883. *Kinetic Isotope Effects in the Addition Reactions of Olefins under Acid Conditions.*

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The hydrogen isotope effect for solvent addition to propene in 90% aqueous formic acid at 100° (k_H/k_T) has been found to be ~4·5. The differences between this result and those of other workers are discussed on the basis that the isotope effect is in the main determined by the zero-point energy of the H–X bond from which a proton (triton) is transferred to olefin during the first phase of the addition reaction.

Several values have been reported for kinetic isotope effects in addition reactions of olefins under acidic conditions. Nash, Taylor, and Doering [1] found that, in the presence of aluminium chloride, the reaction of hydrogen chloride with gaseous propene is 2·2 times as fast as the corresponding reaction of deuterium chloride. Shilov *et al.*[2] showed that the reactions of gaseous ethylene and isobutene with deuterated sulphuric acid result mainly in the formation of monodeuterated products, and that the isotope effect (k_H/k_D) for the ethylene reaction is 2·2. On the other hand, isotope effects (k_H/k_D) differing little from unity were reported by Purlee and Taft [3] for the hydration of 2-methylbut-2-ene and 1-methylcyclopentene in dilute nitric acid. We have investigated the reaction of propene with 90% formic acid at 100° in the presence of various compounds. Some of the mixtures used were chosen in order to reproduce reaction mixtures obtained during other experiments on the solvolysis of n-propyl bromide in 90% formic acid containing sodium formate. The latter reaction results in the formation of small quantities of isopropyl derivatives.[4]

Table 1. *Reaction of propene in 90% formic acid.*

(Mixtures were heated for 20·5 hr. at 100°.)

Expt.	Initial composition of reaction mixture							%
No.	$[Pr^nOH]$	[HBr]	$[H·CO_2Na]$	$10^3[Pr^iOH]$	10^3[Propene]	$10^3[Pr^iOH]$ found	$10^3[Pr^iOH]$ from propene	conversion of propene into Pr^iOH
1	0·10	0·10	0·30	—	13·10	7·36	7·36	56·2
2	0·10	0·10	0·30	—	13·10	6·55	6·55	50·0
3	0·10	0·10	0·30	1·56	5·19	4·43	2·87	55·3
4	0·15	0·15	0·30	2·34	6·20	6·53	4·19	67·7
5	0·25	0·25	0·30	3·90	6·85	9·50	5·60	81·8
6	—	0·10	0·10	—	4·85	4·80	4·80	99·0
7	—	—	—	—	25·9	25·7	25·7	99·3

The results in Table 1 show qualitatively that the rate of conversion of propene into isopropyl derivatives decreases with increasing excess of sodium formate over hydrogen bromide; *i.e.*, hydrogen bromide counteracts the anticatalytic effect of formate ions by the reaction $H·CO_2^- + HBr \longrightarrow H·CO_2H + Br^-$. Experiments 1—5 were carried out in tritiated media, and the alcohol present after the reaction mixtures had been heated was examined for C–T bonds. These bonds may be formed (i) by addition of tritiated solvent to propene (giving isopropyl derivatives containing one C–T bond per molecule), (ii) by the occurrence of exchange reactions between the alcohols and the medium, and (iii) by hydrogen exchange between the olefin and the medium before solvent addition. The formation of C–T bonds by process (iii) seems unlikely in view of the results obtained by Shilov *et al.*[2] for the reactions of deuterated sulphuric acid with ethylene and with isobutene. It was shown that some C–T bonds are indeed formed by process (ii), but these account only for a fraction (1/7—1/2) of the activity found in the experiments with propene. When the mixtures used in experiments 3—5 were heated for 20·5 hr. in the absence of propene, C–T bonds

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[1] Nash, Taylor, and Doering, *J. Amer. Chem. Soc.*, 1949, **71**, 1516.
[2] Shilov, Sabirova, and Gorshkov, *Doklady. Akad. Nauk S.S.S.R.*, 1958, **119**, 533.
[3] Purlee and Taft, *J. Amer. Chem. Soc.*, 1956, **78**, 5807.
[4] Coe and Gold, unpublished work.

were introduced into the alcohols. This activity was determined and the values of the corrections given in Table 2 were thus obtained. These were subtracted from the total activities of the alcohols in order to find the activity due to alcohol formed by addition of radio-active solvent to propene.

