graph Model 90 P gas chromatograph with a Disc chart integrator Model 207.

A weighed amount of *o*-xylene was used as the internal standard; at the end of each run some benzene was added to minimize loss of the volatile butadiene. Aniline was introduced routinely as an inhibitor of radical reactions. At 42°, the retention time of butadiene was 6.15 min while those of the other substances at 136° were 15.5 (benzene), 27.0 (4-vinylcyclohexene), 32.0 (*o*-xylene), 37.0 (cycloocta-1,5-diene), and 41.0 min (aniline).

Gas chromatographic correction factors relative to *o*-xylene were determined by analysis of known mixtures prepared by weight with the exception of butadiene (vacuum system by pressure and volume). Multiplication of the ratio of the integrated peak of material to that of *o*-xylene by the correction factor gives the true weight of material. Correction factors are as follows: cycloocta-1,5-diene, 1.04 ± 0.007; 4-vinylcyclohexene, 1.02 ± 0.008; butadiene, 1.44 ± 0.02.

In preliminary experiments it was found that good material balances and good first-order plots were obtained in the 12-l. Pyrex flask at the highest temperatures provided a tenfold molar excess of aniline was incorporated as an inhibitor. The rate constants at 359.70 and 330.17° were 410.8×10^{-5} and 55.6×10^{-5} sec^{-1}, respectively, whence $\log k_a = 15.40 - 51.6/\theta$ where $\theta = (2.303)\cdot(1.987)(0.001)T$. The ratios of 4-vinylcyclohexene to butadiene were constant for the different runs at the same temperature but varied from 2.92 at 359.70° to 3.57 at 330.17°, corresponding to a greater activation energy for the formation of butadiene of 5 kcal/mol.

The final study of the kinetics was performed without aniline in a 3.5-l. hand-blown flask of lead-potash glass. Mass balance was good at all conversions up to the highest temperatures and strictly first-order plots were obtained. Individual rate constants were calculated by the method of least squares giving weight to individual points in proportion to the extent of reaction. The experimental data are given in Table V[68] in the microfilm edition. The calculated rate constants and activation parameters, calculated by the method of least squares, have been given in Table II.

Acknowledgments. For the support of this work, grateful acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society. Dr. Franck-Neumann expresses his gratitude to the French C.N.R.S. for its support. Dr. Hasselmann expresses his thanks to the Deutsche Forschungsgemeinschaft for the award of a travel grant. R. L. Kaye wishes to express his gratitude to Yale University for a first-year University Fellowship (1964–1965) and to the National Science Foundation for a graduate fellowship (1965–1967).

Cyclohexadienyl Cations. III. Kinetics and Mechanism of the Dienone–Phenol Rearrangement in Concentrated Aqueous Acids[1,2]

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Abstract: Rates of the acid-catalyzed rearrangement of 4,4-dimethylcyclohexadienone (**1**) to 3,4-dimethylphenol in aqueous sulfuric acid (35.5–94.7%) and aqueous perchloric acid (37.9–71.0%) have been measured. 3-Deuterio-4,4-dimethylcyclohexadienone has been prepared and was shown to undergo the dienone–phenol rearrangement faster than **1** in both 97.3 and 55.2% sulfuric acid. These results coupled with earlier published information support a mechanism which involves (a) reversible protonation of **1** to produce a hydroxycyclohexadienyl cation followed by (b) rate-determining methyl migration from C-4 to C-3 and finally (c) rapid loss of a proton from C-3 to produce the aromatic product. In addition, our analysis of the acidity dependence of the dienone–phenol rearrangement in sulfuric and perchloric acids suggests that the transition state is less solvated than the ground state. Activation parameters for the isomerization of **1** in 97.2% sulfuric acid have been determined and are discussed.

The application of acidity function theory to the solution of mechanistic problems in organic chemistry has been and continues to be a challenging problem. Some of the recent work in this area has involved a search for more meaningful parameters associated with the kinetic acidity dependence of acid-catalyzed reactions with a view toward expanding the scope and usefulness of Hammett's original work.[3–5] On the other hand, Kresge, *et al.*, have suggested that detailed structural information concerning the transition state can be obtained from a comparison of the acidity dependence of kinetic and equilibrium protonation reactions for certain acid-catalyzed reactions.[6,7] Very recently in a series of very significant papers it was concluded that the number of water molecules required to form the activated complex in ester[8,9] and amide[10] hydrolysis could be determined from the dependence of the hydrolysis rate on acid concentration and water activity provided that the concentration of protonated ester or amide could be measured or estimated as a function of acid concentration. We were interested in ob-

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(1) For paper II in this series, see: V. P. Vitullo, *J. Org. Chem.*, **35**, 3976 (1970).

