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Kinetic Behavior of Tetrachlorocyclopentadienyl-Type Anions. Deprotonation of 1,2,3,4-Tetrachloro-1,3-cyclopentadiene and Nucleophilic Addition to 1,2,3,4-Tetrachloro-6-phenylfulvene in 50% Me_2SO/50% Water

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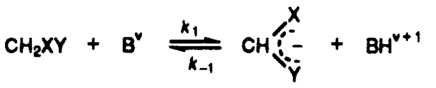
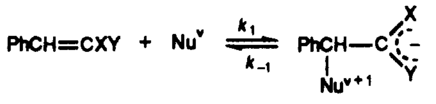
Abstract: The kinetics of the reversible deprotonation of 1,2,3,4-tetrachloro-1,3-cyclopentadiene by OH^-, piperidine, piperazine, 1-(2-hydroxyethyl)piperazine, morpholine, 1-piperazinecarboxaldehyde, *n*-butylamine, 2-methoxyethylamine, 2-chloroethylamine, and glycinamide and of reversible nucleophilic addition of piperidine and morpholine to 1,2,3,4-tetrachloro-6-phenylfulvene have been measured in 50% Me_2SO/50% water at 20 °C. Brønsted coefficients and *intrinsic* rate constants have been determined for both the proton transfers and the nucleophilic additions. The *intrinsic* rate constant for deprotonation of 1,2,3,4-tetrachloro-1,3-cyclopentadiene by the secondary alicyclic amines ($\log k_0 = 3.59$) is about halfway between that for deprotonation by piperidine and morpholine of malononitrile ($\log k_0 \approx 7.0$) and phenylnitromethane ($\log k_0 = -0.25$), while the *intrinsic* rate constant for piperidine and morpholine addition to 1,2,3,4-tetrachloro-6-phenylfulvene ($\log k_0 = 3.34$) lies about halfway between that for piperidine/morpholine addition to benzylidenemalononitrile ($\log k_0 = 4.94$) and α-nitrostilbene ($\log k_0 = 1.42$). The significance of these intrinsic rate constants with respect to resonance effects in the tetrachlorocyclopentadienyl anions and transition-state imbalances is discussed. This paper also reports the first pK_a determination of 1,2,3,4-tetrachloro-1,3-cyclopentadiene ($pK_a = 8.32$).

There is a growing body of kinetic data that suggests a strong similarity in the kinetic behavior of proton transfers that lead to the formation of carbanions (eq 1) and nucleophilic addition to electrophilic olefins that yield carbanionic adducts (eq 2).[1]



$$\mathrm{CH_2XY} + \mathrm{B}^{v} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{CH}{\genfrac{}{}{0pt}{}{\mathrm{X}}{\mathrm{Y}}}^{-} + \mathrm{BH}^{v+1} \qquad (1)$$



$$\mathrm{PhCH{=}CXY} + \mathrm{Nu}^{v} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\mathrm{Nu}^{v+1}}{\mathrm{PhCH}}\!-\!\mathrm{C}{\genfrac{}{}{0pt}{}{\mathrm{X}}{\mathrm{Y}}}^{-} \qquad (2)$$

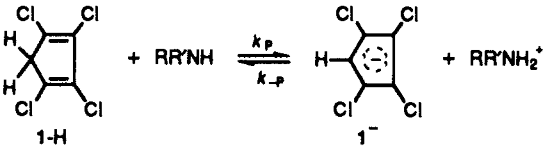
For both types of reactions, the intrinsic rate constant defined as $k_0 = k_1 = k_{-1}$ when $K_1 = 1$[2] (or the intrinsic barrier, defined as $\Delta G_1^{*} = \Delta G_{-1}^{*} = \Delta G_0^{*}$ when $\Delta G^0 = 0$) decreases (increases) with the degree of resonance stabilization of the carbanion. Figure 1 shows a plot of $\log k_0$ for piperidine and morpholine addition to olefins (eq 2) vs $\log k_0$ for proton transfer from CH_2XY to piperidine and morpholine (eq 1) for six XY combinations. The correlation between $\log k_0$ for the two types of reactions is approximated by a straight line of slope 0.46 ± 0.07.

The systems that fit the linear correlation of Figure 1 are all quite similar in the sense that the resonance forms that presumably contribute the most to the stabilization of the carbanion bear the negative charge on oxygen or nitrogen. It is not clear whether the same correlation would extend to systems where the negative charge cannot be shifted to oxygen or nitrogen but is delocalized on carbon atoms. A major motivation for the work described in this paper was to examine this question. The reactions we have investigated are the deprotonation of 1,2,3,4-tetrachloro-1,3-cyclopentadiene by amines (eq 3) and the nucleophilic addition of amines to 1,2,3,4-tetrachloro-6-phenylfulvene (eq 4).

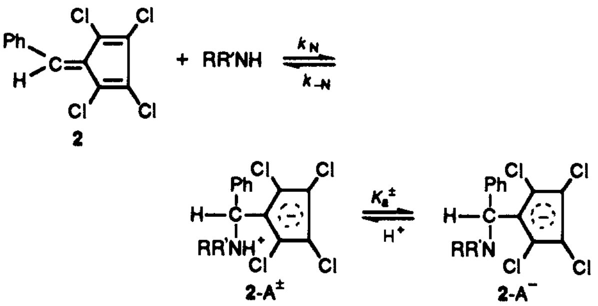
We also report what appears to be the first determination of the pK_a of 1,2,3,4-tetrachloro-1,3-cyclopentadiene.

Results

General Features. All rate and equilibrium measurements were made in 50% Me_2SO/50% water (v/v) at 20 °C and constant ionic strength of 0.5 M maintained with KCl. Pseudo-first-order conditions were used throughout with buffer bases/acids or nucleophiles as the excess components. The observed pseudo-first-order rate constants are tabulated elsewhere.[3]



(3)



(4)

pK_a of 1,2,3,4-Tetrachloro-1,3-cyclopentadiene (1-H). The pK_a was determined spectrophotometrically at 275 nm, which is close to λ_{max} of **1-H** and where **1**$^-$ has only a weak absorption (Figure 2). Basic solutions of **1**$^-$ were too unstable to take spectra or perform the spectrophotometric measurements for the pK_a determination in a conventional spectrophotometer. Hence, they were performed in a stopped-flow spectrophotometer. Figure 3 shows a plot according to eq 5 where A_A is the absorbance of the

$$\mathrm{pH} = pK_a + \log \frac{A - A_A}{A_B - A} \qquad (5)$$

acid form (**1-H**), A_B that of the basic form (**1**$^-$), and A that of a mixture of **1-H** and **1**$^-$ in morpholine buffers in the range of pH 7.58-9.36. The data yield a pK_a of 8.38 ± 0.04. As discussed below, this value is close to the kinetically determined pK_a of 8.32, which is probably more reliable than the spectrophotometric pK_a.

