

Model Calculations of Matrix Effects on the Conversion of Propene Radical Cations into Allyl Radicals in Halocarbon Matrices†

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Salhi-Benachenhou, N., Alvarez-Idaboy, J. R. and Lunell, S., 1997. Model Calculations of Matrix Effects on the Conversion of Propene Radical Cations into Allyl Radicals in Halocarbon Matrices. – Acta Chem. Scand. 51: 242–248. © Acta Chemica Scandinavica 1997.

A comparative study has been undertaken of the conversion of propene radical cations into allyl radicals in the gas phase, and in CCl_4 and CF_4 matrices. The semiempirical UHF/PM3 method, complemented with *ab initio* PMP2/3-21G and PMP2/6-31G(d, p) calculations, is employed to model this process, which is observed to occur through an ion–molecule reaction by a proton transfer from the propene radical cation to a neutral propene molecule. Single molecules of CCl_4 and CF_4 are used to model the influence of the corresponding matrices, following two different pathways depending on which proton is transferred. It is found that the reaction in the gas phase occurs without activation energy. In contrast, a barrier is found on the potential energy curve of the reaction in the CCl_4 matrix. The strongest interactions are found for CCl_4 , resulting in a $6.9 \text{ kcal mol}^{-1}$ activation energy ($2.6 \text{ kcal mol}^{-1}$ for the second pathway). The reaction in CF_4 has an intermediate profile with an activation energy of only $2.0 \text{ kcal mol}^{-1}$ (no barrier for the second pathway). The interactions between the migrating proton and the matrix molecule are interpreted in terms of the basicity of the matrix.

Radical cations are, because of their unpaired electron, generally very reactive. Their observation and characterization are, however, often desirable because they constitute an important class of reaction intermediates. These unstable species can be generated experimentally by radiolysis in frozen matrices and this allows their subsequent study in magnetic resonance experiments. Hence, low-temperature matrix isolation techniques, in combination with EPR spectroscopy, have provided radiation chemistry with a useful tool for the study of the structural properties and the specific reactivity of the radical cations.^{1,2}

The experimental technique comprises dilution to a very low concentration of the neutral species (the solute) in a gaseous solvent, such as SF_6 , a Freon or a noble gas (the matrix), after which the gas mixture obtained is subsequently frozen. The radical cation is then produced after the creation of a positive charge on the solute by γ -irradiation of a sample of the solid solution.

Depending on the nature of the radical cation under

consideration, different choices of the stabilizing matrix can be made. A high melting point is generally advantageous for the matrix compound and, in addition, it is necessary that the matrix has a higher ionization potential than the solute to prevent positive charge transfer from the radical cation. Some chemical processes involving the radical cation (e.g., photoisomerization, oligomerization, deprotonation, methyl transfer or ion–molecule reactions), which may occur in the frozen matrix, are sometimes found to be matrix-dependent. This may be due to the formation of complexes between some matrices and the solute, which can also prevent observation by EPR of the radical cation, in some cases where no reaction is likely to occur. Occasionally, some other factors affecting EPR observation, such as the concentration of the solute and the temperature, may have to be considered. In turn, the theoretical analysis of the EPR spectra requires a detailed understanding of the electronic structure of the radical cation and the distribution of the unpaired electron density, which are of paramount importance in, e.g., processes where regioselectivity is of concern.

We have for some time been involved in theoretical investigations of the geometrical structure and EPR parameters of saturated and unsaturated hydrocarbon

† Contribution at the 14th International Conference on Radical Ions, Uppsala, Sweden, July 1–5, 1996.

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radicals.³⁻⁶ Recently, we have begun to examine the reactivity of alkene radical cations, with a study of the ethene+ethene radical cation,^{7,8} the ethene+1-butene radical cation reactions,⁹ and the isomerization of the 1-butene radical cation into (*Z*)-2-butene,⁹ all of which have been reported to occur in frozen halocarbon matrices.^{10,11} The theoretical models used in these studies did not, however, include the matrix because, according to the experiments, these reactions are observed irrespective of the matrix used. The coincidence between the experimental and the theoretical results largely justifies the neglect of the matrix in these studies, and the simplification thereby introduced in the model allowed the use of high level MO calculations.

