Theoretical Studies of the Structure and Stability of Protonated Olefins in the Gas Phase and in Solution

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The calculation of carbenium and carbonium type cations resulting from the protonation of olefins with growing length and increasing chain branching was carried out by quantum chemical methods which were tested elsewhere.

One result is the distinction of olefins with an equal number of alkyl substituents on both sides of the double bond and other ones with different number. In the latter case generally no bridged structures could be defined.

The influence of nucleophilic solvents on the stability of the cationic structures is simulated on the basis of Klopman's solvaton model. These calculations show that solvents may change the gas phase data in a remarkable way.

Key words: Protonated olefins – Carbenium and Carbonium type ions, existence and stability of ~ – Solvation influence.

1. Introduction

The mechanism of proton transfer to unsaturated systems (and of the electrophilic attack in general) has been described in different ways [1, 2]. The essential reason for this is the inadequate knowledge of the character and the relative stabilities for open and bridged structures (carbenium and carbonium ions [2]) of isolated ions, ions in solution or in the adsorbed state.

In this context an important question is the nature of scrambling processes for protons. Experimental investigations in this field have been undertaken usually in superacid media. Here especially nmr [2, 3, 4] and thermochemical investigations [5, 6] play an important role. So far, studies in the gas phase by means of ion

cyclotron resonance (icr) method [7] which seems to be well suited for an investigation of carbocations, have not given unambiguous results concerning the relative stabilities of the various structural types. Experimental evidence on the mechanism of the protonation of olefins at Broensted type sites on solid surfaces is also not conclusive [8].

The most accurate theoretical studies are available for protonated ethylene. Non-empirical calculations with the CEPA-PNO method including the electron correlation show the bridged structure to be more stable than the open one by about 31 kJ/mole [9]. Almost the same energy difference has been obtained by means of the CNDO/2-FK [10, 11] and MINDO/3 methods [11, 12]. Moreover, the intrinsic structure stabilities calculated by MINDO/3 are in agreement with CEPA-PNO results for a large number of other carbocations [13–15].

Consequently, the above mentioned semiempirical methods were successfully used for the calculation of similar structures in the case of more complicated systems (e.g. aromatics [16, 17]). This led the authors of the present paper to perform extensive quantum mechanical studies on the protonation of nonconjugated double bonds in systems of growing length and increasing branching of the chain.

In order to check the computations with experimental data from solutions medium effects have to be taken into account by the "solvaton model" proposed by Klopman [18].

2. Calculated Structures

In this study cations are considered with two to six carbon atoms which result from ethylene by alkyl-for-H-substitution. The classification of the various protonated forms is given in terms of carbonium ions 1 and isomeric carbonium ions 2a and 2b (cf. Fig. 1) which may be regarded as limiting cases. In this context a structure is defined theoretically as an atomic arrangement which gives rise to a stationary point on the potential energy surface.
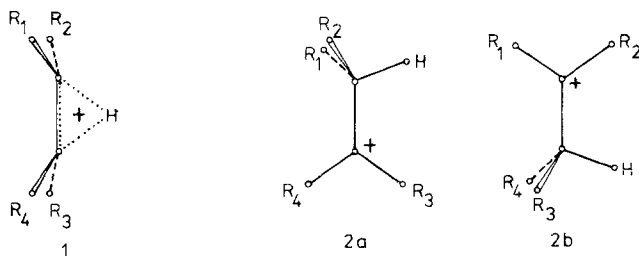
H-bridged: carbonium ion   open: carbenium ions

Fig. 1. Structural types of alkyl-substituted forms of the ethyl cation ($R_i = CH_2$, CH_3, C_2H_5, C_3H_7). Differentiation between structures 2a and 2b is only meaningful if the substituents R_1, R_2 are not equivalent to R_3, R_4

In connection with our classification it should be emphasized that an additional *weaker* complex of a double bond with a proton cannot be derived from an inspection of the potential energy surface for *isolated* cations. Therefore, the bond characteristics of the cations should not be confused with the properties of the well-known complexes of olefins with electron acceptors such as HF and HCl.

3. Calculating Methods

The search of stationary points on the potential energy surface is carried out by the optimization procedures of Murtagh and Sargent [19] and Fletcher [20]. In these methods the gradient of the total energy is the guide for finding the next minimum on the potential energy surface. The energies are computed on the basis of the CNDO/2-FK and MINDO/3 methods. Besides minima also other stationary points of the potential energy surface are determined as far as they are of importance for the present investigation. The geometry optimizations are interrupted when the largest component of the gradient is less than 10^{-3} a.u. In the case of the MINDO/3 method we identify the stationary points directly by using the eigenvalues of the force constant matrix: Minima give only positive, saddle points of the first order (transition states) give one negative, and saddle points of higher order a corresponding higher number of negative eigenvalues.

