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Calculation of thermodynamic properties of the most important forty-seven different solvents to create an information data bank through semi-empirical quantum methods used in determination of theoretical pKa

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In this study, we have calculated the thermodynamic properties, especially in determining the theoretical acidic properties and pKa values of organic compounds, as enthalpy (ΔH, kcal/mol), heat capacity (C, cal/Kmol), entropy (ΔS, cal/Kmol), and free energy (ΔG, kcal/mol) of 47 different solvents with the MOPAC 2016 computer program at 298 K used in semi-empirical quantum methods (PM7, PM6, PM6-DH2, RM1, PM3, AM1, and MNDO). Evaluations are made between these values and the used methods. At the same time, a data bank is created with obtained values for the researchers who will do scientific study for the theoretical pKa.

Keyword: Thermodynamic properties, MOPAC 2016 computer program, Semi-empirical quantum method

For many years, semi-empirical quantum-chemical methods[1] have contributed to computational chemistry, mainly to studies of ground-state properties of large molecules at the self consistent-field molecular-orbital (SCF-MO) level as precious tools. Practices for electronically excited express have been less common, for at least two reasons. First, static electron-correlation effects must be taken into account for excited states, which requires the use of more demanding computational treatments such as configuration interaction (CI) and its multi reference variant (MRCI)[2]. Second, standard semi-empirical methods employ the zero-differential overlap (ZDO) approximation, which leads to a symmetric splitting of bonding and antibonding orbitals, in contrast to ab-initio methods, in which the antibonding orbitals are destabilized to a larger extent than the corresponding bonding orbitals are stabilized[2]. As a result, standard semi-empirical methods commonly tend to acutely underestimate excited-state energies. This can be remedied by special "spectroscopic" parametrizations for vertical excitations, as in the INDO/S methods[3,4] which have been applied successfully in many spectroscopic and related studies[5].

Scouting chemical and biochemical processes that depend on proton transfer is applicable by obtaining knowledge about pKa values of different organic compounds and relatives[6]. However, the rigorous experimental determination of pKa values is not an unimportant task in many cases and may cause substantial experimental challenge[7]. Thus, determining pKa values computationally has become a subject of widespread interest[8]. Parallel with it, we have recently studied and published pKa values of different organic compounds experimentally and theoretically[9-13].

Determination of pKa values, is necessary for understanding many main reactions in chemistry. These values explain the deprotonation state of a molecule in a specific solvent. A lot of scientists are interested in using theoretical methods to calculate the pKa values for many different types of organic molecules with different models and computer programs at various temperatures, although organic molecules and derivatives have not been synthesized. Therefore, experimental pKa determinations are difficult, for larger molecules where the local environment changes the usual pKa values.

Materials and Methods

Computer program

MOPAC (Molecular Orbital Package) 2016 computer program is computational chemistry software with strong semi-empirical quantum chemistry practices for the prediction of chemical properties, calculations of chemical molecules, and

modeling of chemical reactions. MOPAC 2016 computer program is faster and highly reliable software for chemical property predictions and physical property predictions such as Gibbs free energies, activation energies, reaction paths, dipole moments, non-linear optical properties, enthalpy, heat capacity, entropy, and infrared spectra. Also, MOPAC 2016 computer program implements the semi-empirical Hamiltonians PM7, PM6, PM6-DH2, RM1, PM3, AM1, and MNDO. It combines the calculations of vibrational spectra, thermodynamic quantities, isotopic substitution effects, time-dependent effects, and force constants in a fully integrated program[14]. One of the usually used methods to search for the effect of a substituent on an equilibrium process is the practice of the Hammett equation[15] pKa values, which are very important for understanding many fundamental reactions in chemistry, biochemistry, and especially pharmaceutical production and design.

$$HA + S \leftrightarrows SH^+ + A^- \quad \ldots (1)$$

In this reaction, HA is the weak acid, and SH^+ is the protonated acid. S is the used Solvent, and A^- is the conjugated base of weak acids.

$$K_a = \frac{[SH^+][A^-]}{[HA]} \quad \ldots (2)$$

Generally, acid dissociation constants, also known as pKa values, can be determined quite easily experimentally. But, sometimes, chemists are interested in the pKa values of molecules that have not been simply synthesized in the laboratory or for which experiments are not obvious. The skill to computationally determine these pKa values accurately is important for scientific advancements in organic chemistry, biochemistry, and other fields as drug design. Chemical accuracy, though, is hard to achieve[16]. Computationally calculating acid dissociation constants is a demanding and arduous process because an error of 1.36 kcal/mol in the change of free energy of reaction 1 results in an error of 1 pKa unit[17,18]. Generally, three methods, thermodynamic cycles, gas-phase free energy calculations, and the change in free energy of solvation calculations, are used in the theoretical calculation of pKa. In this work, we will discuss the third method, which is the change in free energy of solvation calculations for calculation of pKa. The total free energy change ($\Delta G_{Reaction}$) for (1) reaction is carried out using the following reactions:

$$\Delta G_{Reaction} = \left[\Delta G_{(SH^+)} + \Delta G_{(A^-)}\right] - \left[\Delta G_{(S)} + \Delta G_{(HA)}\right] \quad \ldots (3)$$

$$pK_a = \frac{(\Delta G_{Reaction})}{2.303RT} \quad \ldots (4)$$

In this study, we calculated $\Delta G_{(S)}$ (kcal/mol) and $\Delta G_{(SH^+)}$ (kcal/mol) form of S and SH^+. But earlier, we determined enthalpy (ΔH, kcal/mol) and entropy (ΔS, cal/Kmol) for each solvent at 298 K.