Reaction of 1-H with Hydroxide Ion. Rates were measured at five KOH concentrations from 0.001 to 0.005 M; at higher base concentrations, the reaction became too fast for the stopped-flow method. The observed pseudo-first-order rate constants gave an

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[1] For recent reviews, see: (a) Bernasconi, C. F. *Tetrahedron* **1989**, *45*, 4017. (b) Bernasconi, C. F. *Acc. Chem. Res.* **1987**, *20*, 301.

[2] For proton transfers, a statistical correction is usually applied with $k_0 = k_1/q = k_{-1}/p$ when $pK_a^{BH} - pK_a^{CH_2XY} + \log p/q = 0$; q is the number of equivalent basic sites on B^v, p the number of equivalent protons on BH^{v+1}

[3] Stronach, M. W. Ph.D. Thesis, University of California, Santa Cruz, 1990.

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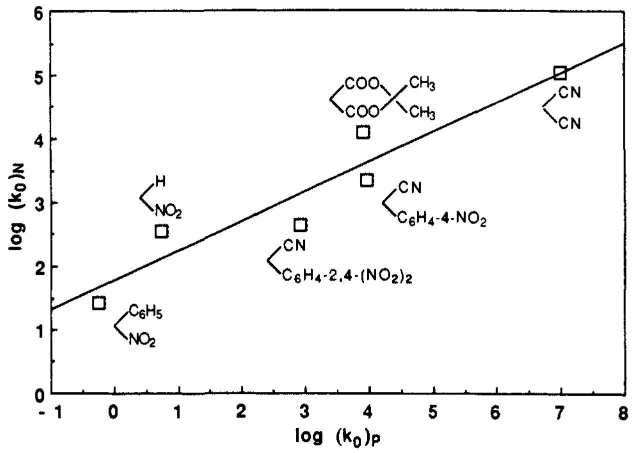

Figure 1. Correlation of intrinsic rate constants for piperidine and morpholine addition to PhCH=CXY (log $(k_0)_N$) with intrinsic rate constants for the deprotonation of CH_2XY (log $(k_0)_p$).

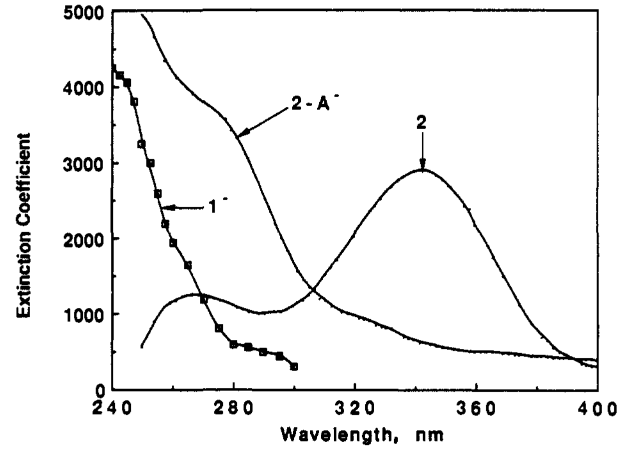

Figure 2. Absorption spectra of 1^-, **2**, and **2-A**$^-$ (A = piperidine). Spectrum of 1^- constructed from stopped-flow traces at 5-nm intervals; see text.

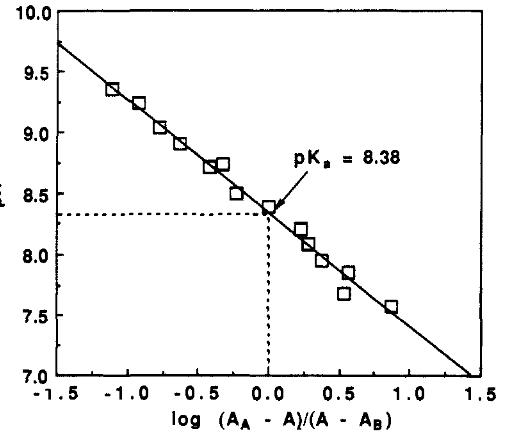

Figure 3. Spectrophotometric determination of the pK_a of **1-H** according to eq 5.

excellent straight line according to $k_{obsd} = k_p^{OH}[OH^-]$ (plot not shown), with $k_p^{OH} = (1.07 \pm 0.03) \times 10^5$ M^{-1} s^{-1} referring to the rate constant of deprotonation by OH^- shown in eq 6. From the kinetic $pK_a = 8.32$ and $pK_w = 15.90$, we obtain $k_{-p}^{H_2O} = k_p^{OH}K_w/K_a = 2.8 \pm 0.1 \times 10^{-3}$ s^{-1}.

$$\textbf{1-H} \underset{k_{-p}^{H_2O}+k_{-p}^{AH}[RR'NH_2^+]}{\overset{k_p^{OH}[OH^-]+k_p^{A}[RR'NH]}{\rightleftarrows}} 1^- \qquad (6)$$

Reactions of 1-H with Amines. k_p^{AH} and k_{-p}^{AH} for piperidine, piperazine, 1-(2-hydroxyethyl)piperazine, morpholine, 1-piperazinecarboxaldehyde, *n*-butylamine, 2-methoxyethylamine, 2-chloroethylamine, and glycinamide were determined. Figure 4 shows a plot of k_{obsd} vs piperidine concentration obtained in piperidine buffers at pH 9.49–9.96. In this pH range, all terms in eq 7 except for $k_p^A[RR'NH]$ are negligible. From the slope,

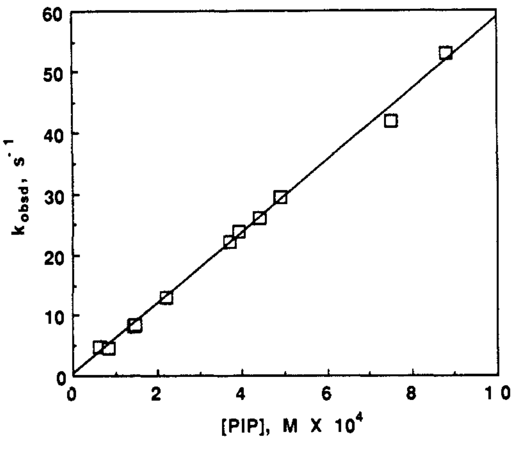

Figure 4. Deprotonation of **1-H** by piperidine in piperidine buffers at pH 9.49–9.96.

$$k_{obsd} = k_p^{OH}[OH^-] + k_{-p}^{H_2O} + k_p^A[RR'NH] + k_{-p}^{AH}[RR'NH_2^+] \qquad (7)$$

we obtain $k_p^A = 6.00 \times 10^4$ M^{-1} s^{-1} and $k_{-p}^{AH} = k_p^A K_a^{AH}/K_a(\textbf{1-H}) = 1.37 \times 10^2$ M^{-1} s^{-1} ($pK_a^{AH} = 11.02$). In a similar way, $k_p^A = 1.05 \times 10^4$ M^{-1} s^{-1} and $k_{-p}^{AH} = 49$ M^{-1} s^{-1} were obtained for *n*-butylamine.