TABLE 2. *Results of radioactivity measurements.*

	Activity (in C–T bonds) of alcohols in 5 ml. of reaction mixture (μc)						
Expt. No.	Total	Part resulting from exchange reactions	In Pr^iOH from propene	$10^3[Pr^iOH]$ from propene	Activity (in C–T bonds) of Pr^iOH from propene (c/mole)	Activity of medium (c/g.-atom exchangeable hydrogen *)	k_H/k_T
1	1·00	~0·13	~0·87	7·36	~0·024	0·106	~4·4
2	0·98	~0·13	~0·85	6·55	~0·026	0·106	~4·1
3	0·49	0·13	0·36	2·87	0·025	0·114	4·6
4	0·76	0·26	0·50	4·19	0·024	0·114	4·7
5	1·48	0·72	0·76	5·60	0·027	0·114	4·2

* It was found that the H atom of the C–H bond in formic acid does not undergo exchange under the conditions of these experiments. The work of Münzberg and Oberst [5] and of Small and Wolfenden [6] suggests that the same is true in the case of sodium formate.

Part of the correction in each case is due to exchange reactions of n-propanol and part to reactions of propan-2-ol. It is important to know how the activity is distributed between the two alcohols in order to estimate what part of the activity of the iso-alcohol formed from propene is due to C–T bonds introduced after solvent addition to the olefin. Separate experiments (using mixtures containing propan-2-ol but no n-propanol) showed that, with propan-2-ol concentrations in the range 5—10 × 10^{-3}M, the part of the correction due to the presence of C–T bonds in propan-2-ol was small, *i.e.*, not more than 10—15% of the total. A more exact assessment is not possible at present owing to the low activities involved, but some of the values of k_H/k_T in Table 2 may be 10—15% too low. Similarly, the corrections to be used in expts. 1 and 2 are not known precisely, but are probably very similar to that used for expt. 3. One further point requiring comment is that the activity attributed to exchange reactions of n-propanol could in fact arise from the presence of impurities (*e.g.*, allyl alcohol) in the n-propanol used. The presence of impurities would not invalidate the corrections applied here, as the same stock solutions were used for the exchange reactions and the experiments with propene.

The existence of an isotope effect is generally ascribed to a difference in zero-point energy between reactants and transition state. In the present case this description is practically equivalent to the conclusion that the transition state for addition to propene in slightly aqueous formic acid contains a looser bonding of the (isotopically replaceable) hydrogen atom than was present in the $H{\cdot}CO_2{-}H$ bond. The rate-controlling phase in olefin additions under the influence of acids is generally accepted to be the formation of a protonated olefin intermediate, and therefore the subsequent step involving the attack of a nucleophilic reagent on the carbonium ion formed is not relevant here. One may attempt to correlate the diverse results obtained by the various studies of the kinetic isotope effects for addition to olefins under acidic conditions by supposing that the transition states in all these cases are rather similar as far as the tightness of the bond to hydrogen is concerned. If this is a reasonable approximation then the various isotope effects should depend on the tightness of the H–X bond from which the proton is transferred during the first and rate-determining phase of the addition reaction. Table 3 suggests that such a correlation does indeed exist.* For the purpose of this comparison

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* It should be pointed out that the values are not absolutely comparable since the first three entries are derived for rate comparison in light and heavy solvents and are therefore subject to a solvent isotope effect, whereas the result for the gas reaction and our value (which is derived from product compositions) are not subject to this effect. The resultant error is probably not greater than ~10% in the isotopic rate ratio.

[5] Münzberg and Oberst, *Z. phys. Chem.*, 1935, *B*, **31**, 18.

[6] Small and Wolfenden, *J.*, 1936, 1811.

the tritium isotope effect (k_H/k_T) obtained in this work has been converted into a deuterium isotope effect (k_H/k_D) by application of the formula,[7] $(k_H/k_T) = (k_H/k_D)^{1{\cdot}442}$. The observed sequence of isotope effects for hydrogen ions, hydrogen chloride, and formic acid is also the sequence of increasing infrared stretching frequencies of the H–X bonds.

TABLE 3.

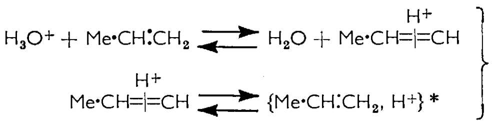
Olefin	Acid	k_H/k_D	Ref.	Olefin	Acid	k_H/k_D	Ref.
$Me_2C{=}CHMe$	H_3O^+ (dilute aq. HNO_3)	1·22	3	$CH_2{=}CH_2$	H_2SO_4	2·2	2
				$CH_2{=}CH_2$	HCl	2·2	1
$Me{\cdot}C{=}CH{\cdot}[CH_2]_3$	,, ,,	0·93	3	$Me{\cdot}CH{=}CH_2$	$H{\cdot}CO_2H$	2·8	This work

Taft[8] has concluded that the transition state for the hydration of isobutene in aqueous nitric acid is composed of the olefin molecule and a proton only. If the same transition-state structure applies to all additions to olefins under the influence of acids, then the reason for the dependence of the isotope effect on the nature of HX alone becomes obvious. On the data available so far it is not possible to say whether the precise correlation expected on this model does apply, or whether the correlation suggested is only approximate and indicates a similarity rather than an identity of transition states.