(2) Supported in part by Grant No. GP-29738X from the National Science Foundation.

(3) J. F. Bunnett, *J. Amer. Chem. Soc.*, **83**, 4956, 4967, 4973, 4978 (1961).

(4) J. F. Bunnett and F. P. Olsen, *Can. J. Chem.*, **44**, 1899, 1917 (1966).

(5) For a review of acidity functions and their use in mechanistic organic chemistry, see: C. H. Rochester in "Acidity Functions," Academic Press, London, and New York, 1970, pp 110–196.

(6) A. J. Kresge, R. A. More O'Ferrall, L. E. Hakka, and V. P. Vitullo, *Chem. Commun.*, 46 (1965).

(7) A. J. Kresge, S. Mylonakis, Y. Sato, and V. P. Vitullo, *J. Amer. Chem. Soc.*, **93**, 6181 (1971).

(8) C. A. Lane, *ibid.*, **86**, 2521 (1964); C. A. Lane, M. F. Cheung, and G. F. Dorsey, *ibid.*, **90**, 6492 (1968).

(9) K. Yates and R. A. McClelland, *ibid.* **89**, 2686 (1967).

(10) K. Yates and J. C. Riordan, *Can. J. Chem.*, **43**, 2328 (1965); K. Yates and J. B. Stevens, *ibid.*, **43**, 529 (1965).

taining similar information for a reaction which (at least formally) does not involve water in the formation of the transition state from the protonated ground state.

Our interest in this point required that we find a model reaction which exhibited the properties of an A-1 reaction, *i.e.*, rapid reversible protonation followed by a simple uncatalyzed rate-determining step not involving a water molecule. We further required that the concentration of the protonated species be directly measurable. Our earlier work[11] on the protonation of 4-dichloromethyl-4-methylcyclohexadienone in sulfuric acid solutions suggested an hydroxycyclohexadienyl cation might be a readily observable intermediate in the dienone–phenol rearrangement. For the acid-catalyzed rearrangement of 4,4-dimethylcyclohexadienone (**1**) this indeed was found to be the case.[12] Clearly the dienone–phenol rearrangement appeared to be a likely candidate for a model A-1 reaction and a detailed study of the kinetics of this rearrangement in solutions of sulfuric and perchloric acids was undertaken to establish the mechanism and acidity dependence of this reaction. The results of these studies are presented here.

Results

We have previously provided evidence for the existence of a protonated cyclohexadienone during the isomerization of **1** to 3,4-dimethylphenol in sulfuric and perchloric acids.[12] The ratios of protonated to neutral forms (α) measured spectrophotometrically for **1** in sulfuric and perchloric acids as a function of medium acidity are given below. (These data were taken from Tables II and III, respectively, in ref 12.) The results allow the fraction of **1** protonated [$\alpha/(1 + \alpha)$] to

$$\text{HClO}_4\text{:}\quad \log \alpha = (0.62 \pm 0.02) \times [(-3.58 \pm 0.10) - H_0] \quad (1)$$

$$\text{H}_2\text{SO}_4\text{:}\quad \log \alpha = (0.61 \pm 0.01) \times [(-3.75 \pm 0.05) - H_0] \quad (2)$$

be computed at any acidity.

Rates of rearrangement of **1** were determined by monitoring the decrease in the absorbance of protonated **1** at either 260 or 295 nm.[12] The reaction was accurately first order in **1** to >90% reaction. The results of our kinetic studies in sulfuric and perchloric acids are given in Tables I and II.[13–15] Also included in these tables is the fraction of dienone which is protonated at the indicated acidity (computed from eq 1 and 2 above).

