54.1, 35.3, 33.8, 32.6, 28.7, 21.5, 19.9, 17.7, 16.6, 12.5 ppm; UV $\lambda_{max}C_2H_5OH$ 220 nm (ϵ 7539); mass spectrum, m/z (M^+) calcd 201.1153, obsd 201.1140.

Anal. Calcd for $C_{13}H_{15}NO$: C, 77.58; H, 7.51. Found: C, 77.31; H, 7.55.

Hydrolysis of 17a. To a magnetically stirred solution of **17a** (16 mg, 0.054 mmol) in ether (2 mL) at room temperature was added a solution of triethylamine (0.02 mL, 0.14 mmol) in methanol. The reaction mixture was stirred for 1 h, the volatiles were evaporated, and the residue was passed through a small column of silica gel (elution with ethyl acetate) to give **17b** as a white solid (9 mg, 82%): IR (CDCl₃, cm⁻¹) 3420, 3200, 2950, 1680; ¹H NMR (300 MHz, CDCl₃) δ 6.19 (br, 1 H), 6.15 (dd, J = 9.8, 5.1 Hz, 1 H), 4.78 (d, J = 9.8 Hz, 1 H), 1.98 (m, 1 H), 1.75 (d, J = 8.8 Hz, 1 H), 1.71-1.30 (series of m, 9 H), 1.04 (ddd,

J = 8.4, 8.4, 4.8 Hz, 1 H), 0.50 (ddd, J = 6.0, 4.8, 4.8 Hz, 1 H); ¹³C NMR (75 MHz, CDCl₃) 174.3, 129.3, 123.3, 54.1, 33.1, 31.9, 26.7, 23.7, 18.0, 17.5, 16.8, 14.0 ppm; mass spectrum, m/z (M^+) calcd 201.1154, obsd 201.1150.

Supplementary Material Available: Tables of bond distances and angles, final fractional coordinates, thermal parameters, and least-squares planes for **12** and **17a** (10 pages). Ordering information is given on any current masthead page.

Diphenylacetaldehyde and Its Enol: Determination of the Keto–Enol and Hydration Equilibrium Constants and the pK_a's of the Aldehyde, Enol, and Hydrate. Comparison with Sterically Hindered Systems

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Abstract: The enol isomer of diphenylacetaldehyde was generated in aqueous solution from its potassium salt, formed by treating the aldehyde with potassium hydride, and rates of ketonization of this enol were measured at 25 °C in perchloric acid and sodium hydroxide solutions and acetic acid and bicarbonate ion buffers. These data, coupled with rates of enolization of the aldehyde measured at 25 °C in acetic acid buffer and sodium hydroxide solutions, lead to duplicate independent determinations of the keto–enol equilibrium constant, K_E = (1.04 ± 0.10) × 10⁻¹, pK_E = 0.98 ± 0.04, the acid dissociation constant of the enol ionizing as an oxygen acid, K_a^E = (4.03 ± 0.11) × 10⁻¹⁰ M, pK_a^E = 9.40 ± 0.01, and the acid dissociation constant of the aldehyde ionizing as a carbon acid, K_a^K = (3.80 ± 0.12) × 10⁻¹¹ M, pK_a^K = 10.42 ± 0.02. The equilibrium constant for formation of the aldehyde hydrate, K_h = 4.7 ± 0.2, was also determined by two independent methods, and the acid dissociation constant of the hydrate ionizing as an oxygen acid, K_a^h = (7.1 ± 0.4) × 10⁻¹⁴ M, pK_a^h = 13.15 ± 0.02, was evaluated from kinetic data. The unusually large values of K_E and pK_a^K for this system are attributed to stabilization of the carbon–carbon double bonds of the enol and enolate ion by the phenyl substituents. Comparison with literature data on sterically hindered, stable, "Fuson" enols bearing mesityl substituents suggests that a substantial portion of the thermodynamic stability of Fuson enols is provided by similar phenyl group stabilization of their double bonds; the methyls of the mesityl substituents of Fuson enols, however, do appear to play a critical role in conferring kinetic stability upon these substances.

The enol isomers of simple monofunctional aldehydes and ketones are generally quite unstable and revert to their carbonyl tautomers rapidly. A notable exception to this behavior is provided by a group of crowded enols studied by Fuson in a classic series of investigations some 40 years ago.[1] Fuson's enols have bulky aryl substituents, such as mesityl or duryl, attached to their carbon–carbon double bonds. They are stable substances that can be isolated, and, if the crowding is sufficiently severe, they resist conversion to their keto isomers strongly. Keto–enol equilibrium constants for some of these crowded systems have been determined only recently,[2] and these new studies have shown that these enols are stable, not only because the barriers for their keto–enol interconversions are high but also because the enols themselves have unusual thermodynamic stability.

It would be of interest to compare the behavior of these crowded enols with that of enols containing unsubstituted phenyl groups on their carbon–carbon double bonds. We report here the beginning of such a study using the diphenylacetaldehyde keto–enol

system (eq 1). We have measured rates of enolization of the

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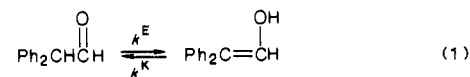
aldehyde, k^E, as well as ketonization of the enol, k^K, with the latter substrate generated from its potassium salt (eq 2); this has provided

(2)
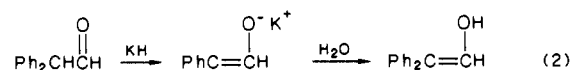
the keto–enol equilibrium constant for the system as the ratio of specific rate constants for these two reactions: K_E = k^E/k^K. Analysis of the rate data obtained in basic solutions has also given the acid dissociation constant of the enol ionizing as an oxygen acid, K_a^E (eq 3), as well as that of the aldehyde ionizing as a carbon

(3)
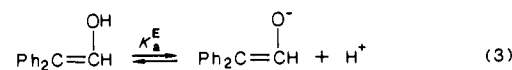
acid, K_a^K (eq 4). Diphenylacetaldehyde is extensively hydrated
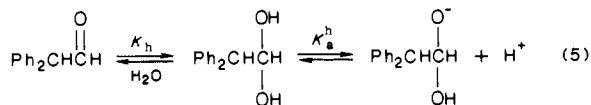

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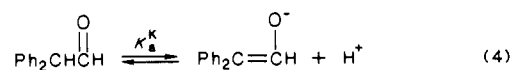
in aqueous solution, and we have therefore also determined the

(1) For a recent summary of this work, see: Hart, H. *Chem. Rev.* **1979**, *79*, 515-528.

(2) (a) Miller, A. R. *J. Org. Chem.* **1976**, *41*, 3599-3602. (b) Biali, S.; Rappoport, Z. *J. Am. Chem. Soc.* **1985**, *107*, 1007-1015. Nugiel, D. A.; Rappoport, Z. *J. Am. Chem. Soc.* **1985**, *107*, 3669-3676. (c) Nadler, E. B.; Rappoport, Z. *J. Am. Chem. Soc.* **1987**, *109*, 2112-2127.

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hydration equilibrium constant, K_h, and the acid dissociation constant of the hydrate, K_a^h (eq 5).

$$\underset{\underset{H_2O}{\overset{K_h}{\rightleftharpoons}}}{\overset{\overset{O}{\overset{\|}{}}}{Ph_2CHCH}} \qquad \underset{\underset{OH}{\overset{OH}{|}}}{\overset{\overset{OH}{\overset{|}{}}}{Ph_2CHCH}} \overset{K_a^h}{\rightleftharpoons} \underset{\underset{OH}{\overset{O^-}{|}}}{\overset{\overset{O^-}{\overset{|}{}}}{Ph_2CHCH}} + H^+ \qquad (5)$$

Experimental Section

Materials. Diphenylacetaldehyde enol was made from its potassium enolate,[3] which was prepared by treating diphenylacetaldehyde with potassium hydride in tetrahydrofuran solution.[4] Enolate stock solutions were stored under argon in Pierce Reacti Vials fitted with Pierce Mininert Valves; samples for kinetic measurement were withdrawn by hypodermic syringe. Diphenylacetaldehyde (Aldrich) was purified by fractional distillation; examination of the distillate by proton NMR showed it to contain 4–5% of another substance, which, in view of the fact that the keto–enol equilibrium constant in aqueous solution is $K_E = 0.1$ (vide infra), presumably was the enol.

