Molecular-orbital Calculations on Proton Abstractions by the Hydride Ion

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Ab initio calculations have been used to examine the electronic structures and energies of the molecules involved in the reactions of simple molecules with negative hydrogen ions. The intermediate structure shows an extended X–H bond character with a relatively strong H–H′ bond. Some useful correlations are discussed.

DURING the past few years, theoretical approaches have been used to study the proton-transfer properties of simple hydrogen molecules. Ritchie and King[1-3] studied the reactions of simple hydrogen molecules with an electron donor, H^-, by means of *ab initio* type calculations. The molecules studied involved H–H, F–H, H_2N–H, HO–H, and H_3C–H. The proton-transfer properties of different hydrogen molecules have also been studied by Bonchev and Cremaschi[4] using a CNDO/2 type method. The electron donors used were NH_3,H_2O, and HF.

No systematic studies, however, have been reported for the properties of complexes formed by the relatively stable hydrogen bond and of the species produced by proton-transfer processes. Therefore, in an attempt to understand the chemical and physical properties involved in the proton-transfer processes, a series of *ab initio* type calculations have been made for a number of small hydrogen molecules using hydride ion, H^-, as proton abstractor. The interaction of the hydrogen molecules with this simplest ion will not only save computational steps but also avoid difficulties often encountered in a large molecular system. In particular, hydride ions have been found to be important secondary ions formed in a negative mass spectrometer[5] and the proton-abstraction mechanism with H^- will give us some insights into the possible chemical reactions in the experimental system.

COMPUTATION

The proton abstractions by hydride ion were studied using a molecular-orbital (m.o.) approach for a series of simple hydrogen molecules by varying the substituent M in (1)

$$\text{M–H} + H^- \longrightarrow [MH_2]^- \longrightarrow M^- + H_2 \qquad (1)$$

where M is H_nX, Y_nX, or H_nY_nX (X and Y are first-row atoms). All the *ab initio* LCAO–MO–SCF calculations were made on an IBM 7094 computer using the SMALLOBE program[6] with the gaussian basis set consisting of S^4 on H and S^2, S^4, and P^4 functions on B, C, N, O, and F. To save computing time, the electronic structures and energies of the molecules, of their possible intermediates, and of the negative ions were computed for the lowest spin states only.

The geometries of all the hydrogenic molecules were optimized by varying the bond lengths and angles in a systematic manner until a minimum energy was obtained. These values were used as a basis for further calculations. The energy of the hydride complexes was obtained by simultaneous variation of the H–H′ bond and the bond attached to the hydrogen, X–H. Further details of these optimizations are discussed in the following section.

RESULTS AND DISCUSSION

Optimized Geometries and Energies.—As mentioned in the previous section, the minimum-energy geometries of the neutral hydrogenic molecules (M–H) were obtained by step-by-step procedures including all the bonds of the molecules. Since the computed results of the molecules were in good agreement with experimental data,† these values were used as a basis for further calculations.

We will describe the proton-transfer reaction as a two-step process as follows (h.a. = hydride affinity):

$$\begin{tikzcd} MH + H^- \arrow[r, "-h.a."'] \arrow[dr, "\epsilon_p"'] & {[MH_2]^-} \arrow[d, "\epsilon_b"] \\ & M^- + H_2 \end{tikzcd}$$

The intermediate negative complexes are assumed to be formed by H · · · H^- interaction. For the relatively

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† The differences in bond lengths and angles computed from the experimental values were *ca.* 0.02 Å and 5°, respectively.

[1] C. D. Ritchie and H. F. King, *J. Amer. Chem. Soc.*, 1968, **90**, 825.

[2] C. D. Ritchie and H. F. King, *J. Amer. Chem. Soc.*, 1968, **90**, 833.

[3] C. D. Ritchie and H. F. King, *J. Amer. Chem. Soc.*, 1968, **90**, 838.

[4] D. Bonchev and P. Cremaschi, *Theor. Chim. Acta*, 1974, **35**, 69.