Table I. First-Order Rate Constants for the Dienone–Phenol Rearrangement of 4,4-Dimethylcyclohexadienone in Aqueous Sulfric Acid at 25.2 ± 0.1°

10^4k_{obsd}, sec^{-1}	Wt % H_2SO_4	$-H_0$[a]	$-\text{Log } a_{H_2O}$[b]	F[c]	10^4k_1, sec^{-1}
9.01	94.70	9.87	4.4195	0.9998	9.01
9.66	94.70	9.87	4.4195	0.9998	9.66
10.6	91.92	9.37	3.9328	0.9996	10.6
8.86	89.11	8.88	3.5066	0.9993	8.86
8.28	86.26	8.41	3.0975	0.9986	8.29
7.12	82.93	7.87	2.6404	0.9970	7.14
6.07	79.92	7.40	2.2606	0.9943	6.10
2.66	72.55	6.26	1.5390	0.9719	3.77
3.02	69.02	5.75	1.2857	0.9439	3.20
1.94	64.77	5.15	1.0168	0.8783	2.21
1.25	61.10	4.67	0.8360	0.7856	1.59
0.745	56.69	4.13	0.6599	0.6310	1.18
0.554	54.33	3.86	0.5800	0.5387	1.03
0.374	52.44	3.66	0.5222	0.4683	0.797
0.398	52.17	3.63	0.5144	0.4577	0.870
0.221	48.04	3.22	0.4062	0.3212	0.688
0.134	44.94	2.94	0.3377	0.2417	0.554
0.0788	41.90	2.68	0.2797	0.1809	0.436
0.0376	37.85	2.36	0.2150	0.1232	0.305
0.0216	35.45	2.18	0.1826	0.0983	0.220

[a] Reference 18. [b] W. F. Giauque, E. W. Horning, J. E. Kunzler, and T. R. Rubin, *J. Amer. Chem. Soc.*, **82**, 60 (1960). [c] Fraction protonated, $\alpha/(1 + \alpha)$, computed from eq 2.

Table II. First-Order Rate Constants for the Dienone–Phenol Rearrangement of 4,4-Dimethylcyclohexadienone in Aqueous Perchloric Acid at 25.2 ± 0.1°

10^4k_{obsd}, sec^{-1}	Wt % $HClO_4$	$-H_0$[a]	$-\text{Log } a_{H_2O}$[b]	F[c]	10^4k_1, sec^{-1}
36.7	70.95	8.03	2.2389	0.9984	36.8
24.9	68.83	7.43	1.9289	0.9961	25.0
19.8	66.80	6.89	1.6702	0.9915	20.0
12.7	64.16	6.21	1.3826	0.9778	13.0
8.36	61.80	5.65	1.1660	0.9530	8.77
5.21	59.72	5.20	1.0025	0.9114	5.72
5.16	59.03	5.05	0.9533	0.8923	5.78
3.33	56.57	4.57	0.7965	0.8059	4.13
1.82	53.62	4.05	0.6415	0.6626	2.75
1.45	52.83	3.92	0.6053	0.6196	2.34
1.04	50.93	3.63	0.5264	0.5176	2.01
0.535	48.13	3.24	0.4284	0.3797	1.41
0.536	47.82	3.20	0.4187	0.3662	1.46
0.257	44.70	2.83	0.3329	0.2533	1.02
0.276	44.54	2.81	0.3290	0.2479	1.13
0.109	41.54	2.51	0.2640	0.1763	0.618
0.0418	37.93	2.18	0.2025	0.1175	0.356

[a] Reference 17. [b] J. F. Bunnett, *J. Amer. Chem. Soc.*, **83**, 4967 (1961). [c] Fraction protonated, $\alpha/(1 + \alpha)$, computed from eq 1.

In order to establish unequivocally the nature of the rate-determining step in the dienone–phenol rearrangement we prepared 3-deuterio-4,4-dimethylcyclohexadienone (**1**-*d*) and compared its rate of rearrangement to **1**. Rearrangement rates were measured for both **1** and **1**-*d* and are collected in Table III.

The predictions are straightforward. If k_1 is rate determining one should observe a small secondary isotope effect probably inverse[16] because of the change of hybridization at the isotopic center. On the other hand, if k_2 were rate determining a large primary isotope effect is expected since a carbon–hydrogen bond is being broken in the rate-determining step.

Now the ratio k_1 to $k_{1\text{-}d}$ does not give the isotope effect directly but it can be obtained from these data in the following way (eq 3–5). The value of k_H/k_D com-

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(11) V. P. Vitullo, *J. Org. Chem.*, **34**, 224 (1969).

(12) V. P. Vitullo, *ibid.*, **35**, 3976 (1970).

