

CALCULATION OF TRANSITION STATE ENERGIES BY MEANS OF SIMPLE
QUANTUM MECHANICAL IC-METHODS

(Transition State Energies of 1,3-Dipolar Additions)

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(Received 5 June 1964)

R. HUISGEN et al.^{1,2} have shown that the well known addition of diazoalkanes to alkenes resulting in pyrazolines follows the mechanism of the so-called 1,3-dipolar addition. In the course of that mechanism there occur simultaneously with the successive formation of the two new σ -bonds (fig. 1) changes in the hybridisation at the four centres of the reaction and at the central N-atom of the diazoalkane. Roughly interpreted the C-atoms change from sp^2 - to sp^3 -states and the N-atoms change from sp - to sp^2 -states. J.D. ROBERTS³ has calculated quantum chemically that the energy Q, arising from the change of hybridisation at the central N-atom, lies in the range

$|2 \alpha_N + 0,83 \beta_{NN}| < Q < |2 \alpha_N + 2,00 \beta_{NN}|$; energy quanta of this order should be available under the usual reaction conditions. R. HUISGEN et al.² have presented kinetic data concerning the 1,3-dipolar addition of 1,1-diphenyldiazomethane to various alkenes.

Fig. 1 shows the model used in our work, of the transition state of these reactions. For simplicity this model is idealized geometrically to some extent by the assumptions: (1) that the lengths of the C-C-bond in the alkene and the C-N- and N-N-bonds in the diazoalkane are equal to d and do not alter during the formation of the activated complex;

(2) that the newly formed σ -bonds have equal lengths r ;
 (3) that the valence angles at the four centres of the reaction are at all stages of the transition state equal to ϕ . So the four centres of the reaction and the central N-atom occupy the corners of an irregular but symmetric pentagon. The valence angle at the central N-atom is called φ .

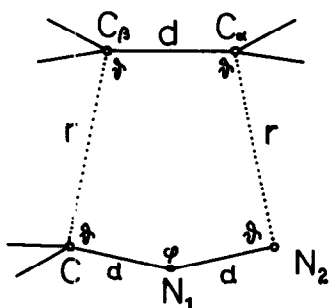


Fig. 1: Slightly idealized model of the transition state in 1,3-dipolar addition of diazoalkanes to alkenes.

If an angle γ is defined by

$$\gamma = \phi - 90^\circ \quad (1)$$

there follows by elementary geometry

$$\varphi = 180^\circ - 4\gamma \quad (2)$$

$$r = d \frac{2 \cos 2\gamma - 1}{2 \sin \gamma} \quad (3)$$

As shown by eqns. (1), (2) and (3) γ may be used as well as r as a measure of the reaction coordinate whereby

$0 \leq \gamma \leq 18^\circ$ corresponds with $\infty \leq r \leq d$.

Two different wave func-

tions $\psi_d(\gamma)$ and $\psi_1(\gamma)$ are used to describe the transition state. Both represent the electrons involved and are simple product functions. In detail, $\psi_d(\gamma)$ represents the electrons of the two reactants without allowance being made for the formation of the two new σ -bonds along r , but $\psi_1(\gamma)$ describes them when the two σ -bonds are formed. Two energies $E_d(\gamma)$ and $E_1(\gamma)$ correspond to both these wave functions. The contributions of π -electrons to these energies are calculated using the simple Hückel method, and those of the σ -electrons are estimated by means of Morse potential functions. Fig. 2 shows the relationship between $E_d(\gamma)$ and $E_1(\gamma)$ respectively, and the angle γ . The intersection of the two curves (point C in fig. 2, corresponding to the energy E_C) is to a first approximation re-

garded as representing the transition state. At this point the equality

$$E_d(\gamma_C) = E_1(\gamma_C) = E_C \quad (4)$$

is exactly fulfilled. The difference in energies $E_C - E_d(0)$ is likewise taken as representing the heat of activation ΔH^\ddagger :

$$\Delta H^\ddagger = E_C - E_d(0) \quad (5)$$

A comparison of the heats of activation calculated by means of eqn. (5) with those observed experimentally by R. HUISGEN et al.² is given in the following table.

$(\Delta H^\ddagger)_{\text{calc.}}$ is always a little high

owing to neglect of the "non-crossing rule"⁴. Configuration interaction (CI) calculations at present in progress will improve the results.

TABLE: HEATS OF ACTIVATION IN THE 1,3-DIPOLAR ADDITION OF 1,1-DIPHENYLDIAZOMETHANE TO ALKENES (in kcal/moles)

Alkenes:	$(\Delta H^\ddagger)_{\text{calc.}}$	$(\Delta H^\ddagger)_{\text{obs.}}$ ²
$C_6H_5-CH=CH-COOEt$	56,6	43,5
$CH_2=CH-COOEt$	49,8	39,6
$C_6H_5-CH=CH_2$	50,5	43,4

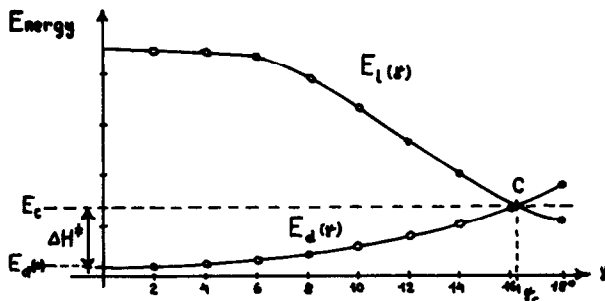


Fig. 2: Energy diagram of the transition state in the reaction of styrene with 1,1-diphenyldiazomethane, γ being the reaction coordinate

To our knowledge this is the first calculation of heats of activation in organic reactions by means of quantum mechanical methods.

A more detailed paper will appear elsewhere.

REFERENCES

- ¹ R. HUISGEN, Naturwiss. Rdschau 1961, 47.
- ² R. HUISGEN, H. STANGL, H.J. STURM und H. WAGENHOFER, Angew. 73, 170 (1961).
- ³ J.D. ROBERTS, Chem.Ber. 94, 273 (1961).
- ⁴ See e.g. C.A. COULSON, Valence, 2nd ed., p. 69, 134, Oxford University Press, 1961.