Lower yields obtained using other alcohols, methanol, 2-propanol, and ethylene glycol in the isobutylene-S_2Cl_2 adduct reaction with sodium hydrosulfide were 2, 15, and 4%, respectively.

B. From 2-Chloro-2-methylpropyl Disulfide. 2-Chloro-2-methylpropyl disulfide (99 g) (obtained from the addition of hydrogen chloride to methallyl disulfide in ethanol as a pale yellow liquid, bp 100–101 °C at 0.05 mm) was added to sodium hydrosulfide (27 g) in 100 mL of ethanol at 45–47 °C; there was obtained a total of 4.8 g (33%) of white solids not depressed in melting point by admixture with solids of part A and having matching infrared and NMR spectra.

C. From Methallyl Disulfide. To 30 g of sodium hydrosulfide in 100 mL of ethanol saturated with hydrogen sulfide was added a solution of 8.7 g of methallyl disulfide in 20 mL of ethanol. From this reaction, there was isolated 3.7 g of the same white solids obtained in A and B above. In addition, 3.5 g of an oil–solids reaction product fraction was estimated to contain about 5% of the same solids (infrared spectrum). In independent experiments, hydrogen sulfide did not add to methallyl disulfide in ethanol and sodium hydrosulfide did not react with methallyl disulfide to form the white solids of A and B in the absence of hydrogen sulfide.

D. From Sodium Methallylthiosulfate (Bunte Salt). A mixture of 95 g of sodium methallylthiosulfate (from the reaction of methallyl chloride with sodium thiosulfate) and 135 g of sodium hydrosulfide in 500 mL of ethanol was stirred and heated at 45–50 °C for 3 h while passing hydrogen sulfide into the reaction mixture. The reaction mixture was filtered; the filtrate was taken up in benzene, refiltered, dried, and concentrated by evaporation of solvents. From the residue there was obtained by direct precipitation and column chromatography over neutral alumina (elution by benzene and dichloromethane and trituration of the solvent-free eluent fractions with 30–60 °C petroleum ether) a total of 4.5 g of **1**.

Reduction of 1 to 2,2-Dimethyl-1,2-ethanedithiol. Thirty grams of **1** in 1 L of tetrahydrofuran was stirred at reflux with 10 g of $LiAlH_4$ for 4 h. The solution was treated with water and 15% sulfuric acid and dried over anhydrous $MgSO_4$ and the solvent was removed. The residue was distilled to afford 20 g of foul-smelling, oily liquid, bp 134–135 °C, which was identified by elemental analysis and ^1H NMR and infrared spectroscopy as 2,2-dimethyl-1,2-ethanedithiol. Anal. Calcd for $C_4H_{10}S_2$: C, 39.34; H, 8.24. Found: C, 40.05; H, 8.22. ^1H NMR (CS_2): δ 1.42 (s, 3, CH_3), 2.69 (d, 2, CH_2), 1.98 (s, 1, CSH), 1.68 (t, 1, CH_2SH). IR (neat, KBr optics): 2960 (s), 2922 (s), 2862 (s), 2545 (m), 1460 (s), 1445 (m), 1435 (m), 1412 (m), 1380 (s), 1275 (m), 1238 (w), 1200 (m), 1146 (w), 1115 (s), 1012 (w), 975 (w), 920 (w), 862 (w), 832 (w), 812 (w), 720 (m), 692 (m), 622 (m), 575 cm^{-1} (m).

Supplementary Material Available: Table I, observed and calculated powder data for polydisulfide I, and Figure 3, comparison of the computed and experimental X-ray diffraction patterns (λ = Cu Kα) of polydisulfide I (3 pages). Ordering information is given on any current masthead page.

