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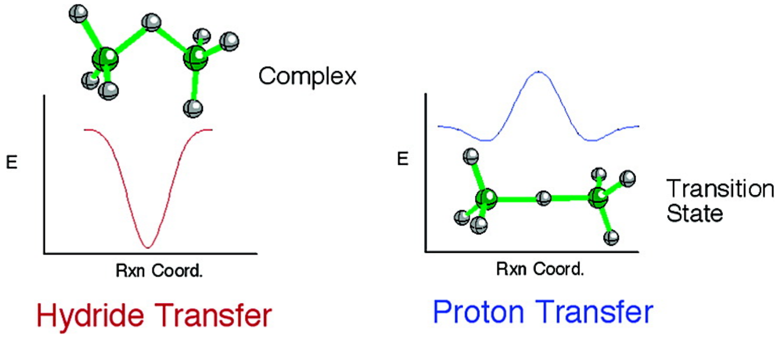

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Identity Hydride-Ion Transfer from C−H Donors to C Acceptor Sites. Enthalpies of Hydride Addition and Enthalpies of Activation. Comparison with C···H···C Proton Transfer. An ab Initio Study

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Abstract: Enthalpies of addition of hydride ion to eleven carbonyl acceptors (X−**C**HO), two conjugate addition sites (X−CH=**C**H_2; X = CHO, NO_2), eight carbenium ion acceptors, fulvene, borane, and SiH_3^+ were calculated at the MP2/6-311+G** level. Correlation between calculated and experimental enthalpies of addition of hydride ion is excellent. Transition states (ts) for the identity hydride transfers between the acceptors and their corresponding hydride adducts (hydride donors) were also calculated. The carbonyl and fulvene reactions have transition states with one imaginary frequency: the hydrogen transfer coordinate. The carbenium ions, borane, and SiH_3^+ gave not transition states but stable compounds upon addition of the hydride donor. Computational differences between these hydride transfers and previously reported proton transfers include shorter partial C···H bonds and a tendency toward bent C···H···C angles for the hydride transfer ts and addition compound structures, particularly when a bent geometry improves interactions elsewhere in the structure. These and other differences are explained by modeling the hydride transfer ts and addition compounds as two-electron, three-center systems involving the transfer termini and the shared hydrogen but the proton transfer ts structures as four-electron, three-center systems. Charge and geometry measures suggest transition states in which these features change synchronously, again in contrast to many proton transfer reactions. For the X−CHO set, polar effects dominate enthalpies of hydride addition, with resonance effects also important for resonance donors; these preferentially stabilize the acceptor, reducing its hydride ion affinity. Activation enthalpies are dominated by resonance stabilization of the acceptors, greatly attenuated in the transition states.

Introduction

Hydride transfer reactions are not as ubiquitous as proton transfers but are nevertheless important in both chemistry and biochemistry. Intramolecular transannular[1] and 1,2-hydride shifts[2] in carbocation chemistry are common and are competitive with other processes especially when the rearranged cation is at least as stable as the original. Intermolecular hydride transfers from hydrocarbon donors to carbocation and related acceptors have long been industrially important.[3] Bartlett clearly recognized their mechanistic interest as well.[3a] Other early work on solution phase hydride transfers involving highly stabilized carbenium ions was reported by McDonough and Dauben[3d] and by Bethell and co-workers.[3e] More recently, Arnett and co-workers have carried out calorimetric studies yielding heats of reaction for hydride transfer to carbenium ions from cycloheptatriene[3f] and cyanoborohydride ion.[3g] These matters have been reviewed by Nenitzescu,[4a] more briefly, by Vogel,[4b] and extensively by Olah, Prakash, and Sommer.[5] Similarly, carbocations may act as hydride acceptors toward alcohols.[4c] Useful carbon-to-carbon hydride transfers in organic synthesis include the Cannizzaro and Tishchenko reactions,[6a] the Meerwein−Pondorf−Verley reduction/Oppenauer oxidation,[6b] and the Clarke−Eschweiler and Leuckart reductive alkylations of amines.[6c] In biochemistry hydride transfer and model hydride transfers involving acceptor coenzymes NAD^+ and $NADP^+$ are

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common and include reactions catalyzed by a variety of dehydrogenases,[7−9] the interconversion of galactose and glucose,[10] and the oxidation of glucose by bacterial glucose dehydrogenase using a quinone cofactor.[11]

Experimental information on the enthalpies of gas-phase hydride ion additions to carbocations[12] and other acceptors, including carbonyl compounds,[13] is readily available. Rates of gas and liquid phase (superacid) intermolecular hydride transfer reactions involving carbenium ions can be difficult to measure because of a number of competing processes including rearrangement, alkylation, dehydrogenation, and disproportionation.[5] However, it has been established that such processes, when exoergic, are very fast in superacid media relative to the rate by which the ion is captured by carbon monoxide.[4a] Additionally, gas-phase studies by Meot−Ner and Field[14] and by Kebarle and co-workers[15] show that hydride transfer from small carbenium ions occurs at or near the collision limit at low temperatures in the thermodynamically favorable direction. Kebarle and co-workers were unable to detect an ion−molecule complex formed from isopropyl$^+$ and isobutane and inferred that the observed production of *tert*-butyl$^+$ has essentially no activation barrier. On the other hand, complexes of isopropyl$^+$/propane, *tert*-butyl$^+$/propane, and *tert*-butyl$^+$/isobutane *were* observed indicating that ergoneutral hydride transfers might take place on an energy surface with a barrier to the transfer event.

Computational work on hydride transfer to carbocations and carbonyl compounds is abundant. Recent work includes the calculation of hydride ion affinities (HIAs) for eighteen sets of *meta*- and *para*-substituted benzylic cations reported by Fujio and co-workers.[16] Corma and co-workers have reported a thorough computational study (B3PW91/6-31G*) of the reactions of small carbenium ions with alkanes.[17] Hypervalent carbonium ion adducts were identified as intermediates leading to transition states for hydride transfer, alkylation, dehydrogenation, and disproportionation. Of these processes hydride transfer is usually the fastest, in part for entropic reasons. Mayr and his colleagues have done an experimental study of the kinetics of hydride transfer to a set of relatively stable, ring-substituted benzhydryl cations[18] and have complemented this with a theoretical study (MP2/6-31+G**//HF/6-31+G**) of hydride transfer between $XYCH{=}CH{-}CH_3$ donors and $XYCH{=}CH{-}CH_2^+$ acceptors.[19] Rosenberg has published "G2/MP2" calculations of the HIAs of a variety of carbonyl compounds.[20]

Transition state modeling of hydride transfer to carbonyl acceptors has a considerable history, often using the transfer of hydride from methoxide anion to formaldehyde (and closely related reactions) as examples. Houk is a pioneer in this area,[21] although his methods have been criticized by Menger.[22] Williams, Miller, and Maggiora made a thorough study of this reaction, albeit at a relatively low computational level.[23] Their paper includes citations of much of the earlier work.

