PROPERTIES AND REACTIVITY OF FIRST AND SECOND ROW HYDRIDES. IV. INTERACTIONS BETWEEN HYDRIDES AND THEIR RADICAL IONS

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Dedicated to Professor Václav Horák on the occasion of his 70th birthday.

The energies and heats of ion–molecule reactions have been calculated (MP4/6-31G**//6-31G** or better level) and compared with the experimental values obtained from the heats of formation. Two main types of reactions have been studied: (i) $AH_n + AH_n^{+\bullet} \rightleftharpoons AH_{n+1}^+ + AH_{n-1}^\bullet$ (A = C to F and Si to Cl), (ii) $AH_n + BH_m^{+\bullet} \rightleftharpoons AH_{n+1}^+ + BH_{m-1}^\bullet$ or $AH_{n-1}^\bullet + BH_{m+1}^+$ (A and B = C to F). In contrast to (i), processes of type (ii) permit easy differentiation between the proton transfer and hydrogen atom abstraction mechanisms. A third type of interaction involves reactions with radical anions (A = Li to F); comparison was made with analogous processes with radical cations. A brief comment is made about the influence of the level of computational sophistication on the energies and heats of reaction, as well as on the stabilization energy of a hydrogen bonded intermediate, a structure which is similar to that of the reaction products.

Ion–molecule reactions play a distinguished role in fundamental research as well as in industrial applications. There is always a dramatic difference between processes taking place in the gas phase and in solutions; only the former are of interest in this work. Ion–molecule interactions can be studied under widely different conditions ranging from molecular beams to reactions in solid inert matrices by using suitable initiation.

Investigations of ion–molecule reactivity have a long tradition. More than 60 years ago Hogness and Harkness studied[1] the interaction between I_2 and its radical ions yielding I_3^+ or I_3^- and the I atom. In the same year a study was published by Barton and Bartlett on the reaction between water and its radical cation[2] leading to hydroxonium cation and the hydroxyl radical. Ion–molecule gas phase reactions have been intensively studied experimentally over the last 30 years[3–5]. Valuable collections of thermochemical and energy characteristics for molecules and gaseous positive and negative ions are available[6,7].

Two processes are, in general, of great importance for ion–molecule reactions: charge transfer and complex (radical cation or radical anion) formation. The complex formed is either stable under the given conditions or decomposes into products, accompanied by a splitting of a covalent or van der Waals bond. There is another very important reaction pathway available to reactants containing hydrogen: this involves proton of hydride transfer or H-atom abstraction.

Reactions between diatomic molecules and their radical-ions represent an important class of reactions. The formation of a radical-ion dimer, e.g. $A_4^{+\bullet}$, and atom transfer leading to, e.g. $A_3^+ + A^\bullet$, belong among the most important reactions. Experimental and theoretical studies have dealt with H_2 (refs[8 - 10]), B_2 (ref.[11]), N_2 (refs[12 - 14]), O_2 (refs[15 - 20]).

Interactions between polyatomic molecules and their radical cations are sometimes connected with remarkable reaction pathway, e.g., interaction between COS and $COS^{+\bullet}$ leading to $S_2^{+\bullet}$, and CO (ref.[21]), N_2O and $N_2O^{+\bullet}$ leading to $NO^{+\bullet}$, NO, and N_2 (ref.[21]), and thiirane and the thiirane radical cation yielding the sulfonated thiirane radical cation and ethylene[22] or to the dimeric thiirane radical cation[23]. The latter process has been studied quantum chemically[24].