The computation of the influence of the solvent on the relative stability of open and H-bridged structures is performed on the basis of Germer's method [21] which is an extension of Klopman's solvaton model. In this model the existence of a fictive charged particle (solvaton) in the vicinity of each atom is assumed. The charge of the solvatons is chosen to be the net negative charge of the atom in order to simulate the polarization effect. In the case of cations the sum of the solvaton charges is equal to the (smeared out) counter ion charge. Germer [21] extended this concept by embedding the solvaton–solute interaction in the iteration procedure of SCF-MO methods.

The inclusion of the interaction with the solvatons in the Hamiltonian results in modified calculations of some matrix elements. In the MINDO/3 method which is used in our computations only the diagonal elements of the H^{core} matrix are modified by the electron–solvaton (S) interaction (3rd term)

$$H_{\mu\mu}^c = U_{\mu\mu}^c - \sum_{B \neq A} Z_B \gamma_{AB} + f \sum_S Q_S \gamma_{AB} \qquad (\mu \in A), \qquad (1)$$

with $f = (\varepsilon - 1)/2\varepsilon$,

$$Q_S = Q_B = Z_B - \sum_\nu P_{\nu\nu} \qquad (\nu \in B),$$

$$\gamma_{AS} = 14.399/[R_{AS}^2 + (7.1995/\gamma_{AA} + 7.1995/\gamma_{BB})^2]^{1/2}.$$

A and B denote the atoms, μ and ν the respective atomic orbitals. $U_{\mu\mu}$ are the one-centre and γ_{AB} are the electron interaction integrals. Z_B stands for the effective core charge, Q_A, Q_B, and Q_S are net charges, $P_{\nu\nu}$ the diagonal elements

of the density matrix, and ε is the permittivity. The nucleus–solvaton interaction is given by

$$C_{NS} = -f \sum_A \sum_S Z_A Q_S [\gamma_{AS} + (14.399/R_{AS} - \gamma_{AS}) \exp(-\alpha_{AS} R_{AS})]. \qquad (2)$$

A check on this procedure reveals, however, that the use of the van der Waals radii in the one-centre integrals as suggested by Germer leads to an incorrectly strong weight of the two-centre terms. The problem can be solved in different ways (cf. Ref. [22]). We use an empirical relation to the atomic charges

$$R_{AS} = R_{vdW}(1 - \alpha Q_S)$$

in order to reduce the atom–solvaton distance in the one-centre integrals.

Simulating a more strongly nucleophilic solvent we assume a value of $\alpha = 0.65$ which gives rise to a greater stability (≈ 40 kJ/mole) of the open structure [22]. The chosen permittivity $\varepsilon = 31.5$ is formally equal to the value of methanol.

5. Results and Discussion

The energy differences between the various protonated structures of the olefins in Fig. 2 are summarized in Table 1.

Structure 2a describes Markovnikov addition (proton addition to the C atom with the largest number of hydrogens) and 2b anti-Markovnikov addition.

