

**1030. *The Mechanism of Vinyl Ether Hydrolysis.***

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First-order rate constants for the acid hydrolysis of vinyl and alk-1-enyl ethers have been determined. Hydrolysis of n-butyl vinyl ether is slower in deuterium oxide than in water by a factor of 2.63. A mechanism of hydrolysis consistent with the results obtained is proposed.

THE hydrolysis of vinyl ethers has been investigated by several workers,<sup>1-5</sup> and it is apparent that it does not take the same course as the hydrolysis of saturated ethers.<sup>6</sup>

<sup>1</sup> Skrabal and Skrabal, *Z. phys. Chem.*, 1938, **181**, A, 449.

<sup>2</sup> Skrabal, *Z. phys. Chem.*, 1939, **185**, A, 81.

<sup>3</sup> Zahorka and Wiemann, *Monatsh.*, 1938, **71**, 229.

<sup>4</sup> Kiprianova and Rekusheva, *Doklady Akad. Nauk S.S.S.R.*, 1962, **142**, 589.

<sup>5</sup> Prilezhaeva, Shapiro, and Shostakovskii, *Zhur. obshchei Khim.*, 1948, **18**, 1663.

<sup>6</sup> Hammett, "Physical Organic Chemistry," McGraw-Hill, New York, 1940, p. 299; Bonhoeffer and Reitz, *Z. phys. Chem.*, 1937, **179**, A, 135.

R. Skrabal<sup>2</sup> and A. Skrabal<sup>7</sup> were able to derive a mathematical expression by which the rates of hydrolysis of mixed saturated ethers, ROR', can be estimated from those of their symmetrical counterparts. R. Skrabal therefore concluded that hydrolysis of vinyl ethers takes place by addition of water to the double bond as Paul<sup>8</sup> had previously proposed, but this could not be verified directly because of the extremely rapid hydrolysis of the hemiacetal produced.<sup>7</sup>

Kiprianova and Rekusheva<sup>4</sup> have found, using H<sub>2</sub><sup>18</sup>O, that the alkyl-oxygen bond in an alkyl vinyl ether is not broken during acid hydrolysis, and Prilezhaeva *et al.*<sup>5</sup> discovered that the hydrolysis of alkyl vinyl ethers is of the second-order; that is, first-order with respect to ether, and first-order with respect to H<sub>3</sub>O<sup>+</sup>. The former authors believe that the initial step in the reaction is an attack by H<sub>3</sub>O<sup>+</sup> on the π electrons of the double bond, whilst the latter authors propose a transition state formed by the interaction of both the ether oxygen and the β-carbon atom of the vinyl group with the H<sub>3</sub>O<sup>+</sup> ion. Neither paper however gives any evidence with regard to the rate-determining step.

We have measured the first-order rate constants with respect to ether. Hydrolyses were carried out at 25° in a solution of dioxan-water (80 : 20) and the reaction was followed by measuring at fixed intervals the carbonyl absorption of the aldehyde or ketone produced.<sup>9</sup> The rates of hydrolysis of several vinyl ethers, CH<sub>2</sub>:CH·OR, are given in Table 1 and of some ethers, RR'C:CR''·OEt in Table 2.

TABLE 1.

R	Bu <sup>t</sup>	Pr <sup>t</sup>	Et	Bu <sup>i</sup>	Bu <sup>n</sup>	Et <sub>2</sub> CH·CH <sub>2</sub>	PhCH <sub>2</sub>	Cl·CH <sub>2</sub> ·CH <sub>2</sub>
10 <sup>4</sup> k <sub>2</sub> * (l. mole <sup>-1</sup> sec. <sup>-1</sup> )	3885	1557	530	409	366	233	81	44

TABLE 2.

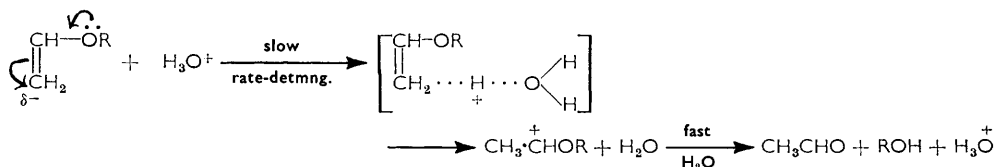
R .....	H	Me	Et	Me	Cl	H
R' .....	H	H	H	Me	H	H
R'' .....	H	H	H	H	H	Me
10 <sup>4</sup> k <sub>2</sub> * (l. mole <sup>-1</sup> sec. <sup>-1</sup> ) .....	530	92	91	8·7	~0·8	1·031 × 10 <sup>7</sup>

$$* k_2 = k_1/[H^+].$$

We have also found that n-butyl vinyl ether hydrolyses 2·63 times faster in water than in deuterium oxide.

