Gas-Phase Ion–Molecule Reactions of Cyclopentadienyl Anion (c-C$_5$H$_5^-$)

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Abstract: Several gas-phase ion–molecule reactions of c-C$_5$H$_5^-$ (CH$_3$O$^-$ + c-C$_5$H$_6$ → c-C$_5$H$_5^-$ + HOCH$_3$) have been studied in a flowing afterglow apparatus at 298 K. In its reactions with alcohols, c-C$_5$H$_5^-$ was rapidly protonated by (CF$_3$)$_2$CHOH in an exoergic proton transfer reaction. However, the alcohols CH$_3$OH, C$_2$H$_5$OH, n-C$_3$H$_7$OH, and (CH$_3$)$_3$COH slowly formed the clusters c-C$_5$H$_5^-$(HOR) when allowed to react with c-C$_5$H$_5^-$; direct H$^+$ transfers are strongly endoergic in these reactions. The rate constants for cluster formation were roughly proportional to the $\Delta H_{acid}°$ of ROH. The reaction of c-C$_5$H$_5^-$ with CF$_3$CH$_2$OH occurs by the sequence c-C$_5$H$_5^-$ + CF$_3$CH$_2$OH $\overset{k_1}{\rightarrow}$ c-C$_5$H$_5^-$(HOCH$_2$CF$_3$) $\overset{k_2}{\rightarrow}$ c-C$_5$H$_6$ + CF$_3$CH$_2$O$^-$(HOCH$_2$CF$_3$) $\overset{k_3}{\rightarrow}$ CF$_3$CH$_2$O$^-$(HOCH$_2$CF$_3$)$_2$, where steps 2 and 3 involve bimolecular reactions with another CF$_3$CH$_2$OH molecule, and k_1 = (2.7 ± 0.2) × 10^{-10} cm^3 molecule^{-1} s^{-1} = k_3 = $^1/_2k_2$. Although the direct H$^+$ transfer between c-C$_5$H$_5^-$ and CF$_3$CH$_2$OH is endoergic (8 kcal mol^{-1}), this sequential process of "indirect" H$^+$ transfer is related to the role of solvation on acid–base equilibria in the gas and condensed phases. c-C$_5$H$_5^-$ is shown to be a poor nucleophile in S$_N$2 reactions with CH$_3$X molecules and in Michael (conjugate) addition reactions with H$_2$C=CHCN and H$_2$C=CHCO$_2$CH$_3$. Michael addition of c-C$_5$H$_5^-$ with H$_2$C=CHCN produces the adduct c-C$_5$H$_5$CH$_2$CHCN$^-$ (m/z 118), while addition of c-C$_5$H$_5^-$ to H$_2$C=CHCO$_2$CH$_3$ yields the (M − 2) adduct c-C$_5$H$_4$CHCHCO$_2$CH$_3^-$ (m/z 149). These different results from apparently similar reactions are rationalized in terms of conformationally allowed rearrangement followed by elimination (−H$_2$) reactions from the adduct c-C$_5$H$_5$CH$_2$CHCO$_2$CH$_3^-$ which are not possible from c-C$_5$H$_5$CH$_2$CHCN$^-$. The basic and nucleophilic properties of c-C$_5$H$_5^-$ are compared with those of the hypovalent anion radical species, c-C$_5$H$_4^{-}$·. The upper limit of EA(C$_6$F$_6$) <41 kcal mol^{-1} was determined.

The gas-phase preparation of cyclopentadienyl anion (c-C$_5$H$_5^-$) is readily accomplished by proton abstraction from cyclopentadiene (c-C$_5$H$_6$) using bases with proton affinities (PA) which exceed that of c-C$_5$H$_5^-$.[1] The physical properties of c-C$_5$H$_5^-$ (PA = 356.1 ± 2 kcal mol^{-1},[1c] $\Delta H_f°$ = 21.3 ± 3 kcal mol^{-1},[1a,c] EA(c-C$_5$H$_5$·) = 41.17 ± 0.46 kcal mol^{-1} [2]) have been determined. To our knowledge, however, the gas-phase chemistry of this delocalized anion has not been reported.

Our interest in the chemical reactivity of c-C$_5$H$_5^-$ stems from our study of the gas-phase generation, characterization, and reactions of cyclopentadienylidene anion radical (c-C$_5$H$_4^{-}$·).[3] One of the intriguing questions about hypovalent anion radicals is how the properties and chemistry of R$_2$C$^-$· differ from those of the corresponding carbanion R$_2$CH$^-$. We wish to report our results of ion–molecule reactions of c-C$_5$H$_5^-$ with selected reagents chosen to facilitate the comparison with c-C$_5$H$_4^{-}$·.

Experimental Section

The flowing afterglow used in these investigations has been previously described.[3] Gas-phase anions were prepared by dissociative electron attachment with small concentrations of neutral reagents added to the upstream end of the flow tube in helium as the buffer gas. The flow pressure (P_{He}) and flow velocity ($\bar{v}$) were maintained in the stainless-steel flow tube (120 × 7.15 cm i.d.) by a Stokes Roots blower–mechanical pump system (Model 1722-S) but could be varied from P_{He} = 0.2–1.2 torr and $\bar{v}$ = 30–80 m s^{-1} by throttling a gate valve and/or altering the helium inlet flow. Our standard operating conditions were P_{He} = 0.5 torr and $\bar{v}$ = 80 m s^{-1} at 298 K.