(13) Some of these results were presented earlier in preliminary form: (a) V. P. Vitullo, *J. Chem. Soc. D*, 688 (1970); (b) V. P. Vitullo and N. Grossman, *Tetrahedron Lett.*, 1559 (1970). Subsequent to this, Waring and Cook have reported some rate and equilibrium protonation data for **1** in aqueous sulfuric acid solutions: K. L. Cook and A. J. Waring, *ibid.*, 1675 (1971).

(14) Prior to our work kinetic data on the dienone–phenol rearrangement covered only a limited range of acidity: H. Hemetsberger, *Monatsh. Chem.*, **99**, 1724 (1968); G. Farges and A. S. Dreiding, *Helv. Chim. Acta*, **49**, 552 (1966).

(15) For a discussion of possible mechanisms of the dienone–phenol rearrangement, see: A. J. Waring, *Advan. Alicycl. Chem.*, **1**, 207 (1966).

(16) A. Streitweiser, R. H. Jagow, R. C. Fahey, and S. Suzuki, *J. Amer. Chem. Soc.*, **80**, 2326 (1958).

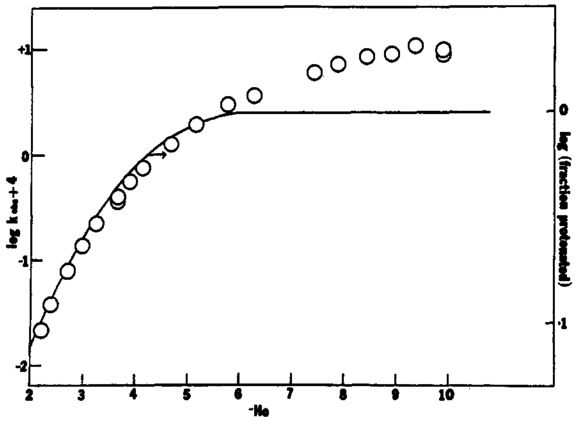


Figure 1. Plot of log k_{obsd} *vs.* $-H_0$ for the acid-catalyzed isomerization of 4,4-dimethylcyclohexadienone in sulfuric acid.

$$k_1 = 2k_H \qquad (3)$$

$$k_{1\text{-}d} = k_H + k_D \qquad (4)$$

$$k_D/k_H = [2(k_{1\text{-}d}/k_1) - 1] \qquad (5)$$

puted in this way is 0.87 ± 0.04 and is independent of acidity. This unequivocally establishes that the rate-determining step in the dienone–phenol rearrangement is the intramolecular migration of a methyl group.

Table III. Deuterium Isotope Effects for the Dienone–Phenol Rearrangement of 4,4-Dimethylcyclohexadienone in Aqueous Sulfuric Acid

10^4k_1, sec^{-1}	$10^4k_{1\text{-}d}$, sec^{-1}	Wt % H_2SO_4	T, °C
9.00	9.90	97.29	25.2 ± 0.1
9.27	9.79	97.29	25.2 ± 0.1
8.97	9.89	97.29	25.2 ± 0.1
9.00	9.48	97.29	25.2 ± 0.1
9.06 ± 0.15	9.76 ± 0.20	k_H/k_D = 0.866 ± 0.041	
0.660	0.716	55.24	25.8 ± 0.1
0.651	0.695	55.24	25.8 ± 0.1
0.644	0.692	55.24	25.8 ± 0.1
0.652 ± 0.009	0.701 ± 0.014	k_H/k_D = 0.868 ± 0.039	

Rates of rearrangement of **1** were also determined as a function of temperature and these results are recorded in Table IV. At this acidity (97.2% H_2SO_4) **1** is completely protonated and the activation parameters obtained from these data refer solely to the isomerization of 1-hydroxy-4,4-dimethylcyclohexadienyl cation. The activation parameters computed from these data are $\Delta H^{\ddagger} = 21.9 \pm 0.4$ kcal/mol and $\Delta S^{\ddagger} = 1.0 \pm 1.1$ eu.

Table IV. Activation Parameters for the Dienone–Phenol Rearrangement of 4,4-Dimethylcyclohexadienone in 97.24% Sulfuric Acid[a]

10^4k_{obsd}, sec^{-1}	T, °C
57.2	40.7
55.2	40.7
53.9	40.6
54.2	40.6
55.3	40.8
23.2	33.5
23.3	33.5
22.9	33.3
22.8	33.3
9.00	25.2
9.27	25.2
8.97	25.2
9.00	25.2

[a] $\Delta H^{\ddagger} = 21.9 \pm 0.4$ kcal/mol; $\Delta S^{\ddagger} = 1.0 \pm 1.1$ eu.

