146. Properties and Reactivity in Groups of the Periodic System: Ion-Molecule Reactions $CH_3X + CH_3X^{+\cdot}$ (X = F through At)

by Rudolf Zahradník* and Libuše Šroubková
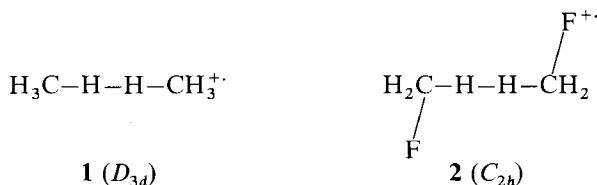
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The reactions indicated in the title have been studied in terms of direct processes and complex formation. Quantum-chemical methods have been applied to the passage of an acid (H^+, CH_3^+, X^+) from $CH_3X^{+\cdot}$ to CH_3X, and the abstraction of a radical ($H^\cdot$, $CH_3^\cdot$, $X^\cdot$) from CH_3X by $CH_3X^{+\cdot}$. It has been shown that a complex represented by a dimer of a methyl-halide radical cation, $(CH_3X)_2^{+\cdot}$, with a two-center three-electron bond X—X, has fairly high stability. These investigations were based on non-empirical quantum-chemical calculations, the results being systematically compared with experimental determinations. Some calculations included all electrons (X=F, Cl, Br), others were based on relativistic pseudopotentials (X=F through At). The two sets of calculations agree qualitatively with each other and with experimental observations.

Introduction. – Although the most familiar interactions in chemistry and molecular physics occur between molecules, ion-molecule interactions are also important [1]. These may occur in solution, with extensive solvation of the ionic species, or in the gas phase (as in molecular beam experiments), where the environment in the absence of solvation is dramatically different.

Ten years ago, a quantum-chemical study elucidated [2] the structure of the metastable radical cation dimer **1** formed by the interaction between CH_4 and its radical cation. This result was confirmed by the independent calculations of *Kamiya* and *Morokuma* [3]. Later, we became interested in the corresponding interactions between CH_3F

$$H_3C-H-H-CH_3^{+\cdot}$$

1 (D_{3d})

$$H_2C-H-H-CH_2 \quad \text{with} \quad \overset{F^{+\cdot}}{\underset{F}{|}} \text{ and } \overset{|}{\underset{F}{|}}$$

2 (C_{2h})

and CH_3Cl and their radical cations [4]. A structurally analogous radical cation, dimer **2**, was identified on the potential-energy surface (PES) of $(CH_3F)_2^{+\cdot}$. It is worth mentioning that the central H—H bond in **1** and **2** is very short (0.92 Å for both the systems), whereas the C—H (central) bonds are somewhat longer than usual (1.28 and 1.31 Å for **1** and **2**, resp.) [4]. The energetics of process (*1*) was studied [4] by more sophisticated methods.

$$CH_3X + CH_3X^{+\cdot} \rightleftharpoons (C_2H_6X_2)^{+\cdot} \rightleftharpoons CH_3XH^+ + CH_2X^\cdot \qquad (1)$$
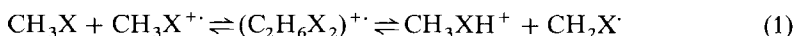
Our attempts to localize a minimum of type **2** on the PES of the methyl-chloride radical cation dimer failed [4]. Although the cited results [4] remain valid, it has been found than *Eqn. 1* does not represent all the important reaction pathways. Here, we are considering one additional intermediate complex (a radical cation dimer with a two-center three-electron (2c–3e) bond; for a more specific information, see [5–7]) and two additional reaction pathways with the entire set of methyl halides.

The reaction between CH_3F and $CH_3F^{+\cdot}$ was studied experimentally by a threshold-electron – secondary-ion-coincidence technique (abbreviated TESICO) [8]. The contribution of the proton-transfer mechanism increases slightly with an increase in the total energy of the reactants. The internal and collision energy dependence for two microscopic reaction mechanisms in the $MH + MH^{+\cdot} = MH_2^+ + M^\cdot$ $(M = CH_4, CH_3F, CH_3Cl)$ process was investigated by the same technique [9]. The two peaks found in the time-of-flight coincidence spectra of the product, MH_2^+, were interpreted in terms of the H abstraction and proton transfer for MH_2^+ formation. By means of mass spectrometry, an exciting gas-phase ion-molecule association, $CH_3I + CH_3I^{+\cdot} \rightleftharpoons H_3C–I–I–CH_3^{+\cdot}$ was analyzed to provide the thermodynamic characteristics of the formation of the 2c–3e bond [10]. In our previous paper [4] (dealing with the F and Cl derivatives), the possibility of formation of the 2c–3e bond was not considered, but related reactions between hydrogen halides and their radical cations have been thoroughly studied in our laboratory [11].

