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).

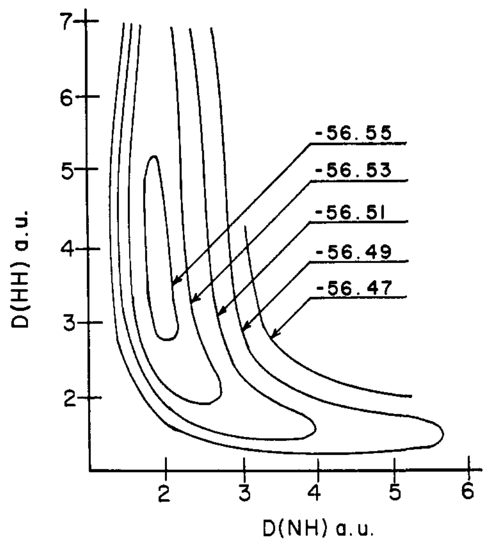

Figure 1. Energy contour diagram for the NH_4^- system. The HNH angles are 107°, and the lengths of the nonreacting NH bonds are 1.91 au for all points. Results are from the small basis set computations.

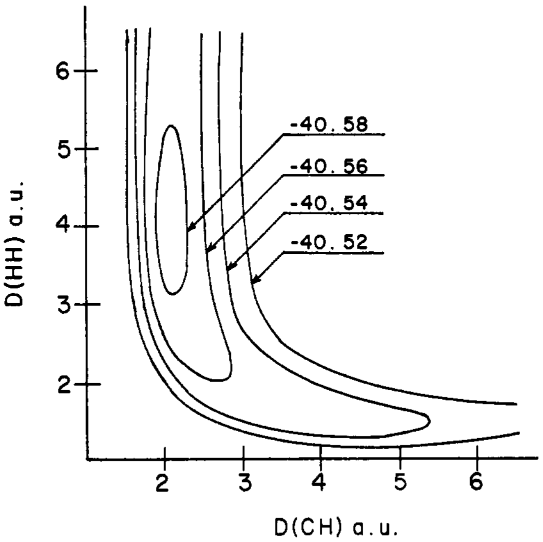

Figure 2. Energy contour diagram for the CH_5^- system. The HCH angles are tetrahedral and the lengths of the nonreacting CH bonds are 2.12 au for all points. Results are from the small basis set computations.

A series of calculations, using the small basis sets, were carried out to determine the optimal geometries of both amide ion and methide ion. The results of these computations are shown in Table II.

Table II. Energies of Amide and Methide Ions[a]

Angle, deg	D(NH)[b]	$-E_{\text{calcd}}$[b]
	A. Amide Ion	
HNH		
103	2.05	55.3538
103	1.95	55.3539
103	1.85	55.3470
110	1.95	55.3518
95	1.95	55.3523
103	2.00	55.3545
	B. Methide Ion	
HCH		
105	2.10	39.4043
109.5	2.10	39.4034
115	2.10	39.3991
109.5	2.12	39.4042
109.5	2.20	39.3991
109.5	2.30	39.3883

[a] All calculations with small basis sets. [b] Energies and distances are in atomic units.

In view of previous experience,[1,2] only those configurations of the systems corresponding to approach of hydride ion along the N–H, or C–H, bond axis were considered in computing the potential energy surfaces. One calculation for the NH_4^- system in which hydride was placed on the C_3 axis at a distance of 2.75 au from nitrogen on the side of the hydrogens gave an energy *ca.* 0.16 au higher than that of separated ammonia and hydride ion.

Since the results shown in Table II indicate that the energies of the anions are relatively insensitive to small changes in bond angles and distances, the potential energy surfaces were computed without allowing these angles and distances to vary. For the NH_4^- system, the HNH angles are kept at 107° and N–H bond distances for the nonreacting hydrogens are kept at 1.91 au. For the CH_5^- system, tetrahedral angles are used, and the C–H distance for the nonreacting hydrogens is 2.12 au. It seems unlikely that optimization of these angles and distances would change any of the calculated energies by more than *ca.* 0.001 au.

