A flash photolytic investigation of the photosolvolysis of α-(2,6-dimethoxyphenyl)vinyl chloride. Characterization of the 2,6-dimethoxyacetophenone keto–enol system

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Photosolvolysis of α-(2,6-dimethoxyphenyl)vinyl chloride in trifluoroethanol solution at 25°C was found to produce the α-(2,6-dimethoxyphenyl)vinyl cation as a transient species with the lifetime $\tau = 1$ μs. Addition of water reduced this lifetime markedly, until, at compositions greater than 80% water, it was too short to measure ($\tau < 20$ ns); extrapolation of the data suggests $\tau = 9$ ns in pure water. Hydration of this cation gave the much longer lived enol of 2,6-dimethoxyacetophenone, whose rates of ketonization were measured in dilute perchloric acid and sodium hydroxide solutions. These data, when combined with rates of enolization of the ketone determined by iodine scavenging, give $\mathrm{p}K_{\mathrm{E}} = 6.98$ for the keto–enol equilibrium constant in the 2,6-dimethoxyacetophenone system, $\mathrm{p}K_a^{\mathrm{E}} = 10.72$ for the acidity constant of the enol ionizing as an oxygen acid, and $\mathrm{p}K_a^{\mathrm{K}} = 17.70$ for the acidity constant of the ketone ionizing as a carbon acid; these constants refer to wholly aqueous solution at 25°C and ionic strength = 0.10 M.

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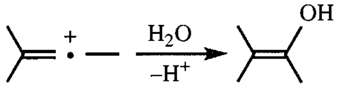
On a trouvé que la photosolvolyse du chlorure de α-(2,6-diméthoxyphényl)vinyle en solution dans le trifluoroéthanol, à 25°C, conduit au cation α-(2,6-diméthoxyphényl)vinyle comme espèce transitoire dont le temps de vie, $\tau = 1$ μS. L'addition d'eau au milieu réactionnel réduit ce temps de vie d'une façon importante jusqu'à des compositions en eau supérieures à 80% alors que les temps de vie deviennent trop courts pour être mesurés ($\tau < 20$ ns); l'extrapolation des données suggère que $\tau = 9$ ns dans l'eau pure. L'hydratation de ce cation conduit à l'énol de la 2,6-diméthoxyacétophénone dont la longueur de vie est beaucoup plus longue et dont on a mesuré les vitesses de cétonisation dans des solutions diluées d'acide perchlorique et d'hydroxyde de sodium. Lorsqu'on combine ces données avec les vitesses d'énolisation de la cétone telles que déterminées par piégeage d'iode, elles fournissent des valeurs de $\mathrm{p}K_{\mathrm{E}} = 6{,}98$ pour la constante d'équilibre céto–énolique du système 2,6-diméthoxyacétophénone, de $\mathrm{p}K_a^{\mathrm{E}} = 10{,}72$ pour la constante d'acidité de l'énol s'ionisant sous la forme d'une oxyacide et de $\mathrm{p}K_a^{\mathrm{K}} = 17{,}70$ pour la constante d'acidité de la cétone s'ionisant sous la forme d'une acide carboné; ces constantes se réfèrent à des solutions entièrement aqueuses, à 25°C et à une force ionique de 0.10 M.

[Traduit par la rédaction]

Vinyl cations have been observed as short-lived transient species formed by flash photolytic photosolvolysis of vinyl halides or photohydration of acetylenes in organic solvents such as acetonitrile (1, 2), acetic acid (2), and trifluoroethanol (3). There is evidence that they are formed by these reactions in aqueous solution as well, for their enol hydration products, eq. [1], have been observed as transients in this medium; the ions themselves, however, have not been seen in this solvent, presumably because none of the systems examined so far give vinyl cations with sufficiently long lifetimes to allow detection by the methods that have been employed.



