back side of the fluorine nucleus.[23] Separate contour diagrams for the σ- and π-electron systems of hydrogen fluoride molecule show that the π system simply undergoes a general contraction from that in fluoride ion, and that nearly all of the detailed shifts shown in Figure 11 occur in the σ system. The diagrams suggest that there is a large amount of charge transfer from a p,σ orbital of fluoride to the s orbital of the hydrogen. The charge transfer from fluorine to hydrogen molecule is indicated even for rather large distances as shown in Figure 15. Similar types of electron density shifts are found in the reactions of other first-row hydrides with hydride ion, as will be reported in separate papers, and it appears that the charge transfer observed for the H_2F^- system is fairly general.

It will also be shown in the following papers that the potential energy surface for the H_2F^- system is typical of those for several proton-transfer reactions and that the well-known potential energy surface characteristic of the H_3^- and H_3 systems is atypical.

Acknowledgments. We are grateful to the Computer Center of the State University of New York at Buffalo for the generous donation of computer time which made this study possible. The Computer Center is partially supported by grants from Public Health Service, NIH (FR-00126), and from National Science Foundation (GP-7318). Professor R. E. Stanton has provided both moral and intellectual support throughout the course of this work, and we are indebted to him for many helpful suggestions and discussions.

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[23] This behavior may be contrasted to the shifts of electron densities which occur when two neutral atoms form a molecule. See, for example, P. R. Smith and J. W. Richardson, *J. Phys. Chem.*, **69**, 3346 (1965); R. F. W. Bader and W. H. Henneker, *J. Am. Chem. Soc.*, **88**, 280 (1966).

Theoretical Studies of Proton-Transfer Reactions. II. The Reaction of Water with Hydride Ion

Calvin D. Ritchie and Harry F. King

Contribution from the Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214. *Received September 1, 1967*

Abstract: The results of computation of the potential energy surface for the reaction of water with hydride ion are described. The LCAO-MO-SCF method, using Gaussian basis functions, with all integrals analytically evaluated has been used, and the final calculations are believed to be quite close to the Hartree–Fock limits. The computations show the absence of a classical activation barrier for the reaction. The theoretical results are compared with experimental data which have been reported in the literature, and it is found not only that the results are consistent, but that the theoretical results provide an explanation of otherwise puzzling isotope effects on the solution reaction. Attention is called to the role of solvent in providing activation energies for proton-transfer reactions in solution.

In the preceding paper of this series,[1] we described the computations of potential energy surfaces for the reactions of hydride ion with hydrogen molecule and with hydrogen fluoride. The theoretical results, which are completely nonempirical, were shown to be consistent with the limited amount of experimental data available for the systems. The most interesting part of the results, the absence of an activation barrier in the reaction of hydrogen fluoride with hydride ion, could not be substantiated because of the absence of experimental data for that system.

In the present paper, we report the results of *ab initio* LCAO-MO-SCF calculations of the potential energy surface for the reaction of water molecule with hydride ion to produce hydroxide ion and hydrogen molecule. In this case, experimental data concerning the reaction in both gas and solution phases have been reported.[2-4]

Methods and Results

Descriptions of the computer programs used and of the method of choosing basis sets for the computations have previously appeared.[1,5] In the present study, as in that of the H_2F^- system,[1] the potential energy surface was mapped using a limited basis set, and final calculations with an extensive basis set were carried out for points along the minimum energy path on the surface. Only enough points off the minimum energy path were examined with the large basis calculations to be sure that the path was being reproduced.

Both the small and large basis sets used are those presented in a previous paper.[5] The basis functions centered on the hydride ion are identical with those centered on the water protons.

The experimental energies, estimated Hartree–Fock limits, and energies calculated with both small and large basis sets for the various species involved in the reaction studied are shown in Table I.

A series of initial calculations with the small basis set were carried out to determine the optimum direction of approach of hydride ion to water molecule, and of

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

[2] J. F. Paulson, "Ion-Molecule Reactions in the Gas Phase," Advances in Chemistry Series, No. 58, American Chemical Society, Washington, D. C., 1966, Chapter 3.

[3] W. K. Wilmarth, J. C. Dayton, and J. M. Fluornoy, *J. Am. Chem. Soc.*, **75**, 4549 (1953).