In the present investigation, the mechanisms of the reactions between alkyl halide and alkyl-halide radical cations are studied and compared with the corresponding hydrogen-halide hydrogen-halide radical cation interactions. Structural features, physical properties, and reactivity among the halogens are analyzed, and the description by relativistic pseudopotentials (in comparison with the all-electron treatment) is investigated.

Calculations. – In this study, basis sets, relativistic pseudopotentials, and the degree of refinement employed in the calculations were chosen in the light of our recent work on interaction energies for rare-gas dimerization (He through Rn) [12], hydrogen halide dimerization [13], and reactions between HX and $HX^{+\cdot}$ (F through At in both series) [11] (see *Fig. 1*). As in earlier investigations [11–13], relativistic pseudopotentials (PS) were used in the entire group (F through At), whereas all-electron (AE) calculations were carried out for the derivatives of the three lightest halogens (F through Br). Gaussian 94 program package [14] was used throughout (frozen-core procedure was not adopted) and was connected with the 6-311G ** basis set (AE) [15] or with *Christiansen*'s average relativistic effective pseudopotential (AREP) [16]. The nature of stationary points of the F- and Cl-containing systems was investigated along standard lines [2] [4]. The force-constant matrices permitted also to establish the role of including zero-point energies. It turned out that this role was of negligible importance. Being interested in this study in tendencies in the group of the periodic system and in semiquantitative features of the processes under study, we did not carry out vibrational analyses.

Results. – In general, cation-molecule reactions are associated with the processes outlined in *Scheme 1*. In the case of hydrogen halides, the specification is unambiguous [11], because only one energetically accessible reaction pathway and two intermediate complexes are available. In contrast, three reaction pathways are possible with methyl
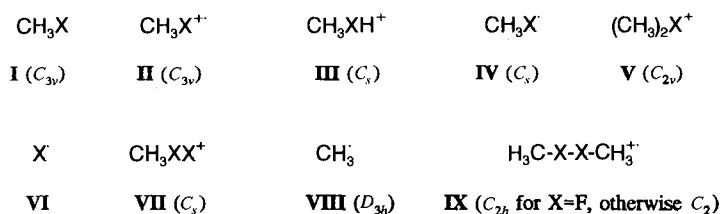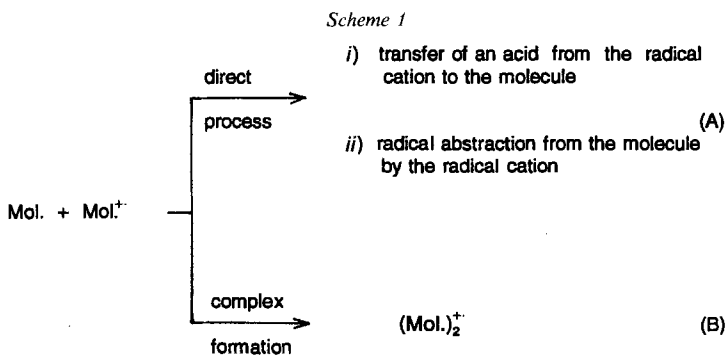
$$CH_3X \qquad CH_3X^{+\cdot} \qquad CH_3XH^+ \qquad CH_3X^\cdot \qquad (CH_3)_2X^+$$

$$\mathbf{I}\ (C_{3v}) \qquad \mathbf{II}\ (C_{3v}) \qquad \mathbf{III}\ (C_s) \qquad \mathbf{IV}\ (C_s) \qquad \mathbf{V}\ (C_{2v})$$

$$X^\cdot \qquad CH_3XX^+ \qquad CH_3^\cdot \qquad H_3C\text{-}X\text{-}X\text{-}CH_3^{+\cdot}$$

$$\mathbf{VI} \qquad \mathbf{VII}\ (C_s) \qquad \mathbf{VIII}\ (D_{3h}) \qquad \mathbf{IX}\ (C_{2h}\ \text{for}\ X{=}F,\ \text{otherwise}\ C_2)$$

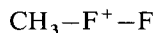Fig. 1. *The molecules, ions, radicals, and radical ions under study*

halides, because three kinds of acidic species can be cleaved from the radical cation: the proton and two *Lewis* acids, the methyl cation, and the halogen cation. Similarly, three different radicals (H$^\cdot$, CH$_3^\cdot$, X$^\cdot$) can be abstracted from the CH$_3$X molecules. These processes are shown in *Scheme 2*.