We have investigated the flash photolysis of α-(2,6-dimethoxyphenyl)vinyl chloride, **1**, in the hope that the stabilizing effect of the two *ortho* methoxyl groups in the vinyl cation formed from this substrate, **2**, eq. [2], coupled with the steric hindrance that these groups might provide to attack of water at the cationic center, would be sufficient to permit observation of this ion in wholly aqueous solution. This hope, unfortunately, was not realized: we were able to see this ion in trifluoroethanol solution and also in trifluoroethanol–water mixtures up to a water content of 80%; above this point, however, the lifetime of the ion became less than 20 ns, which is the limit of detection of our system.

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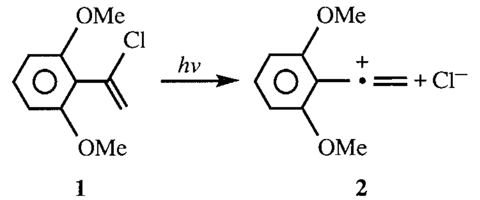

1 **2**

Although we did not see this ion in wholly aqueous solution, we could observe its enol hydration product, **3**, in this medium. We therefore studied the ketonization of this enol, eq. [3], and the results we obtained, in combination with information on enolization of the corresponding ketone, 2,6-dimethoxyacetophenone, **4**, have allowed us to characterize this keto–enol system. These results are of special interest

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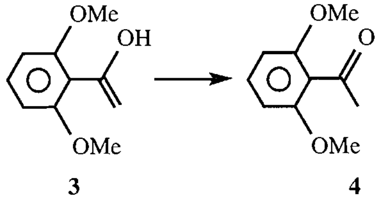
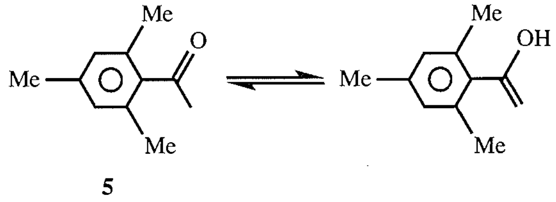


in connection with corresponding information on the 2,4,6-trimethylacetophenone, **5**, keto–enol system, eq. [4] (4*b*), and also on the hydrolysis of methyl α-(2,6-dimethoxyphenyl)vinyl ether, (**6**), eq. [5] (5).

[4]



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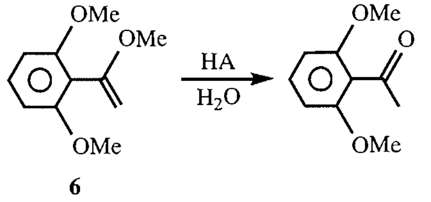

Experimental section

Materials

α-(2,6-Dimethoxyphenyl)vinyl chloride was prepared by treating 2,6-dimethoxyacetophenone with phosphorus pentachloride under conditions that prevent chlorination of the benzene ring (6). All other materials were best available commercial grades and were used as received.

Kinetics

Flash photolysis was performed using a conventional flash lamp system for the slower reactions and a laser system for the faster ones. Details of the conventional system have already been published (7). The laser system used a Lumonics Ex-510 excimer laser operating at λ = 248 nm for excitation and a pulsed Oriel model 66002 Xenon-arc lamp as monitoring light source. The monitoring light, after leaving the sample, was passed through an Oriel model 77250 monochrometer and onto a Hamamatsu 1P28 photomultiplier whose output was fed into a Tektronix model SCD1000 transient digitizer. Data analysis was performed with a Tektronix PEP 301 computer using Enzfitter software (Elsevier-BIOSOFT) for fitting to exponential functions. Reaction mixtures were contained in quartz cuvettes placed in a brass holder whose temperature was controlled at 25.0 ± 0.1°C by water circulating from a constant temperature bath.

