

CALCULATION OF REACTION ENERGIES FOR ION-MOLECULE PROCESSES OF FIRST-ROW IONS AND THEIR HYDRIDES

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Dedicated to late Academician Eduard Hála.

Reaction energies calculated by quantum chemical methods are compared with reaction enthalpies obtained on the basis of experimental heats of formation. Fifty six ion-molecule reactions ($X^+ + H_2$, $XH^+ + H_2$, where X is boron, carbon, or nitrogen, and reactions involving $C_2H_2^{*+}$, $C_2H_4^{*+}$, and $C_2H_6^{*+}$) have been arranged into structurally related sets. Moreover, nine processes important in connection with the C_2H_2 formation in interstellar clouds are treated.

Reaction enthalpies represent an important basic information on reactive processes. Reaction enthalpy is defined as a difference between the sums of heats of formation (ΔH_f) of products (p) and reactants (r) of a process (R) in question

$$\Delta H_R = \sum(\Delta H_f)_p - \sum(\Delta H_f)_r.$$

Enthalpies have been generally used for ion-molecule processes in the single-collision limit, because under these extreme non-equilibrium conditions it is energy, in its various forms, which makes the reaction go.* Information on reaction enthalpies come mostly from spectroscopic data, measurements of ionization potentials of atoms, molecules and radicals and appearance potentials of ions; thermochemical cycles, employing in addition standard heats of formation of neutrals, are used to derive the respective quantities for ions. In some cases, like in the estimation of proton affinities, kinetic data, occurrence or non-occurrence of a series of suitably chosen ion-molecule reactions, have been used. Thermochemical data on isomeric ions have been obtained by analysis of experimental data and kinetics of particular processes in which the formation of the species in question is unambiguous. The over-all accuracy of estimation of reaction enthalpies is, at the present time, within a few kcal/mole in favourable cases.

* For a recent discussion of reaction enthalpy and reaction Gibbs energy changes in ion-molecule processes, evaluation of temperature dependence of reaction rate constants under many-collision conditions, *entropy-driven* reactions etc. see, e.g., ref.¹.

However, it is remarkable, how many values of reaction enthalpies remain quite uncertain. This holds in particular for reactions of small ionic species which originate from molecules by extensive fragmentation. The appearance potential measurements may lead then to considerable overestimation of the heat of formation of ions in question. Very often then confrontation of experimental data with results of theoretical calculations becomes very useful.

Theoretical calculations of thermochemical data on ions have become a valuable source of information in particular for supplying missing and needed data. A certain problem arises in connection with various methods used in obtaining particular data and accuracy of calculated values of different origin.

Therefore, we find it useful to summarize series of calculations over a set in homological series by one particular theoretical method, comparing trends and internal consistency of data in such a series, and confronting the data with experimental values, whenever possible. One expects that in this way general tendencies, relative accuracy of data as well as occasional deficiency (or even breakdown) of calculation procedure may emerge.

The aim of this paper is to summarize data on experimental reaction enthalpies and calculated reaction energies (i.e. zero-point energies are not involved) of ion-molecule processes of the first-row cations and their hydrides with hydrogen, and of the cations of acetylene, ethylene and ethane with hydrogen and various neutral partners, including CH, CH₃ etc. (Table I). In connection with investigating the role of ion-molecule processes for evolution of molecular species in dense interstellar clouds, formation of acetylene was pointed out specifically². Table II concerns energetics of the possible processes involved.

Whenever possible, calculated values of reaction energies are accompanied by reaction enthalpy values derived from tabulated or experimentally determined heats of formation of the species involved.

RESULTS

The calculations were performed along the same lines as described recently in detail³. In addition, it turned out that many of needed quantum chemical energy values were available in *Archive* by Pople and co-workers⁴. In the present work we are interested rather in tendencies than in attempts to reach the best quantitative agreement between calculated and observed energy characteristics. Therefore, zero-point energies and temperature effects are not considered in the calculated data. Another, more quantitative consideration is in preparation.

