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QUANTUM CHEMICAL CALCULATIONS ON THE INTERACTION OF DIAZOMETHANE WITH PROTON ACIDS

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Abstract—Diazoalkanes may form H-bonded associates with weak proton acids, whereas with strong acids proton transfer leads to the diazonium ion. In order to get information about protonation and association at C and N, the corresponding energy balances, electron charge distributions and bond strengths have been calculated by means of quantum chemical *ab initio* methods with diazomethane as substrate and HF, NH_4^+, OH_3^+ as acids.

The reaction of diazoalkanes with proton acids has been well examined experimentally.[1] It is generally described in the simplified form of eqn (1) where the ratio k_2/k_{-1}, determined by the nature of the substituent R, determines the reversibility of protonation.

$$\underset{\mathbf{1}}{\text{R–CHN}_2} + \text{H}^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\mathbf{2}}{\text{R–CH}_2\text{N}_2{}^+} \xrightarrow{k_2} \text{products.} \qquad (1)$$

There are, however, also examples of interaction of diazoalkanes with H-acid compounds which are not related to the simple scheme of eqn (1):

A reversible N protonation has been suggested for the mechanistic interpretation of the action of diazoalkanes as basic catalysts.[2] The results, however, can also be interpreted by eqn (1) but with a reversible C protonation ($k_{-1} \gg k_2$).

Besides protonation, a second kind of interaction between diazoalkanes and proton acids seems to be the formation of H-bonds. They are seen to be responsible for the increase of nucleophilicity of alcohols[3] and phenols[4] by diazoalkanes. In the same way, alcohols and phenols catalytically accelerate intramolecular rearrangements of diazoalkanes.[5] Investigations with deuterated substrates gave evidence that with the formation of an H-bond, nitrogen in the diazoalkane acts as an acceptor.[6]

These examinations give us qualitative indications that the interaction of proton acids with diazoalkanes may proceed via proton transfer as well as via formation of H-bonded associates. A quantitative statement is possible for the reaction[7] of olefines with aryldiazoalkanes in the presence of proton acids.[8] According to Scheme 1 the ratio between formation of associates and proton transfer can be determined experimentally by means of the balance of products.

In order to get information about energy balances, electron charge distributions and bond strengths for the various possibilities of interaction of diazoalkanes with proton acids, quantum chemical calculations have been investigated *ab initio* with diazomethane as substrate.

Method of calculation

The basis for the discussion of reactivity of diazomethane is *ab initio* calculations by use of the SCF-MO method with pure Gaussians.[9] The basis set {7s, 3p} for the atoms C and N, and {3s} for H was taken from earlier calculations.[10]

For the discussion of the interaction with proton acids there were three methods used which differ essentially in their results and reliability.

(1) *Mullikan's population analysis.* This yields atomic electron charges and is therefore used for preliminary results concerning electrophilic sites of attack or positions of association.

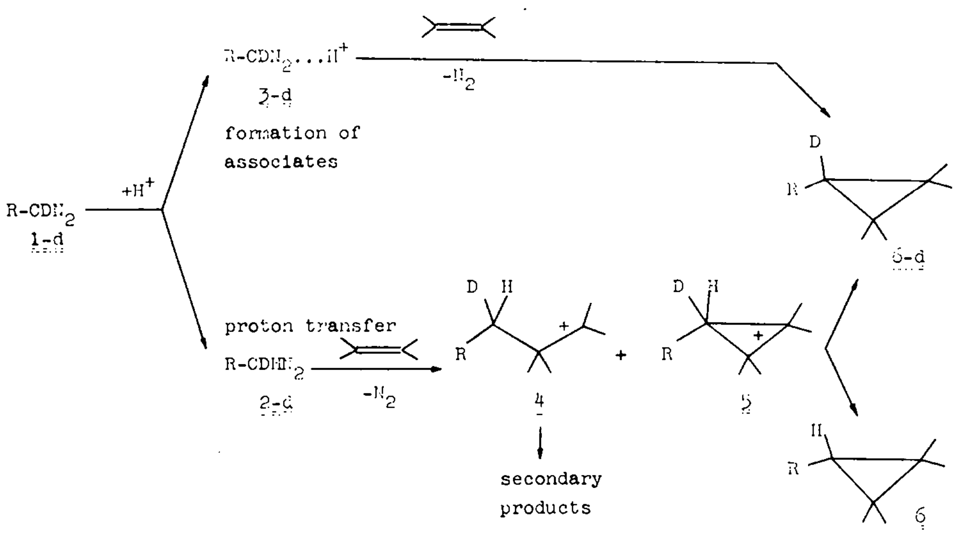
(2) *The interaction energy* E(**R**) *between a proton and a molecule in* 1st *and* 2nd *order of perturbation theory*

