

A Semi-empirical Method for Calculating Activation Energies

By J. N. BRADLEY

(Department of Chemistry, University of Essex, Wivenhoe Park, Colchester)

THE major difficulty in estimating rate constants for chemical reactions lies in determining the appropriate potential-energy surfaces. The earliest transition-state calculations¹ used the London equation to obtain such surfaces from the energy curves for the constituent pairs of atoms. This necessitated the assignment of an arbitrary value to the ratio of the Coulomb and exchange terms and many of the resulting discrepancies can be attributed to this approximation. Numerous improvements² have been made to the theory, with varying degrees of success, the most recent³ making use of energy curves for both ground and excited states of the diatomic species.

The success of the Hückel theory for calculating the properties of aromatic molecules suggests that a more profitable approach might be based on molecular-orbital theory although the Hückel method itself is unsatisfactory because it is based on a one-electron Hamiltonian and neglects electron interactions. Roothaan⁴ overcame this difficulty by developing an iterative procedure for solving the Hartree-Fock self-consistent-field equations based on a set of LCAO molecular orbitals. This method has been extended to open-shell systems (radicals) by Pople and Nesbet.⁵

In the present approach, the integrals involved are simplified by making similar approximations to Pariser and Parr⁶ and Pople⁷ so that they can be replaced by terms obtained empirically from

simpler systems. Briefly, the approximations made are as follows (χ_μ denotes an atomic orbital centred on nucleus μ):

(i) Overlap integrals $\int \chi_\mu \chi_\nu dv$ are not included explicitly although the effects of overlap are implicit in obtaining empirical values for the various integrals as functions of internuclear separation.

(ii) All interactions involving non-adjacent nuclei are omitted, *i.e.*, electron-nuclear attractions, $\int \chi_\mu H \chi_\nu dv$, electron-electron repulsions $\iint \chi_\mu(1) \chi_\nu(2) \left(\frac{1}{r_{12}} \right) \chi_\mu(1) \chi_\nu(2) dv$, and nuclear repulsions $\frac{1}{R_{\mu\nu}}$.

(iii) The zero differential overlap approximation is assumed in order to simplify the electron repulsion terms, *i.e.*, charge distributions $\chi_\mu(1) \chi_\nu(1)$ are neglected if $\mu \neq \nu$.

(iv) The Coulomb penetration integrals $\int \chi_\mu(1) \left(-\frac{1}{r_{1\nu}} \right) \chi_\mu(1) dv$ are set equal in magnitude but opposite in sign to the corresponding electron repulsion terms $\iint \chi_\mu(1) \chi_\nu(2) \left(\frac{1}{r_{12}} \right) \chi_\mu(1) \chi_\nu(2) dv$.

(v) Different spatial orbitals are allocated to electrons with different spins *i.e.*, the molecular

orbitals are represented in LCAO approximation by $\psi_i^\alpha = \sum_\mu c_{i\mu}^\alpha \chi_\mu$ and $\psi_i^\beta = \sum_\mu c_{i\mu}^\beta \chi_\mu$ where $c_{i\mu}^\alpha$ and $c_{i\mu}^\beta$ denote different sets of coefficients.

The procedure leaves only four types of integrals to be evaluated: the nuclear attraction terms, $V_{\mu\mu}$, and the electron repulsion terms, $\gamma_{\mu\mu}$, associated with a single centre μ , and the corresponding terms, $\beta_{\mu\nu}$ and $\gamma_{\mu\nu}$ associated with a pair of centres μ, ν .

procedure. The computations were carried out on the N.I.R.N.S. Atlas Computer. The maximum energy along the reaction co-ordinate corresponded to a symmetrical transition state and the results obtained are shown in the Table.