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Stopped-Flow Kinetics of Proton Transfer Involving Cyclopentadiene Derivatives

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Abstract: Rates of protonation of cyclopentadienide ions and deprotonation of cyclopentadienes in aqueous solution have been measured by the stopped-flow method at 30 °C. Substrates investigated include 1-nitro-, 1-formyl-, 1-acetyl-, 1-methoxycarbonyl-, and 1,2-bis(methoxycarbonyl)cyclopentadienes, whose pK_as were found to be 3.25, 7.40, 8.84, 10.35, and 5.00, respectively. Plots of the logarithms of the rate constants against pK_a were found to be roughly linear, falling in the range of scattering of those found previously with nonconjugated nitro and carbonyl compounds. General acid–base catalyses obeyed the Brønsted law with substantial downward deviations of the H_3O^+, H_2O, and OH^- plots. The reasons for the reduction in rate of proton transfer to and from carbon have been discussed.

Proton transfers between electronegative atoms such as N and O are very fast and diffusion controlled if the process is thermodynamically favorable, whereas those involving carbon are usually quite slow.[1] Numerous examples of such slow proton transfers have been known ever since the first discovery by Hantzsch[2] with nitromethane. Reasons for the reduction in rate of proton transfer involving carbon acids have been discussed by a number of investigators.[1,3-6] The reasons considered include (1) the small hydrogen-bonding ability of carbon acid, (2) the electronic and structural reorganization on going from the acid to its conjugate base (carbanion), and (3) the accompanying reorientation of solvent molecules. The second one is established to be important and the electronic delocalization in carbanions is often emphasized as a crucial factor to retard the proton transfer. If this is in fact the case, the process involving a carbanion of electronic structure quite different from the others may exhibit some anomalies in its rate.

As a class of carbon acids with such a possibility, we here choose cyclopentadiene derivatives, **1a–5a.** Their conjugate bases, **1b–5b,** are cyclopentadienide ions of 6π aromatic electron delocalization. The rates of proton transfers involving these compounds were directly measured by means of stopped-flow spectrophotometry. Most of the rate measurements so far made with carbon acids have been indirect and limited to nitro alkanes and carbonyl compounds. Cyano and

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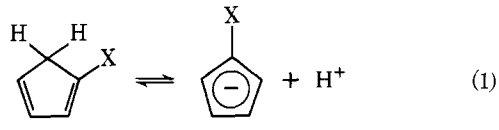
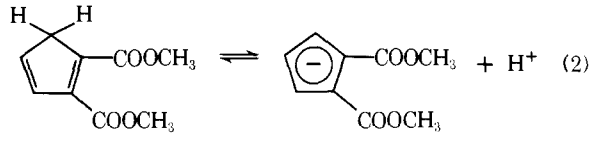


(1)

1a, X = NO_2 **1b**, X = NO_2
2a, X = CHO **2b**, X = CHO
3a, X = CH_3CO **3b**, X = CH_3CO
4a, X = CH_3OCO **4b**, X = CH_3OCO



(2)

5a **5b**

sulfonyl derivatives showed behavior different from that of typical carbon acids.[6]

The present results in comparison with related data have indicated that the nuclear (structural) reorganization on going from the acid to its conjugate base is a main cause of the activation barrier against proton transfer involving usual carbon acids but that the electronic delocalization in carbanions is only the result of the nuclear reorganization and is not essential in determining the rate of proton transfer.

Experimental Section

Materials. Sodium nitrocyclopentadienide (**1b**) was prepared by the reaction of ethyl nitrate with sodium cyclopentadienide.[7] NMR: δ (D_2O) 6.50 (m) and 6.21 (m). UV: λ_{max} (H_2O) 232 and 362 nm; conjugate acid (**1a**), 335 nm.

Sodium formylcyclopentadienide (**2b**) and acetylcyclopentadienide (**3b**) were obtained by the reaction of sodium cyclopentadienide with ethyl formate and ethyl acetate, respectively.[8] NMR: δ (D_2O) **2b**, 8.58 (s), 6.56 (m), 6.23 (m); **3b**, 6.61 (m), 6.15 (m), 2.28 (s). UV: λ_{max} (H_2O) **2b**, 307 nm; **2a**, 294 nm; **3b**, 314 nm; **3a**, 292 nm.