All reaction energies and enthalpies are given in kcal/mole (1 kcal/mole = 4.184 kJ/mole). For our discussion only the MP2/SCF characteristics are important. Nonetheless, the SCF characteristics are presented, too, in order to suggest the role the correlation energy plays in the treatment of the reactions under study: in the tables,

TABLE I

Calculated reaction energies of ion-molecule processes and comparison with available thermochemical data (kcal/mole)

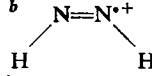
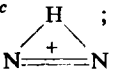
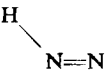
Reaction	SCF ^a	MP2/SCF	Exp.	Ref.	Eq.
$B^+(^1S) + H_2(^1\Sigma^+) \rightleftharpoons B(^2S) + H_2^+(^2\Sigma)$	156.17	171.00	164.5	5	(1)
$\rightleftharpoons BH_2^+(^1)$ (association)	-67.77	-66.21	-52	6	(2)
$\rightleftharpoons BH^+(^2\Sigma) + H(^2S)$	31.83	49.25	63	5	(3)
			56.7	6	
$\rightleftharpoons BH(^1S) + H^+$	150.09	157.00	147.5	5	(4)
$C^+(^2P) + H_2(^1\Sigma^+) \rightleftharpoons C(^1) + H_2^+(^2\Sigma)$	105.78	118.68	96.3	5	(5)
$\rightleftharpoons CH_2^+(^2A_1)$ (association)	-95.50	-100.78	-98	5	(6)
$\rightleftharpoons CH^+(^1\Sigma^+) + H(^2S)$	14.21	13.54	0.2	7	(7)
			24.1	5	
			13.1	9	
$\rightleftharpoons CH^+(^2\Pi) + H^+$	92.95	91.08	77.4	5	(8)
$N^+(^3P) + H_2(^1\Sigma^+) \rightleftharpoons N(^4S) + H_2^+(^2\Sigma)$	14.82	20.81	21	5	(9)
$\rightleftharpoons NH_2^+(^3B_1)$ (association)	-133.97	-147.58	-144	5	(10)
$\rightleftharpoons NH^+(^2\Pi) + H(^2S)$	9.16	5.58	(9.9)	5	(11)
			(~0)	8, 10	
$\rightleftharpoons NH(^3\Sigma^-) + H^+$	25.66	10.55	-3	5	(12)
$BH^+(^2\Sigma) + H_2(^1\Sigma^+) \rightleftharpoons BH(^1\Sigma) + H_2^+(^2\Sigma)$	142.49	148.50	130.5	5	(13)
			137	6	
$\rightleftharpoons BH_3^+(^2)$ (association)	-19.53	-23.12	(54)	5	(14)
$\rightleftharpoons BH_2^+(^2A_1) + H^+$	129.97	117.89	(81)	5	(15)
$\rightleftharpoons BH_2^+(^1) + H(^2S)$	-14.97	-14.31	-2.9	5	(16)

$\text{CH}^+(^1\Sigma^+) + \text{H}_2(^1\Sigma^+) \rightleftharpoons \text{CH}^+(^2\Pi) + \text{H}_2^+(^2\Sigma^+)$	102.97	118.29	99.4	5	(17)
$\rightleftharpoons \text{CH}_3^+(^1A_1)$ (association)	-130.16	-138.02	110	9	
$\rightleftharpoons \text{CH}_2(^1A_1) + \text{H}^+$	81.14	80.76	-139	5	(18)
$\rightleftharpoons \text{CH}_2(^3B_1) + \text{H}^+$	64.87	67.33	-128	9	
$\rightleftharpoons \text{CH}_2^+(^2A_1) + \text{H}^+(^2S)$	-25.08	-13.17	70	5	(19)
			81	9	
			60.7	5	(20)
			72	9	
			-10.9	5	(21)
			~0	9	
$\text{NH}^+(^2\Pi) + \text{H}_2(^1\Sigma^+) \rightleftharpoons \text{NH}(^1\Delta) + \text{H}_2^+(^2\Sigma^+)$	87.96	87.55	-	-	(22)
$\rightleftharpoons \text{NH}(^3\Sigma^-) + \text{H}_2^+(^2\Sigma^+)$	40.74	45.73	46	10	(23)
			53	5	
$\rightleftharpoons \text{NH}_3^+(^2A_2'')$ (association)	-164.94	-184.14	-174	5, 10	(24)
$\rightleftharpoons \text{NH}_2^+(^2B_1) + \text{H}^+$	35.91	15.97	10	5, 10	(25)
$\rightleftharpoons \text{NH}_2^+(^3B_1) + \text{H}^+(^2S)$	-7.07	-13.13	-37	10	(26)
			-22	5	
$\text{H}_2^+(^2\Sigma) + \text{N}_2(^1\Sigma^+) \rightleftharpoons \text{H}_2(^1\Sigma^+) + \text{N}_2^+(^2\Sigma^+)$	25.78	-8.33	3	5	(27)
$\rightleftharpoons \text{N}_2\text{H}_2^+(^2)^b$ (association)	-104.49	-84.70	(-59)	5	(28)
$\rightleftharpoons \text{HN}_2^+(^1)^c + \text{H}^+(^2S)$	-60.25	-63.28	-52.4	5, 11	(29)
$\rightleftharpoons \text{HN}_2^+(^2)^d + \text{H}^+$	68.63	79.27	-	-	(30)
$\text{H}_2(^1\Sigma^+) + \text{N}_2^+(^2\Sigma^+) \rightleftharpoons \text{HN}_2^+(^1)^c + \text{H}^+(^2S)$	-86.03	-54.96	-55.4	5, 11	(31)
$\rightleftharpoons \text{HN}_2^+(^2)^d + \text{H}^+$	42.85	87.60	-	-	(32)