Rates of enolization of 2,6-dimethoxyacetophenone were determined by iodine scavenging in the presence of iodide ion using the absorbance of I_3^- to monitor the reaction. Absorbance measurements were made with a Cary model 118C spectrometer whose cell compartment was thermostatted at 25.0 ± 0.1°C. Iodine concentrations in the reaction mixtures were 3×10^{-5} M; iodide ion concentrations, 7×10^{-4} M; and 2,6-dimethoxyacetophenone concentrations, 7×10^{-4} M. Reactions were followed to about 1% completion and zero-order rates of change of absorbance with time, $\Delta A/\Delta t$, were converted into observed first-order rate constants, k_{obs}, according to eq. [6]. In this expression K_{I_3} (= 1.5×10^{-3} M) (8) is the equilibrium constant for dissociation of I_3^- into I_2 and I^-, ϵ_{351} (= 2.6×10^4 M^{-1} cm^{-1}) (8) is the extinction coefficient of I_3^- at λ = 351 nm, the wavelength at which the measurements were made, and [S] is the concentration of 2,6-dimethoxyacetophenone.

$$[6] \quad k_{obs} = (\Delta A/\Delta t)(1 + K_{I_3}/[I_3^-])/\epsilon_{351}[S]$$

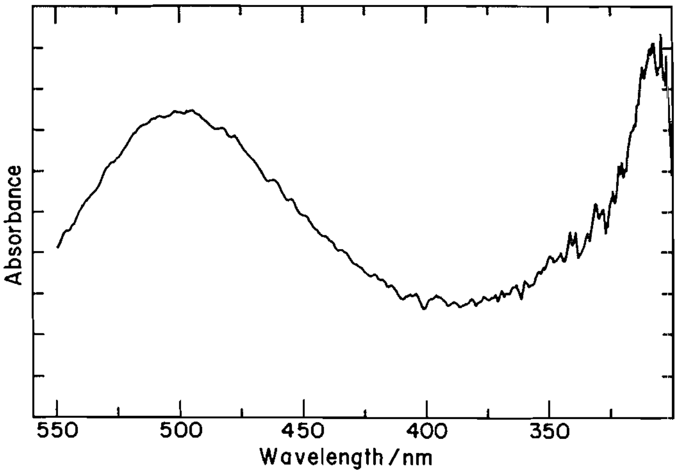

FIG. 1. Absorption spectrum of the shorter lived of the two transients produced upon flash photolysis of α-(2,6-dimethoxyphenyl)vinyl chloride in trifluoroethanol solution.

Results

The UV spectrum of α-(2,6-dimethoxyphenyl)vinyl chloride dissolved in water consists of an absorption maximum at λ = 280 nm, plus strong end absorption at low wavelengths with a shoulder at λ = 240 nm. Upon irradiation of an aqueous solution with a few pulses from our conventional flash photolysis apparatus, these spectral features move to lower wavelengths and give a spectrum similar to that of an authentic sample of 2,6-dimethoxyacetophenone, with λ_{max} = 265 nm and a shoulder at λ = 220 nm. This shows that photolysis of α-(2,6-dimethoxyphenyl)vinyl chloride in aqueous solution gives 2,6-dimethoxyacetophenone as an ultimate reaction product. Flash photolytic examination of this transformation shows that it occurs via short-lived vinyl cation and enol intermediates.

Vinyl cation

Flash photolysis of α-(2,6-dimethoxyphenyl)vinyl chloride dissolved in trifluoroethanol produces a transient species with absorption maxima at λ = 300 and 500 nm (Fig. 1) and a lifetime of τ ≅ 1 μs. Degassing the solution has no effect on this lifetime, but addition of chloride ion or water shortens it markedly. This behavior indicates that this transient is the α-(2,6-dimethoxyphenyl)vinyl cation, **2**, formed as expected according to eq. [2]. In the absence of added reagents, the lifetime of this ion is governed by its reaction with the solvent to give the corresponding trifluoroethyl vinyl ether, and also by its reaction with chloride ion produced by the photoionization to regenerate the starting material. Addition of chloride ion to the photolysis solution speeds up the latter reaction, shortening the lifetime of the vinyl cation. Water has a similar lifetime-shortening effect through its reaction with the cation to give enol according to eq. [1].