Experimental solution phase studies of hydride transfer from alkoxide donors to carbonyl acceptors are complicated by aggregation of the M^+RO^- reactants and competing side reactions, including nucleophilic addition and proton-transfer chemistry. Watt and co-workers have been able to measure the rates of intramolecular hydride transfer for several cage ketoalkoxides, finding activation energies ranging from 14 to 22 kcal/mol,[24] interpreted by Menger to depend on the distance between the transfer termini.[22] Gas-phase hydride transfers from C−H donors to carbonyl acceptors have been studied by several groups. DePuy, Bierbaum, and co-workers identified the cyclohexadienyl anion ($C_6H_7^-$) as capable of reducing aldehydes to alkoxides, forming benzene as the byproduct.[25a] The same reductant reacts with α,β-unsaturated carbonyl compounds by both nucleophilic addition and hydride addition.[25b] The hydride addition was shown to occur at the β-carbon, that is, in the 1,4 (Michael) fashion, giving enolate products. Ingemann, Kleingeld, and Nibbering showed that methoxide ion could donate a hydride to benzaldehyde giving benzyloxide anion and, presumably, formaldehyde.[26] A gas-phase Cannizzaro reaction was reported by Sheldon et al., upon treatment of benzaldehyde or pivaldehyde with hydroxide ion at sufficiently high substrate pressure.[27]

We were prompted to carry out a computational study of hydride transfer reactions partly as a complement to our earlier work on proton transfers[28] and partly as a systematic effort to determine the electronic effects of substituents on the intrinsic barriers to these reactions. In this paper we report ab initio computations at the MP2/6-311+G** level on identity hydride transfers between eight small carbenium ions and their conjugate hydrocarbon donors and a set of eleven carbonyl acceptors, $X{-}CH{=}O$ reacting with their conjugate donors, $X{-}CH_2O^-$. Two examples of "Michael" hydride transfer between the β-carbons of $CH_2{=}CH{-}X$ and $(CH_3{-}CH{-}X)^-$ were also studied, as was the transfer of hydride from methylcyclopentadienide ion to fulvene. Enthalpies of hydride addition, donor−acceptor compound formation, and activation are reported. The major emphasis in this paper is on structure−reactivity relationships within the carbonyl set.

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Methods

All structures were built and optimized at HF/3-21 or HF/6-31G* levels using the MacSpartan Plus software package.[29] Conformational preferences were established at these or higher levels, before completing the geometry optimizations at the HF/6-311+G** and MP2/6-311+G** levels using the GAUSSIAN 98 or GAUSSIAN 03 quantum mechanical packages.[30,31] Frequencies and zero-point vibrational energy (zpve) corrections were calculated at HF/6-311+G** with the latter scaled by 0.9135.[32] In two cases (the borane plus borohydride reaction set and the allyl cation plus propene transition state), MP2/6-311+G** frequencies were calculated, but in general, our computational resources do not allow calculation of MP2 frequencies. No thermal corrections were made to the resulting enthalpies. Thus, all enthalpies of reaction reported here refer to 0 °K. With three exceptions all species had the correct number of imaginary frequencies: none for the reactants and complexes and one (the transfer coordinate) for the transition states. The exceptions are the ion−molecule complex, **2cx**, formed from formaldehyde and methoxide ion, the "perpendicular" transition state, **1ts** (perp, D_{2d}), for hydride transfer between CO_2 and formate$^-$, and the C_{2v} "syn" transition state, **2ts** (syn), for hydride transfer between methoxide$^-$ and formaldehyde. Structure **2cx** had $i\upsilon = -6\ cm^{-1}$ (torsion about the methoxy C−O bond). The MP2 structure had no negative eigenvalue. Transition states **1ts** (perp) and **2ts** (syn) each had an imaginary frequency corresponding to the transfer coordinate, plus a low-frequency motion corresponding in each case to an internal rotation leading to the more stable ts structures, **1ts** (planar, D_{2h}) and **2ts** (anti, C_{2h}), respectively. **1ts** (perp) and **2ts** (syn) were obtained by the use of symmetry-enforcing constraints.

The electronic energies calculated by these methods are tabulated in Table S1 of the Supporting Information.[33] These results agree well with published computational values[20] where comparisons are possible.

The multiparameter relationships between substituent constants and computed ΔH values were obtained by the use of the "Solver" function within the Excel spreadsheet software package.

Results

Energetics. Our results allow calculation of several enthalpies of reaction or activation at 0 K, that is, changes in electronic energies corrected by the corresponding changes in (scaled) zero-point energy contributions. These are explicitly defined here. They include ΔH_{ADD}, defined as the enthalpy difference between hydride acceptor and the hydride adduct (the conjugate donor). For convenience in comparison with experimental HIA values, the sign of ΔH_{ADD} is made positive. We also define ΔH_{CX} as the enthalpy of reaction for donor and acceptor combining to form a noncovalent ion−molecule complex. This quantity is distinguished from ΔH_{CPD}, the enthalpy of formation of covalent addition compounds from acceptors and donors. These electron-deficient species result from combination of carbenium ions, SiH_3^+, and BH_3 with their respective conjugate donors. Finally, $\Delta H^{\ddagger}$ is the activation enthalpy for hydride transfer between acceptor and conjugate donor. Hydride transfer transition states were found for the reactions of the carbonyl acceptors and fulvene with their conjugate donor anions but not for the reactions of the carbenium ions, SiH_3^+, and BH_3 with their conjugate donors.

Table 1 lists experimental gas-phase hydride ion affinities (HIAs), computed enthalpies of hydride ion addition (ΔH_{ADD}), and computed activation enthalpies ($\Delta H^{\ddagger}$) for hydride transfer for the X−CHO systems considered in this study. For the carbenium ion acceptors enthalpies of compound formation (ΔH_{CPD}) between donor and acceptor are also given in Table 1. Because the electronic energy of H^- is not well computed at the MP2/6-311+G** level, ΔH_{ADD} is here defined simply as the difference between the enthalpies of the acceptor and the hydride adduct (the donor). HIA values for a number of carbonyl compounds, relative to that of formaldehyde, were computed by Rosenberg using a G2(MP2) method.[20] A plot of our results against his gives an excellent correlation, eq 1, in which the intercept is closely matched by our value for formaldehyde, $\Delta H_{ADD} = 357.5$ kcal/mol.

$$\Delta H_{ADD} = -1.02\ (\mathrm{G2/MP2}) + 358.1,\ r^2 = 0.998\ (n = 8) \qquad (1)$$

$$\Delta H_{ADD} = 1.02\ (\mathrm{HIA})_{exp} + 317.6,\ r^2 = 0.999\ (n = 15) \qquad (2)$$

Comparison of our results with experimental gas-phase HIA values was possible for fifteen systems: six carbonyl compounds, eight carbenium ions, and borane. This correlation is also excellent, see eq 2. Using this correlation we can estimate that the hydride ion affinity of fulvene is approximately 79 kcal/mol, unusually high for a neutral hydrocarbon. By contrast the HIAs for 3-methylene-1,4-cyclohexadiene and 5-methylene-1,3-cyclohexadiene which produce nonaromatic conjugated carbanions upon addition of hydride are estimated at 52 and 56 kcal/mol, respectively. Values for the carbonyl compounds and the carbenium ions are well separated from one another, but both sets give good correlations as well: $r^2 = 0.992$ for the carbonyl set and 0.986 for the carbenium ions. The computed value for acrolein fits the correlation only when hydride addition occurs at the β-carbon, giving the enolate of propanal, apparently as

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[33] See paragraph concerning Supporting Information at the end of this paper.

Table 1. Calculated[a] and Experimental Enthalpies of Hydride Addition and Calculated Enthalpies of Activation for Identity Hydride Transfer Reactions in This Study, kcal/mol