In the present experiments, CH$_3$O$^-$ was prepared by dissociative electron attachment to CH$_3$ONO which was flowed past the ionizer. Cyclopentadiene (from freshly cracked dimer) was then added 10 cm downstream of the ionizer in sufficient quantity to completely convert CH$_3$O$^-$ (m/z 31) to c-C$_5$H$_5^-$ (m/z 65). The ions (I$^-$) are thermalized by collisions with the buffer gas as they flow 25 cm downstream before neutral reactant gases, N, are added through a fixed inlet. The inlet for N is located 61 cm from the first sampling nose cone and is the distance (time) for the pseudo-first-order (N in large excess) ion–molecule reaction to occur. This reaction distance is held constant as variable con-

centrations of N are added, and the ion signals of c-C$_5$H$_5^-$ and products are recorded at each concentration of N. The slope of the plot of log I$^-$ vs. concentration of N is then converted into the bimolecular rate constant for the ion–molecule reaction of I$^-$ + N by the equations previously given.[3]

Preparation of CH$_3$O$^-$ from dissociative electron attachment with CH$_3$ONO has several problems. Besides the m/z 31 signal, ions m/z 46 (NO$_2^-$) and 60 (CH$_2$NO$_2^-$) are also observed in a ratio of 1:1:1.[4] Addition of 5 × 10^{11} molecules cm^{-3} of CH$_3$ONO to the helium buffer gas flowing past the ionizer (10-mA filament to grounded grid current) did not eliminate all electrons since addition of SF$_6$ 30 cm downstream of the discharge produced SF$_6^-$. Since EA(CH$_3$O·) = 36.2 ± 0.5 kcal mol^{-1} and EA(SF$_6$) < 23 kcal mol^{-1},[5a] electron transfer from CH$_3$O$^-$ to SF$_6$ cannot occur. Penning ionization by He*(2^{3}S) appears to be the major contributor to forming electrons downstream of the ionizer. This problem is eliminated when c-C$_5$H$_6$ was added to the flow (see above) because of its low IP (196 kcal mol^{-1}).[5b] The electrons released from Penning ionization of c-C$_5$H$_6$ can undergo dissociative attachment with CH$_3$ONO present in the flow to give CH$_3$O$^-$ and finally c-C$_5$H$_5^-$ by reaction with c-C$_5$H$_6$.

Results and Discussion

Reactions of c-C$_5$H$_5^-$ with Alcohols. The reaction of c-C$_5$H$_4^{-}$· with CH$_3$OH proceeded exclusively by H· abstraction from the O–H group while the reactions of c-C$_5$H$_4^{-}$· with C$_2$H$_5$OH, n-C$_3$H$_7$OH, and (CH$_3$)$_3$COH gave varying amounts of H· abstraction and proton transfer.[3] The overall rate constants for these four reactions were essentially the same ((6.1–8.3) × 10^{-10} cm^3 molecule^{-1} s^{-1}). The amount of the proton-transfer product forming channel was dependent on the acidity ($\Delta H_{acid}°$) of the alcohol,[1c] while the extent of H· abstraction was essentially constant since $\delta D°$(RO–H) ≈ 0 kcal mol^{-1} in these alcohols.[6] It was suggested that both H· and H$^+$ transfers to c-C$_5$H$_4^{-}$· by ROH molecules could be rationalized by a single intermediate (c-C$_5$H$_4^{-}$·(HOR)) with the ROH hydrogen bonded to the delocalized π-anion of c-C$_5$H$_4^{-}$·.[3] Therefore, it was of interest to determine

(1) (a) di Domenico, A.; Harland, P. W.; Franklin, J. L. *J. Chem. Phys.* **1972**, *56*, 5299. (b) Bohme, D. K.; Lee-Ruff, E.; Young, L. B. *J. Am. Chem. Soc.* **1972**, *94*, 5153. (c) Bartmess, J. E.; Scott, J. A.; McIver, R. T. *Ibid.* **1979**, *101*, 6046.

(2) Engelking, P. C.; Lineberger, W. C. *J. Chem. Phys.* **1977**, *67*, 1412.

(3) McDonald, R. N.; Chowdhury, A. K.; Setser, D. W. *J. Am. Chem. Soc.* **1980**, *102*, 6491.

(4) Jager, K.; Hengelein, A. *Z. Naturforsch., A* **1967**, *22A*, 700.

(5) (a) Janousek, B. K.; Brauman, J. I. In "Gas Phase Ion Chemistry"; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 2, Chapter 10. (b) Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T., *J. Phys. Chem. Ref. Data*, **1977**, *6*, Suppl 1.