Interactions between hydrides and their radical cations have been investigated for years in connection with the dynamics of ion reactions on the basis of molecular beam scattering and state-selective studies. These studies were carried out to provide a deeper understanding of the molecular collision mechanism of elementary reactions as well as the energy transformation in these reactions: very extensive attention has been paid to the reaction[25 - 27] between CH_4 and $CH_4^{+\bullet}$. The reaction heat and the structure of the $C_2H_8^{+\bullet}$ intermediate have been studied quantum chemically[28 - 30]. HD_2O^+ is formed in molecular beams from $D_2O^{+\bullet}$ and NH_3 by direct H-atom transfer and by the decomposition of the $(D_2O\ .\ NH_3)^{+\bullet}$ complex[31]. It was suggested on the basis of scattering experiments that the complex is a prolate, near-linear system[31], $(D_2OH)^+\ .\ (NH_2)^\bullet$. The potential energy surfaces of the $(H_2O)_2^{+\bullet}$ complex were studied theoretically in two electronic states[32]. The equilibrium structure of $(NH_3)_2^{+\bullet}$ and the ionization of the parent dimer have been studied theoretically[33,34]. The electronic structure of the $(NH_3)_2^{+\bullet}$, $(H_2O)_2^{+\bullet}$, and $(HF)_2^{+\bullet}$ and analogous second row dimers have been studied nonempirically (MP2/6-31G* optimizations)[35]. Hydrogen bonds are preferred by the first-row dimers, while complexes with heavier atoms frequently have a structure with a bond between the heavy atoms (two-center, three-electron bond, 2c–3e). In addition, analogous dications have been studied theoretically[36]. Except for the $(HF)_2^{2+}$ dimer, all the other dimers are expected to spontaneously dissociate into two radical cations. Finally, an extensive set of experimental rate constants for exothermic reactions between C^+ and N^+ with molecules has become available[37].

In relation to our special interest in hydrides, some recent quantum chemical studies must be cited. These studies dealt with neutral AH_n molecules and their dimers[38 - 40] with ammoniated NH_5^+ (ref.[41]), H_4O^+ and H_4O^{2+} (ref.[42]), and SiH_5^- and CH_5^- (ref.[43]).

It is the purpose of this study (for a broader context see ref.[44]) to obtain quantum chemical energy characteristics which would permit a discussion of the heats of reactions between the hydrides of atoms of the first and (partly) second row elements and their radical ions, mostly radical cations.

$$AH_n + AH_n^{+\bullet} \rightleftharpoons AH_{n+1}^{+} + AH_{n-1}^{\bullet} \qquad (A)$$

Medium-level theoretical description will be used for establishing the trends between the equilibria and structural features (position of atom A in the Periodic System) as well as for comparison between the calculated and observed heats of reaction. Moreover, marginal attention will be paid to the structure of the complexes formed by association of reactants in Eq. (*A*), $A_2H_2^{+\bullet}$, i.e. the radical ion dimers.

RESULTS AND DISCUSSION

Calculations

The geometry of all the systems studied was optimized, unless stated otherwise, at the Hartree–Fock level (6-31G** basis set) and single point calculations were carried out at the MP4/6-31G** level.

Cation–Molecule Interactions: Homogeneous Pairs

We have theoretically investigated extensive sets of cation–molecule reactions. The energies of reactions of type (*A*) are, semiquantitatively speaking, rather insensitive to the size of the basis set used. Inclusion of electron correlation also does not lead to dramatic changes. The situation is less clear for the intermediates, i.e. the radical cation dimers. Therefore, some attention is paid to this point in the last paragraph.

In the entries of Table I, fair agreement can be seen between the MP4 enthalpy values (zero-point energy included) at zero Kelvin and the experimental enthalpy changes at 298 K, obtained from the heats of formation[6,7,28 – 30]. What is peculiar and still remains unexplained is the completely different shape of the dependence of ΔH on the atomic number of A in the AH_n hydrides for the representatives of the first (C through F) and second (Si through Cl) row hydrides (Fig. 1). There is no reason for unease, because the calculated and experimental ΔH values follow the same pattern but the difference between their shapes is provocative. Investigation of the dependences of the heats of formation, ionization potentials, and proton affinities (cf. refs[45,46]) on the atomic numbers reveals interesting relationships, but the above-mentioned difference still remains unelucidated.

TABLE I
Calculated ΔE and ΔH_0 (in kcal/mol) values for reaction (*A*) and the experimental heats of reaction[6,7,28 – 30]. A in Eq. (*A*) stands for C, N, O, F and Si, P, S, Cl