hydride acceptor[b]	HIA,[c,d] expt	ΔH_{ADD},[e] calcd	$\Delta H^{\ddagger}$ or ΔH_{CPD},[f] calcd
1 $\mathbf{C}O_2$	51.6 ± 2.3	368.7	5.2 (planar), 6.2 (perp)
2 $H_2\mathbf{C}{=}O$	40.9 ± 1.1	357.5	−7.25
3 $CH_3\mathbf{C}H{=}O$	38.6 ± 1.1	356.6	−6.3 (R,R), −6.2 (R,S)
4 $CH_2F\mathbf{C}H{=}O$	NA	369.0	−6.2 (R,R), −8.3 (R,S)
5 $CF_3\mathbf{C}H{=}O$	63.8 ± 3.0	385.3	−11.5 (R,R), −10.9 (R,S)
6 $CH_3CH_2\mathbf{C}H{=}O$	40.5 ± 2.2	357.9	NA
7 $(CH_3)_2\mathbf{C}{=}O$	38.6 ± 1.1	356.8	−6.7
8 $CH_2{=}CH\mathbf{C}H{=}O$	NA	358.9	−5.7 (R,R), −5.2 (R,S)[g]
8 $\mathbf{C}H_2{=}CHCH{=}O$	−62.5[h]	382.1	0.7
9 $HO\mathbf{C}H{=}O$	NA	355.7	−5.0 (R,R), 1.9 (R,S)
10 $CH_3O\mathbf{C}H{=}O$	NA	354.5	6.3 (R,R), 3.4 (R,S)
11 $H_2N\mathbf{C}H{=}O$	NA	348.7	−0.2 (R,R), 2.9 (R,S)
12 $\mathbf{C}H_2{=}CHNO_2$	NA	395.9	−8.1, 2.2[i]
13 $\mathbf{B}H_3$	74.2 ± 2.8	392.8	−32.3[j] (−32.9)
14 $\mathbf{Si}H_3^+$	NA	578.4	−33.9[j]
15 $\mathbf{C}H_3^+$	314.6	634.1	−39.5[j]
16 $CH_3\mathbf{C}H_2^+$	276.7	592.1	−15.0[j]
17 $(CH_3)_2\mathbf{C}H^+$	250.0	576.0	−16.8[j]
18 $(CH_3)_3\mathbf{C}^+$	232.0	560.9	−16.2[j]
19 $CH_2{=}CH\mathbf{C}H_2^+$	256.0	578.7	−10.8[j]
20 $Ph\mathbf{C}H_2^+$	238.0	563.7	−21.0[j]
21 $HC{\equiv}C\mathbf{C}H_2^+$	272.6	597.9	−14.9[j] (MP2//HF)
22 $CH_2{=}C\mathbf{C}H(CH_3)^+$	237.0	561.6	−12.0[j]
23 fulvene[k]	NA	398.2	−0.3
24 homofulvene[k]	NA	371.4	NA
25 isohomofulvene[k]	NA	375.6	NA

[a] Electronic energies were calculated at the MP2/6-311+G** level and are in hartrees; 1 hartree = 627.51 kcal/mol. Vibrational frequencies and zero-point energies were calculated at the HF/6-311+G** level. The ZPVE values were scaled by 0.9135 as recommended by Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502. [b] Hydride acceptor atoms are bold. For identity reactions the donor is identical with the hydride−acceptor adduct. Transition state structures with stereocenters at the transfer termini are identified with the usual descriptors. (R,R) and (R,S) structures are diastereomeric. [c] HIA = hydride ion affinity = $-\Delta H$ for the reaction H^- + acceptor → adduct. [d] Experimental values are from Bartmess, J. E. In *NIST Standard Reference Database Number 69;* Mallard, W. G., Linstrom, P. J., Eds.; National Institute of Standards and Technology (http://webbook.nist.gov): Gaithersburg, MD, 2003. [e] $\Delta H_{ADD} = -(H_{ADDUCT} - H_{ACCEPTOR})$. The enthalpy of H^- is not well calculated at MP2/6-311+G** and is omitted from the listed quantity. [f] Enthalpies of activation or addition compound formation for the identity hydride transfer between the hydride donor and hydride acceptor. [g] A third, centrosymmetric ts was calculated giving $\Delta H^{\ddagger} = -4.7$ kcal/mol. The unsymmetrical hydride transfer between the CO carbon of allyloxide anion and the β-carbon of acrolein giving acrolein + the enolate of propanal has $\Delta H_{RXN} = -23.2$ kcal/mol and $\Delta H^{\ddagger} = -10.2$ kcal/mol. [h] The experimental value for hydride addition to the β-carbon of acrolein was estimated using heats of reaction and formation involving propanal, propanal enolate, and acrolein.[d] [i] The first entry is for the ts in which the two $CHNO_2$ groups are syn to each other, and the second is for the centrosymmetric ts in which they are anti to each other. [j] Structures **13ad** through **22ad** are not hydride transfer transition states but stable adducts of donor and acceptor at the MP2 level (see text). These have either no imaginary frequency (HF) or no negative eigenvalue (MP2). The ethyl cation is a symmetrical hydrogen-bridged structure. Frequencies and ZPVEs for the borane system were calculated at MP2/6-311+G**, and the ZPVEs were scaled by 0.96 as recommended by Scott and Radom.[a] The ΔH_{CPD} value for BH_3 in parentheses is calculated using HF ZPVE corrections. [k] Hydride addition occurs at the exocyclic carbon for fulvene, homofulvene (3-methylene-1,4-cyclohexadiene), and isohomofulvene (5-methylene-1,4-cyclohexadiene).

assumed in the experimental work.[34] The excellent correlation shown between experimental and computational results supports the adequacy of the computational level used in this work, particularly for comparative purposes.

For several systems diasteroisomeric and conformationally distinct transition state structures were found. Diastereomeric ts structures are generated in many cases because the hydride transfer termini become stereocenters upon partial bonding with the transferred hydrogen. For many of the X groups in the X−CHO set there are different orientations possible between the two C−X units in the transition states. They can be more-or-less anti or more-or-less syn or gauche to one another. Still other conformational possibilities were studied at the HF/3-21G and 6-31G* levels before full optimization at the MP2/6-311+G** level. The resulting differences are identified in the footnotes to Tables 1 and 2.

Geometries. Selected geometric features for hydride acceptors, donors, addition compounds, and transition states are given in Table 2. These include C−H distances, C−O distances for the carbonyl set, partial C···H distances and C···H···C angles for transition states and addition compounds, and other information. Once again, data for distinct stereoisomeric transition states are listed where pertinent. The most stable transition states for the formic acid (**9**) and formamide (**11**) systems profit from internal hydrogen bonding, especially attractive in the C_2 (R,R) ts for formic acid; see Figure 1, where two short (1.63 Å), strong hydrogen bonds exist between the OH group of one-half of the structure and the carbonyl oxygen in the other half providing 6.9 kcal/mol stabilization relative to the (R,S) ts.

For the X−**C**HO and X−CH═**C**H$_2$ acceptors the fractional changes in C−O and C−X distances attained at the transition states relative to the changes in the same distances occurring between the acceptor and the donor were used to calculate "distance-based" transition state progress parameters, $\mathbf{f_o}$ and $\mathbf{f_x}$. These are presented in Table 3 and are defined explicitly in the Discussion section below.

The formaldehyde/methoxide anion system has been modeled by others[21,22a] as possessing a C_{2v} structure with a bent C···H···C angle and with the oxygens syn to one another. In fact, this structure is a second-order saddle point having two imaginary frequencies, one at −1439 cm^{-1} (hydrogen transfer) and one at −130 cm^{-1} corresponding to a complex motion about the axis separating the two CH_2O moieties. This motion leads to a centrosymmetric, C_{2h} transition state with a linear C···H···C angle, anti oxygens, one imaginary frequency, and lying 2.6 kcal/mol below the C_{2v} structure. An important influence on these two structures is the need to separate the two negative oxygens. The C_{2v} ts minimizes this problem by bending the C···H···C angle to 152° and opening the H···C−O angle to 115°, allowing the syn oxygens to be 4.2 Å apart. The C_{2h} ts has a linear C···H···C angle with the opposed oxygens 4.4 Å apart

Some of the transition states in the X−CHO series are not exactly symmetrical with respect to the two C···H partial bond distances and other properties within the two halves of the ts. Some of these transition states nevertheless do connect identical or enantiomeric reactant and product ion−molecule complexes. Others, those with bent C···H···C angles *and* which are conformationally asymmetric, connect reactant and product complexes which are diastereomeric. These complexes are not precisely energy equivalent, and the hydride transfer event is therefore not a true identity reaction. The energetic consequences of this lack of symmetry appear to be small.

We draw attention to three general trends in the transition state structures. It is common, though not universal, for the two substituent groups *not* to be anti to each other; that is, the X−C·

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(34) (a) Zimmerman, A. H.; Reed, K. J.; Brauman, J. I. *J. Am. Chem. Soc.* **1977**, *99*, 7203. (b) Alconcel, L. S.; Deyerl, H.-J.; Continetti, R. E. *J. Am. Chem. Soc.* **2001**, *123*, 12675.