(6) (a) Batt, L.; Christie, K.; Milne, R. T.; Summers, A. J. *Int. J. Chem. Kinet.* **1974**, *6*, 877. (b) Benson, S. W.; Cruickshank, F. R.; Golden, D. M.; Haugen, G. R.; O'Neal, H. E.; Rogers, A. S.; Shaw, R.; Walsh, R. *Chem. Rev.* **1969**, *69*, 279.
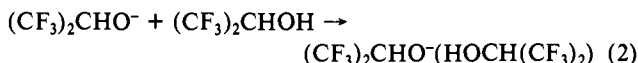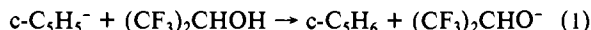
Table I. Summary of Rate Constants and Thermochemical Data for the Reactions of c-$C_5H_5^-$ with Alcohols

alcohol	k_{total},^{a} cm^3 molecule^{-1} s^{-1}	$\Delta H_{acid}°$-(ROH),^{e} kcal mol^{-1}	ΔH_{rx} for c-$C_5H_5^-$ + ROH,^{d} kcal mol^{-1}
$(CF_3)_2CHOH$	$(1.2 \pm 0.1) \times 10^{-9}$	<351	≤-5
CF_3CH_2OH	$(2.7 \pm 0.2) \times 10^{-10b}$	364.4 ± 2	8.3 ± 4
$(CH_3)_3COH$	$(1.5 \pm 0.3) \times 10^{-12}$	373.3 ± 2	17.2 ± 4
n-C_3H_7OH	$(6.9 \pm 0.5) \times 10^{-12}$	374.7 ± 2	18.6 ± 4
C_2H_5OH	$(4.7 \pm 0.2) \times 10^{-12}$	376.1 ± 2	20.0 ± 4
CH_3OH	$(5.9 \pm 0.2) \times 10^{-13c}$	379.2 ± 2	23.1 ± 4

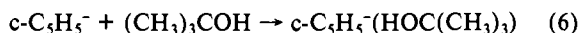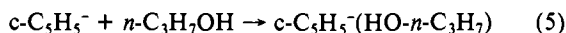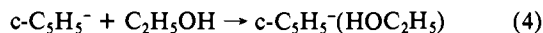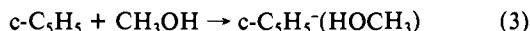^{a} Rate constants are for the decay of c-$C_5H_5^-$ and are estimated to be accurate to ±30%. Errors are standard deviations from multiple determinations. ^{b} This k_{total} was found to be independent of P_{He} from 0.5 to 1.1 torr. ^{c} Measured at $\bar{v} = 52$ m s^{-1}, $P_{He} = 0.76$ torr. ^{d} $\Delta H_{rx} = \Delta H_{acid}°(ROH) - 356.1 \pm 2$ kcal mol^{-1} ($\Delta H_{acid}°$(c-C_5H_6)).^{1c} ^{e} References 1c and 7.

if c-$C_5H_5^-$ would give observable clusters with ROH molecules which could not effect an exoergic proton transfer reaction.

The first reaction of c-$C_5H_5^-$ and an ROH molecule examined was with $(CF_3)_2CHOH$ (Table I). As expected, a fast proton-transfer reaction occurred since this process is exoergic.[7] The initial product of the proton transfer $(CF_3)_2CHO^-$ (m/z 167) (eq 1) subsequently associates with another alcohol molecule to yield the cluster ion m/z 335 (eq 2) with $k_2 = 1 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}.

$$c\text{-}C_5H_5^- + (CF_3)_2CHOH \rightarrow c\text{-}C_5H_6 + (CF_3)_2CHO^- \quad (1)$$

$$(CF_3)_2CHO^- + (CF_3)_2CHOH \rightarrow$$
$$(CF_3)_2CHO^-(HOCH(CF_3)_2) \quad (2)$$

Since the desired c-$C_5H_5^-$(HOR) cluster could not be observed in the above reaction, we turned to those reactions where the direct proton transfer between the collision partners would be endoergic. Cluster formation was observed in the reactions of c-$C_5H_5^-$ with CH_3OH, C_2H_5OH, n-C_3H_7OH, and $(CH_3)_3COH$, (eq 3–6).

$$c\text{-}C_5H_5 + CH_3OH \rightarrow c\text{-}C_5H_5^-(HOCH_3) \quad (3)$$

$$c\text{-}C_5H_5^- + C_2H_5OH \rightarrow c\text{-}C_5H_5^-(HOC_2H_5) \quad (4)$$

$$c\text{-}C_5H_5^- + n\text{-}C_3H_7OH \rightarrow c\text{-}C_5H_5^-(HO\text{-}n\text{-}C_3H_7) \quad (5)$$

$$c\text{-}C_5H_5^- + (CH_3)_3COH \rightarrow c\text{-}C_5H_5^-(HOC(CH_3)_3) \quad (6)$$

These four cluster-forming reactions occur with small rate constants with the largest (n-C_3H_7OH) having a reaction efficiency of 2×10^{-2}.[8] No evidence for formation of higher clusters, c-$C_5H_5^-$(HOR)$_x$ ($x > 1$), was observed in these reactions. The rate constants determined for the first three of these clustering reactions (eq 3–5; Table I) parallel the increases in the acidity of ROH. However, this is not maintained in the reaction with $(CH_3)_3COH$ (eq 5; Table I). This breakdown of the k vs. $\Delta H_{acid}°$ correlation for $(CH_3)_3COH$ is assumed to result from the steric bulk of the *tert*-butyl group. On this basis, we describe the structure of the clusters as hydrogen-bonded complexes **1**, rather than as an edge, or a corner complex, or a simple charge–dipole complex.
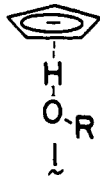
The reaction of c-$C_5H_5^-$ with CF_3CH_2OH proceeded rapidly

(7) Bartmess, J. E.; McIver, R. T. In "Gas Phase Ion Chemistry"; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 2, Chapter 11.

