enolisation is found here. The aromatic protons occurs at $\tau = 2.95$ and the enol hydroxyls at $\tau = -6.8$.

The reason why (I) prefers the 7-membered chelate ring to the 6-membered one as in (II) may lie in a resonance possibility where a benzenoid (quinol) structure participates, formed by establishing an ordinary $O-H$ bond between the quinone oxygen and the enol proton (IV). Such a structure leads to some degree of charge separation, which makes it less probable, but it may well be of sufficient importance to give structure (I) the edge over a structure with hydrogen bonding only within the side-chains.

Experimental. The NMR-spectra were recorded in approximately 10 % solutions in d_6-dimethyl sulphoxide on a Varian A 60 spectrometer. Infra-red spectra were recorded on a Beckman IR-5A apparatus. The investigated substances were prepared according to published methods.[1,2]

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Kinetics of the Hydrolytic Cleavage of the Furan Ring

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In a recent discussion of the acid-catalyzed hydrolysis of vinyl ethers,[1] it was pointed out that the proton transfer mechanism of vinyl ether hydrolysis would be extremely difficult to apply to furans because of their initial aromatic stabilization.

In order to obtain direct experimental information about the hydrolytic cleavage of the furan ring, the kinetics of the acid-catalyzed hydrolysis of 2,5-dimethylfuran in water and the deuterium solvent

$$HC-CH \quad + H_2O \longrightarrow CH_3COCH_2CH_2COCH_3$$

isotope effect thereon have been studied. A few comparative experiments were also made with furan itself, although its low reactivity towards water made it less suitable for more extensive studies. The hydrolysis rate coefficients of the former compound in 15 and 25 % ethanol-water mixtures at 25°C, and those of the both compounds in moderately concentrated acids have been previously measured.[2,3]

Furan and *2,5-dimethylfuran* were commercial products of Koch-Light Laboratories, Ltd., which were purified by careful fractional distillations in a Todd precision fractionation assembly. The following physical constants were recorded: furan, b.p. $31.2-31.6°C/746$ torr, n_D^{20} 1.4212, d_4^{20} 0.9373; 2,5-dimethylfuran, b.p. $41-42°C/134$ torr, n_D^{20} 1.4122, d_4^{20} 0.8505. The purities of the compounds were also controlled by gas chromatography.

In the kinetic experiments the rate of disappearance of the furan was followed by spectrophotometry. As it was observed that ultraviolet light interfered by bringing about photochemical side reactions, it was necessary to conduct the reactions in the dark, excepting the short periods of time needed for the photometric analysis of the samples withdrawn from the reaction mixtures. Owing to the relatively low solubilities of the investigated furans, the initial concentrations were 0.005 M or less. The optical measurements were made on a Beckman DK 2A Ratio Recording Spectrophotometer at a constant wavelength of approximately 235 mμ. The cell housing of the photometer was at the same temperature as the thermostat in which the reactions were carried out. The concentration of the catalyst hydrochloric acid was about 0.2 M in most experiments. First-order kinetics were strictly obeyed in all cases, the standard errors of the rate coefficients being less than 2 %. In a number of additional rate measurements it was confirmed that the directly measured first-order rate coefficient was proportional to the concentration of the hydrochloric acid up to 0.2 M. The results of the kinetic measurements are shown in Tables 1 and 2.

The value obtained for furan shows that this compound hydrolyzes slower than its aliphatic analog, divinyl ether,[2] by a factor of about 10^4. This is in agreement with the partial aromatic character of the furan

Table 1. Rate coefficients for the hydronium ion-catalyzed hydrolysis of furans in water.

	°C	No. of runs	$10^3 \times k_{H_3O^+}$ $M^{-1}s^{-1}$
2,5-Dimethylfuran	25	2	0.181
»	35	2	0.583
»	45	5	2.03
$E = 22.8$ kcal/mole; $\Delta S^{\ddagger} = -1.3$ e.u.			
Furan	45	2	0.0081

Table 2. Rate coefficients for the lyonium ion-catalyzed hydrolysis of 2,5-dimethylfuran in H_2O-D_2O mixtures. n = deuterium atom fraction of the solution.

n	No. of runs	$10^3 \times k_{L_3O^+}$ $M^{-1}s^{-1}$
0.000	5	2.03
0.200	1	2.43
0.398	1	2.22
0.599	3	2.70
0.774	1	2.91
0.981	2	4.21

$k_D/k_H = 2.15$

ring, the stabilizing influence of which is lost in the transition state of the hydrolysis.[1] The aromaticity of the furans is even more strikingly illustrated by a comparison of their rates of hydrolysis with those of the corresponding dihydrofurans, which latter were found to be higher by factors of 10^6 to 10^7.