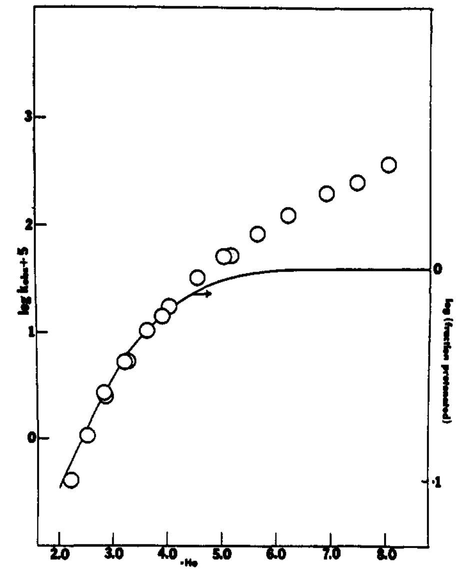


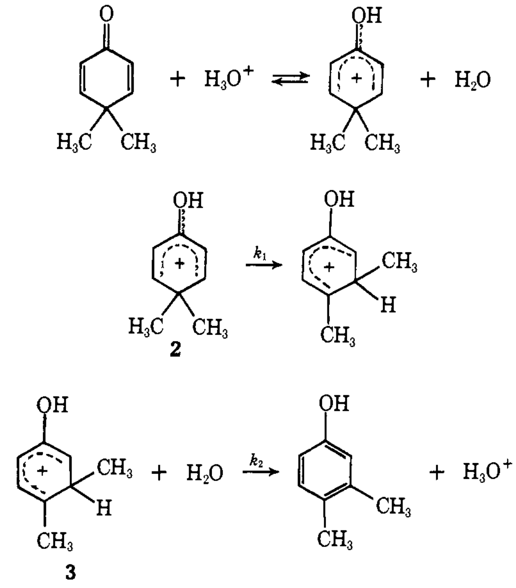
Figure 2. Plot of log k_{obsd} *vs.* $-H_0$ for the acid-catalyzed isomerization of 4,4-dimethylcyclohexadienone in perchloric acid.

Discussion

Reaction Mechanism. That the dienone–phenol rearrangement is an acid-catalyzed reaction is abundantly evident from an examination of Figures 1 and 2 in which log k_{obsd} is plotted against $-H_0$, the Hammett acidity function. For our purposes in this paper the choice of the acidity function H_0 is irrelevant and our choice was based on the fact that this is perhaps the best known and most carefully measured acidity function. Precise H_0 values are now available for both perchloric[17] and sulfuric[18] acids.

The deuterium isotope effects reported in Table III demonstrate that k_1 of Scheme I is indeed rate deter-

Scheme I



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[17] K. Yates and H. Wai, *Can. J. Chem.*, 43, 2131 (1965).

[18] M. J. Jorgenson and D. R. Hartter, *J. Amer. Chem. Soc.*, **85**, 878 (1963).

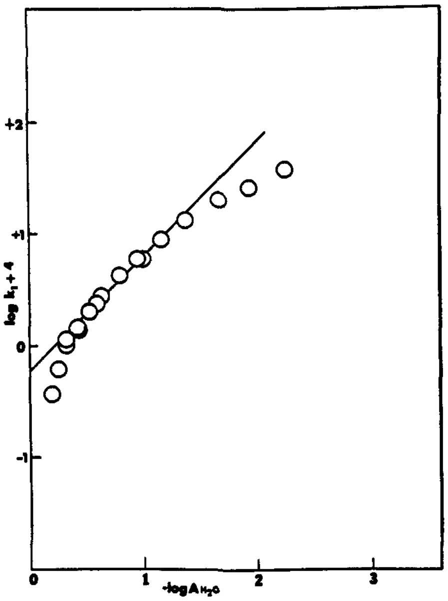

Figure 3. Plot of log k_1 *vs.* $-\log a_{H_2O}$ for the acid-catalyzed isomerization of 4,4-dimethylcyclohexadienone in perchloric acid.

mining. Both the direction (inverse) and magnitude of the isotope effect are consistent with a change of hybridization at the isotopic center $sp^2 \rightarrow sp^3$. For example, α-deuterium isotope effects in solvolysis reactions ($sp^3 \rightarrow sp^2$) are normal, $k_H/k_D \approx 1.15$.[19] This isotope effect is completely inconsistent with k_2 as the rate-determining step.