Decay of this transient absorbance attributed to the vinyl

TABLE 1. Rates of reaction of the α-(2,6-dimethoxyphenyl)vinyl cation in trifluoroethanol–water mixtures at 25°C[a]

% Trifluoroethanol	$k/10^6\ s^{-1}$
100	1.18,[b] 1.58
100[c]	1.18
100[d]	3.31
80	5.83
60	9.33
40	15.7
20	49.8

[a] Monitored at λ = 500 nm unless otherwise indicated.

[b] Monitored at λ = 340 nm.

[c] Solution degassed.

[d] With 0.004 M NaCl.

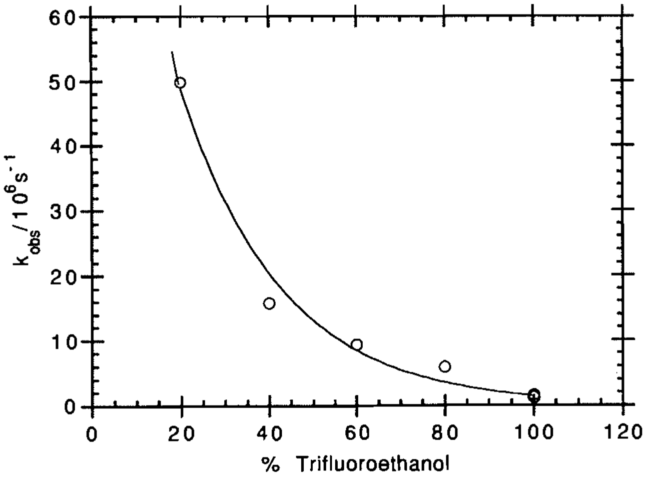

FIG. 2. Relationship between solvent composition and rates of decay of the α-(2,6-dimethoxyphenyl)vinyl cation in trifluoroethanol–water mixtures.

cation conformed to the first-order rate law, and first-order rate constants were determined in trifluoroethanol–water mixtures of increasing water content. The data are summarized in Table 1 and are displayed in Fig. 2. It may be seen that the rate of reaction increases markedly with water content, especially in the more water-rich mixtures, suggesting an exponential dependence of rate upon water content. As Fig. 3 shows, there is a reasonably good linear relationship between the logarithms of observed rate constants and percent trifluoroethanol, $\log(k_{obs}/s^{-1}) = 8.07 - 0.0190$ (% TFE), which allows extrapolation to a wholly aqueous solvent. The result of this extrapolation, $k_{obs} = (1.2 \pm 0.3) \times 10^8\ s^{-1}$, gives $\tau = 9$ ns as the lifetime of the α-(2,6-dimethoxyphenyl)vinyl cation in aqueous solution. This is shorter, by about a factor of two, than the shortest excitation pulse available from our flash photolysis apparatus, and that renders this ion unobservable in wholly aqueous solution with our equipment.

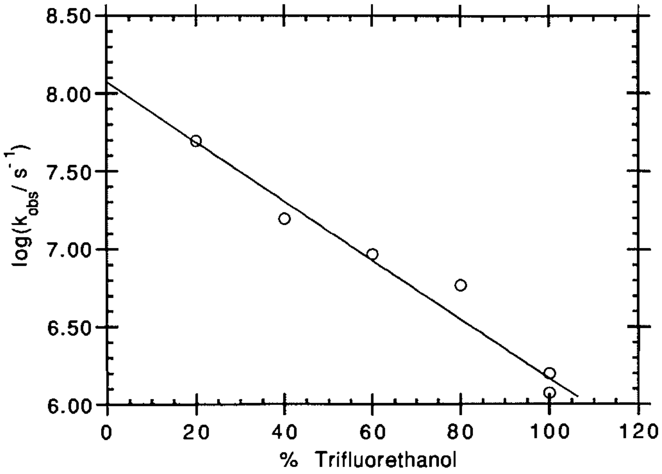

FIG. 3. Logarithmic relationship between solvent composition and rates of decay of the α-(2,6-dimethoxyphenyl)vinyl cation in trifluoroethanol–water mixtures.

