

Interactions between Ions and Molecules: Gas-Phase Theoretical Studies

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When speaking about chemical reactivity, there is still a tendency to think primarily of molecule–molecule interactions. In fact, however, ion–molecule reactions frequently play an outstanding role. Since the 1920's these reactions have received great attention.¹ Electrophilic and nucleophilic transformations in solution have played a great role in all branches of chemistry. In the last quarter of this century a very significant increase in interest in gas-phase ion–molecule reactions has been observed. It is well-known that there is a great deal of difference between ion–molecule reactions taking place in the gas or in the condensed phase; typical reaction profiles are presented in Figure 1. The reaction conditions we are interested in are those which operate in interstellar space and in molecular-beam experiments. Therefore, this report deals mainly with quantum chemical studies of gas-phase processes; influence of solvent molecules will be mentioned only marginally. We are aware of the differences between ions (electronic closed-shell) and radical ions (electronic open-shell)–enhanced reactivity and special computational tools needed for theoretical treatment—but we shall not stress these differences too strongly.

The structure of this Account is as follows: the processes under study are classified, then the theoretical features of the individual prototypes are outlined (and compared with experimental data, if available), and finally, the main characteristics of ion–molecule reactions are summarized and tempting possibilities for the near future are mentioned.

The Processes under Study

Reactions between closed-shell ions and molecules are widespread in chemistry and are studied in solution as well as in the gas phase. Reactants and products of gas-phase processes are separated by an activated complex (in the Eyring sense), and this complex is, in general, “framed” by ionic van der Waals (vdW) species² when going along the reaction path (cf. Figure 1). The role of distinguished vdW species is less significant in solution because all species along the reaction path are solvated, which is especially true of the ionic species. The following five processes will be mentioned explicitly: (a) ion solvation (where the vdW species formed represent “reaction product”) (b)

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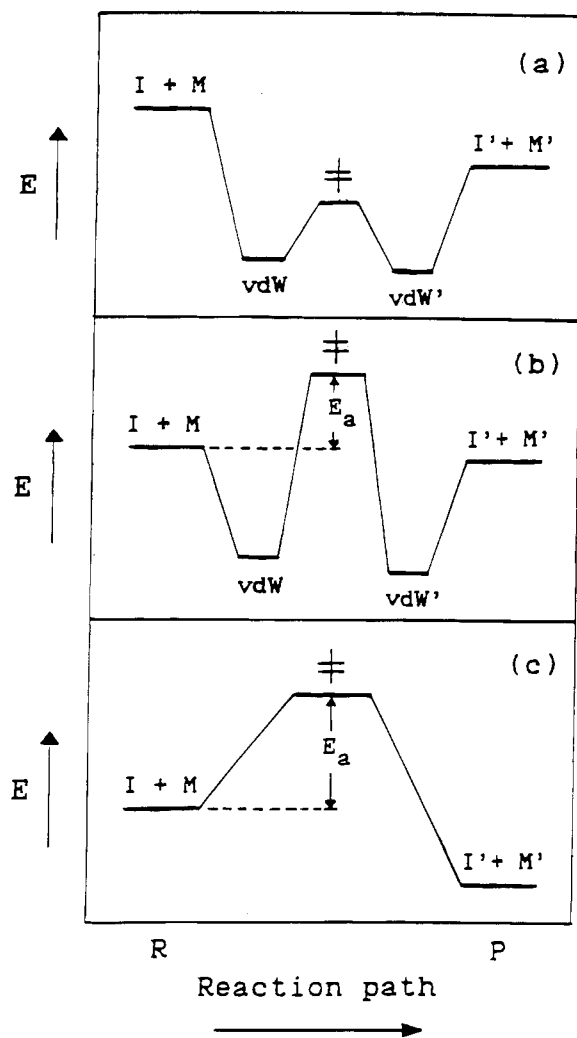


Figure 1. Reaction profiles of typical ion–molecule reactions. Gas-phase processes: (a) downhill process; (b) process with energy barrier; (c) reaction in solution. E is potential energy, E_a is activation energy, vdW (vdW') is van der Waals complex between ion I (I') and molecule M (M') ‡ is Eyring's activated complex, and R and P mean reactants and products.

protonization of rare-gas atoms, (c) classical S_N2 substitution, (d) reactions between cations and anions derived from the first-row hydrides and H_2 , and (e) some pseudocatalytic reactions.