Scheme 1

Mol. + Mol.$^{+\cdot}$

direct process →
i) transfer of an acid from the radical cation to the molecule
ii) radical abstraction from the molecule by the radical cation
(A)

complex formation → (Mol.)$_2^{+\cdot}$
(B)

Obviously, protonation of CH$_3$X leads either to an X-acid (protonation at the halogen) or to a halogen derivative of the nonclassical cation, CH$_5^+$ (*Reactions 1* and *2* in *Scheme 2*). Abstraction of an H-atom from CH$_3$X leads to the same products. Without isotope labelling, it is not easy to distinguish between proton transfer and H-atom abstraction. The pathways involving H$^+$ (H$^\cdot$), CH$_3^+$ (CH$_3^\cdot$), and X$^+$ (X$^\cdot$) are available in the halogen group (*Scheme 2* and *Fig. 2*). However, in complex formation (*Scheme 2*, *Reactions 5–9*), only *Reaction 7*, the X–X bond formation (2c–3e bond) is of general importance in the entire group.
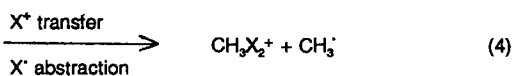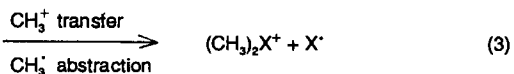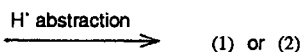
The total MP2 energies (based on all electron and pseudopotential treatments) are given in *Table 1*, the differences needed for construction of the energy profiles (*cf. Fig. 2*) in *Table 2*.

The first member in the group, CH$_3$F, assumes its usual, somewhat special position. Obviously, because of the electronegativity of F, all cationic forms of F-containing species are energetically rather unfavorable. The same is true for systems with σ double-bonded fluorine. The most unfavorable system, **3**, is handicapped in both ways: it is a cation and one of the F-atoms is σ double-bonded. Another special feature of F-containing systems is the occurrence of two types of intermediate complexes. In an earlier

$$CH_3-F^+-F$$
3

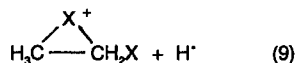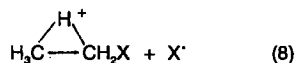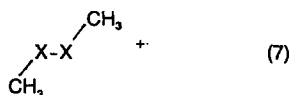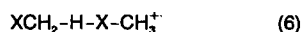Scheme 2

Direct processes (A)

$$CH_3X + CH_3X^{+\cdot} \xrightarrow{\text{H}^+ \text{ transfer}} CH_2X^\cdot + CH_3XH^+ \tag{1}$$

$$\xrightarrow{\phantom{\text{H}^+ \text{ transfer}}} CH_2X^\cdot + CH_4X^+ \tag{2}$$

$$\xrightarrow{\text{H}^\cdot \text{ abstraction}} (1) \text{ or } (2)$$

$$\xrightarrow[\text{CH}_3^\cdot \text{ abstraction}]{\text{CH}_3^+ \text{ transfer}} (CH_3)_2X^+ + X^\cdot \tag{3}$$

$$\xrightarrow[\text{X}^\cdot \text{ abstraction}]{\text{X}^+ \text{ transfer}} CH_3X_2^+ + CH_3^\cdot \tag{4}$$

Complex formation (B)

$$CH_3X + CH_3X^{+\cdot} \rightarrow CH_2\text{-H-H-}CH_2X^{+\cdot} \tag{5}$$

$$XCH_2\text{-H-X-}CH_3^{+\cdot} \tag{6}$$

$$\begin{array}{c} CH_3 \\ / \\ X\text{-}X \quad\quad\quad {}^{+\cdot} \\ / \\ CH_3 \end{array} \tag{7}$$

$$\begin{array}{c} H \quad + \\ / \ \backslash \\ H_3C\text{——}CH_2X \ + \ X^\cdot \end{array} \tag{8}$$