The relationship of Fig. 3 gives $k = (1.5 \pm 0.2) \times 10^6\ s^{-1}$ as the rate constant for decay of the present vinyl cation in 100% trifluoroethanol solution; this is similar to $k = 1.3 \times 10^6\ s^{-1}$ reported for reaction of the α-(*p*-methoxyphenyl)-vinyl cation in the same solvent (3).

Enol

This very rapid reaction of the α-(2,6-dimethoxyphenyl)-vinyl cation in wholly aqueous solution appeared as an instantaneous rise in absorbance at lower wavelengths, in the vicinity of λ = 300 nm, where the enol is expected to absorb. This rise, which took place within the excitation pulse, was then followed by an additional further increase in absorbance as the enol was converted to the still more strongly absorbing ketone. This latter absorbance change is similar to that observed in the hydrolysis of the vinyl ether analog of this enol, ethyl α-(2,6-dimethoxyphenyl)vinyl ether, (5) **6**, which gives the same ketone as its reaction product (eq. [5]).

Rates of ketonization of the enol were measured in dilute perchloric acid and sodium hydroxide solutions; these data are summarized in Tables 2 and 3. As Fig. 4 shows, observed first-order rate constants determined in perchloric acid solutions proved to be accurately proportional to acid concentration. This is the behavior expected for enol ketonization; it represents rate-determining protonation of the enol on its β-carbon atom followed by rapid removal of the oxygen-bound proton of the ketone conjugate acid thus formed, eq. [7] (9). Linear least-squares analysis of the data gave $k^{K}_{H^+} = 120\ M^{-1}\ s^{-1}$ as the hydronium-ion catalytic coefficient for this ketonization reaction.

Ketonization was also catalyzed by sodium hydroxide but, as Fig. 5 demonstrates, observed first-order rate constants

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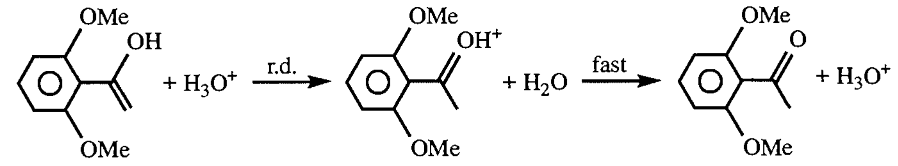


TABLE 2. Rates of ketonization of 2,6-dimethoxyacetophenone enol in aqueous perchloric acid solutions at 25°C[a]

$[HClO_4]/10^{-2}$ M	k_{obs}/s^{-1}
10.0	13.2, 13.3, 12.9
8.00	11.2, 10.7, 11.1, 11.2
5.00	7.01, 7.33, 6.93, 7.15
3.00	4.22, 5.17, 4.67, 5.05
1.00	2.57, 2.26, 2.48, 2.65

$k_{obs}/s^{-1} = 1.22 \pm 0.12 + (120 \pm 2)[HClO_4]$

[a] Ionic strength = 0.10 M.

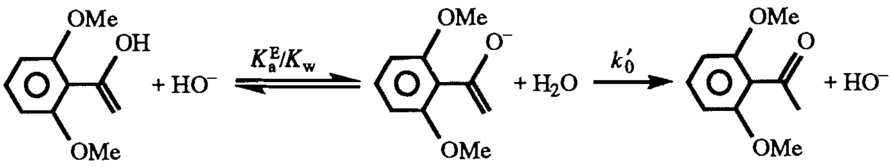
TABLE 3. Rates of ketonization of 2,6-dimethoxyacetophenone enol in aqueous sodium hydroxide solutions at 25°C[a]

$[NaOH]10^{-3}$ M	$k_{obs}/10^2 s^{-1}$
10.0	28.7, 30.2, 26.9
2.00	24.9, 25.4
1.00	19.3, 18.9, 17.2
0.600	13.1, 13.0, 13.6
0.400	9.78, 10.5, 9.07
0.200	5.25, 4.35. 3.79