5.1. Isolated Cations in the Gas Phase

The protonation of the olefins VI to X leads to differently stabilized carbenium ions 2a and 2b, the double bonds of which are asymmetrically substituted with respect to the number of alkyl groups. Bridged structures, however, could not be defined in this case, i.e. no stationary points on the potential energy surface of the cations were found which would correspond to these species. For some typical representatives of the two kinds of carbenium ions, experimental energy differences were reported which are given in Table 1. These values are 67 and 75 kJ/mole for the primary and secondary cations of protonated propene (VI) and 1-butene (VII), respectively. The corresponding energy difference between the primary and the tertiary isobutene (VIII) cations is about 134 kJ/mole. These differences are in good agreement with the results of the MINDO/3 computations. The values according to the CNDO/2-FK method are slightly higher. Also on other alkyl-substituted ethylene molecules, both calculations gave differences of similar magnitude between cation forms of types 2a and 2b. The smallest differences with values between 36 and 71 kJ/mole result for the secondary and the tertiary cation of the protonated trimethylethylene (X). The markedly different stabilities of the open cationic structures are one of the reasons for the lack of activation barriers concerning the proton migrations to the less alkylated carbon atom. This effect has already been described for protonated propene [24]. It should be mentioned here that theoretical studies [25, 13] showed
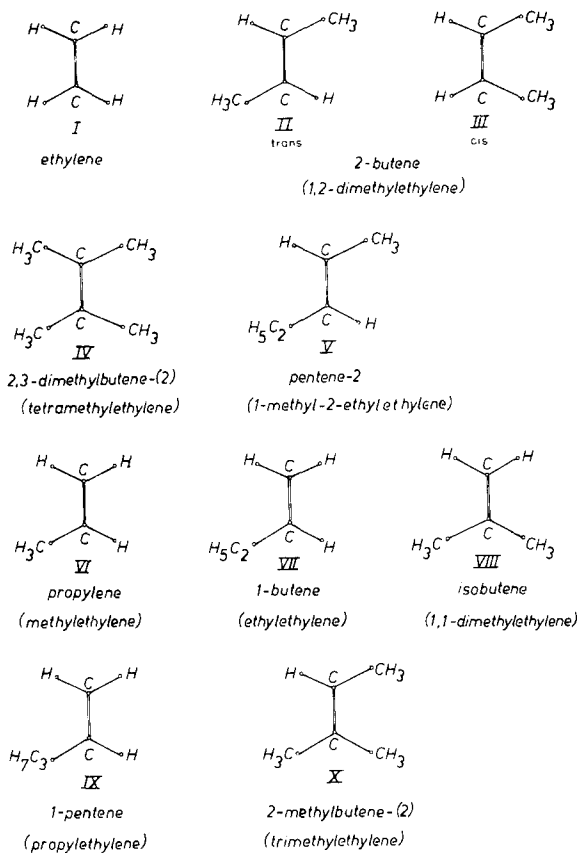
Fig. 2. Summary of the studied olefins

the protonated cyclopropane to come next in stability to the secondary carbenium ion of protonated propene.

In the case of the olefins I to V the two types of carbenium ions (2a and 2b) have an equal or nearly equal stability because of the equal number of alkyl groups on both sides of the double bond. The influence due to the different size of alkyl groups is small as in the case of 2-pentene. Furthermore, for the protonated forms of I to V we find well-defined H-bridged structures. Calculations by the aid of the two semiempirical methods show (cf. Table 1) that the energy of these bridged structures (i.e. carbonium ions) is in general somewhat less than that of the open ones.

The energy minimum for structure 1 of the carbonium ions, however, becomes more and more shallow (according to CNDO/2-FK) as the number of substituents increases and disappears for protonated tetramethylethylene (MINDO/3, CNDO/2-FK). The result for the latter compound resembles most that obtained for protonated benzene [26].

In the completely optimized ions the alkyl groups at the original double bond are twisted by an angle up to 25° with respect to the possible symmetrical forms. The energy gain is about 13 kJ/mole for highly alkylated open structures. Concerning a possible barrier between such open and bridged cations, explicit calculations have not yet been undertaken for the larger systems. But experience shows that there should be no appreciable barriers between the structures of types 1 and 2. The trend derived is not in contradiction with the few results of non-empirical calculations on ethyl and 2-butyl cations (Table 1). The SCF energy values indicate the bridged structure of protonated butene-2 to be slightly disfavoured in comparison with protonated ethylene. But the estimated greater correlation energy of the H-bridged structure of protonated butene-2 overcompensates this effect. This case shows the importance of an accurate calculation of the correlation energy with non-empirical methods even in the study of analogous structure elements in molecules of different size. Unfortunately, the present determination of the correlation energy for protonated 2-butene [14] is not yet sufficient to be a theoretical standard.

5.2. Solution

Results concerning the solvent influence on the relative stability of the isolated cationic structures are also given in Table 1. The energy differences in solutions calculated for the primary and secondary carbenium ions and for the secondary and tertiary ones are less than that without solvent influence.

So it is not surprising that ethylene molecules which are asymmetrically substituted with respect to the number of alkyl groups show a tendency to form a barrier

Table 1. Relative energies (kJ/mole) of the structures 1, 2a, and 2b after protonation of studied olefins (cf. Fig. 2) The lower index for the energy values E refers to the structure and the upper one indicates the case of isolated cation (isol) or that in solution (solv)

Structure	Method	$E_{2b}^{isol} - E_{2a}^{isol}$	$E_1^{isol} - E_2^{isol}$	$E_{2b}^{solv} - E_{2a}^{solv}$ Germer-solvaton-model, MINDO/3	$E_1^{solv} - E_2^{solv}$
I	CNDO/2-FK	0	−39	—	—
	MINDO/3	0	−33	0	41
	SCF+corr.[a]	0	−31[b]	—	—
II	CNDO/2-FK	0	−26	—	—
	MINDO/3	0	−21	0	23
	SCF+corr.[a]	0	−26[c]	—	—
III	CNDO/2-FK	0	−25	—	—
	MINDO/3	0	−17	0	26
IV	CNDO/2-FK	0	−0.5[e]	—	—
	MINDO/3	0	−0.9[e]	0	38
V	CNDO/2-FK	8.7[f]	1–2a: −10 1–2b: −18	—	—
	MINDO/3	0.3[f]	1–2a: −24 1–2b: −24	−9	1–2a: 17 1–2b: 26