1-Methoxycarbonylcyclopentadiene (**4a**) was prepared from Theile's dimeric acid which was obtained by the method of Ziegler et al.[9] The dimeric acid was esterified in methanol.[10] The dimeric ester, melting at 85 °C (lit.[11] mp 85 °C), was then subjected to the degradative distillation under reduced pressure by maintaining the receiver at −70 °C. The sample of **4a** obtained was stored as an acetonitrile solution in a refrigerator to avoid dimerization. UV: λ_{max} (H_2O) 278 nm; **4b**, 294 nm.

Sodium 1,2-bis(methoxycarbonyl)cyclopentadienide (**5b**) was prepared from cyclopentadienide and methyl chloroformate.[12] NMR: δ (D_2O) 6.75 (2 H, d, J = 3.8 Hz), 5.93 (1 H, t, J = 3.8 Hz), 3.70 (6 H, s). NMR spectra showed that the product contained 20% of 1,3 isomer [δ 7.17 (1 H, t, J = 2.3 Hz), 6.46 (2 H, d, J = 2.3 Hz), 3.70 (6 H, s)]. UV: λ_{max} (H_2O) 225 and 309 nm; **5a**, 282 nm.

Protonation of 2b and 3b. A sample of 200 mg of **2b** or **3b** was dissolved in 5 mL of water, followed by successive additions of 5 mL of 1 M aqueous HCl and 5 mL of CCl_4 with shaking. The resulting organic phase was separated, filtered through a layer of $MgSO_4$, and immediately subjected to ^1H NMR analysis: δ (CCl_4) **2a**, 3.22 (2 H, m), 6.7 (2 H, m), 7.3 (1 H, m), 9.85 (1 H, s); **3a**, 2.26 (3 H, s), 3.18 (2 H, m), 6.6 (2 H, m), 7.2 (1 H, m).

pK_a Measurements. Values of pK_a were determined spectrophotometrically at 30 °C with use of a Shimadzu spectrophotometer UV-200 equipped with a water-jacketed cell holder. An aqueous stock solution of a cyclopentadienide (**1b–3b** and **5b**) was diluted with a buffer solution of varying pH. The ionic strength of the resulting solution was adjusted to 0.5 by adding KCl. With **4a**, a stock solution in acetonitrile was used; the sample solutions used contained 5 vol % of CH_3CN. From the absorption at an appropriate wavelength (λ_{max} of cyclopentadienide), the fraction of the conjugate base (cyclopentadienide) was calculated and plotted against pH. A sigmoid curve thus obtained gave pK_a as the pH value at an inflection point. With **2**, whose absorbances changed gradually ($t_{1/2}$ > 10 h), the absorbance readings were extrapolated to the time of sample preparation.

Kinetics. The rates of proton transfer were measured by means of a stopped-flow spectrophotometer Union RA-1100. Decrease and increase of the absorbance at λ_{max} of cyclopentadienide were followed at lower and higher pH regions, respectively. The stock solutions of conjugate base and acid were used accordingly. Thus the sample base solutions were prepared by dissolving an appropriate amount of a cyclopentadienide (**1b–3b** and **5b**) in 0.5 M aqueous KCl or by diluting a CH_3CN solution of **4a** with 0.001 M aqueous NaOH of ionic strength of 0.5 (KCl), the resulting solution containing 1 vol % of CH_3CN. In the same manner, the acid solutions were prepared by dissolving a cyclopentadienide in 0.001 M HCl (μ = 0.5) or by diluting a CH_3CN solution of **4a** with 0.5 M aqueous KCl.