Reactions between molecules and open-shell ions, i.e., radical cations and radical anions, have been studied for about 30 years in the gas phase, and mostly

(1) Ingold, C. K. *Structure and Mechanism in Organic Chemistry*; Bell and Sons Ltd.: London, 1953.

(2) Zahradník, R.; Hess, B. A., Jr. *J. Mol. Struct.: THEOCHEM* **1991**, 230, 387.

in molecular beams. Typically, the high reactivity of radical ions prevents one from investigating these processes in solution. Frequently, but not always, the studied processes involve interactions between a molecule and a radical ion (mostly cation) derived from ionization. For purely pragmatic reasons, we shall distinguish between reaction of species not containing hydrogen and hydrides (in the sense of hydrogen-containing systems) of different sorts. The reason for this is that in the latter group proton, hydride, or H-atom transfer plays a significant role. The following processes will be presented for illustration: (i) $\text{H}_2\text{-H}_2^+$ as a prototype of interactions between diatomics and radical cations derived from them, (ii) COS-COS^+ as a prototype of triatomics not containing hydrogen, (iii) reactions between hydrides having one heavy atom (mostly atoms ranging from Li to Cl) and radical cations thereof, (iv) analogous processes including radical anions, (v) reactions involving alkylated or arylated hydrides, and (vi) interactions of hydrides having more than one heavy atom.

Quantum Chemical Calculations

In our laboratory for years energy and molecular characteristics calculations have been carried out by nonempirical quantum chemical procedures mostly at three levels. For geometry optimization these levels have been SCF/6-31G** (level A), SCF/6-31++G** (level B), and MP2/6-31++G** (level C). Single-point MPn ($n = 2, 3, 4$) and CCSD energy calculations have been carried out for optimized structures (see, e.g., ref 3). Open-shell systems have been studied by spin-unrestricted open-shell procedures, unless stated otherwise. Level A offers semiquantitatively correct information for a majority of cations and molecules, while reliable treatment of anions requires level C. The standard Pople's basis sets not only are convenient but also permit straightforward comparison with published data.

Nowadays, of course, basis sets which are better and more advanced are available and applicable. However, we believe that the above mentioned types of calculations are good enough for semiquantitative purposes. What seems more important to us is exploitation of chemical feeling, experience, and intuition for selecting problems, as well as proper interpretation of computational data.

Closed-Shell Ions

(a) Complexes between alkali-metal (Li^+-Rb^+), alkaline-earth-metal ($\text{Be}^{2+}-\text{Sr}^{2+}$), trivalent-metal (Al^{3+} , Ga^{3+}), and Cu^+ , Zn^{2+} , and Sc^{3+} ions with H_2O and NH_3 can be semiquantitatively described⁴ at the Hartree-Fock level with small basis sets (MINI-1 and MIDI). Investigation of geometry and stability relationships between the various cation complexes suggests that the ion charge and radius are not always the only factors determining the nature of complexes: for transition-metal cations, the different behavior of d electrons in shielding the core charge also influences the above characteristics. This might play a signifi-

(3) Hess, B. A., Jr.; Zahradník, R. *Int. J. Quantum Chem.* **1991**, *40*, 643.

(4) Hofmann, H.-J.; Hobza, P.; Cammi, R.; Tomasi, J.; Zahradník, R. *J. Mol. Struct.: THEOCHEM* **1989**, *201*, 339.