All other materials were best available commercial grades. Aqueous solutions were prepared with deionized water purified further by distillation.

Kinetics of Ketonization. Rates of ketonization of diphenylacetaldehyde enol were measured spectroscopically, for the most part by monitoring the decrease in absorbance of the enol at its maximum, $\lambda_{max} = 260$ nm. These determinations were made with a Cary Model 118C spectrometer whose cell compartment was thermostated at 25.0 ± 0.05 °C. Acid or buffer solutions contained in quartz cuvettes were first allowed to come to temperature equilibrium with the spectrometer cell compartment; a few microliters of diphenylacetaldehyde potassium enolate in tetrahydrofuran solution was then added, the mixture was shaken briefly and was replaced in the spectrometer, and the recording of absorbance was begun. Final concentrations of enol in the reaction mixtures were of the order of $(2–3) \times 10^{-4}$ M, and the amount of tetrahydrofuran in these solutions was always well below 1%. Reactions were usually followed to completion; these data fit the first-order rate law well, and rate constants were obtained by least-squares fitting to a linear form of the first-order rate law. In some cases, however, final absorbance values were not measured and the data were then analyzed either by linear least-squares fitting using the Guggenheim method[5] or by nonlinear least-squares fitting to an exponential function.[6]

Rates of ketonization of diphenylacetaldehyde enol in sodium hydroxide solution were too fast to be measured in this way, and stopped-flow techniques were therefore used instead. In these basic solutions, moreover, the enol, whose pK_a is 9.4 (vide infra), was largely ionized, and that shifted the keto–enol equilibrium strongly away from the aldehyde tautomer; little aldehyde therefore existed at equilibrium in these solutions, and the ketonization reaction consequently proceeded only to a small, sometimes negligible, extent. This difficulty was overcome by using a scavenger (semicarbazide) to react with the aldehyde as it formed and thus force ketonization to completion. Measurements were made with a Durrum–Gibson stopped-flow spectrometer operating at 25.0 ± 0.1 °C. Aqueous sodium hydroxide solution containing semicarbazide (0.30 M) was placed in one drive syringe, and this was mixed in a 1:1 ratio with enol stock solution from the other drive syringe. The enol solution was prepared by adding a small amount of potassium enolate in tetrahydrofuran to a much larger volume of water containing a sufficient excess of perchloric acid to give a final acid concentration of 1×10^{-4} M; at this acidity, the lifetime of the enol is ca. 30 min. Once again, the amount of tetrahydrofuran in the final reaction mixtures was well below 1%. Ketonization was monitored at the absorption maximum of the enolate, $\lambda_{max} = 295$ nm, and the reactions were followed to completion. These changes fit the first-order rate law well, and first-order rate constants were calculated by least-squares fitting to a linear expression.

Kinetics of Enolization. Rates of enolization of diphenylacetaldehyde were measured in acetic acid buffer solutions and also in sodium hydroxide solutions. The determinations in acetic acid buffers were performed using iodine to scavenge the enol as it formed. Measurements were made spectroscopically with a Cary Model 118C spectrometer whose cell compartment was thermostated at 25.0 ± 0.05 °C. The reactions were carried out under first-order conditions with the iodine in twofold excess over aldehyde: $[I_2] = (4–5) \times 10^{-5}$ M and $[aldehyde] = (2–3) \times 10^{-5}$ M. The reaction mixtures also contained iodide ion

$([I_2]/[I^-] = 0.01)$ so that the strong triiodide ion absorbance at $\lambda_{max} = 351$ nm could be monitored. Kinetic runs were conducted by first allowing 3.0-mL portions of buffer and iodine–iodide solutions, contained in quartz cuvettes, to come to temperature equilibrium with the spectrometer cell compartment and then adding 3.0-μL quantities of stock solution of diphenylacetaldehyde dissolved in tetrahydrofuran to initiate reaction. These enolizations were followed for 4–5 half-lives, and first-order rate constants were evaluated by the Guggenheim method[5] with least-squares fitting.

A scavenger was not used to measure rates of enolization of diphenylacetaldehyde in sodium hydroxide solutions because the concentration of enol plus enolate could itself be monitored by following the appearance of enolate absorbance at $\lambda_{max} = 295$ nm: the solutions used were sufficiently basic to allow appreciable amounts of the aldehyde, whose pK_a is 10.4 (vide infra), to exist in the ionized, enolate, form. The reactions were too rapid for rate measurement by conventional (slow) UV spectroscopy, and a Durrum–Gibson stopped-flow spectrometer, operating at 25.0 ± 0.1 °C, was therefore used. These enolizations were monitored for at least 4–5 half-lives and often were followed to completion; rate constants were evaluated by least-squares fitting either to a linear form of the first-order rate equation or to the Guggenheim expression.[5]

Hydration Equilibrium Constant. The position of equilibrium between diphenylacetaldehyde and its hydrate, 2,2-diphenylethane-1,1-diol, was determined by proton NMR and also by a kinetic method based upon reaction of free aldehyde with semicarbazide. In the NMR method, the area of signals from the aldehydic proton at $\delta = 10.62$ and the corresponding proton of the hydrate at $\delta = 6.54$ were compared. Measurements were made at 400 MHz (Varian XL400 spectrometer) on a saturated solution of diphenylacetaldehyde in D_2O containing 0.01 M DCl to ensure complete equilibration. A pulse acquisition time of 1.8 s was employed, and 10^3 transients were accumulated.

The kinetic method made use of the fact that semicarbazide at the concentration employed (0.1 M) in the solutions investigated (aqueous acetic acid buffers) reacts with diphenylacetaldehyde more rapidly than the aldehyde hydrate undergoes dehydration. Consequently, when semicarbazide was added to an equilibrated mixture of aldehyde and hydrate, there was at first a rapid formation of aldehyde semicarbazone from reaction of semicarbazide with the free aldehyde, and this was then followed by a slower semicarbazone formation as the hydrate underwent dehydration and provided more free aldehyde. Rates of this slower formation of semicarbazone were measured by monitoring the increase in semicarbazone absorbance at $\lambda = 235$ nm. The data conformed to the first-order rate law well. They were analyzed by least-squares fitting to an exponential function by a method[6] that calculates the final absorbance, A_∞, and the absorbance at zero time, A_0, in addition to the first-order rate constant, and hydration equilibrium constants were evaluated as $K_h = [hydrate]/[aldehyde] = (A_\infty - A_0)/A_0$. Measurements were made with a Cary 118C spectrometer whose cell compartment was thermostated at 25.0 ± 0.05 °C. Aldehyde plus buffer solutions contained in 3.0-mL cuvettes were first allowed to come to temperature and hydration equilibrium, and reactions were then initiated by adding 60 μL of a solution of 2 M semicarbazide hydrochloride in 2 M NaOH.

Results

Hydration Equilibrium Constant. The extent of hydration of diphenylacetaldehyde in aqueous solution, and thus its hydration equilibrium constant K_h (eq 5), was determined by proton NMR and also by semicarbazide scavenging. The NMR method involved integrating the signals of the aldehydic ($RCHO$) and hydrate ($RCH(OH)_2$) protons from an equilibrated solution of aldehyde and hydrate in D_2O. This gave $K_h = 5.4$, with an estimated uncertainty of about 5%.

This result may be converted to a value of K_h for H_2O solution by using the relationship $(K_h)_{D_2O}/(K_h)_{H_2O} = \phi^2$, in which ϕ is the fractionation factor for the hydrogens of the hydroxyl groups in the hydrate. With $\phi = 1.08$,[7] this gives $K_h = 4.6 \pm 0.2$ for H_2O solution.

The scavenging method of determining K_h used semicarbazide to react rapidly with the free aldehyde of an equilibrated aqueous (H_2O) solution and then more slowly with the additional aldehyde formed by dehydration of the hydrate. The appearance of aldehyde semicarbazone was monitored spectroscopically, and rate constants of the dehydration reaction were also determined; these were consistent with literature values for other aliphatic aldehyde

(3) Chiang, Y.; Kresge, A. J.; Walsh, P. A. *J. Am. Chem. Soc.* **1982**, *104*, 6122–6123; **1986**, *108*, 6314–6320. Pruszynski, P.; Chiang, Y.; Kresge, A. J.; Schepp, N. P.; Walsh, P. A. *J. Phys. Chem.* **1986**, *90*, 3760–3766.