$$\mathrm{E}(\mathbf{R}) = \sum_k \mathrm{Z}_k/|\mathbf{R}_k - \mathbf{R}| - 2\sum_i^{\mathrm{OCC}} \langle\Phi_i|1/|\mathbf{r}-\mathbf{R}||\Phi_i\rangle$$
$$+ 2\sum_i^{\mathrm{OCC}}\sum_j^{\mathrm{VIR}} |\langle\Phi_i|1/|\mathbf{r}-\mathbf{R}||\Phi_j\rangle|^2/(\mathrm{e}_i - \mathrm{e}_j). \qquad (2)$$

The first term represents the classic electrostatic repulsive interaction of the proton with the nuclei of the molecule, the second term describes the electrostatic interaction of the proton with the electrons,[11] whereas the third term is concerned with the polarisation energy as it occurs in the Hartree–Fock approximation with a perturbing field.[12]

(3) *The energy hypersurface for two interacting molecules.* A complete energy surface would be unwarranted in this context, owing to the amount of work as well as the accuracy of the results. If one is interested only in the energy difference between reactants and products, a crude estimation of the positions of minima on the energy surface (molecular structure) by means of observed molecular structures of analogue compounds is better than theoretical data obtained from energy variation.

The above methods differ essentially in their range of application. With the population analysis the arrangement



Scheme 1.

of atoms is disregarded. Furthermore the shape of the electron distribution (s- and p-character) is neglected, which can have considerable influence on reactions and structures of associations. The method of perturbation theory would be reliable in this context as long as molecular deformation can be neglected, which is justifiable with weak and medium associations (distance atom-proton ~2 Å). With associations, moreover, the charge transfer contribution may sometimes play a significant role.[13] Different attacking cations cannot be distinguished in perturbation theory because the interaction energy E(**R**) is concerned with a point charge and can be seen as a molecular property which needs only one MO calculation. In principle, the energy hypersurface can give reaction energies, but owing to inevitable approximations (Hartree–Fock approximation, truncated basis, assumed molecular structure, neglect of zero point vibration) these are in general only of qualitative nature.

RESULTS AND DISCUSSION

(1) *Paths of an attacking proton.* The diazomethane molecule has been calculated with interatomic distances reported in[14] (C–N = 1.32; N–N = 1.12 Å). In Fig. 1 the atomic electron charges as well as the curves for E(**R**), computed by eqn (2), are drawn for various paths of attack. If a lone pair at the proton acceptor is seen to be necessary for the formation of association, the C atom cannot be a proton acceptor despite the pronounced excess electron charge. Hence, the inner N atom which shows, in contrast to the outer N atom, a small excess electron charge would be the slightly favoured proton acceptor. The curve of E(**R**), however, shows that there is only one distinct favoured site for the formation of association: the outer N atom which just has the least electron charge in the molecule. This path has the direction of the N–N bond. But this direction may be changed by the neglected charge transfer contribution which is biggest in path (3b) whereas the most unfavoured position is in path (3c). The true angle N_2–N_3...H probably lies between 90° and 180°, which will be taken into account later. The curves E(**R**) predict the position of association well, because the range of application of perturbation theory extends down so far to include distances $|\mathbf{R}| = 2$ Å. Experience has shown that the deformation of the proton acceptor may in general be neglected in associations. Finally, it should be noted that the energies E(**R**) are concerned with a bare proton and therefore energies should be seen only in sequence.

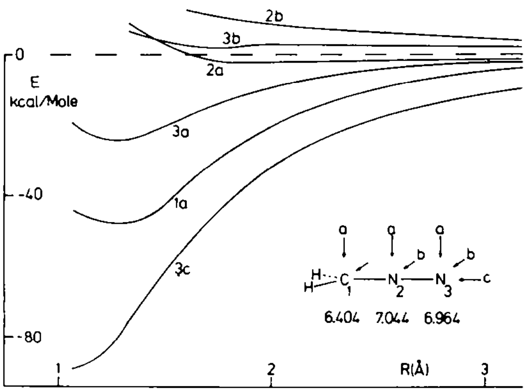


Fig. 1. Interaction energy E(**R**), computed by eqn (2), for various paths of attack of a proton. R represents the distance between the proton and an atom, indicated by an arrow, in the diazomethane molecule.