Reaction	ΔE			ΔH_0^{MP4}	ΔH^{exp}
	6-31G**	MP4	higher level[a]		
$CH_4^{+\bullet} + CH_4 \rightleftharpoons CH_5^+ + CH_3^\bullet$	0.18	0.58	–0.81[b]	–2.41	–4.16; –6; –2.4
$NH_3^{+\bullet} + NH_3 \rightleftharpoons NH_4^+ + NH_2^\bullet$	–18.78	–17.99	–18.34[c]	–16.82	–17.1
$H_2O^{+\bullet} + H_2O \rightleftharpoons H_3O^+ + OH^\bullet$	–29.22	–27.94	–24.78	–26.21	–24.9
$HF^{+\bullet} + HF \rightleftharpoons H_2F^+ + F^\bullet$	–44.56	–43.0	–37.37	–41.19	–36.8
$SiH_4^{+\bullet} + SiH_4 \rightleftharpoons SiH_5^+ + SiH_3^\bullet$	–12.14	–19.68	–	–19.91	–17.5
$PH_3^{+\bullet} + PH_3 \rightleftharpoons PH_4^+ + PH_2^\bullet$	–19.91	–19.16	–	–18.56	–19.0
$H_2S^{+\bullet} + H_2S \rightleftharpoons H_3S^+ + SH^\bullet$	–7.07	–5.56	–	–3.73	–7.8
$HCl^{+\bullet} + HCl \rightleftharpoons H_2Cl^+ + Cl^\bullet$	–12.73	–11.61	[d]	–9.81	–11; –13.8

[a] MP4/6-311+G**//6-31G**. [b] MP4/6-31G**//MP2/6-31G** value equals 0.28 kcal/mol, after including the zero-point energy, –2.71 kcal/mol. [c] CCD/6-31G** value: –20.18 kcal/mol. [d] CCD/6-31G** value: –11.63.

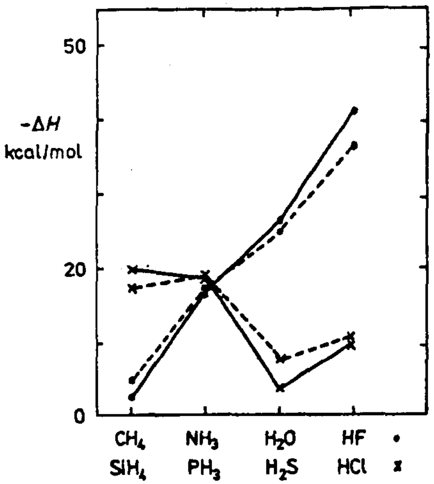

FIG. 1
MP4 Calculated (full line) and Experimental (broken line) heats of reaction plotted against atomic number of A in AH_n hydrides

Cation–Molecule Interactions: Heterogeneous Pairs

The equilibria between molecules and molecular radical cations can be rather easily described theoretically at a semiquantitative level; again, the calculated reaction energies show little sensitivity to the quality of the basis set and to the inclusion of the electron correlation.

The situation is slightly more complicated when attempts are made to obtain quantitative agreement between the calculated and experimental heats of reaction. It can be seen from Table II that passing from level A to level B and inclusion of the zero-point energy are desirable.

Let us discuss the entries in Table II. $CH_4^{+\bullet}$ is a powerful acid and, therefore, NH_3 and H_2O are protonated quantitatively. H-atom tranfer to $CH_4^{+\bullet}$ can hardly take place because CH_5^+ is not thermodynamically favorable. However, the basicity of HF is so low that it is not protonated even by $CH_4^{+\bullet}$.

In the ensemble of the cations studied, $NH_3^{+\bullet}$ represents a weak acid; it cannot even protonate water. On the other hand, the H-atom affinity of $NH_3^{+\bullet}$ is high enough and therefore H-atom abstraction from H_2O and especially from CH_4 should occur smoothly.

$H_2O^{+\bullet}$ is capable to protonize NH_3 and to abstract the H-atom from H_2O, NH_3, and HF. $HF^{+\bullet}$ is, no doubt, an extremely strong acid but, simultaneously its electron affinity is very high. Therefore the dominant interaction with CH_4 and NH_3 is charge transfer.

Let us close this paragraph by saying there is satisfactory agreement between the calculated ΔH_0^{MP4} and experimental ΔH^{exp} values.