[4] J. M. Fluornoy and W. K. Wilmarth, *ibid.*, **83**, 2257 (1961).

[5] C. D. Ritchie and H. F. King, *J. Chem. Phys.*, **47**, 564 (1967).

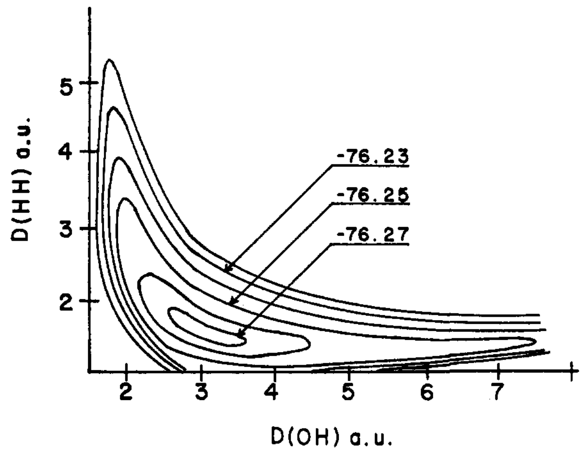


Figure 1. Energy contour diagram for the H_3O^- system. Energy is given in atomic units. The HOH angle is 105° and the length of the nonreacting OH bond is 1.8 au for all points. Results are from the small basis set computations.

hydrogen molecule to hydroxide ion. The results of these calculations are shown in Table IIA.

Table I. Calculated and Experimental Energies for the H_3O^- System

Species	Basis[a]	$-E_{calcd}$[b]	$-E_{HF}$[c]	$-E_{nr}$[d]
H_2O	Small	75.767	76.06	76.438
	Large	76.034		
H^-	Small	0.434	0.488	0.526
	Large	0.480		
OH^-	Small	75.133	75.417	75.804
	Large	75.377		
H_2	Small	1.122	1.134	1.174
	Large	1.1310		

[a] The basis sets are those detailed in ref 5. [b] Calculated energies in atomic units. [c] Estimated Hartree–Fock limits; see ref 1 and 5. [d] Experimental energies corrected for zero-point and relativistic energies; see ref 1 and 5.

The system is seen to prefer a linear O–H–H configuration and a bent H–O–H arrangement for all distances of approach. The energy of the system is not very sensitive to the H–O–H angle when the distance of the hydrogen molecule from oxygen is more than *ca.* 3.2 au, but the optimum angle is between 105 and 120°. Shorter O–H distances begin to heavily favor an angle of *ca.* 105°. The O–H bond not involved in the reaction appears to have an optimum length of *ca.* 1.8 au throughout the course of the reaction.

The remainder of the calculations were then carried out for the linear O–H–H and 105° H–O–H arrangement and a bond length of 1.8 au for the nonreacting OH bond. The potential energy is then a function of D(O–H) and D(H–H) and may be plotted as a two-dimensional contour diagram. The diagram constructed from point-by-point computations with the small basis set is shown in Figure 1. The surface shows no activation barrier but rather indicates the existence of a stable H_3O^- complex with $D(OH) = 3.0$ and $D(HH) = 1.5$ au, with an energy 0.016 au (*ca.* 10 kcal) below that of the separated hydroxide ion and hydrogen molecule. The surface is quite similar in all respects to that found for the H_2F^- system in our earlier study.[1]

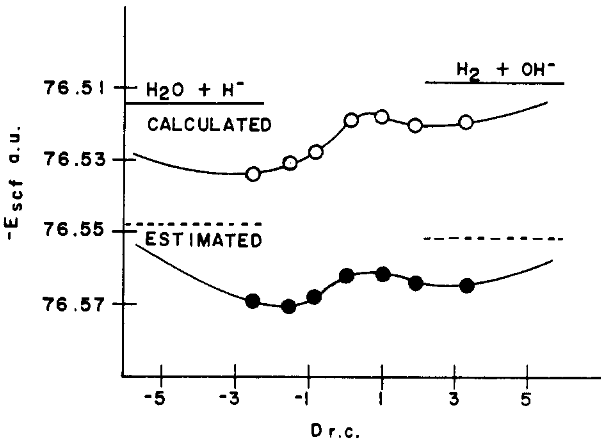
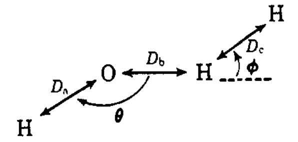


Figure 2. Energy as a function of distance along the minimum energy path for the H_3O^- system. All results are from the large basis set computations. $D_{rc} = (2)^{1/2}[D(OH) - D_0(OH) - D(HH) + D_0(H_2)]$.