It is necessary to consider the formic acid molecule as the reagent acid species in the above discussion of isotope effects, since this is the molecular form in which the bulk of the acidic hydrogen atoms of the system are stored. However, this does not imply that we must regard the transition state as being formed directly from formic acid and olefin without intervening equilibria. The fact that the rate of reaction is markedly depressed by the addition of sodium formate suggests that the reaction depends on the acidity of the medium rather than on the concentration of formic acid molecules. It could be that the important pre-equilibrium is the generation of a low concentration of hydroxonium ions which then attack olefin in the rate-determining step. However, on the assumption that the reaction velocity in all media follows Hammett's acidity function (as it does over a limited range of acidity in aqueous solution), the processes which precede the formation of the transition state are likely to be of such a nature that the transition state is composed of olefin and proton only. The precise nature of these steps cannot be rigorously deduced from measurements of reaction velocities. The only equilibrium which is directly relevant to the kinetics is the formation of the transition state from the reactants

$$H{\cdot}CO_2H + Me{\cdot}CH{:}CH_2 \rightleftharpoons \{Me{\cdot}CH{:}CH_2, H^+\}^* + H{\cdot}CO_2^- \quad . \; . \; . \; . \; . \; . \quad (1)$$

(the asterisk denoting a transition state). A chemical equilibrium constant may always be expressed as the product of equilibrium constants of intermediate stages, whether these steps have physical reality or not. Thus, Purlee and Taft[3] would dissect the above equilibrium (with hydrogen ion in place of formic acid) into the components



$$\left.\begin{array}{l} H_3O^+ + Me{\cdot}CH{:}CH_2 \rightleftharpoons H_2O + Me{\cdot}CH{=}\overset{H^+}{|}{=}CH \\ Me{\cdot}CH{=}\overset{H^+}{|}{=}CH \rightleftharpoons \{Me{\cdot}CH{:}CH_2, H^+\}^* \end{array}\right\} \quad . \; . \; . \; . \; . \; . \; . \quad (2)$$

and assign opposed isotope effects to these two steps. The procedure is unexceptionable, but it follows from the discussion of the analogous problem in aromatic hydrogen isotope exchange[9,10] that any scheme of this kind has physical significance only for calculation purposes and does not necessarily express the sequence of reaction steps on the molecular scale.

If we then take the view that {olefin, $H^+\}^*$ expresses the composition of all transition

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[7] Swain, Stivers, Reuwer, and Schaad, *J. Amer. Chem. Soc.*, 1958, **80**, 5885.
[8] Taft, *J. Amer. Chem. Soc.*, 1952, **74**, 5372.
[9] Melander and Myhre, *Arkiv Kemi*, 1959, **13**, 507.
[10] Gold, Lambert, and Satchell, *J.*, 1960, 2461.

states and restrict our discussion to the overall equilibria, the small isotope effect with hydrogen ions implies that the proton is held about equally loosely in the aqueous hydrogen ion and in the transition state, *i.e.*, that the ratio of equilibrium constants K_H^*/K_D^* for reaction (1) is close to unity, and the ratio 2·8 with formic acid implies that this is the value of the ratio of the equilibrium constants K_H^*/K_D^* for reaction (2). If this interpretation is correct, and if it is indeed correct to assume that a value ~1 would apply to the hydrogen-ion catalysed hydration of propene (and not only to the two olefins studied by Purlee and Taft [3]), then the ratio 2·8/~1 should be equal to the ratio of dissociation constants $K_{H\cdot CO_2H}/K_{H\cdot CO_2D}$. The experimental value [11] for this ratio is 2·5. The agreement must be regarded as very close, in view of the neglect of the solvent isotope effect on the reaction velocity.

EXPERIMENTAL

Materials.—Formic acid, propan-2-ol, propene, and tritiated water were obtained as described previously.[12] n-Propanol (May & Baker) was distilled at atmospheric pressure; it had b. p. 96·8—97·0°.

Preparation and Treatment of Reaction Mixtures.—Reaction media were prepared by mixing standard solutions of propan-2-ol, n-propanol, and hydrogen bromide in water or formic acid to give the required composition. Weighed quantities of sodium formate were dissolved in such mixtures. Propene samples were sealed in calibrated thin-walled bulbs, and the latter broken by shaking after sealing with 5 ml. quantities of reaction medium in glass tubes. The same stock solutions were used in the experiments with propene as for determining the corrections given in Table 2. The tubes were heated in a water-bath at 100°, cooled, and broken by shaking in a stopped reagent bottle at slightly reduced pressure. The contents were then diluted and used for the estimation of isopropyl derivatives (alcohol and formate together) and for radioactivity measurements by the methods previously described.[12]

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[11] Schwarzenbach, Epprecht, and Erlenmeyer, *Helv. Chim. Acta*, 1936, **19**, 1292.
[12] Coe and Gold, *J.*, 1960, 4185.