For the reaction with morpholine, measurements were made at constant $[MorH^+] = 0.01$ M and variable [Mor] in the pH range 8.63–9.56. Under these conditions, the first two terms in eq 7 are again negligible while the fourth one is constant and a plot of k_{obsd} vs [Mor] (not shown) yields $k_p^A = 8.86 \times 10^3$ M^{-1} s^{-1} from the slope. With pK_a^{AH}, we obtain $k_{-p}^{AH} = 4.1 \times 10^3$ M^{-1} s^{-1}. An alternative method for determining k_{-p}^{AH} was to use kinetic data obtained between pH 7.58 and 8.20 and calculate k_{-p}^{AH} from eq 8. This method yields $k_{-p}^{AH} = 3.50 \times 10^3$ M^{-1} s^{-1}, in good

$$k_{-p}^{AH} = \frac{k_{obsd} - k_p^A[\text{Mor}]}{[\text{MorH}^+]} \qquad (8)$$

agreement with k_{-p}^{AH} obtained above. If one uses this k_{-p}^{AH} value in conjunction with k_p^A to calculate a pK_a for **1-H**, one obtains $pK_a = 8.32$, in good agreement with the value 8.38 determined spectrophotometrically.

With piperazine, 1-(2-hydroxyethyl)piperazine, 2-methoxyethylamine, and glycinamide, kinetic determinations were made at constant buffer ratio $[RR'NH]/[RR'NH_2^+] = 1.00$. Under these conditions, the slopes of plots of k_{obsd} vs [RR'NH] are given by $k_p^A + k_{-p}^{AH}$. k_p^A and k_{-p}^{AH} were then calculated in conjunction with $k_p^A/k_{-p}^{AH} = K_a(\textbf{1-H})/K_a^{AH}$. With 1-piperazinecarboxaldehyde, the rates were measured at $[RR'NH]/[RR'NH_2^+] = 4.00$. In this case, the slopes were given by $k_p^A + 0.25\ k_{-p}^{AH}$. The various rate constants are summarized in Table I.

Reaction of 1,2,3,4-Tetrachloro-6-phenylfulvene (2) with Amines. In basic piperidine or morpholine solutions, **2** is quantitatively converted to **2-A**$^-$ according to eq 4. Evidence for the structure of **2-A**$^-$ includes the following: (1) The UV spectrum of **2-A**$^-$ is similar to that of 1^- except that it is red-shifted relative to the latter, as shown in Figure 2 for the piperidine adduct. This red shift is characteristic for amine adducts of olefins of the general structure PhCH=CXY.[4,5] (2) When a basic solution of **2-A**$^-$

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(4) (a) Bernasconi, C. F.; Kanavarioti, A. *J. Am. Chem. Soc.* **1986**, *108*, 7744. (b) Bernasconi, C. F.; Murray, C. J.; Fox, J. P.; Carré, D. J. *J. Am. Chem. Soc.* **1983**, *105*, 4349.

(5) (a) Bernasconi, C. F.; Fornarini, S. *J. Am. Chem. Soc.* **1980**, *102*, 5329. (b) Bernasconi, C. F.; Carré, D. J. *J. Am. Chem. Soc.* **1979**, *101*, 2698.

Table I. Rate Constants for the Proton-Transfer Reactions of 1,2,3,4-Tetrachloro-1,3-cyclopentadiene with Hydroxide Ion and Amines in 50% Me_2SO/50% Water (v/v) at 20 °C[a]

base	pK_a^{AH}	k_p^A,[c] $M^{-1}\,s^{-1}$	k_{-p}^{AH},[c] $M^{-1}\,s^{-1}$
OH^-	17.34	1.07×10^5	2.8×10^{-3} [b]
piperidine	11.02	6.00×10^4	1.37×10^2
piperazine	9.90	3.04×10^4	8.00×10^2
1-(2-hydroxyethyl)piperazine	9.51	2.41×10^4	1.56×10^3
morpholine	8.72	8.86×10^3	3.50×10^3
1-piperazinecarboxaldehyde	7.97	3.34×10^3	5.82×10^3
n-butylamine	10.65	1.05×10^4	4.90×10^1
2-methoxyethylamine	9.62	2.44×10^3	1.22×10^2
2-chloroethylamine	8.70	1.20×10^3	5.00×10^2
glycinamide	8.27	4.60×10^2	5.20×10^2

[a] μ = 0.5 M (KCl). [b] Units are s^{-1}. [c] Estimated error is ±5% or less.

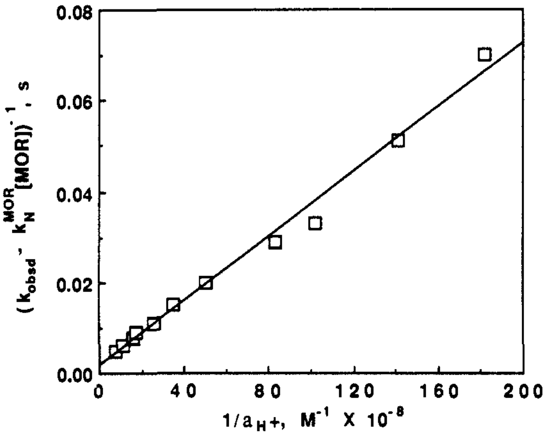

Figure 5. pH-jump data for the reaction of 1^- with morpholinium ion. Plot according to eq 10.

is acidified immediately after its preparation (pH-jump experiment), **2** is recovered almost quantitatively, but after being allowed to stand for extended periods of time, **2-A**$^-$ decomposes; this decomposition was not investigated further, although the likely products are benzaldehyde, 1^-, and amine. (3) The kinetic behavior is characteristic of the scheme of eq 4, as discussed below (see, e.g., eq 9).

Rates of nucleophilic addition were measured in 0.009 M KOH (piperidine) or 0.099 M KOH (morpholine) solutions. Plots of k_{obsd} vs amine concentration (10 concentrations from 0.001 to 0.01 M with piperidine, 0.01 to 0.1 M with morpholine) were strictly linear (not shown) with negligible intercepts and afforded $k_N^{Pip} = 1.15 \times 10^4$ $M^{-1}\,s^{-1}$ and $k_N^{Mor} = 3.07 \times 10^3$ $M^{-1}\,s^{-1}$.

$k_{-N}^{Pip} = 46.7$ s^{-1} for the breakdown of the piperidine adduct could be obtained from a pH-jump experiment by quenching **2-Pip**$^-$ with an acetate buffer at pH 5.78 in the stopped-flow apparatus. Under these conditions eq 9, which is the general expression for k_{obsd} describing eq 4, simplifies to $k_{obsd} = k_{-N}$.

$$k_{obsd} = k_N[RR'NH] + k_{-N}\frac{a_{H^+}}{K_a^{\pm} + a_{H^+}} \qquad (9)$$

By conducting pH-jump experiments in *p*-chlorophenol buffers (pH 9.58–10.81), we also determined $pK_a^{\pm}$ and k_{-N} from an inversion plot according to

$$(k_{obsd} - k_N[RR'NH])^{-1} = \frac{1}{k_{-N}} + \frac{K_a^{\pm}}{k_{-N}a_{H^+}} \qquad (10)$$

This procedure yielded $pK_a^{\pm} = 9.80$ and $k_{-N}^{Pip} = 41.7$ s^{-1}. We note the good agreement between the two k_{-N}^{Pip} values; since the first one (46.7 s^{-1}) is considered more reliable, we shall adopt its value for k_{-N}^{Pip} as well as $pK_a^{\pm} = 9.75$, which is calculated from the slope of the plot according to eq 10 with $k_{-N}^{Pip} = 46.7$ s^{-1}.

