

# APPROXIMATE CALCULATIONS ON A PROTONATION STEP IN THE REDUCTION OF PROPADIENES

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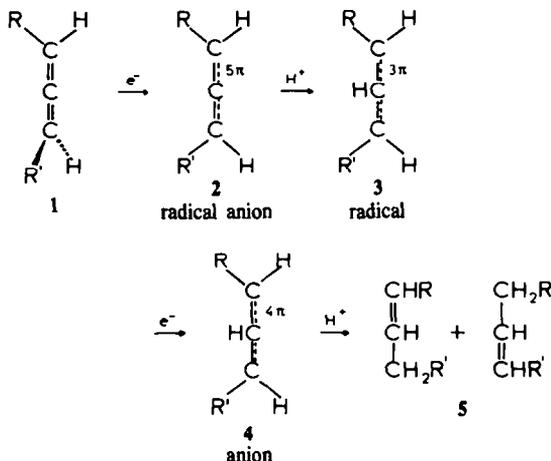
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**Abstract**—The protonation of the radical anion produced as an intermediate by electron transfer to 1,3-dimethylpropadiene is studied by calculating the electrostatic molecular potential to which higher order perturbation terms are added (induction energy). The preferred protonation site is at the central carbon atom, producing a planar allyl radical, in agreement with experimental evidence. A different conclusion is reached if the induction energy is neglected.

## INTRODUCTION

1,3-Substituted propadienes (1) may be reduced to alkenes by alkali metal in liquid ammonia<sup>1-3</sup> as well as by electrochemical reduction<sup>4</sup> in the presence of a proton donor. Experimental evidence suggests a reaction via the intermediates 2, 3 and 4 by alternate electron transfer and protonation:



According to this scheme the protonation of 2 takes place at the central C atom. Protonation at a terminal C atom would produce an isopropenyl radical which, however, is not observed.<sup>4</sup> As to the stereo-chemical aspects we note that propadiene (1) has its substituents in perpendicular planes whereas the allyl radical (3) is coplanar.

We performed a quantum chemical study of the protonation of the radical anion (2), covering the site of protonation and the stereochemical aspects of this process. Perturbation theory was applied to describe the approach of the proton to the radical anion. To minimize the computational effort we took  $R = R' = \text{methyl}$  and used one-electron methods for calculations on the unperturbed radical anion. In all the calculations only valence electrons were taken into account.

### Geometry of the radical anion

The experimentally determined bond lengths and angles of the related methylpropadiene<sup>5</sup> were adopted for 2, apart from the angles  $\alpha$  and  $\theta$  (defined in Fig. 1) which were optimized. For simplicity we restricted  $C_3$  to the plane defined by  $Me_1$ ,  $C_1$  and  $C_2$ . A few test calculations

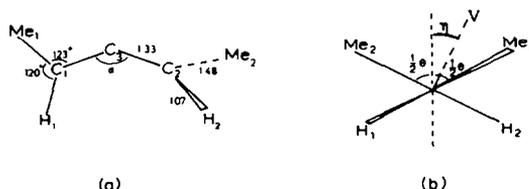


Fig. 1. Geometrical parameters for the radical anion (bond lengths in Å). Me denotes a methyl group, having a C-H bond eclipsing the C=C bond. In Fig. (b) plane V passes through  $C_1C_2$ , which is taken perpendicular to the paper; Me<sub>1</sub> and H<sub>1</sub> are above the paper, Me<sub>2</sub> and H<sub>2</sub> below.  $\theta = \angle(\text{Me}_1C_1C_2, \text{Me}_2C_2C_1)$ .

showed there is not much to be gained by relaxing this condition.

The Extended Hückel method was considered suitable for optimization of  $\alpha$  and  $\theta$ .<sup>6-8</sup> Applying Hoffmann's parameter scheme<sup>9</sup> we obtained the optimum values  $\theta = 40^\circ$  or  $\theta = 140^\circ$  for the dihedral angle of the substituent planes. In both cases the bending of the carbon chain could be neglected, so we took  $\alpha = 180^\circ$ . Similar results have been reported by Hoffmann<sup>7</sup> for propadiene, but his energy minima are less pronounced than ours.

## PROTONATION OF THE RADICAL ANION THEORY AND RESULTS

In order to study the site of protonation we have to compare the free energy differences for various proton approaches. Although the reactions take place in solution, we neglect the solvation energy terms since we expect them to be similar for the alternative proton approaches. On similar grounds entropy terms are omitted,<sup>10</sup> whereas enthalpy is replaced by energy.<sup>11</sup> So we concentrate on the energy change arising on protonation of an isolated radical anion. This energy change was calculated by perturbation theory.

The unperturbed wave function of the radical anion in its optimum configuration was generated by an iterative Extended Hückel (IEH) calculation, adopting parameters from Rein *et al.*<sup>12</sup> The non-iterative EH-method was considered unsuitable here as it is known to produce unrealistic charge distributions,<sup>8</sup> which does not apply to the iterative method.<sup>13,14</sup> A population analysis of the IEH-wave function shows that the negative charge on the unsaturated carbon chain has a slight preference for the central atom.