Apart from oligomerization, no other reaction is observed in frozen halocarbon matrices for the ethene radical cation, whereas an alternative process may occur in the case of the radical cations of propene and higher olefins. For instance, in parallel with the dimerization of the isobutene radical cation by addition of a neutral parent molecule, the formation of the 2-methylallyl radical is possible in an irradiated CCl₂FCClF₂ matrix solution of isobutene at 103 K.¹¹ Similarly, the formation of allyl radical in concentrated solutions of propene in the CCl₃F and SF₆ matrices has been reported by Shiotani *et al.*¹²

From their EPR study of the stereospecific conversions of butene radical cations into methylallyl radicals, Fujisawa and coworkers¹¹ found these reactions to be very sensitive to the nature of the matrix. However, the differences between the matrices in which the reaction is prevented and those in which it is actually observed are reported to be very small: the substitution of one fluorine atom for one chlorine atom is, in some instances, enough to alter the influence of the matrix on the reaction. On the other hand, the concentration of the solute is also found to affect this kind of reaction.¹² Furthermore, the formation of allyl radical from the propene radical cation has been reported to occur in CCl₃F¹² whereas, although it is favored by hyperconjugation by the methyl group, the formation of the 2-methylallyl radical from the isobutene radical cation is not observed in the same matrix,¹¹ which suggests that the occurrence of the reaction might depend not only on the kind of the matrix but also on other experimental factors, such as the temperature.

From experimental evidence,^{11,12} such processes could be represented as an ion-molecule reaction between the radical cation and the parent olefin molecule giving, as products, the protonated olefin together with the allyl radical in the case of propene, and with the 2-methylallyl radical in the case of isobutene, provided that the matrix is inert enough not to be the final proton acceptor. Interactions with the matrix must obviously be included in the theoretical models. Nevertheless, the mechanism of the reaction, as well as the role of the matrix, remain unknown. In this connection, modelling of the reaction in the gas phase will help to elucidate whether the

matrices in which the reaction is possible play the role of a catalyst or, on the contrary, if other matrices, in which the reaction is not observed, quench the reaction by forming stable associations with the reactants. Moreover, if one or a few molecules of the matrix are included in the model system studied, this may provide some information about the nature of these interactions.

The aim of this paper is to model the role of the matrix in the conversion of the propene radical cation into an allyl radical, by transfer of one proton from the propene cation to a neutral parent molecule, in the gas phase and including the effect of different matrices. For simplicity, no mixed chloro-fluoro hydrocarbon matrix is involved in the present model study. Instead, only two alternative models are described, in addition to the study in the gas phase: 1, reaction occurring in the presence of a chlorinated hydrocarbon matrix (using one molecule of CCl₄ to model the influence of the matrix) and 2, reaction occurring in the presence of a fluorinated hydrocarbon matrix (using one molecule of CF₄ to model the influence of the matrix).

Furthermore, depending on whether the migrating proton is directly attached to the matrix molecule or not, two different pathways are investigated for each model matrix.

Method

The system under study is of medium size, as the modelling of the reaction in the gas phase concerns six carbon atoms and twelve hydrogen atoms. Coordinates between non-bonded atoms are, however, also included in the geometry optimization calculations which consequently become time consuming because, although the gradients for these parameters are small, the displacements they induce are very large. On the other hand, when one or two matrix molecules are involved in the model, *ab initio* level calculations with a reasonable basis set are prevented because the system becomes too large.

We therefore chose to work with the semiempirical UHF/PM3¹³ method which has, in many instances, proved to give results comparable to those obtained at the *ab initio* PMP2 level.^{7,9} All stationary points were fully optimized using gradient techniques. The reaction profiles in the gas phase, in a CCl₄ matrix and in a CF₄ matrix were calculated by means of the reaction coordinate method implemented in the MOPAC program,¹⁴ going first from reactants to products. A transition state structure was thereby identified and refined, and subsequently checked by means of a frequency calculation. Finally, the reactants and products were found from the transition state in a second reaction coordinate calculation, similar to the well-known intrinsic reaction coordinate (IRC) method.¹⁵ In all the calculations the gradient norm was kept below 0.05 kcal Å⁻¹ (or kcal radian⁻¹).

In the second step, the stationary point geometries of the gas phase study were re-optimized at the *ab initio* UMP2¹⁶⁻¹⁸ level in conjunction with the 3-21G basis

set,¹⁹ because the distance found between the two molecules in the products was unnaturally small at the PM3 level (see below). This was furthermore complemented with single-point UMP2 calculations of the points of interest on the potential energy surface of the reaction in the gas phase, using the 6-31G(d, p) basis.²⁰ Spin annihilation was included in the final energy calculations to correct for unbalanced spin contamination in different parts of the potential energy surface, which, for some intermediate structures with elongated bonds, has previously been found to be very important.⁷ The UMP2 calculations performed were within the frozen core approximation, using the program package GAUSSIAN 92.²¹

Results and discussion

Starting from the propene radical cation and a neutral parent molecule, an allyl radical and a protonated propene molecule are obtained after a proton transfer from the methyl group in the radical cation to the non-substituted unsaturated carbon atom in the second molecule.