[5] R. C. Dougherty and J. Dalton, *Org. Mass. Spectrometry*, 1972, **6**, 1171; J. G. Dillard, *Chem. Rev.*, 1973, **73**, 589.

[6] QCPE No. 239, obtained from the Quantum Chemistry Program Exchange, Indiana University, Bloomington, Indiana.

TABLE 1

Geometries and energies of the negative hydride complex ions, $[MH_2]^-$ *

M–H · · · H′	Geometry $R_{H-H'}$	R_{X-H}	R_{Y-X}	θ_{YXH}	$\theta_{XHH'}$	Energy
H–H · · · H	1.134	1.134			180.0	1.3373
B–H · · · H	0.821	2.294			180.0	25.3729
C–H · · · H	1.189	1.304			172.0	38.1721
N–H · · · H	1.161	1.273			180.0	54.6798
O–H · · · H	1.352	1.080			180.0	74.6812
F–H · · · H	1.022	1.241			179.9	99.0579
HB–H · · · H	1.051	2.305	1.288	180.0	(180.0)	25.8616
HC–H · · · H	1.012	1.350	1.181	95.3	(180.0)	38.9220
HN–H · · · H	1.323	1.325	1.089	93.2	(180.0)	55.1601
HO–H · · · H	1.131	1.129	1.013	96.7	177.88	75.5253
HF–H · · · H	1.056	1.233	1.538	181.0	(180.0)	99.3524
H_2B–H · · · H	1.413	1.776	1.277	127.7	(180.0)	26.5146
H_2C–H · · · H	1.233	1.355	1.157	109.0	(180.0)	39.4613
H_2N–H · · · H	1.192	1.239	1.073	96.3	(180.0)	56.0146
H_2O–H · · · H	1.018	1.265	1.128	105.7	(180.0)	75.8373
NC–H · · · H	0.994	2.014	1.204	(180.0)	(180.0)	92.5484
OC–H · · · H	1.015	1.490	(1.219)	(121.6)	(180.0)	112.4606
ON–H · · · H	1.051	1.108	(1.243)	(105.5)	(180.0)	128.8534
FC–H · · · H	1.123	1.580	(1.306)	(101.6)	(180.0)	136.6229
HC_2–H · · · H	1.014	1.337	(1.259)	(180.0)	(180.0)	76.6874

* Energy in negative atomic units, R in Å, and θ in °. Values in parentheses are not optimized.

small complexes, the energy was optimized for all the bonds, while for the larger complexes optimization was only for H–H′ and X–H bonds assuming X–H–H′ bonds are linear and the rest of the neighbouring bonds are not influenced. Such assumptions seem justified because the complete optimization showed a relatively large increase in the X–H bond without significant change in the neighbouring bond and preference for approximate linearity of the X–H–H′ bonds. The near linearity of these bonds has also been observed by Ritchie and King.[1,2] The occurrence of linearity implies the importance of the electrostatic effect on the H–H′ bond formation.[7] The computed results are in Tables 1 and 2. Because of the greatly extended X–H bonds with strong H–H′ bonds in the intermediate complexes, the negative ion, M^-, is expected to appear as a possible ion in the reaction system.