An appropriate sample solution of either acid or base and a buffer solution (μ = 0.5) were thermally equilibrated at 30 °C in separate reservoirs of the stopped-flow apparatus and then mixed by the pressure drive. The change in absorbance of the mixture with time was recorded by means of a high-speed memory unit Union RA-108S and displayed on an x-y recorder National VP-6421A. The first-order plots of absorbance with respect to time were linear over 90% reactions when the absorbance at infinite time (i.e., equilibrium) was stable. With **4** and **5** at higher pH, the absorbance at equilibrium happened to be unstable, so a modified Guggenheim analysis[13] was adopted to obtain the first-order rate constants.

Results

Rates of proton transfer were measured in aqueous solutions at the ionic strength of 0.5 (KCl) and 30 °C. Spectral change due to the formation (at higher pH) or the disappearance (at lower pH) of the cyclopentadienide ion was followed directly by means of the stopped-flow spectrophotometry. Observed first-order rate constants, k_{obsd}, were buffer dependent in the whole pH region. Extrapolation of k_{obsd} to zero buffer concentration gives the buffer-independent rate constant, k_0.

$$k_{obsd} = k_0 + k_{Buf}[Buf] \tag{3}$$

Figures 1 and 2 show plots of log k_0 against pH for the substrates **1–5**. The buffer-independent reaction is accelerated by both hydronium and hydroxide ions.

$$k_0 = k_{H_3O^+}[H_3O^+] + k_{OH^-}[OH^-] + k_{H_2O} \tag{4}$$

Clearly, the buffer-independent reactions include

$$CH + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C^- + H_3O^+ \tag{5}$$

and

$$CH + OH^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} C^- + H_2O \tag{6}$$

where CH and C^- stand for a cyclopentadiene and a cyclopentadienide ion, respectively, and where k_{-1} and k_2 are the second-order rate constants while both k_1 and k_{-2} are the pseudo-first-order rate constants. Water acts both as a base and as an acid.

Assuming that the concentrations of H_3O^+ and OH^- stay constant during reaction, we can derive from reaction formulas 5 and 6 the following expression for the rate of formation (or destruction) of C^-:

$$d[C^-]/dt = -k_0([C^-] - [C^-]_e) \tag{7}$$

Here, k_0 is given by

$$k_0 = k_{-1}[H_3O^+] + k_2[OH^-] + k_1 + k_{-2} \tag{8}$$

and $[C^-]_e$ is the concentration of C^- at equilibrium. The ratios k_1/k_{-1} and k_2/k_{-2} are related to the acid dissociation constant K_a of CH by

$$K_a = k_1/k_{-1} = K_\omega k_2/k_{-2} \tag{9}$$

where K_ω is the ionic product of water (pK_ω = 13.83 at 30 °C[14]). The rate constants appearing in eq 4 can thus be identified as follows:

$$k_{H_3O^+} = k_{-1} \tag{10}$$

$$k_{OH^-} = k_2 \tag{11}$$

$$k_{H_2O} = k_1 + k_{-2} \tag{12}$$

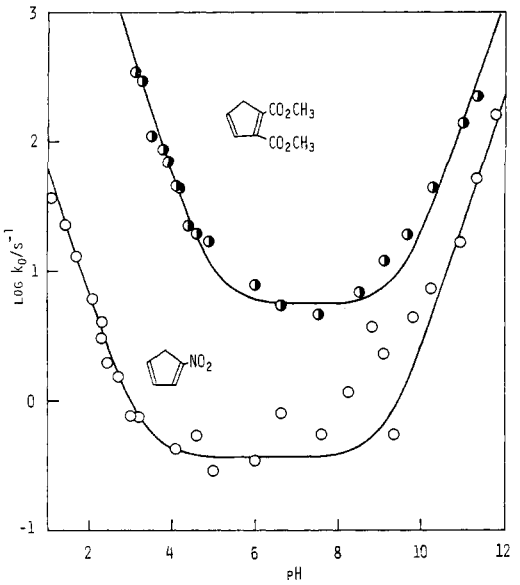


Figure 1. pH-rate profiles for the proton transfer with **1** (○) and **5** (◑). Curves are calculated from eq 8, using constants of Table I.