Table 1 *contd.*

Structure	Method	$E_{2b}^{isol} - E_{2a}^{isol}$	$E_1^{isol} - E_2^{isol}$	$E_{2b}^{solv} - E_{2a}^{solv}$ $\quad$ $E_1^{solv} - E_2^{solv}$ Germer-solvaton-model, MINDO/3	
VI	CNDO/2-FK	107	—	—	—
	MINDO/3	78	1–2a: 15 ⎫ d 1–2b: −63 ⎭ 61		1–2a: 56 1–2b: −5
	SCF + corr.[a]	69	—	—	—
	Exp.	67[g]			
VII	CNDO/2-FK	—	—	—	—
	MINDO/3	80	1–2a: 18 ⎫ d 1–2b: −61 ⎭ 52		1–2a: 51 1–2b: −1
	Exp.	75[g]			
VIII	CNDO/2-FK	181	—	—	—
	MINDO/3	132	1–2a: 45 ⎫ d 1–2b: −87 ⎭ 82		1–2a: 72 1–2b: −10
	Exp.	134[g]			
IX	CNDO/2-FK	130	—	—	—
	MINDO/3	82	1–2a: 15 ⎫ d 1–2b: −67 ⎭ 55		1–2a: 82 1–2b: 27
X	CNDO/2-FK	59 (71)[h]	—	—	—
	MINDO/3	36 (48)[h]	1–2a: 0.3 ⎫ d (12)[h] ⎬ 18(−46)[h] 1–2b: −36 ⎭ —		1–2a: 32 (−32)[h] 1–2b: 14

[a] SCF (extended basis) + correlation energy (CEPA)
[b] cf. Ref. [9]
[c] cf. Ref. [14]
[d] Structure 1 is no stationary point on the calculated potential surface. The energy values are found by fixing H over the centre of the bond.
[e] H-eclipsed conformation of structure 2. The bisected form of this cation has almost the same energy (i.e. no rotational barrier).
[f] 2a corresponds to the central position of the trigonal carbon.
[g] cf. Ref. [23]
[h] The eclipsed structure 2a of X (all methyl groups in a plane) is energetically unfavoured in comparison to a distorted one. It has to be checked yet whether this bridged form (the shifted H is in a position perpendicular to its carbon atom) is an artifact of the used theoretical methods or not.

for the H shifts between the structures 2a and 2b in protonated olefins which modifies the gas phase results for some systems (cf. VII, IX, X). To enable the calculation of the bridged structure, in each case the proton was fixed in the centre of the double bond.

For symmetrically substituted ethylenes the influence of nucleophilic solvents leads in all cases considered to an appreciably higher stability of the open structures. With the exception of the ethyl cation, the solvation energies are relatively constant which might be generalized to give a rough estimate of the

solvent influence. From this it follows, in agreement with the former explanations, that the bridged structures (type 1) act as a barrier for the H shift between the cationic structures of type 2 in solution.

If one extrapolates these results to more weakly nucleophilic solvents about the same stability for open and bridged structures is expected for the ethyl and the butyl cations, while the protonated tetraalkylated ethylenes form equilibrating tertiary carbenium ions in the course of solvation. These conclusions are in accordance with the ^{13}C-nmr investigations of Olah et al. [27] in which the spectrum measured for n-butylcations in superacid media was interpreted as being due to a fast 1,2-H shift between the carbons 1 and 2. Furthermore, the free energies of activation $\Delta G^{\neq}$ for the 1, 2-H shift of tertiary alkylcations in solution which were derived by Saunders and Kates [3] from carbon-13 resonance spectra do not contradict the present data although the former results (viz. values of $\Delta G^{\neq}$ from 13 to 19 kJ/mole for the transition states) cannot directly be compared with our data.

6. Conclusion

1. The calculations performed for isolated cations suggest the distinction between two types of protonated olefins: For the olefins I to V, which have the same number of alkyl substituents on both sides of the double bond of the parent olefins, open and H-bridged structures can be defined on the potential energy surface. On the other side, the olefins VI to X with asymmetrically substituted double bond of the parent olefins show no energy minima or saddle points (transition states) for the H-bridged structures. Energy differences of 36 to 181 kJ/mole between the primary and the secondary carbenium ions and between the secondary and the tertiary ones prevent the appearance of additional stationary points of the potential energy in the bond region.