The activation parameters cited in Table IV are in complete accord with k_1 as the rate-determining step. At this acidity **1** is completely protonated and one would expect that the isomerization of **2** to **3** would be accompanied by only modest changes in entropy especially at low water activities (*vide supra*). The entropy change upon activation in 97.2% sulfuric acid is very close to zero ($\Delta S^{\ddagger} = 1.1 \pm 1.0$ eu). On the other hand, if deprotonation of **3** were rate determining, $\Delta S^{\ddagger} < 0$ is expected. Thus, the acid-catalyzed dienone-phenol is an example of an authentic A-1 reaction in which a measurable amount of the protonated intermediate is present during the reaction.

Kinetic Acidity Dependence. For an A-1 reaction k_1 is related to k_{obsd} through eq 8.

$$S + H^+ \rightleftharpoons SH^+ \xrightarrow{k_1} \text{products} \qquad (6)$$

$$k_{obsd} = [\text{fraction protonated}]k_1 \qquad (7)$$

$$\begin{aligned} k_{obsd} &= [\alpha/(1 + \alpha)]k_1 \\ \alpha &= [SH^+]/[S] \end{aligned} \qquad (8)$$

In highly concentrated acid solutions k_1 is expected to be independent of acidity only if the ratio of ground-state and transition-state activity coefficients remains constant.[20] This will in general be the case when (a) the transition state and the protonated intermediate are similar structurally and (b) there is little or no change in "solvation" attending the formation of the transition state.[21–26] At first glance the dienone–phenol rearrangement would seem to represent a case in which both of these criteria would be fulfilled. Since the rate-determining step involves the isomerization of **2** to **3** the transition state should bear a striking resemblance to the protonated dienone. Superficially, at least, water plays no significant role in this process.

$$k_1 = k_1^{\circ}(f_{SH^+}/f_{\pm}) \qquad (9)$$

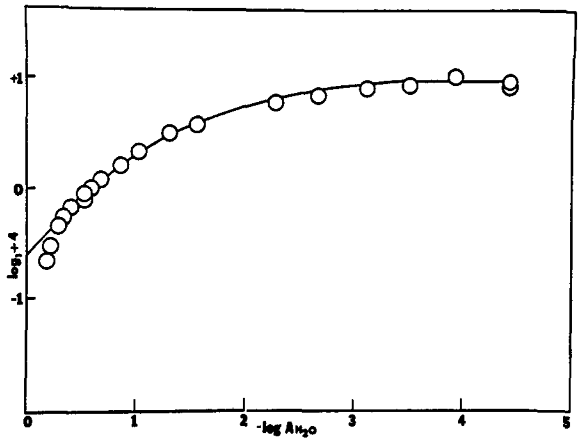

Figure 4. Plot of log k_1 *vs.* $-\log a_{H_2O}$ for the acid-catalyzed isomerization of 4,4-dimethylcyclohexadienone in sulfuric acid.

Values of k_1 computed according to eq 8 for sulfuric and perchloric acids are collected in Tables I and II, respectively. In sulfuric acid k_1 is constant only in >90% sulfuric acid and in general decreases with decreasing sulfuric acid concentration. Qualitatively the results in perchloric acid are similar, although the limiting value of k_1 is experimentally inaccessible.

It seems to us extremely unlikely that the increase of k_1 with increasing acid concentration represents superimposed acid catalysis of the decomposition of SH^+. On the other hand these results suggest that the transition state is less solvated than the protonated ground state resulting in a specific increase of f_{SH^+}[21–26] relative to $f_{\pm}$ as the water activity is reduced. Since water activity and acidity are related in an inverse way this effect would result in an increase of k_1 with increasing acid concentration as observed. The variation of k_1 with water activity is given in Figures 3 and 4 for perchloric and sulfuric acids. In sulfuric acid solutions k_1 at first increases with decreasing water activity but eventually k_1 becomes independent of water activity. In fact the solid line in Figure 4 was calculated from eq 10.[27]

$$k_1 = \frac{(2.67 \pm 0.08) \times 10^{-5}\ \text{sec}^{-1}}{(0.0268 \pm 0.0068) + a_{H_2O}} \qquad (10)$$

In the light of these results is it reasonable that the transition state should be less solvated than the protonated ground state? Consider first the conversion of **2** to **3**. Since **1** is a weak base **2** must be a fairly strong acid. Since a reasonably large fraction of the positive

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(19) V. J. Shiner in "Isotope Effects in Chemical Reactions," C. J Collins and N. S. Bowman, Ed., Van Nostrand Reinhold Co., New York, N. Y., 1970, pp 90–155.