A series of computations, using the large basis set, for points along the indicated minimum energy path were then carried out. The results are presented in Table III, and a "reaction coordinate" diagram constructed from the data is shown in Figure 2.

Table II. Calculated Energies for Various Configurations of the H_3O^- System[a]



D_a	D_b	D_c	θ, deg	ϕ, deg	$-E_{calcd}$
		A. Small Basis			
1.8	1.8	∞	105	0	76.201
1.8	3.2	1.5	105	0	76.271
1.8	3.2	1.5	105	30	76.263
1.8	3.2	1.5	105	−30	76.266
1.8	3.2	1.5	90	0	76.268
1.8	3.2	1.5	120	0	76.272
1.8	3.2	1.5	135	0	76.270
1.8	3.2	1.5	150	0	76.270
1.9	1.9	3.6	105	−33.5	76.162
1.9	1.9	2.47	105	0	76.251
1.9	1.9	2.04	105	0	76.242
1.9	1.9	2.90	105	0	76.252
1.85	1.9	2.00	150	0	76.228
1.8	2.1	2.1	105	0	76.257
1.8	2.2	2.0	180	0	76.246
1.9	1.9	2.0	180	0	76.221
1.8	2.0	2.5	105	0	76.256
1.8	2.0	3.4	105	0	76.250
1.8	1.8	2.3	105	0	76.239
1.8	1.8	2.7	105	0	76.245
		B. Large Basis			
1.8	2.7	1.7	90	0	76.516
1.8	2.7	1.7	105	0	76.518
1.8	2.7	1.7	110	0	76.519
1.8	2.7	1.7	120	0	76.518
1.8	2.7	1.7	130	0	76.517
1.8	2.7	1.7	180	0	76.510

[a] All quantities are in atomic units.

Since a small hump is found in the "reaction coordinate," a further series of calculations were carried out to see if the energy at the "hump" could be lowered

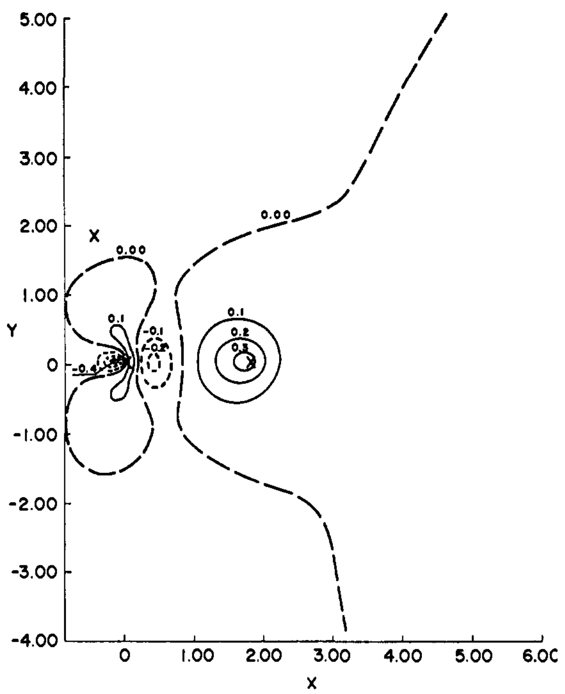


Figure 3. Electron density difference contour diagram for the H_3O^- system at various points along the minimum energy path. The locations of nuclei are marked by X's. The central hydrogen nucleus is located at $x = 0$, $y = 0$. The electron densities of hydroxide ion superimposed on the nonreacting OH moiety, and of hydride ion superimposed on the right-most hydrogen nucleus, are subtracted from the total electron density of the H_3O^- system. The plane shown contains the entire system. The distance (au) along the minimum energy path, defined as for Figure 2, is $-\infty$. All results are from the large basis set computations.

by changing bond angle. The results are shown in Table IIB. The hump found is apparently real and is not due to a poor bond angle choice.

