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A Semi-Empirical Calculation of the Potential Surface for the $CH_3^{\cdot} + CH_2{=}CH_2$ Reaction

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A model for the reaction $CH_3^{\cdot} + CH_2{=}CH_2$ is studied including the hybridization change of the reaction center. The interaction energy is devided into two parts. The first is a stabilization energy – the contribution due to the π-electron delocalization (including the hybridization effects). It is computed by the PPP method. The second part is an exchange repulsion due to all valence electrons of the three carbon atoms. Correlation corrections are considered. A potential energy surface is constructed, giving a saddle point value close to the experimental activation energy. A discussion is given of the approximations involved. The method suggested is a generalization of the reactivity indices method of the theory of chemical reactivity. It can be regarded as a justification of this more empirical approach.

Ein Modell für die Reaktion $CH_3^{\cdot} + CH_2{=}CH_2$ wird untersucht, einschließlich der Änderung der Hybridisation des Reaktionszentrums. Die Wechselwirkungsenergie wird in zwei Teile zerlegt. Der erste Teil ist eine Stabilisationsenergie – der Beitrag, der der Delokalisierung des π-Elektrons (einschließlich Hybridisationseffekte) entspricht. Der zweite Teil ist eine Austauschabstoßung, die von allen Valenzelektronen der drei Kohlenstoffatome herrührt. Korrellationskorrekturen werden berücksichtigt. Eine Fläche der potentiellen Energie wird konstruiert mit einem Sattelpunktswert, der dicht an der experimentellen Aktivierungsenergie liegt. Die verwendeten Näherungsmethoden werden diskutiert. Die vorgeführte Methode ist eine Verallgemeinerung der Methode der Reaktivitätsindices aus der Theorie der chemischen Reaktivität. Sie kann als eine Rechtfertigung dieser mehr empirischen Näherung angesehen werden.

Etude d'un modèle pour la réaction $CH_3^{\cdot} + CH_2{=}CH_2$ où l'on tient compte du changement d'hybridation du centre réactif. L'énergie d'interaction est divisée en deux termes. Le premier est une énergie de stabilisation; c'est la contribution dela délocalisation des électrons π (effets d'hybridation compris). Il est calculé par la méthode PPP. Le second terme est une répulsion d'échange dûe à tous les électrons de valence des trois atomes de carbone. Les corrections de corrélation sont introduites.

Une surface d'énergie potentielle est construite; elle fournit une valeur de l'énergie d'activation proche de celle obtenue expérimentalement. Les approximations utilisées sont discutées. La méthode proposée est une généralisation de celles des indices de réactivité. On peut la considérer comme justifiant cette approche plus empirique.

Introduction

The modern theory of chemical reactivity operates with the so called reactivity indices. The best of these indices is the stabilization energy Δ [1, 2] – the difference of π-energies in the delocalised transition state and in the reagents. If a bimolecular reaction

$$A + B \rightarrow AB^{\neq} \rightarrow \text{products}$$

is considered, we have

$$\Delta = E_{\pi}^{AB^{\neq}} - E_{\pi}^{A} - E_{\pi}^{B} . \tag{1}$$

The stabilization energy gives a good semi-empirical description of the relative rates of reactions including conjugated molecules [3, 4]. It may be shown [5] that the other indices can be derived from Δ.

We wish to use the conception of delocalisation in the transition state for an absolute calculation of activation energies. Some preliminary results have been reported elsewhere [4]. The results presented here are based on the theory and data given in [6].

There exist several difficulties. First, the Δ value, if calculated by usual methods, does not take into account the exchange repulsion. It decreases with the intermolecular distance and it is impossible to get a maximum at the potential curve corresponding to an activation energy. This problem had been discussed in [6]. The expression derived for the interaction energy

$$U=\Delta+\gamma\sum S^2 \tag{2}$$

(where S are the *inter*molecular overlap integrals and γ is a parameter) can already be used as the basis for an absolute calculation.

Secondly the transition state of the radical addition reaction we intend to concern is not really a π-system. We discuss this problem in the next section.