With the restrictions stated in the last paragraph, the energy of either the NH_4^- or CH_5^- system is a function of two variables, the X–H distance and the H–H distance for the reacting centers. The three-dimensional potential energy surfaces constructed from point-by-point computations are shown as contour diagrams in Figures 1 and 2.

The energies calculated for the various isolated species involved in the systems are shown in Table III along with estimates of the Hartree–Fock limits and experimental energies. The evaluations of the experimental energies for the NH_2^- and CH_3^- ions are detailed in the Appendix.

Table III. Experimental and Calculated Energies for Isolated Species

Species	Basis[a]	$-E_{\text{calcd}}$[b]	$-E_{\text{HF}}$[b]	$-E_{\text{nr}}$[c]
H^-	Small	0.434	0.488[d]	0.526[d]
	Large (NH_4^-)	0.480		
	Large (CH_5^-)	0.477		
H_2	Small	1.122	1.134[d]	1.174[d]
	Large (NH_4^-)	1.131		
	Large (CH_4^-)	1.126		
NH_3	Small	56.098	56.23[e]	56.563[e]
	Large	56.200		
CH_4	Small	40.141	40.23[e]	40.513[e]
	Large	40.180		
NH_2^- [f]	Small	55.354	?	55.930
	Large	55.508		
CH_3^- [g]	Small	39.404	?	39.877[h]
	Large	39.463		

[a] The basis sets are described in ref 3 and in Table I. [b] Energies in atomic units. [c] Experimental energies excluding zero-point and relativistic energies. [d] References 1 and 2. [e] Reference 3. [f] HNH angle = 107°, D(NH) = 1.91 au. [g] HCH angle = 109.5°, D(CH) = 2.12 au. [h] See Appendix for details.

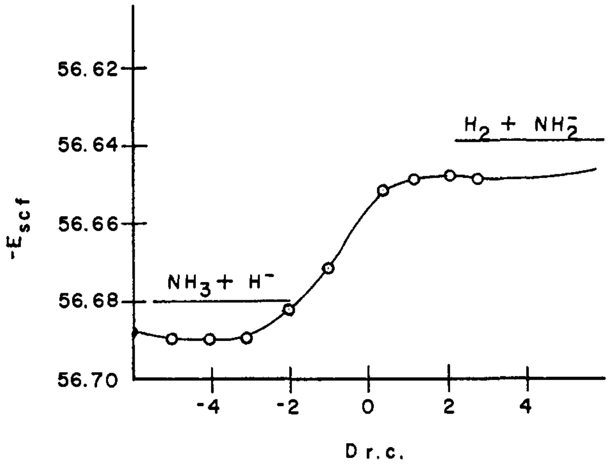

Figure 3. Energy as a function of distance along the minimum energy path for the NH_4^- system. Results are from the large basis set computations. $D_{rc} = (2)^{1/2}[D(NH) - D_0(NH) - D(HH) + D_0(H_2)]$.

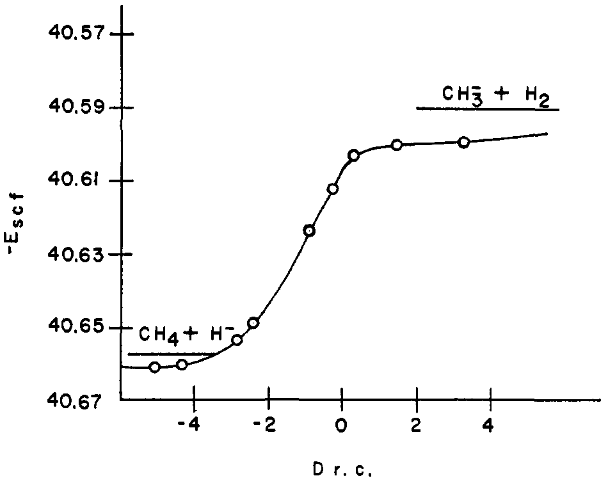

Figure 4. Energy as a function of distance along the minimum energy path for the CH_5^- system. Results are from the large basis set computations. $D_{rc} = (2)^{1/2}[D(CH) - D_0(CH) - D(HH) + D_0(H_2)]$.