EPR studies of radical alkyl formation from the parent alkane radical cation have shown that the reaction occurs exclusively through an ion-molecule reaction of the radical cation with a parent neutral molecule by deprotonation. The structure of the singly occupied molecular orbital (SOMO) of the cation has been found to be unambiguously related to the site selectivity of such a process.^{22,23} Hence, 'a high unpaired electron density in a particular carbon-hydrogen bond, leads to proton transfer from that site giving rise to a particular alkyl radical'.²⁴

Similarly, in the reaction investigated here, migration is observed of one of the hydrogen atoms of the methyl group, these being more acidic than the other hydrogen atoms of the propene radical cation. Indeed, the EPR spectra of $C_3H_6^+$ in CCl_3F and in SF_6 have been interpreted by Shiotani and co-workers in terms of higher isotropic hyperfine coupling constants on the hydrogen atoms of the methyl group.¹² This was furthermore confirmed in a theoretical study at the MP2 and SDCI levels, using relatively large basis sets.⁶

Gas phase study. A loose complex formed by the reactants at large distances apart, was first optimized using the PM3 method. The optimized structure is displayed in Fig. 1. The distance between the migrating proton, labelled H7 in the figure, and the accepting carbon atom C4 was kept fixed at 3.5 Å, which is well beyond the sum of the van der Waals radii of the hydrogen and the carbon atoms. In the second step, this distance was decreased stepwise from its initial value using the reaction coordinate method. No transition state structure was found on the gas phase reaction profile thereby obtained, as depicted in Fig. 2. Instead, the energy decreases monotonically along the curve to give the reaction products.

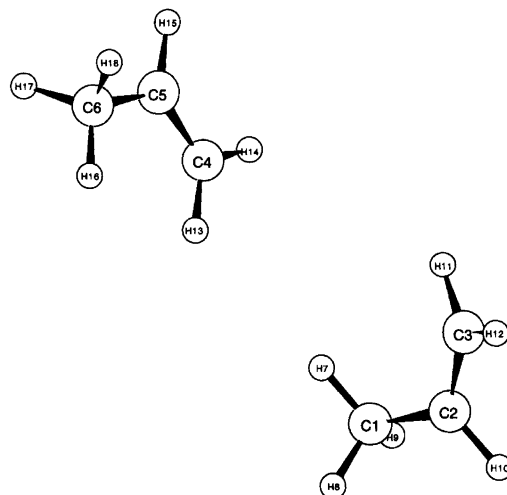


Fig. 1. Geometry of the PM3 optimized reactant complex of the reaction in the gas phase. The distance between the migrating proton in the propene radical cation, H7, and the accepting carbon atom in the neutral propene molecule, C4, is frozen to 3.5 Å.

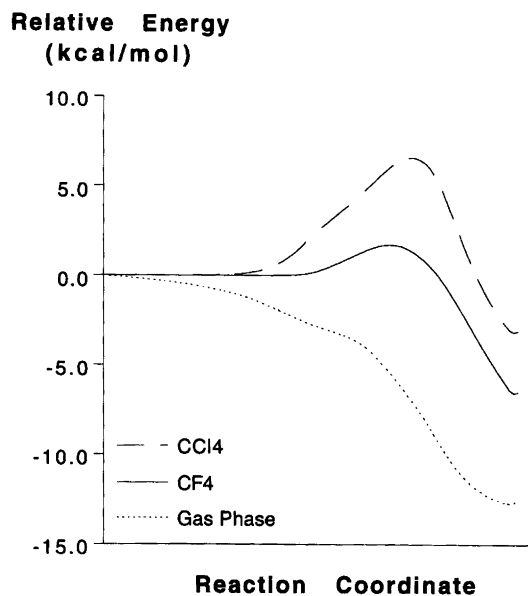


Fig. 2. The reaction profile of allyl radical formation: in the gas phase (lower line), and, following the first pathway, in CF_4 matrix (middle line) and in CCl_4 matrix (upper line). The energy of the bimolecular reactant complex is used as the zero level in the gas-phase reaction and, in the other two cases, the energy of the trimolecular reactant complex is used.