Anion–Molecule versus Cation–Molecule Interactions

In the realm of ion–molecule reactions almost all the attention has been paid for years to cation interactions. It is usually significantly easier to deal with cations than with anions; this is true of both experiments and computations. Thus, studies involving anions are frequently a real challenge. The purpose of Table III is similar to the purpose of our recent study of LiH plus $LiH^{-\bullet}$ interaction[47], namely to draw attention to anion–molecule interactions and to increase the experimental investigation of these processes. To obtain quantitative information on processes involving anions, a significantly higher level of approach than that used in Table III is necessary. Specifically, electron correlation should be used from the very beginning of the geometry optimization process. However, on the basis of experience, it is fair to say that the entries in Table III represent reliable qualitative indicators. The ΔE values in Table III are plotted against the atomic number in Fig. 2. It can be seen that the passage from reactants to products in Table III is always much more favorable for the cations. But it is also true that, except for two instances, anion–molecule reactions of the type under study are also feasible from a thermochemical point of view. The two instances mentioned concern CH_5^- and

TABLE II

Calculated ΔE and ΔH_0 (in kcal/mol) for cation–molecule interactions[a]: 1 proton transfer, 2 H-atom abstraction, 3 charge-transfer

Reaction			Proc.	ΔE^A	ΔE^B	ΔH_0^B [b]	ΔH^{exp} [c]
$CH_4^{+\bullet} + NH_3$	$\rightleftharpoons$	$NH_4^+ + CH_3^\bullet$	1	-86.30	-83.31	-79.12	-74.2
		$CH_5^+ + NH_2^\bullet$	2	1.17	1.17	0.00	1.1
		$CH_4 + NH_3^{+\bullet}$	3	-67.55	-63.10	-59.83	(-54.2)[d]
$CH_4^{+\bullet} + H_2O$	$\rightleftharpoons$	$H_3O^+ + CH_3^\bullet$	1	-46.68	-42.55	-39.95	-37.4
		$CH_5^+ + OH^\bullet$	2	6.43	10.59	11.05	12.1
		$CH_4 + H_2O^{+\bullet}$	3	-14.90	-6.37	-3.66	(2.3)[d]
$CH_4^{+\bullet} + HF$	$\rightleftharpoons$	$H_2F^+ + CH_3^\bullet$	1	-1.03	9.50	9.79	12.1
		$CH_5^+ + F^\bullet$	2	18.40	25.38	28.31	29.1
		$CH_4 + HF^{+\bullet}$	3	61.85	73.02	75.81	(81.4)[d]
$NH_3^{+\bullet} + CH_4$	$\rightleftharpoons$	$CH_5^+ + NH_2^\bullet$	1	68.89	64.27	59.86	55.7
		$NH_4^+ + CH_3^\bullet$	2	-18.74	-20.31	-19.39	-19.6
		$NH_3 + CH_4^{+\bullet}$	3	67.55	63.10	60.03	(54.2)[d]
$NH_3^{+\bullet} + H_2O$	$\rightleftharpoons$	$H_3O^+ + NH_2^\bullet$	1	19.63	22.53	22.11	20.7
		$NH_4^+ + OH^\bullet$	2	-12.90	-8.92	-6.16	-5.1
		$NH_3 + H_2O^{+\bullet}$	3	52.65	56.73	56.17	(56.5)[d]
$NH_3^{+\bullet} + HF$	$\rightleftharpoons$	$H_2F^+ + NH_2^\bullet$	1	69.33	74.54	71.81	71.0
		$NH_4^+ + F^\bullet$	2	-0.93	5.9	11.13	11.9
		$NH_3 + HF^{+\bullet}$	3	130.40	136.12	135.64	(135.6)[d]
$H_2O^{+\bullet} + CH_4$	$\rightleftharpoons$	$CH_5^+ + OH^\bullet$	1	21.32	16.96	14.71	10.1
		$H_3O^+ + CH_3^\bullet$	2	-33.78	-36.18	-36.29	-39.4
		$H_2O + CH_4^{+\bullet}$	3	14.90	6.37	3.66	(-2.3)[d]
$H_2O^{+\bullet} + NH_3$	$\rightleftharpoons$	$NH_4^+ + OH^\bullet$	1	-66.56	-65.65	-62.33	-61.7
		$H_3O^+ + NH_2^\bullet$	2	-33.03	-34.20	-34.06	-35.9
		$H_2O + NH_3^{+\bullet}$	3	-52.65	-56.73	-56.17	(-56.5)[d]
$H_2O^{+\bullet} + HF$	$\rightleftharpoons$	$H_2F^+ + OH^\bullet$	1	21.77	27.23	26.65	25.4
		$H_3O^+ + F^\bullet$	2	-15.96	-9.99	-5.79	-7.9
		$H_2 + HF^{+\bullet}$	3	76.75	79.39	79.47	(79.1)[d]
$HF^{+\bullet} + CH_4$	$\rightleftharpoons$	$CH_5^+ + F^\bullet$	1	-43.46	-47.64	-47.50	-52.1
		$H_2F^+ + CH_3^\bullet$	2	-60.82	-63.55	-66.05	-68.3
		$HF + CH_4^{+\bullet}$	3	-61.85	-73.02	-75.81	(-81.4)[d]
$HF^{+\bullet} + NH_3$	$\rightleftharpoons$	$NH_4^+ + F^\bullet$	1	-130.30	-130.30	-124.59	-123.9
		$H_2F^+ + NH_2^\bullet$	2	-60.07	-61.58	-63.83	-64.8
		$HF + NH_3^{+\bullet}$	3	-129.40	-136.12	-135.64	(-135.5)[d]
$HF^{+\bullet} + H_2O$	$\rightleftharpoons$	$H_3O^+ + F^\bullet$	1	-92.71	-89.38	-85.26	-87.1
		$H_2F^+ + OH^\bullet$	2	-54.98	-52.16	-52.82	-53.8
		$HF + H_2O^{+\bullet}$	3	-76.75	-79.39	-79.47	(-79.1)[d]