Table 2. Selected Geometric Features for Identity Hydride Ion Transfer Structures in This Study (Å, deg)[a]

	ts	ts	acceptor		ts		donor		ts
system, acceptor[b]	d(C···H)[c]	Φ(C···H···C)[d]	d(C–X)	d(CH–O)	d(C–X)	d(CH–O)	d(C–X)	d(CH–O)	other features
1 $\mathbf{C}O_2$ (planar ts)	1.348, 1.348	180.0	NA	1.170	NA	1.217	NA	1.258	d(O−C) = 1.217 Φ(OCO) = 143.9°
1 $\mathbf{C}O_2$ (perpendicular ts)	1.354, 1.354	180.0	NA	1.170	NA	1.217	NA	1.258	d(O−C) = 1.217 Φ(OCO) = 143.5°
2 $H_2\mathbf{C}{=}O$	1.315, 1.315	180.0	1.105	1.213	1.119	1.274	1.133	1.345	C_{2h} symmetry
3 $CH_3\mathbf{C}H{=}O$, (R,R)	1.305, 1.324	180.0	1.505	1.215	1.534	1.275	1.556	1.340	dihedral C**C**·**C**C = 63°
3 $CH_3\mathbf{C}H{=}O$, (R,S)	1.313, 1.313	180.0	1.505	1.215	1.534	1.274	1.556	1.340	C_{2h} symmetry
4 $CH_2F\mathbf{C}H{=}O$, (R,R)	1.325, 1.327	167.2	1.517	1.213	1.529	1.272	1.533	1.350	virtual C_2 symmetry
4 $CH_2F\mathbf{C}H{=}O$, (R,S)	1.330, 1.348	177.8	1.517	1.213	1.524	1.270	1.533	1.350	dihedral C**C**·**C**C=179°
5 $CF_3\mathbf{C}H{=}O$, (R,R)	1.345, 1.345	179.8	1.537	1.206	1.535	1.260	1.534	1.329	C_2 symmetry
5 $CF_3\mathbf{C}H{=}O$, (R,S)	1.332, 1.365	180.0	1.537	1.206	1.535	1.259	1.534	1.329	dihedral C**C**·**C**C = 131.3°
6 $CH_3CH_2\mathbf{C}H{=}O$	NA	NA	1.507	1.216	NA	NA	1.558	1.341	NA
7 $(CH_3)_2\mathbf{C}{=}O$	1.317, 1.317	180.0	1.516	1.219	1.539	1.278	1.555	1.341	C_{2h} symmetry
8ts1 $CH_2{=}CH\mathbf{C}H{=}O$,[e] (R,R)	1.293, 1.401	159.6	1.477	1.219	1.505	1.273	1.531	1.333	vinyl groups gauche
8ts1 $CH_2{=}CH\mathbf{C}H{=}O$,[e] (R,S)	1.319, 1.364	161.2	1.477	1.219	1.506	1.273	1.531	1.333	vinyl groups anti
8ts1 $CH_2{=}CH\mathbf{C}H{=}O$,[f] (R,S)	1.335, 1.334	180.0	1.477	1.219	1.501	1.276	1.531	1.333	virtual C_{2h} symmetry
8ts2 $\mathbf{C}H_2{=}CHCH{=}O$[g]	1.321, 1.321	177.8	1.345[g]	1.219	1.416[g]	1.246	1.506[g]	1.274	vinyl dihedral = 144.1°
8ts2 $\mathbf{C}H_2{=}CHCH{=}O$[g,h]	1.320, 1.320	180.0	1.345[g]	1.219	1.416[g]	1.246	1.506[g]	1.274	C_{2h} symmetry
8ts3 $CH_2{=}CHCH{=}O$[i]	1.236, 1.580	138.6							not an identity reaction
9 $HO\mathbf{C}H{=}O$, (R,R)	1.361, 1.361	132.4	1.348	1.205	1.388	1.274	1.519	1.312	C_2, d(OH···O) = 1.632[j]
9 $HO\mathbf{C}H{=}O$, (R,S)	1.265, 1.458	135.4	1.348	1.205	1.426	1.256	1.519	1.312	d(OH···O) = 2.052[j]
10 $CH_3O\mathbf{C}H{=}O$, (R,R)	1.321, 1.367	151.2	1.343	1.208	1.446	1.245	1.540	1.295	dihedral O**C**··**C**O = 111.3°
10 $CH_3O\mathbf{C}H{=}O$, (R,S)	1.315, 1.352	168.3	1.343	1.208	1.440	1.252	1.540	1.295	dihedral O**C**··**C**O = 99.1°
11 $H_2N\mathbf{C}H{=}O$, (R,R)	1.326, 1.326	153.3	1.364	1.217	1.452	1.274	1.526	1.327	C_2 symmetry
11 $H_2N\mathbf{C}H{=}O$, (R,S)	1.299, 1.309	180.0	1.364	1.217	1.460	1.268	1.526	1.327	dihedral N**C**··**C**N = 178.1° close to C_i symmetry
12ts1 $\mathbf{C}H_2{=}CHNO_2$	1.325, 1.325	180.0	1.332[g]	1.232[g]	1.402[g]	1.257[g]	1.497[g]	1.282[g]	C_{2h} symmetry
12ts2 $\mathbf{C}H_2{=}CHNO_2$	1.375, 1.376	148.8	1.332[g]	1.232[g]	1.417[g]	1.252[g]	1.497[g]	1.282[g]	dihedral C**C**··**C**C = 7.3°
13[k] $\mathbf{B}H_3$	1.308, 1.308	126.5	NA	NA	NA	NA	NA	NA	staggered about B··B axis
14[k] $\mathbf{Si}H_3$	1.606, 1.606	180.0	NA	NA	NA	NA	NA	NA	C_{2h} symmetry
15[k] $\mathbf{C}H_3^+$	1.232, 1.232	103.2	NA	NA	NA	NA	NA	NA	staggered about C···C axis
16[k,l] $CH_3\mathbf{C}H_2^+$	1.238, 1.238	122.4	NA	NA	NA	NA	NA	NA	C_2 symmetry
17[k] $(CH_3)_2\mathbf{C}H^+$	1.241, 1.243	165.8	NA	NA	NA	NA	NA	NA	virtual C_2 symmetry
18[k] $(CH_3)_3\mathbf{C}^+$	1.254, 1.254	180.0	NA	NA	NA	NA	NA	NA	C_{2h} symmetry
19[k] $CH_2{=}CH\mathbf{C}H_2^+$	1.272, 1.272	176.3	NA	NA	NA	NA	NA	NA	dihedral C**C**··**C**C = 150.6°
20[k] $Ph\mathbf{C}H_2^+$	1.310, 1.312	164.1	NA	NA	NA	NA	NA	NA	dihedral C**C**··**C**C = 12.7°
21[k,m] $HC{\equiv}C\mathbf{C}H_2^+$	1.288, 1.287	177.1	NA	NA	NA	NA	NA	NA	dihedral C**C**··**C**C = 177°
22[k] $CH_2{=}CH\mathbf{C}H(CH_3)^+$, (R,S)	1.272, 1.272	180.0	NA	NA	NA	NA	NA	NA	C_{2h} symmetry
23[n] fulvene	1.318, 1.318	180.0	NA	NA	NA	NA	NA	NA	C_{2h} symmetry

[a] All geometries were optimized at the MP2/6-311+G** level. Average values are used for d(C−X) and d(CH−O) in unsymmetric transition states. All transition states had one imaginary frequency corresponding to the hydrogen transfer coordinate. [b] The acceptor atom is in bold type. Transition state structures with stereocenters at the transfer termini are identified with the usual descriptors. (R,R) and (R,S) structures are diastereomeric. [c] Distances between the transferred hydrogen and the transfer termini. [d] Angles described by the transfer termini and the shared hydrogen. [e] Transfer occurs between the CO carbons. The descriptors gauche and anti refer to the relative orientation of the vinyl groups about the **C···C** axis. [f] This transition state lies 0.5 kcal/mol above the other (R,S) ts. [g] Transfer occurs between the β-carbons. For **8ts2** and **12ts** the d(C−X) distances are between the β- and α-carbons. For **12ts** the d(CH−O) distances are the average N−O distances. [h] This transition state lies 0.03 kcal/mol above the other **8ts2** structure. [i] This is the transition state for the nonidentity hydride transfer between the CO carbon of allyloxide anion and the β-carbon of acrolein. [j] These are hydrogen-bonding distances between the OH group of one formyl moiety and the O atom of the other. There are two such interactions in the C_2, (R,R) structure and one in the (R,S) structure. [k] ts structures for systems **13** through **22** are not transition states but stable donor-acceptor adducts. [l] The ethyl cation is a symmetrical hydrogen-bridged structure. [m] Geometry for the propargyl system is at the HF/6-31+G** level. [n] Hydride addition occurs at the exocyclic carbon for fulvene.