(8) Reaction efficiency is defined as k/k_{ADO} where k_{ADO} is the collision limit rate constant calculated from the average dipole orientation theory (Su, T.; Bowers, M. T. *J. Chem. Phys.* 1973, *58*, 3027; *Int. J. Mass Spectrom. Ion Phys.* 1973, *12*, 374); k_{ADO} for the reaction of c-$C_5H_5^-$ + n-C_3H_7OH is 1.7 × 10^{-9} cm^3 molecule^{-1} s^{-1}.
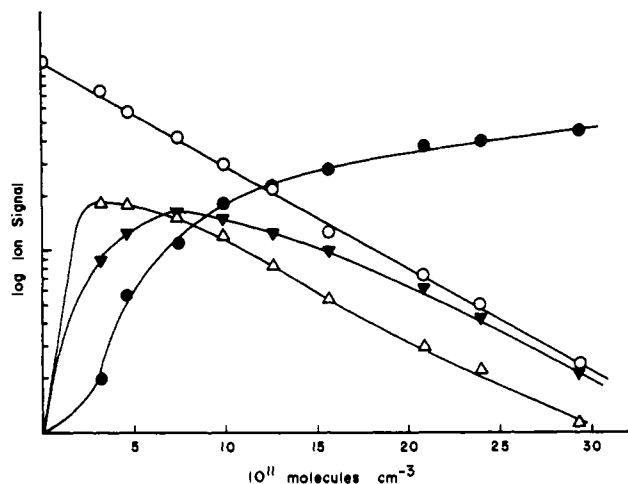

Figure 1. Semilog plot of the decay of c-$C_5H_5^-$ (O) and formation of products (m/z 165, △; m/z 199, ▼; m/z 299, ●) for the reaction of c-$C_5H_5^-$ + CF_3CH_2OH as a function of added alcohol. Ion signals are in arbitrary units.

with the formation of three cluster anions, c-$C_5H_5^-$(HOCH$_2$CF$_3$) (m/z 165), $CF_3CH_2O^-$(HOCH$_2$CF$_3$) (m/z 199), and CF_3CH_2-O^-(HOCH$_2$CF$_3$)$_2$ (m/z 299). The rate constant for the decay of c-$C_5H_5^-$ and for formation of the ions m/z 165 and 199 were independent of the helium buffer gas pressure (P_{He} varied from 0.5 to 1.1 torr) and the flow velocity ($\bar{v} = 80$ or 50 m s^{-1}). Direct proton transfer between c-$C_5H_5^-$ and CF_3CH_2OH followed by clustering of $CF_3CH_2O^-$ with CF_3CH_2OH as the source of the $CF_3CH_2O^-$(HOCH$_2$CF$_3$)$_x$ is unlikely due to the endoergicity of the first step (eq 7). Also, we were unable to directly detect the

$$c\text{-}C_5H_5^- + CF_3CH_2OH \rightarrow c\text{-}C_5H_6 + CF_3CH_2O^- \quad (7)$$
$$(m/z \ 99)$$
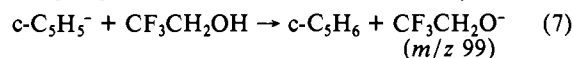
$$\Delta H_{rx} = +8.3 \pm 4 \text{ kcal mol}^{-1}$$

anion $CF_3CH_2O^-$ (m/z 99) when small concentrations ((3–5) × 10^{11} molecules cm^{-3}) of CF_3CH_2OH were added to the flow containing c-C_5H_5. Under similar conditions, the exoergic proton transfer reaction between c-$C_5H_4^-$· and CF_3CH_2OH produced $CF_3CH_2O^-$ as a readily observed anion, although it subsequently forms the $CF_3CH_2O^-$(HOCH$_2$CH$_3$)$_x$ clusters quite rapidly. The definitive evidence that reaction 7 was *not occurring* is shown in Figure 1 (semilog plot) where the total ion composition of the reaction mixture is plotted against the concentration of added CF_3CH_2OH. While good pseudo-first-order decay of c-$C_5H_5^-$ (m/z 65) is observed, it is clearly evident that the three product ions are produced *sequentially*, first cluster c-$C_5H_5^-$(HOCH$_2$CF$_3$) (m/z 165) is formed, followed by cluster $CF_3CH_2O^-$(HOCH$_2$CF$_3$) (m/z 199), with final clustering to yield $CF_3CH_2O^-$(HOCH$_2$CF$_3$)$_2$ (m/z 299).