TABLE 2

Reaction energies and other computed results *

M–H	$E_{l.u.m.o.}$	$E_{l.u.m.o.}{}^{\sigma}$	H.a.	$-E_p$	E_b
H–H	0.6270	0.6270	0.0066	0.0000	0.0066
B–H	−0.0074	−0.0074	0.3810	0.3770	0.0040
C–H	0.1153	0.4994	0.1334	0.1337	−0.0003
N–H	0.1685	0.5060	0.1156	0.0571	0.0585
O–H	0.5149	0.5149	0.1111	0.0026	0.1085
F–H	0.5359	0.5359	0.1002	−0.0617	0.1619
HB–H	0.0971	0.3402	0.2104	0.2542	−0.0438
HC–H	0.1749	0.3511	0.2007	0.2144	−0.0107
HN–N	0.1328	0.5359	0.1473	0.1536	−0.0063
HO–H	0.5368	0.5368	0.1154	0.0326	0.0828
HF–H	0.0430	0.5070	0.1084	0.1003	0.0081
H_2B–H	0.5265	0.5265	0.0947	0.1168	−0.0221
H_2C–H	0.5543		0.1451	0.1534	−0.0083
H_2N–H	0.5641		0.1064	−0.0342	0.1406
H_2O–H	0.1398	0.5025	0.1485	0.1139	0.0346
NC–H	0.2463	0.2463	0.2751	0.3039	−0.0288
OC–H	0.1983	0.4823	0.2284	0.2386	−0.0102
ON–H	0.1656	0.4665	0.1354	0.1536	−0.0182
FC–H	0.1384	0.4813	0.1348	0.1448	−0.0100
HC_2–H	0.2680	0.2680	0.2718	0.2643	0.0075

* Energies in atomic units. Definitions of the terms are given in the text.

TABLE 3

Charge distributions and bond orders of $[MH_2]^-$ complexes

M–H–H′	Charge distribution C_Y	C_X	C_H	$C_{H'}$	Bond orders P_{Y-X}	P_{X-H}	$P_{H-H'}$
H–H–H		−0.539	0.078	−0.539		0.369	0.369
B–H–H		−0.917	0.098	−0.181		0.060	0.721
C–H–H		−0.685	0.147	−0.462		0.280	0.243
N–H–H		−0.549	0.129	−0.580		0.221	0.356
O–H–H		−0.560	0.072	−0.512		0.215	0.182
F–H–H		−0.454	0.159	−0.695		0.193	0.226
H–B–H–H	−0.087	−0.843	0.120	−0.190	0.736	0.039	0.628
H–C–H–H	−0.033	−0.614	0.156	−0.509	0.499	0.191	0.479
H–N–H–H	−0.071	−0.642	0.008	−0.295	0.331	0.270	0.223
H–O–H–H	−0.009	−0.555	0.170	−0.606	0.248	0.245	0.331
H–F–H–H	−0.358	−0.285	0.073	−0.430	0.009	0.130	0.348
H_2–B–H–H	−0.030	−0.620	−0.172	−0.486	0.760	0.181	0.399
H_2–C–H–H	−0.020	−0.724	0.099	−0.330	0.594	0.361	0.330
H_2–N–H–H	0.022	−0.626	0.174	−0.592	0.414	0.266	0.369
H_2–O–H–H	−0.156	−0.374	0.141	−0.456	−0.126	0.131	0.435
N–C–H–H	−0.490	−0.439	0.114	−0.185	0.950	0.040	0.654
O–C–H–H	−0.401	−0.367	0.092	−0.324	0.472	0.121	0.521
O–N–H–H	−0.288	−0.314	0.205	−0.573	0.350	0.150	0.464
F–C–H–H	−0.182	−0.487	0.113	−0.444	0.153	0.190	0.466
HC–C–H–H	−0.458	−0.420	0.192	−0.414	1.197	0.026	0.640

Electron-density Distribution.—Charge distributions and bond strengths for $[MH_2]^-$ complexes are listed in Table 3 and the change in these parameters caused by the proton abstraction is summarized in Table 4. For the change of charge distribution on the formation of the complexes by the H–H′ bond, the main electron-acceptor site in the hydrides is the atom attached to the hydrogen, X. The hydrogen atom involved in the direct bond formation does not noticeably contribute to the charge distribution in the complex and is still slightly positively charged. The decrease in X–H bond order (ΔP_{X-H}) is probably due to repulsion of X by the negatively charged H′ atom. This may cause considerable lengthening of the X–H bond, except for $[HFH]^-$ and $[H_2OH]^-$ systems, which have antibonding character in the neutral states.