Large basis set calculations were carried out for the minimum energy paths indicated in Figures 1 and 2 for the NH_4^- and CH_5^- systems, and the results are reported in Tables IV and V. As with previous systems, enough points off the minimum energy path were checked to be sure that the path was being reproduced. The "reaction coordinate" diagrams constructed from the calculations are shown in Figures 3 and 4.

Table IV. Large Basis Calculations for the NH_4^- System[a]

D(NH)	D(HH)	$-E_{calcd}$[b]	$-E_{small\ basis}$[c]
1.90	∞	56.680	56.532
1.90	6.40	56.688	56.540
1.95	5.20	56.690	56.549
2.00	4.40	56.690	56.552
2.10	4.00	56.685[d]	
2.00	3.70	56.690	56.555
1.80	3.30	56.685[d]	
2.10	3.00	56.683	56.552
2.25	2.50	56.672	56.543
2.60	2.40	56.653[d]	
2.60	1.80	56.652	56.529
3.00	1.65	56.649	56.520
4.00	1.50	56.649	56.509
∞	1.40	56.639	56.476

[a] HNH angles are 107°, and the nonreacting NH bond distances are constant at 1.91 au for all calculations. [b] Large basis set values. [c] Small basis set values (interpolated). [d] These points are off the minimum energy path.

Table V. Large Basis Calculations for the CH_5^- System[a]

D(CH)	D(HH)	$-E_{calcd}$[b]	$-E_{small\ basis}$[c]
2.12	∞	40.658	40.576
2.12	5.00	40.661	40.586
2.10	4.45	40.660	40.586
2.20	4.05	40.656[d]	
2.00	3.70	40.656[d]	
2.15	3.45	40.654	40.583
2.18	3.15	40.659	40.580
2.25	2.70	40.639	40.576
2.15	2.55	40.635[d]	
2.40	2.30	40.624	40.568
2.70	2.25	40.614[d]	
3.00	1.90	40.603	40.555
3.40	1.70	40.600	40.552
4.567	1.08	40.565[d]	
4.50	1.50	40.601	40.550
∞	1.40	40.589	40.526

[a] HCH angles are tetrahedral and the CH distances for nonreacting hydrogens are 2.12 au for all calculations. [b] Large basis set values. [c] Small basis set (interpolated) values. [d] These points are off the minimum energy path.

Electron density difference contour diagrams analogous to those presented for the earlier systems[1,2] are shown in Figures 5–9 for the NH_4^- system and in Figures 10–14 for the CH_5^- system. The diagrams are constructed by substracting from the electron density of the system in a given configuration the electron densities of the two anions involved in the reactions. The diagrams, therefore, show the shifts in electron densities which occur when amide ion, or methide ion, and hydride ion interact with each other and with a proton between them. All of the diagrams are constructed from the results of the large basis set calculations.

Discussion

It is rather surprising, in view of intuitive feelings about acidity, to find that the experimental energies of reaction for hydride ion with water, ammonia, and methane are very nearly equal. From the data in Table III, we can calculate that the reactions of hydride ion with ammonia and with methane are exothermic by 0.015 and 0.012 au (9.4 and 7.5 kcal), respectively. The reaction of water with hydride ion is exothermic by 0.014 au (8.8 kcal).[2] The inclusion of zero-point energies gives the following $\Delta E_0°$ values.

$$\begin{gathered} H_2O + H^- \rightleftharpoons OH^- + H_2 \\ \Delta E_0° = -0.019 \text{ au} = -11.8 \text{ kcal/mole} \end{gathered} \tag{1}$$

$$\begin{gathered} NH_3 + H^- \rightleftharpoons NH_2^- + H_2 \\ \Delta E_0° = -0.022 \text{ au} = -13.7 \text{ kcal/mole} \end{gathered} \tag{2}$$

$$\begin{gathered} CH_4 + H^- \rightleftharpoons CH_3^- + H_2 \\ \Delta E_0° = -0.019 \text{ au} = -11.8 \text{ kcal/mole} \end{gathered} \tag{3}$$

In the gas phase, then, water and methane have equal acidities, and ammonia is slightly more acidic than either of these. The large basis set Hartree–Fock calculations give energies of reaction for reactions 1, 2, and 3 of +3.8, +25.6, and +42.6 kcal, respectively.