Cluster formation of c-$C_5H_5^-$ with CF_3CH_2OH is readily understood in view of the other c-$C_5H_5^-$(HOR) clusters **1** (eq 3–6). The additional clustering of RO$^-$(HOR) to RO$^-$(HOR)$_2$ species is also a well-known process in the gas phase.[9] It is the second step of the sequence, conversion of c-$C_5H_5^-$(HOCH$_2$CF$_3$) to $CF_3CH_2O^-$(HOCH$_2$CF$_3$), which deserves further comment. To complete the overall stoichiometry of the second step, we must include an additional CF_3CH_2OH molecule. This step must involve the bimolecular reaction shown in eq 8, which requires

$$c\text{-}C_5H_5^-(HOCH_2CF_3) + CF_3CH_2OH \rightarrow$$
$$c\text{-}C_5H_6 + CF_3CH_2O^-(HOCH_2CF_3) \quad (8)$$
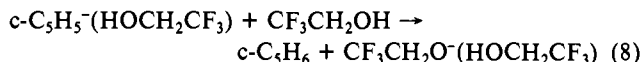
that a proton be transferred to the clustered c-$C_5H_5^-$ moiety yielding c-C_5H_6 and the homoconjugate product $CF_3CH_2O^-$(HOCH$_2$CF$_3$). It is also reasonable to conclude that the proton to be transferred is that which is hydrogen-bonded in the c-$C_5H_5^-$(HOCH$_2$CF$_3$) cluster. These requirements and considerations lead to the mechanism shown in Scheme I where the structure of the intermediate or transition state considered most

(9) Kebarle, P. *Annu. Rev. Phys. Chem.* 1977, *28*, 445.

Table II. Summary of Kinetic and Product Data for the Ion-Molecule Reactions of c-$C_5H_5^-$ with CH_3X and CH_2=CHX Molecules

rxn	neutral ion + reactant		product ion + [assumed neutral]	$k,^{a,b}$ cm^3 molecule^{-1} s^{-1}	$\Delta H_{rx},^c$ kcal mol^{-1}
1	c-$C_5H_5^-$ + CH_3Br	→	Br^- [+ c-$C_5H_5CH_3$]	$(2.5 \pm 0.7) \times 10^{-12}$	−38
2	c-$C_5H_5^-$ + CH_3Cl	→	no rxn obsd	⩽10^{-13}	−32
3	c-$C_5H_5^-$ + CH_3F	→	no rxn obsd	⩽10^{-13}	−2
4	c-$C_5H_5^-$ + H_2C=CHCN	→	c-$C_5H_5CH_2CHCN^-$	$(1.8 \pm 0.5) \times 10^{-11}$	−7^d
5	c-$C_5H_5^-$ + H_2C=CHCO$_2$CH$_3$	→	c-$C_5H_4CHCHCO_2CH_3^-$ [+H_2]	$(1.7 \pm 0.5) \times 10^{-12}$	e

^{a} See description in Table 1. ^{b} All data obtained at P_{He} = 0.5–0.6 torr, $\bar{v}$ = 80 m s^{-1}. ^{c} Calculated from group additivities in ref 15a. ^{d} See ref 19. ^{e} See text.
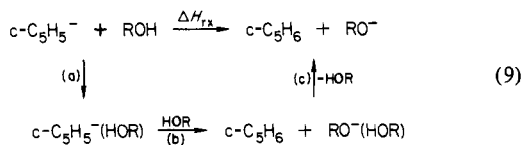
Scheme I
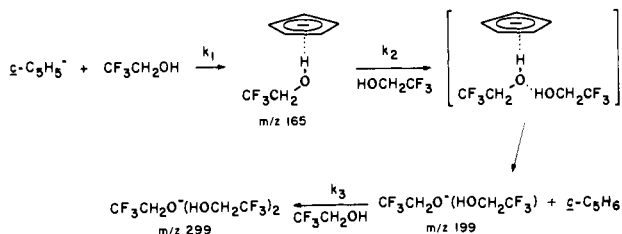
reasonable for this cluster-to-cluster (m/z 165 → m/z 199) transformation is shown. The anion transferred in this cluster-to-cluster reaction is not the original anion in the m/z 165 cluster. Regarding this as an example of an "anion-switching mechanism" accounts for the absence of the unsolvated anion $CF_3CH_2O^-$ (m/z 99) as a product of this reaction.

Computer fitting of the data in Figure 1 was carried out to determine the three rate constants in Scheme I ($k_1 = k_{total}$, the decay constant for c-$C_5H_5^-$, Table I). Since some mass discrimination at the larger masses is obvious in Figure 1, only the maxima of the ion signals vs. CF_3CH_2OH concentration for ions m/z 165 and 199 were employed in the computer calculation.[10] The relative rate constants for the mechanism in Scheme I were found to be $k_1 = k_3 = {}^1/_2k_2$.

The thermochemical cycle (eq 9) shows the processes given in Scheme I with the associated thermochemical steps. In this cycle, the "anion-switching" proton transfer (step b) can only occur if the binding energy of RO^-(HOR) exceeds that of c-$C_5H_5^-$(HOR) by $\geq \Delta H_{rx}$. Although the binding energies $D°$(c-$C_5H_5^-$–HOR) and $D°$(RO^-–HOR) are unknown, it appears reasonable that $D°$(RO^-–HOR) should be similar to that of the homoconjugate cluster HO^-(HOH) which is 24 kcal mol^{-1}.[9,11] If we assume that $D°$($CF_3CH_2O^-$–$HOCH_2CF_3$) = 24 kcal mol^{-1}, we calculate that $16 \geq D°$(c-$C_5H_5^-$–HOR) ≥ 7 kcal mol^{-1}, using the CF_3CH_2OH and $(CH_3)_3COH$ data to set the limits. This bracketed value for $D°$(c-$C_5H_5^-$–HOR) seems to be appropriate compared with the binding energies of certain other delocalized anion–water clusters ($D°$(NO_3^-–HOH) = 10.2 kcal mol^{-1} and $D°$(NO_2^-–HOH) = 14.3 kcal mol^{-1}).[11b] The fact that the rate constant (k_2) for step b in eq 9 is twice that for step a in the reaction of c-$C_5H_5^-$ with CF_3CH_2OH would seem to require that ΔH_{rx} for step b also be exoergic. On the basis of this, $D°$(c-$C_5H_5^-$–$HOCH_2CF_3$) may be at the lower end (7–12 kcal mol^{-1}) of the above bracket. With the CH_3OH to $(CH_3)_3COH$ alcohols, the $D°$(RO^-–HOR) are not sufficient to overcome their larger endoergic ΔH_{rx}'s, and only the formation of the simple clusters c-$C_5H_5^-$(HOR) is observed.