The structure of the whole complex in the vicinity of the last point on the reaction profile was then fully optimized. A complex of the two products is obtained (see Fig. 3) where the distance between the migrating proton H7 and the donating carbon atom C1 is optimized to 1.56 Å, which is now less than the sum of the van der Waals radii of the hydrogen and the carbon atoms. Moreover, the distance between H7 and C4 (1.26 Å) is much longer than a 'normal' C-H bond length. This suggests that the

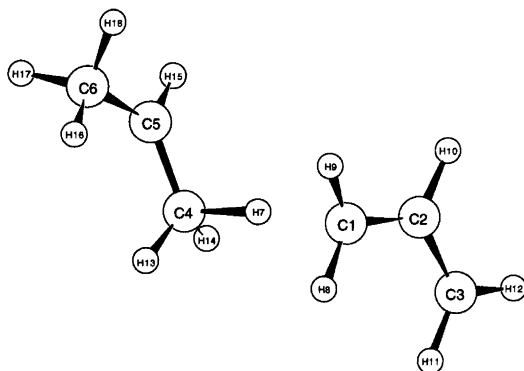


Fig. 3. PM3-optimized geometry of the products of the reaction in the gas phase.

proton is found at the PM3 level to migrate only partially between the donating and the accepting carbon atoms.

In order to remove any possible ambiguity with regard to the nature of the stationary point found under these conditions for the products of the reaction, a force calculation was performed on the supermolecule displayed in Fig. 3. All the frequencies were computed with a positive sign which indicates that the geometry obtained for the products corresponds to a minimum.

In addition, the validity of these PM3 results was checked by performing geometry optimization calculations at the MP2/3-21G *ab initio* level. When releasing the C4–H7 distance in the PM3 optimized reactant complex, this converged directly to the products. The C1–H7 distance converged to 2.52 Å which corresponds closely to the sum of the van der Waals radii of the two atoms, while the C4–H7 distance optimized to 1.09 Å. Hence, the *ab initio* results definitely show that two separate molecules are obtained, with a total transfer of the proton from the propene radical cation to the neutral propene molecule, and furthermore lend support to the PM3 predictions that no other stationary point is found between the reactants and products of the reaction in the gas phase.

Finally, single-point PMP2/6-31G(d, p) calculations were performed on the reactants and on the products. The relative energies of the reaction products with respect to the reactants are collected in Table 1. As is also reported in the profile (cf., Fig. 2), the reaction in the gas phase proceeds without any activation energy since, irrespective of the method, the products are calculated to be more stable than the reactants. The quantitative

Table 1. Relative energies in (kcal mol⁻¹) of the reaction products with respect to the reactants at a fixed distance of 3.5 Å (cf., Fig. 1), obtained at different levels of calculation for the reaction in the gas phase.

Method	Reactant complex	Products
PM3	0.0	-12.1
PMP2/3-21G	0.0	-6.7
PMP2/6-31G**//MP2/3-21G	0.0	-6.8

difference in the predicted heat of reaction is, in this connection, of less importance.

The results of this modelling lead us to conclude that the reaction in the gas phase is expected to be a one-step process that occurs without activation energy. The same behaviour should be expected, at a high enough temperature for diffusion to be possible, for the reaction in a truly inert matrix, such as a noble gas. No experimental results have, however, yet been reported for these conditions.

Influence of the matrix. The most significant result of the modelling in the gas phase is that the matrix can be expected only to have a retarding influence on the reaction studied, i.e., the radical cation forms some type of complex with the matrix so that its ability to react with the neutral molecule and to form an allylic radical is diminished. We therefore studied the formation of such a complex between one of the acidic protons of the propene radical cation and a Cl or a F atom of a CCl₄ and a CF₄ matrix molecule. The migration of the proton bonded to the CCl₄ or CF₄ matrix molecule (labelled H7) was studied first. The numerical results are summarized in Tables 2 and 3. In Fig. 2, the reaction profiles are drawn for the reaction in both CCl₄ and CF₄ matrices, together with that from the gas-phase study. The geometries corresponding to the stationary points of the reaction in CCl₄ are displayed in Figs. 4, 6 and 7. A schematic energy profile for the reaction in CCl₄ is represented in Fig. 5. An alternative pathway is also possible for the proton transfer, where the migrating proton is not directly attached to the matrix molecule in the reactant complex. Therefore, we have also modelled the reaction

Table 2. PM3 relative energies in (kcal mol⁻¹) of the reaction species with respect to the reactants in different matrices. The zero point is, in the gas-phase reaction, the energy of the bimolecular reactant complex in Fig. 1 and, in the other two cases, the energy of the trimolecular reactant complex (cf., Fig. 4).