Proton Donor Strength of M–H.—Since the X–H group

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[7] C. A. Coulson, *Research* (*London*), 1957, **10**, 149.

behaves as a proton donor and the negative ion as an electron donor in the proton-abstraction reaction, the hydride affinity calculated (Table 2) could indicate the proton donor strength of the studied molecules for a fixed electron donor. If so, the following h.a. orders, which in fact are similar to the previous study,[4] can be suggested from the present computation: for M = X, B > C > N > O > F > H; M = H_nX, CH_2 > CH_3 > CH_4 *; M = YX, HCN > HC_2H > HCO_2H * > CH_4. This relation eventually allows us to suggest that the X–H–H′ bonds examined have no principal differences from the ordinary hydrogen bond, although the bond strengths are generally much higher.

TABLE 4

Change of charge distribution and bond order by the MH · · · H′ complex formation *

M–H	ΔC_H	ΔC_X	ΔC_M	ΔP_{X-H}
H–H	−0.078	0.539	0.461	0.440
B–H	−0.003	0.822	0.822	0.720
C–H	−0.033	0.571	0.571	0.237
N–H	0.010	0.410	0.410	0.091
O–H	0.098	0.390	0.390	0.073
F–H	0.022	0.283	0.283	0.029
HB–H	0.013	0.577	0.797	0.797
HC–H	0.061	0.650	0.747	0.502
HN–H	0.207	0.213	0.499	0.261
HO–H	0.037	0.141	0.357	0.125
HF–H	−0.043	0.225	0.733	−0.149
H_2B–H	−0.079	0.342	0.588	0.643
H_2C–H	0.039	0.235	0.541	0.380
H_2N–H	0.005	0.090	0.404	0.195
H_2O–H	−0.078	0.185	0.623	−0.180
NC–H	0.159	0.326	0.656	0.714
OC–H	0.092	0.365	0.584	0.380
ON–H	−0.026	0.248	0.453	0.305
FC–H	−0.009	0.435	0.565	0.359
HC_2–H	0.037	0.191	0.549	0.770

* Positive values represent increasing electronegativity on the appropriate group or atom and decreasing bond order by the complex formation.

Stability of $[MH_2]^-$ *Complex*.—Considering the extremely weakened X–H bond with increasing H–H′ bond strength (Figure 1), one may view the structure as a complex of M^- and H_2 connected by a weak X–H bond. If the electrostatic energy between M^- and H_2 is considered to be sufficient to account for the whole energy of the bond, the X–H bond energy is expected to vary with X–H bond length similar to a Morse curve. Thus, at large separations of X and H atoms increasing electrostatic attraction stabilizes the X–H bond as the X–H bond length decreases. However, at a sufficiently short distance of the X and H atoms the rapidly increasing repulsive force may decrease the X–H bond stability.

An interesting feature is the variation of the total X–H–H′ bond length as the length of the X–H bond varies, as illustrated in Figure 2. This particular curve certainly suggests, although there is a large-scale scattering of the data, the presence of a critical bonding distance for the X–H–H′ system. At large distance of the X–H bond, this bond length decreases without much change in the H–H′ bond; thus the total X–H–H′ bond length decreases until the X–H bond length reaches the critical point of *ca.* 1.2 Å. When the X–H bond length becomes shorter than the critical length, the H–H′ distance increases with a subsequent increase in the total X–H–H′ distance. Therefore, at the critical point, the complex has the most compact configuration and is most strongly bonded. Among the ions studied, $[HF_2]^-$ with X–H = 1.241 and X–H–H′ = 2.263 Å has the greatest stability close to the critical point. It is also interesting to note that $[H_2F]^-$ has the maximum bond energy, E_b. Essentially, $[HHF]^-$ is quite similar to $[FHF^-]$ which has been observed to carry a maximum hydrogen-bonding character with F–H = 1.23 Å.[8]