(4) Brown, C. A. *J. Org. Chem.* **1974**, *39*, 3913–3918.

(5) Guggenheim, E. A. *Philos. Mag.* **1926**, *2*, 538–543.

(6) Swain, C. G.; Swain, M. S.; Berg, L. F. *J. Chem. Int. Comput. Sci.* **1980**, *20*, 47–51.

(7) Bone, R.; Wolfenden, R. *J. Am. Chem. Soc.* **1985**, *107*, 4772–4777.
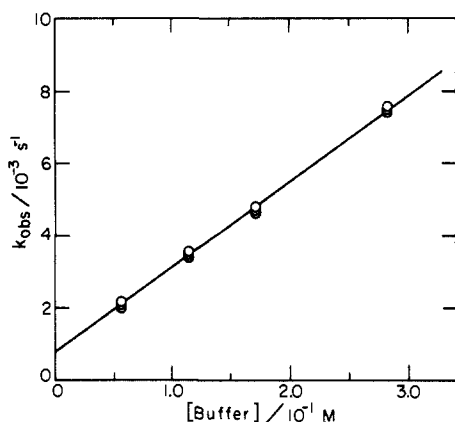
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Figure 1. Relationship between buffer concentration and observed first-order rate constants for the ketonization of diphenylacetaldehyde enol in aqueous acetic acid buffer solutions ([HOAc]/[OAc⁻] = 1.83).

Figure 2. Relationship between buffer catalytic coefficients and fraction of buffer present in basic form for the enolization of diphenylacetaldehyde (O) and ketonization of its enol (●) in acetic acid buffer solutions.

dehydration reactions.[8] Measurements were made in a series of acetic acid buffer solutions of constant buffer ratio but different buffer concentrations (0.012–0.10 M). The data are summarized in Table S1.[9]

The results of 21 separate determinations made in this way give K_h = 4.78 ± 0.24. This is in good agreement with the number obtained by NMR, K_h = 4.6 ± 0.2, and the weighted average of the two results is K_h = 4.69 ± 0.17. This value is considerably greater than an estimate that can be made from a correlation of aldehyde hydrate dissociation constants using Taft polar and steric substituent constants,[10] K_h = 0.089, but it is nicely consistent with K_h = 6 recently measured for 9-formylfluorene[11] (**1**), which resembles diphenylacetaldehyde (**2**) closely.
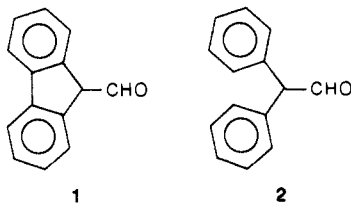
Keto–Enol Equilibrium Constant. The position of equilibrium between a carbonyl compound and its enol isomer, for example, that of the process shown in eq 1, is independent of the concentration or type of catalyst used to effect reaction. The equilibrium constant for such a process may therefore be evaluated as the ratio of forward, k^E, to reverse, k^K, rate constants, $K_E = k^E/k^K$, by using specific rates for any catalyst, or collection of catalysts, as long as this is the same for the forward as for the reverse process.

We tried at first to determine k^E and k^K in perchloric acid solutions, where the hydronium ion and water are the only catalytically effective species. We found, however, that, whereas rates of ketonization could be measured readily in these solutions (vide infra), rates of enolization could not: both diphenylacetaldehyde and the iodine scavenger needed to monitor enolization were not stable at the acidities required to effect reaction. We therefore turned to acetic acid buffer solutions, where, because this keto–enol interconversion is catalyzed strongly by bases even as weak as acetate ion, rates of reaction are comparable to those in ca. 1 M perchloric acid solutions.

Rate measurements were made in series of solutions with constant ionic strength (0.10 M) and constant buffer ratio but changing buffer concentration (fivefold variation). Four series were used with [HOAc]/[OAc⁻] = 0.44, 0.64, 1.1, and 1.8, and

rates of enolization and ketonization were measured with each. The data are summarized in Tables S2 and S3.[9]

Marked buffer catalysis was found for both enolization and ketonization, and for both reactions observed first-order rate constants were accurately proportional to buffer concentration; Figure 1 shows a typical example. The data were therefore fitted to eq 6 by linear least-squares analysis. The buffer catalytic

$$k_{obsd} = k_0 + k_{cat}[\text{buffer}] \qquad (6)$$

coefficients, k_{cat}, so obtained were in turn fitted to eq 7, in which

$$k_{cat} = k_{HA} + (k_B - k_{HA})f_B \qquad (7)$$

k_{HA} and k_B are operational general-acid and general-base catalytic coefficients, respectively, and f_B is the fraction of buffer present in the basic form. Least-squares analysis gave good linear relationships with zero intercepts (Figure 2), which shows that buffer catalysis is of the general-base type only: for enolization, k_{cat} = (0.001 ± 1.227) × 10⁻⁴ + (1.60 ± 0.22) × 10⁻³f_B; and for ketonization, k_{cat} = -(2.72 ± 2.99) × 10⁻³ + (7.49 ± 0.55) × 10⁻²f_B.

These results lead to the catalytic coefficients $(k_{OAc^-}^E)_{eff}$ = (1.60 ± 0.26) × 10⁻³ M⁻¹ s⁻¹ and $k_{OAc^-}^K$ = (7.22 ± 0.62) × 10⁻² M⁻¹ s⁻¹. The enolization rate constant $(k_{OAc^-}^E)_{eff}$ refers to unit concentration of a rapidly interconverting equilibrium mixture of diphenyl-acetaldehyde and its hydrate; it may be converted to a true catalytic coefficient based upon unit concentration of aldehyde alone by multiplying by (1 + K_h), where K_h is the hydration equilibrium constant determined for this system as described above: $k_{OAc^-}^E$ = $(k_{OAc^-}^E)_{eff}(1 + K_h)$ = (9.1 ± 1.5) × 10⁻³ M⁻¹ s⁻¹. Combination of this rate constant, corrected for hydration, with the ketonization catalytic coefficient $k_{OAc^-}^K$ then leads to the keto–enol equilibrium constant K_E = (1.26 ± 0.23) × 10⁻¹.

Another estimate of K_E may be obtained from the zero buffer concentration intercepts gotten by fitting the data to eq 6. These intercepts show no systematic variation with buffer ratio; they therefore contain no contribution from catalysis by hydronium or hydroxide ions and thus represent a solvent-initiated or "uncatalyzed" reaction. The ratio of their averages, $(k_0^E)_{eff}$ = (1.27 ± 0.12) × 10⁻⁵ s⁻¹ and k_0^K = (7.32 ± 0.37) × 10⁻⁴ s⁻¹, corrected for aldehyde hydration, gives K_E = (0.99 ± 0.11) × 10⁻¹, which is nicely consistent with the result obtained from the acetate ion catalytic coefficients. The weighted average of the two values is K_E = (1.04 ± 0.10) × 10⁻¹, pK_E = 0.98 ± 0.04.

An interpretation at the molecular level of the rate constants determined here may be made on the basis of the generally accepted two-step mechanism for the base-catalyzed enolization of carbonyl compounds (eq 8).[12] Acetate ion catalyzed enolization

(8) Bell, R. P.; Rand, M. H.; Wynne-Jones, K. M. A. *Trans. Faraday Soc.* **1956**, *52*, 1092–1102. Gruen, L. C.; McTigue, P. T. *J. Chem. Soc.* **1963**, 5224–5229. Sorensen, P. E.; Jencks, W. P. *J. Am. Chem. Soc.* **1987**, *109*, 4675–4690.

(9) Supplementary material; see paragraph at the end of this paper regarding availability.

(10) Bell, R. P. *Adv. Phys. Org. Chem.* **1966**, *4*, 1–29.