For the morpholine adduct, k_{-N}^{Mor} could not be determined by the first pH-jump method because the breakdown of **2-Mor**$^{\pm}$ is too fast for the stopped-flow technique. pH-jumps into a series of DABCO buffers (pH 7.87–9.70) and plotting the data according to eq 10 gave the plot shown in Figure 5. It yields $pK_a^{\pm} \approx 7.7$ and $k_{-N}^{Mor} \approx 600$ s^{-1}; the smallness of the intercept ($1/k_{-N}^{Mor}$) introduces a considerable uncertainty in these parameters. An alternative method is to calculate $pK_a^{\pm}$ for the morpholine adduct from the relationship in eq 11. This relationship has been shown

$$pK_a^{\pm}(Pip) - pK_a^{\pm}(Mor) \approx pK_a^{PipH} - pK_a^{MorH} \qquad (11)$$

to hold fairly well in several similar systems.[6,7] It yields $pK_a^{\pm}(Mor) \approx 7.45$ from which we obtain $k_{-N}^{Mor} \approx 10^3$ s^{-1}. We shall adopt this latter value. All rate and equilibrium constants are summarized in Table II.

Table II. Rate and Equilibrium Constants for the Reaction of Amines with 1,2,3,4-Tetrachloro-6-phenylfulvene in 50% Me_2SO/50% Water (v/v) at 20 °C[a]

parameter	morpholine (pK_a = 8.72)	piperidine (pK_a = 11.02)
k_N, $M^{-1}\,s^{-1}$	$(3.07 \pm 0.09) \times 10^3$	$(1.15 \pm 0.04) \times 10^4$
k_{-N}, s^{-1}	$(1.0 \pm 0.1) \times 10^3$	$(4.7 \pm 0.2) \times 10^1$
K_N, M^{-1}	3.1 ± 0.2	$(2.5 \pm 0.1) \times 10^2$
$pK_a^{\pm}$	7.45 ± 0.05	9.75 ± 0.02
$K_NK_a^{\pm}$	$(1.1 \pm 0.1) \times 10^{-7}$	$(4.4 \pm 0.2) \times 10^{-8}$

[a] μ = 0.5 M (KCl).

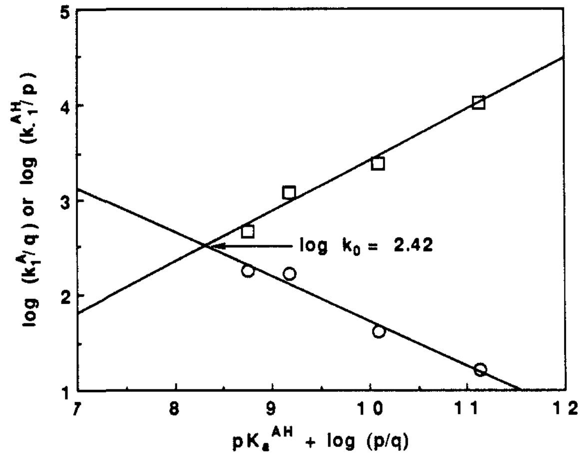

Figure 6. Brønsted plots for the reaction of **1-H** with primary amines: □, k_1^A/q; ○, k_{-1}^{AH}/p.

Discussion

pK_a of 1,2,3,4-Tetrachloro-1,3-cyclopentadiene. Despite a thorough search of the literature, we were somewhat surprised not to find any report on the pK_a of **1-H**. This is probably because the very short lifetime of the anion 1^- precludes the use of standard procedures of pK_a determinations. This instability of 1^- was already noted 35 years ago.[8] By applying a common spectrophotometric method in the *stopped-flow apparatus* that allows measurement of the absorption of 1^- a few milliseconds after its generation, we were able to determine the pK_a quite easily, and its value of 8.38 was confirmed kinetically. Since the kinetic pK_a is probably more accurate, we will adopt this latter value (8.32). This pK_a, which is substantially lower than that of the parent cyclopentadiene (16.0 in water,[9] 18.0 in Me_2SO[10]), shows the expected acidifying effect of the chlorines.

Proton Transfer from 1,2,3,4-Tetrachloro-1,3-cyclopentadiene. Rate constants referring to eq 6 are summarized in Table I. Figure 6 shows Brønsted plots for k_p^A and k_{-p}^{AH} where A are primary

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(6) (a) Bernasconi, C. F.; Panda, M. *J. Org. Chem.* **1987**, *52*, 3042. (b) Bernasconi, C. F.; Renfrow, R. A. *Ibid.* **1987**, *52*, 3035.

(7) Bernasconi, C. F.; Carré, D. J. *J. Am. Chem. Soc.* **1979**, *101*, 2698.

(8) McBee, E. T.; Meyers, R. K.; Baranauckas, C. F. *J. Am. Chem. Soc.* **1955**, *77*, 86.

(9) Streitwieser, A., Jr.; Nebenzahl, L. L. *J. Am. Chem. Soc.* **1976**, *98*, 2188.

(10) Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456.

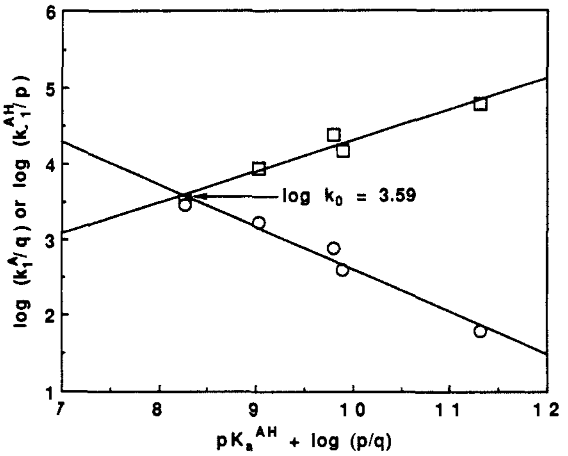


Figure 7. Brønsted plots for the reaction of **1-H** with secondary alicyclic amines: □, k_1^A/q; ○, k_{-1}^{AH}/p.