In the previous papers of this series, we have discussed the two approximations involved in the LCAO–

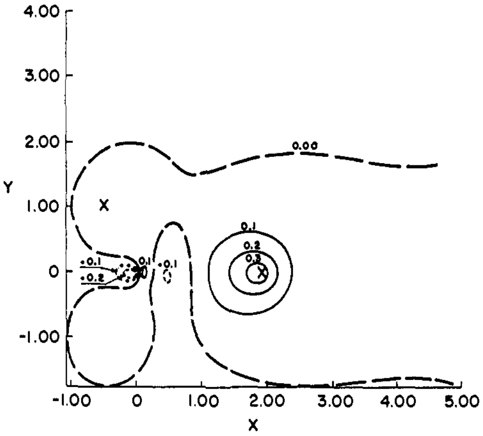

Figure 5. Electron density difference contour diagram for the NH_4^- system at various points along the minimum energy path. The electron densities of amide ion superimposed on the nonreacting NH_2 moiety, and of hydride ion superimposed on the rightmost hydrogen nucleus, are subtracted from the total electron density of the NH_4^- system. The plane shown bisects the nonreacting HNH angle and contains the nitrogen and reacting hydrogen nuclei. The locations of the nuclei are marked by ×'s. The projection of the two nonreacting hydrogen nuclei onto the plane is also indicated by an ×. The central hydrogen nucleus is located at $x = 0$, $y = 0$. All results are from the large basis set computations. This distance (au) along the minimum energy path, as defined for Figure 3, is $-\infty$.

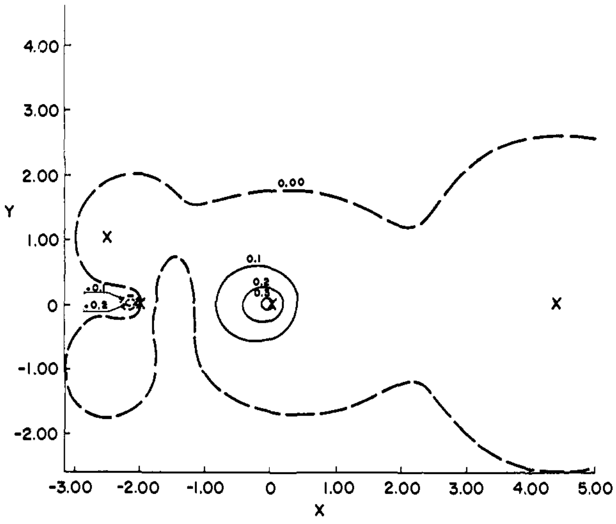

Figure 6. Electron density difference contour diagram (see caption to Figure 5); distance, -4.12.

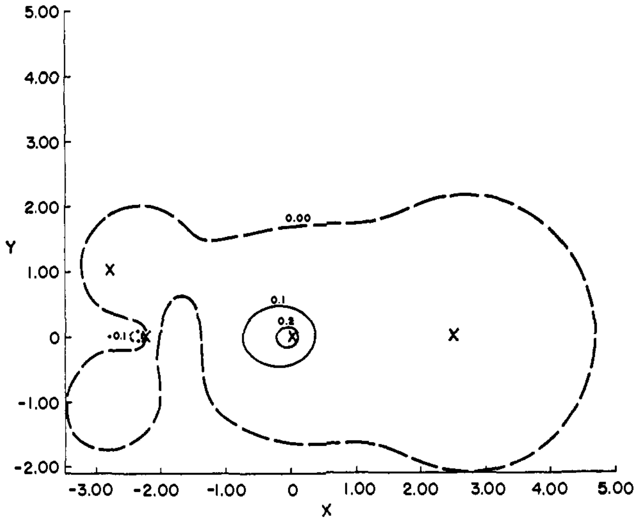

Figure 7. Electron density difference contour diagram (see caption to Figure 5); distance, -1.08.