In the search for protonation sites of the diazomethane molecule, the curves E(**R**) may no longer be used without modification. The protonation to the methyldiazonium ion implies a tetrahedral Me group, so that an essential molecular deformation occurs.

On the other hand no significant deformation can be expected with protonation at the outer N atom. To decide between C protonation or outer N protonation, two points on the energy hypersurface for the system $[H_2CN_2 + H]^+$ have been calculated, both of which can be seen as possible products. The structural data of both cations were taken as follows:[14] $H_3CN_2^+$: C–N = 1.424 Å from H_3CNC, N–N = 1.10 Å from N_2; $H_2CN_2H^+$: C–N = 1.32 Å from H_2CN_2, N–N = 1.24 Å from N_3H, NNH = 111° from N_3H. Similar data have been obtained by semiempirical methods.[15] The total energies are in a.u.

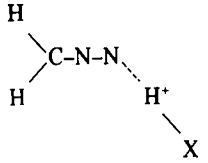
$$\begin{tikzcd}
 & \begin{matrix} H_2CN_2 + H^+ \\ -147.183396 \end{matrix} \arrow[dl] \arrow[dr] & \\
\begin{matrix} H_3CN_2^+ \\ -147.436401 \end{matrix} & & \begin{matrix} H_2CN_2H^+ \\ -147.323959 \end{matrix}
\end{tikzcd}$$

Hence, the protonation of diazomethane yields the methyldiazonium ion with a stability of 70 kcal/mole with respect to the N protonated species. This means, in terms of E(**R**) in Fig. 1, that the curves (1a and 3c) would intersect in the range of bond distances if the molecular deformation were taken into account. The range of validity of only the electrostatic molecular potential (first and second term in eqn 2) has been disregarded until now so that the corresponding discussions are of doubtful value.[16,17]

(2) *Interaction with proton acids.* For the reactive behaviour of the diazomethane molecule in the presence of a proton acid molecule there are two distinct possibilities. On the one hand diazomethane can be protonated to the methyldiazonium ion; on the other hand diazomethane can form an associate together with the acid molecule. As a first criterion for deciding between these two possibilities we have the proton affinities $E(XH^+) - E(X)$. These are given in the following Table 1.

With diazomethane the calculation confirms the experimentally approximated value. Owing to the corresponding proton affinities, the HF molecule might be incapable of protonating the diazomethane molecule, whereas for the hydronium ion H_3O^+ a proton transfer might be possible.

More precise statements can be made by considering the other possibility, that of association. Thus, associates of the form



have been investigated. The angle N–N ... H was taken to be 111°; the N ... X distances have been taken as follows: F^-: 2.75 Å, NH_3: 2.70 Å, H_2O: 2.5 Å. The total energy shows an extremely small alteration with respect to the N ... X distance which can be explained by the weak H-bond. This justifies assumed N ... X distances which were taken from the associates $H_3N \ldots HF$, $H_3N \ldots HNH_3^+$, $H_3N \ldots HOH_2^+$.[20,21] The bond energies of the associates are reported in Table 2.

The intermolecular bonds turn out to be relatively weak, which can be explained by the fact that the properties of the N–N bond in diazomethane are similar to those of molecular nitrogen, which is not a proton acceptor in the sense of association. The electron charges in the diazomethane molecule in Table 3 allow us to conclude that with the formation of associates the C–N bond will be weakened by a deficiency of electrons which might increase the reactivity.

A more precise statement about the electron distribution is given by the calculated electron density (Table 4). The decrease of electron charge at the C atom is mainly caused by electron displacements in the C–N π_z bond so that the π contribution of the C atom indicates an electron deficiency. A slight polarisation of the C–N σ bond in the same direction also occurs. The loss of electron density in the molecular plane might be caused by electron displacements in the N–N π_y bond. The discussed differences $\Delta\rho$ between two electron distributions are small in amount, so that the familiar plotted densities, as they are presented in the literature,[22] would fail here.