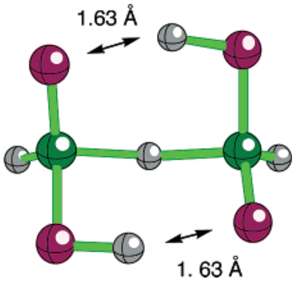

Figure 1. Structure of the C_2, (R,R) transition state for the identity hydride ion transfer between the monoanion of formaldehyde hydrate and formic acid showing short, strong intramolecular hydrogen bonds.

Table 3. Transition State Progress Parameters:[a] Fractional Charge Development ($\mathbf{f_q}$),[b] Fractional Change in C−X Bond Length ($\mathbf{f_x}$),[c] and Fractional Change in C−O Bond Length ($\mathbf{f_o}$)[d]

acceptor	f_q	f_x	f_o
1 $\mathbf{C}O_2$	0.47	NA	0.53
planar ts			
perp ts	0.48	NA	0.53
2 $H\mathbf{C}HO$	0.52	0.50	0.46
3 $CH_3\mathbf{C}HO$	0.52	0.57	0.48
4 $CH_2F\mathbf{C}HO$	0.46	0.44	0.42
5 $CF_3\mathbf{C}HO$	0.42	0.67[e]	0.44
7 $(CH_3)_2\mathbf{C}O$	0.52	0.59	0.47
8 $CH_2{=}CH\mathbf{C}HO$	0.49	0.52	0.47
8[f] $\mathbf{C}H_2{=}CHCHO$	0.50	0.44	0.49
9[g]$HO\mathbf{C}HO$	0.52	0.23, 0.46	0.64, 0.48
10 $CH_3O\mathbf{C}HO$	0.49	0.49	0.51
11 $H_2N\mathbf{C}HO$	0.53	0.54	0,52
12ts1[h] $\mathbf{C}H_2{=}CHNO_2$	0.50	0.39	0.49
12ts2[h] $\mathbf{C}H_2{=}CHNO_2$	0.42	0.53	0.60

[a] All structures were optimized at the MP2/6-311 + G** level. The acceptor atom is bold. The most stable stereoisomer found was used here in all cases except as indicated. [b] $\mathbf{f_q}$ = [(charge on oxygen)^{ts} − (charge on oxygen)^{acceptor}]/[(charge on oxygen)^{donor} − (charge on oxygen)^{acceptor}], that is, the fractional change in charge on oxygen reached at the ts relative to that attained in the donor. [c] $\mathbf{f_x}$ = [d(C−X)^{ts} − d(C−X)^{acceptor}]/[d(C−X)^{donor} − d(C−X)^{acceptor}]. [d] $\mathbf{f_o}$ = [d(C−O)^{ts} − d(C−O)^{acceptor}]/d(C−O)^{donor} − d(C−O)^{acceptor}]. [e] The changes in C−X bond length were so small that this figure is but poorly determined. [f] X = CHCHO for hydride transfer between the β-carbons. [g] The first entry is for the (R,R) ts stereoisomer, the second for the (R,S) ts. The (R,R) structure has two short intramolecular hydrogen bonds between the OH and O fragments; the (R,S) ts has none. [h] X = $CHNO_2$ for hydride transfer between the two β-carbons. **12ts1** is a centrosymmetric structure with the $CHNO_2$ units anti to each other. **12ts2** has the $CHNO_2$ units syn to each other.

$\cdot\cdot$C−X dihedrals are often substantially less than 180°, the two C−X groups being more-or-less gauche to one another. The same tendency was observed in our study of identity proton-transfer reactions[28] and by Houk in his study of hydride transfer in NAD^+/NADH model systems.[8c] In our cases the energetic preference for the best orientation of the C−X groups is usually not large and is presumably determined by a combination of dipolar and polarizability effects. The benzyl$^+$ donor−acceptor compound and fulvene transition state structure illustrate the balance of effects for hydrocarbon systems. In the benzyl$^+$/toluene addition compound the phenyl groups can be described as gauche to each other, the appropriate dihedral being 13°. In the fulvene ts the cyclopentadienyl rings are exactly anti to one another about the hydride transfer axis. In both cases reduced electrostatic repulsion requires maximum separation of the charged moieties, but the benzyl$^+$ compound is a valence-electron deficient structure that could profit from a weak bonding interaction between the rings.

We note two other trends by contrast with proton-transfer transition states. The partial C$\cdots$H$\cdots$C bonds in hydride transfers are shorter by almost 0.1 Å on average than those calculated[28] for proton transfers. In addition, the C$\cdots$H$\cdots$C angle in the hydride transfer transition states is often (but not always) bent, whereas for proton transfers[28] this angle always exceeds 175°. These results will be discussed below.

Charges. Atomic charges for the optimized MP2/6-311+G** structures were calculated by the natural population analysis (NPA) method. A portion of these results is found in Table S2 of the Supporting Information.[33] Of interest is the fact that the charge on the transferred hydrogen in the transition state, $q(\mathbf{H})^\ddagger$, is small, ranging from 0.03 to 0.13 for the X−**C**HO series. These values contrast with those found for the transferred proton in identity proton transfers between carbons which range from 0.25 to 0.30.[28] The smaller values reflect the fact that whereas proton-transfer transition states have a significant charge triplet contribution[28] to their structures ($C^-\ H^+\ C^-)^\ddagger$, the analogous $(C^+\ H^-\ C^+)^\ddagger$ contribution to hydride transfer transition state structure is relatively unimportant.

Values in Table S2 were used to calculate a “charge-based” transition state progress parameter, $\mathbf{f_q}$, for the X−**C**HO and X−CH═**C**H_2 sets. Combined with the two distance-based ts progress parameters mentioned above, these results are given in Table 3 and will be explicitly defined and discussed below.

Discussion

Reaction Energy Surfaces: The X−CHO Set. An ion−molecule complex formed from methoxide anion and formaldehyde was calculated to have ΔH_{CX} = −15.5 kcal/mol, the complex lying more than 8 kcal/mol below the transition state enthalpy. We take this result to be representative of the X−CHO and X−CH═CH_2 series, thus those systems have double well energy surfaces with an enthalpic barrier to hydride transfer.

Reaction Energy Surfaces: The Carbenium Ion Set. For the reactions between carbenium ions and their hydride addition products we found no barrier to hydride transfer at the HF/6-311+G** level for the methyl$^+$, ethyl$^+$, and isopropyl$^+$ acceptors. Rather, the calculated structures are donor−acceptor addition compounds. The other systems produced structures with imaginary frequencies corresponding to the hydrogen transfer motion at the HF level. However, these frequencies were suspiciously low compared with those found for the carbonyl transition states. Moreover, at the MP2/6-311+G** level these structures characteristically have either a single very small negative eigenvalue or none at all, suggesting that the calculated MP2 structures are not true transition states but addition compounds. To test this point we computed MP2/6-311+G** frequencies for the allyl$^+$/propene transition state. Whereas for the HF/6-311+G** structure an imaginary frequency = 493 cm^{-1} was found, the MP2 structure had $i\upsilon = 22\ cm^{-1}$ and no negative eigenvalues. Likewise, calculation of the transition state for the hydride transfer to 1-methylallyl$^+$ from 1-butene produced no negative eigenvalue at the MP2/6-311+G** level. These results show that at the MP2 level identity hydride transfer reactions to simple carbenium ions have little or no barrier.