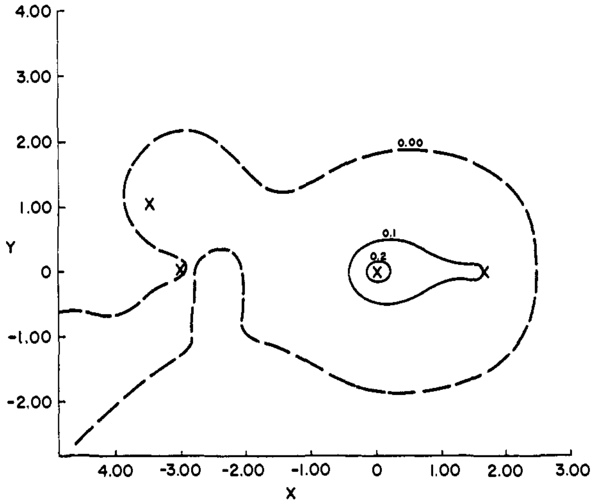

Figure 8. Electron density difference contour diagram (see caption to Figure 5); distance, $+1.19$.

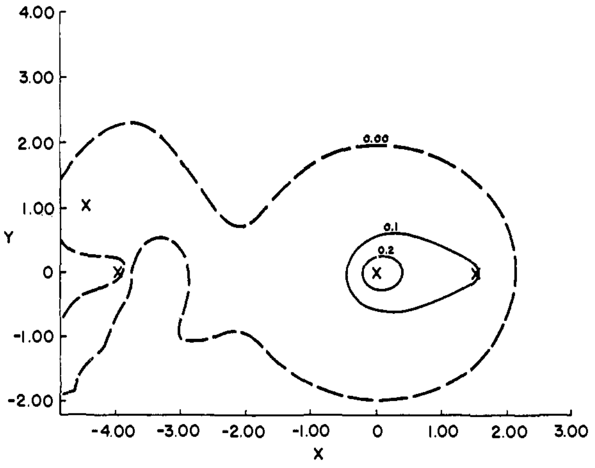

Figure 9. Electron density difference contour diagram (see caption to Figure 5); distance, $+2.82$.

MO–SCF method used in these studies. In the previously discussed systems, we were able to make reasonable estimates of the magnitudes of the errors arising from either electron correlation energy changes, or from the use of limited basis sets, with fair confidence. In the NH_4^- and CH_5^- systems, we can estimate the contributions of each of these errors to the energies of all species except the amide and methide ions. For these latter two species, reliable Hartree–Fock estimates are not available. The problem of estimating the correlation energies of these two anions is considered in a separate paper.[4]

We have pointed out previously that either source of error in the calculations is not expected to cause major qualitative features of the potential energy surfaces to change from the true features. In particular, it appears highly unlikely that the true surfaces will show barriers in those cases where the fairly accurate Hartree–Fock calculations indicate them to be absent.

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(4) C. D. Ritchie and H. F. King, submitted for publication.

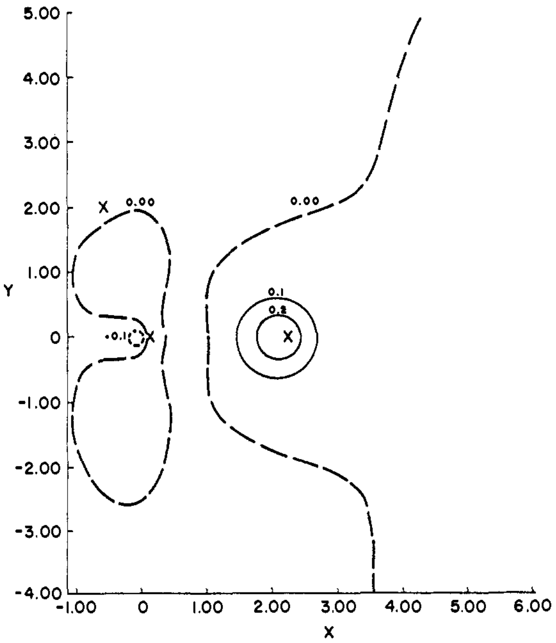

Figure 10. Electron density difference contour diagrams for the CH_5^- system at various points along the minimum energy path. The electron densities of methide ion superimposed on the nonreacting CH_3 moiety, and hydride ion superimposed on the rightmost hydrogen, are subtracted from the total electron density for the CH_5^- system. The plane shown contains the carbon and reacting hydrogen nuclei and one of the nonreacting hydrogen nuclei. The location of the nuclei in the plane are marked by X's. The central hydrogen nucleus is located at $x = 0$, $y = 0$. Results are from the large basis set computations. The distance (au) along the minimum energy path, as defined for Figure 4, is $-\infty$.