Table III. Large Basis Calculations for the H_3O^- System[a]

D(OH)	D(HH)	$-E_{\text{calcd}}$
1.8	∞	76.514
2.0	3.4	76.534
2.1	2.8	76.531
2.2	2.4	76.528
2.5	2.0	76.519
2.8	1.7	76.518
3.2	1.5	76.520
4.2	1.45	76.519
2.7	1.7	76.518
∞	1.4	76.508
2.5	2.3	76.514[b]
2.6	1.7	76.518[b]
3.1	1.8	76.514[b]
3.6	1.6	76.518[b]

[a] All calculations are for a linear O-H-H and 105° H-O-H, with the bond length of the nonreacting OH 1.8 au. [b] These points are off the minimum energy path.

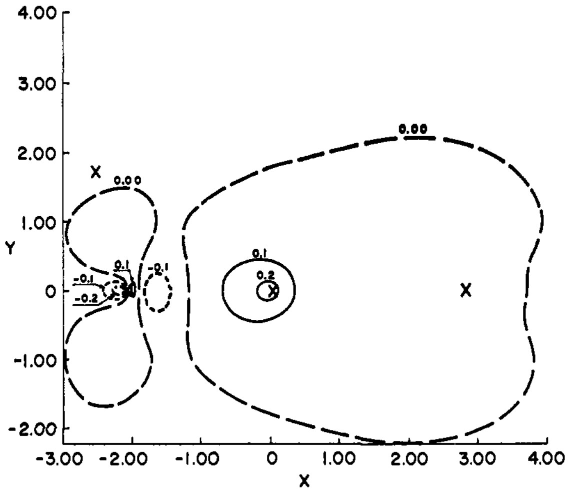


Figure 4. Electron density difference contour diagrams (see caption to Figure 3); distance, −1.56.

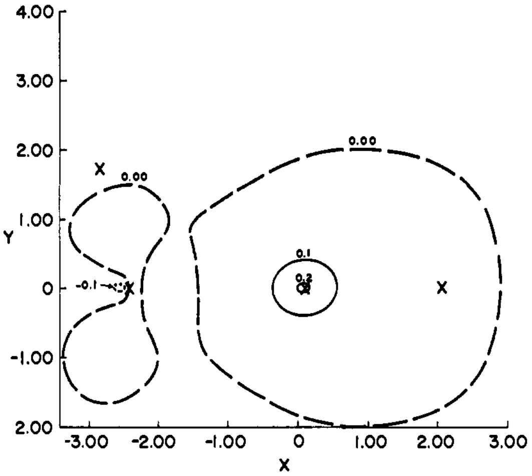


Figure 5. Electron density difference contour diagrams (see caption to Figure 3); distance, +0.142.

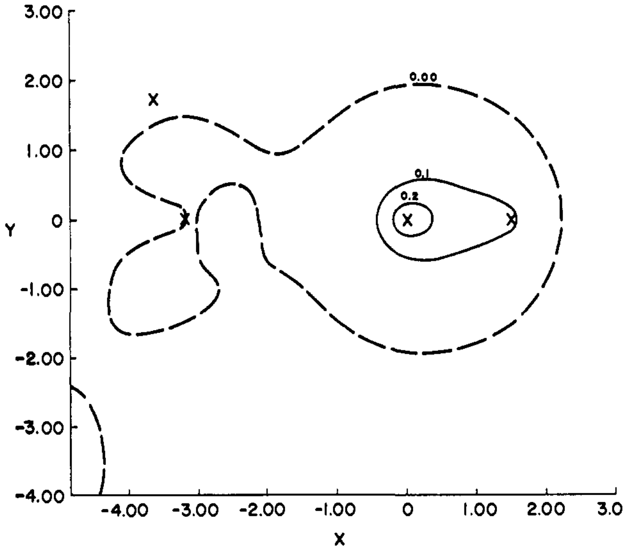


Figure 6. Electron density difference contour diagrams (see caption to Figure 3); distance, +1.84.