Table III. Brønsted Coefficients and Intrinsic Rate Constants for the Proton-Transfer Reactions of 1,2,3,4-Tetrachloro-1,3-cyclopentadiene with Amines and the Nucleophilic Addition of Piperidine and Morpholine to 1,2,3,4-Tetrachloro-6-phenylfulvene in 50% Me_2SO/50% Water (v/v) at 20 °C[a]

	secondary alicyclic amines	primary amines
$\mathbf{1\text{-}H} + A \rightleftharpoons \mathbf{1}^- + AH^{+}$[b]		
$\beta = d \log k_p^A / d\ pK_a^{AH}$	0.41 ± 0.06	0.53 ± 0.06
$\alpha = d \log k_{-p}^{AH} / d \log K_a^{AH}$	0.59 ± 0.06	0.47 ± 0.06
$\log k_0$	3.59 ± 0.08	2.50 ± 0.08
$\mathbf{2} + A \rightleftharpoons \mathbf{2\text{-}A}^{\pm}$[c]		
$\beta_{nuc} = d \log k_N / d\ pK_a^{AH}$	0.25 ± 0.02	
$\beta_{lg} = d \log k_{-N} / d\ pK_a^{AH}$	−0.58 ± 0.04	
$\beta_{eq} = d \log K_N / d\ pK_a^{AH}$	0.83 ± 0.06	
$\beta_{nuc}^{n} = \beta_{nuc}/\beta_{eq}$	0.30 ± 0.02	
$\beta_{lg}^{n} = \beta_{lg}/\beta_{eq}$	−0.70 ± 0.05	
$\log k_0$	3.34 ± 0.06	

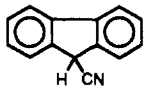
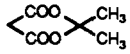
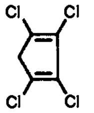
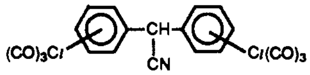
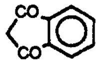
[a] μ = 0.5 M (KCl). [b] Errors are standard deviations. [c] Errors are estimated.

amines, while Figure 7 shows similar plots for the secondary alicyclic amines. Brønsted coefficients are reported in Table III. The β value for the secondary alicyclic amines (0.41 ± 0.06) is somewhat lower than that for the primary amines (0.53 ± 0.06), in agreement with similar findings reported for the deprotonation of a variety of carbon acids.[11,12]

The Brønsted plots allowed a determination of the intrinsic rate constants ($k_0 = k_p^A/q = k_{-p}^{AH}/p$ at $pK_a^{AH} - pK_a^{CH} + \log (p/q) = 0$), which are also reported in Table III. The $\log k_0$ value for the primary amines is 1.1 units lower than for the piperidine/morpholine pair. The reduced intrinsic rate constant for primary amines is part of a general pattern that has been observed in numerous systems.[11-14] It has commonly been attributed to the stronger solvation of the ammonium ions derived from primary amines and the assumption that the solvation of the incipient ammonium ion at the transition state lags behind charge development.[1b,15-17]

It is interesting to compare $\log k_0$ for the deprotonation of **1-H** by the secondary alicyclic amines with $\log k_0$ for the deprotonation of several carbon acids by the piperidine/morpholine pair under the same reaction conditions. These $\log k_0$ values, which are summarized in Table IV, fall into three ranges: a very high value of ~7.0 for malononitrile, a cluster of values in the midrange between 2.75 and 4.58 comprising eight carbon acids, and four very low values for nitromethane (0.73), phenylnitromethane (−0.25), and 2,4,4′-trinitro-2′-X-diphenylmethane (−0.1 for X = NO_2, −0.55 for X = H). $\log k_0$ = 3.70 for **1-H** fits just about into the center of the midrange.

Table IV. Intrinsic Rate Constants for the Proton-Transfer Reactions of Carbon Acids, CH_2XY, with Piperidine and Morpholine ($(\log k_0)_p$) and for the Nucleophilic Addition of the Same Amines to Olefins, PhCH=CXY ($\log (k_0)_N$), in 50% Me_2SO/50% Water (v/v) at 20 °C

$<^{X}_{Y}$	$\log (k_0)_p$	$\log (k_0)_N$
$<^{CN}_{CN}$	≈7.0[a]	4.94[b]
	4.58[c]	
	3.9[d]	4.10[e]
$<^{CN}_{C_6H_4\text{-}4\text{-}NO_2}$	≈3.70[f]	≈3.35[g]
	3.59[h]	3.34[h]
	3.30[i]	
	3.13[j]	
$<^{CN}_{C_6H_3\text{-}2,4\text{-}(NO_2)_2}$	2.75[f]	2.65[g]
$<^{COCH_3}_{COCH_3}$	2.75[k]	0.30[l]
$<^{H}_{NO_2}$	0.73[m]	2.55[n]
$<^{C_6H_3\text{-}2,4\text{-}(NO_2)_2}_{C_6H_3\text{-}2,4\text{-}(NO_2)_2}$	−0.10[o]	
$<^{C_6H_5}_{NO_2}$	−0.25[m]	1.42[p]
$<^{C_6H_4\text{-}4\text{-}NO_2}_{C_6H_3\text{-}2,4\text{-}(NO_2)_2}$	−0.55[o]	

[a] In water: Hibbert, F. *Compr. Chem. Kinet.* **1977**, *8*, 97. [b] Bernasconi, C. F.; Fox, J. P.; Fornarini, S. *J. Am. Chem. Soc.* **1980**, *102*, 2810. [c] Reference 11b. [d] Bernasconi, C. F.; Oliphant, N. Unpublished results. [e] Reference 5a. [f] Reference 34. [g] Reference 4b. [h] This work. [i] Reference 11a. [j] Reference 12b. [k] Reference 12a. [l] Reference 4a. [m] Reference 36. [n] Reference 35. [o] Reference 13, at 25 °C. [p] Reference 6b.

It has been pointed out before that, by and large, the trend toward lower intrinsic rate constants parallels the trend toward increased resonance stabilization of the carbanion.[1b,17] This trend has been attributed to an imbalanced transition state in which the development of resonance of the carbanion lags behind charge transfer. As has been elaborated upon elsewhere,[1b,17] the relationship among $\log k_0$, imbalance, and resonance may be expressed in the form of eq 12. $\delta \log k_0^{res}$ represents the difference between

$$\delta \log k_0^{res} = (\alpha_{res} - \beta)_p\ \delta \log K_p^{res} \qquad (12)$$

$\log k_0$ for the reaction under consideration ($\log k_0^{res}$) and $\log k_0$ for a (hypothetical) reference reaction in which the carbanion is stabilized by polar effects only ($\log k_0^{pol}$), i.e., $\delta \log k_0^{res} = \log k_0^{res} - \log k_0^{pol}$; $\delta \log K_p^{res}$ is the increase in the equilibrium constant of the reaction that is caused by the resonance effect; β is the Brønsted β value defined earlier and is assumed to be an approximate measure of charge transfer at the transition state;[18] and

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α^{res} (not to be confused with the Brønsted α = d log k_1^A/d log K_a^{AH} or d log k_1^A/d log K_a^{CH}) is a measure of progress in the resonance development at the transition state. When this progress lags behind charge transfer, we have $\alpha^{res} < \beta$, and hence, δ log $k_0^{res} < 0$ for δ log $K_p^{res} > 0$. For a given $(\alpha_{res} - \beta)_p$, the decrease in log k_0 is, thus, proportional to the resonance stabilization δ log K_p^{res}.