The "almost π-Electron Approximation"

Fig. 1 shows the model we assumed for the addition reaction of a methyl radical to ethylene. When the distance R between the C_1 and C_2 atoms is great, the configuration of the reacting molecules is retained and their planes are parallel. As the distance is reduced, a change in the geometry is advantageous, a change that is to be characterised by a single parameter – namely the angle φ, through which each of the six σ-bonds adjacent to the reaction center deflects from its initial direction (the direction of the $C_1 \ldots C_2$ bond is to be fixed).

Our model differs from the usually applied one. The consideration of the geometry changes allows to follow the real reaction path. In the reaction treated the angle φ changes from 0 in the reagents to 19° 28′ in the product and so it does in our model.

Such a system is not really a π-electron system, since first one-electron interactions between the orbitals of the σ- and the π-systems from different molecules appear, and secondly in each reagent the planar structure is distorted, thus intramolecular σ-π-interaction is involved.

If the interactions are small it is possible to choose three AO's belonging to the three carbon atoms, from the 12 carbon orbitals of the combined system (Fig. 1) in such a manner that they convert into the corresponding $2p_z$ AO's when the interactions vanish. We choose the other nine AO's to convert into the trigonal AO's of the σ-bonds of the reagents when the interactions vanish. Let us call these AO's the "π-orbitals" and the "σ-orbitals" respectively. There exist several possibilities to determine such orbitals. We shall use the additional condition that the one-electron "σ-π"-interactions are minimal. This corresponds to the maximum overlap principle, i.e. to orbitals directed along the σ-bonds.

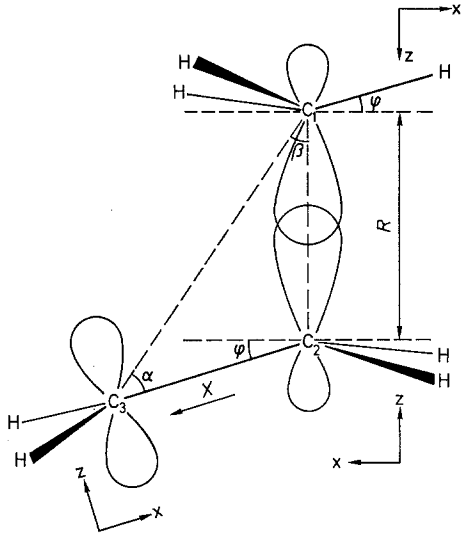

Fig. 1. $CH_3^{\cdot} + CH_2{=}CH_2$ reaction. The model and coordinates

Let us rewrite (2) in the form

$$U = \Delta_\pi + \Delta_\sigma + \gamma \sum_{\sigma,\pi} S^2 . \tag{3}$$

Δ_π is the part of stabilization energy due to the three "π-orbitals", it should be directly calculated. Δ_σ characterizes the energy change of the σ-bonds due to the hybridization change; it should be empirically estimated. The last sum corresponding to the exchange repulsion is to be evaluated over all 12 valence AO's of the carbon atoms. It is invariant with respect to the choice of the basis AO's.

In (3) we have neglected the part of the stabilization energy due to the one-electron σ-π-interactions.

The exchange repulsion due to carbon valence electrones is taken into account. We have also not considered all the intermolecular interactions due to hydrogen 1s-orbitals. Although a more accurate treatment could involve these at least in the S^2 sum, such a complication would be undersirable in our semiempirical procedure. We would like to point as a justification that in the range of intermolecular separations we are studying the respective C–H and H–H distances are close to or more than the sum of the Van der Waals radii for the given atom pairs.

Calculational Details

Let us introduce a hybridization parameter a for the two carbon atoms, adjacent to the reaction center:

$$a = \sqrt{2}\, \mathrm{tg}\varphi .$$

Provided that the σ-bonds are moving synchronously (the same angle for all six bonds) we get the orbitals

$$\begin{aligned}
c_{r1} &= a s_r + \sqrt{1-a^2}\, z_r\,, \\
c_{r2} &= \sqrt{\frac{1-a^2}{3}}\, s_r - \frac{a}{\sqrt{3}}\, z_r + \sqrt{\frac{2}{3}}\, x_r\,, \\
c_{r3} &= \sqrt{\frac{1-a^2}{3}}\, s_r - \frac{a}{\sqrt{3}}\, z_r - \frac{1}{\sqrt{6}}\, x_r + \frac{1}{\sqrt{2}}\, y_r\,, \\
c_{r4} &= \sqrt{\frac{1-a^2}{3}}\, s_r - \frac{a}{\sqrt{3}}\, z_r - \frac{1}{\sqrt{6}}\, x_r - \frac{1}{\sqrt{2}}\, y_r\,,
\end{aligned} \tag{4}$$