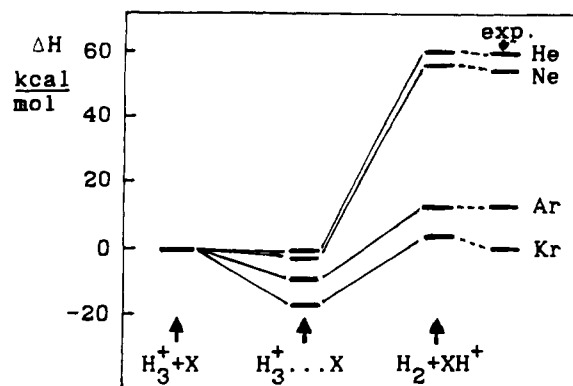
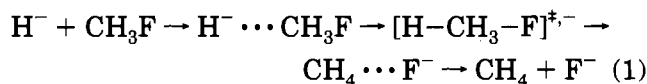


Figure 2. Energy profile for the process $\text{H}_3^+ + \text{X} \rightleftharpoons \text{H}_3^+ \cdots \text{X} \rightleftharpoons \text{H}_2 + \text{H-X}^+$: MP2 stabilization enthalpies (MP2/6-31G**//MP2/6-31G**) for the complex formation ($\text{H}_3^+ \cdots \text{X}$; X = He, Ne, Ar, Kr) from H_3^+ and X and reaction heats of the $\text{H}_2 + \text{XH}^+$ formation. For the latter process experimental values are also presented.

cant role in gas-phase studies of pseudocatalytic reactions (*vide infra*).

(b) Reactions between rare-gas atoms and H_3^+ are endoergic,⁵ which means that protonated rare gases are stronger acids than H_3^+ . The reactions proceed via the $\text{X} \cdots \text{H}_3^+$ complex, which, in the case of X = Ar and Kr, are quite stable. Calculated and experimental energy characteristics are summarized in Figure 2. Three equivalent $\text{X} \cdots \text{H}_3^+$ minima are separated by three equivalent saddle points. All the stationary points assume C_{2v} symmetry. The calculated energy barrier height is negligible for the He and Ne complexes and amounts to 4.3 and 8.1 kcal/mol for the isomerization between equivalent structures of $\text{Ar} \cdots \text{H}_3^+$ and $\text{Kr} \cdots \text{H}_3^+$. Quantum chemical energy characteristics permit straightforward interpretation of these and related experimentally studied processes.

(c) **Classical $\text{S}_{\text{N}}2$ Substitution.** Gas-phase substitution of F^- in CH_3F by the hydride ion exhibits five stationary points along the reaction path (\cdots denotes a vdW bond):^{6,7}



All the necessary data for evaluation of the rate constants within the framework of statistical theories were calculated. It appears that C_{3v} symmetry of the reaction path is not conserved in the product region. Using two kinetic models we obtained values of rate constants (300 K) for the overall process (2.1×10^{-12} and $4.5 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$), which are in reasonable agreement with the experimental estimate at 300 K from flowing afterglow measurements by Tanaka et al.⁸ ($1.5 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$).

(d) **Reactions between Cations and Anions, Derived from the First-Row Hydrides, with H_2 .** The two series of ions under study were Li^+ , BeH^+ ,

(5) (a) Hobza, P.; Zahradník, R.; Smith, D. *Chem. Phys. Lett.* **1993**, *208*, 497. (b) Bogey, M.; Bolvin, H.; Demuyne, C.; Destombes, J. L. *Chem. Phys.* **1988**, *88*, 4120. (c) Smith, D.; Spanel, P.; Bedford, D. K. *Chem. Phys. Lett.* **1992**, *191*, 587.

(6) Havlas, Z.; Merkel, A.; Kalcher, J.; Janoschek, R.; Zahradník, R. *Chem. Phys.* **1988**, *127*, 53.

(7) Merkel, A.; Havlas, Z.; Zahradník, R. *J. Am. Chem. Soc.* **1988**, *110*, 8355.

(8) Tanaka, K.; Mackay, G. I.; Payzant, J. D.; Bohme, D. K. *Can. J. Chem.* **1976**, *54*, 1643.