The simplest interpretation of the trends in Table IV is to assume that $(\alpha_{res} - \beta)_p$ is more or less independent of the carbon acid, and hence, there is a direct proportionality between δ log k_0^{res} and δ log K_p^{res}. This is likely to be an oversimplification, but in the absence of quantitative measures of the resonance effects, which are also strongly influenced by solvation,[17,26-28] this assumption serves us well as a first approximation. Thus, the ordering of the log k_0 values in Table IV indeed reflects the expected strength of the resonance effect in the carbanions. This is most obvious when comparing the log k_0 values for the three clusters of carbon acids referred to earlier: The malononitrile anion, even though not devoid of resonance, derives most of its stabilization from the polar effect of the cyano groups. The seven carbon acids in the midrange all lead to carbanions with substantial resonance stabilization. With the nitronate ions, the resonance effect is maximal, particularly in a hydroxylic solvent with $CH_2{=}NO_2^-$ and $PhCH{=}NO_2^-$ because of strong hydrogen-bonding solvation to the oxygens.

Within the midrange group, an exact rank ordering according to the strength of the resonance effect is perhaps not completely unambiguous a priori, especially because of the different effects of solvation on enolate ions compared to, say, aromatic anions. Nevertheless, even within this group there are clearcut correlations of log k_0 with expected resonance effects. For example, the lower log k_0 for 2,4-dinitrophenylacetonitrile compared to 4-nitrophenylacetonitrile undoubtedly reflects a stronger resonance effect in the carbanion and so do the lower log k_0 values for 1,3-indandione and acetylacetone compared to that for Meldrum's acid.[29]

Our current finding that log k_0 for 1,2,3,4-tetrachloro-1,3-cyclopentadiene is $\approx$1 log unit lower than for 9-cyanofluorene also fits into this trend: The pK_a values of the parent hydrocarbons cyclopentadiene (16.0 in water,[9] 18.0 in Me_2SO[10]) and fluorene (23.04 in CsCHA,[30] 23.0 in Me_2SO[10]) indicate that the resonance stabilization of the cyclopentadienyl anion is substantially stronger than that of the fluorenyl anion. Substituting the hydrogens with chlorines in the cyclopentadienyl anion is not expected to alter the resonance effect significantly, while substituting a 9-hydrogen with a 9-cyano group may add a slight amount of resonance stabilization to the fluorenyl anion, but probably not enough to bring it close to that of the 1,2,3,4-tetrachloropentadienyl anion. In fact, in view of the accumulating number of examples that show a direct correlation between log k_0 and resonance in the carbanion,[31] we may take the lower k_0 for the deprotonation of **1-H** compared to the deprotonation of 9-cyanofluorene as evidence for a larger resonance effect in **1**$^-$ compared to the 9-cyanofluorenyl anion.

In terms of a more general proposition, our results suggest that the lag in the resonance development at the transition state and its effect of lowering k_0 is quite independent of whether the resonance stabilization occurs through delocalization of the negative charge onto electronegative atoms such as oxygen or nitrogen, or onto carbon. What seems to matter the most is the magnitude of the resonance effect, i.e., δ log K_p^{res} in eq 12, whereas $(\alpha_{res} - \beta)_p$ appears to be quite independent of the type of resonance. We suggest, therefore, that in cases where an independent assessment of resonance effects in a carbanion may be difficult to come by, log k_0 of its proton transfer reaction could serve as an approximate measure of this resonance effect.

Nucleophilic Addition to 1,2,3,4-Tetrachloro-6-phenylfulvene. Rate and equilibrium constants as defined in eq 4 are summarized in Table II. β_{nuc}, β_{lg}, β_{eq}, β_{nuc}^n, and β_{lg}^n values are collected in Table III; log k_0 with the intrinsic rate constant defined as $k_0 = k_N = k_{-N}$ when $K_N = k_N/k_{-N} = 1$ is also given in Table III. Since the main purpose of our studying amine addition to **2** was to determine k_0 for the piperidine/morpholine pair rather than to construct an accurate Brønsted plot based on a large number of amines, the various Brønsted coefficients are necessarily not very accurate and, therefore, not too much significance should be attached to their numerical values. Nevertheless, we note that $\beta_{nuc}^n = 0.30$ falls into the range of β_{nuc}^n values observed before for piperidine/morpholine addition to several olefins with comparable equilibrium constants.[1a]

Regarding the intrinsic rate constant, we note that, just as log k_0 for the deprotonation of **1-H** falls about halfway between the two extreme values for proton transfers (Table IV), so does log k_0 for piperidine/morpholine addition to **2** when compared with piperidine/morpholine addition to other electrophilic olefins (Table IV). In fact, log $(k_0)_N$ for **2** is the same as for α-cyano-4-nitrostilbene, just as log $(k_0)_p$ for **1-H** is virtually the same as for 4-nitrophenylacetonitrile! Hence, the correlation line in Figure 1 remains essentially unchanged when the **2**/**1-H** pair is included. (Regarding the exclusion of the benzylideneacetylacetone/acetylacetone point from the correlation, see ref 4a.)

The good fit of the **2**/**1-H** pair with the other olefin/carbon acid pairs is an important result because it shows that the correlation between the log k_0 values for the two kinds of reactions is not restricted to systems whose carbanions are all characterized by resonance forms bearing negative charge on oxygen or nitrogen. This result is perhaps not surprising in view of our conclusions reached above regarding log k_0 for the deprotonation of **1-H**, in particular the finding that the type of resonance (delocalization of the negative charge onto electronegative atoms or carbon) does not seem to have a significant effect on how much its development in the transition state lags behind charge transfer and, hence, how much this lag depresses k_0.

The straight-line correlation shown in Figure 1 suggests that an equation similar to eq 12 for proton transfers should be valid

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(18) This is the traditional interpretation of β in proton transfers (or β_{nuc}^n in nucleophilic addition), which usually also equates degree of bond formation with degree of charge transfer.[19,20] However, the presumption that bond order and charge transfer are linearly related has been criticized;[21] more seriously, the relationship between charge transfer and Brønsted coefficients has been questioned, particularly in nucleophilic reactions, even in cases where the charge transfer occurs without the involvement of resonance effects.[21-23] When resonance and also strong solvation effects are involved that lead to imbalances between charge transfer and the development (or disappearance) of resonance or solvation, the Brønsted coefficients are well-known not to be good measures of the charge transfer.[1,17,24,25]

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(31) Besides Table IV, see also ref 13 and: Bunting, J. W.; Stefanidis, D. *J. Am. Chem. Soc.* **1988**, *110*, 4008.