$k_{obs} = k_0' \mathrm{K}_a^E[HO^-]/(K_a^E[HO^-] + 1.59 \times 10^{-14})^b$
$k_0' = (3.21 \pm 0.11) \times 10^3 s^{-1}$
$K_a^E = (1.91 \pm 0.19) \times 10^{-11}$ M
$pK_a^E = 10.72 \pm 0.04$

[a] Ionic strength = 0.10 M.
[b] See eq. [9]; $1.59 \times 10^{-14} = K_w/f_{H^+}f_{HO^-}$ using values of the activity coefficients $f_H{}^+$ and $f_{HO}{}^-$ for ionic strength = 0.10 M recommended by Bates (10).

were proportional to hydroxide-ion concentration only at low basicity; at progressively higher basicities this proportionality gave way to saturation of catalysis, and rate constants approached a constant value. This again is as expected for enol ketonization; it represents reaction through the much more reactive enolate ion under conditions where the initial state shifts from enol at low basicity to enolate at high basicity, as shown in eq. [8] (9). The rate law that applies in this situation is given as eq. [9], in which k_0' is the rate constant for carbon protonation of the enolate ion by water, K_a^E is the acidity constant of the enol, and K_W is the autoprotolysis constant of water. Nonlinear least-squares fitting of the data to this expression gave $k_0' = 3.21 \times 10^2$ s^{-1} and $K_a^E = 1.91 \times 10^{-11}$, $pK_a^E = 10.72$; the latter is a concentration dissociation constant that applies at the ionic strength of the measurements (0.10 M).

[8] 

[9] $k_{obs} = k_0'K_a^E[HO^-]/(K_a^E[HO^-] + K_W)$

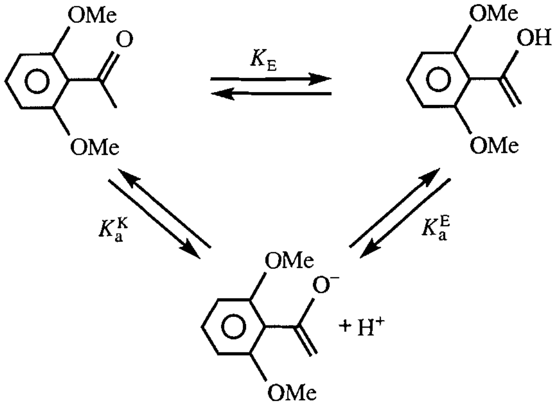
Enolization

Rates of enolization of 2,6-dimethoxyacetophenone were measured in dilute perchloric acid solutions; the data are summarized in Table 4. Observed first-order rate constants proved to be proportional to acid concentration, as expected for enolization of a ketone (9), and linear least-squares analysis of the data gave $k_{H^+}^E = 1.26 \times 10^{-5}$ M^{-1} s^{-1} as the hydronium-ion catalytic coefficient for this enolization reaction.

Discussion

The amount of enol tautomer in equilibrium with a simple ketone, such as 2,6-dimethoxyacetophenone, in aqueous solution is generally very small, and it is consequently often difficult to evaluate keto–enol equilibrium constants in such systems by direct determination of enol concentration. An equilibrium constant, however, can also be evaluated as the ratio of rate constants for the reaction in the forward and reverse directions, and the hydronium-ion catalytic coefficients determined here for the enolization of 2,6-dimethoxyacetophenone and ketonization of its enol may therefore be used to determine the keto–enol equilibrium constant for this system: $K_E = k_{H^+}^E/k_{H^+}^K = (1.05 \pm 0.06) \times 10^{-7}$, $pK_E = 6.98 \pm 0.02$.

This enolization reaction plus the acid dissociation of the enol, whose equilibrium constant was determined here by the ketonization rate measurements in sodium hydroxide solutions, form two legs of a thermodynamic cycle whose third member is ionization of the ketone as a carbon acid, eq. [10]. The equilibrium constant for this carbon acid ionization,

[10] 

K_a^K, may therefore be evaluated as the product of the equilibrium constants for the other two reactions: $K_a^K = K_E K_a^E = (2.00 \pm 0.23) \times 10^{-18}$, $pK_a^K = 17.70 \pm 0.05$.