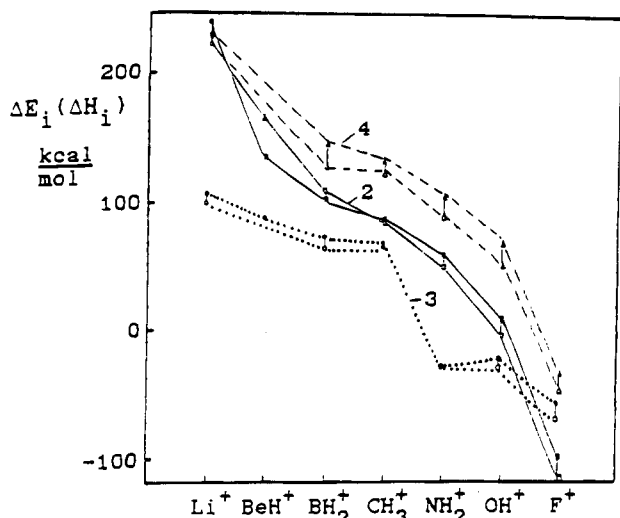
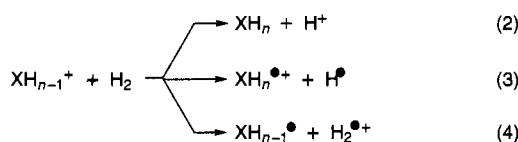


Figure 3. MP4/6-31G** reaction energy (■, ●, ▲) and experimental heats of the reaction (□, ○, △) of XH_{n-1}^+ with H_2 for the reactive channels 2, 3, and 4, respectively.

BH_2^+ , CH_3^+ , NH_2^+ , OH^+ , F^+ , and Li^- , BeH^- , BH_2^- , CH_3^- , NH_2^- , OH^- , F^- . In each of the series three members are "natural" (e.g., Li^+ , F^-) and three are "unnatural" (e.g., Li^- , F^+) ions; in the case of methyl ions, both forms, cation and anion, are natural. Three reaction channels, 2–4, were considered for cations:⁹



Channels 2 and 3 differ in the distribution of the positive charge and are both characterized by one broken (H–H) and one formed chemical bond (X–H). Channel 4 is an electron transfer process. The reactions can be interpreted in terms of electron attachment to XH_{n-1}^+ , electron detachment from H^\bullet , XH_n , and H_2 , and the bond energy difference in bond energies of H–H and X–H. Nonempirical calculations provided reaction energy profiles in good agreement with values derived from experimental gas-phase ionization potentials and heats of formation (Figure 3). The preferred reaction channel in eqs 2–4 depends on the relationship of the adiabatic ionization potentials of H^\bullet , XH_n , and H_2 . For the cations with X ranging from Li to O, the formation of $XH_n^{\bullet+} + H^\bullet$ is favored over the formation of $XH_n + H^+$. The gas-phase reaction course is predicted to be different from that in solution. In the latter, proton-generating channels are favored due to the high solvation energy of H^+ . The situation with anions differs significantly.¹⁰ The reaction between the CH_3^- anion and H_2 represents the exoergic process in the set; Li^- and F^- have strongly endoergic balances. The parabolic shape of the dependence of the anionic reaction energy on X (in XH_{n-1}^-) contrasts sharply with that of the corresponding cations.

(e) Pseudocatalytic Reactions. The importance of catalytic reactions is overwhelming. Unfortunately,

(9) Mehlhorn, A.; Hess, B. A., Jr.; Zahradník, R. *J. Mol. Struct.: THEOCHEM* **1992**, 258, 1.

(10) Mehlhorn, A.; Hess, B. A., Jr.; Zahradník, R. *J. Mol. Struct.: THEOCHEM* **1992**, 277, 67.

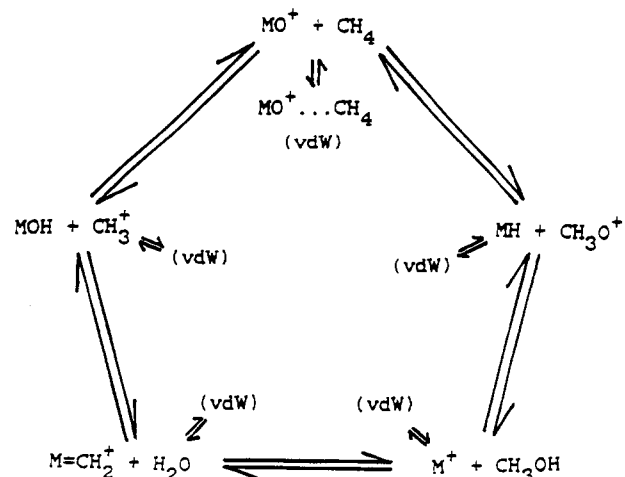
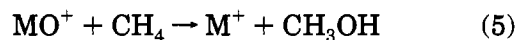