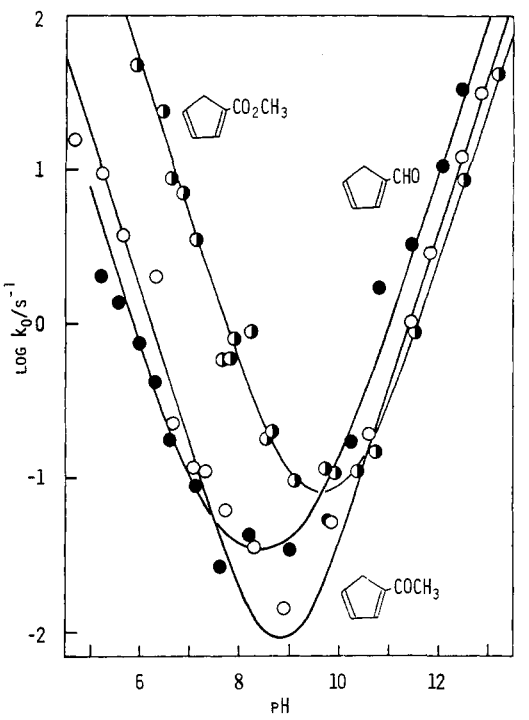


Figure 2. pH-rate profiles for the proton transfer with **2** (●), **3** (○), and **4** (◑). Curves are calculated from eq 8, using constants of Table I.

Table I. Rate Constants and pK_a Values[a]

substrate	pK_a[b]	k_{-1}, M^{-1} s^{-1}	k_2, M^{-1} s^{-1}	k_1, s^{-1}	k_{-2}, s^{-1}
1	3.25	6.5×10^2	1.5×10^4	3.7×10^{-1}	3.9×10^{-7}
2	7.40	8.3×10^5	6.8×10^2	4.0×10^{-2}	2.5×10^{-4}
3	8.84	1.7×10^6	2.0×10^2	2.5×10^{-3}	2.0×10^{-3}
4[c]	10.35	5.1×10^7	1.7×10^2	2.3×10^{-3}	5.6×10^{-2}
5	5.00	5.5×10^5	1.0×10^5	5.5	1.5×10^{-4}

[a] 30 °C, ionic strength = 0.5 (KCl). [b] Accurate to within ±0.03 pK_a unit. [c] pK_a measured in 5 vol % aqueous CH_3CN and kinetics in 1 vol % aqueous CH_3CN.

The observed rate constants k_{-1} and k_2 and the constants k_1 and k_{-2} calculated therefrom by the aid of eq 9 are summarized in Table I, together with the pK_a values. Solid curves in Figures 1 and 2 are theoretical ones calculated by eq 8 using the rate constants given in Table I.

The buffer-dependent rate constants, k_{Buf}, can be partitioned into catalytic constants by general base B and acid BH^+, k_B and k_{BH}, in the usual way.

$$k_{Buf}[Buf] = k_B[B] + k_{BH}[BH^+] \quad (13)$$

$$CH + B \underset{k_{BH}}{\overset{k_B}{\rightleftharpoons}} C^- + BH^+ \quad (14)$$

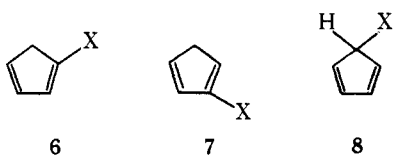
Both base- and acid-catalyzed reactions were observed at pHs near pK_a. At higher and lower pHs, only the base and acid catalyses were found, respectively. Such catalytic constants obtained for **1** are given in Table II.