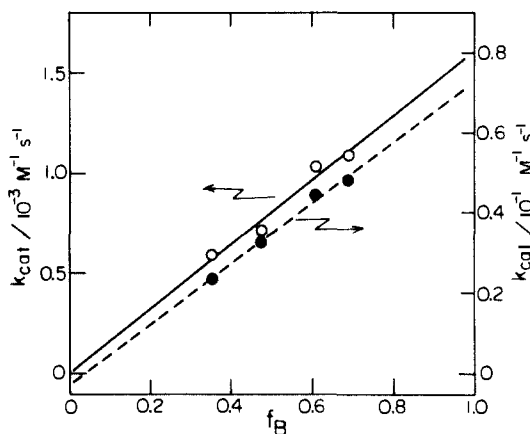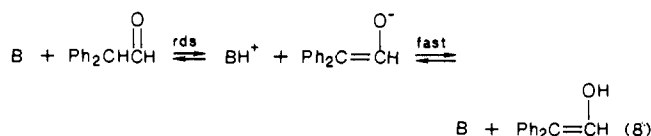(11) Harcourt, M.; More O'Ferrall, R. A. *J. Chem. Soc., Chem. Commun.* **1987**, 822–823.

Diphenylacetaldehyde and Its Enol

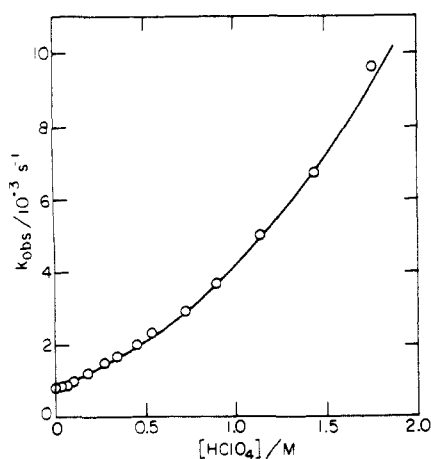*J. Am. Chem. Soc., Vol. 110, No. 8, 1988* 2603

Figure 3. Relationship between acid concentration and observed first-order rate constants for the ketonization of diphenylacetaldehyde enol in aqueous perchloric acid solutions.

then becomes a process whose rate-determining step involves proton transfer from diphenylacetaldehyde to acetate ion with the rate constant $k_{OAc^-}^E = (9.1 \pm 1.5) \times 10^{-3}$ M^{-1} s^{-1}, and the uncatalyzed enolization reaction involves rate-determining proton transfer from diphenylacetaldehyde to a water molecule with the rate $k_0^E = (7.23 \pm 0.73) \times 10^{-5}$ s^{-1}. The principle of microscopic reversibility requires ketonization to occur by the same reaction mechanism, and acetate ion catalyzed ketonization then becomes a process that involves proton transfer to acetate ion from the enol hydroxyl group followed by rate-determining carbon protonation of the enolate ion by acetic acid. This makes the operational general-base catalytic coefficient for this reaction, $k_{OAc^-}^K$, equal to $(K_a^E/K_{HOAc})k'_{HOAc}$, in which K_a^E, the acid dissociation constant of the enol at the ionic strength of the experiments (0.10 M), and K_{HOAc}, the acid dissociation constant of acetic acid at ionic strength $= 0.10$,[13] make up the equilibrium constant for the rapid step, and k'_{HOAc} is the rate constant for proton transfer from acetic acid to enolate carbon. The value of $k_{OAc^-}^K$ measured here, coupled with $K_a^E = 4.2 \times 10^{-10}$ M determined as described below, then leads to $k'_{HOAc} = (4.87 \pm 0.45) \times 10^3$ M^{-1} s^{-1}. Similarly, the "uncatalyzed" ketonization reaction is a process involving proton transfer from enolate oxygen to a water molecule followed by rate-determining protonation of enolate on carbon by the hydronium ion thus formed. This makes $k_0^K = K_a^E k'_{H^+}$ in which k'_{H^+} is the rate constant for carbon protonation of enolate by the hydronium ion; use of $k_0^K = (7.92 \pm 0.12) \times 10^{-4}$ s^{-1}, which is the weighted average of the value determined in acetic acid buffers and a result obtained from rate measurements in perchloric acid solutions (vide infra), then leads to $k'_{H^+} = (1.97 \pm 0.06) \times 10^6$ M^{-1} s^{-1}.

Ketonization in Perchloric Acid Solutions. Rates of ketonization of diphenylacetaldehyde enol were measured in aqueous perchloric acid solutions over the concentration range $[HClO_4] = 0.001-1.8$ M. The data are summarized in Table S4[9] and are displayed in Figure 3.

The results show that the rate of ketonization remains essentially constant and independent of acidity up to $[HClO_4] \simeq 0.1$ M and that observed first-order rate constants in this region are similar to the specific rate of the "uncatalyzed" ketonization reaction observed in acetic acid buffers, $k_0^K = 7.3 \times 10^{-4}$ s^{-1}. Above $[HClO_4] = 0.1$ M, however, observed rate constants increase strongly with increasing acidity, and the increase in rate, moreover, is faster than in direct proportion to acid concentration. Such

sharply accelerating acidity dependence is not uncommon for acid-catalyzed reactions in concentrated acids, and it may be handled by using an acidity function to correlate the data. The X_0 scale[16] appears to be the best function currently available for this purpose.[17] The data were therefore fitted to eq 9, which is

$$\log \{(k_{obsd} - k_0)/[H^+]\} = \log k_{H^+} + mX_0 \qquad (9)$$

the standard expression generally used to correlate k_{obsd} with X_0 for the present kind of reaction,[18] modified by inclusion of an additional rate constant k_0 to allow for the "uncatalyzed" reaction observed below $[HClO_4] \simeq 0.1$ M. Least-squares analysis gave $k_0 = (7.98 \pm 0.12) \times 10^{-4}$ s^{-1}, $k_{H^+} = (2.10 \pm 0.03) \times 10^{-3}$ M^{-1} s^{-1}, and $m = 0.815 \pm 0.017$. These parameters were used to draw the line shown in Figure 3; it is apparent that they correlate the experimental data well.

The value of k_0 obtained in this way is consistent with $k_0^K = (7.32 \pm 0.37) \times 10^{-4}$ s^{-1} obtained for the "uncatalyzed" ketonization reaction in acetic acid buffer solutions. The two rate constants may therefore be taken to represent the same ketonization process; their weighted average is $k_0^K = (7.92 \pm 0.12) \times 10^{-4}$ s^{-1}.

Enol Acidity Constants. The acid dissociation constants of enols may be determined by kinetic experiments by virtue of the fact that their ketonization reactions show apparent base catalysis.[3,19] This catalysis is brought about by ionization of the enol to the much more reactive enolate ion followed by ketonization of that through rate-determining proton transfer to enolate carbon (eq 10). At sufficiently high hydroxide ion concentrations, however,
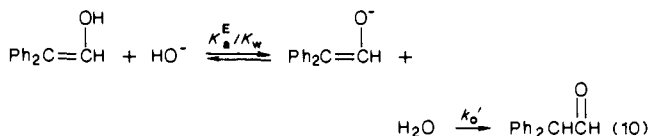
this catalysis becomes saturated because the ionization equilibrium is shifted completely to the right and further formation of the more reactive species is no longer possible. Straightforward treatment of rate data obtained in the region of transition from catalysis to no catalysis then leads to the equilibrium constant for the ionization step, K_a^E/K_w, from which the enol acidity constant may be extracted.

We first measured rates of ketonization of diphenylacetaldehyde enol in sodium hydroxide solutions. Determinations were made over the concentration range $[NaOH] = 0.002-0.01$ M; these data are summarized in Table S5.[9]

Observed first-order rate constants obtained in this way increased only very slightly with increasing hydroxide ion concentration, indicating that the equilibrium step of the process of eq 10 was already shifted largely to the right. This contrasts with the behavior of other enols we have studied whose ketonization shows marked hydroxide ion catalysis over this concentration range,[3,19] but it is consistent with the expected greater acid strength of the present enol. We therefore moved to lower hydroxide ion concentrations, which required the use of buffer solutions.

