Contribution from the Department of Pure and Applied Chemistry,
University of Strathclyde, Glasgow, C. 1., United Kingdom

The Mechanism of Formation of the Complexes BF_3,NH_3, and BH_3,NR_3

P. G. Perkins and J. J. Stewart

Received August 4, 1969

The addition reaction between BF_3, BH_3, and NH_3 are studied by the SCFMO method including all valence electrons. It is concluded that no primary reorganisation of the acceptor is necessary and the energy due to formation of the donor acceptor bond at all distances offsets both the reorganisation energy and the mutual repulsion energy of the two moieties. A curve having the general shape of the Morse potential is obtained for the variation of the energy with the length of the D–A bond in both cases. The absence of activation energy for such reactions is thereby accounted for.

Introduction

Adducts such as $BF_3 . NH_3$ are generally formed when the two components are mixed in the gas-phase and during the formation of $BF_3 . NH_3$ the BF_3 moiety changes from a planar to a pramidal shape. This process involves an increase in energy of the molecule (the reorganisation energy) and various estimates of its magnitude have been published.[1,2,3] The most recent of these stems from a full self-consistent field *ab initio* calculation of the electronic structure of boron trifluoride[3] and is the overall energy required to convert planar boron trifluoride to a pyramidal structure with F–B–F angles of 111° (as in $BF_3 . NH_3$[4]). This was found to be 34.2 kcal/mole^{-1}. A similar calculation has yielded the value 13.2 kcal/mole^{-1} for the reorganisation energy of BH_3 where the only changes are in the σ energy of the compound.[5]

The most interesting feature arising from kinetic observations of the reaction of BF_3 with NH_3 (and other amines) is that these processes are extremely fast and appear to take place virtually without action energy.[6] This is surprising because it might be expected that primary distortion of the BF_3 molecule from planarity would be necessary before the addition of amine could take place. (In this context ammonia is already pyramidal so little reorganisation of this portion of the new adduct is necessary).

In order to explain the experimental results Lockhart[6] has suggested that, since such complexes are (by the Mulliken definition) of charge-transfer type, then an addition reaction can be resolved into two conflicting processes:

(i) the mutual repulsion of unreorganised BF_3 and amine at short distances, assuming no bonding. This situation is represented by the Mulliken «no-bond» wave function. (ii) the transfer of an electron from the donor molecule to the acceptor at infinite distance and the subsequent attraction of the oppositely charged entities. This hypothetical molecule would be represented by the completely ionic wave function. The energy curves corresponding to these two functions cross as the B–N distance decreases and Lockhart explains the absence of activation energy on the basis of an intersystem crossing from the no-bond to the ionic form when the B–N distance approaches the known equilibrium value. It is assumed that, to reach the crossing point, little energy need be expended.

This approach though valid, is non-quantitative and is not able to take account of a number of important factors. Because the final wave function is of the ionic type no allowance for orbital mixing in the B–N bond is made. Perhaps most important, it suggest that the addition reaction is non-adiabatic since it crosses from a spin-paired «covalent» system to an ionic state.

In order to throw more light on the mechanism of this reaction we have investigated the reaction coordinate for BF_3, BH_3, and NH_3 using a variation of the CNDO SCF method.[7]

The total energy of a series of systems in which an acceptor and a donor molecule mutually approach are calculated, the line of approach of the two systems being made to coincide with their common C_3 axes, because this will be the lowest energy path for the reaction.[8] There are a large number of degrees of freedom in the total system (hence a multidimensional reaction hypersurface) but these may be reduced to one only by maintaining the NH_3 moiety unchanged during the process and by reorganising the BX_3 molecule in a systematic manner as the B–N internuclear separation decreases.

The reorganisation was arranged by moving the

---

(1) F. A. Cotton and J. R. Leto, *J. Chem. Phys.*, *30*, 993 (1959).
(2) D. R. Armstrong and P. G. Perkins, *J. Chem. Soc.* (A), 1218, (1967).
(3) D. R. Armstrong and P. G. Perkins, *Chem. Comm.* in the press.
(4) Interatomic Distances in Molecules and Ions, *Chem. Soc. Special* Publ. London, No. 11., 1958.
(5) D. R. Armstrong and P. G. Perkins, *J. Chem. Soc.*, (A), 1064, (1969).
(6) J. C. Lockhart, « Introduction to Inorganic Reaction Mechanisms », Butterworths, London, 1966, Ch. 2.
(7) J. A. Pople, D. P. Santry and G. A. Segal, *J. Chem. Phys.*, *43*, S 129, (1965).
(8) S. Glasstone, K. J. Laidler and H. Eyring, « The Theory of Rate Processes' McGraw Hill, New York, 1941, Ch. 3.

boron atom out of the plane of the three X atoms at a constant rate as the B–N distance was simultaneously decreased. The geometrical limits, *e.g.*, for $BF_3 . NH_3$ were set at FBF = 120° and B–F = 1.36 Å when B–N = 1.6 Å. The linear change in the height of the BF_3 pyramid induces an approximately quadratic change in both B–F distance and F–B–F angle. This necessarily makes the exact form of the potential energy surface somewhat arbitrary but it does reduce its dimension to unity. If the developing complex is described well at all B–N distances by molecular orbital theory then mixing of the orbitals producing the B–N bond gradually occurs and the reaction can remain adiabatic throughout the whole reaction coordinate. This results from our allowing for orbital mixing, nuclear repulsion and electronic repulsion at all distances.