Matrix	Reactant complex	Transition state	Products
Gas phase	0.0	—	-12.1
CF ₄ (pathway 1)	0.0	2.0	-6.5
CCl ₄ (pathway 1)	0.0	6.9	-3.2
CF ₄ (pathway 2)	0.0	—	-6.5
CCl ₄ (pathway 2)	0.0	2.6	-3.2

Table 3. Orbital energy of the HOMO of the CCl₄ and CF₄ matrices, the distance between the halogen and the migrating hydrogen atom attached to the matrix molecule (pathway 1), and the total interaction energy, as obtained from the PM3 calculations.

Matrix	$E_{\text{HOMO}}/\text{eV}$	d (Halogen–H7)/Å	$E_{\text{int}}/\text{kcal mol}^{-1}$
CF ₄	-16.79	1.80	-2.4
CCl ₄	-10.98	1.63	-8.7

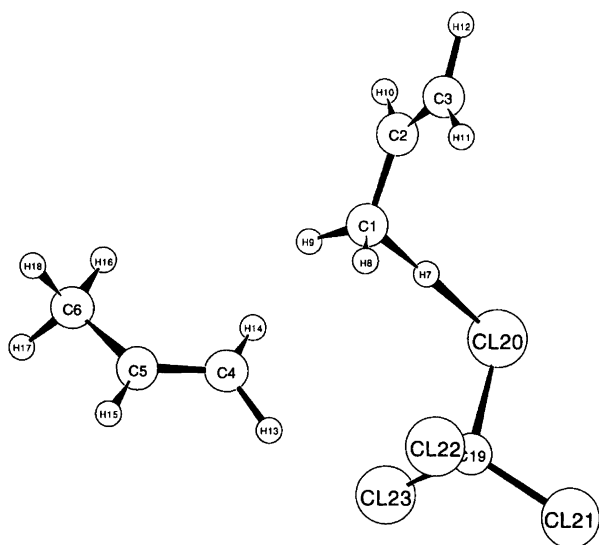


Fig. 4. PM3-optimized geometry of the complex of the reactants in CCl_4 matrix (pathway 1).

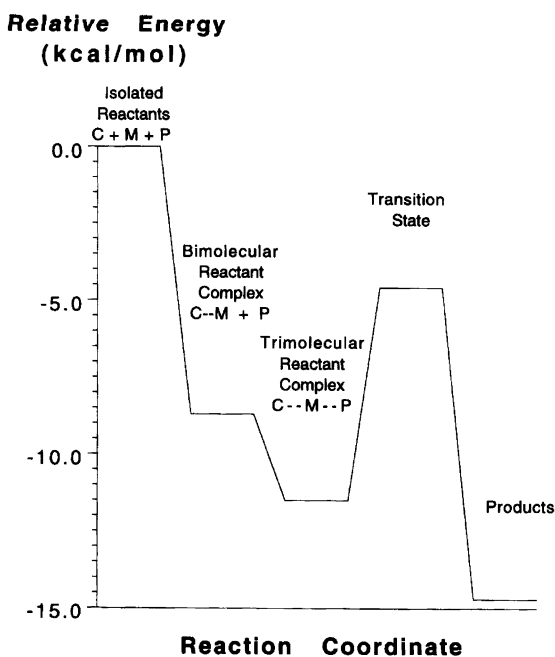


Fig. 5. Schematic energy profile of the reaction in CCl_4 matrix along the first pathway: C, propene radical cation; M, a CCl_4 matrix molecule; P, neutral propene.

of transfer of H8, with H7 connecting the propene cation to the matrix molecule. Selected results, obtained for the second pathway are reported in Table 2 and Fig. 8. Throughout the investigation, only one molecule of the matrix was involved in the calculations.