We chose bicarbonate–carbonate buffers for this purpose. Rates of ketonization were measured in series of buffer solutions of constant ionic strength and constant buffer ratio but varying buffer concentration. Six such series of solutions were used, covering the buffer ratio range $[HCO_3^-]/[CO_3^{2-}] = 1-7$. These data are summarized in Table S6.[9]

Observed first-order rate constants determined in this way proved to be linear functions of buffer acid concentration. The

(12) Bell, R. P. *The Proton in Chemistry*, 2nd ed.; Cornell University Press: Ithaca, NY, 1973; p 171. Toullec, J. *Adv. Phys. Org. Chem.* **1982**, *18*, 1–77.

(13) $K_{HOAc} = 2.72 \times 10^{-5}$ M on the basis of $pK_a = 4.756$[14] and activity coefficients recommended by Bates.[15]

(14) Harned, H. S.; Ehlers, R. W. *J. Am. Chem. Soc.* **1933**, *55*, 652–656.

(15) Bates, R. G. *Determination of pH. Theory and Practice*; Wiley: New York, 1973; p 49.

(16) Cox, R. A.; Yates, K. *Can. J. Chem.* **1981**, *59*, 2116–2124.

(17) Kresge, A. J.; Chen, H. J.; Capen, G. L.; Powell, M. F. *Can. J. Chem.* **1983**, *61*, 249–256.

(18) Cox, R. A.; Yates, K. *Can. J. Chem.* **1979**, *57*, 2944–2951.

(19) (a) Chiang, Y.; Kresge, A. J.; Tang, Y. S.; Wirz, J. *J. Am. Chem. Soc.* **1984**, *106*, 460–462. Chiang, Y.; Kresge, A. J.; Wirz, J. *J. Am. Chem. Soc.* **1984**, *106*, 6392–6395. (b) Chiang, Y.; Hojatti, M.; Keeffe, J. R.; Kresge, A. J.; Schepp, N. P.; Wirz, J. *J. Am. Chem. Soc.* **1987**, *109*, 4000–4009.

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data were therefore fitted to a linear expression in $[HCO_3^-]$. The zero-buffer-concentration intercepts obtained from this treatment, $(k_{obsd})_{[HCO_3^-]=0}$, which represent reaction by the process of eq 10, did increase with decreasing buffer ratio, and therefore increasing hydroxide ion concentration, thus substantiating the conclusion reached above that the lack of catalysis observed in sodium hydroxide solutions did represent essentially complete conversion of enol to enolate in these media.

The rate law that applies to the process of eq 10 is given in eq 11. Taking reciprocals of both sides of this expression leads to

$$(k_{obsd})_{[HCO_3^-]=0} = \frac{k_0'(K_a^E/K_w)[HO^-]}{1 + (K_a^E/K_w)[HO^-]} = \frac{k_0'K_a^E}{[H^+] + K_a^E} \quad (11)$$

eq 12, which requires $(k_{obsd})^{-1}$ to be a linear function of $[H^+]$. As

$$1/(k_{obsd})_{[HCO_3^-]=0} = (1/k_0') + [H^+]/k_0'K_a^E \quad (12)$$

Figure 4 shows, the data from these bicarbonate buffer experiments combined with the results obtained in sodium hydroxide solutions fit this expression well; least-squares analysis gives $(k_{obsd})^{-1} = (9.31 \pm 0.17) + (2.30 \pm 0.05) \times 10^{10}[H^+]$, which leads to $K_a^E = (4.04 \pm 0.11) \times 10^{-10}$ M[20] and $k_0' = (1.08 \pm 0.02) \times 10^{-1}$ s^{-1}.[21]

Another estimate of K_a^E may be obtained from the slopes of the linear relationships between $[HCO_3^-]$ and observed first-order rate constants determined in these series of bicarbonate buffer solutions. These slopes are rate constants for a process similar to that shown in eq 10, but with HCO_3^- rather than H_2O as the proton donor in the second (rate determining) step. They will therefore vary with the hydroxide ion concentration of the buffers, and a plot such as that of Figure 4 will give slope and intercept parameters from which K_a^E and the rate constant for the second step can be evaluated. Least-squares analysis of the relevant data led to the results $K_a^E = (2.99 \pm 0.86) \times 10^{-10}$ M[20] and $k_{HCO_3^-}' = 2.78 \pm 0.66$ M^{-1} s^{-1}. This value of K_a^E, though considerably more uncertain than that obtained from the intercepts, is nevertheless consistent with it; the weighted average of the two determinations is $K_a^E = (4.03 \pm 0.11) \times 10^{-10}$ M, $pK_a^E = 9.40 \pm 0.01$.[20]

Aldehyde Acidity Constant. The keto–enol equilibrium of a carbonyl compound such as diphenylacetaldehyde and the acid ionization of the enol form two parts of a thermodynamic cycle whose third member is ionization of the carbonyl compound as a carbon acid (eq 13). The equilibrium constants for these three
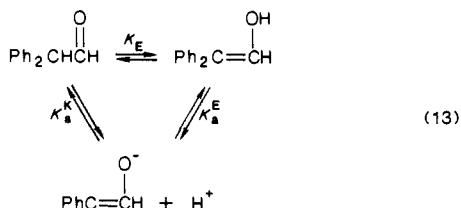
reactions are therefore related, $K_E K_a^E = K_a^K$, and knowledge of any two provides an estimate of the third. Use of the values of K_E and K_a^E for diphenylacetaldehyde determined as described above then leads to $K_a^K = (4.03 \pm 0.47) \times 10^{-11}$ M. This estimate implies that diphenylacetaldehyde is sufficiently acidic to undergo ionization in dilute aqueous sodium hydroxide solutions and that it should thus be possible to determine K_a^K directly in such media.

This proved to be the case: we were able to obtain two independent, directly determined values of K_a^K from rates of enolization of diphenylacetaldehyde measured in sodium hydroxide solutions, one from the ratio of forward to reverse rate constants and another from a spectrophotometric titration curve. The data consist of rates of approach to equilibrium measured over the concentration
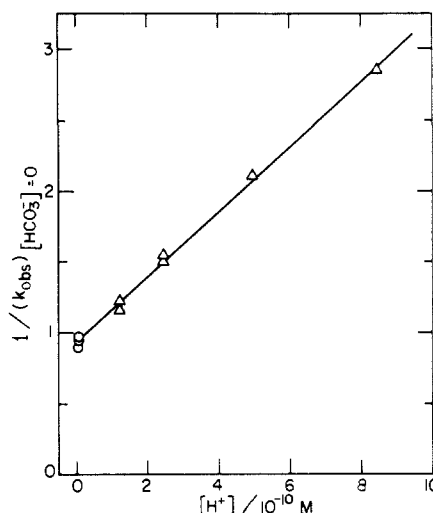
Figure 4. Rate data for the ketonization of diphenylacetaldehyde enol in sodium hydroxide (O) and bicarbonate buffer (△) solutions plotted according to eq 12.
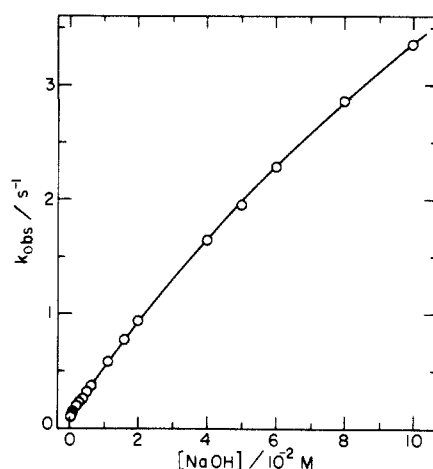
Figure 5. Relationship between hydroxide ion concentration and observed first-order rate constants for enolization of diphenylacetaldehyde in aqueous sodium hydroxide solutions.

range [NaOH] = 0.0004–0.10 M at a constant ionic strength of 0.10 M; they are summarized in Tables S7 and S8[9] and are displayed in Figure 5.