Figure 4. Relevant channels on the CH_4OM^+ potential energy surface. Except for $MO^+ \cdots CH_4$ van der Waals complexes are indicated by the abbreviation vdW. Numerous possible saddle points (Eyring's activated complexes) are not depicted.

it is still hardly possible to investigate elementary steps of these processes under very well defined conditions. Recently a proposal was made¹¹ to investigate processes of type 5 in molecular beams. Pro-



cesses of this type (where M is a metal atom ranging from Li to U) assume a significant feature of steps in catalytic processes. Pioneering attempts with processes of this sort are due to Schwarz and associates.¹² Process 5 is seemingly simple. In reality, the overall reaction picture is much more complicated because, for instance, for $M = Li$ quite a few reaction channels are possible (Figure 4); moreover, ion–molecule pairs form van der Waals species. Not only that: thorough investigation of the ground state potential energy surface (PES) must be supplemented by the lowest electronic excited state PES because with some systems the energy gap between the ground state and first excited state is small. Beauchamp et al.¹³ and Schwarz et al.¹⁴ established yields for three channels connected with the $FeO^+ - CH_4$ interaction. The lack of correspondence between the calculated and observed reaction enthalpies suggests kinetic rather than thermodynamic control.¹¹

Open-Shell Ions

Investigations of radical ion–molecule reactivity were started about 65 years ago¹⁵ with the study of the interaction between I_2 and its radical ions yielding $I_3^{\bullet+}$ or $I_3^{\bullet-}$, and the I^\bullet atom. Experimental study of reactions between H_2O and $H_2O^{\bullet+}$ is of the same age.¹⁶ Ion–molecule gas-phase reactions have been intensively studied experimentally over the last 35 years; some key references are reviewed in a recent work.¹⁷

(11) Zahradník, R. *J. Mol. Catal.* **1993**, 82, 265.

(12) Blum, O.; Stöckigt, D.; Schröder, D.; Schwarz, H. *Angew. Chem.* **1992**, 104, 637.

(13) Irikura, K. K.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1989**, 111, 75.

(14) Schröder, D.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1990**, 29, 1433.

(15) Hogness, T. R.; Harkness, R. W. *Phys. Rev.* **1928**, 32, 784.

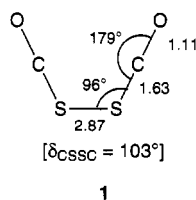
(16) Barton, H. A.; Bartlett, J. H. *Phys. Rev.* **1928**, 31, 822.

For evaluation of experimental reaction heats, valuable collections of thermochemical and energy characteristics for molecules and gaseous positive and negative ions are available.^{18,19}

In general, three processes are of great importance for radical ion–molecule reactions: charge transfer, atom (or atomic group) transfer, and complex (radical cation or radical anion) formation. The complex formed either is stable under the given conditions or decomposes into products. This decomposition is accompanied by a splitting of a covalent (or van der Waals) bond. Radical ion–molecule reactions involving reactants containing hydrogen, proton, or hydride or hydrogen atom transfer are an important reaction pathway.

