, little information is available on this type of reaction involving esters of phosphorous acid. Diethyl hydrogen phosphite (phosphonate) has been reported[4] to undergo an exchange reaction with aliphatic alcohols with the formation of mixed dialkyl hydrogen phosphites, but the literature does not contain any information on a similar exchange reaction of trialkyl phosphites. However, triaryl phosphites are known to undergo transesterification with aliphatic alcohols[5,6] yielding mixed alkyl aryl esters. In general, mixed trialkyl esters of phosphorous acid have been prepared in the past from phosphorochloridites or -dichloridites and alcohols or sodium alkoxides in yields varying between 13 and 50%.[5,7]

The present investigation was undertaken to determine the usefulness of the transesterification reaction between alcohols and trialkyl phosphites as a practical method for the preparation of mixed trialkyl phosphites and to elucidate a mechanism for this reaction. The technique used in this study for transesterifying trialkyl phosphites with alcohols was similar to that applied by Kosolapoff[4a] in the transesterification of diethyl hydrogen phosphite. The trialkyl phosphites were refluxed at atmospheric pressure with alcohols having larger alkyl groups than the starting ester, and the lower alcohol was distilled from the reaction mixture at the rate of its formation.

The results of our investigation indicate that the transesterification of trialkyl phosphites is a general reaction which can be applied advantageously to the preparation of mixed trialkyl phosphites. Since the exchange reaction proceeds in three steps with apparently equal or almost equal rates, only a

$$R'OH + (RO)_3P \rightleftarrows R'OP(OR)_2 + ROH$$

$$R'OH + R'OP(OR)_2 \rightleftarrows (R'O)_2POR + ROH$$

$$R'OH + (R'O)_2POR \rightleftarrows (R'O)_3P + ROH$$

moderate yield of the monotransesterification product is obtained, if the phosphite and alcohol are used in equimolar amounts. However by a proper choice of the ratio of the reactants any one of the three transesterification products can be made the main reaction product.

A limitation of the transesterification reaction as a preparative method is the fact that the alcohol to be exchanged must have a boiling point which is not too close to that of the exchanging alcohol; otherwise, the reaction cannot be forced by distilling off the originally esterified alcohol, and difficulty is encountered in the separation of the products from the original phosphite. An example of

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[1] The material presented in this paper represents a portion of a thesis submitted by Richard J. Ess to the University of Maryland in partial fulfillment of the requirements of the M.S. degree, July, 1955.

[2] Presented in part at the 129th Meeting of the American Chemical Society in Dallas, Texas, April 8–13, 1956.

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[4] (a) G. M. Kosolapoff, THIS JOURNAL, **73**, 4989 (1951). (b) B. A. Arbuzov and V. S. Vinogradova, *Doklady Akad. Nauk S.S.S.R.*, **83**, 79 (1952); *C. A.*, **47**, 2685*a* (1953). (c) V. K. Kuskov and T. Kh. Gradia, *ibid.*, **92**, 323 (1953); *C. A.*, **49**, 155g (1955).

[5] S. R. Landauer and H. N. Rydon, *J. Chem. Soc.*, 2224 (1953).

[6] F. C. Gzemski, U. S. Patent 2,253,558 (1944); *C. A.*, **38**, 6548^6 (1944).

[7] The literature on this subject has been reviewed by Kosolapoff in "Organic Phosphorus Compounds," John Wiley and Sons, Inc., New York, N. Y., 1950, pp. 184–187.