In a perturbation treatment the energy of protonation is separated into three parts:<sup>15,16</sup> the first order term (Coulomb energy), the higher order terms (induction

energy) and a rest term commonly called the charge transfer energy. The Coulomb energy—better known in this context as electrostatic molecular potential—has been shown recently to be capable of predicting the approach channels of a positively charged reagent (e.g.<sup>17,18</sup>). However, for unsaturated substrate molecules like ethene inclusion of the induction energy can lead to qualitatively different predictions.<sup>19</sup> In the present work the protonation is described on the basis of Coulomb and induction energy terms. No attempt has been made to evaluate the charge transfer energy, since this would require relatively large computational efforts.

**Coulomb energy.** The first order energy was calculated according to the formula introduced by Bonaccorsi *et al.*<sup>17,18</sup> The (unperturbed) doublet ground state wave function of 2 which enters this formula was taken to be a single determinant of the IEH-M.O.'s obtained above.

The proton positions for which the Coulomb energy was calculated are grouped in planes passing through the unsaturated carbon chain. These planes V are defined by a dihedral angle  $\eta$  (Fig. 1b).

Analysis of the energy patterns revealed a local minimum in each plane, at a nearly constant distance (1.19–1.27 Å) from the carbon chain. However, the set of local minima varies in depth and position along the carbon chain. These features are displayed in Fig. 2 for the optimum configuration  $\alpha = 180^\circ$ ,  $\theta = 140^\circ$ . The Coulomb energy alone is seen to favour approach of the proton towards the centre of the C<sub>2</sub>C<sub>3</sub> bond in the plane  $\eta = 35^\circ$  and towards the centre of the C<sub>1</sub>C<sub>3</sub> bond in the plane  $\eta = 160^\circ$ .

**Induction energy.** The induction energy was approximated by second order Rayleigh–Schrödinger perturbation theory or by Brillouin–Wigner perturbation theory.<sup>16,19</sup> This approach is much faster than the variational treatment applied elsewhere<sup>20–22</sup> and sufficiently accurate for our purpose. The formulas needed

here for a doublet open shell molecule are collected in the appendix.

The single excitation energies entering these formulas were treated in an approximate manner, which is permissible because the induction energy is primarily determined by the nuclear attraction integral values. The approximation consisted of:

$$\Delta E_{i-j} = \epsilon_j - \epsilon_i + c$$

where  $\epsilon_i$  and  $\epsilon_j$  are the M.O. eigenvalues produced by the IEH calculation and  $c$  is a positive constant. This formula is used because one-electron methods tend to underestimate the energy gap between occupied and virtual orbitals and produce excitation energies that are too low.<sup>9</sup> For excitations to and from the half-occupied M.O. separate constants  $c'$  and  $(c-c')$  respectively were introduced instead of  $c$ . On the basis of extensive test calculations† we choose  $c = 10$  eV and  $c' = 5$  eV. These values fall into the range where fair excitation energy values are obtained, besides producing perturbation results that are rather insensitive to the precise parameter values.

According to the scheme outlined above we calculated the induction energy for over 100 different proton positions. Figure 2 displays in a condensed form the total interaction energies ( $E_C + E_I$ ) obtained with Brillouin–Wigner perturbation theory. The results are strikingly different from those based on Coulomb energy only. We now predict the proton approach to be preferably in the plane  $\eta = 90^\circ$  towards the central carbon atom. The minimum in this approach channel is favoured by 13 kcal/mole over the local minimum in the plane  $\eta = 180^\circ$  and by 17 kcal/mole over that in  $\eta = 0^\circ$ . The local minima of Coulomb + induction energy collected in Fig. 2b are at a distance of 1.09–1.11 Å from the carbon chain.

With the radical anion in the optimum configuration  $\alpha = 180^\circ$ ,  $\theta = 40^\circ$  we find on the other hand the total interaction energy to have an unfavourable local minimum in the plane  $\eta = 90^\circ$ , the minima at  $\eta = 0^\circ$  and  $180^\circ$  being 9 and 20 kcal/mole lower respectively. The latter minima correspond to approaches towards the central carbon atom, whereas the Coulomb energy alone predicts again favoured approaches towards the centres of the bonds C<sub>1</sub>C<sub>3</sub> and C<sub>2</sub>C<sub>3</sub>.

Application of Rayleigh–Schrödinger perturbation theory leads to the same general conclusions although there are minor quantitative differences.

## DISCUSSION

Our treatment clearly indicates the central carbon atom as the preferred protonation site, in agreement with experimental evidence.<sup>4</sup> In addition, for both optimum configurations of 2 the proton will approach at such dihedral angles ( $\eta$ ) that a planar allyl radical is easily formed. Protonation of the configuration  $\alpha = 180^\circ$ ,  $\theta = 140^\circ$  thus produces a 1,3-dimethyl substituted allyl radical in *cis-trans* geometry, while the *trans-trans* geometry originates from  $\alpha = 180^\circ$ ,  $\theta = 40^\circ$  upon a proton approach at  $\eta = 0^\circ$ . The latter configuration also has a favoured proton approach at  $\eta = 180^\circ$ , but this would lead to a sterically prohibited *cis-cis* geometry.<sup>23</sup> At this stage the limitations of our model should be realized: the interaction energies calculated are able to describe the first stages of the protonation process. The molecular geometry is kept rigid, however, so we have omitted the effect of a change in geometry accompanying the

†Details are available upon request.