(32) The log $(k_0)_N$ for benzylideneacetylacetone shows a strong negative deviation and is not included in Figure 1. This deviation has been attributed to strong intramolecular hydrogen bonding in the adduct, which is poorly developed in the transition state, and a steric effect that is strongly developed in the transition state.[4a] More on this type of steric effect below.

for nucleophilic addition (eq 13). Here β_{nuc}^{n} is used as the

$$\delta \log k_0^{res} = (\alpha_{res} - \beta_{nuc}^{n})_N \, \delta \log K_N^{res} \qquad (13)$$

measure for charge transfer at the transition state.[18] The fact that the slope of the line in Figure 1 is only 0.46 instead of unity may be interpreted in different ways. One extreme view is that the reduced dependence of log $(k_0)_N$ on XY is entirely due to $(\alpha_{res} - \beta_{nuc}^{n})_N$ in eq 13 being only 0.46 times as large as $(\alpha_{res} - \beta)_p$ in eq 12. This view implies that the resonance stabilization of the carbanions formed in the nucleophilic additions ($\delta \log K_N^{res}$) and in the proton transfers ($\delta \log K_p^{res}$) is the same but that the lag in the development of this resonance behind charge transfer is much smaller in the nucleophilic addition reactions. This is the point of view that has been emphasized in previous discussions.[1,33]

At the other extreme is the notion that it is $(\alpha_{res} - \beta_{nuc}^{n})_N$ and $(\alpha_{res} - \beta)_p$ that are the same, while $\delta \log K_N^{res}$ is only 0.46 as large as $\delta \log K_p^{res}$. The true state of affairs is probably somewhere in the middle: i.e., $(\alpha_{res} - \beta_{nuc}^{n})_N$ is somewhat smaller than $(\alpha_{res} - \beta)_p$, and $\delta \log K_N^{res}$ is somewhat smaller than $\delta \log K_p^{res}$. As shown in the Appendix, the slope of the line in Figure 1 is then equal to uv with $u = (\alpha_{res} - \beta_{nuc}^{n})_N/(\alpha_{res} - \beta)_p$ and $v = \delta \log K_N^{res}/\delta \log K_p^{res}$.

A reduction in the resonance stabilization ($\delta \log K_N^{res}$) in the olefin adducts is most likely to arise from a steric effect that hinders optimal π-overlap with the XY groups. A direct manifestation of this effect can be seen from comparisons of equilibrium constants for addition to olefins (K_N) with pK_a values of carbon acids. For example, K_N for piperidine addition to α-cyano-2,4-dinitrostilbene is only 36.1-fold larger than K_N for piperidine addition to α-cyano-4-nitrostilbene,[4b] while the acidity constants of 2,4-dinitrophenylacetonitrile and 4-nitrophenylacetonitrile differ by a factor of 3.63×10^4.[34] Similar conclusions can be reached when K_N for piperidine addition to β-nitrostyrene[35] and α-nitrostilbene[6b] are compared with the pK_a difference between nitromethane and phenylnitromethane.[36]

With respect to the lag in resonance development, there are two main factors that can make $(\alpha_{res} - \beta_{nuc}^{n})_N$ smaller than $(\alpha_{res} - \beta)_p$. The first is the sp^2 hybridization of the procarbanionic carbon in the olefin that facilitates π-overlap with X and Y in the transition state and, hence, reduces the lag in the resonance development. The second is hydrogen bonding in the transition state of the proton transfers. As has been discussed in more detail previously,[37] this hydrogen bonding may stabilize the negative charge on the carbon, thereby exacerbating the lag in resonance development and, hence, increase the absolute magnitude of $(\alpha_{res} - \beta)_p$ compared to a situation in which such hydrogen bonding is absent.

Considering that both $(\alpha_{res} - \beta_{nuc}^{n})_N$ and $\delta \log K_N^{res}$ in eq 13 differ from the corresponding quantities in eq 12, it is perhaps remarkable that, despite some significant scatter, the correlation in Figure 1 is as good as it is. One potential source of the scatter is that the reduction in $\delta \log K_N^{res}$ caused by steric hindrance probably varies significantly from one olefin to another. According to eq 13, $\delta \log k_0^{res}$ should be less negative if $\delta \log K_N^{res}$ is sterically reduced. This would translate into a *positive* deviation from the line in Figure 1.

However, it appears that the olefins with the bulkier XY groups deviate *negatively* from the line. This suggests that the steric effects may increase $(\alpha_{res} - \beta_{nuc}^{n})_N$ in such a way as to overcompensate for the decrease in the absolute magnitude of $\delta \log K_N^{res}$ or more likely to lower k_0 by a separate mechanism. As elaborated upon elsewhere,[4a] steric effects that develop ahead of charge transfer at the transition state provide such a mechanism; i.e., they lower k_0 in addition reactions. This can be expressed by eq 14

$$\delta \log k_0^{st} = (\alpha_{st} - \beta_{nuc}^{n}) \, \delta \log K_N^{st} \qquad (14)$$

in which $\delta \log K_N^{st}$ is the reduction in the equilibrium constant that is caused by the steric effect and α_{st} is the progress in the development of the steric effect at the transition state. Equation 14 shows that $\delta \log k_0^{st} < 0$ for $\alpha_{st} > \beta_{nuc}^{n}$ and $\delta \log K_N^{st} < 0$. Inasmuch as the rigidity of the π-system in the olefin already forces the XY groups into an arrangement that will lead to steric crowding in the transition state and adduct, this situation is indeed tantamount to an early development of the steric effect.

Experimental Section

Materials. Substrates were prepared according to literature procedures.[8,38] 1,2,3,4-Tetrachloro-1,3-cyclopentadiene gave a mp 61–62 °C (lit.[8] mp 62–63 °C). 1,2,3,4-Tetrachloro-6-phenylfulvene (prepared by adapting a literature procedure[8]), crystallized in long needles from ethanol, had a deep metallic iodine color, mp 80–81 °C, and a ^{1}H NMR spectrum in CCl$_4$ (Varian EM-360, 60 MHz) with two unresolved peaks centered at 7.2 and 7.4 ppm downfield from TMS. Morpholine, piperidine, *n*-butylamine, and 2-methoxyethylamine were purified and stored as described previously.[5b] Piperazine was recrystallized from 95% hexanes/5% acetone. Glycinamide and 2-chloroethylamine buffers were prepared from their hydrochloride salts. 1-(2-Hydroxyethyl)piperazine and 1-piperazinecarboxaldehyde were used without further purification. Me$_2$SO was stored over 4-Å molecular sieves or distilled from CaH$_2$ prior to use.

Reaction Solutions. 50% Me$_2$SO/50% water (v/v) solutions were prepared by adding appropriate amounts of aqueous stock solutions to a volumetric flask containing a measured amount of Me$_2$SO that would correspond to 50% of the final volume and then diluting to the mark with water. Ionic strength was maintained at 0.5 M with added KCl.

pH and pK_a Measurements. All pH measurements were performed on an Orion Research 611 digital pH meter with a Corning No. 476022 glass electrode and a Beckman No. 39400 calomel reference electrode. The pH meters were calibrated for 50% Me$_2$SO/50% water solutions with standard buffer solutions described by Hallé et al.[39] The pK_a's of piperazine, 1-(2-hydroxyethyl)piperazine, 1-piperazinecarboxaldehyde, and 2-chloroethylamine were determined by averaging the pH measurements for six solutions with $[AH^+]/[A] = 1$ for concentrations of amine between 0.001 and 0.01 M.