Along the first pathway, the interaction of a chlorine atom of the CCl_4 matrix with the radical cation creates a complex (cf., Fig. 4) that has a weak H7–Cl bond (1.63 Å), though still within the range of a chemical bond. The H7–Cl bond is, on the other hand, very elongated (1.29 Å). The C4–H7 distance was kept frozen

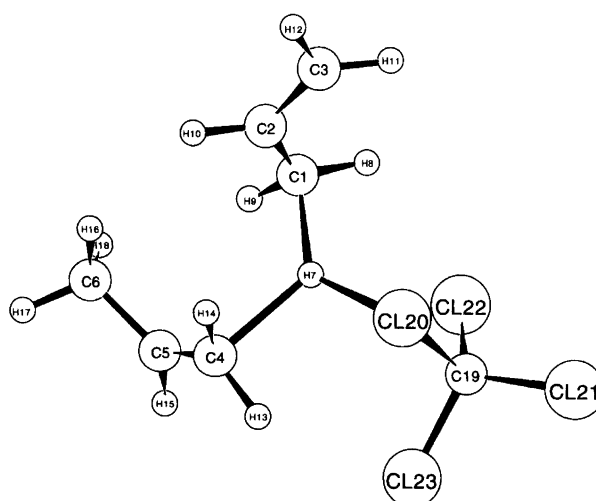


Fig. 6. Transition-state complex of the reaction in CCl_4 matrix (pathway 1), optimized by PM3.

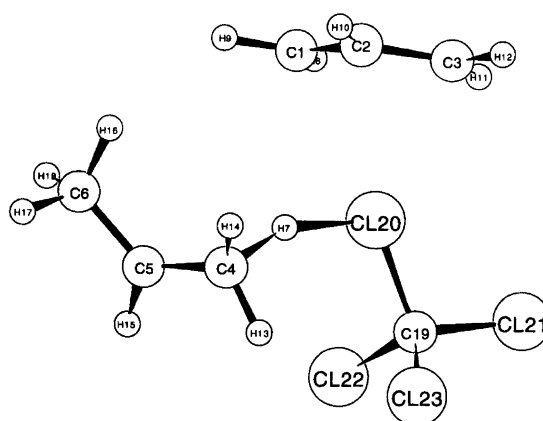


Fig. 7. PM3-optimized product complex of the reaction in CCl_4 matrix (pathway 1).

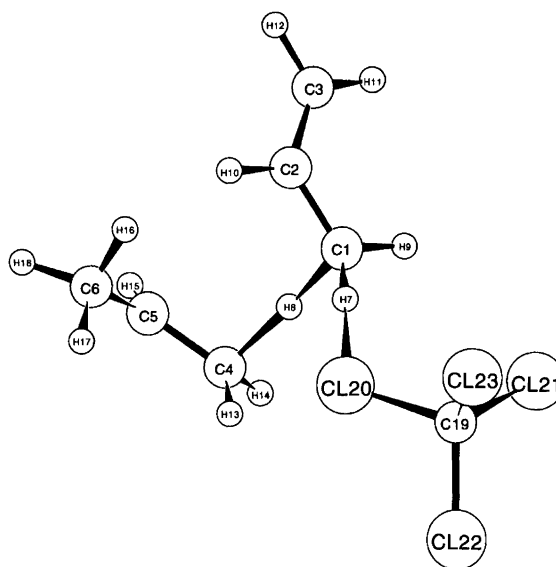


Fig. 8. Transition-state complex of the reaction in CCl_4 matrix (pathway 2), optimized by PM3.

at 3.5 Å, as discussed above for the gas-phase study. The total stabilization energy of this bimolecular system with respect to the isolated radical cation plus a matrix molecule is 8.7 kcal mol⁻¹, as reported in Table 3. The energy of the initial trimolecular reactant complex (cf., Fig. 4) with respect to the free molecules is -11.5 kcal mol⁻¹, as reported in Fig. 5.

The next step of the reaction, i.e., the approach of a neutral propene molecule to the acidic hydrogen atom H7 in the complex formed by the propene radical cation and the matrix, was then considered. The C4-H7 distance was decreased stepwise from its initial value in the reactant complex, using the reaction coordinate method. The energy of the system increased to give a transition state at a C4-H7 distance of 1.85 Å, the C1-H7 distance being now 1.53 Å (cf., Fig. 6). The relative energy of the transition state complex with respect to the trimolecular reactant complex amounts to +6.9 kcal mol⁻¹, as reported in Table 2 (see also Figs. 2 and 5). Such an activation energy is large enough to make the reaction difficult in this case, although the total energy of the system in this transition state is 4.6 kcal mol⁻¹ lower than the energy of the three isolated reactants, as shown in Fig. 5.

Owing to the larger abundance of the matrix molecules compared with the neutral propene molecules, the addition complex of CCl₄ with the radical cation is formed with a high probability before the attack of the neutral molecule and the energy released could be absorbed by the medium. When this relaxation occurs, the complex plus isolated neutral propene is 4.1 kcal mol⁻¹ more stable than the transition state (cf., Fig. 5). In contrast, if concentration of the solute is increased, the probability of the bimolecular reaction competing with matrix complexation increases. This could be the reason for the fact that in the experimental studies some reactions occur only in concentrated solutions.