$$\begin{array}{c} X \quad + \\ / \ \backslash \\ H_3C\text{——}CH_2X \ + \ H^\cdot \end{array} \tag{9}$$
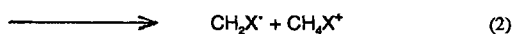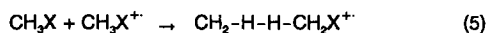
publication [4], we demonstrated the significance of structure **2**, which is a close analog of the well-established complex **1** participating in the $CH_4 + CH_4^{+\cdot}$ interaction [17]. Furthermore, complex **2** corresponds to the deepest minimum on the $C_2H_6F_2^{+\cdot}$ PES. This type of complex has not been found on the PES of systems containing Cl through At. Finally, electron removal from CH_3F presents such an energetic handicap that all the remaining systems (except $CH_3F_2^+ + CH_3^\cdot$) are energetically favored (*Fig. 2*).

In the alkyl halides (Cl through At), only complexes containing the X−X bond were identified; all other imaginable products turned out to be energetically less favorable. The formation of the dimethylhalogen (halonium) cations is feasible in the entire series, with little sensitivity to the identity of the halogen atom. This is the only dependence showing a shallow minimum between F and At, probably due rather to the lack of a tendency of CH_3F to form $(CH_3)_2F^{+\cdot}$ than to the enhanced reactivity of CH_3Cl. Only the F and At derivatives show *two* exothermic reaction paths, in the other cases there is just one. Protonation of CH_3F and CH_3At at the halogen represents the most and least

Table 1. *Total MP2 Energies (H_a) of the Systems under Study*[a]) (see *Fig. 1*)

System									
X	Method[b])	I	II	III	IV	V	VI	VII	IX
F	AE	−139.47556	−139.01593	−139.71748	−138.81027	−178.93373	−99.57262	−238.59225	−278.50954
	PS	−63.88220	−63.42007	−64.10775	−63.22271	−103.28965	−24.02864	−87.46137	−127.32348
Cl	AE	−499.49411	−499.08478	−499.74830	−498.82877	−538.97673	−459.63376	−958.78848	−998.62325
	PS	−54.62690	−54.21868	−54.86632	−53.96924	−94.05605	−14.82634	−69.10998	−108.89099
Br	AE	−2612.68962	−2612.30568	−2612.94789	−2612.02278	−2652.17813	−2572.84616	−5185.22571	−5225.04293
	PS	−52.99967	−52.61988	−53.24684	−52.34053	−92.43519	−13.21533	−65.90535	−105.66653
I	PS	−51.02140	−50.67289	−51.27542	−50.36045	−90.46439	−11.25628	−61.99030	−101.72790
At	PS	−50.66091	−50.33056	−50.91479	−49.99971	−90.04777	−10.96743	−61.34638	−101.03233

[a]) Total energies for **VIII**: −39.72567 (AE), −39.66963 (PS). [b]) AE = all-electron, PS = pseudopotential.

Table 2. *Energy Differences Required for Energy Profile Construction* (in kJ/mol)

X[a])	Method	ΔE			
		1	3	4	7
F	AE	−95.0	−38.9	455.5	−47.3
	PS	−73.7	−41.9	449.7	−55.7
CL	AE	4.6	−82.9	170.0	−116.4
	PS	26.4	−96.7	173.3	−119.3
Br	AE	64.9	−76.2	115.1	−125.2
	PS	84.6	−81.2	116.8	−123.5
I	PS	153.2	−69.1	90.4	−114.3
At	PS	201.8	−62.4	−64.5	−107.2

[a]) Halogen atom in the species participating in *Reactions 1, 3, 4,* and *7* (see *Scheme 2*).
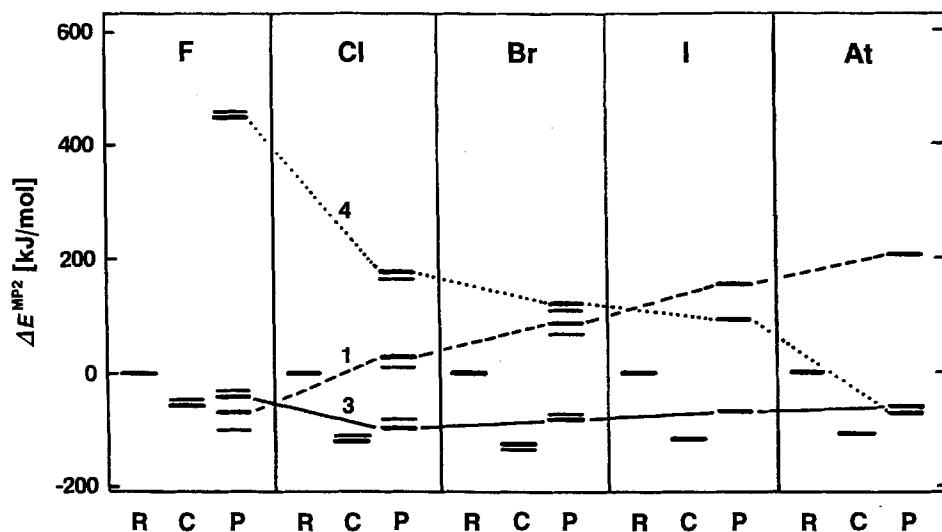