which are directed along the respective bonds. For the carbon $2s$, $2p_z$, $2p_x$ and $2p_y$ AO's, the abbreviations s, z, x and y are used. The index r indicates the number of the carbon atom. The directions of coordinate axes are shown in Fig. 1. The parameter a describes the continuous transition of the reaction center from the initial sp^2-state ($a=0$) to the ultimate sp^3-state ($a=0.5$). For the third carbon atom C_3 ($r=3$), sp^2-hybridization is retained and $a=0$ during the whole reaction path.

To calculate Δ_π we need the matrix elements of the one-electron hamiltonian $\boldsymbol{h}$ in the basis of the three AO's c_{11}, c_{21}, c_{31}. Neglecting the terms of order a^3 we have

$$\begin{aligned}
\alpha_r &= \langle c_{r1}|\boldsymbol{h}|c_{r1}\rangle = W_p + a^2(W_s - W_p)\,, \\
\beta_{12} &= \langle c_{11}|\boldsymbol{h}|c_{21}\rangle = \langle \sigma_1|\boldsymbol{h}|\sigma_2\rangle + 2a\langle \sigma_1|\boldsymbol{h}|s_2\rangle \\
&\quad + a^2[\langle s_1|\boldsymbol{h}|s_2\rangle - \langle \sigma_1|\boldsymbol{h}|\sigma_2\rangle]\,, \\
\beta_{23} &= \langle c_{21}|\boldsymbol{h}|c_{31}\rangle = \langle \pi_2|\boldsymbol{h}|\pi_3\rangle\,(1-\tfrac{3}{4}a^2)\,, \\
\beta_{13} &= \langle c_{11}|\boldsymbol{h}|c_{31}\rangle = [\langle \sigma_1|\boldsymbol{h}|\sigma_3\rangle \sin\alpha\cos\beta \\
&\quad - \langle \pi_1|\boldsymbol{h}|\pi_3\rangle \cos\alpha\sin\beta]\,(1-\tfrac{1}{2}a^2) + a\langle \sigma_3|\boldsymbol{h}|s_1\rangle \sin\alpha\,.
\end{aligned} \tag{5}$$

W_s and W_p are the energies of $2s$ and $2p$ AO's, σ_r and π_r are the $2p$ AO's directed along the corresponding bond or perpendicular to it. The angles α and β are shown in Fig. 1.

The Δ_π value was calculated by the Roothaan method [7] in the zero differential overlap approximation [8] with and without correlation (by perturbation theory). The values of the two-center integrals $(rr|ss)$ were taken from [8, 6]. Their dependence on the type or orientation of AO's was not taken into account. The β value for ethylene (i.e. $\langle \pi_1|\boldsymbol{h}|\pi_3\rangle$) was put equal to -2.78 eV. The other β_{rs} were evaluated according to (5) supposing them to be proportional to S_{rs}:

$$\beta_{rs} = -9.19\, S_{rs}\ \text{eV}\,.$$

Slater orbitals were used with effective charge $Z=3.18$.

A complete analysis of the interactions between the orbitals (4) has shown [4] Δ_σ to be proportional to a^2. If $\Delta E_\sigma(sp^3)$ is the energy change of six σ-bonds adjacent to the reaction center when its hybridization changes from sp^2 to sp^3, then

$$\Delta_\sigma = \frac{\Delta E_\sigma(sp^3)}{0.25}\, a^2\,, \tag{6}$$

since a changes from 0 to 0.5.

To estimate the value of $\Delta E_\sigma(sp^3)$, we made use of the data given by Dewar [9, 10] or Lorquet [11]. In the first case $\Delta E_\sigma(sp^3) \approx 1$ eV, and in the second case $\Delta E_\sigma(sp^3) \approx 0$.

The value of the sum $\gamma \sum S^2$ as pointed out above is invariant with respect to a transformation of the basic AO's. The calculations are simplified if the initial $2s$- and $2p$-AO's are used instead of hybride orbitals. The parameter γ was estimated according to Dewar or Lorquet [6].