Two points of particular interest become evident from Tables 1 and 2. First, the value of the activation entropy of 2,5-dihydrofuran does not differ significantly from those determined earlier for a number of aliphatic and cyclic vinyl ethers.[1] The low rate is thus primarily due to the relatively high activation energy. Second, the deuterium solvent isotope effect,* $k_D/k_H = 2.15$, is the inverse of that on the reaction of "normal" vinyl ethers, for which k_D is *smaller* than k_H by a factor of about 2.5. This must be the result of

differences in the transition state structures involved. As an additional point it may be mentioned that, in contrast to other vinyl ethers, general acid catalysis was not detected in the hydrolysis of furans.

Because the reaction is, apparently at least, specifically catalyzed by hydronium ion, two mechanistic alternatives are to be considered:

A) A rate-determining proton transfer from the catalysing hydronium ion with a Brønsted α of almost unity.

B) Pre-equilibrium protonation which is at least slightly faster than the subsequent rate-determining reaction of the protonated intermediate I^+.
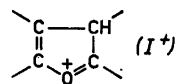
As the intermediate I^+, regardless of the rate-determining stage of the overall reaction, has lost the delocalization energy of the furan ring, its energy level is relatively high. As a consequence of the Hammond principle,[4] this implies that the free energy difference between I^+ and the transition state of the proton transfer step must be relatively small, which means that the proton transfer is almost complete (α about 1) in the transition state in question.

If the proton transfer step determined the overall rate (mechanism *A*), as is the case with other vinyl ethers, the similar magnitudes of the activation entropies would be easily understood. It should also be remembered that in the case of furans, in contrast to other vinyl ethers, we had a product-like transition state, which might account for the exceptional isotope effect. However, Bunton and Shiner[5] have estimated that, for a product-like transition state resulting from a proton transfer from the hydronium ion to a carbon-carbon double bond, the value of k_D/k_H can hardly exceed 1.6, which is still small in com-

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* An obvious explanation for the controversy between the present result and that reported by Stamhuis et al.[3] is in photochemical side reactions, not accounted for by these authors. It was observed in the present study that, if the reactions were carried out directly in the cell of the spectrophotometer, the apparent rate coefficients increased by factors of 2 to 50.

parison with our experimental value of 2.15.

If, alternatively, the subsequent reaction of I^+ were slower than its formation from the reactants (mechanism B), the magnitude and direction of the isotope effect could be better understood. However, the value of the activation entropy as well as the fact that the structural influence of an α-methyl substituent on the rate is of the same magnitude as for other vinyl ethers [1] could be explained only if the structure of the transition state of the rate-determining subsequent step were relatively close to that of I^+, and the free energy difference between these structures were not large.
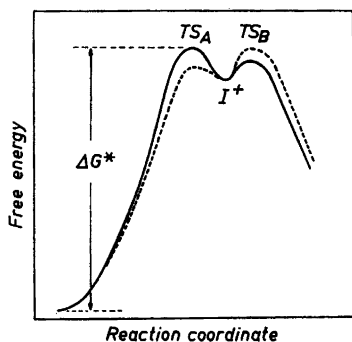

Fig. 1. Free energy profiles for the hydrolysis of furans. TS_A and TS_B are transition states in the mechanisms A and B, respectively, and I^+ is the protonated intermediate.

The two mechanistic possibilities discussed above are illustrated in Fig. 1. Although, at first sight, the magnitude of the isotope effect seems to favor mechanism B, mechanism A cannot be wholly excluded because of the approximations made when predicting values for the different transition state structures. The conclusion can be drawn, however, that the energy level of the actual transition state cannot differ much from that of the protonated intermediate I^+.

The above conclusion is also supported by approximate energy calculations. It was estimated earlier [6] that the free energy of protonation of a vinyl ether is roughly 10 kcal/mole. The corresponding free energy change for furan must exceed this value by the delocalization energy of furan, about 17 kcal/mole,[7] since this energy is lost in the conjugate acid of furan. Although the result of this estimation, 27 kcal/mole, may be in error by several kilocalories, it is seen to be relatively close to the free energy of activation of furan, which is about 26 kcal/mole at 25°C.

Finally, it is worth mentioning that in the case of a gross isotope effect of the present magnitude ($k_D/k_H = 2.15$), the experiments in mixed H_2O-D_2O solvents do not furnish mechanistic information in addition to that obtained from the experiments in the pure waters alone.[8]

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