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[a] Level A: MP4/6-31G**//6-31G**; level B: MP4/6-311+G**//6-31G**; [b] zero point energy (6-31G** values) included; [c] heats of formation from refs[4,6]; [d] a value obtained as the difference of the experimental vertical ionization potentials[4] for the respective radical cations.

TABLE III
Anion/cation–molecule reactions: MP4 reaction energy changes[a] (in kcal/mol)

Reaction	ΔE
$LiH + LiH^{-\bullet} \rightleftharpoons LiH_2^- (D_{\infty h}) + Li^\bullet$	−12.76[b]
$LiH + LiH^{+\bullet} \rightleftharpoons LiH_2^+ + Li^\bullet$	−67.09
$BeH_2(D_{\infty h}) + BeH_2^{-\bullet}(C_{2v}) \rightleftharpoons BeH_3^-(D_{3h}) + BeH^\bullet$	0.72[c]
$BeH_2 + BeH_2^{+\bullet} \rightleftharpoons BeH_3^+ + BeH^\bullet$	−21.22
$BH_3 + BH_3^{-\bullet} \rightleftharpoons BH_4^- + BH_2^\bullet$	4.78
$BH_3 + BH_3^{+\bullet} \rightleftharpoons BH_4^+(C_{3v}) + BH_2^\bullet$	−2.67
$CH_4 + CH_4^{-\bullet}(C_{3v}) \rightleftharpoons CH_5^-(C_1) + CH_3^\bullet$	32.37
$CH_4 + CH_4^{+\bullet} \rightleftharpoons CH_5^+ + CH_3^\bullet$	0.58
$NH_3 + NH_3^{-\bullet}(C_{2v}) \rightleftharpoons NH_4^- + NH_2^\bullet$	(−2.64)[d]
$NH_3 + NH_3^{+\bullet} \rightleftharpoons NH_4^+ + NH_2^\bullet$	−17.99
$H_2O + H_2O^{-\bullet}(C_{\infty v}) \rightleftharpoons H_3O^- + OH^\bullet$	−3.15 (exp.−6.79)
$H_2O + H_2O^{+\bullet} \rightleftharpoons H_3O^+ + OH^\bullet$	−27.94
$HF + HF^{-\bullet} \rightleftharpoons FH_2^- + F^\bullet$	20.19
$HF + HF^{+\bullet} \rightleftharpoons FH_2^+ + F^\bullet$	−44.03

[a] MP4/6-31G**//6-31G**; [b] ΔH_0 (zero-point energy included) amounts to −11.92 kcal/mol. [c] ΔH_0 = 0.41 kcal/mol; [d] MP4/6-311++G**//6-31G**.