(i) Reactions between diatomics (A_2) and radical ions thereof represent an attractive reaction class. With cations, the formation of a radical ion dimer ($A_4^{+\cdot}$) and atom transfer leading to $A_3^+ + A^\cdot$ belong to the most important reactions. Poshusta and Matsen²⁰ investigated the structure of $H_4^{+\cdot}$ as early as the 1960s. Since that time much attention has been paid to the process $H_2 + H_2^{+\cdot} \rightarrow H_4^{+\cdot} \rightarrow H_3^+ + H^\cdot$; the respective references are presented in a CI and MCSCF study²¹ of the PES of $H_4^{+\cdot}$. It was shown that the optimal distorted square geometries are slightly different from those obtained by following the Jahn–Teller modes of the initial square geometry of $H_4^{+\cdot}$. (This subject is topical in connection with Jahn–Teller distortion of the cyclobutane radical cation, *vide infra*.) The very shallow global minimum corresponds to triangular H_3^+ forming a planar C_{2v} complex with hydrogen atom (stabilized by about 1 kcal/mol with respect to free H_3^+ and H^\cdot). It must be added that the energy dependence on the H^\cdot distance to H_3^+ is very flat. This explains the uncertainty in predicting this distance (the published calculated values lie in the range 1.5–1.8 Å).

(ii) Interactions between polyatomic molecules and their radical cations are in some instances connected with remarkable reaction pathways. This can be illustrated by the reaction $COS + COS^{+\cdot}$ leading to CO^\cdot and $S_2^{+\cdot}$ and the reaction $N_2O + N_2O^{+\cdot}$ leading to N_2 plus NO^\cdot and NO^+ . The formation of CO and $S_2^{+\cdot}$ from COS and $COS^{+\cdot}$ is exoergic by about 10 kcal/mol (level B, *vide supra*);²² the binding energy of dimer 1, with respect to COS and $COS^{+\cdot}$, amounts to about 20 kcal/mol.²³ When ionization potentials of diatomics



formed and atom electronegativities are taken into consideration, it is possible to make an estimate,

(17) Zahradník, R. *Collect. Czech. Chem. Commun.* **1993**, *58*, 1.

(18) Franklin, J. L., Ed. *Ion-Molecule Reaction*; Plenum Press: New York, 1972; Vols. 1 and 2.

(19) Lias, S. G.; Bartmess, J. E.; Liebmann, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17* (S1), 1.

(20) Poshusta, R. D.; Matsen, F. A. *J. Chem. Phys.* **1967**, *47*, 4795.

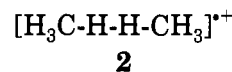
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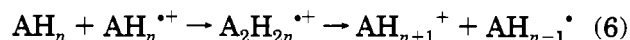
(23) McKee, M. L. *Chem. Phys. Lett.* **1991**, *179*, 559.

without calculations, on the course of analogous interactions between triatomics.

(iii) Investigations of interactions between hydrides and radical cations thereof have a long tradition in connection with investigations of the dynamics of ion–molecule reactions by means of molecular beam scattering and state-selective studies. Fundamental studies by Z. Herman and his colleagues should be mentioned here (see, e.g., ref 24). On the basis of his request, the peculiar structure **2** of the complex between CH_4 and $CH_4^{+\cdot}$, $C_2H_8^{+\cdot}$, was elucidated quantum chemically²⁵ (see also ref 26). A sophisticated



structural study on related radical cation dimers ($A_2H_{2n}^{+\cdot}$, where A is N, O, F or P, S, Cl) was published by Radom.²⁷ In general, the processes under study can be written^{17,28}



The structure of $A_2H_{2n}^{+\cdot}$ is not simple. Firstly, there are two types of hydrogen-bonded isomers of this dimer, one structurally related to reactants (in eq 6) and one to products. These minima on the PES of the dimer are separated by a saddle point, the Eyring activated complex. Secondly, besides the H-bonded dimers, there exists an isomer possessing a two-center, three-electron ($2c-3e$) bond. The importance of the latter isomer increases rapidly with increasing atomic mass in a given column of the periodic system. Specifically, when going from $(HF)_2^{+\cdot}$ to $(HCl)_2^{+\cdot}$ to $(HBr)_2^{+\cdot}$, the H-bonded dimer is dominant with $(HF)_2^{+\cdot}$ while with the last system it is the $[H-Br-Br-H]^{+\cdot}$ form, i.e., the structure with the $2c-3e$ bond (called also a hemibond), which predominates.