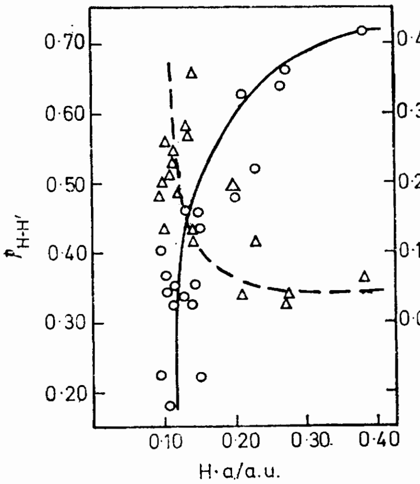

FIGURE 1 Change of hydride affinity plotted against X–H (△) and H–H′ bond order (○) in $[MH_2]^-$ complexes

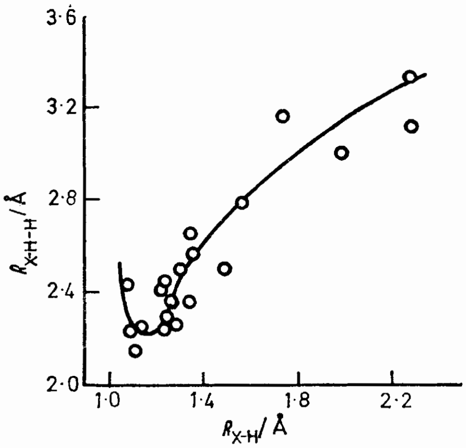

FIGURE 2 Change of total X–H–X′ distance plotted against X–H distance in $[MH_2]^-$ complexes

Charge Distribution in $[MH_2]^-$ *Complex*.—The charge distributed in the M group of $[MH_2]^-$ does not correlate with hydride affinities but has reasonable correlations with the proton-transfer energy, E_p, for a series of

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* With limited optimization, hydride affinities of the molecules CH_4 and HCO_2H are obtained as 0.096 and 0.145 a.u. (1 a.u. = 4.360 × 10^{-18} J).

[8] S. H. Bauer, J. Y. Beach, and J. H. Simmons, *J. Amer. Chem. Soc.*, 1939, **61**, 19.

molecules (Figure 3). If the proton-transfer capability of the molecule is related to the charge of the M group in the intermediate complex, the charge distributed in the M group must indicate the possibility of proton transfer to the neutral molecules.

Molecular-orbital Energy and Hydride Affinity.—Suppose a charge transfer from the negative hybride ion to the neutral molecule occurs before the relaxation procedure. Then the first step in the proton transfer can be expressed as two hypothetical reaction paths [equation (2)], and the hydride affinity can be defined as in (3) and (4) where E_{rel} is the relaxation energy of the

$$MH + H^- \longrightarrow [MH]^- + H \longrightarrow [MH_2]^- \qquad (2)$$

$$\text{h.a.} = \text{e.a.}_{MH}{}^{\text{vert}} + \text{i.p.}_{H^-}{}^{\text{vert}} + E_{\text{rel}} \qquad (3)$$

$$\Delta\text{h.a.} \simeq \Delta(\text{e.a.}_{MH}{}^{\text{vert}}) + \Delta E_{\text{rel}} \qquad (4)$$

product and the electrostatic interaction energy of the reactants, and e.a. and i.p. represent the vertical electron affinity of M–H and the ionization potential of H^-, respectively. If the second term in equation (4) can be neglected for these simple hydrogen molecules, one should find a linear correlation between the hydride affinity and the energy of the lowest unoccupied molecular orbital ($E_{\text{l.u.m.o.}}$) according to Koopman's theorem [9] as in (5). For planar molecules, however, the