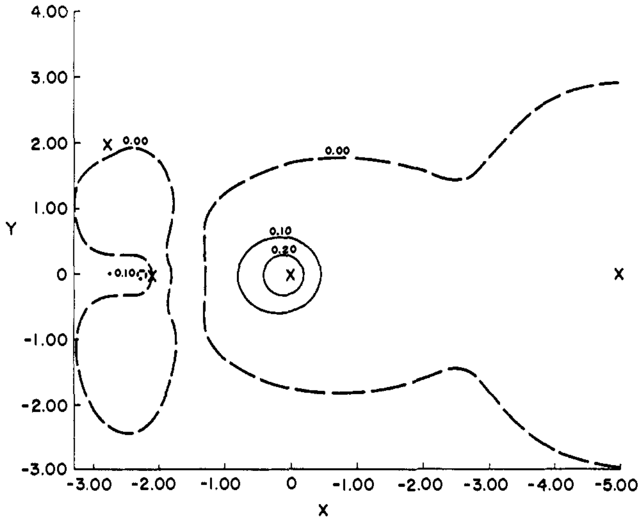

Figure 11. Electron density difference contour diagram (see caption to Figure 10); distance, -5.10.

The results for the NH_4^- and CH_5^- systems, reported here, are quite similar to those found for earlier systems. In all of the systems studied, with the exception of the reaction of hydrogen molecule with hydride ion, the approach of hydride ion to the neutral molecules, or the approach of hydrogen molecule to the anions, results in a lowering of the energy of the system such that weak complexes are formed. Classical activation barriers to the proton transfers are not found.

The electron density shifts which occur along the minimum energy paths for the reactions of ammonia and

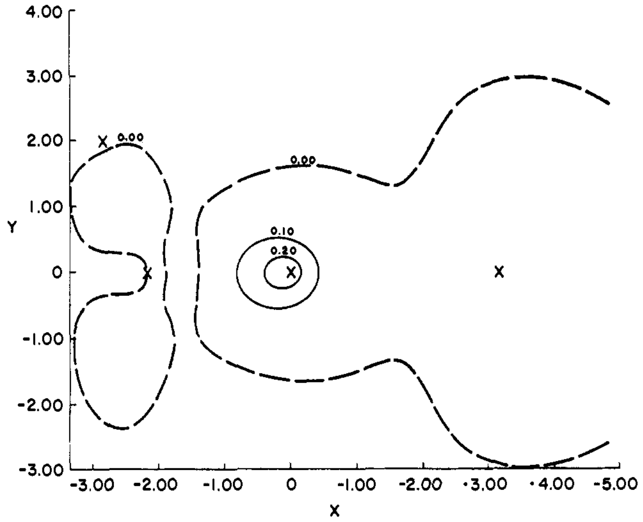

Figure 12. Electron density difference contour diagram (see caption to Figure 10); distance, -2.40.

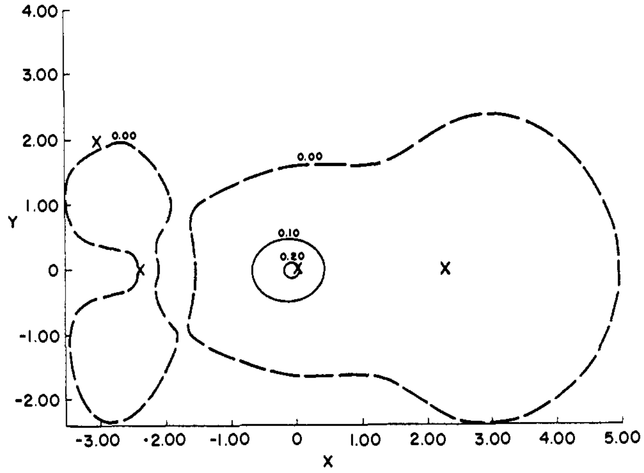

Figure 13. Electron density difference contour diagram (see caption to Figure 10); distance, -0.88.

