where $k_{00}{}^{H_2O} = k_{00}(H_2O)$ and K_W is the ionization constant of water. Using the measured pK's of fumaric acid,[2] the k_{hyd} data shown in Figure 1 were fitted by the method of least squares to obtain equations in the form of eq 2. The solid curves shown in Figure 1 were calculated from these equations. The values determined for the rate constants at 117.8° are $k_{00}{}^{H^+} = 7.85 \times 10^{-6}$ sec^{-1} M^{-1}, $k_{00}{}^{H_2O} = 1.09 \times 10^{-7}$ sec^{-1}, and $k_{00}{}^{OH^-} = 2.17 \times 10^2$ sec^{-1} M^{-1}. Also shown in Figure 1 are the rate constants at 117.8° for the individual reactions as a function of pH.

The rate constants determined in these investigations for the acid-catalyzed hydration reaction ($k_{00}{}^{H^+}$) are very similar to those determined by Rozelle and Alberty.[1] The ratio of the rate constants for the addition of hydroxide ion to neutral fumaric acid ($k_{00}{}^{OH^-}$) and the fumarate dianion[2] ($k_{--}{}^{OH^-}$) can be compared to $k_{00}{}^{NH_3}$ and $k_{--}{}^{NH_3}$ calculated for the amination reaction.[5] For both OH^- and NH_3, the rates of addition to fum^{00} are much greater than the rates of addition to fum^{--}. However, at 135° $k_{00}{}^{OH^-}/k_{--}{}^{OH^-} = 2.8 \times 10^7$ while $k_{00}{}^{NH_3}/k_{--}{}^{NH_3} = 2.7 \times 10^4$. This 10^3 difference can be explained as follows. The ratio $k_{00}{}^{OH^-}/k_{00}{}^{NH_3}$ gives the relative nucleophilicity of OH^- compared to NH_3. This ratio is 2.1×10^3 at 135.3°. However, $k_{--}{}^{OH^-}/k_{--}{}^{NH_3}$ at this temperature is only 1.9. The ratio $k_{--}{}^{OH^-}/k_{--}{}^{NH_3}$ is smaller than $k_{00}{}^{OH^-}/k_{00}{}^{NH_3}$ because of an electrostatic term in the free energy of activation for OH^- addition to fum^{--}. This electrostatic free energy, $\Delta F_{el}{}^{\ddagger}$, is the free energy required to bring together OH^- and fum^{--} from infinite separation. For OH^- addition to fum^{00} and NH_3 addition to both fum^{00} and fum^{--}, $\Delta F_{el}{}^{\ddagger}$ can be approximated as zero. This electrostatic free energy term can be written as

$$\begin{aligned}\Delta F_{el}{}^{\ddagger} &= (\Delta F_{--}{}^{\ddagger} - \Delta F_{00}{}^{\ddagger})_{OH^-\text{addn}} - \\ &\qquad (\Delta F_{--}{}^{\ddagger} - \Delta F_{00}{}^{\ddagger})_{NH_3\,\text{addn}} \\ &= RT \ln \{2.81 \times 10^7/2.73 \times 10^4\} = 5.6 \text{ kcal/mol}\end{aligned}$$

$\Delta F_{el}{}^{\ddagger}$ can be estimated theoretically from[8,9]

$$\Delta F_{el}{}^{\ddagger} = \frac{Z_{OH^-}Z_{fum^{--}}e^2N}{Dr_{\ddagger}}$$

Substituting $\Delta F_{el}{}^{\ddagger} = 5.6$ kcal/mol in this expression gives $Dr_{\ddagger} = 1.2 \times 10^{-6}$ cm. Using the value[10] $D = 45$ at 135° gives $r_{\ddagger} = 2.7$ Å which is of the expected magnitude. Therefore most of the 10^3 difference between $k_{00}{}^{OH^-}/k_{--}{}^{OH^-}$ and $k_{00}{}^{NH_3}/k_{--}{}^{NH_3}$ can be accounted for by the electrostatic free energy.