2. Solvation is important for the stabilization of the carbenium ions with respect to the carbonium ions. The energy minimum which exists between the open structures for the protonated systems I to V (and which was attributed to the bridged structure) can become more shallow or changes to a saddle point under the influence of the solvent. This result is in agreement with experimental data for tetraalkylethylenes in solution for which a fast H shift between the two types of carbenium ions was found.

3. The calculations indicate the possibility of a high mobility of the H-atoms in the carbon chain of open and bridged protonated structures in certain media if the H shifts lead to cations which are stabilized due to the same number of alkyl groups (degenerated proton shifts). Here the formation of isoenergetical regions with respect to H migrations along the skeleton of carbons is possible.

4. The calculations show a preferential solvation of primary relative to secondary carbenium ions and of secondary relative to tertiary ones due to stronger electrostatic interactions with the sterically favoured carbenium ions. Similarly the decreasing solvent stabilization of benzenium ions with an increasing size of

para-substituted alkyl groups could be explained on the basis of this model [22]. The reduced energy difference between the open forms of VI to X in solution could give rise to barriers for the H-shifts in some of these compounds.

References

1. Lowry, Th. H., Schueller Richardson, K.: Mechanism and theory in organic chemistry, chapt. 7. New York: Harper & Row 1976
2. Olah, G. A.: Karbokationen und elektrophile Reaktionen. Weinheim: Verlag Chemie 1974
3. Saunders, M., Kates, M. R.: J. Am. Chem. Soc. **100**, 7082 (1978)
4. Brouwer, D. M., Hogeveen, H.: Prog. Phys. Org. Chem. **9**, 197 (1972)
5. John Ch. S., Marsden, Ch. E., Dickinson, R.: J. Chem. Soc. (London), Faraday Trans. I **72**, 2923 (1976)
6. Arnett, E. M., Petro, C.: J. Am. Chem. Soc. **100**, 5408 (1978)
7. Dunbar, R. C.: in: Chemical reactivity and reaction path, G. Klopman, Ed., pp. 339–366. New York: Wiley 1974
8. Barthomeuf, D.: in: ACS Symp. Ser., No. 40 Molecular Sieves—II, J. R. Katzer, Ed., pp. 453–472. New York: 1977
9. Köhler, H.-J., Heidrich, D., Lischka, H.: Z. Chem. **17**, 67 (1977)
10. Kollmar, H., Smith, H. O.: Theoret. Chim. Acta (Berl.) **20**, 65 (1971)
11. Heidrich, D., Grimmer, M., Köhler, H.-J.: Tetrahedron **32**, 1193 (1976)
12. Radom, L., Poppinger, D., Haddon, R. C.: in: Carbonium ions, Vol. 5, G. A. Olah, P. v. R. Schleyer, Eds., (a) p. 2343, (b) p. 2338. New York: Wiley-Interscience 1976
13. Lischka, H., Köhler, H.-J.: J. Am. Chem. Soc. **100**, 5297 (1978)
14. Köhler, H.-J., Lischka, H.: J. Am. Chem. Soc. **101**, 3479 (1979)
15. Lischka, H., Köhler, H.-J.: Chem. Phys. Letters **58**, 175 (1978)
16. Heidrich, D., Grimmer, M.: Int. J. Quantum Chem. **9**, 923 (1975)
17. Heidrich, D., Deininger, D.: Tetrahedron Letters **42**, 3751 (1977)
18. Klopman, G.: Chem. Phys. Letters **1**, 200 (1967)
19. Murtagh, B. A., Sargent, R. W. H.: Computer J. **13**, 185 (1970)
20. Fletcher, R.: Comput. J. **13**, 317 (1970)
21. Germer Jr., H. A.: Theoret. Chim. Acta (Berl.) **34**, 145 (1974)
22. Heidrich, D., Göring, U., Förster, W., Weiss, C.: Tetrahedron **35**, 651 (1979)
23. Lossing, F. P., Semeluk, G. P.: Canad. J. Chem. **48**, 955 (1970)
24. Al-Khowaiter, S. H., Wellington, C. A.: Tetrahedron **33**, 2843 (1977)
25. Hariharan, P. C., Radom, L., Pople, J. A., Schleyer, P. v. R.: J. Am. Chem. Soc. **96**, 599 (1974)
26. Heidrich, D., Hobza, P., Čarsky, P., Zahradnik, R.: Collect. Czech. Chem. Commun. **43**, 3020 (1978)
27. Olah, G. A., Donovan, D. J.: J. Am. Chem. Soc. **99**, 5026 (1977)