Table II. Catalytic Constants, k_B and k_{BH}, for the Proton Transfer Involving **1**

B	pK_{BH^+}	k_B, M^{-1} s^{-1}	k_{BH}, M^{-1} s^{-1}
$ClCH_2CO_2^-$	2.71		13.8
HCO_2^-	3.58	8.9	5.3
$CH_3CO_2^-$	4.59	15.8	1.2
pyridine	5.41	104	
$HONH_2$	6.09	115	
HPO_4^{2-}	6.62	140	
imidazole	7.17	71	
$(HOCH_2CH_2)_3N$	8.03	820	
$(HOCH_2)_3CNH_2$	8.25	176	
$(HOCH_2CH_2)_2NH$	9.10	2600	
$HOCH_2CH_2NH_2$	9.63	900	
CO_3^{2-}	9.78	700	
CH_3NH_2	10.62	2040	

Discussion

Site of Protonation. Protonation of a monosubstituted cyclopentadienide in principle gives rise to three possible isomers **6–8.** The structure of various cyclopentadiene derivatives was previously investigated by several workers.[7a,8,9,15-18] Protonation of **1b** and **4b** was concluded to give 1-derivatives **6** (**1a** and **4a**).[7a,9] On the other hand, based on the IR observations, **2b** and **3b** were considered to give mixtures of three isomers **6–8** on protonation.[8,15] However, ^1H NMR spectra of protonated **2b** and **3b** showed a pattern similar to those of **1a**[7a] and 1-cyanocyclopentadiene.[18] That is, the conjugate acids of **2b** and **3b** must mainly be 1 isomers, **2a** and **3a.** Products of some electrophilic reactions of **3b** have recently been found to be derivatives of the 1 isomer.[19]



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The ^1H NMR spectrum of **5b** showed that it was contaminated with 20% of the 1,3 isomer. The literature does not mention that the same preparation resulted in the contamination with the 1,3 isomer but that the 1,2 structure was determined by its IR and UV spectra as well as by the chemical transformations.[12] The determination must have not been decisively quantitative. Since the separation of these isomers was difficult, the kinetic studies were conducted with the mixture. Nevertheless, the pseudo-first-order plots showed satisfactory linearities. Both the isomers must be similar in their protonation rates.

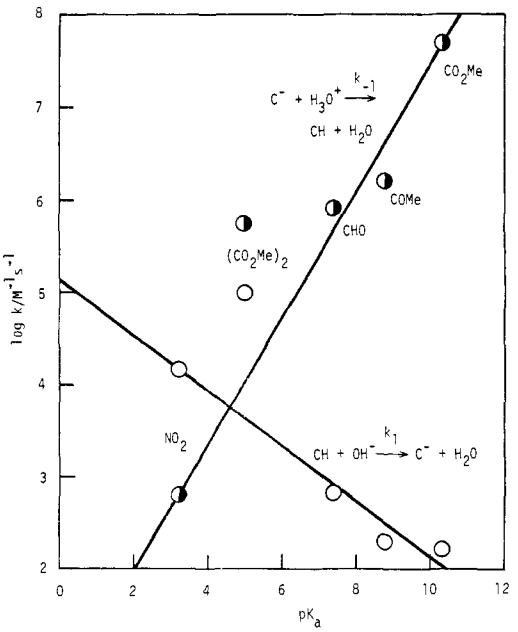

Figure 3. Rate constants for the deprotonation of CH, k_2 (○), and for the protonation of C^-, k_{-1} (◑).

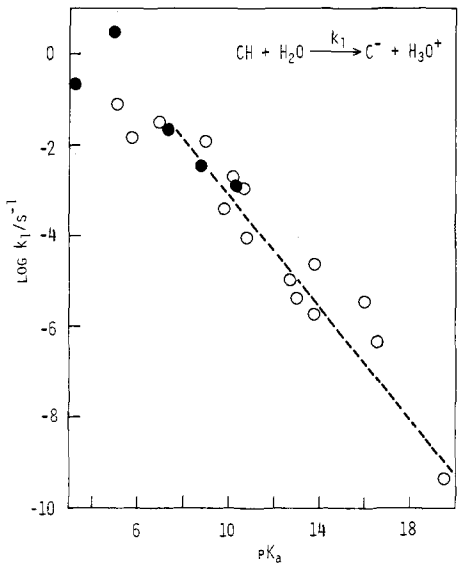

Figure 4. Rate constants k_1 for cyclopentadienes (●) and simple nitro and carbonyl compounds (○).