Simple graphical interpolation was used in obtaining the necessary interaction terms and more precise methods would probably lead to further improvement, particularly in the interatomic distance, but these preliminary results are adequate to indicate the potentialities of the

TABLE

| | Activation energy (kcal/mole) | Internuclear distance (Å) | Reference |
|--|-------------------------------|---------------------------|-----------|
| This work (S.C.F. procedure) | 13 ^a | 0.96 | — |
| This work (Hückel coeffs.) | 39 ^a | 0.96 | — |
| Best theoretical estimate (Boys and Shavitt) .. | 14.8 | 0.942 | 9 |
| Semi-empirical value (Cashion and Herschbach) .. | 8.9 | 0.963 | 3 |
| Experimental value | 8.0 ^b | — | 10 |

^a Zero-point energy corrections have been made using the values given in ref. 3.

^b The experimental value is expected to lie below the estimated values as the allowance for quantum mechanical tunnelling has not been included in the latter.

The calculations have been carried out for the $H + H_2$ reaction, assuming that the transition state is linear. The electronic energies of the ground and excited states of H_2^+ and H_2 are known for a range of internuclear distances⁸ and, in terms of the integrals above, may be written:

$$H_2^+ (1\sigma_g) : V_{\mu\mu} + \beta_{\mu\nu} - \gamma_{\mu\nu}$$

$$H_2^+ (2p\sigma_u) : V_{\mu\mu} - \beta_{\mu\nu} - \gamma_{\mu\nu}$$

$$H_2 ({}^1\Sigma) : 2V_{\mu\mu} + 2\beta_{\mu\nu} - \frac{3}{2}\gamma_{\mu\nu} + \frac{1}{2}\gamma_{\mu\mu}$$

$$H_2 ({}^3\Sigma^+) : 2V_{\mu\mu} - \gamma_{\mu\nu}$$

Values for all four terms can thus be obtained for each internuclear distance.

The energy of the H_3 complex was then evaluated as a function of internuclear separation using both the Hückel coefficients and the self-consistent-field coefficients obtained by the usual iteration

method. Comparable results to those of Cashion and Herschbach might have been predicted since they are based on similar potential-energy curves.

The $H + H_2$ reaction was selected for the preliminary analysis because of the fund of material available for comparison, although the method should prove more profitable for comparing the activation energies of a series of related reactions. The results show that the molecular-orbital approach is at least as promising as the valence-bond treatment for this type of work. However, the present procedure should be more easily extended to other systems because the diatomic potential-energy curves are reduced to interaction terms with a direct physical significance. Further details of the methods and the results obtained, will be presented later.

(Received, November 29th, 1965; Com. 747.)

¹ e.g., M. Polanyi, "Atomic Reactions," Williams and Northgate, London, 1932; S. Glasstone, K. J. Laidler, and H. Eyring, "The Theory of Rate Processes," McGraw-Hill, New York, 1941.

² S. Sato, *J. Chem. Phys.*, 1958, **23**, 592, 2465; *Bull. Chem. Soc. Japan*, 1955, **28**, 450; R. E. Weston, *J. Chem. Phys.*, 1959, **31**, 892.

³ J. K. Cashion and D. R. Herschbach, *J. Chem. Phys.*, 1964, **40**, 2358.

⁴ C. C. J. Roothaan, *Rev. Modern Phys.*, 1951, **23**, 69.

⁵ J. A. Pople and R. K. Nesbet, *J. Chem. Phys.*, 1954, **22**, 571.

⁶ R. Pariser and R. G. Parr, *J. Chem. Phys.*, 1953, **21**, 466, 767.

⁷ J. A. Pople, *Trans. Faraday Soc.*, 1953, **49**, 1375; A. Brickstock and J. A. Pople, *ibid.*, 1954, **50**, 901.

⁸ D. R. Bates, K. Ledsham, and A. L. Stewart, *Phil. Trans.*, 1954, *A*, **246**, 215; W. Kolos and C. C. J. Roothaan, *Rev. Modern Phys.*, 1960, **32**, 219.

⁹ I. Shavitt, *J. Chem. Phys.*, 1959, **31**, 1359.

¹⁰ R. E. Weston, *J. Chem. Phys.*, 1959, **31**, 892.