Much attention has been paid to the mechanism of molecule–cation reactions. Transition of the reactants to the products in eq 6 takes place either via proton transfer (from the cation to the molecule) or via H-atom abstraction (from the molecule by the cation).¹⁷ In order to distinguish between the two mechanisms with homogeneous pairs (e.g., $H_2O + H_2O^{+\cdot}$), labeling by D is helpful. With heterogeneous pairs (e.g., $HF^{+\cdot} + CH_4$), the products of the two processes are different, either $CH_5^+ + F^\cdot$ (H^+ transfer) or $H_2F^+ + CH_3^\cdot$ (H^\cdot transfer).

In the case of homogeneous pairs, there is good agreement between calculated and observed enthalpy changes¹⁷ for a set of equilibria between reactants and products of process 6. In Figure 5, calculated and observed reaction heats are plotted against atomic number of A in AH_n hydrides. The completely different shape of the dependence for the first-row (C through F) and second-row (Si through Cl) hydrides still remains unexplained.

(24) (a) Henschman, M.; Smith, D.; Adams, N. G.; Paulson, J. F.; Herman, Z. *Int. J. Mass Spectrom. Ion Processes* **1989**, *92*, 15. (b) Vančura, J.; Herman, Z. *Chem. Phys.* **1991**, *151*, 249. (c) Herman, Z.; Koyano, I. *J. Chem. Soc., Faraday Trans. 2* **1987**, *83*, 127.

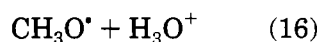
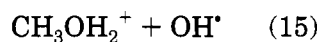
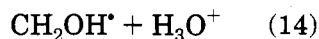
(25) Havlas, Z.; Bauwe, E.; Zahradník, R. *Chem. Phys. Lett.* **1985**, *121*, 330.

(26) Kamiya, K.; Morokuma, K. *Chem. Phys. Lett.* **1986**, *123*, 331.

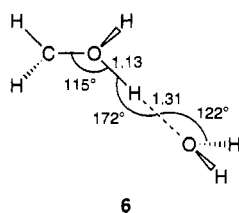
(27) Gill, P. M. W.; Radom, L. *J. Am. Chem. Soc.* **1988**, *110*, 4931.

(28) Zahradník, R.; Havlas, Z.; Hess, B. A., Jr.; Hobza, P. *Collect. Czech. Chem. Commun.* **1990**, *55*, 869.

bonded, and the last one possesses a hemibond. Convincing evidence was accumulated which shows that $\text{CH}_3\text{OH}^{\bullet+}$ acts rather like a C-acid than an O-acid. With interaction between $\text{CH}_3\text{OH}^{\bullet+}$ and H_2O the following channels are important:

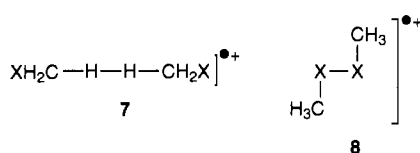


The most stable form of complex **4** has structure **6**. The most stable complex for **5** has C_s symmetry, with the linear H-bond between the proton of the phenol moiety and the oxygen in H_2O . For this structure harmonic vibrational frequencies were calculated; for some soft intermolecular modes anharmonicity was calculated as well. These calculations made possible assignment of vibrational frequencies observed in ZEKE photoelectron spectra.



6

Much attention has also been paid to the radical cations derived from CH_3X ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$).^{37,38} While for $(\text{CH}_3\text{F})_2^{\bullet+}$ the energy of stabilization for structures of type **7** and **8** is roughly the same (about 15 kcal/mol), all remaining systems assume only structure **8**. There is good agreement between the



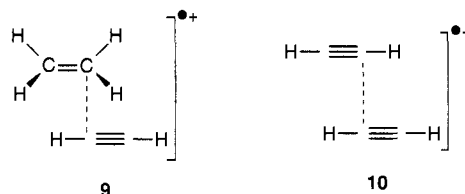
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calculated and observed³⁹ I-I bond energy in **8** ($\text{X} = \text{I}$). The final products of interaction ($\text{X} = \text{F}$) are $\text{CH}_3\text{-FH}^+$ and $\text{CH}_2\text{F}^{\bullet}$ ($\Delta E = -13$ kcal/mol) rather than $(\text{CH}_3)_2\text{F}^+ + \text{F}^{\bullet}$ (-10 kcal/mol).