Reactions of c-$C_5H_5^-$ with CH_3X Molecules. The S_N2 reactions of nucleophiles with methyl halies[12,13] and related neutral molecules[12] in the gas phase are well-known processes. The wide varition in rate constants observed for these reactions require a barrier on the potential surface with the traditional substitution complex located at the top of this barrier.[12–14] On the basis of charge delocalization, c-$C_5H_5^-$ would be expected to be a poor nucleophile toward saturated carbon.[12,13] In terms of thermodynamic considerations, the CH_3^+ affinity of c-$C_5H_5^-$ (258 kcal mol^{-1})[15] is smaller than that of CN^- (261 kcal mol^{-1}) which is itself a relatively poor nucleophile toward saturated carbon.[12,13]

The reaction of c-$C_5H_5^-$ with CH_3Br (Table II) occurred with a rate constant that is 1 order of magnitude smaller than the corresponding reaction of CN^- ($k = 3 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}).[12,13] No reaction was observed between c-$C_5H_5^-$ and CH_3Cl or CH_3F even though ΔH_{rx} = −32 kcal mol^{-1} for the CH_3Cl reaction.

Reactions of c-$C_5H_5^-$ with Acrylonitrile and Methyl Acrylate. The reaction between c-$C_5H_5^-$ and acrylonitrile occurred slowly (Table II). The only anionic product was the adduct m/z 118 believed to be formed by conjugate addition of the delocalized anion to C_β of acrylonitrile (eq 10). The analogous reaction

$$c\text{-}C_5H_5^- + H_2C=\!\!\!=\!CH\!-\!CN \longrightarrow c\text{-}C_5H_5\!-\!CH_2\!-\!\bar{C}H\!-\!C\!=\!\!\!=\!N \quad (10)$$
$$(m/z\ 118)$$

$$c\text{-}C_5H_5^- + H_2C=\!\!\!=\!CHCO_2CH_3 \xrightarrow{(a)} c\text{-}C_5H_5\!-\!CH_2\!-\!\bar{C}HCOCH_3 \xrightarrow{(b)}$$
$$c\text{-}\bar{C}_5H_4\!-\!CH\!-\!CHCOCH_3 + H_2 \quad (11)$$
$$(m/z\ 149)$$

between c-$C_5H_5^-$ and methyl acrylate had a rate constant 10 times smaller than that for the reaction with acrylonitrile (Table II). Further, the observed anionic product of the reaction with methyl acrylate was not the adduct but rather the (M − 2) species (m/z 149). The most reasonable structure for this m/z 149 anion is that of the delocalized fulvene enolate anion **2**, formed by loss of the ring C_1–H and C_β–H as molecular hydrogen from the conjugate addition adduct.

Loss of a molecular fragment from the product of an ion-molecule reaction is caused by excess energy in the initial product as a result of the chemical activation. Such eliminations normally have large activation energies which should be lowered in these cases due to the increased delocalization in the product anion (e.g., **2**). However, this does not explain why H_2 is lost from the addition of c-$C_5H_5^-$ to methyl acrylate (eq 11) but is not eliminated in the analogous reaction with acrylonitrile (eq 10).[16]

The thermochemical cycle (eq 9) shows the processes given in

$$c\text{-}C_5H_5^- + ROH \xrightarrow{\Delta H_{rx}} c\text{-}C_5H_6 + RO^-$$
$$(a)\downarrow \qquad\qquad (c)\uparrow\text{-HOR} \qquad\qquad (9)$$
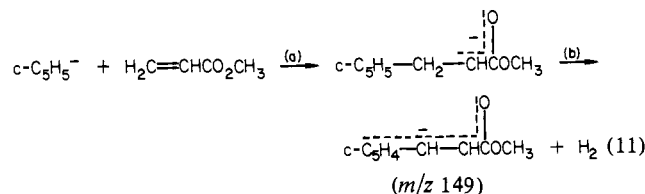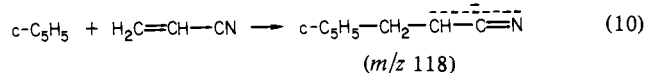$$c\text{-}C_5H_5^-(HOR) \xrightarrow[(b)]{HOR} c\text{-}C_5H_6 + RO^-(HOR)$$

(10) While mass discrimination can lead to errors in evaluating branching ratios for reactions, it is not important in determining the maxima of ion signals for intermediate species and rate constants in the consecutive pseudo-first-order processes described here.