Although the term k_{0-}(fum^{0-})(H_2O) = $k_{0-}{}^{H_2O}$(fum^{0-}) is kinetically equivalent to $k_{00}{}^{OH^-}$(fum^{00})(OH^-), it does not appear in the rate expression given in eq 1. This can be accounted for on the following basis. The ratio of $k_{00}{}^{NH_3}/k_{0-}{}^{NH_3}$ at 135.3° is 5.75.[5] Assuming the same ratio for $k_{00}{}^{H_2O}/k_{0-}{}^{H_2O}$ gives an estimated value for $k_{0-}{}^{H_2O}$ at 135.3° of 4.5×10^{-8} sec^{-1}. At pH 4, this gives 3.2×10^{-8} sec^{-1} for the maximum rate of addition of H_2O to fum^{0-} at 135.3°. This is about 4% of the measured k_{hyd} at this pH. On the basis of these considerations, $k_{00}{}^{OH^-}$(fum^{00})(OH^-) appears to be the dominant term with only a small contribution from the kinetically equivalent term $k_{0-}{}^{H_2O}$(fum^{0-}).

These results cannot exclude the β-malolactonic acid mechanism. However, the addition of NH_3 to fum^{0-} has been shown to be nonstereoselective[5] which is inconsistent with the stereochemistry expected for the β-malolactonic acid mechanism.[11] It seems unlikely that there should be two different mechanisms for the amination and hydration of fumaric acid. The mechanism[5] for the amination of fumaric acid has been classified as AdN2, and a similar mechanism can be written for the hydration reaction. The relative rates of the amination and hydration of the various ionic forms of fumaric acid differ because of the different nucleophilicities of NH_3, OH^-, and H_2O and because of electrostatic effects.[12]

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(8) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley & Sons, Inc., New York, N. Y., 1961, p 144.

(9) The Z's are the respective charges on OH^- and fum^{--}, e the charge on an electron, N Avogadro's number, D the dielectric constant of the surrounding media, and $r_{\ddagger}$ the equilibrium distance between OH^- and fum^{--} in the activated complex.

(10) C. G. Malmberg and A. A. Maryott, *J. Res. Natl. Bur. Std.*, **56**, 1 (1956).

(11) The β-malolactonic acid mechanism proposed by Bender and Connors predicts stereoselective *cis* addition.[3]

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Jeffrey L. Bada, Stanley L. Miller
Department of Chemistry, University of California, San Diego
La Jolla, California 92037

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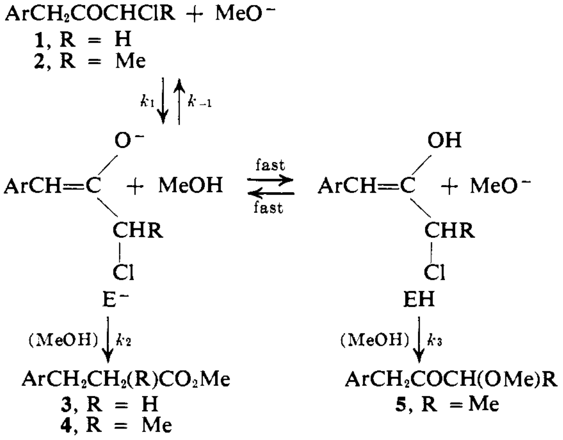
Mechanistic Change in the Favorskii Rearrangement on Methyl Substitution

Sir:

Recently it was demonstrated that in the ionization of X^- from the enolate ion ArCH=C(O$^-$)CH$_2$X the C—X bond developed a high degree of ionic character in the transition state ($\rho \cong -5$).[1] It follows that substitution of a methyl group for hydrogen, as in ArCH=C(O$^-$)CHXMe, should greatly facilitate this ionization.[2] This prediction has now been confirmed and, as a consequence of this rate change, a dramatic change in the mechanism and products formed under Favorskii rearrangement conditions has been observed (Table I).

The differences summarized in Table I can be accommodated by a common mechanistic scheme for **1** and **2** in which the presence of the methyl group plays a decisive role on the course of the reaction.