TABLE I
 (Continued)

Reaction	SCF ^a	MP2/SCF	Exp.	Ref.	Eq.
$C_2H_2^+(^2\Pi_u) + CH(^2\Pi) \rightleftharpoons C_2H_2(^1\Sigma^+) + CH^+(^1\Sigma^+)$	9.05 ^a	-15.95	-17.2	5, 9	(33)
$\rightleftharpoons C_3H_3^+(^1)$ (association)	-175.21 ^a	-218.08	-204 ^e	5, 12	(34)
$\rightleftharpoons C_2H^*(^2) + CH_2^+(^2A_1)$	7.23 ^a	9.25	-15	5	(35)
$\rightleftharpoons C_2H^+(^3) + CH_2(^1A_1)$	31.39 ^a	46.18	33	5	(36)
$\rightleftharpoons C_2H^+(^1) + CH_2(^3B_1)$	49.90 ^a	64.31	-	-	(37)
$C_2H_2^+(^2\Pi_u) + CH_3(^2A_2) \rightleftharpoons C_2H_2(^1\Sigma^+) + CH_3^+(^1A_1')$	-16.70 ^a	-36.94	-36	5	(38)
$\rightleftharpoons C_3H_5^+(^1)^f$ (association)	-107.52 ^a	-133.11	-134	5	(39)
$\rightleftharpoons C_3H_5^+(^1)^g$ (association)	-64.62 ^a	-102.86	-111	5	(40)
$\rightleftharpoons C_3H_3^+(^1) + H_2(^1\Sigma^+)$	-70.27 ^a	-101.39	-95	5	(41)
$\rightleftharpoons C_2H^*(^2) + CH_4^*(^2)$	106.36 ^a	109.63	36	5	(42)
$\rightleftharpoons C_2H^+(^1) + CH_4(^1A_1)$	62.69 ^a	64.89	(31)	5	(43)
$C_2H_2^+(^3\Pi_u) + C_3H_3(^1\Sigma^+) \rightleftharpoons C_3H_3^+(^1) + CH^*(^2\Pi)$	5.49 ^a	25.03	26	5, 12	(44)
$\rightleftharpoons C_2H^*(^2) + C_2H_3^+(^1)$	27.54 ^a	49.64	10	5	(45)
$\rightleftharpoons C_2H^+(^1) + C_2H_3^*(^2)$	102.69 ^a	144.31	(93)	5	(46)
$C_2H_2^+(^2\Pi_u) + C_2H_4(^1A_g) \rightleftharpoons C_2H_2(^1\Sigma^+) + C_2H_4^+(^2)$	-22.32 ^a	-22.11	-22.3	5	(47)
$\rightleftharpoons C_3H_5^+(^1) + CH^*(^2\Pi)$	22.87 ^a	40.75	29	5	(48)
$\rightleftharpoons C_3H_3^+(^1) + CH_3^*(^2A_2'')$	-44.82 ^a	-44.22	-41.3	5	(49)