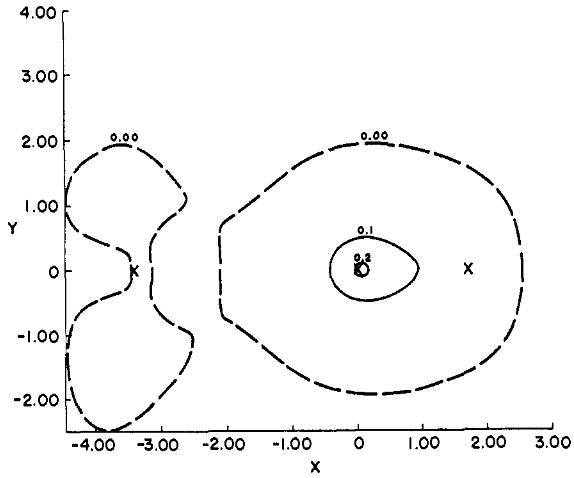

Figure 14. Electron density difference contour diagram (see caption to Figure 10); distance, $+1.39$.

methane with hydride are also similar to those found with other systems; again, the hydrogen molecule–hydride ion system is atypical. The decrease in electron density which occurs along the bond axis of the newly formed X-H bond on protonating amide or methide ions is less pronounced than found for the protonation of hydroxide of fluoride ions but is still in marked contrast to the shifts which occur on protonating hydride ion.

There appear to have been no studies of the reactions of hydride ion with either ammonia or methane in the gas phase, although these reactions should be observable by the use of the same techniques used to study the reaction of water and hydride ion.[5] Our results lead us to predict that these reactions will be encounter controlled, and it should be possible, under proper conditions, to observe the intermediates.

Experimental studies of the reactions of hydrogen molecule in ammoniacal amide solutions to give either *ortho-para* conversion or isotope exchange have been reported.[6–9] The results are qualitatively similar to those which were discussed for the reactions in aqueous hydroxide solution.[2] Some of the details are very interesting, however, in connection with our earlier interpretations of the aqueous reactions.[2] The data are summarized in Table VI.

Table VI. Reactions of H_2 in Ammoniacal Amide Solutions

Reaction observed[a]	k_2[b]	E_2[c]
$p\text{-}H_2 = o\text{-}H_2$[d]	1.3	6.4
$HD = H_2$[d]	0.47	7.4[e]
$D_2 = HD$[d]	0.82	7.4[e]

[a] The data given are for −50°. Other temperatures are reported in the original references. [b] Second-order rate constant in units of M^{-1} sec^{-1}. [c] Activation energy in kcal/mole. [d] Reference 6. [e] Reference 7.

The isotope effects found in the reactions of hydrogen molecule with amide solutions ($k_{H_2}/k_{D_2} = 1.6$, $k_{HD}/k_{D_2} = 0.57$) are very nearly the same as those found for the reactions with aqueous hydroxide solutions ($k_{H_2}/k_{D_2} = 1.65$, $k_{HD}/k_D = 0.63$), even though the reactions with amide ion are at −50°, and those with hydroxide solution are at +100°. Even more enlightening, the activation energies for the reactions of HD, HT, and D_2 with amide are 7.4, 7.4, and 7.6 kcal, respectively.[7] These isotope effects, and the small activation energies, strongly indicate that the proton transfer does not occur in the rate-determining step and that free hydride ion is not involved in the reaction. The same conclusion can be reached by a consideration of equilibrium isotope effects analogous to those applied to the reactions with hydroxide ion solutions.[2] Rather large isotope effects on the equilibria of the reactions to produce hydride ion, in conjunction with the small isotope effects on the forward rates which are observed would require that the reverse rates, *i.e.*, the rate of reaction of hydride ion with ammonia, have large inverse isotope effects.