(20) J. N. Bronsted, *J. Phys. Chem. (Leipzig)*, **119**, 19 (1926).

(21) R. H. Boyd, *J. Amer. Chem. Soc.*, **85**, 1555 (1963).

(22) A. J. Kresge, G. W. Barry, K. R. Charles, and Y. Chiang, *ibid.*, **84**, 4343 (1962).

(23) W. M. Schubert and R. H. Quacchia, *ibid.*, **85**, 1278 (1963).

(24) E. M. Arnett and R. D. Bushick, *ibid.*, **86**, 1564 (1964).

(25) R. W. Taft, Jr., *ibid.*, **82**, 2965 (1960).

(26) W. M. Schubert, H. Burkett, and A. L. Schy, *ibid.*, **86**, 2520 (1964).

(27) The constants in eq 10 were calculated from a least-squares plot of $1/k_1$ *vs.* a_{H_2O}.

charge in **2** resides on oxygen it is probable that the OH group is strongly hydrogen bonded to at least one water molecule. The very shallow acidity dependence for the protonation of **1** (eq 1 and 2) supports this hypothesis. In **3** delocalization of the nonbonded electrons on oxygen into the electron-deficient ring is not possible and the acidity of the OH group in **3** ought to be much reduced compared to **2**. Thus, as the methyl group migrates from C-4 to C-3 the acidity and hence the solvation requirements of the hydroxy group are continously changing. It is possible that at some stage of methyl migration (*before*[28] the critical transition state is reached) the acidity of the hydroxy group has been reduced to a point such that one less molecule of water is involved in its solvation. The continual readjustment of solvation as the reaction coordinate is traversed is, of course, a basic tenet of transition-state theory.

An alternative explanation for the inverse dependence of k_1 on water activity involves the loss of a single water molecule from **2** before methyl migration has begun. Desolvated **2** should, of course, be more reactive than **2** since the positive charge in desolvated **2** is more highly concentrated in the ring and less "diffuse" than in **2**. If rearrangement takes place through desolvated **2** k_1 would also be expected to be proportional to $a_{H_2O}^{-1}$. This analysis for the sulfuric acid data would suggest that the constant in the denominator of eq 10 is the effective equilibrium constant for desolvation of **2**.

$$DH \cdot H_2O^+ \rightleftharpoons DH^+ + H_2O \qquad K = (2.7 \pm 0.7) \times 10^{-2} \quad (11)$$

The limiting value of k_1 observed in very concentrated solutions of sulfuric acid suggests that in these solutions there is no change in solvation attending the formation of the transition state. It is probable that in these solutions **2** is effectively desolvated and, therefore, k_1 becomes independent of water activity. The activation entropy observed in 97.2% sulfuric acid is in complete accord with this notion.

The results in perchloric acid are in general agreement with this analysis although it is unfortunate that perchloric acid–water mixtures of >72% perchloric acid are not readily available. It is for this reason that the constants in eq 10 for perchloric acid are not available.

Upon closer examination of Figures 3 and 4 it becomes apparent that at very high water activities in both perchloric and sulfuric acids k_1 is no longer proportional to $a_{H_2O}^{-1}$. Since the dependence of k_1 on water activity is apparently steeper this would suggest that more than one water molecule is lost in the activation process. In solutions of high water activity the solvation number of **2** is expected to be larger. Thus, the incursion of a higher order activity of water terms in the rate law is not surprising.

In conclusion, our results demonstrate unequivocally that the rate constant (k_1) for decomposition of the protonated intermediate in this simple A-1 reaction is not independent of the medium. In fact, the variation of k_1 with water activity can give valuable information concerning solvation changes attending the formation of the transition state. Finally, we suggest that "desolvation catalysis" suggested in this work may be a general phenomenon and can in part explain the extraordinary catalytic properties of concentrated aqueous acids.