(11) (a) Payzant, J. D.; Yamdagni, R.; Kebarle, P. *Can J. Chem.* **1971**, *49*, 3308. (b) Yamdagni, R.; Kebarle, P. *J. Am. Chem. Soc.* **1971**, *93*, 7139.
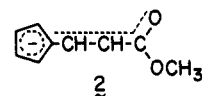
(12) Tanaka, K.; Mackay, G. I.; Payzant, J. D.; Bohme, D. K. *Can. J. Chem.* **1976**, *54*, 1643.

(13) Olmstead, W. M.; Brauman, J. I. *J. Am. Chem. Soc.* **1977**, *99*, 4219.

(14) Pellerite, M. J.; Brauman, J. I. *J. Am. Chem. Soc.* **1980**, *102*, 5993.

(15) (a) The $\Delta H_f°$(c-$C_5H_5CH_3$) = 25.1 kcal mol^{-1} was calculated from group additivities in: Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley: New York, 1976. (b) $\Delta H_f°$(CH_3^+) = 262 kcal mol^{-1}.[5b]

There is insufficient energy in the system for stepwise elimination of two hydrogen atoms. Therefore, the loss of H_2 must follow a concerted reaction pathway. Since a 1,2-elimination ($_\sigma 2_s$ + $_\sigma 2_s$) of H_2 is forbidden from orbital symmetry considerations,[17,18] we seek an explanation in the structural differences in the –CN and –CO_2CH_3 groups of the initially formed adducts. In the adduct **3** produced by conjugate addition of c-$C_5H_5^-$ to methyl

$$\text{(12)}$$
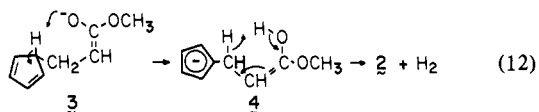
acrylate a ready proton transfer from ring C_1 and O of the enolate anion can occur yielding cyclopentadienyl–enol anion **4**. From **4**, H_2 can be eliminated via another six-membered-ring transition state producing the observed product anion **2** (eq 12). The related proton-transfer in c-$C_5H_5CH_2CHCN^-$ (eq 10) from ring C_1 to N is not possible since C_α-C=N^- is a linear unit and cannot easily achieve a six-membered ring conformation for proton transfer as in **3**.

Using group additivities,[15a] we calculate that the conjugate addition of c-$C_5H_5^-$ to acrylonitrile has $\Delta H_{rx} \geq -7.1$ kcal mol^{-1} (eq 10).[19] For the corresponding addition of c-$C_5H_5^-$ to methyl acrylate yielding **3** (eq 11a), $\Delta H_{rx} \geq -6.7$ kcal mol^{-1}.[20] However, the intramolecular proton transfer of **3** → **4** would be exoergic by 15 kcal mol^{-1} based on the $\delta\Delta H_{acid}°$'s for $CH_3CO_2CH_3$ and c-C_5H_6.[7] The net exoergicity of ≥ 21.7 kcal mol^{-1} of c-$C_5H_5^-$ + H_2C=$CHCO_2CH_3$ → **4** must then drive the final elimination of H_2 to produce **2** via the available reaction channel in eq 12. The fact that both addition reactions are slow compared to their collision limits[8] requires a barrier in the rate-limiting step separating the loose collision complexes and the covalently bonded addition products.

Establishing a New Upper Limit on the Electron Affinity of C_6F_6. In our bracketing of the IP of c-$C_5H_4^-$· (EA(c-C_5H_4)), the lower limit was set when electron transfer was not observed in the reaction of c-$C_5H_4^-$· with C_6F_6.[3] The overlapping values for the EA's of c-C_5H_5· (41.2 ± 0.5 kcal mol^{-1})[2] and C_6F_6 ($\geq 41.5 ± 7$ kcal mol^{-1})[21] predict that electron transfer should occur between

(16) That these results are not a function of different stabilizing abilities of the –CN and –CO_2CH_3 groups on the α anion is seen in the very similar proton affinities of $^-CH_2CN$ (PA = 372.2 ± 2 kcal mol^{-1})[7] and $^-CH_2CO_2CH_3$ (PA = 371.0 ± 2 kcal mol^{-1}).[7]

(17) Woodward, R. B.; Hoffmann, R. "The Conservation of Orbital Symmetry"; Academic Press: New York, 1970.

(18) Bierbaum, V. M.; DePuy, C. H.; Shapiro, R. H.; Stewart, J. H. *J. Am. Chem. Soc.* **1976**, *98*, 4229 arrived at similar conclusions in the elimination of H_2 from the adducts formed in the reactions of HO$^-$ and H_2N^- with ethylene oxide.

(19) $\Delta H_f°$(c-$C_5H_5CH_2CH_2CN$) = 52.9 kcal mol^{-1} (calcd).[15a] With the assumption that $\Delta H_{acid}°$(c-$C_5H_5CH_2CH_2CN$) $\leq$ ($\Delta H_{acid}°$(CH_3CN) = 372.2 kcal mol^{-1}),[7] $\Delta H_f°$(c-$C_5H_5CH_2CHCN^-$) $\leq$ 57.9 kcal mol^{-1} is calculated; $\Delta H_f°$(H_2C=$CHCN$) = 43.7 kcal mol^{-1},[6b] and $\Delta H_f°$(c-$C_5H_5^-$) = 21.3 kcal mol^{-1}.[7]

(20) $\Delta H_f°$(H_2C=$CHCO_2CH_3$) = –73.9 kcal mol^{-1} (calcd);[15a] $\Delta H_f°$ $\Delta H_f°$(c-$C_5H_5CH_2CH_2CO_2CH_3$) = –63.1 kcal mol^{-1} (calcd).[15a] With the assumption that $\Delta H_{acid}°$(c-$C_5H_5CH_2CH_2CO_2CH_3$) $\leq$ ($\Delta H_{acid}°$($CH_3CO_2CH_3$) = 371.0 kcal mole^{-1}),[7] $\Delta H_f°$(c-$C_5H_5CH_2CHCO_2CH_3^-$) $\leq$ –59.3 kcal mol^{-1} is calculated.