$$\Delta\text{h.a.} \simeq \Delta E_{\text{l.u.m.o.}} \qquad (5)$$

main proton-donor group of the reactants, X–H, should be situated in the σ plane with the electron donor, H^-. If so, the hydride affinity will be determined more probably by the energy of the σ-type l.u.m.o. ($E_{\text{l.u.m.o.}}{}^{\sigma}$). The hydride affinities computed are compared with these two l.u.m.o.s in Table 2. The close linear correlation with the σ-type l.u.m.o.s rather than the general l.u.m.o.s for planar molecules (Figure 4) seems to justify our argument. A similar relation chould be applicable to protonation of the same molecules. An almost linear dependence on the energy of the highest occupied molecular orbital ($E_{\text{h.o.m.o.}}$) is also obtained (Figure 5). The correlation for proton affinity has a gradient of unity. A similar correlation has been reported previously.[10] For proton-transfer reactions, the correlation has a gradient of less than unity. The explanation for the difference in correlation gradients is not obvious to us at this time.

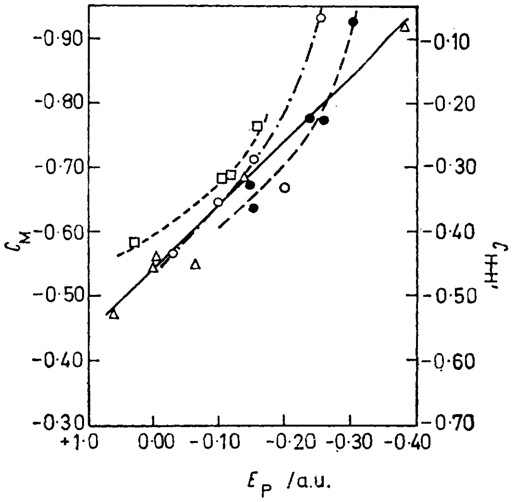

FIGURE 3 Charge of M group in $[MH_2]^-$ complexes plotted against the energy of the negative ion formation for (△) X–H, (○) NX–H, (□) H_2X–H, and (●) YX–H type molecules

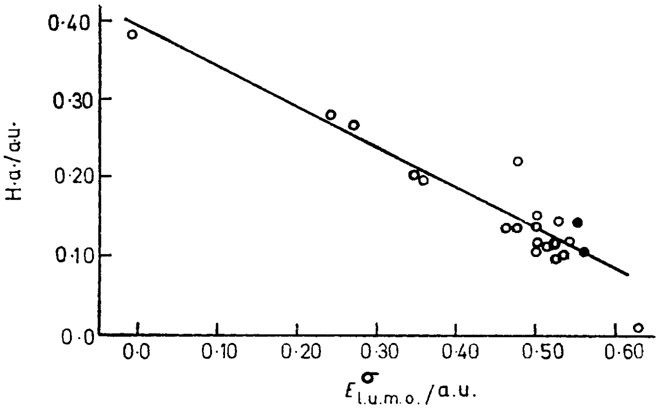

FIGURE 4 Dependence of hydride affinity on the energy of the σ-type lowest unoccupied molecular orbital (l.u.m.o.) for planar (○) and non-planar molecules (●)

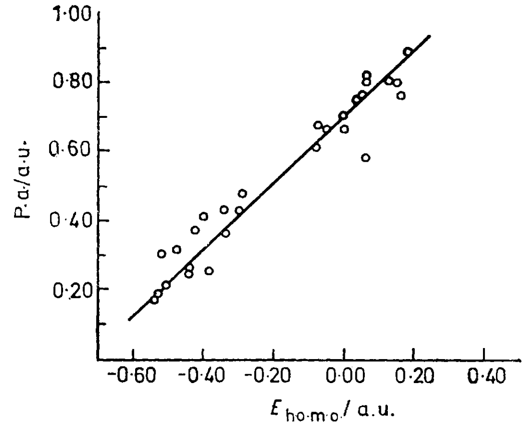

FIGURE 5 Dependence of proton affinity on the energy of the highest occupied molecular orbitals (h.o.m.o.)

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[5/2348 *Received, 2nd December*, 1975]

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[9] T. A. Koopmans, *Physica*, 1933, **1**, 104.

[10] D. W. Davis and J. W. Rabalais, *J. Amer. Chem. Soc.*, 1974, **96**, 5305.