(vi) For quite some time now, we have been interested in a qualitative discussion (based, e.g., on correlation diagrams) dealing with $\text{C}_2\text{H}_4 + \text{C}_2\text{H}_4^{\bullet+}$, $\text{C}_2\text{H}_2 + \text{C}_2\text{H}_4^{\bullet+}$, and $\text{C}_2\text{H}_2 + \text{C}_2\text{H}_2^{\bullet+}$. Now, together with Prof. Thomas Bally, in our respective laboratories, a more quantitative project is realized. Reaction between ethylene and its radical cation has been intensively studied experimentally. Ethylene radical cation dimer is known to be the primary product (a π -complex bound by about 18 kcal/mol with respect to C_2H_4 and $\text{C}_2\text{H}_4^{\bullet+}$). The mechanism of further transformations, leading to methyl radical and the allyl cation and to the butenyl cation and H atom, was

studied in great detail.⁴⁰ The π -complex decomposes either via cyclobutane radical cation or, via 1,3 H-shift, to the 1-butene radical cation. No minimum corresponding to the frequently postulated tetramethylene radical cation intermediate was found.

Now, along similar lines, a detailed study of PES is carried out for the remaining two processes, including radical cations **9** and **10** as intermediates



9

10

Concluding Remarks

1. Gas-phase interactions between molecules (M) and ions (I) lead frequently to another molecule-ion pair (M', I'). Electron transfer and proton, H-atom, or hydride transfer belong to the most frequent processes. With these systems, and also with species (molecules, ions) not containing hydrogen atoms, formation of a dimer having a two-center three-electron bond is a widespread process. The majority of studied processes have concerned molecule-cation processes.

2. With ion-molecule processes involving hydrogen-containing systems, at least two hydrogen-bonded intermediates are formed, $I \cdots M$ and $I' \cdots M'$ (labeled vdW and vdW' in Figure 1), and these are separated by an activated complex.

3. Processes explicitly including anions are tempting, but well-known difficulties of experimental as well as theoretical treatment of anions are probably responsible for limited activity in this area. The process $\text{BH}_3 + \text{BH}_3^{\bullet-}$ seems, on the basis of calculations, most promising.

4. On the basis of experience various regularities concerning ion-molecule reactivity in the first and second period of atoms have been uncovered.

Summary and Prospects

Passing from the world of molecules into the world of radical ions is just as exciting as passing into the world of electronically excited molecules, i.e., into the realm of photophysics and photochemistry. Indeed, radical ions and electronically excited species do assume some significant common features, e.g., short lifetimes, high reactivity, special physical characteristics, and frequently quite unexpected structural features. Clearly these features are astonishing only seemingly because structural rules concerning molecules in ground states are deeply fixed in our chemical minds.

Ion-molecule gas-phase interactions are ideally suited for molecular beam investigations; this is true of both reactivity and spectroscopy. Combination of experiments with contemporary quantum chemistry computational tools is extremely rewarding and makes progress in the area very rapid. It seems that within a few years it will be possible to offer a very compact

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summary of rules and regularities on ion–molecule reactivity and structural features of radical ions.

In the near future two areas of enhanced activities are to be expected. First, our knowledge concerning regularities in the first and second periods of atoms must be completed by analogous knowledge in groups of the periodic system. Therefore, experimental and quantum chemical investigations of sets of cationic dimers of the $(\text{HX})_2^{*+}$ [$\text{X} = \text{F}, \dots, \text{I}, \text{At}$], $(\text{H}_2\text{Y})_2^{*+}$ [$\text{Y} = \text{O}, \dots, \text{Te}, \text{Po}$] and $(\text{H}_3\text{Z})_2^{*+}$ [$\text{Z} = \text{N}, \dots, \text{Sb}, \text{Bi}$] types is very topical. Both electron correlation and relativistic effects will play a key role in theoretical description. Second, systematic investigations of dimeric radical

anions can fill out another regrettable gap in our chemical knowledge. Radical anions represent a real challenge for both experimentalists and theorists.

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