The reaction scheme that applies to this system in these solutions is shown as eq 14. Rate-determining reaction of aldehyde with
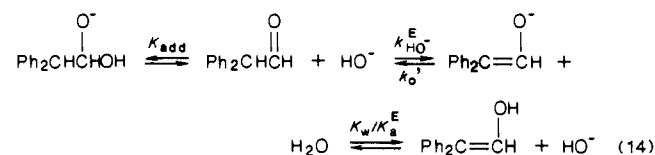
hydroxide ion to give enolate occurs with a rate constant $k_{HO^-}^E$, and re-formation of the aldehyde by carbon protonation of enolate occurs with the rate constant k_0'. At the lower end of the hydroxide ion concentration range employed, a small amount of enolate will also be protonated on oxygen to give enol, but this will be a fast process after the slow step, and it can be treated as a subsequent equilibrium with equilibrium constant K_w/K_a^E. There will also be another fast equilibrium reaction, significant only at the higher hydroxide ion concentrations, in which hydroxide ion adds to the carbonyl atom of the aldehyde; the equilibrium constant for this process is designated K_{add}. In addition to these reactions, the aldehyde will be in equilibrium with its hydrate, but the extent of this process does not depend upon hydroxide ion concentration and it therefore does not have to be included explicitly in this kinetic analysis; it can be allowed for subsequently by applying the correction $(1 + K_h)$ to quantities that it will effect, much as

(20) This is a concentration dissociation constant referred to a standard state of unit molarity at ionic strength = 0.10 M.

(21) Values of $[H^+]$ in the bicarbonate buffers needed for this analysis were obtained by calculation using $pK_a = 10.329$[22] and activity coefficients recommended by Bates.[15]

(22) Harned, H. S.; Scholes, S. R., Jr. *J. Am. Chem. Soc.* **1941**, *63*, 1706–1709.
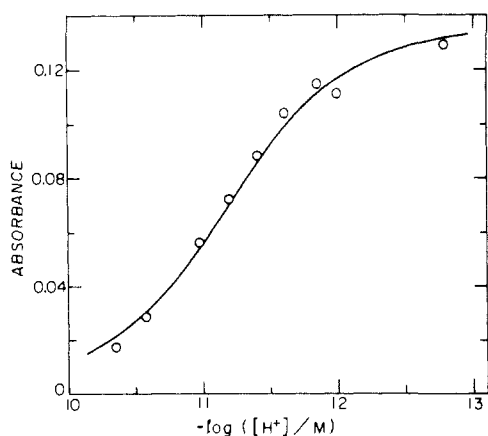
Figure 6. Spectrophotometric titration curve for the ionization of diphenylacetaldehyde in aqueous sodium hydroxide solutions (25 °C, ionic strength = 0.10 M).

was done above for K_E, $k_{OAc^-}^E$, and k_0^E.

The rate law that applies to this reaction scheme is given as eq 15. There are four parameters in this expression governing

$$k_{obsd} = \frac{k_{HO^-}^E[HO^-]}{1 + K_{add}[HO^-]} + \frac{k_0'[HO^-]}{[HO^-] + K_w/K_a^E} \quad (15)$$

the dependence of k_{obsd} upon $[HO^-]$. One of these parameters, K_w/K_a^E, affects the relationship between these two variables only in a minor way, inasmuch as its value is small compared to even the lowest hydroxide ion concentration used, and it therefore cannot be determined at all well from the fit of k_{obsd} to $[HO^-]$. This parameter, however, is already known, for K_a^E has been determined from ketonization rate measurements made in bicarbonate buffer and sodium hydroxide solutions. A least-squares analysis was therefore carried out with K_w/K_a^E supplied as (1.59 × 10^{-14})/(4.03 × 10^{-10}) = 3.9 × 10^{-5} M; the results are $k_{HO^-}^E/(1 + K_h)$ = 44.6 ± 0.2 M^{-1} s^{-1} ($k_{HO^-}^E$ = 254 ± 8 M^{-1} s^{-1}), k_0' = 0.105 ± 0.002 s^{-1}, and $K_{add}/(1 + K_h)$ = 3.69 ± 0.07 M^{-1} (K_{add} = 21.0 ± 0.7 M^{-1}). These parameters were used to draw the line shown in Figure 5; they reproduce the experimental data well. The value of k_0' obtained, moreover, is in good agreement with k_0' = 0.108 ± 0.002 s^{-1} determined from rates of ketonization measured in bicarbonate buffer and sodium hydroxide solutions; the weighted average of the two results is k_0' = 0.106 ± 0.001 s^{-1}.
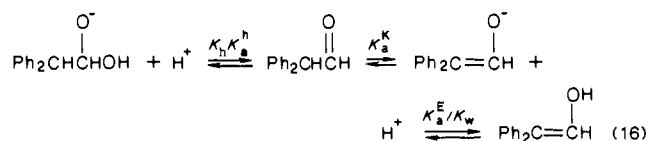
The equilibrium constant K_{add} is related to the acid dissociation constant of diphenylacetaldehyde hydrate ionizing as an oxygen acid, as shown in eq 5: $K_{add}K_w = K_h K_a^h$. A value of K_a^h may therefore be obtained from K_{add} determined by this fit. The result, K_a^h = (7.10 ± 0.36) × 10^{-14} M, pK_a^h = 13.15 ± 0.02,[20] is in remarkably good agreement with a value that may be estimated from a correlation of acid dissociation constants of aldehyde hydrates using Taft polar substituent constants, pK_a^h = 13.13.[23]

The slow step of the reaction scheme of eq 14 involves the ionization of diphenylacetaldehyde as a carbon acid, and the acidity constant of diphenylacetaldehyde may therefore be obtained from the ratio of forward to reverse rate constants for this step, $k_{HO^-}^E/k_0' = K_a^K/K_w$. The result is K_a^K = (3.83 ± 0.14) × 10^{-11} M.

This acidity constant may also be evaluated from final absorbance readings made at the ends of the kinetic runs carried out to measure these rates of approach to aldehyde–enolate equilibrium in sodium hydroxide solutions. The rate measurements were made at λ = 295 nm, which is λ$_{max}$ for the enolate ion. Since the aldehyde has negligible absorbance at this wavelength, the final absorbance readings were due almost entirely to enolate ion, and they therefore reflected the position of the aldehyde–enolate equilibrium. Figure 6 shows that these final absorbances, when

plotted against $-\log [H^+]$ of the solutions in which they were measured, describe a sigmoid titration curve. The inflection point of this curve is related to pK_a^K.

It is convenient, for the purpose of analyzing the data, to recast the changes described in eq 14 in terms of H^+ rather than HO^-; this is done in eq 16. There is, as before, still another equilibrium

$$Ph_2CHCHOH + H^+ \overset{K_h K_a^h}{\rightleftharpoons} Ph_2CHCH \overset{K_a^K}{\rightleftharpoons} Ph_2C=CH +$$
$$H^+ \overset{K_a^E/K_w}{\rightleftharpoons} Ph_2C=CH \quad (16)$$

expressing the hydration of diphenylacetaldehyde, but this reaction is not affected by the $[H^+]$ level of the medium, and once again it can be left out for the sake of simplicity. The final absorbance, A_f, will be the sum of the absorbances of all the relevant substrate species: aldehyde, A; enolate, E$^-$; enol, E; and hydrate anion, h$^-$. Each of these absorbances may be written as a concentration times the relevant molar extinction coefficient, as shown in eq 17.

$$A_f = \epsilon_A[A] + \epsilon_{E^-}[E^-] + \epsilon_E[E] + \epsilon_{h^-}[h^-] \quad (17)$$

Expressing this in terms of total substrate concentration, $[S]_{tot}$, then leads to eq 18.

$$A_f = \frac{\{(\epsilon_A + \epsilon_E K_E)[H^+] + \epsilon_{E^-}K_a^K + \epsilon_{h^-}K_h K_a^h\}[S]_{tot}}{(1 + K_E)[H^+] + K_a^K + K_h K_a^h} \quad (18)$$

The last term in braces in the numerator of this expression, $\epsilon_{h^-}K_a^h$, will be very much smaller than the term immediately preceding it, $\epsilon_{E^-}K_a^K$, because ϵ_{h^-} is very much smaller than ϵ_{E^-} at λ = 295 nm and also because $K_h K_a^h$ [=(5)(7 × 10^{-14} M)] is 2 orders of magnitude less than K_a^K (=4 × 10^{-11} M from the kinetic analysis described above). The latter difference also implies that $K_h K_a^h$ will make a negligible contribution to the denominator of this expression. Making these simplifications and supplying an approximate value of K_E in the denominator of this expression[24] then lead to eq 19. Least-squares fitting of the data[25] to this

$$A_f = \frac{(\epsilon_A + \epsilon_E K_E)[S]_{tot}[H^+] + \epsilon_{E^-}[S]_{tot}K_a^K}{1.02[H^+] + K_a^K} \quad (19)$$

expression then gives $(\epsilon_A + \epsilon_E K_E)[S]_{tot}$ = 0.0057 ± 0.022, $\epsilon_{E^-}[S]_{tot}$ = 0.135 ± 0.047, and $K_a^K/(1 + K_h)$ = (6.45 ± 0.40) × 10^{-12} M (K_a^K = (3.67 ± 0.25) × 10^{-11} M). These parameters were used to draw the line shown in Figure 6; they reproduce the experimental data well. The operational extinction coefficient for the enolate ion thus obtained is considerably greater than that of aldehyde plus enol, as expected, and the value of K_a^K is in very good agreement with the result obtained from the kinetic analysis described above, K_a^K = (3.83 ± 0.14) × 10^{-11} M. The weighted average of the two determinations is K_a^K = (3.80 ± 0.12) × 10^{-11} M, pK_a^K = 10.42 ± 0.02.