UV-Visible Spectra. UV-visible spectra of **2** and **2-A**$^-$ were obtained on a Perkin-Elmer 559A UV-visible spectrophotometer. A spectrum of **1**$^-$ in 50% *p*-dioxane/50% H$_2$O at 20.0 °C with $\mu = 0.5$ M was taken on a Durrum-Gibson D-110 stopped-flow spectrophotometer by injecting **1** in 0.01 M HCl before mixing in the stopped flow to give a final solution of **1**$^-$ in 0.01 M KOH. The spectrum was constructed from traces obtained at 5-nm intervals.

Kinetic Measurements. All kinetic runs were performed with a Durrum-Gibson D-110 stopped-flow spectrophotometer with computerized data acquisition and analysis. The deprotonation of **1-H** ($\epsilon = 2900$) was monitored at 275 nm (λ_{max} of **1** is 259 nm in 50% *p*-dioxane/50% water, $\epsilon = 4500$) and the nucleophilic addition to **2** at 340 nm (λ_{max} of **2** is 343 nm).

Acknowledgment. This research was supported by Grant No. CHE-8921739 from the National Science Foundation.

Appendix

The straight line plot in Figure 1 can be expressed as

$$\log (k_0)_N = c + \text{slope} \times \log (k_0)_p \qquad (A1)$$

Equation A1 follows directly from eqs 12 and 13 if the following conditions are met: (1) $(\alpha_{res} - \beta_{nuc}^{n})_N$ is a constant fraction of $(\alpha_{res} - \beta)_p$, i.e., independent of XY (eq A2). (2) $\delta \log K_N^{res}$ is

$$\frac{(\alpha_{res} - \beta_{nuc}^{n})_N}{(\alpha_{res} - \beta)_p} = u \qquad (A2)$$

a constant fraction of $\delta \log K_p^{res}$; i.e., eq A3 holds. According

$$\frac{\delta \log K_N^{res}}{\delta \log K_p^{res}} = v \qquad (A3)$$

to eq 12, log $(k_0)_p$ is given by

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$$\log (k_0)_p = a + \delta \log k_0^{res} = a + (\alpha_{res} - \beta)_p \, \delta \log K_p^{res} \quad (A4)$$

with *a* being $\log (k_0)_p$ for a reference acid in which the carbanion is stabilized by polar effects only. In a similar way, eq A5 holds for nucleophilic additions.

$$\log (k_0)_N = b + \delta \log k_0^{res} = b + (\alpha_{res} - \beta_{nuc}{}^{n})_N \, \delta \log K_N^{res} \quad (A5)$$

Substituting $u(\alpha_{res} - \beta)_p$ for $(\alpha_{res} - \beta_{nuc}{}^{n})_N$ (eq A2) and $v(\delta \log K_p^{res})$ for $\delta \log K_N^{res}$ in eq A5 yields

$$\log (k_0)_N = b + uv(\alpha_{res} - \beta)_p \, \delta \log K_p^{res} \quad (A6)$$

From eq A4 we obtain

$$(\alpha_{res} - \beta)_p \, \delta \log K_p^{res} = \log (k_0)_p - a \quad (A7)$$

Combining eqs A6 and A7 leads to

$$\log (k_0)_N = c + uv \log (k_0)_p \quad (A8)$$

which is equivalent to eq A1 with slope = *uv* and *c* = *b* − *auv*.

Kinetic Method for the Measurement of the pK_R Value of the Triphenylmethyl Cation in the Aqueous Standard State

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Abstract: A kinetic method is presented for the measurement directly in the aqueous standard state of the equilibrium constant K_R for the reaction $Ph_3C^+ + H_2O = Ph_3COH + H^+$. The basis of the procedure is direct measurement of the rate constant k_f for the reaction proceeding in the forward direction with the technique of laser flash photolysis. The rate constant k_r for the reverse reaction is measured by following oxygen exchange in a labeled alcohol in a weakly acidic (0.005 M HCl) solution. At 25 °C in water, $k_f = (1.68 \pm 0.06) \times 10^5\ s^{-1}$, $k_r = (5.79 \pm 0.29) \times 10^{-2}\ M^{-1}\ s^{-1}$, and the value for p$K_R$ calculated from their ratio is −6.46 ± 0.03. The value for k_r is based on a slight extrapolation from 5% acetonitrile in water. The value for k_f is measured in water. This directly measured value for pK_R provides a test of the validity of the acidity function and excess acidity methods commonly employed to determine p*K* values for weak bases where the equilibrium with the conjugate acid form can only be studied in strong acids. Values of pK_R previously reported for Ph_3C^+ based upon these approaches vary from −5.85 to −6.89, although the range is smaller, −6.44 to −6.89, if data obtained in concentrated HCl are omitted. The conclusion is that these methods *do* lead to pK_R values in reasonable agreement with the directly measured number.

The measurement of the equilibrium constant pK_R for a carbenium ion–carbinol equilibrium (eqs 1a,b) can be carried out in a straightforward manner when the value lies within the range of about 2–12. In such a case, R^+ and ROH coexist at equilibrium in significant amounts in some aqueous solution that is ideal or close to ideal. Thus, when their concentrations (or ratio of concentrations) are measured, the equilibrium constant can be calculated from eq 1b with use of the known $[H^+]$ concentration. This situation is found with highly stabilized carbenium ions,[2] such as tropylium ions and triarylmethyl cations bearing at least one *p*-dimethylamino substituent. However, for less stable carbenium ions, nondilute acids are required in order to obtain solutions with significant amounts of cation present, for example, >45% H_2SO_4 in the case of the parent triphenylmethyl cation.[3] In such solutions, concentrations cannot be equated to activities,[4] and some form of extrapolation is needed to obtain the thermodynamic pK_R value in the aqueous standard state. The same problem arises in the measurement of pK_a values of the conjugate acids of weak bases which protonate only in concentrated acids. These pK_a and pK_R values have considerable importance in the understanding of quantitative structure–activity relationships as well as in the analysis of the mechanisms of reactions that occur in nondilute acids. In consequence, there has been an extensive effort to develop methods for their determination. This has generally involved the establishement of acidity scales that incorporate the necessary activity coefficients and activities in such a way that p*K* values can be calculated from knowledge of the measured ionization ratios $[R^+]$:[ROH] or $[BH^+]$:[B]. A number of approaches have been suggested, with two now the most widely used, the Hammett acidity function method and the excess acidity method. These procedures, particularly those involving acidity functions, have been reviewed on a number of occasions.[5] The details will not be discussed here; the acidity scales are usually based on some assumption of equivalency or proportionality of a ratio of activity coefficients and activities. In general, the acidity function and excess acidity methods give p*K* values that are in reasonable agreement, although differences are occassionally large for systems that require study in very concentrated acids. The acidity function method has been critized because, even for structurally related systems, there is frequently not the exact parallelism of log (ionization ratios) required by the basic postulate.[6] It has also been pointed out that the various acidity function scales do not

$$R^+ + H_2O \underset{k_r}{\overset{k_f}{\rightleftharpoons}} ROH + H^+ \quad (1a)$$

$$K_R = \frac{[ROH][H^+]}{[R^+]} = \frac{k_f}{k_r} \quad (1b)$$

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