Table 1. Calculated and observed[18,19] proton affinities for various proton acceptors

Proton acceptor X	Proton affinity [kcal/mole] calculated	observed
F^-	399	361
NH_3	185	206
H_2O	152	151
H_2CN_2	159	(152)

Table 2. Bond energies of H-bonded associates with diazomethane

Associate	Bond energy [kcal/mole]
$H_2CN_2 \ldots HF$	3.4
$H_2CN_2 \ldots HNH_3^+$	1.3
$H_2CN_2 \ldots HOH_2^+$	4.9

Table 3. Atomic electron charges for the diazomethane molecule in various associates

H	C	N	N	Proton acid
0.79	6.40	7.04	6.96	–
0.77	6.39	7.03	7.02	HF
0.74	6.36	7.02	7.06	HNH_3^+
0.72	6.34	7.00	7.09	HOH_2^+

Consequences for chemical reactivity

The results presented for calculations with isolated molecules and associates show, in agreement with experimental evidence for reactions in solution, that by strong acids diazomethane is converted to the methyldiazonium ion **2** (R=H). The small amount of change in the energy obtained from the difference of calculated proton affinities, agrees with the observed reversibility of the reaction.[23] A qualitative agreement with experiment is also shown by the energy balance of the interaction with weak acids, which in this case does not favour the proton transfer to the diazonium ion **2**.

Both strong and weak acids can form H-bonds to the outer N atom in diazoalkane. An increase of electron charge in the donor and a decrease in the acceptor of the H-bond is generally caused by this kind of association. The increase of the electron charge in the donor agrees with the observed increase of nucleophilicity of the O atom in alcohols and phenols caused by diazoalkanes.[3,4]

The expected decrease of the electron charge in the acceptor diazoalkane is confirmed by calculations; a considerable decrease of electron charge is shown by the C atom in diazomethane. Consequently the strength of the C–N bond is weakened, as can be seen in the change of the electron density. This facilitates the splitting off of nitrogen, which leads to the observed "carbenoid"

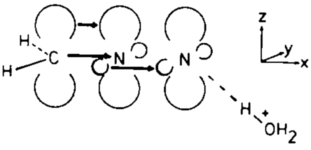


Fig. 2. Electron displacements in the diazomethane molecule associated with a proton acid molecule.

Table 4. Change of the electron density (a.u.) in the C–N bond in diazomethane associated with H_3O^+. ($x = 0$ and $x = 2.49447$ a.u. are the x coordinates for C and N, respectively. The values $\Delta\rho(\pi_z)$ and $\Delta\rho(\pi_y)$ are related to a parallel displacement of the x axis by 1.5 a.u. in the z and y direction, respectively, as is shown in Fig. 2)

x	$\Delta\rho(\sigma)$	$\Delta\rho(\pi_z)$	$\Delta\rho(\pi_y)$
0.00000	0.15565	-0.00885	0.00043
0.12472	0.05925	-0.00861	0.00117
0.24945	0.00726	-0.00805	0.00162
0.37417	-0.00021	-0.00721	0.00185
0.49889	-0.00214	-0.00617	0.00188
0.62362	-0.00245	-0.00502	0.00178
0.74834	-0.00231	-0.00385	0.00159
0.87306	-0.00205	-0.00271	0.00133
0.99779	-0.00169	-0.00157	0.00103
1.12251	-0.00119	-0.00073	0.00068
1.24724	-0.00052	0.00010	0.00028
1.37196	0.00034	0.00085	-0.00018
1.49668	0.00136	0.00146	-0.00075
1.62141	0.00252	0.00201	-0.00144
1.74613	0.00381	0.00247	-0.00226
1.87085	0.00515	0.00284	-0.00320
1.99558	0.00608	0.00309	-0.00422
2.12030	0.00552	0.00320	-0.00525
2.24502	0.00294	0.00315	-0.00619
2.36975	0.00557	0.00294	-0.00693
2.49447	0.05020	0.00257	-0.00736

reaction behaviour of diazoalkanes in the presence of acids. With phenyldiazomethane 1 (R=Ph) it has been shown by experiments[7] that in this case with olefins cyclopropanes are formed. However, this reaction does not proceed via a free carbene because without an acid catalysis no reaction takes place. The increase in reactivity of diazoalkane is caused rather by the formation of associate 3 (Scheme 1).

Another reaction path to cyclopropane 6, as is shown in Scheme 1, also leads through proton transfer and the protonated cyclopropane 5.[8] With deuterated substrates, an experimental estimation of the partitioning of association and proton transfer in product formation is possible. In agreement with the present calculated results the reaction path via proton transfer is favoured more and more as the strength of the acid increases.[7,8]

The results presented consequently allow a mechanistic interpretation of the various possibilities of reaction of diazoalkanes of the diazomethane type with proton acids. Strong acids lead via C protonation to the diazonium ion and its secondary products, N protonation does not take place. Weak acids lead to H-bonded associates at the outer N atom. This on the one hand implies the observed catalytic effects of diazoalkanes on the nucleophilicity of alcohols and phenols, and on the other hand indicates their carbenoid reaction behaviour.

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