It has been established<sup>10</sup> that the rate-determining step in the hydration of olefins is the formation of a carbonium ion which is rapidly attacked by water. Furthermore the maximum value of  $k_{H_2O}/k_{D_2O}$  to be expected for a slow proton transfer from a hydronium ion is, according to Bunton and Shiner,<sup>11</sup> ~3·6 and the same authors show that in the olefin hydration reaction the only transition state which could give rise to a high value is that in which the proton interacts electrostatically with both the water and the unsaturated centre.

On this basis, the annexed mechanism for the acid-hydrolysis of vinyl ethers is suggested. The high reactivity of the vinyl ethers is due to a mesomeric effect, which



<sup>7</sup> Skrabal, *Ber.*, 1939, **72**, 446.

<sup>8</sup> Paul, *Bull. Soc. chim. France*, 1934, 971.

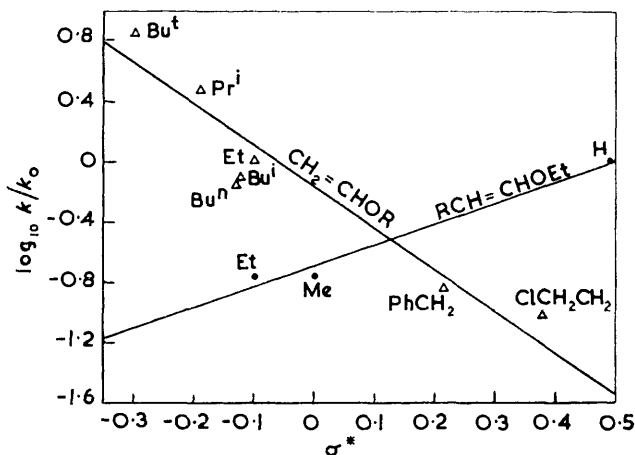
<sup>9</sup> Kreevoy and Taft, *J. Amer. Chem. Soc.*, 1955, **77**, 3146.

<sup>10</sup> Taft, *J. Amer. Chem. Soc.*, 1952, **74**, 5372; Taft, Purlee, Reisz, and De Fazio, *ibid.*, 1955, **77**, 1584.

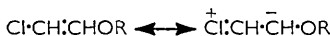
<sup>11</sup> Bunton and Shiner, *J. Amer. Chem. Soc.*, 1961, **83**, 3214.

produces a partial negative charge on the  $\beta$ -carbon atom of the vinyl group, thus facilitating proton interaction. As the electron-releasing power of R in  $\text{CH}_2\text{:CH}\cdot\text{OR}$  is increased, the mesomeric effect is assisted. This observation is in agreement with nuclear magnetic resonance studies.<sup>12</sup>

The presence of alkyl substituents upon the  $\beta$ -carbon atom of the vinyl group leads to a decrease in the hydrolysis rate, because the mesomeric effect is opposed, possibly by



hyperconjugation, whilst in the case of 2-chlorovinyl ethyl ether, which is hydrolysed extremely slowly, additional, unfavourable mesomeric forms involving the chlorine atom are possible, *e.g.*,



On the other hand, ethyl isopropenyl ether is hydrolysed approximately 20,000 times faster than ethyl vinyl ether, and it seems likely that this reaction is assisted by hyperconjugation.

The data in Tables 1 and 2, when substituted in the Hammett-Taft equation,<sup>13</sup> lead to linear relationships between  $\log k/k_0$  and  $\sigma^*$ , where  $k_0$  is the rate constant for ethyl vinyl ether and  $\sigma^*$  the appropriate substituent coefficient. This supports the view that the substituent effects are predominantly polar in character (Figure).