An important detail should be stressed. In principle there exist two possible ways to calculate the interaction energy U: a) as a difference of the total energies of the unified system and the isolated reagents, and b) as a difference of their atomisation (i.e. bonding) energies. We must follow the second method because our estimation of Δ_σ by (6) has already included bonding energies. Thus the Δ_π value is to be considered as a bonding energy difference. In (1) the unified system's π-energy $E_\pi^{AB^*}$ is to be related to the energies α_r (5) of the hybride orbitals:

$$E_\pi^{AB\ddagger} = \mathcal{E}_\pi^{AB\ddagger} - \sum_{r=1}^{3} \alpha_r .$$

Similarly for the isolated reagents

$$E_\pi^A + E_\pi^B = E_\pi^0 = \mathcal{E}_\pi^0 - 3W_p .$$

Here $\mathcal{E}_\pi^{AB\ddagger}$ and $\mathcal{E}_\pi^0$ are the total π-energies.

Results and Discussion

The Table gives the potential surfaces calculated with the Lorquet estimations of $\Delta E_\sigma(sp^3)$ and $\gamma(\Delta E_\sigma(sp^3)=0$; $\gamma=8.51$ eV without correlation, $\gamma=9.89$ eV with correlation). If the Dewar estimations are used, the energy at the saddle point greatly exceeds the experimental activation energy value for the reaction under study. The value of activation energy obtained, 7—10 kcal/mol, is fully satisfactory (the experimental value is equal to 8 ± 1 kcal/mol [12—16]). Such a good agreement with the experiment should not be overestimated, especially considering the large number of approximations involved in our calculation, of which the neglect of one-electron σ-π-interactions is the most hazardous one.

The σ-π-interaction energy can be devided into intermolecular and intramolecular parts. The intramolecular interactions due to the geometry changes of the reagents are proportional to a^2 [4]. They appear to be indirectly involved in the Δ_σ value as calculated by (6). At any rate the corresponding corrections are small up to the very saddle point ($a^2=0.04$—0.06).

The intermolecular σ-π (and σ-σ) interactions are more dangerous. The matrix elements of $\boldsymbol{h}$ which determine their values are of the same order of magnitude as β_{12} and β_{13} in (5) which dermine the Δ_π value. However the energy levels of the σ-bonds lie lower than the levels of the π-bonds (the last being of order of β_{23}), so the stabilization energy correction due to the interactions concerned should be less than Δ_π. Using the analogy with the conjugation and hyperconjugation energies this correction appear to contribute 20—30% of Δ_π. Near the saddle point such an error may give 3—4 kcal/mole reducing the activation energy.

The empirical estimate of the σ-bonds energy may also be a source of error. We could see the Dewar estimations to be invalid at all. All these difficulties may be overcome only by the complete treatment of all valence electrons. In our procedure the errors would be the less the closer the saddle point to the beginning of the reaction path.

It should be noted that the zero temperature corrections increase the activation energy by ~2 kcal/mole [17]. As a result the errors partly compensate.

This discussion showes the errors involved to be systematic. They can be eliminated at least partly by means of the parameter choice, for example, by the change of the γ value in (3). This problem needs further investigation.

On the other hand the activated complex geometry is quite insensitive to the calculational details. It follows from the comparison of the surfaces given in the Table and from the data reported in [4]. Thus the values obtained: $R^{\neq}=2.3$ Å, Table. *Potential energy surface for the reaction* $CH_3^{\cdot} + CH_2{=}CH_2$ (in eV)

with correlation									without correlation							
R, Å \ φ^0	0	2	4	6	8	10	12	14	R, Å \ φ^0	0	2	4	6	8	10	12
2.1									2.1					0.39	0.24	0.05
2.2						0.43	0.32	**0.15**	2.2				0.46	0.37	0.30	0.23
2.3					0.48	0.43	**0.42**	0.35	2.3		0.48	0.44	0.36	0.32	**0.30**	0.31
2.4				0.44	0.42	**0.42**	0.44	0.45	2.4	0.43	0.35	0.32	0.30	**0.28**	0.29	0.33
2.5		0.37	0.36	**0.35**	**0.35**	0.38	0.44		2.5	0.30	0.25	0.24	**0.23**	0.24	0.28	
2.6	0.31	0.28	**0.27**	0.28	0.31	0.37			2.6	0.22	0.19	**0.18**	0.19	0.22		
2.7	0.23	**0.20**	0.21	0.23	0.28				2.7	0.15	**0.13**	0.14	0.17			
2.8	0.16	**0.15**	0.16						2.8	0.11	**0.10**	0.11	0.12			
2.9	0.11	**0.11**	0.13						2.9	0.08	**0.07**	0.09				
3.0	**0.07**	0.07	0.10						3.0	**0.05**	0.05	0.08				
3.1	**0.05**	0.06							3.1	**0.04**	0.04	0.06				