Internal Consistency. Three equilibrium constants, K_E, K_a^E, and K_a^K, were determined in this study, each by two independent methods. It was pointed out above that these three constants are interrelated, $K_E K_a^E = K_a^K$ (see eq 13), and the results obtained can therefore be examined for internal consistency. This may be done, for example, by combining the constants as $K_E K_a^E/K_a^K$, which, for a self-consistent set of values, should be equal to unity. The results obtained to give a value that is unity within the combined experimental uncertainties: 1.10 ± 0.12. This attests to the essential validity of the various methods used to obtain these results.

Discussion

Keto–Enol Equilibria. The results of the present study, summarized in Table I, show that the keto–enol equilibrium constant

(23) Perrin, D. D.; Dempsey, B.; Serjeant, *pK_a Predictions for Organic Acids and Bases*; Chapman and Hall: London, 1981; p 60. Barlin, G. B.; Perrin, D. D. *Q. Rev. Chem. Soc.* **1966**, *20*, 75–101.

(24) Because the hydration equilibrium was not included in the scheme of eq 16, $K_E/(1 + K_h)$ = 1.8 × 10^{-2} must be used, and the coefficient of $[H^+]$ then becomes $1 + (1.8 \times 10^{-2}) \simeq 1.02$.

(25) The data, listed in Table S8, consist of 52 pairs of A_f and $[H^+]$ determined over the concentration range [NaOH] = 0.00036–0.10 M.

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Table I. Summary of Rate and Equilibrium Constants for the Diphenylacetaldehyde System in Aqueous Solution[a]

Process	Constant
$Ph_2CHCHO \rightleftharpoons Ph_2C=CHOH$	$K_E = 1.04 \times 10^{-1}$; $pK_E = 0.98$
$Ph_2C=CHOH \rightleftharpoons Ph_2C=CHO^- + H^+$	$K_a^E = 4.03 \times 10^{-10}$ M; $pK_a^E = 9.40$
$Ph_2CHCHO \rightleftharpoons Ph_2C=CHO^- + H^+$	$K_a^K = 3.80 \times 10^{-11}$ M; $pK_a^K = 10.42$
$Ph_2CHCHO + H_2O \rightleftharpoons Ph_2CHCHOH_2$ (OH)	$K_h = 4.69$; $pK_h = -0.67$
$Ph_2CHCHOH_2$ (OH) $\rightleftharpoons Ph_2CHCHOH$ (O$^-$) $+ H^+$	$K_a^h = 7.10 \times 10^{-14}$ M; $pK_a^h = 13.15$
$Ph_2CHCHO \xrightarrow{HO^-} Ph_2C=CHO^-$	$k_{OH^-}^E = 2.54 \times 10^2$ M^{-1}s^{-1}
$Ph_2CHCHO \xrightarrow{OAc^-} Ph_2C=CHO^-$	$k_{OAc^-}^E = 9.1 \times 10^{-3}$ M^{-1}s^{-1}
$Ph CHCHO \xrightarrow{H_2O} Ph_2C=CHO^-$	$k_0^E = 7.23 \times 10^{-5}$ s^{-1}
$Ph_2C=CHOH$ (OH) $\xrightarrow{H^+} Ph_2CHCHO$	$k_{H^+}^K = 2.10 \times 10^{-3}$ M^{-1}s^{-1}
$Ph_2C=CHO^-$ $\xrightarrow{H^+} Ph_2CHCHO$	$k_{H^+}^* = 1.97 \times 10^6$ M^{-1}s^{-1}
$Ph_2C=CHO^-$ $\xrightarrow{HOAc} Ph_2CHCHO$	$k_{HOAc}^* = 4.87 \times 10^3$ M^{-1}s^{-1}
$Ph_2C=CHO^-$ $\xrightarrow{HCO_3^-} Ph_2CHCHO$	$k_{HCO_3^-}^* = 2.78$ M^{-1}s^{-1}
$Ph_2C=CHO^-$ $\xrightarrow{H_2O} Ph_2CHCHO$	$k_0^* = 1.06 \times 10^{-1}$ s^{-1}

[a] At 25 °C, ionic strength = 0.10 M.

for diphenylacetaldehyde in aqueous solution is unusually large: $K_E = 0.10$. This is orders of magnitude greater than keto–enol equilibrium constants for simple aldehydes and ketones usually are; for example, $K_E = 5.9 \times 10^{-7}$ for acetaldehyde itself.[19b] 9-Formylfluorene, however, whose structure is quite similar to that of diphenylacetaldehyde (cf. **1** and **2**), has $K_E = 18.$[11]

Phenyl substituents are known to stabilize carbon–carbon double bonds, and it would seem reasonable to attribute these unusually large keto–enol equilibrium constants to phenyl-group stabilization of the enol isomers through interaction with their double bonds. It is significant, then, that the ratio of K_E for 9-formylfluorene to that for acetaldehyde corresponds to 10.2 kcal mol^{-1} or a substituent effect of 5.1 kcal mol^{-1} per phenyl group, in very good agreement with Hine's double-bond stabilization parameter for phenyl, $D = 4.9$ kcal mol^{-1}.[26] Comparison of K_E for diphenylacetaldehyde with that for acetaldehyde gives a phenyl-group effect somewhat less than this, 3.6 kcal mol^{-1}, but steric crowding in this system undoubtedly prevents a completely coplanar arrangement of the phenyl and double bond groups, thereby reducing conjugative interaction and lowering the phenyl-group effect.

It is interesting to compare this effect of unsubstituted phenyl groups on enol stability with that of mesityl or duryl substituents in sterically hindered Fuson enols. Keto–enol equilibrium constants for those substances have so far been measured only in hexane solution at elevated temperatures,[2b,c] whereas the present studies were done in water at 25 °C, but the difference in solvent, at least, may have little effect, for a value of K_E that can be estimated for acetaldehyde in the gas phase does not differ significantly from that measured in aqueous solution.[19b] The keto–enol equilibrium constant determined for dimesitylacetaldehyde, $(2,4,6-(CH_3)_3-C_6H_2)_2CHCHO$, in hexane solution at 80 °C is $K_E = 20,$[2b] and combination of that with the value for acetaldehyde gives an enol-stabilizing substituent effect of 5.3 kcal mol^{-1} to each mesityl group. This is only half again as large as the value determined above for an unsubstituted phenyl group, and it would seem therefore that the influence of the phenyl group itself makes up a substantial portion of the enol-stabilizing effect of mesityl substituents.

These arguments are based upon equilibrium constants, and they therefore deal with thermodynamic stability. Kinetic stability is something else, and there the mesityl group would appear to surpass unsubstituted phenyl by an impressively greater margin.

Table II. Composition of Aqueous Solutions of Diphenylacetaldehyde[a]

	%	
species	acid solution	0.1 M HO$^-$
aldehyde	17	0.40
enol	1.8	0.042
enolate ion		97
aldehyde hydrate	81	1.9
hydrate anion		0.85

[a] At 25 °C, ionic strength = 0.10 M.