It is interesting that this equilibrium constant, as well as those for the other two reactions of the scheme shown in eq. [10], are quite similar to the corresponding values for

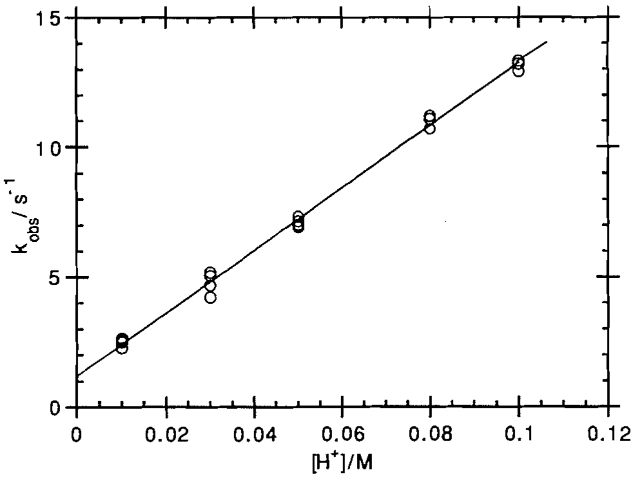


FIG. 4. Relationship between perchloric acid concentration and rates of ketonization of 2,6-dimethoxyacetophenone enol in aqueous solution at 25°C.

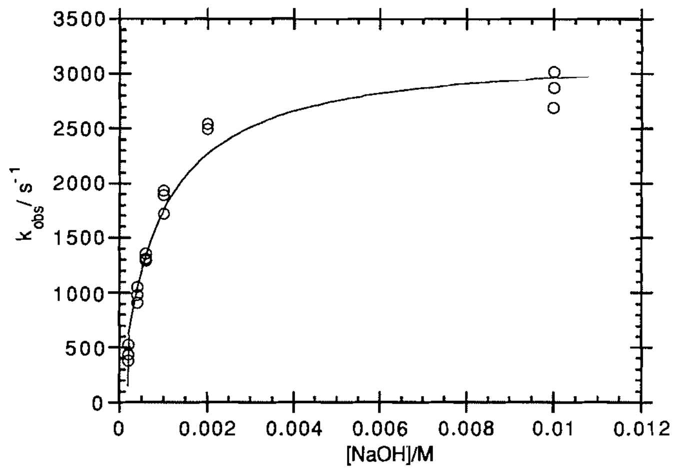


FIG. 5. Relationship between sodium hydroxide concentration and rates of ketonization of 2,6-dimethoxyacetophenone enol in aqueous solution at 25°C.

TABLE 4. Rates of enolization of 2,6-dimethoxyacetophenone in aqueous perchloric acid solutions at 25°C[a]

$[HClO_4]/10^{-2}$ M	$k_{obs}/10^{-7}$ s^{-1}
10.5	14.0, 15.5, 14.9, 14.9, 12.3
8.36	9.43, 11.8, 10.5, 10.5, 11.0, 11.4
6.27	9.08, 8.51, 8.54, 7.30, 7.43
4.18	7.75, 7.67, 7.22, 5.38, 5.81
2.09	3.86, 3.53, 2.72, 2.36, 2.88

$$k_{obs}/s^{-1} = (6.99 \pm 4.76) \times 10^{-8} + (1.26 \pm 0.07) \times 10^{-5} [HClO_4]$$

[a] Ionic strength = 0.10 M.

the 2,4,6-trimethylacetophenone (**5**) keto–enol system: the numbers, listed in Table 5, show hardly any differences at all. There are, on the other hand, significant differences between these two ketones and the parent, unsubstituted acetophenone, values for whose reactions are also listed in Table 5.