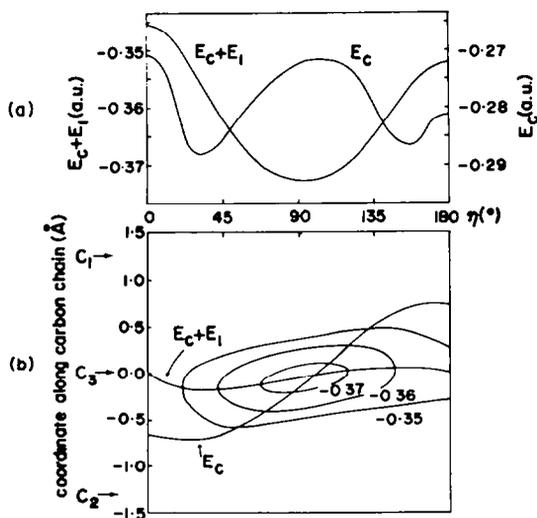


Fig. 2. (a) Depth of the local minima in the Coulomb energy ( $E_C$ ) and in the Coulomb + induction energy ( $E_C + E_I$ ) for radical anion 2 ( $\alpha = 180^\circ$ ,  $\theta = 140^\circ$ ), as a function of  $\eta$ . (b) Positions of the local minima of  $E_C$  and  $E_C + E_I$ , together with contours of constant  $E_C + E_I$  (energy values in a.u.). The surface laid down in this figure is a nearly cylindrical surface around the carbon chain C<sub>1</sub>C<sub>3</sub>C<sub>2</sub> and is defined by lines parallel to C<sub>1</sub>C<sub>3</sub>C<sub>2</sub> and passing through the local minima.

formation of the protonated species. Such an effect may sometimes dominate the last stages of the protonation and rule out an otherwise favourable proton approach.

The mixture of *trans-trans* and *cis-trans* allyl radicals mentioned above may account for the experimentally observed product composition, but here the analysis is obscured by possible isomerization of 3 and 4.<sup>1</sup>

The importance of including the induction energy is shown by the qualitatively different results obtained by taking into account only Coulomb energy. This confirms similar observations in calculations on ethene<sup>19</sup> and aza-aromatics,<sup>24</sup> in contrast with calculations on 3-membered ring molecules<sup>20</sup> and formamide.<sup>21</sup>

It is satisfying to note the relative insensitivity of the results to modifications of some of the approximations applied in this work, e.g. Brillouin-Wigner versus Rayleigh-Schrödinger perturbation theory or our method of estimating single excitation energies.

The present study may serve to illustrate the applicability of semi-empirical wave functions to a perturbation treatment of the protonation of rather large molecules.

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#### APPENDIX

Following the arguments given above the induction energy on approach of a proton p is approximated by the second order energy in Rayleigh-Schrödinger perturbation theory:

$$E_1 = - \sum_{k \neq 0} \langle \Psi_0^0 | - \sum_{i=1}^n 1/r_{ip} | \Psi_k^0 \rangle^2 / \Delta E_{0-k} \quad (A1)$$

$\Psi_0^0$  and  $\Psi_k^0$  are unperturbed ground and excited state wave functions of the substrate molecule (with n electrons) and the denominator represents the corresponding excitation energy. With reference to the doublet ground state  $\Psi_0^0$  the molecular orbitals fall into three groups: doubly occupied, singly occupied and unoccupied orbitals, denoted here by r, q and s respectively. Excited states contributing to the summation in Eqn (A1) are singly excited doublet states. Three types of single excitation can be distinguished: r → q, q → s, r → s. The excitation r → s results in two degenerate (orthogonal) doublet states, which contribute both to the summation in Eqn (A1). Evaluation in terms of M.O.'s results in:

$$E_1 = - \sum_r h_{qr}^2 / \Delta E_{r-q} - \sum_q h_{qs}^2 / \Delta E_{q-s} - 2 \sum_r \sum_q h_{rs}^2 / \Delta E_{r-s} \quad (A2)$$

where the nuclear attraction integral  $h_{uv} = \langle t | -1/r_p | u \rangle$ .

In Brillouin-Wigner perturbation theory, however, we replace the denominators in Eqns (A1) and (A2) in a first approximation by:<sup>22</sup>

$$\Delta E_{0-k} + (E'_k - E'_0) \quad (A3)$$

where the prime indicates the first order energy correction. The induction energy thus found is subtracted from the energy defined by Eqn (A3), the new denominators are inserted into Eqn (A2) and the calculation is repeated once.<sup>16</sup>