Electron density difference contour diagrams constructed from the results of the large basis set calculations are shown in Figures 3–7. The diagrams were constructed by subtracting from the electron densities of the H_3O^- systems the electron densities of hydroxide ion superimposed on the OH moiety and of hydride ion superimposed on the extreme hydrogen of the system. The diagrams, therefore, show the shifts in electron densities which occur when hydroxide ion and hydride ion interact with each other and with a proton in be-

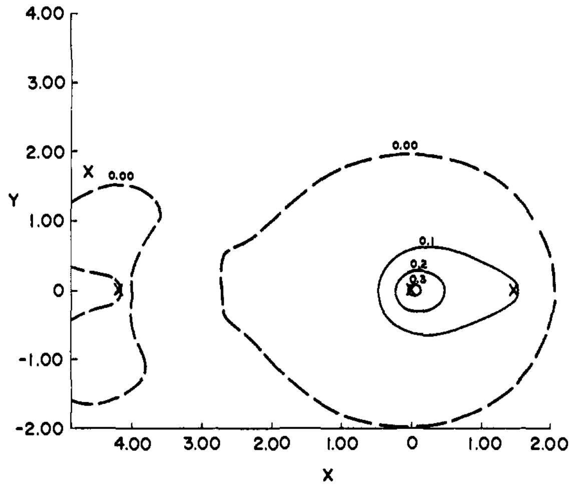


Figure 7. Electron density difference contour diagrams (see caption to Figure 3); distance, +3.32.

tween them. In all of the figures, the plane shown is that containing the entire H_3O^- system.

Discussion

The general details of the potential energy surface and of the electron density shifts for the H_3O^- system are quite similar to those previously reported for the H_2F^- system. The major difference in the two systems is the appearance of the hump along the minimum energy path (amounting to *ca.* 1.2 kcal above the highest minimum) for the H_3O^- system. Since the top of the "hump" is lower than the energy of either separated reactants or products, there is still no classical activation barrier for the reaction. Both the potential energy surface and the electron density shifts are completely unlike those for the classical H_3^- and H_3 systems.

It is interesting to note in Figure 3 that the protonation of hydroxide ion causes an increase in electron density in the hydroxide bond but leads to a decrease in electron density at points in the newly formed bond. The latter behavior is quite similar to that found for the protonation of fluoride ion but is somewhat less pronounced in the present case. It appears that the electron shifts are due to a charge transfer from a σ p-type orbital of oxygen to s-type orbitals on the incoming proton and to general contraction of the entire wave function. It is somewhat surprising, then, to find less transfer from hydroxide than from fluoride.

Before proceeding to a comparison of the present theoretical results with experimental data for the reaction of water with hydride, it is worthwhile to examine the possible sources of error in our calculations. A general discussion of the two approximations used in our study was given in the previous paper.

In the present system, electron correlation energies of water plus hydride ion, and of hydroxide ion plus hydrogen molecule, are very nearly equal, having estimated magnitudes of 0.416 and 0.427 au, respectively. The difference between these two quantities, 6.9 kcal, however, is appreciable in comparison to the experimental energy difference of 8.8 kcal between the reactants and products of the reaction and decreases the Hartree–Fock energy difference to *ca.* 2 kcal.

In the small basis set calculations, the error introduced by the use of a limited basis set is quite appreciable as can be readily seen on comparing Figures 1 and 2. The small basis calculations show an intermediate H_3O^- configuration with an energy nearly 45 kcal lower than that of the reactants and *ca.* 12 kcal lower than that of the products. Calculations with the large basis set show an optimal intermediate with bond lengths different from those found with the small basis and with an energy *ca.* 12 kcal lower than that of the reactants. As in the case of the calculations for the H_2F^- system,[1] it appears that the primary deficiency in the small basis set is the absence of very diffuse functions which are necessary to produce good wave functions for the anions. The energy of hydride ion calculated with the small basis set is particularly poor for this reason.

Although the large basis set gives energies quite close to the estimated Hartree–Fock limits for all of the species involved, the small amount of error introduced into the calculated difference in energy between reactants and products is significant in comparison with the experimental difference. This error of *ca.* 0.009 au (5.6 kcal), together with the small error introduced by differences in correlation energies discussed above, causes the calculated value for the energy of the reaction of hydride ion plus water molecule to produce hydroxide ion and hydrogen molecule to be *ca.* 13 kcal greater than the experimental value. Thus, we calculate that the reaction is endothermic by 3.8 kcal, while the experimental data shown in Table I allow us to calculate that the reaction is exothermic by 8.8 kcal.