The energy of the trimolecular system then decreases to give the products of the reaction (cf., Figs. 2 and 5). The allyl radical now forms a separate molecule while a complex is built between the protonated propene and the CCl₄ molecule as seen in Fig. 7. The interatomic distances C1-H7, C4-H7 and Cl-H7 optimized to 2.63 Å, 1.23 Å and 1.73 Å, respectively. The relative energy of the products with respect to the reactant complex is -3.2 kcal mol⁻¹ (cf., Table 2 and Figs. 2 and 5).

Analogous modelling using one CF₄ molecule showed intermediate behaviour between the results in the gas phase and in the CCl₄ matrix (cf., Fig. 2). The complex CF₄ + radical cation obtains its minimum energy for an F-H7 distance of 1.80 Å. Causing H7 to approach further the matrix molecule destabilizes the system. Also, the stabilization energy is only 2.4 kcal mol⁻¹ in this case (cf., Table 3). The larger distance and the weaker interaction energy indicate inert behaviour of the fluorinated matrix compared with the CCl₄ matrix.

A transition-state structure is indeed found, but the activation energy is only 2.0 kcal mol⁻¹, at a C4-H7 distance of 2.02 Å. The transition state is, in this case, 'earlier' because the interactions with the matrix molecule, which could hamper the reaction, are weaker. The products of the reaction finally lie some 6.5 kcal mol⁻¹ lower than the reactant complex (cf., Table 2 and Fig. 2).

The reactivity of the radical cation in the CF₄ matrix thus resembles more closely that in the gas phase, as can also be seen from the relative energies collected in Table 2. While no transition state structure is found at all for the reaction in the gas phase, a small activation energy (2.0 kcal mol⁻¹) is computed for the reaction in CF₄ whereas it is found to be as high as 6.9 kcal mol⁻¹ for the same reaction in CCl₄.

For both the CCl₄ and CF₄ matrices, the results obtained for the reaction along the second pathway are less pronounced but qualitatively very similar to those of the first pathway described above: a barrier of 2.6 kcal mol⁻¹ is computed on the reaction profile of the reaction in CCl₄ while no activation energy is found for the reaction in CF₄, as reported in Table 2. It should be mentioned that, in either matrix, the relative energy of the product with respect to the reactant is the same for both pathways (see Table 2). This reaction profile seems to be closer to the experimental results. In any case the aim of this work is to show the different behaviour of the two systems, not to find accurate activation energies.

In Fig. 8 is displayed the geometry of the transition state structure of the reaction in CCl₄ along the second pathway. The migrating proton, H8, lies 1.38 Å and 1.41 Å apart from the donor (C1) and the acceptor (C4) carbon atoms, respectively. The distance between the proton attached to the matrix molecule, H7, and the chlorine atom of the matrix is found to be 1.38 Å whereas the C1-H7 distance is now 1.13 Å (cf., Fig. 8).

Compared with the first pathway, less accentuated effects are found for the reaction along the second pathway, as expressed by the smaller barrier and the larger chlorine-H7 distance in the transition state.

Along either pathway, however, the interactions with the chlorinated matrix are much stronger than might be expected from an intuitive point of view, since a halocarbon molecule is playing the role of a base which is not common in everyday chemistry. This unexpected interaction between an 'inert' matrix and the radical cation seems to be responsible for the changing behaviour of the cation in different halocarbon matrices, and might explain why the conversion reaction studied does not occur in some of these matrices.

In order to rationalize this result, and being mainly motivated by the above-mentioned experiences of regio-specificity of the deprotonation process in connection with the shape of the SOMO in the alkyl radical formation,²²⁻²⁴ we looked further into the orbital energies of the propene radical cation, CCl₄ and CF₄. At the PM3 level, the energy of the β-LUMO of the propene cation is -8.92 eV, a value that is very low compared with the

energy of the LUMO of the hydronium ion H_3O^+ , which is -6.76 eV. This means that the radical cation is a very strong electrophile and, consequently, the proton involved in the reaction is very acidic, as has already been discussed above in connection with the isotropic hyperfine coupling constants.

The energy of the HOMO of CCl_4 is -10.98 eV, which is high enough to allow for a strong interaction to take place. On the other hand, the energy of the HOMO of CF_4 , -16.78 eV, is too low to induce strong interactions. The 'basicity' of the matrix seems thus to be responsible for the inhibition of allyl radical formation in the chlorinated halocarbon matrix.