$C_2H_4^+(^2) + CH_3(^2A_2'')$	$\rightleftharpoons C_3H_7^+(^1)^h$ (association)	-49.83 ^a	-93.07	-88	5, 11	(50)
	$\rightleftharpoons C_3H_7^+(^1)^i$ (association)	-50.07 ^a	-79.73	-77	5	(51)
	$\rightleftharpoons C_2H_4(^1) + CH_3^+(^1A_1')$	5.62 ^a	-14.82	-14	5	(52)
$C_2H_4^+(^2) + C_2H_4(^1A_g)$	$\rightleftharpoons C_2H_3^+(^2) + C_2H_5^+(^1)$	26.69 ^a	35.63	19	5	(53)
	$\rightleftharpoons C_2H_3^+(^1) + C_2H_5^+(^2)$	37.76 ^a	31.70	29	5	(54)
$C_2H_6^+(^2) + C_2H_6(^1)$	$\rightleftharpoons C_2H_5^+(^2) + C_2H_7^+(^1)$	15.19 ^a	10.36	1	5, 11	(55)
	$\rightleftharpoons C_2H_5^+(^1) + C_2H_7^+(^2)$	203.07 ^a	201.78	-	-	(56)

^a 6-31G** values, 6-31G* values are labeled "a"; ^b ; ^c ; ^d ; ^e cyclopropenylium; ^f allyl; ^g corner protonated

cyclopropene; ^h edge-protonated cyclopropane; ⁱ 1-propyl radical.

TABLE II
Calculated reaction energy of ion-molecule processes of interstellar interest²

Process ²	Reaction	SCF ^a	MP2/SCF	Exp.	Ref.	Eq.
C ⁺ ↓	C ⁺ (² P) + CH ₂ (¹ A ₁) → C ₂ H ⁺ (¹) + H ⁺ (² S)	-40.02	-59.76	(-61)	4	(57)
	C ⁺ (² P) + CH ₂ (³ B ₁) → C ₂ H ⁺ (³) + H ⁺ (² S)	-25.45	-44.72	-	-	(58)
	C ⁺ (² P) + CH ₃ (² A ₁ ') → C ₂ H ⁺ (¹) + H ₂ (¹ Σ ⁺)	-5.49	-22.51 ^b	-65	4	(59)
C ₂ H ⁺ ↓	C ₂ H ⁺ (¹) + H ₂ (¹ Σ ⁺) → C ₂ H ₂ ⁺ (² Π _u) + H ⁺ (² S)	-65.81	-71.42 ^b	-26	4	(60)
	C ⁺ (² P) + CH ₄ (¹ A ₁) → C ₂ H ₂ ⁺ (² Π ₁) + H ₂ (¹ Σ ⁺)	-68.71	-86.09	-96	4	(61)
C ₂ H ₂ ⁺ ↓	C ₂ H ₂ ⁺ (² Π _u) + H ₂ (¹ Σ ⁺) → C ₂ H ₃ ⁺ (¹) + H ⁺ (² S)	4.36	4.44	8	4	(62)
	C ⁺ (² P) + CH ₄ (¹ A ₁) → C ₂ H ₃ ⁺ (¹) + H ⁺ (² S)	-64.34	-81.65	-88	4	(63)
C ₂ H ₃ ⁺ ↓	C ₂ H ₃ ⁺ (¹) + e(²) → C ₂ H ₂ (¹ Σ ⁺) + H ⁺ (² S)	-142.43	-157.02	-159	4	(64)
	C ₂ H ₃ ⁺ (¹) + NH ₃ (¹) → C ₂ H ₂ (¹ Σ ⁺) + NH ₄ ⁺ (¹) ^c	-49.40	-61.99	-53	4, 11	(65)
C ₂ H ₂						

^a 6-31G**. ^b It is worth-mentioning that when passing to more sophisticated calculations C_{2v} instead of C_{∞v} structure becomes minimum for C₂H⁺; this could cause heavy discrepancy between calculated and experimental values. ^c An example of proton-transfer, terminating reaction.

the first value concerns SCF (either 6-31G* or 6-31G**) and the second one is the MP2/SCF value.

The species involved in the ion-molecule processes are specified (in parentheses after the species) by their simplified spectroscopic notation or at least by their spin multiplicity.

Last columns of the tables summarize reaction enthalpies calculated from generally accepted tabulated⁵ or literature data on heats of formation of the species in question which, in turn, are based on experimentally determined quantities. In some cases, newer data from the current literature have been used, and several values are then listed with one process, with respective references. These data show sometimes a remarkable spread of values, even for simple processes. If the reaction enthalpy is questionable (because the heat of formation of an ion may be in doubt), the observed value is given in parenthesis.