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(1) F. G. Bordwell, W. R. Springer, and R. G. Scamehorn, *J. Am. Chem. Soc.*, **91**, 2087 (1969).

(2) For *lim* solvolyses the rate acceleration brought about by methyl substitution is of the order of 10^6; see, *e.g.*, A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 74.

Table I. Effect of Methyl Substitution on the Reaction of $ArCH_2COCH_2X$ with Sodium Methoxide in Methanol

	$ArCH_2COCH_2X$ (**1**)	$ArCH_2COCHXMe$ (**2**)
Relative rates (X = Cl)[a]	1	>250[b]
Deuterium exchange,[c] %	~80	~5
k_{Br}/k_{Cl}	63	0.9
Hammett ρ	−5.0	+0.95
Product with		
2 *M* NaOMe	100% $ArCH_2CH_2CO_2Me$ (**3**)	100% $ArCH_2CH(Me)CO_2Me$ (**4**)
0.05 *M* NaOMe	100% **3**	**4** and $ArCH_2COCH(OMe)Me$ (**5**)
0.0001 *M* NaOMe[d]	100% **3**	100% **5**

[a] For chloride ion release. [b] This is a minimum value; a change in rate-determining step precludes an exact determination (see text). [c] Exchange prior to loss of chloride ion. [d] Addition of 0.05 *M* NaOMe over a 6-hr period to a solution of **1** or **2** in methanol.

For **1** formation of E^- is reversible (*i.e.*, $k_{-1} > k_2$), making k_2 rate determining, which explains the extensive deuterium exchange, large Br/Cl rate ratio, and large negative ρ. For **2** formation of E^- is irreversible because methyl substitution has increased the rate of enolate (and enol) solvolysis causing k_2 (and k_3) to become larger than k_{-1}.[3] Proton abstraction by methoxide ion is now rate determining, which explains the lack of deuterium exchange, the absence of a Br/Cl leaving group effect, and the positive ρ. For **1**, $k_2 \gg k_3$, and product **3** is formed at both high and low methoxide concentrations. For **2**, k_2 and k_3 are more nearly equal,[5] and formation of **5** occurs at low [MeO⁻] where the $E^- \rightleftarrows EH$ equilibrium is more favorable to the enol.[7]

According to the mechanistic scheme the relative yields of **4** and **5** depend on the concentrations of E^- and EH, *i.e.*, $[E^-]k_2/[EH]k_3 = \%\,\mathbf{4}/\%\,\mathbf{5}$. Since the ratio, $[E^-]/[EH]$, is directly proportional to the methoxide ion concentration, the mechanism predicts that the ratio, % **4**/% **5**, will increase linearly with increasing methoxide concentration. A plot of $[MeO^-]$ from 0.020 to 0.20 *M* *vs.* % **4**/% **5** was linear. The correlation coefficient was 0.994 for Ar = Ph and 0.998 for Ar = p-$MeOC_6H_4$.

Electron-donating substitutents (p-MeO, p-Me, p-F) in **2** caused the yield of methoxy ketone (**5**) produced with 0.05 *M* NaOMe to increase at the expense of the Favorskii ester (**4**); m-Cl and m-NO_2 substituents had the opposite effect. These changes are caused, according to the mechanistic scheme, by changes in the position of the enolate–enol equilibrium and changes in the relative values of k_2 and k_3. A plot of log (% **4**/% **5**) *vs.* σ was linear (correlation coefficient 0.956) with $\rho = 1.83$. This ρ value is reasonable for the enolate–enol equilibrium, which indicates that the ρ values for the reactions $E^- \rightarrow \mathbf{4}$ and $EH \rightarrow \mathbf{5}$ are similar in sign and magnitude. This is to be expected. For $E^- \rightarrow \mathbf{4}$, ρ should be *ca.* −5 by analogy with the $ArCH_2COCH_2Cl$ system. A value of this order of magnitude for the reaction $EH \rightarrow \mathbf{5}$ is expected by analogy with the value of −6.08 for the acid-catalyzed rearrangement of $ArCH(OH)CH{=}CH_2$ to $ArCH{=}CHCH_2OH$.[8]