Remarks. Saddle point is characterised by the following values of geometric and energy variables: with correlation $R^{\neq} = 2.3$ Å, $\varphi^{\neq} = 12°$, $U^{\neq} = 9.7$ kcal/mol, without correlation $R^{\neq} = 2.3$ Å, $\varphi^{\neq} = 10°$, $U^{\neq} = 7$ kcal/mol. Reaction path is shown by faced numbers.

$\varphi^{\neq}=10$—$12°$ seem to be realistic. We can add that there are no experimental sources to get this last information.

At last we would like to discuss briefly the dependence of the potential energy on the shift of the methyl radical in the direction X from C_2 to C_3 atoms along the ethylene molecule (Fig. 1). An accurate treatment of such configurations of the reacting system requires introduction of new geometric conditions, which are quite different from those we have accepted. For instance, our model with the same hybridisation for C_1 and C_2 atoms would be a poor approximation in this case.

The hybridisation changes are of little importance for such configurations if we consider a small shift ΔX in the vicinity of our reaction path at $\varphi=a=0$; thus we will neglect them at all. Keeping the intermolecular separation R fixed, the variations of interatomic distances are small, and we can regard the electron repulsion terms as constant. The change of β_{12} is of the order of $(\Delta X/R)^2$. This is true also for the corrections in the overlap and resonance integrals due to the changes of angles between the z-axes and bond directions. Neglecting these terms, we have by the perturbation theory:

$$\Delta U=2p_{13}\Delta\beta_{13}+2\gamma\sum_{1,3} S\Delta S$$

where the bond order p_{13} and S are calculated at $\Delta X=0$ and the sum is over all 1—3 interactions. This simple estimation shows the energy change ΔU to be positive for all $R-s$ considered. Thus we conclude that the reaction path presented at our potential surfaces is energetically favoured, at least as long as the ratio $\Delta X/R$ is small.

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References

1. Evans, M., J. Gegerly, and E. Seaman: J. Polym. Sci. **3**, 866 (1948).
2. Bagdasaryan, Kh. S.: Zh. Fiz. Khim. **23**, 1375 (1949). (in Russian).
3. Fukui, K.: Molecular orbitals in chemistry, physics and biology. Acad. Press 1964.
4. Basilevsky, M. V.: Radiospectroscopic and quantum chemical methods in structural research, pp. 40, 50. Moscow: Nauka 1967 (in Russian).
5. — Dokl. Acad. Nauk SSSR **172**, 1405 (1967). (in Russian).
6. — Theoret. chim. Acta (Berl.) **13**, 409 (1969).
7. Roothaan, C. C. J.: Rev. modern. Physics **32**, 179 (1960).
8. Hoyland, J. R., and L. Goodman: J. chem. Physics **36**, 12 (1962).
9. Dewar, M. J. S., and H. N. Schmeising: Tetrahedron **11**, 96 (1960).
10. Chung, A. L. H., and M. J. S. Dewar: J. chem. Physics **42**, 756 (1965).
11. Lorquet, A. J.: Theoret. chim. Acta (Berl.) **5**, 192 (1966).
12. Hogg, A. M., and P. Kebarle: J. Amer. chem. Soc. **86**, 4558 (1964).
13. Brinton, R. K.: J. chem. Physics **29**, 781 (1958).
14. Mandelcorn, L., and E. W. R. Steacie: Canad. J. Chem. **32**, 474 (1954).
15. Landers, L. C., and D. H. Volman: J. Amer. chem. Soc. **79**, 2996 (1957).
16. Endrenyi, L., and D. J. Le Roy: J. physic. Chem. **71**, 1334 (1967).
17. Ainbinder, B. Yu., and M. V. Basilevsky: Zh. Strukt. Khim. **9**, 513 (1968). (in Russian).

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