The HOMO energy, the distance between the migrating proton (H7) in the radical cation and the halogen atom of the matrix molecule, and the interaction energy for the first pathway and for the two halocarbon matrices considered in the present investigation, i.e., CCl_4 and CF_4 , are collected in Table 3. As the energy of the HOMO increases, the basicity gets stronger. Hence CF_4 is the less basic molecule while CCl_4 is the more basic one. The interaction energies also correlate perfectly with the HOMO energies: stronger interactions are found on going from CF_4 to CCl_4 and, quite naturally, where the interaction is stronger, the migrating proton gets closer to the matrix molecule.

Acknowledgements. This research was supported by the Swedish Natural Science Research Council (NFR), and by the Swedish Agency for Research Cooperation with Developing Countries (SAREC).

References

- For a recent review, see, e.g., Lund, A. and Shiotani, M., Eds., *Radical Ionic Systems, Properties in Condensed Phases*, Kluwer, Dordrecht 1991.
- See, e.g., Wertz, J. and Bolton, J. R. *Electron Spin Resonance, Elementary Theory and Practical Applications*, Chapman and Hall, New York 1986.
- Lunell, S., Huang, M.-B. and Lund, A. *Faraday Discuss. Chem. Soc.* 78 (1984), 35.
- Lunell, S., Feller, D. and Davidson, E. R. *Theor. Chim. Acta* 77 (1990) 111.
- Lunell, S. and Huang, M.-B. *Chem. Phys. Lett.* 168 (1990) 63.
- Lunell, S., Eriksson, L. A. and Huang, M.-B. *J. Mol. Struct. (Theochem)* 230 (1991) 263.
- Alvarez-Idaboy, J. R., Eriksson, L. A., Fängström, T. and Lunell, S. *J. Phys. Chem.* 97 (1993) 12737.
- cf., Jungwirth, P. and Bally, T. *J. Am. Chem. Soc.* 115 (1993) 5783.
- Alvarez-Idaboy, J. R., Eriksson, L. A. and Lunell, S. *J. Phys. Chem.* 97 (1993) 12742.
- Fujisawa, J., Sato, S. and Shimokoshi, K. *Chem. Phys. Lett.* 124 (1986) 391.
- Fujisawa, J., Sato, S., Shimokoshi, K. and Shida, T. *J. Phys. Chem.* 89 (1985) 54816.
- Shiotani, M., Nagata, Y. and Sohma, J. *J. Phys. Chem.* 88 (1984) 4078.
- Stewart, J. J. P. *J. Comput. Chem.* 10 (1989) 209.
- Stewart, J. J. P. Program No. 581, *QCPE*, Indiana University, Bloomington, IN.
- Fukui, K. *Acc. Chem. Res.* 14 (1981) 363.
- Møller, C. and Plesset, M. S. *Phys. Rev.* 46 (1934) 618.
- Binkley, J. S. and Pople, J. A. *Int. J. Quantum Chem.* 9 (1975) 229.
- Pople, J. A., Binkley, J. S. and Seeger, R. *Int. J. Quantum Chem., Symp.* 10 (1976) 1.
- Binkley, J. S., Pople, J. A. and Hehre, W. J. *J. Am. Chem. Soc.* 102 (1980) 939.
- Hariharan, P. C. and Pople, J. A. *Theor. Chim. Acta* 28 (1973) 213.
- GAUSSIAN 92, Revision C, Frisch, M. J., Trucks, G. W., Head-Gordon, M., Gill, P. M. W., Wong, M. W., Foresman, J. B., Johnson, B. G., Schlegel, H. B., Robb, M. A., Replogle, E. S., Gomperts, R., Andres, J. L., Raghavachari, K., Binkley, J. S., Gonzalez, C., Martin, R. L., Fox, D. J., Defrees, D. J., Baker, J., Stewart, J. J. P. and Pople, J. A. Gaussian, Inc., Pittsburgh PA, 1992.
- Toriyama, K., Nunome, K. and Iwasaki, M. *J. Phys. Chem.* 90 (1986) 6833.
- Iwasaki, M., Toriyama, K., Fukaya, M., Muto, H. and Nunome, K. *J. Phys. Chem.* 89 (1985) 5278.
- Stienlet, D. and Ceulemans, J. *J. Phys. Chem.* 97 (1993) 8595 and references therein.

Received July 11, 1996.