The error introduced from these sources into the calculations for intermediate configuration of the H_3O^- system cannot be directly evaluated and is difficult to even estimate. We may fairly confidently predict that correlation energy will increase as separated species approach each other simply because the number of pair-wise interactions of electrons increases. This effect would tend to lower the middle of the true potential energy surface relative to the Hartree–Fock surface, and the shape of the diagram shown in Figure 2 would be altered, therefore, in that the energy at the middle of the diagram would be lowered with respect to that at both ends. We have no reliable way of estimating the magnitude of the effect, however.

If we compare the improvement in energy gained by going from the small basis set to the large basis set for each of the points shown in Figure 2, we find that the improvement for water plus separated hydride is 0.290 au, and for the points, in order from left to right, the corresponding improvement is 0.284, 0.275, 0.267, 0.254, 0.247, 0.250, 0.252, and 0.253, respectively, with the last value being for hydroxide ion plus separated hydrogen molecule. Thus, to a fair approximation, the improvement in energy for intermediate configurations of the system is intermediate between that of the separated reactants and products. We may guess, therefore, that a further improvement in basis set would result in lowering the line shown in Figure 2, with the extent of the lowering increasing monotonically from left to right. Such a correction would result in the curve shown by dotted lines in Figure 2.

On the basis of these arguments, we believe that the true potential energy surface for the system will retain the two important features shown in our present results, the absence of a barrier, and the existence of an intermediate which is at least 12 kcal lower in energy than either reactants or products. These are exactly the primary features found in the computations for the H_2F^- system.

The absence of any appreciable activation barrier for the reaction of hydride ion with water molecule is confirmed by an experimental study of this reaction in the gas phase.[2] It appears that the reaction occurs at, or close to, an encounter-controlled rate.

The *ortho–para* conversion, or isotope exchange of hydrogen molecule in aqueous base solution,[3,4] is interesting in connection with our present results. The experimental data are shown in Table IV.

Table IV. Reactions of Hydrogen Molecule in Aqueous Hydroxide[a]

Reaction observed	Temp, °C	$k_2 \times 10^3$ [b]
p-H_2 = o-H_2	70	5.3[c]
	100	9.4[d]
D_2 = HD	100	5.7[d]
HD = H_2	100	3.6[d]

[a] All data is taken from ref 3 and 4. [b] Second-order rate constants in units of M^{-1} sec^{-1}. [c] Estimated activation energy is 23–25 kcal/mole. [d] Reference 4.

From the data in Table I, the energy of the reaction of hydride ion with water to produce hydrogen molecule and hydroxide ion is exothermic by 8.8 kcal/mole. The inclusion of zero-point energies raises this value to *ca.* 11 kcal/mole, and a consideration of partition functions indicates that the value is not temperature dependent to an appreciable extent. In order to calculate the heat of reaction in aqueous solution, we need several pieces of information; namely, the heat of solution of hydroxide ion, hydride ion, and hydrogen molecule, and the heat of vaporization of water. The latter two quantities are well known. The heat of solution of hydrogen molecule in water at 80–100° is very close to zero, and the heat of vaporization of water is 10.4 kcal/mole. The heat of ionization of water in water is 13.35 kcal/mole[6] at 25°, and the proton affinity of hydroxide ion in the gas phase is 390 kcal/mole.[7] These values, in combination with an estimated value of 267 kcal/mole for the heat of solution of the proton in water,[8] lead to a heat of solution of hydroxide ion of 119 kcal/mole. The heat of solution of hydride ion can be estimated from a consideration of ionic radii to be intermediate between those of bromide and iodide ions,[8] to give a value of *ca.* 65 kcal/mole.

Combination of the above values leads to a value of 54.6 kcal/mole for the exothermicity of the reaction of hydride ion with water in aqueous solution at about 25°. This value is not expected to change greatly with temperature. Although different methods of estimating the heat of the reaction lead to values that differ from the above by as much as 10 kcal, the magnitude is still much greater than the energy of activation for the hydrogen exchange reaction reported in Table IV. It, therefore, appears quite unlikely that hydride ion is actually formed in the exchange reactions.