Our computational results stand in contrast to those of Mayr et al.[19] These workers reported activation enthalpies for a number of identity and nonidentity hydride transfers between substituted allyl cations and a set of 1-substituted propene donors. There are two major possibilities for the discrepancy. First, all of Mayr's cations are more stable than those studied by us. Second, as shown also by Mayr, the computational existence of a transition state for these reactions seems to depend on whether electron correlation is employed in computing the optimized structure, and perhaps also on the size of the basis set. As mentioned above, we find that transition states for the *tert*-butyl, allyl, 1-methylallyl, and benzyl systems were located at the HF/6-311+G** level (albeit with suspiciously low imaginary frequencies compared with the those for the X−CH═O set) but that these disappear at the MP2/6-311+G** level. Mayr's highest level calculation, a G3MP2 calculation for the 3,3-dimethylallyl case, shows a transition state lying only a fraction of 1 kcal/mol above an ion−molecule complex, indicating once again that if a barrier to hydride transfer exists in these systems it is a very small one.

An ion−molecule complex, different from the addition compound, was calculated for the allyl reactants with $\Delta H_{CX} \approx -32$ kcal/mol, placing this complex well below the addition compound for which $\Delta H_{CPD} = -11$ kcal/mol. The complex formed from allyl$^+$ and propene owes its great stability to the fact that it is actually an unsymmetrical π-complex. One end of the allyl moiety lies 1.72 Å from C1 and 2.09 Å from C2 of the propene portion. The secondary C2−H unit in the propene portion has acquired +0.42 NPA charge, more than any other CH_n unit in the complex. This species presumably leads to a transition state for Markovnikov addition of allyl$^+$ to propene. We did not search for other complexes between these two reactants.

The *tert*-butyl$^+$ energy surface was also explored. We found two noncovalent ion−molecule complexes formed from *tert*-butyl cation and isobutane. One of these complexes is calculated to lie 10.7 kcal/mol above the addition compound, and the other is 10.4 kcal/mol higher. We did not search for other complexes, but it may well be that an abundance of complexes characterizes the interaction of saturated nonpolar neutrals with simple carbenium ions because the ion will not discriminate decisively between a collection of similar C−H and C−C units in the neutral.

Correlations Involving ΔH Values. An attempted linear correlation between ΔH_{ADD} and $\Delta H^{\ddagger}$ (ΔH_{CPD}) gave essentially a scatter plot, $r^2 = 0.379$. A similarly poor result was obtained between computed ΔH_{ACID} and $\Delta H^{\ddagger}$ values for a set of identity proton-transfer reactions.[28] These results are not surprising in view of the fact that in the transition states and addition compounds, bimolecular interactions occur which have no counterparts in the separated reactants. These interactions must vary somewhat from system to system, hence the lack of a general relationship.

Transition State Geometry: Comparison With Proton Transfer. Two geometric features are systematically different between the identity hydride transfer transition states and addition compounds reported here and the identity proton-transfer transition states, computed at the same level, and reported earlier.[28] First, the partial bonds between the transferred hydrogen and the donor and acceptor carbons are computed to be shorter on average by about 0.1 Å in the hydride transfer transition states and addition compounds. Second, the angle formed by the two terminal carbons and the transferred hydrogen is often far from linear in the hydride transfers, whereas in proton transfers that angle was always found to lie between 175° and 180°. Both features bring the terminal carbons closer to each other in the hydride transfer structures. The idea that hydride transfers might have bent transition states was suggested early on by Lewis and co-workers[35] as well as by More O'Ferrall.[36]

These differences can be understood by modeling the hydride transfer transition state and addition compound structures as having a two-electron, three-center array in which two electrons are shared by the terminal groups and the transferred hydrogen in the HOMO.[37] By the same token the proton-transfer ts has a *four*-electron, three-center array. Swain, Wiles, and Bader gave a simple pictorial σ-orbital description of these differences in which the HOMO in the proton-transfer ts is antibonding, whereas that for the hydride transfer is bonding.[38] For proton transfer, the result is repulsion between the termini because the wave function at these negatively charged sites is out of phase. In hydride transfer the wave function at the terminal centers in the HOMO is in phase allowing for a bonding interaction which can be improved if those sites are closer. Sorensen provided a similar analysis likening the hydride transfer between an alkane and a carbenium ion (modeled as a μ-H-bridged addition compound) to the allyl cation for which the HOMO = π_1 is bonding.[1b] Extending the analogy, the proton-transfer ts can be likened to the allyl anion where HOMO = π_2 and is antibonding. As the model predicts, the allyl anion is calculated (MP2/6-311+G**) to have a larger C−C−C angle (132°) and a greater $C_1 \cdots C_3$ distance (2.55 Å) than the allyl cation (117° and 2.37 Å).

In Figure 2 we show the HOMOs calculated for two of the systems studied here, the addition compound formed from methyl cation and methane and the transition state for hydride transfer between methoxide anion and formaldehyde. Both show that the terminal centers interact constructively with each other.

It is noteworthy that the hydride transfers for the carbonyl set do have significant activation barriers, whereas those for the carbenium set do not. Carbenium ions not only are positively charged but also have an unfilled valence shell. The opportunity to (partly) remedy this situation by formation of a three-center, two-electron bond must present a powerful driving force for no-barrier compound formation. The carbonyl acceptors also form three-center, two-electron arrays, but from much less electron deficient starting materials; hence these structures are transition states, not stable compounds. The hydride transfer from methylcyclopentadienide to fulvene demonstrates that formation of a transition state is not a feature of the X−CH═O and X−CH═CH_2 systems alone but can be the preferred path for a hydrocarbon acceptor as well. Like the carbonyl acceptors, fulvene has a complete valence electron count. It is therefore not electron deficient in the same sense as a carbenium ion, and the benefit of the three-center, two-electron bonding arrangement is not fully expressed.

Transition State Progress Measures. We define three measures of "transition state progress" for the X−**C**HO and X−CH═**C**H_2 series. Two are based on fractional changes in

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(35) (a) Lewis, E. S.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1958**, *80*, 4296. (b) Lewis, E. S.; Symons M. C. R. *Q. Rev. Chem. Soc.* **1958**, *12*, 230.

(36) More O'Ferrall, R. *J. Chem. Soc. B* **1967**, 985.

(37) The idea is concisely expressed by Lipscomb: The localized multicenter orbital... is particularly useful when there are more valence orbitals than electrons in a molecule or transition state. Lipscomb, W. N. In *Hypercarbon Chemistry*; Olah, G. A.; Prakash, G. K. S.; Wade, K., Eds.; Wiley-Interscience: New York, 1987; Foreword.

(38) Swain, C. G.; Wiles, R. A.; Bader, R. F. W. *J. Am. Chem. Soc.* **1961**, *83*, 1945.

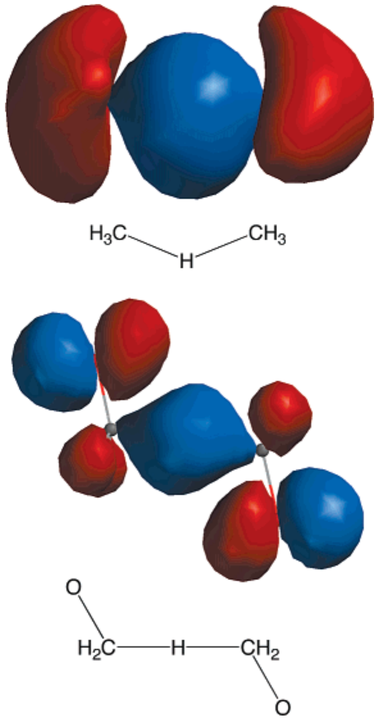


Figure 2. (a) HOMO for the addition product of methyl cation to methane showing constructive overlap between the terminal CH_3 groups, $d(C\cdots C) = 1.93$ Å. (b) HOMO for the transition state (C_{2h}) in the identity hydride transfer between formaldehyde and methoxide anion showing constructive overlap between the reaction termini, $d(C\cdots C) = 2.63$ Å.