In divinyl ether, the charge requirements of the two vinyl groups are in opposition<sup>14</sup> and the compound therefore hydrolyses about 350 times more slowly than ethyl vinyl ether.<sup>15</sup>

#### EXPERIMENTAL

**Materials.**—Ethyl vinyl ether and n-butyl vinyl ether were obtained from B.D.H. Ltd.; isobutyl vinyl ether, 2-ethylhexyl vinyl ether, and 2-chloroethyl vinyl ether were obtained from L. Light & Co. Ltd. These reagents were distilled from sodium.

2-Chlorovinyl ethyl ether<sup>16</sup> was synthesised from 1,2-dichloroethyl ether, which had been prepared by passing chlorine through ethyl vinyl ether at  $0^\circ$ , until the C:C stretching absorption

<sup>12</sup> Feeney, Ledwith, and Sutcliffe, *J.*, 1962, 2021.

<sup>13</sup> Taft, in "Steric Effects in Organic Chemistry," ed. Newman, Wiley & Sons, New York, 1956, p. 556.

<sup>14</sup> Ingold, "Structure and Mechanism in Organic Chemistry," Cornell Univ. Press, New York, 3rd edn., 1957, p. 117; Baricelli and Bastiansen, *Acta Chem. Scand.*, 1949, 3, 201.

<sup>15</sup> Jacobs and Searle, *J. Amer. Chem. Soc.*, 1944, 66, 686.

<sup>16</sup> Arens, *Rec. Trav. chim.*, 1955, 74, 271.

disappeared from an infrared spectrum of the liquid. Other vinyl ethers were synthesised.<sup>17</sup> All compounds were >98% pure (gas-liquid chromatography). Stereoisomers, when these occurred, were not separated.

*Procedure.*—Sufficient of the vinyl ether to give a 0.05M solution was weighed into a 10 ml. graduated flask, which was transferred to a thermostat at 25°. Dioxan (8 ml.), water (1 ml.), and acid catalyst (1 ml.) were added to the flask, all having been previously brought to 25°. After being well mixed, part of the vinyl ether solution was transferred to a 1 cm. silica cell, which was placed in a thermostatted cell housing attached to a Unicam S.P. 500 spectrophotometer. Readings of optical density at 280 m $\mu$  due to the carbonyl absorption of the aldehyde or ketone produced in the hydrolysis were taken at intervals over about 75% of the reaction, and the first-order rate constant for the reaction was obtained from a plot of  $\log a/(a-x)$  against time where  $a$  = optical density at infinite time and  $x$  = optical density at time  $t$ . Duplicate determinations agreeing within about 2.5% were obtained.

The catalyst was 0.1N-perchloric acid (1 ml.), except in the case of ethyl isopropenyl ether, when a buffer solution of 95% 0.2M-acetic acid and 5% 0.2M-sodium acetate (v./v.) was employed. The latter catalyst produced a hydrogen-ion concentration of  $1.88 \times 10^{-8}$  mole/l., this value being calculated by a published method.<sup>18</sup> Only an approximate value for the rate constant of 2-chlorovinyl ethyl ether was found as the reaction was extremely slow.

For the experiments in which D<sub>2</sub>O was used, the procedure was slightly modified. Sufficient 70% perchloric acid to give an approximately 0.01N solution was accurately weighed into a 10 ml. graduated flask, which was placed in a thermostat at 25°. Dioxan (8 ml.) and D<sub>2</sub>O (2 ml.) were added, and finally n-butyl vinyl ether (0.1 ml.). Duplicate determinations were made, and a parallel set of experiments was carried out using water (2 ml.). The value of  $k_{H_2O}/k_{D_2O}$  was found to be 2.63.

A typical set of results is in Table 3. The perchloric acid concentration is 0.01N.

TABLE 3.

## Hydrolysis of t-butyl vinyl ether.

$t$ (min.)	1.5	2	2.5	3	3.5	4
$x$	0.463	0.549	0.563	0.602	0.636	0.672
$t$ (min.)	4.5	5	5.5	6	$\infty$	
$x$	0.697	0.717	0.745	0.761	0.900	

$$k_1 = 3.93 \times 10^{-3} \text{ sec.}^{-1}.$$

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<sup>17</sup> Nazarov, Makin, Krupstov, and Miranov, *J. Gen. Chem. (U.S.S.R.)*, 1959, **29**, 116; Watanabe and Conlon, *J. Amer. Chem. Soc.*, 1957, **79**, 2828.

<sup>18</sup> Kreevoy and Taft, *J. Amer. Chem. Soc.*, 1955, **77**, 5590.