pK_a and Rate Constants. The rate constants k_{-1} of protonation of various cyclopentadienides (C^-) by H_3O^+ increase with their basicity, while those (k_2) of deprotonation from CH by OH^- decrease with pK_a. Figure 3 shows such correlations. The change in k_{-1} is much greater than that in k_2, slopes being roughly 0.7 and −0.3, respectively. The transition state of proton transfer will be closer to the acid form (CH). Points for the disubstituted substrate, **5**, deviate upward from the lines.

Existence of a similar correlation between k_1 and pK_a is shown in Figure 4, including other classes of carbon acids, nitro and carbonyl compounds.[20] Points for cyclopentadienes,[21] filled circles, fall within a scattering of the literature points. The kinetics of proton transfer involving cyclopentadienes does not seem to show any anomaly deviating from that of simple nitro and carbonyl compounds. Both equilibrium and kinetic acidities are similar between substituted acetones, CH_3COCH_2X,[22] and 1-substituted cyclopentadienes. The extent of electron delocalization influences greatly the stability of carbanions, i.e., equilibrium acidity, and affects the kinetics accordingly. In other words, the extent of delocalization contributes to a reaction barrier only as "thermodynamic effects".[5] The difference in electronic structure of carbanions does not induce any substantial effects on the rate of proton transfer. The nuclear (structural) reorganization which is accompanied by the rehybridization of the carbon must be a primary factor to introduce an activation barrier against proton transfer involving carbon acids.

The Brønsted Relation. The general base and acid catalytic constants summarized in Table II are correlated with pK_a of catalyst acids in Figure 5. Slopes of the lines are 0.4 (β) and −0.6 ($-\alpha$) for the base and acid catalyses, respectively.

In Figure 5, the points for H_2O, OH^-, and H_3O^+ uniformly deviate downward from the lines. Such downward deviations have often been found with the proton transfer to and from carbon.[23] They have been interpreted either by the Marcus curved correlation[24-27] or by the anomalous behavior of solvent-dependent catalytic species.[23,28-32] The present results are not detailed enough to distinguish between the above possibilities. However, it is suggested that the transition state structure is not largely changed while carbon acids are widely varied in their structure and pK_a. This does not seem to conform to the Marcus theory which presumes a sensitive change in the transition state structure with changing pK_a of catalyst. The anomalies may most reasonably be accounted for on the basis of the hydrogen-bonded structure of liquid water.[32]

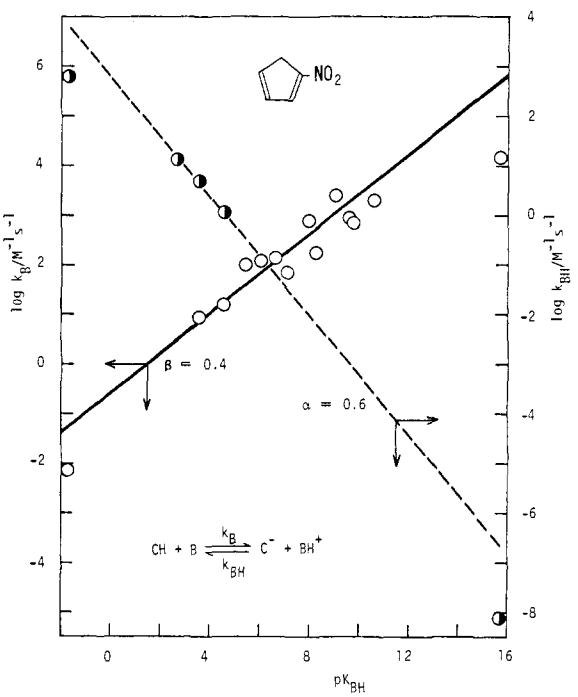

Figure 5. The Brønsted plots for the deprotonation of CH (○) and for the protonation of C^- (◑).