Experimental Section

2-Isopropyl-1,3-dithiane.[29] In a 500-ml flask equipped with a reflux condenser, stirrer, and a gas inlet tube was placed 36.3 ml (0.4 mol) of freshly distilled isobutyraldehyde, 300 ml of chloroform, and 40 ml (0.393 mol) of 1,3-propanedithiol. While the flask was cooled in ice anhydrous HCl was admitted for 8 min. The reaction mixture was then stirred for an additional 0.5 hr at room temperature, and washed with two 100-ml portions of water and three 100-ml portions of 10% KOH. After drying over $MgSO_4$ the solvent was removed on a rotary evaporator and the residue distilled: 44.2 g (68%); bp 96–8° (0.7 mm); ir 910 cm^{-1} (dithiane[29]); nmr δ 3.75 (d, J = 5 Hz), methine H.

2-Deuterio-2-isopropyl-1,3-dithiane.[29] The following is a representative run. In a 50-ml flask equipped with a nitrogen inlet and a dropping funnel was placed 2.0 g of 2-isopropyl-1,3-dithiane and 20 ml of dry tetrahydrofuran (THF). The flask was cooled in ice water and 10.0 ml of 1.6 M butyllithium in hexane (Foote Chemical Co.) was added dropwise. After the butyllithium was added the solution was allowed to stir for an additional 1.1 hr. At this time 2.0 ml of D_2O (99.8% D) was added. The solution was allowed to stir for an additional 20 min, the precipitate was filtered and washed with THF, and the combined filtrate and washings were dried over Na_2SO_4. After removal of the THF on a rotary evaporator and distillation of the residue there was obtained 1.10 g (55%) of product; bp 106–107° (1.75 mm). The nmr peak at δ 3.75 was absent indicating >98% deuteration.

Isobutyraldehyde-1-*d*.[29,30] In a 1000-ml flask equipped with an overhead stirrer, a dropping funnel, and a distillation head was placed 150 ml of water and 27.2 g (0.1 mol) of $HgCl_2$. The reaction mixture was warmed to effect solution and 9.67 g (0.059 mol) of 2-deuterio-2-isopropyl-1,3-dithiane was added dropwise. The reaction mixture was heated and 3.0 ml (0.02 mol, 33%) of labeled isobutyraldehyde was collected by distillation. The aldehyde was taken up in pentane and stored over Na_2SO_4.

3-Deuterio-4,4-dimethylcyclohex-3-enone. The title compound was prepared from the labeled aldehyde in the same way as previously published for 4,4-dimethylcyclohex-3-enone.[12] In this way there was obtained 1.60 g of product: bp 85–89° (25 mm); nmr, vinyl region, δ 5.8 (t, J = 1.2 Hz). The doublet at δ 6.7 in unlabeled 4,4-dimethylcyclohexenone was absent.

3-Deuterio-4,4-dimethylcyclohexadienone. This material was prepared as described earlier[12] for the unlabeled dienone by oxidation with 2,3-dichloro-5,6-dicyanobenzoquinone. The product was purified by glpc (10% diethylene glycol succinate, 100°): ir 1680, 2250 cm^{-1} (C–D); deuterium analysis, 0.98 D/molecule (Josef Nemeth, University of Illinois). The glpc-purified material was used for the kinetics.

4,4-Dimethylcyclohexadienone. This material was available from a previous study.[12] It was purified by glpc for the isotope effect studies.

Kinetics. A small volume (5–20 μl) of a solution (~0.1 M) of the dienone in water was introduced into a clean, dry cuvette. Three milliliters of previously equilibrated acid of the desired concentration was added to the cuvette and the absorbance[12] at either 260 or 295 nm monitored as a function of time in either a Cary-16 or Gilford-2400 spectrophotometer. The kinetic data in most cases were processed using a nonlinear regression analysis program written for the Wang 700 computer. In most cases the standard deviation of the rate constant was <2%. Product studies in both perchloric and sulfuric acids have been reported.[12]

The activation parameters were calculated in the usual way using a nonlinear regression analysis program written for the Wang 700.

Acid concentrations were determined by mixing carefully weighed amounts of standardized acid and distilled water or by titrating with standard base the actual kinetic solutions.

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[28] This suggestion rests on the assumption that the dependence of k_1 on water activity truly reflects the molecular composition of the transition state. This assumption, although common,[8–10] may not be justified in concentrated acid solutions.

[29] D. Seebach, B. W. Erickson, and G. Singh, *J. Org. Chem.*, **31**, 4034 (1966).

[30] An improved method for this hydrolysis has recently been published: E. Vadejs and P. L. Fuchs, *ibid.*, **36**, 366 (1971).