Fig. 2. *Energy profiles of* Process 1, 3, *and* 4 (protonation, methylation, and halogenation) *of CH₃X based on ΔE values obtained with pseudopotentials; for X=F, Cl, Br, also ΔE based on all-electron calculations are presented* (thin lines). R, C, and P mean reactants, complex having a 2c−3e bond, and products, respectively.

convenient pathway, respectively. On the other hand, although the $CH_3FF^+ + CH_3^-$ formation is energetically unfavorable, the analogous process (2) with X = At is exothermic by *ca.* 64.5 kJ/mol. Semiquantitative considerations are offered below.

$$CH_3At + CH_3At^{+\cdot} \rightleftharpoons CH_3AtAt^+ + CH_3^- \qquad (2)$$

The essential geometric characteristics of the systems under study are shown in *Table 3*, the electric dipole moments in *Table 4*.

Table 3. *Selected Bond Lengths* [Å], *Bond Angles, and Dihedral Angles* (both in Degrees) *of the Systems under Study*

System		I[a])			II	III			IV		
X	Method	C–X	C–H	HCX	C–X	C–X	X–H	CXH	C–X	C–H	HCX
F	AE	1.380	1.091	109.2	1.295	1.594	0.943	116.4	1.339	1.081	114.4
	PS	1.401	1.090	108.2	1.312	1.621	0.970	117.1	1.359	1.081	113.3
Cl	AE	1.775	1.088	109.0	1.757	1.840	1.294	99.3	1.700	1.077	117.5
	PS	1.785	1.087	108.6	1.782	1.855	1.303	100.4	1.709	1.078	116.8
Br	AE	1.932	1.087	108.4	1.933	1.978	1.427	96.9	1.849	1.078	117.4
	PS	1.947	1.087	108.0	1.955	1.994	1.441	96.8	1.863	1.079	116.9
I	PS	2.160	1.087	107.8	2.164	2.183	1.634	96.4	2.066	1.079	117.6
At	PS	2.371	1.090	105.7	2.400	2.413	1.750	92.7	2.270	1.084	115.1

System		V		VII			IX			
X	Method	C–X	CXC	C–X	X–X	CXX	C–X	X–X	CXX	CXXC
F	AE	1.513	119.6	1.655	1.423	108.5	1.431	1.941	107.0	180.1
	PS	1.531	119.8	1.700	1.436	106.8	1.463	1.898	105.2	180.1
Cl	AE	1.810	102.9	1.814	2.024	102.5	1.793	2.626	99.3	124.4
	PS	1.823	103.5	1.838	2.030	102.8	1.807	2.602	99.2	159.8
Br	AE	1.955	99.6	1.962	2.300	100.1	1.948	2.845	96.5	110.0
	PS	1.971	99.5	1.982	2.300	100.4	1.965	2.846	97.8	116.2
I	PS	2.167	95.9	2.177	2.707	97.8	2.169	3.250	94.7	106.0
At	PS	2.398	95.2	2.410	2.965	96.2	2.386	3.441	95.8	105.4

[a]) Experimental values for the three geometry characteristics are: for X = F: 1.39, 1.09, 110; for X = Cl: 1.78, 1.11, 111; for X = Br: 1.94, 1.11, 111; for X = I: 2.16, 1.10, 111.5. (From *Tables of Interatomic Distances*, Special Publ. No. 11, The Chemical Society, London, 1958.)

Table 4. *Observed*[a]) *and MP2-Calculated Dipole Moments of Methyl Halides* (in Debyes). The values for the corresponding hydrogen halides are in parentheses [11].