DISCUSSION

The agreement between calculated energy values and values obtained from thermochemical tabulated data of reaction enthalpies of more than sixty ion-molecule processes is reasonably good. In some instances of importance, in particular where thermochemical data are well established (e.g., processes (6), (9), (29), (33),(38), (39), (44), (47), (52)) the agreement with the calculated MP2/SCF values is quite remarkable and may be used in estimating the probable structure of the isomeric ion product (reactions (34), (39), (44), (51)) or in deciding between several other estimations of a reaction enthalpy (reaction (7)).

In several instances a disagreement stems from a uncertain value of the heat of formation of an ion. This is presumably the case with reactions involving C_2H^+ and C_2H^* species ($\Delta H_f(C_2H^+) = 399$ kcal/mole (ref.⁴) appears to be too high). Also, data on some reactions involving C^{*+} , CH^+ seem to show a rather large scatter of results.

Table II concerns a series of reactions thought to be of possible importance in the build-up of molecular species in interstellar clouds². The remarkable feature of the set of reactions leading to C_2H_2 is that, except for one process (reaction (62)), all are exoergic. The reaction in question is between acetylene radical cation and hydrogen molecule. The cited authors note that it is almost thermoneutral and believed to be of importance because of high density of hydrogen in the clouds. Reaction (65) is just one representative of a possible proton-transfer process; the authors² mention also reactions with H_2O , HCN , and H_2CO .

It would be premature to try to go at present farther in comparison between calculated and observed energy characteristics. This will be topical after improving calculated energy values (more extensive basis set, MP calculations through fourth order, inclusion of zero-point energy, consideration of temperature effects) and

analyzing more critically experimental enthalpies values. However, on the basis of partial investigation along these lines it is possible to say that no dramatic changes are to be expected.

It is a privilege of the authors to contribute to this volume and dedicate this contribution to late Academician Eduard Hála on the occasion of his unattained seventieth birthday. One of the authors (R.Z.) appreciates that forty years ago E. Hála, a young teacher at the Technical University, devoted more than one hour to explain to him, a beginning student then, that chemistry in the second half of the twentieth century would be significantly influenced by the impact of quantum and statistical mechanics. The other author (Z. H.) gratefully acknowledges constant stimulation from contacts with Professor Hála, in particular during the years spent in the same institute whose congenial and unforgettably unique atmosphere E. Hála helped to create.

REFERENCES

1. Ausloos P., Lias S. G. (Eds): *Structure, Reactivity and Thermochemistry of Ions*. NATO ASI Series C, Vol. 193. p. 381. D. Reidel Publ. Co., Dordrecht 1987.
2. Koyano I., Tanaka K., Yamazaki H.: *Annu. Rev. Inst. Mol. Sci., Okazaki 1978*, 77.
3. Zahradník R., Havlas Z., Hobza P.: Unpublished results.
4. Whiteside R. A., Frisch M. J., Pople J. A.: *The Carnegie-Mellon Quantum Chemistry Archive*, 3rd ed. Carnegie-Mellon University, Pittsburgh 1983.
5. Franklin J. L., Dillard J. G., Rosenstock H. M., Herron J. T., Draxl K.: *Ionization Potentials, Appearance Potentials and Heats of Formation of Gaseous Ions*. NSRDS, NBS — 26, Washington 1969.
6. Friedrich B., Herman Z.: *Chem. Phys.* 69, 433 (1982).
7. Gislason E. A., Mahan B. H., Chi-Wing Tsao, Weiner A. S.: *J. Chem. Phys.* 54, 3899 (1971).
8. Mahan B. H., Sloane T. M.: *J. Chem. Phys.* 59, 5661 (1973).
9. Herzberg G., Johns J. V. C.: *Astrophys. J.* 158, 399 (1969).
10. Erwin K. M., Armentrout P. B.: *J. Chem. Phys.* 86, 2673 (1987).
11. Lias S. G., Liebman J. F., Levin R. D.: *J. Phys. Chem. Ref. Data* 13, 695 (1984).
12. Smith D., Adams N. G., Ferguson E. E.: *Int. J. Mass Spectrom. Ion Process.* 61, 15 (1984)

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