A consideration of the observed isotope effects on the exchange reaction also shows that it is unlikely that hydride ion is formed in a rate-determining step. The equilibrium isotope effect on the reaction of hydroxide ion with hydrogen molecule may be calculated with the aid of the eq 1–3. The equilibrium isotope effect,

$$OH^- + D_2 \overset{K_D}{\rightleftarrows} HDO + D^- \tag{1}$$

$$OH^- + HD \overset{K_H}{\rightleftarrows} HDO + H^- \tag{2}$$

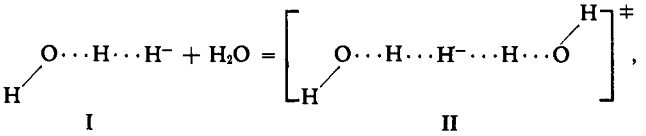
$$HD + D^- \overset{K_3}{\rightleftarrows} D_2 + H^- \tag{3}$$

K_H/K_D, is seen to be equal to K_3, the equilibrium constant for the exchange reaction 3. This latter equilibrium constant can be easily calculated for the gas-phase reaction from spectroscopic data[9] and is found to give $K_3 = 1.6$ at 373°K.

Since the ratio of the forward rate constants, shown in Table IV, is less than the equilibrium ratio, K_H/K_D, then, if the reaction of hydroxide ion with hydrogen molecule to form hydride ion were rate determining, the reverse rate constants (*i.e.*, the reverse rate constants for reactions 1 and 2) would have to show an inverse isotope effect with deuteride reacting 2.5 times as fast as hydride with HDO.[10]

Even without the formation of hydride ion in the exchange reactions, we must bear in mind that the observed isotope effect is so small that no appreciable motions of the protons are involved in the motion along the reaction coordinate in the rate-determining step. Using the theoretical results presented above, we may attempt to formulate an acceptable mechanism.

As we noted in discussing Figure 2, there appears to be an intermediate formed in the reaction of hydride ion with water, or the reaction of hydroxide ion with hydrogen molecule, which is *ca.* 12 kcal more stable than isolated hydroxide and hydrogen. This intermediate is formed without activation energy and has an optimal geometry with an O–H bond length of *ca.* 2.0 au, and an H–H bond length of *ca.* 3.4 au. It seems quite likely that the attack of a water molecule on this complex could result in hydrogen exchange as indicated in eq 4, where structure II indicates the possible



$$\mathrm{HO\cdots H\cdots H^- + H_2O = [HO\cdots H\cdots H^-\cdots H\cdots OH]^{\ddagger}},$$

I

II

etc. (4)

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(6) L. G. Hepler in "Solvent Interactions," J. F. Coetzee and C. D. Ritchie, Ed., Marcel-Dekker, Inc., New York, N. Y., in press.

(7) R. Gaspar, I. Tamassy-Lentei, and Y. Kruglyak, *J. Chem. Phys.*, **36**, 740 (1962). A value of 389.3 kcal/mole can be calculated from the heat of formation of hydroxide radical, 9.3 kcal/mole, and the electron affinity of the hydroxide radical, 42.2 kcal/mole; see J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966); J. Kay and F. M. Page, *Trans. Faraday Soc.*, **62**, 3081 (1966).

(8) R. M. Noyes, *J. Am. Chem. Soc.*, **84**, 513 (1962).

(9) The parameters used in the calculation are those given in W. J. Moore, "Physical Chemistry," 2nd ed, Prentice-Hall, Inc., Englewood Cliffs, N. J., p 367, Problem 6. We find the pertinent partition function ratios at 373°K to have the following values, $Q_{rot}(D_2)/Q_{rot}(HD) = 0.752$; $Q_{trans}(D_2 + H^-)/Q_{trans}(HD + D^-) = 0.541$, where the rotational partition function for D_2 is calculated for an equilibrium ratio of the *ortho* to *para* form.

(10) Wilmarth[3] pointed out that the *ortho–para* conversion cannot be validly compared with the isotope exchange, since it seems likely that spin conversion could occur without complete formation of hydride ion.

transition state for this step, with structure I the intermediate indicated by theory.

It is unlikely, however, that II represents the transition state *in the rate-determining step* of the reaction, since one would expect normal isotope effects if this were the case. We suggest that the formation of the intermediate I is the rate-determining step of the reaction. The formation of I essentially involves replacing one of the water molecules in the solvation shell of hydroxide ion with hydrogen molecule.