X	F	Cl	Br	I	At
μ (AE)	2.14	2.25	2.16		
μ (PS)	2.38	2.41	2.17	1.98	2.10
μ (exp.)[a])	1.85 (1.82)	1.87 (1.08)	1.81 (0.82)	1.62 (0.44)	

[a]) 'Handbook of Chemistry and Physics', 57th edn., CRC Press, Cleveland, Ohio, 1976–1977; A.L. McClellan, in 'Tables of Experimental Dipole Moments', W.H. Freeman, San Francisco, 1963.

Discussion. – *Reactivity.* In contrast to the methane radical cation dimer, complexes of type **IX** (with the 2c–3e bond) assume a nonlinear structure with C_{2h} or C_2 symmetry (*vide infra*). Except for the F derivative, they are stabilized (ΔE) by *ca.* 107–125 kJ/mol. Specifically, a ΔE for **IX** (X = I) amounts to –114.3 kJ/mol (*Table 2*), which agrees well with the experimental enthalpy change of –96 to –109 kJ/mol at 503 K [10]. In addition, the calculated entropy change (–98.8 J/mol K) matches the experimental value (–83.7 to –104.7 J/mol K). The significantly smaller stabilization energy of –47.3 kJ/mol for **IX** (X = F) (*Table 2*), is obviously due to the lack of a tendency to form an F–F bond. Indeed, the $(CH_3F)_2^{+\cdot}$ prefers [4] a structure possessing an H–H bond. Its stabilization energy, using a basis set closely related to our (MP2/6-31G**), is –59.5 kJ/mol. It should again be stressed that we did not succeed in identifying this type of dimer (with an H–H bond) with any $(CH_3X)_2^{+\cdot}$ system containing the heavier halogens.

Reaction 1 (*Scheme 2*), with protonation of the halogen atom, is energetically favorable only for CH_3F. Indeed, the protonated form of methyl fluoride, CH_3FH^+, is the most stable product in the $CH_3F + CH_3F^{+\cdot}$ interaction. The reactivity of the heavier halogen-containing species (in the sense of *Reaction 1*) rapidly falls between F and At. The trend of the experimental heats of reaction (obtained from the heats of formation [18]) is matched by the calculated energy change (*Table 5*). Protonation leading to non-classical ions CH_4X^+ is energetically more demanding.

Table 5. *Experimental Heats of Reaction and MP2 Energy Changes of Protonation of Alkyl Halides by* $CH_3X^{+\cdot}$: $CH_3X + CH_3X^{+\cdot} \rightleftharpoons CH_3XH^+ + CH_2X^\cdot$ *in kJ/mol*

X	ΔH_{298}[a])	ΔE (AE)	ΔE (PS)
F	–62.8	–95.0	–73.7
Cl	–22.6	4.81	26.4
Br	33.9	64.9	84.6
I			153.2
At			201.8

[a]) Values calculated from experimental heats of formation [18].

Reaction 3 (*Scheme 2*), connected with the CH_3^+ (or CH_3^-) transfer, is exothermic throughout the series. The exothermicity depends little on the identity of the halogen. In *Table 6*, the calculated ΔE (*cf. Table 2*) and the observed ΔH_{298} values are compared; agreement is satisfactory. The ΔH_{298} values were again derived from the respective experimental ΔH_f values [18]. These are less reliable than for *Reaction 1*, having been estimated [18] from the results of a study of the gas-phase stabilities of halonium ions [19] (this paper is incorrectly quoted in [18]). This is true of ΔH_f for $(CH_3)_2F^+$ and $(CH_3)_2Cl^+$. Moreover, our estimated values for $(CH_3)_2Br^+$ and $(CH_3)_2I^+$ are based on the heats of formation of the isomeric species.

The calculated protonation energies of both methyl and hydrogen halides are in approximate agreement with the experimental proton affinities [20] (*Table 7*). The proton affinity (*PA*), that is, the tendency to protonation, increases between F and At; the values for I and At derivatives are practically identical. The *PA* for CH_3X is higher than for HX; this is obviously due to an electron shift from CH_3 to X in methyl halides. This effect is also clearly visible for the ionization potentials (*IP*) shown in *Table 8*. The decrease in the ionization potential from F to At is given by both sets of calculations.

Table 6. *Experimental Heats of Reaction and MP2-Calculated Energy Changes of Formation of Dimethylhalogen Cations:* $CH_3X + CH_3X^{+\cdot} \rightleftharpoons (CH_3)_2X^+ + X^{\cdot}$ *in kJ/mol*

X	ΔH_{298}[a])	ΔE (AE)	ΔE (PS)
F	−14.7	−38.9	−41.9
Cl	−74.9	−82.9	−96.7
Br	(−84.8)[b])	−76.2	−81.2
I	(−64.5)[b])		−69.1
At			−62.4

[a]) Values calculated from experimental heats of formation [16].　[b]) Estimated values, *cf.* the text.