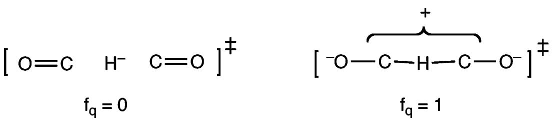
bond lengths which have occurred at the transition state as the hydride acceptor, X−CH═O, becomes the hydride adduct (donor). One of these ($\mathbf{f_x}$) is the fractional change in the X−C bond length. The other ($\mathbf{f_o}$) is the fractional change in the C═O (or NO for X = NO_2) bond length. Additionally a charge-based measure ($\mathbf{f_q}$) is defined as the fractional change in the NPA charge on the oxygen atom(s), q_o, attained at the ts as the acceptor turns into the donor. Equations 3−5 give the definitions. The resulting **f** values are given in Table 3.

$$\mathbf{f_x} = [d(\mathrm{C{-}X})^{\mathrm{ts}} - d(\mathrm{C{-}X})^{\mathrm{acceptor}}]/[d(\mathrm{C{-}X})^{\mathrm{donor}} - d(\mathrm{C{-}X})^{\mathrm{acceptor}}] \quad (3)$$

$$\mathbf{f_o} = [d(\mathrm{C{-}O})^{\mathrm{ts}} - d(\mathrm{C{-}O})^{\mathrm{acceptor}}]/[d(\mathrm{C{-}O})^{\mathrm{donor}} - d(\mathrm{C{-}O})^{\mathrm{acceptor}}] \quad (4)$$

$$\mathbf{f_q} = [(q_o)^{\mathrm{ts}} - (q_o)^{\mathrm{acceptor}}]/[(q_o)^{\mathrm{donor}} - (q_o)^{\mathrm{acceptor}}] \quad (5)$$

All three measures are close to 0.5 for all members of the series. The average values, respectively, are $\mathbf{f_x} = 0.51 \pm 0.04$, $\mathbf{f_o} = 0.49 \pm 0.03$, and $\mathbf{f_q} = 0.49 \pm 0.03$. Limiting cases for the charge-based parameter can be evaluated by imagining two extreme transition state models. One may be said to have a "hypovalent", negative hydrogen. The other has a "hypervalent" hydrogen. These models and the appropriate $\mathbf{f_q}$ values are shown schematically below for the carbonyl set.



These transition state progress measures, together with the small charges on the transferred hydrogen, indicate that the hydride transfer ts in these systems is central and that the transfer may be described as synchronous, with the bonding changes paralleling one another, even in the X−CH═CH_2 systems where the opportunity exists for resonance delocalization in the ts. Again, this result lies in contrast to many proton transfers in which "transition state imbalance" is found, particularly when the conjugate base of the acid has a delocalized or relocalized charge.[28, 39]

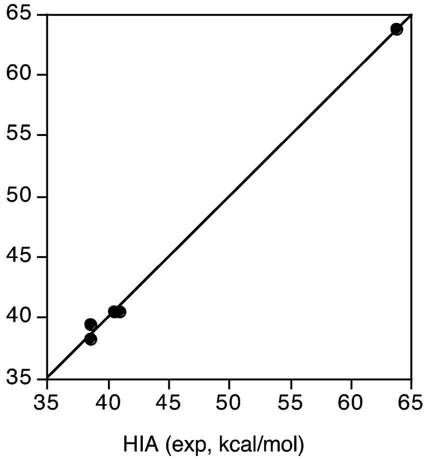


Figure 3. Plot of predicted hydride ion affinities (HIAs) using gas-phase polar, resonance (σ^+), and polarizability substituent constants against experimental HIA values[13] for the X−CHO set. See eq 6.

Substituent Effects on ΔH_{ADD} and $\Delta H^{\ddagger}$. Gas-phase substituent constants[40] were used to carry out a multiparameter substituent effect analysis of the effects of substituents, X, on the experimental HIA values, the computed enthalpies of hydride addition, and the computed activation enthalpies for identity hydride transfers in the X−CHO set. A three-parameter fit was sought to determine the relative importance of polar effects (σ_F), resonance effects (σ_{R+}), and polarizability effects (σ_α).[41] The correlations are shown as eqs 6−8

$$\mathrm{HIA_{EXP}} = 49.9\sigma_F + 37.9\sigma_{R+} - 5.4\sigma_\alpha + 40.5 \qquad r^2 = 0.998\ (n = 5) \quad (6)$$

$$\Delta H_{\mathrm{ADD}} = 54.6\sigma_F + 39.0\sigma_{R+} - 9.3\sigma_\alpha + 356.7 \qquad r^2 = 0.970\ (n = 10) \quad (7)$$

$$\Delta H^{\ddagger} = -6.0\sigma_F - 30.4\sigma_{R+} + 6.4\sigma_\alpha - 6.8 \qquad r^2 = 0.990\ (n = 9) \quad (8)$$

and graphically as Figures 3−5. For two systems, **9** (formic acid acceptor) and **11** (formamide acceptor), the most stable transition states were not used in correlation 8 because these structures profit from internal hydrogen bonding between the two halves of the structure (see Geometries above), an interaction not represented in the data set by which the σ values were evaluated.

In correlations 6 and 7 the processes are so defined that positive $\rho\sigma$ combinations signify increased hydride ion affinity,

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(39) (a) Bernasconi, C. F. *Acc. Chem. Res.* **1987**, *20*, 301. (b) Albery, W. J.; Bernasconi, C. F.; Kresge, A. J. *J. Phys. Org. Chem.* **1988**, *1* 29. (c) Bernasconi, C. F. *Acc. Chem. Res.* **1992**, *25*, 9. (d) Bernasconi, C. F. *Adv. Phys. Org. Chem.* **1992**, *27*, 119.

(40) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165.

(41) Because σ_α values are negative,[40] a negative ρ value results in $\rho\sigma_\alpha > 0$. This enhances HIA but raises the barrier to hydride transfer.

Table 4. Polar, Resonance, and Polarizability Substituent Effects (kcal/mol)[a] on −HIA (expt),[b] $-\Delta H_{ADD}$ (calcd),[c] and $\Delta H^{‡}$ (calcd)[d] for the Identity Hydride Transfer Reactions between X−CHO and $X-CH_2O^-$ in This Study; See Equations 6−8 in the Text

	−HIA (expt)			$-\Delta H_{ADD}$ (calcd)			$\Delta H^{‡}$ (calcd)		
system, X	$\rho_F\sigma_F$	$\rho_R\sigma_R^+$	$\rho_\alpha\sigma_\alpha$	$\rho_F\sigma_F$	$\rho_R\sigma_R^+$	$\rho_\alpha\sigma_\alpha$	$\rho_F\sigma_F$	$\rho_R\sigma_R^+$	$\rho_\alpha\sigma_\alpha$
2 H	-0-	-0-	-0-	-0-	-0-	-0-	-0-	-0-	-0-
3 CH_3	0.0	3.0	−1.9	0.0	3.1	−3.3	0.0	2.4	−2.2
4 CH_2F	NA	NA	NA	−12.0	1.2	−2.8	−1.3	0.9	−1.9
5 CF_3	−22.0	0.0	−1.4	−24.0	0.0	−2.3	−2.6	0.0	−1.6
6 CH_2CH_3	0.0	2.7	−2.6	0.0	2.7	−4.6	NA	NA	NA
7[e] CH_3, CH_3	0.0	6.1	−3.8	0.0	6.2	−6.5	0.0	4.9	−4.5
8 $CH{=}CH_2$	NA	NA	NA	−3.3	6.2	−4.7	−0.4	4.9	−3.2
9[f] OH	NA	NA	NA	−16.4	14.8	−0.3	−1.8	11.6	−0.2
10 OCH_3	NA	NA	NA	−13.7	16.4	−1.6	−1.5	12.8	−1.1
11[f] NH_2	NA	NA	NA	−7.6	20.3	−1.5	−0.8	15.8	−1.0