This process of replacing water in the solvation sheath of anions has previously been suggested to be important in accounting for the activation energy of reactions.[11] An energy of *ca.* 20 kcal has been estimated[11] for the process of replacing one water molecule from the shell around hydroxide ion with methyl iodide. This energy, plus the activation energy for diffusion of hydroxide ion, *ca.* 2–3 kcal, is then estimated as the activation energy for formation of the intermediate I in good agreement with the experimental value of 23–25 kcal. Equation 4 must have an activation energy of less than 2–3 kcal if the formation of I is to be rate determining. This does not seem at all unreasonable, since we have found that several proton transfers can occur without activation energy.[1]

Acknowledgments. We are grateful to the Computer Center of the State University of New York at Buffalo for the generous donation of computer time which made the present work possible. The Computer Center is partially supported by grants from Public Health Service, NIH (FR-00126), and from National Science Foundation (GP-7318).

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(11) See, for example, R. A. Ogg and M. Polyanyi, *Trans. Faraday Soc.*, 31, 604 (1935); E. A. Moelwyn-Hughes and D. Glew, *Proc. Roy. Soc.* (London), **A212**, 260 (1952); E. F. Caldin, *J. Chem. Soc.*, 3345 (1959).

Theoretical Studies of Proton-Transfer Reactions.
III. The Reactions of Hydride Ion with Ammonia and Methane

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Contribution from the Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214. *Received September 1, 1967*

Abstract: The results of *ab initio* computations of the potential energy surfaces for the reactions of hydride ion with ammonia and with methane molecules, to form hydrogen molecule and amide, and methide ions, respectively, are described. The potential surfaces and electron density shifts for these reactions are quite similar to those found for the reactions of hydrogen fluoride and of water molecules with hydride ion. They are in distinct contrast to the results found for the classical reactions of hydrogen molecule with either hydride ion or hydrogen atom. No barriers to reactions are found in the present calculations.

In the preceding papers of this series, we have reported the results of completely nonempirical computations of the potential energy surfaces for the reactions of hydride ion with hydrogen, hydrogen fluoride, and water molecules.[1,2] The striking result reported is that the potential energy surfaces for the last two reactions show no barriers to the proton transfer.

In the present paper, we report the results of analogous computations for the reactions of hydride ion with ammonia and methane molecules.

Methods and Results

The methods used in the present study are completely analogous to those reported for other systems.[1,2] The GTO basis sets for the NH_4^- system have been reported[3] previously.

In the study of the CH_5^- system, the small basis set used in the construction of the potential energy surface is that reported earlier.[3] The large basis set which was used to obtain an estimate of the Hartree–Fock limit for methane,[3] however, proved too extensive for the computations on the CH_5^- system to be carried out in a reasonable amount of time. We have, therefore, used a basis set which is slightly reduced from the large set used in the previous study.[3] The basis set used is detailed in Table I.

Table I. Large Basis Set for the CH_5^- System

Center[a]	Type[a]	Exponent[a]
Carbon	1s	Set A, frozen core[b]
	1s	0.294
	1s	0.813
	1s	3.82
	1s	13.67
	2p	0.150
	2p	0.500
	2p	2.00
	2p	12.00
Hydrogen	1s	0.148
	1s	0.657
	1s	4.2397
	1s	0.070[c]
	2p	1.00

[a] The Gaussian-type basis functions are of the form: $A \exp[-\alpha(x-a)^2 - \alpha(y-b)^2 - \alpha(z-c)^2]$, where α is designated by the exponent value in the table, a, b, and c are the Cartesian coordinates of the center on which the function is located, and A is 1, $(x-a)$, $(y-b)$, or $(z-c)$ depending on whether the function is a 1s, $2p_x$, $2p_y$, or $2p_z$ function, respectively. [b] The frozen core is a linear combination of 1s-type GTO's, detailed in ref 3. [c] Used only on the hydride hydrogen center.

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(1) C. D. Ritchie and H. F. King, *J. Am. Chem. Soc.*, 90, 825 (1968).
(2) C. D. Ritchie and H. F. King, *ibid.*, 90, 833 (1968).
(3) C. D. Ritchie and H. F. King, *J. Chem. Phys.*, 47, 564 (1967).