(i) *Boron trifluoride-ammonia.* Figure 1 illustrates the sum of all the energy changes, electronic, nuclear, and the reorganisation energy as the distance between the BF_3 and NH_3 moieties lessens. At a B–N distance of 5 Å the BF_3 and NH_3 molecules are not associated and the eigenvectors for the system contain contributions from only one entity or the other. This distance was therefore used as the point at which the reorganisation process was initiated. The curve calculated for a series of B–N distances is of the normal Morse type and has a minimum at 1.6 Å (experimental value 1.6 Å[4]). The form of this curve shows that, at all distances, the energy gained from donor-acceptor bonding offsets both the nuclear repulsion energy between the two molecules and the reorganisation energy. This means that there need be no activation energy for the process of complex formation and, moreover, the reactants and product stay in the $^1A_1$ electronic state throughout the reaction.

In a separate series of calculations on BF_3 in which the B–F bonds were bent and stretched to distort the molecule to pyramidal form the energy gain for this perturbation was found to be 28 kcal/mole^{-1} recently calculated *ab initio* using Gaussian type atomic orbitals.[3]

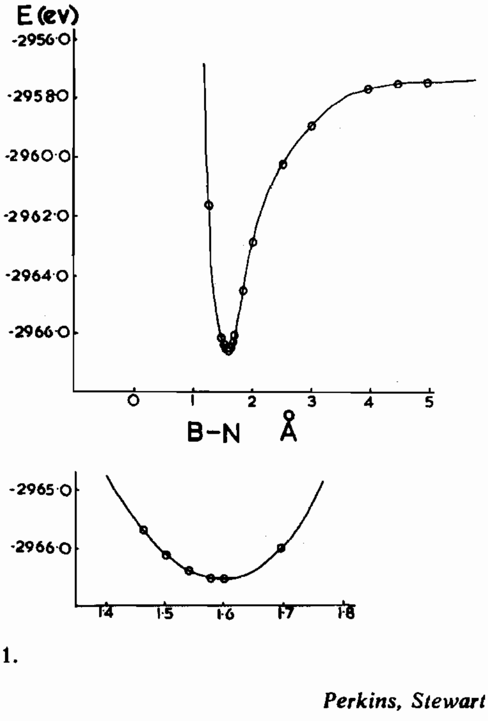

Figure 1.

Orbital-Orbital bond orders in the B–N bond. It is interesting to examine the development of the orbital-orbital bond orders which make-up the B–N bond as the two species mutually approach. The way in which the bond orders between the boron and nitrogen orbitals increase with decreasing B–N distance gives interesting information on the relative strengths of the donor-acceptor bond at various distances. Reorganisation of BF_3 to C_{3v} form removes σ–π separability and the original $2p_\pi{}^B$–$2p_\pi{}^F$ bonds become mixed with the σ components. Figure 2 shows how the bond orders vary with increase in the B–N bond distance. These quantities are high or at a maximum near the equilibrium bond distance but decrease by a factor of ~2 when the B–N length increases by ~1 Å.

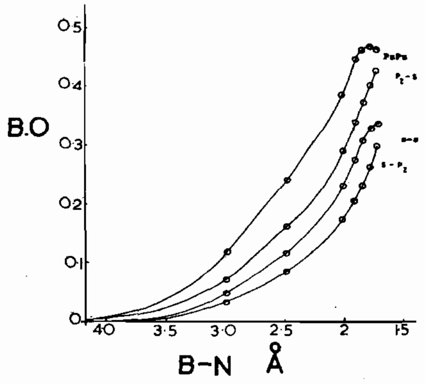

Figure 2.

(ii) *Borane-Ammonia.* The direct reaction of B_2H_6 with ammonia does not yield $BH_3 . NH_3$: trimethylamine however does form the 1 : 1 complex, $BH_3 . NM_3$, presumably after dissociation of B_2H_6. It would therefore be expected that this type of addition reaction would require activation energy because of the necessity of the latter dissociation and this is indeed found to be the case.[6] However, although this is

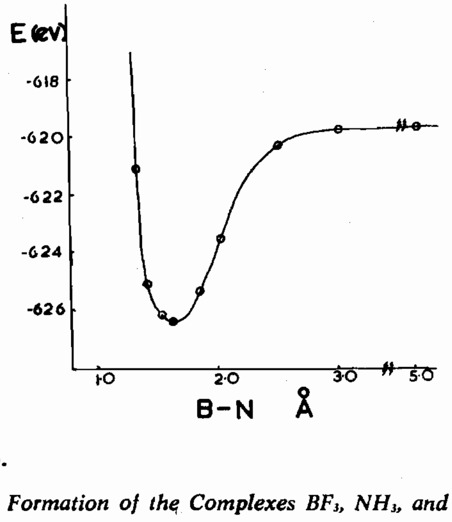

Figure 3.

consistent there are other interpretations of this energy which are possible. Since as stated earlier, the amine in the donor-acceptor reaction does not require drastic reorganisation we can take the direct addition of NH_3 to BH_3 as a model for the whole class of reactions.

The reorganisation energy of BH_3 stems from changes in the σ energy only and amounts to 13.2 kcal/mole^{-1}.[5] The present calculations on the addition reaction followed the same pattern as for $BF_3 . NH_3$ and Figure 3 records the variation of total energy of the molecule with the B–N bond length. The minimum occurs at $\sim$1.6 Å.

There is some doubt about the experimental value of the B–N length for this compound but a recent *ab initio* calculation[5] has estimated it to be 1.665 Å. The curve is again of the simple Morse type and shows no deviation due to the reorganisation energy.

It seems therefore that, despite reorganisation energy, donor acceptor reactions of this type, where no primary dissociation process need be brought about, should be extremely fast and should proceed without activation energy.

Acknowledgments. One of us (J.J.S.) thanks the Scottish Education Department for a maintenance grant.