The small observed isotope effects on the reactions of hydrogen with amide solutions led Bar-Eli and Klein[7] to suggest a mechanism[10] for the reaction as shown in eq 4, with step 4a being rate determining. This mechanism is

$$D_2 + NH_2^- = [D\text{—}D\text{—}NH_2^-] \qquad (4a)$$

$$[D\text{—}D\text{—}NH_2^-] + NH_3 = [H_2N\text{—}H\text{—}D\text{—}D\text{—}NH_2^-]^{\ddagger} = [H_2N\text{—}H\text{—}D^-] + NH_2D, \text{ etc.} \qquad (4b)$$

completely analogous to that which we suggested[2] for the reactions in aqueous hydroxide solutions. The formation of the intermediate in step 4a is in accord with the results of our calculations which show the favorable energy of such a species. As in the previous case,[2] we ascribe the relative slowness of step 4a to the necessity of partially desolvating amide ion in order to form the complex with hydrogen molecule.

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 work reported here possible. The Computer Center is partially supported by grants from Public Health Service, NIH (FR-00126), and from National Science Foundation (GP-7318).

Appendix

The heat of formation of amide radical has been evaluated[11] at 40 ± 2 kcal/mole. The electron affinity of amide radical at 0°K is estimated[12] at 27.6 kcal. These values, together with the heats of formation of the composite atoms,[13] give

$$N + 2H + e^- = NH_2^-$$

$$\Delta E_0{}^\circ = -0.323 \text{ au} = -202.7 \text{ kcal/mole}$$

The experimental energies of the separated atoms total −55.614 au, and the relativistic energy is 0.025 au.[14]

Ammonia molecule has vibrational frequencies (cm^{-1}) of 3337 (A type), 3414 (E type), 940 (A type), and 1627 (E type).[15] We estimate from these that the frequencies (cm^{-1}) of amide ion are close to 3300 (symmetric stretch), 3400 (antisymmetric stretch), and 1400 (bending). The zero-point energy is then estimated at 0.018 au.

The above values give $E_{exp}((NH_2^-) = -55.930$ au, excluding zero-point and relativistic energies.

The heat of formation of CH_3 at 0°K is 35 kcal/mole.[13,16] The electron affinity of methyl radical is 26 kcal at 0°K,[17] and we can then calculate: $C + 3H + e^- = CH_3^- + 0.503$ au ($\Delta E_0{}^\circ = -315.5$ kcal/mole).

We estimate the frequencies (cm^{-1}) for CH_3^- to be *ca.* 10% lower than those for ammonia to obtain 2900 (A-type stretch), 3000 (E-type stretch), 850 (A-type bending), 1450 (E-type bending). These frequencies produce a zero-point energy of 0.029 au.

The relativistic energy is estimated as 0.012 au,[14] leading to the value of −39.877 au for the experimental energy of methyl anion, excluding zero-point and relativistic energies.

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(5) 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.

(6) W. K. Wilmarth and J. C. Dayton, *J. Am. Chem. Soc.*, **75**, 4553 (1953).

(7) K. Bar-Eli and F. S. Klein, *J. Chem. Soc.*, 1378 (1962).

(8) R. Delmas, P. Courvoisier, and J. Ravoire, *J. Chim. Phys.*, **62**, 1423 (1965).

(9) G. Dirian, F. Botter, J. Ravoire, and P. Crandcollot, *ibid.*, **60**, 139 (1963).

(10) Other workers[6,8,9] have preferred a mechanism involving the formation of free hydride ion.

(11) J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966).

(12) F. M. Page, *Trans. Faraday Soc.*, **57**, 1254 (1961).

(13) G. N. Lewis and M. Randall, "Thermodynamics," revised by K. S. Pitzer and L. Brewer, McGraw-Hill Book Co., Inc., New York, N. Y., 1961.

(14) C. W. Scherr, J. N. Silverman, and F. A. Matsen, *Phys. Rev.*, **127**, 830 (1962).

(15) G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Co., Inc., New York, N. Y., 1945.

(16) D. M. Golden, R. Walsh, and S. W. Benson, *J. Am. Chem. Soc.*, **87**, 4053 (1965).

(17) A. F. Gains and F. M. Page, *Trans. Faraday Soc.*, **62**, 3086 (1966).