The maximum lifetime of acetaldehyde enol in aqueous solution at 25 °C is 25 s, and that of diphenylacetaldehyde, 20 min;[19b,27] introducing two unsubstituted phenyl groups thus raises the lifetime by a factor of 50. No quantitative data are available for dimesitylacetaldehyde, but equilibrium of keto and enol isomers in hexane solution at 80 °C is reported to have required 48 h.[2b] Taking this to be equal to 10 half-lives and assuming that the rate doubles for each 10 °C rise in temperature then lead to a lifetime estimate of 10^4 h at 25 °C. This is 10^6 times longer than the lifetime of acetaldehyde and 3 × 10^4 times longer than the lifetime of diphenylacetaldehyde. This big difference between the effect of mesityl groups and that of unsubstituted phenyls implies that the steric shielding provided by the methyls of the mesityl groups plays an important role in determining the kinetic stability of Fuson enols.

Acid Dissociation Constants. The acid dissociation constant of diphenylacetaldehyde is also unusually large: $pK_a^K = 10.42$; this makes diphenylacetaldehyde more than 10^6 times more acidic than acetaldehyde, for which $pK_a^K = 16.73$.[19b] In this respect diphenylacetaldehyde is again like 9-formylfluorene; the latter, in fact, with $pK_a^K = 6.2,$[11] is even substantially more acidic.

These enhanced acidities, just like the unusually large keto–enol equilibrium constants, appear to be the result of carbon–carbon double-bond stabilization by phenyl substituents. This may be seen by viewing acid ionization of the aldehydes as a two-step process: conversion of the aldehyde to its enol, followed by ionization of the enol as an oxygen acid (eq 20). Although di-

$$\underset{\text{(O)}}{\overset{K_E}{\rightleftharpoons}} \underset{\text{(OH)}}{\overset{K_a^E}{\rightleftharpoons}} \underset{\text{(O}^-\text{)}}{\ } + H^+ \qquad (20)$$
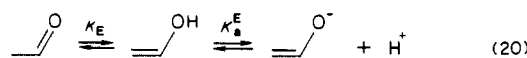
phenylacetaldehyde enol is a stronger oxygen acid than acetaldehyde enol, the difference is not great: $pK_a^E = 9.40$ vs 10.50.[19b] Thus, the substituent effect of two phenyl groups on the overall reaction of eq 20 is expressed largely in the first step, and diphenylacetaldehyde is as strong an acid as it is mainly because the phenyl groups stabilize the double bond of the enolate ion acid ionization product. In the case of diphenylacetaldehyde, some 80% of the substituent effect on pK_a^K appears in pK_E, and for 9-formylfluorene, 70%. The slightly lower percentage for 9-formylfluorene is consistent, of course, with the expected additional ability of the fluorenyl group to stabilize enolate negative charge through cyclopentadienyl anion type resonance.

Because of its acidity, basic solutions of diphenylacetaldehyde will contain large amounts of the enolate ion. Calculations based upon the equilibrium constants determined here, summarized in Table II, show that in 0.1 M aqueous hydroxide ion solutions, 97% of stoichiometric aldehyde exists as enolate and less than 1% is present in the free aldehyde form. Free aldehyde is also a minor form in acid solutions, where aldehyde hydrate is the dominant species.

(26) Hine, J. *Structural Effects on Equilibria in Organic Chemistry*; Wiley: New York, 1975; p 273.
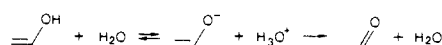
(27) These lifetimes are based upon rates of the so-called "uncatalyzed" reactions that form the lowest, horizontal regions of ketonization rate profiles, near neutral pH. Ketonization in such solutions actually occurs by a self-catalyzed mechanism that is the reverse of eq 8 with B = H_2O:

$$\underset{\text{(OH)}}{\ } + H_2O \rightleftharpoons \underset{\text{(O}^-\text{)}}{\ } + H_3O^+ \longrightarrow \underset{\text{(O)}}{\ } + H_2O$$

Supplementary Material Available: Rate and equilibrium data for the dehydration of diphenylacetaldehyde hydrate in aqueous acetic acid buffer solutions at 25 °C (Table S1), rate data for enolization of diphenylacetaldehyde in aqueous acetic acid buffer solutions at 25 °C (Table S2), rate data for ketonization of diphenylacetaldehyde enol in aqueous acetic acid buffer solutions at 25 °C (Table S3), rate data for ketonization of diphenyl-acetaldehyde enol in aqueous perchloric acid solutions at 25 °C (Table S4), rate data for the ketonization of diphenylacetaldehyde enol in aqueous sodium hydroxide solutions at 25 °C in the presence of semicarbazide scavenger (Table S5), rate data for the ketonization of diphenylacetaldehyde enol in aqueous bicarbonate–carbonate buffer solutions at 25 °C (Table S6), rate data for the enolization of diphenylacetaldehyde in aqueous sodium hydroxide solutions at 25 °C (Table S7), and absorbance changes during the enolization of diphenylacetaldehyde in aqueous sodium hydroxide solutions at 25 °C (Table S8) (12 pages). Ordering information is given on any current masthead page.
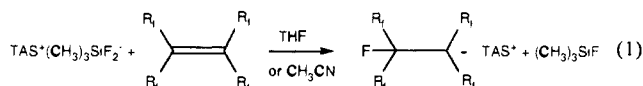
Molecular and Electronic Structure of an Isolated Perfluorocarbanion. Crystal Structure of Tris(dimethylamino)sulfonium 1,3-Bis(trifluoromethyl)-2,2,3,4,4-pentafluorocyclobutanide

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Abstract: The title compound has been synthesized, and its crystal structure has been determined by X-ray diffraction. This is the first experimental structure of a perfluorocarbanion and shows good evidence for fluorine negative anionic hyperconjugation. The C–C bond distances to the planar carbanion carbon are short, $r(C^--CF_2)$ = 1.428 Å and $r(C^--CF_3)$ = 1.443 Å. The C–F bonds on the CF₂ groups are long, $r(C-F)$ = 1.388 and 1.405 Å, and $\theta(FCF)$ is small, 100.9°. Ab initio calculations with a DZ + D_C basis set were done on a model compound obtained by substitution of a F for the 3-CF₃ group. The agreement between the theoretical model and experimental structures is excellent. Two conformers of the CF₃ group bonded to the carbanion carbon were found to have almost the same energy. This is consistent with the observed disorder of this CF₃ group in the crystal structure.

Perfluoroalkyl carbanions are well-recognized reactive intermediates in fluorocarbon chemistry.[1] We recently employed the general reaction in eq 1 for the synthesis and characterization of

several TAS perfluoroalkyl carbanion salts where TAS is [(CH₃)₂N]₃S⁺, tris(dimethylamino)sulfonium.[2] While the physical properties of the reported tertiary carbanions enable convenient isolation and solution studies, crystals of sufficient quality for X-ray diffraction analysis were not produced. We now report the crystal and molecular structure of tris(dimethylamino)sulfonium 1,3-bis(trifluoromethyl)-2,2,3,4,4-pentafluorocyclobutanide (2), prepared from the bicyclobutane 1[3] by using a fluoride-promoted C–C cleavage reaction (eq 2).

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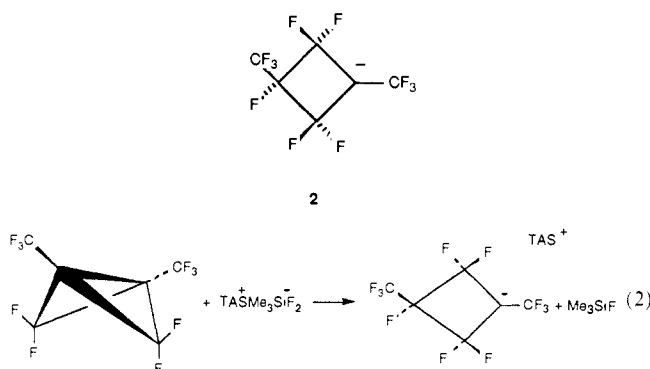
We have also been interested in characterizing the molecular properties of fluorocarbons[4] by use of ab initio molecular orbital theory. We have previously reported theoretical evidence for negative anionic hyperconjugation in fluorocarbanions based on our calculated structures.[5,6] We have previously shown structural

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