Table 7. *Experimental Proton Affinities (PA)* [20] *and MP2-Calculated Protonation Energies of Alkyl Halides in kJ/mol. Values for the respective hydrogen halides in parentheses* [11].

X	PA	−ΔE (AE)	−ΔE (PS)
F	628	635.1	592.0
	(490)	(522.9)	(499.1)
Cl	703	667.4	628.4
	(564.4)	(552.7)	(556.4)
Br	693.8	677.8	649.0
	(569.4)	(571.9)	(573.2)
I	716		667.0
	(628)		(600.0)
At			666.5
			(602.5)

Table 8. *Observed* [18] *and Calculated Adiabatic Ionization Potentials of Methyl Halides in kJ/mol. Values in parentheses correspond to the parent hydrogen halides* [11].

X	F	Cl	Br	I	At
AE	52.34	46.60	43.71		
	(64.18)	(51.08)	(47.69)		
PS	52.59	46.52	43.25	39.69	37.60
	(65.27)	(51.08)	(47.60)	(43.17)	(40.65)
exp	52.21	46.98	44.13	39.94	
	(67.16)	(53.38)	(48.82)	(43.50)	

Electron Distribution and Geometry. Mulliken atomic populations do not provide ideal information about electron density. However, these populations do describe tendencies with essential correctness, which is important here (*Fig. 3*). The only system in which a F-atom bears a positive charge is that with the central F-atom in system **VII** (X = F). The only system in which the I-atom has a surplus negative charge is CH_3I (**I**, X = I). As a first approximation, the population changes gradually between F and I derivatives. As might be expected from halogen electronegativities, the difference between the population of F- and Cl-atoms is always the most significant. For all the
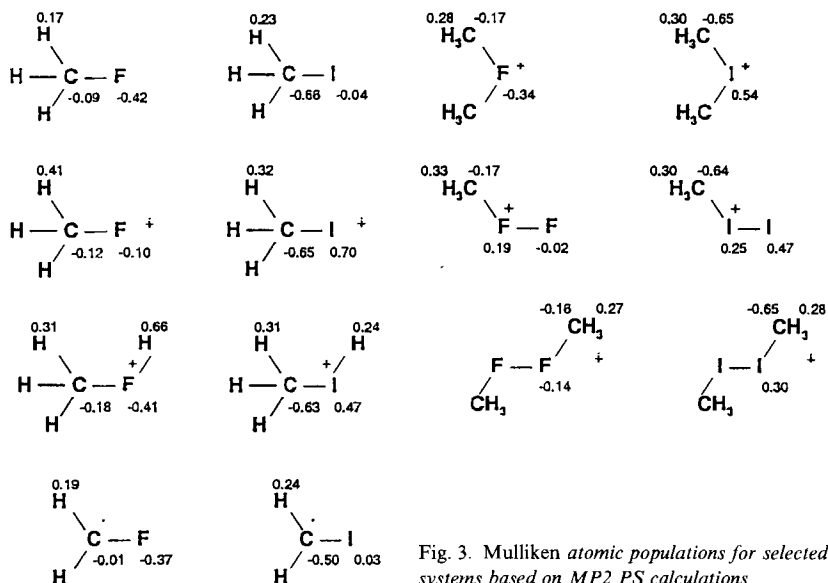
Fig. 3. Mulliken *atomic populations for selected systems based on MP2 PS calculations*

systems under study, the extreme value in the atomic population attained for I; for At, reverses the trend. The dependence of the ionization potentials of the atoms, mentioned below is helpful in evaluating the reliability of the observed values.

Both sets of calculations match the observed bond lengths and angles for methyl halides. The σ double bonding of halogen atoms is worth mentioning (systems **III, V, VII, IX**). In all cases, the angles associated with X (the halogen atom) assume values close to those typical for sp^2 hybridization (systems **III** and **V**) or sp^3 hybridization (systems **VII** and **IX**) for the F derivatives. In the F–At sequence, the values typical for hybridization gradually change to those which are typical for bonding through nonhybridized p_z orbitals. The dihedral angle, CXXC, for **IX** also deserves attention. System **IX** is planar for X = F (C_{2h}), whereas all the remaining systems are structurally related to hydrogen peroxide (C_2).