[a] Negative $\rho\sigma$ values indicate that the substituent aids the reaction; positive values indicate that it inhibits reaction. Gas phase substituent constants are taken from Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165. See also: Taft, R. W.; Topsom, R. D. *Prog. Phys. Org. Chem.* **1987**, *16*, 1. Calculated values refer to structures optimized at the MP2/6-311+G** level with ZPVE corrections calculated at the HF/6-311+G** level and scaled by 0.9135 as recommended by Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502. [b] −HIA is the enthalpy of reaction for the addition of hydride ion to the acceptor. Experimental values are from Bartmess, J. E. In *NIST Standard Reference Database Number 69;* Mallard, W. G., Linstrom, P. J., Eds.; National Institute of Standards and Technology (http://webbook.nist.gov): Gaithersburg, MD, 2003. [c] $-\Delta H_{ADD} = (H_{ADDUCT} - H_{ACCEPTOR})$. The enthalpy of H^- is not well calculated at MP2/6-311+G** level and is omitted from the listed quantity. [d] Enthalpies of activation for the identity hydride transfer between the hydride donor (adduct) and hydride acceptor. [e] The acceptor is acetone; the donor is 2-propanoxide ion. [f] The more stable stereoisomeric transition state is used in all cases except for X = OH, NH_2. In these cases superior inter-moiety hydrogen bonding occurs in the more stable structures and is not reflected in the σ values.

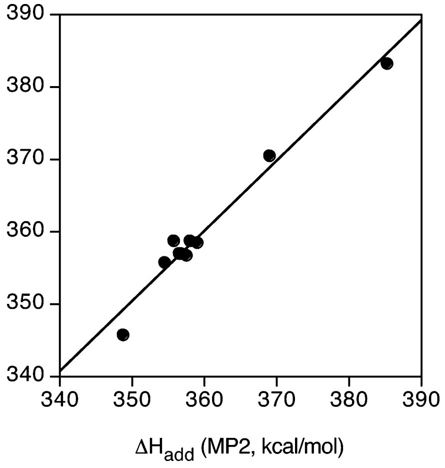

Figure 4. Plot of predicted ΔH_{ADD} values using gas-phase polar, resonance (σ^+), and polarizability substituent constants against calculated (MP2/6-311+G**) ΔH_{ADD} values for the X−CHO set. See eq 7.

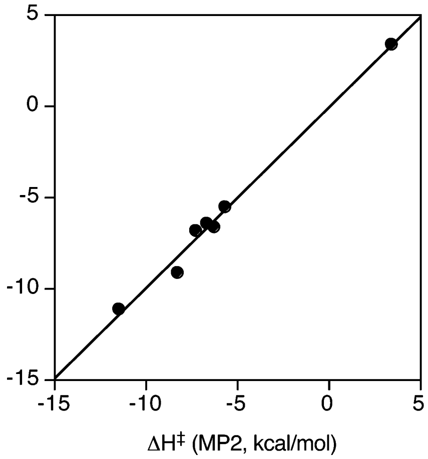

Figure 5. Plot of predicted $\Delta H^{‡}$ values using gas-phase polar, resonance (σ^+), and polarizability substituent constants against calculated (MP2/6-311+G**) $\Delta H^{‡}$ values for the X−CHO set. See eq 8.

whereas in eq 8 negative combinations signify a lower barrier to the hydride transfer. Thus, electron withdrawing groups increase hydride ion affinity and accelerate hydride transfer, while electron donors reduce hydride ion affinity as well as raising the barrier to hydride transfer. These results are in general agreement with those of Mayr et al.[19] Of course the exact energetic consequences depend not only on the signs and magnitudes of the ρ coefficients but also on those of the σ values as well. These consequences are seen more clearly in Table 4, where it is seen that polarizability effects, helpful in all cases, can be important, even dominant, despite relatively low ρ_α values.

It is gratifying that the fractional influence of the various substituent effects, as measured by their ρ coefficients, is almost the same for the experimental HIAs and the computed ΔH_{ADD} quantities. For eq 6 the percent contributions are 53.5% polar, 40.7% resonance, and 5.8% polarizability. For eq 7 it is 53.1% polar, 37.9% resonance, and 9.0% polarizability. In eq 8 the influences of polar and resonance effects are reversed: 14.0% polar, 71.0% resonance, and 15.0% polarizability. In this process resonance stabilization of the acceptor reactant, X−CH=O, is largely missing in the transition states with the effect that the barriers for X = OH, OCH_3, and NH_2 are especially high.

We also performed the multiparameter substituent effect analysis on Fujio and co-workers' computational results.[16] They computed stabilization energies, $\delta_X\Delta E$, for the isodesmic reaction shown in eq 9. *Para*- and *meta*-substituents must be considered separately in this analysis. The results are given as eqs 10 and 11.

$$PhCH_2^+ + ArCH_3 \rightarrow PhCH_3 + ArCH_2^+ \text{ (MP2/6-31G*//RHF/6-31G*)} \quad (9)$$

$$\delta_X\Delta E\ (para) = -24.9\sigma_F - 52.6\sigma_{R+} - 6.1\sigma_\alpha + 0.01 \qquad r^2 = 0.999\ (n = 11) \quad (10)$$

$$\delta_X\Delta E\ (meta) = -26.1\sigma_F - 21.9\sigma_{R+} - 3.0\sigma_\alpha + 0.26 \qquad r^2 = 0.994\ (n = 6) \quad (11)$$

Clearly the multiple substituent effect treatment using gas-phase σ values does an excellent job predicting substituent effects on the stabilization energies of benzylic cations. The persistence of resonance effects in the *meta*-substituted set is notable and calls to mind such effects on the ionization of benzoic acids in aqueous solution. The σ_m constant for the NH_2 group, for example, is -0.16.[42] If the resonance donating substituents in Fujio's *meta*-set were rotated so that conjugation with the ring was not possible, this residual resonance should be erased.

Conclusions

The major conclusions drawn from this work include the following:

(1) Transition states for identity hydride transfer reactions in the $X{-}CH{=}O$ and $X{-}CH{=}CH_2$ series are central with respect to development of bond length and charge changes attained at the transition state. These changes appear to occur in a synchronous manner, in contrast to many identity proton transfer reactions between carbon centers, especially those in which substantial charge delocalization occurs in the conjugate base structures, and for which ion-triplet structures, $(C^{-}\cdots H^{+}\cdots C^{-})^{\ddagger}$, make an important contribution to the transition state.[28,39]

(2) Hydride transfer to simple carbenium ions from their conjugate donors occurs with little or no activation barrier. Stable donor−acceptor addition compounds are formed rather than transition states.

(3) Differences between ts structures for hydride transfer and proton transfer include systematically shorter C···H bonds to the transferred hydrogen and a more flexible geometry about the C···H···C triad, often with angles considerably less than 180° for hydride transfers. These differences can be explained using a two-electron, three-center model for hydride transfer and a four-electron, three-center model for proton transfer.[1b,38]

(4) For the $X{-}CHO$ series polar effects are somewhat more important than resonance effects in determining enthalpies of hydride addition, but resonance donors are nevertheless important in stabilizing the acceptor reactant. Activation enthalpies are dominated by resonance effects, again most dramatically realized with resonance donors. These stabilize the acceptor more than the transition state. Polarizability effects can also be important, especially when polar and resonance σ values are small.

(5) The multiparameter substituent effect analysis using gas-phase substituent constants does a very good to excellent job correlating both experimental and calculated gas-phase enthalpies of reaction and activation not only for the hydride transfers reported here but also for proton-transfer reactions[28] and for the relative stabilization energies of ring-substituted benzylic cations calculated by Fujio and co-workers.[16]

Acknowledgment. Support from the National Science Foundation (CHE-0348809) is gratefully acknowledged by S.G.

Supporting Information Available: Tables S1 (electronic energies, zero-point viibrational energies, imaginary frequencies) and S2 (selected NPA charges). This material is available free of charge via the Internet at http://pubs.acs.org.

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(42) Hine, J. *Structural Effects on Equilibria in Organic Chemistry*; Wiley-Interscience: New York, 1975; p 66.