(21) Lifshitz, C.; Tiernan, T. O.; Hughes, B. M. *J. Chem. Phys.* **1973**, *59*, 3182.

Table III. Relative Reaction Rate Constants for c-$C_5H_4^-$· and c-$C_5H_5^-$ with CH_3X and CH_2=CHX Molecules

neutral reactant	k(c-$C_5H_4^-$·)^a/ k(c-$C_5H_5^-$)	neutral reactant	k(c-$C_5H_4^-$·)^a/ k(c-$C_5H_5^-$)
CH_3Cl	b	CH_2=CHCN	39
CH_3Br	40	CH_2=CHCO$_2$CH$_3$	59

^{a} Rate constants for substitution (CH_3X) and addition (CH_2=CHX) by c-$C_5H_4^-$· from ref 3. ^{b} for c-$C_5H_4^-$· + CH_3Cl, $k \simeq 10^{-13}$ cm^3 molecule^{-1} s^{-1}, while $k < 10^{-13}$ cm^3 molecule^{-1} s^{-1} for c-$C_5H_5^-$ + CH_3Cl (Table II).

c-$C_5H_5^-$ and C_6F_6. When C_6F_6 was added to a helium flow containing c-$C_5H_5^-$, we did *not* observe formation of $C_6F_6^-$·. This establishes EA(C_6F_6) $\leq$ 41 kcal mol^{-1}. Also, this result supports our expectation that c-$C_5H_4^-$·, a π-anion, σ-radical ground-state electronic configuration, and c-$C_5H_5^-$ will have similar IP's since related π-MO's are involved in the two molecules.

Conclusions

Comparison of c-$C_5H_5^-$ and c-$C_5H_4^-$· in Related Reactions. In comparing the properties of the carbene anion radical, c-$C_5H_4^-$·, with those of the corresponding carbanion, c-$C_5H_5^-$, the difference in their proton affinities of 21 kcal mol^{-1} is most striking.[3] The greater PA of c-$C_5H_4^-$· arises from the heats of reaction for protonation of these two species; in this comparison the acid is omitted. The product from reaction of c-$C_5H_4^-$· with an acid is the delocalized radical, c-C_5H_5·, and is exothermic ($\Delta H_f°$(c-C_5H_5·) – $\Delta H_f°$(c-$C_5H_4^-$·)) $\approx$ –10 kcal mol^{-1}) while the reaction of c-$C_5H_5^-$ with that acid yields cyclopentadiene and is endothermic ($\Delta H_f°$(c-C_5H_6) – $\Delta H_f°$(c-$C_5H_5^-$)) $\approx$ +11 kcal mol^{-1}).[3]

The ability of c-$C_5H_5^-$ to function as a nucleophile is compared with c-$C_5H_4^-$· for this same property in Table III. While c-$C_5H_4^-$· is characterized kinetically as a moderate-to-good nucleophile in both addition and substitution reactions, c-$C_5H_5^-$ must be considered to be a poor nucleophile in both reaction types.[12,13] This lower kinetic performance of c-$C_5H_5^-$ as a nucleophile compared to c-$C_5H_4^-$· is probably related to the thermochemistry of the respective processes. Although the effects of methyl substitution on the $\Delta H_f°$'s of c-C_5H_5· and c-$C_5H_5^-$ are unknown, it is reasonable to assume that reaction 13 will be *less* exoergic than reaction 14

$$\text{c-}C_5H_5^- + CH_3Br \rightarrow \text{c-}C_5H_5CH_3 + Br^- \qquad (13)$$

$$\text{c-}C_5H_4^-\cdot + CH_3Br \rightarrow \text{c-}C_5H_4CH_3\cdot + Br^- \qquad (14)$$
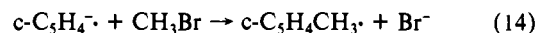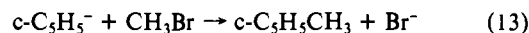
for similar reasons to those given in the above discussion of the PA's of c-$C_5H_5^-$ and c-$C_5H_4^-$·. For c-$C_5H_5^-$, the energies of the transition-state structures must "feel" the increased $\Delta H_f°$ of the neutral reaction product compared to the starting ion c-$C_5H_5^-$ as in eq 13. With c-$C_5H_4^-$· (eq 13), we start with a species which has a large $\Delta H_f°$ (70.7 ± 3.2 kcal mol^{-1})[3] and proceed to a neutral product which should have a lower $\Delta H_f°$. A portion of this overall thermochemistry will be realized in the transition states for the related processes with these two reactant anions and will lead to larger rate constants for the reactions of c-$C_5H_4^-$· compared to those of c-$C_5H_5^-$.