In conclusion, the nuclear reorganization or the rehybridization of the carbon is a main factor to retard the proton transfer involving carbon acids and the contribution of solvation is of secondary importance.

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Conformational Effects on Acetolysis of Bicyclo[3.2.0]hept-6-en-2-yl and Bicyclo[3.2.0]hept-2-yl Derivatives. Homoallylic Participation vs. σ Participation[1]

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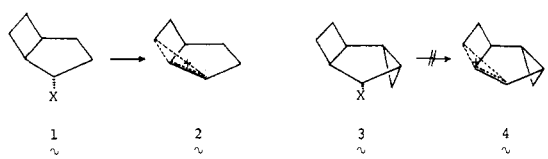
Abstract: The acetolysis reactions of *anti,exo-* and *anti,endo*-tricyclo[5.2.0.0^{2,5}]non-3-en-6-yl tosylates (**7** and **8**), *anti*-tricyclo[5.2.0.0^{2,5}]non-6-yl tosylate (**9**), and *syn,exo,exo-* and *syn,exo,endo*-tetracyclo[5.4.0.0^{2,5}.0^{8,11}]undeca-3,9-dien-6-yl tosylates (**10** and **11**) have been studied to obtain a direct insight into anchimeric assistances by cyclobutane and cyclobutene rings. As important factors to influence the reactivity of the tosylates, homoallylic and σ participations, inductive effect, and conformational change have been discussed. The homoallylic participation (**33**) is more effective for stabilization of the transition state than the σ participation (**34**) ($\Delta\Delta G^{\ddagger}$ = ca. 1.1 kcal/mol at 25 °C) in contrast to the result in the bicyclic system. The ordering of anchimeric stabilization by small-ring compounds in a similar geometrical system is estimated to be cyclopropane (700) > cyclobutene (7) > cyclobutane (1.0). The acetolysis product studies also support the importance of anchimeric assistances by cyclobutene and cyclobutane.

Solvolysis studies of small-ring compounds have long intrigued organic chemists because of their unique properties caused by conjugative interaction between a strained bonding orbital and an adjacent carbonium ion. Although solvolysis reactions of cyclopropylcarbinyl derivatives have been extensively investigated,[2,3] much less attention has been given to those of cyclobutylcarbinyl derivatives.[4] An original work about cyclobutylcarbinyl derivatives was carried out by Winstein and co-workers[4a] in solvolysis of bicyclo[3.2.0]heptyl *p*-bromobenzenesulfonate (**1**), suggesting the stabilized carbonium ion (**2**) by the cyclobutane (σ participation). The



1 2 3 4

molecular orbital calculations have also provided some evidence for the stabilizing effects by cyclobutane rings.[5] Paquette and co-workers,[3e] however, have suggested that anchimeric assistance by the cyclobutane (**4**) is not significant, when compared to that by the cyclopropane, in the solvolysis of the tricyclo[4.2.0.0^{2,4}]oct-5-yl derivative (**3**) which is partially similar to **1**.

Recently cyclobutenylcarbinyl cation **6**, which is stabilized by the double bond (homoallylic participation), has received a considerable amount of attention.[6] However, when one compares the rate of solvolysis of *exo*-bicyclo[3.2.0]heptenyl derivative **5** to that of **1**, both the rates are essentially identical[6e]

5 6

in spite of the fact that their transition states are quite different. Here questions arise as to whether the σ participation and the π participation are in nature significant in solvolysis of **1** and **5** and, if any, to what extent they are important as compared to a model compound.

In order to obtain direct insight into the above questions one has to investigate solvolysis reactions of the bicyclo[3.2.0]-heptenyl and bicyclo[3.2.0]heptyl derivatives in a rigid ring system eliminating complications due to conformational factors.[6f] Thus, we undertook to synthesize *anti,exo-* and *an-*

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