The largest difference occurs in the pK_E values: the keto–enol equilibrium constants for the substituted ketones are an order of magnitude greater than that for acetophenone. This difference may be understood by making a further comparison with acetaldehyde, which has no aromatic substituent and for which $pK_E = 6.23$ (7). There is thus a marked decrease in keto–enol equilibrium constant upon introduction of a phenyl substituent; this can be attributed to a difference in stabilization of the keto and enol forms produced by conjugation with the phenyl group. Conjugation of phenyl with the carbonyl group of the keto isomer is strong because the carbonyl carbon atom bears a partial positive charge, whereas conjugation with the neutral double bond of the enol is considerably weaker. The keto isomer is thus stabilized relative to the enol form, and the keto–enol equilibrium constant is decreased. *Ortho* substituents, such as those in 2,6-dimethoxyacetophenone and 2,4,6-trimethylacetophenone, inhibit this conjugation and shift the equilibrium constant back toward that of the acetaldehyde system.

It is significant that most of this increase in keto–enol equilibrium constant upon introduction of *ortho* substituents appears as a decrease in the rate of ketonization and that rates of enolization are hardly affected: the data of Table 5 show $k_{H^+}^{K}$ values for 2,6-dimethoxyacetophenone and 2,4,6-trimethylacetophenone that are an order of magnitude less than those for acetophenone but $k_{H^+}^{E}$ values that are virtually the same. This is consistent with little conjugative effect on the stability of the enol isomer and a stronger effect on both the keto isomer and the transition state of the reaction. The effect on the transition state and the keto isomer might, in fact, be expected to be of similar strength because both species have partial positive charges in positions where charge can be delocalized into the phenyl group; this similarity of conjugative effect on ketone and transition state is attested to by the fact that a Yukawa–Tsuno correlation of rates of acid-catalyzed enolization of ring-substituted acetophenones gives a resonance ρ value that is vanishingly small (12).

There are also differences in pK_a^E and pK_a^K values between acetophenone and *ortho*-substituted derivatives, but these are smaller than the differences in pK_E. The slightly weaker acidity of the enols of 2,6-dimethoxyacetophenone and 2,4,6-trimethylacetophenone may be attributed to the electron-supplying nature of their methoxyl and methyl groups, which will tend to destabilize the enolate ions. This effect, however, is overwhelmed in the carbon acid ionization of the ketones, for here 2,6-dimethoxyacetophenone and 2,4,6-trimethylacetophenone are stronger acids than acetophenone. This inversion of relative acidity can be ascribed to the conjugative effects discussed above, which destabilize the substituted ketones relative to the parent acetophenone.

The acid-catalyzed ketonization of enols bears a close mechanistic resemblance to the acid-catalyzed hydrolysis of vinyl ethers: both reactions occur by rate-determining proton transfer from the catalysts to the β-carbon atom of the substrate, and mechanistic differences occur only after this step (9, 13). The effects of structure on reactivity for the two reactions might therefore be expected to be similar, and this, in fact, is the case: hydronium-ion catalytic coefficients for enol ketonization have been found to parallel those for methyl vinyl ether hydrolysis over a wide range of structural vari-

Table 5. Comparison of related keto–enol systems[a]

Parameter	2,6-Dimethoxy-acetophenone	2,4,6-Trimethyl-acetophenone[b]	Acetophenone[c]
pK_E	6.98	6.92	7.96
pK_a^E	10.72	10.69	10.34
pK_a^K	17.70	17.61	18.31
$k_{H^+}^E/10^{-5}\ M^{-1}\ s^{-1}$	1.26	1.30	1.21
$k_{H^+}^K/10^3\ M^{-1}\ s^{-1}$	0.120	0.109	1.25

[a] Ionic strength = 0.10 M; equilibrium constants are concentration quotients at this ionic strength.

[b] Reference 4*b*.

[c] Reference 11.

ation spanning five orders of magnitude in reactivity, with the ketonisation reactions consistently 10–100 times faster than the hydrolyses (9). A comparison of the two reactions can be made for the present system, for the hydronium-ion catalytic coefficient has recently been measured for the hydrolysis of methyl α-(2,6-dimethoxyphenyl)vinyl ether, **6** (5). This comparison shows the present enol to be 42 times more reactive than the vinyl ether, which is nicely consistent with previous experience.

Acknowledgement

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