Changing the solvent from methanol to 50% v/v H_2O–MeOH caused the rate of chloride ion release from **1** (Ar = Ph) to be accelerated 110-fold (0.05 *M* base), but there was no change in product composition.[1] On the other hand, the corresponding solvent change for **2** (Ar = Ph) caused only about a sixfold increase in rate, but the product composition was almost reversed. It changed from 61% **4** and 39% **5** to 32% **4** and 68% **5**. The mechanistic scheme predicts little change in rate for **2** on dilution of the methanol with water since the basicity of the medium is not changed greatly. To explain the change in product composition it is necessary to assume that k_3 is more sensitive to changes in the ionizing power of the solvent than is k_2. This is not unreasonable since in at least one instance solvolysis of halide ion from a negatively charged species has been found to show a remarkably low sensitivity to solvent ionizing power.[9]

An effect of methoxide ion concentration on product distribution similar to that observed with **2** has been found previously with $PhCH_2COCHClPh$[10a] and with 6-tosyloxyisophorone.[10b] The results were interpreted in terms of a dipolar ion intermediate which reacted with methoxide ion to give Favorskii ester and with methanol to give methoxy ketone.[10,11] It is difficult to accommodate the present results with this mechanism. Furthermore, our mechanistic scheme has stood up to numerous additional experimental tests, the results of which are difficult, if not impossible, to explain on the basis of the dipolar ion mechanism.[12,13]

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[3] Methyl substitution at the α position causes a rate acceleration of 1.3×10^3 in the ethanolysis of $CH_3CH{=}CHCH_2Cl$.[4]

[4] R. H. deWolfe and W. G. Young, *Chem. Rev.*, **56**, 786 (1956).

[5] We are assuming that the accelerating effect of methyl substitution is less in the methanolysis of E^- than of EH. A possible analogy here is that the t-BuBr/i-PrBr methanolysis rate ratio is *ca.* 10^4, whereas the $Me_2CBrCO_2^-/MeCHBrCO_2^-$ methanolysis rate ratio is only *ca.* 2.[6]

[6] E. Grunwald and S. Winstein, *J. Am. Chem. Soc.*, 70, 841 (1948).

[7] A possible model for the effect of charge on the methanolysis rate may be obtained from the $PhCHBrCO_2^-/PhCHBrCO_2H$ hydrolysis rate ratio of 14/1 observed by S. Widequist, *Arkiv Kemi*, **19**, 551 (1962).

[8] H. H. Jaffé, *Chem. Rev.*, 53, 204 (1953).

[9] The Winstein-Grunwald m values for the solvolysis of $PhCHBrCO_2^-$ and $PhCHBrCH_2CO_2^-$ are each about 0.2 in aqueous ethanol: A. C. Knipe, unpublished results. On the other hand the m values for $CH_3CH{=}CHCH_2Cl$ and $H_2C{=}CHCHClCH_3$ are 0.655 and 0.875 in this solvent system (ref 4, p 790).

[10] (a) A. W. Fort, *J. Am. Chem. Soc.*, 84, 2620 (1962); (b) A. W. Fort, *ibid.*, 84, 2625 (1962).

[11] See also R. C. Cookson, M. J. Nye, and G. Subrahmanyan, *J. Chem. Soc., C*, 473 (1967).

[12] F. G. Bordwell and M. W. Carlson, *J. Am. Chem. Soc.*, **91**, 3951 (1969).

[13] Methanolysis of an enol allylic chloride was considered previously as a possible route to the conversion of $PhCH_2COCHClPh$ to $PhCH_2COCH(OMe)Ph$ at low methoxide concentrations, but was rejected.[10a] In the complete paper it will be shown that the grounds for its rejection are invalid.

F. G. Bordwell, Merle W. Carlson, A. C. Knipe
Department of Chemistry, Northwestern University
Evanston, Illinois 60201

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