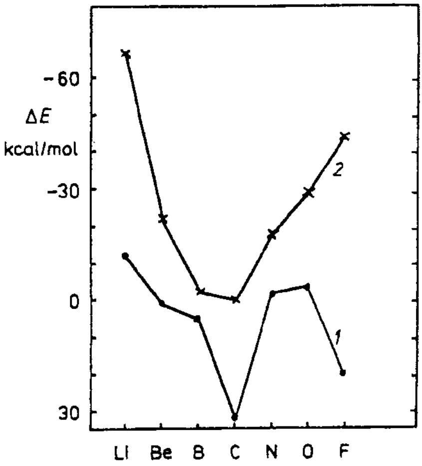

FIG. 2
Dependence of calculated reaction energy changes, ΔE, on the atomic number of the heavy atom (cf. Table III): *1* anions, *2* cations

FH_2^-: this might be due to the fact that both these systems represent very weak van der Waals ions. These ions might be viewed as CH_3^- . . . H_2, and F^- . . . H_2, respectively.

The experimental ΔH value[4] for the process $H_2O + H_2O^{-\bullet} \rightleftharpoons H_3O^- + OH^\bullet$ equals −6.79 kcal/mol; the agreement between the calculated and observed values is fair (cf. Table III).

A Methodological Remark on Energy Stabilization of Intermediates in Cation–Molecule Reaction: Illustrative Calculation

For four selected processes, ΔE (ΔH_0) and ΔE^s (ΔH^s) were calculated at five levels: (a) 6-31G** optimization, (b) MP2/6-31G** (full core) optimization, (c) MP2/6-31G** (frozen core) optimization, (d) compensation of basis set superposition error by the function counterpoise method, (e) correction of the (a) values for the zero-point energy, i.e. passing from energy to enthalpy changes. The frequencies of the normal vibrational modes were calculated at the 6-31G** level.

The reaction profile of the processes under study is depicted schematically in Fig. 3. ΔE^s refers to the dimer formation. In general, at least three isomers of this dimer play a role. For the purposes of this study only hydrogen bonded dimers resembling the products (i.e. structures of the AH_{n+1}^+ . . . $AH_{n-1}^\bullet$ type) were considered. Energy changes based on (i) through (e) calculations are summarized for four processes (A = N, P, F, Cl) in Table IV. The entries in Table IV demonstrate convincingly that the energy characteristics of the hydrogen-bonded intermediate are also rather insensitive to the basis set used and to the inclusion of various corrections. However, it must be kept in mind that intermediates with a 2c–3e bond are very sensitive to the inclusion of the electron correlation[35,48].

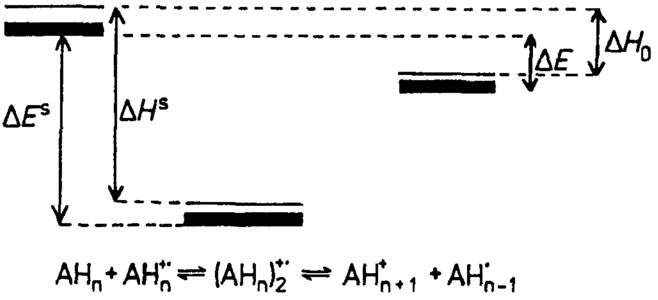

FIG. 3
Reaction profile of the process under study (cf. Table IV)

TABLE IV

Energy changes accompanying the process indicated in Fig. 3 (in kcal/mol). Levels (a) through (e) are defined in the text

A	Level	$-\Delta E^s$ (ΔH^s)	$-\Delta E$ (ΔH_0)	A	Level	$-\Delta E^s$ (ΔH^s)	$-\Delta E$ (ΔH_0)
N	a	41.17	18.77	F	a	54.98	44.80
	b	45.19	19.82		b	57.46	43.06
	c	45.09	19.84		c	57.65[a]	43.39[a]
	d	40.02	–		d	52.90	–
	e	37.48	17.60		e	52.24	42.99
P	a	25.78	19.90	Cl	a	16.91	11.03
	b	25.82	18.47		b	21.29	11.85
	c	25.95	19.01		c	21.28[b]	11.85[b]
	d	25.70	–		d	16.85	–
	e	24.22	44.20		e	38.71	16.97

[a] MP4 calculation (frozen core) for MP2 optimized geometry leads to 57.42 and 43.04 kcal/mol for ΔE^s and ΔE, respectively; [b] analogously as in footnote[a] 20.81 and 11.69 kcal/mol.

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