Extension Beyond the Region of Classical Elements. We have long believed that quantum-chemical interpretations and predictions have a significant value for experimentalists. Experimental work on transuranium elements will probably be always severely limited [21–25] primarily because of spontaneous decay. Only a few atoms were obtained [22] for recently prepared elements having $Z = 110$ and 111 and probably also $Z = 112$. However, islands of stability might exist in the region of superheavy elements with nuclei in which both protons and neutrons assume 'magic' values ('double magic' nuclei) [25]. These regions of stability are expected to be near elements with $Z = 114$ and 164.

In this context, two elements may be mentioned, eka-astatine ($Z = 117$) and the element with $Z = 171$; both belong to the VIIb group. It would be difficult but interesting to predict the properties of molecules containing these elements. In any case, such an undertaking requires reliable pseudopotentials. In *Fig. 4*, the ionization potentials and

electron affinities are plotted against the position of the atom in the group, which is, of course, merely a semiquantitative parameter. To increase the significance of this plot, data for VIb elements and rare gases have been included; electron affinities have also been considered. All exhibit a break, experimental ionization potentials and electron affinities [26] as well as those calculated for the superheavy elements [25]. Nonetheless, the breaks are most probably real. Attempts to interpret this phenomenon are under way in our laboratory.
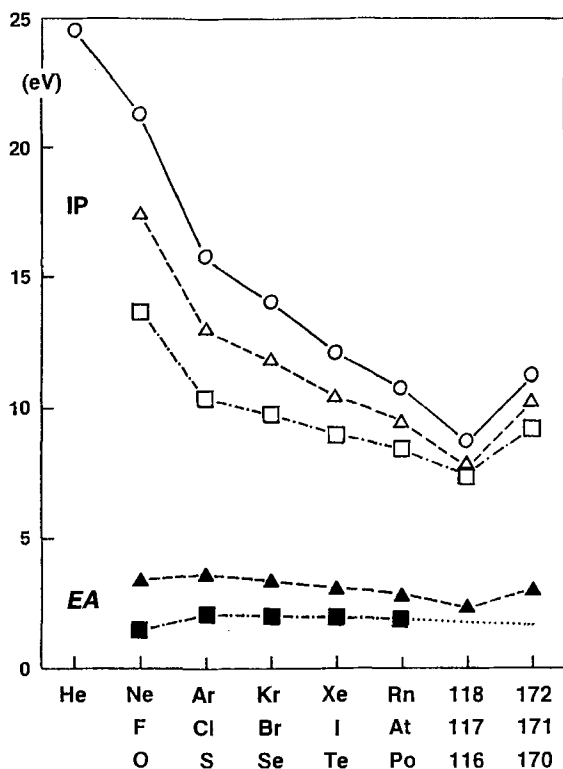

Fig. 4. *Ionization potentials* (empty symbols) *and electron affinities* (full symbols) *of atoms plotted against position of the atoms in the Groups VIb* (squares), *VIIb* (triangles), *and 0.* The characteristics for atoms with $Z < 100$ are experimental [22] for atoms with $Z > 100$ calculated.

Conclusions. – *1*) Gas-phase reactions between alkyl halides (CH_3X, X = F through At) and the corresponding radical cations lead to *i*) protonated CH_3X, *ii*) dimethylhalonium cations, and *iii*) halogenated methyl halides, CH_3X-X^+. These transformations may occur by transfer either of an acidic species from $CH_3X^{+\cdot}$ to CH_3X or of a radical from CH_3X to $CH_3X^{+\cdot}$.

2) In all instances a radical cation dimer, $(CH_3X)_2^{+\cdot}$, represents a minimum on the potential energy surface. For X = Cl through At, the dimer is at a global minimum. Only in case of the F derivative, a dimer possessing the $-C-H-H-C-^{+\cdot}$ bridge represents a global minimum. We attempted without success to identify analogous dimer structures for the heavier halogen systems.

3) The importance of the individual reaction pathways (*cf. 1* above) changes dramatically from F to At derivatives. Protonation on F is highly favored energetically, but not on CH_3At. On the contrary, formation of CH_3At-At^+ is exoenergetic, whereas formation of CH_3-F-F^+ is significantly endoenergetic and, therefore, not to be expected. The formation of dimethylhalonium cations is exothermic throughout with little dependence on the identity of the halogen.

4) For the systems under study, quantum-chemical calculations are in fair agreement with experimental heats of reaction and physical properties. An attempt was made to use quantum chemistry for both, interpretations and predictions.

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