$$\Delta G = \Delta H - T\Delta S \quad \ldots (5)$$

We have taken 47 different solvents and, different solvent groups, and calculated them with the MOPAC 2016 computer program at 298 K using semi-empirical quantum chemical methods (PM7, PM6, PM6-DH2, RM1, PM3, AM1, and MNDO). After the solvent molecule was optimized, calculation was made. Each solvent was individually optimized in both forms (S and SH^+). Also, we calculated heat capacity (C, cal/Kmol) values for each solvent form of S and SH^+. Thus, the enthalpy (ΔH) and entropy (ΔS) values obtained for the each solvents have been very important data for scientists working on pKa in computational chemistry with semi-empirical quantum chemical methods. We have already created a data bank of our purpose. Also, we think that we have achieved the creation of a data bank for these 47 solvents. The names and molecular formulas of the studied solvents are given in Table 1.

Acid dissociation constants of a compound depend on many factors. The two most important factors are the solvent effect and molecular structure. In this study, we selected the most used solvents, especially in the literature. At the same time, these solvents are available in the MOPAC 2016 computer program. Therefore, we calculated the thermodynamic properties, especially in determining the theoretical acidic properties and pKa values of organic compounds, as enthalpy (ΔH, kcal/mol), heat capacity (C, cal/Kmol), entropy (ΔS, cal/Kmol), and free energy (ΔG, kcal/mol) of 47 different solvents with the MOPAC 2016 computer program at 298 K used in semi-empirical quantum chemical methods (PM7, PM6, PM6-DH2, RM1, PM3, AM1, and MNDO). Each calculation was made with 3 replicates, and the average values are given in all tables. Thermodynamic values for each model obtained for these 47 different solvents are given in Table 2 – 8 as separately for S and SH^+ forms. The graphs of the S form using the data in these tables are given in Fig. 1 – 4 for each model.

Table 1 — Determined solvents and molecular formulas in this study

Number	Solvent	Number	Solvent
1	Water (H_2O)	25	Dichloroethane($ClCH_2CH_2Cl$)
2	Acetic Acid (CH_3COOH)	26	Ethylene Glycol ($HOCH_2CH_2OH$)
3	Acetone (CH_3COCH_3)	27	Formamide ($HCONH_2$)
4	Acetonitrile (CH_3CN)	28	Formic Acid (HCOOH)
5	Ammonia (NH_3)	29	Glycerol ($C_3H_8O_3$)
6	Aniline ($C_6H_5NH_2$)	30	Hexamethyl Phosphoramide ($C_6H_{18}N_3OP$)
7	Benzene (C_6H_6)	31	Hexane (C_6H_{14})
8	Benzyl Alcohol ($C_6H_5CH_2OH$)	32	Hydrazine (N_2H_4)
9	Bromoform ($CHBr_3$)	33	Methanol (CH_3OH)
10	Butanol (C_4H_9OH)	34	Methyl Ethyl Ketone ($CH_3CH_2COCH_3$)
11	Iso-Butanol ($(CH_3)_2CHCH_2OH$)	35	Dichloromethane (CH_2Cl_2)
12	Tert-Butanol ($(CH_3)_3COH$)	36	Methyl Formamide ($HCONHCH_3$)
13	Carbon Disulphide (CS_2)	37	Methyl Pyrrolidinone (C_5H_9NO)
14	Carbon Tetrachloride (CCl_4)	38	Nitrobenzene ($C_6H_5NO_2$)
15	Chloroform ($CHCl_3$)	39	Nitromethane (CH_3NO_2)
16	Cyclohexane (C_6H_{12})	40	Phosphoryl Chloride ($POCl_3$)
17	Cyclohexanone ($C_6H_{10}O$)	41	Iso-Propanol ($(CH_3)_2CHOH$)
18	Dichlorobenzene ($C_6H_4C_{l2}$)	42	Pyridine (C_5H_5N)
19	Diethyl Ether ($(CH_3CH_2)_2O$)	43	Sulfolane ($C_4H_8SO_2$)
20	Dioxane ($C_4H_8O_2$)	44	Tetrahydrofuran (C_4H_8O)
21	Dimethyl Formamide ($(CH_3)_2NCHO$)	45	Toluene ($C_6H_5CH_3$)
22	Dimethyl Sulfoxide ($(CH_3)_2SO$)	46	Triethylamine ($(CH_3CH_2)_3N$)
23	Ethanol (CH_3CH_2OH)	47	Trifluoroacetic Asid (CF_3COOH)
24	Ethyl Acetate($CH_3COOCH_2CH_3$)		

Table 2 — Thermodynamic values of S and SH^+ forms in PM7 semi-empirical quantum chemical methods at 298 K

No	Type	ΔH (kcal/mol)	C (cal/Kmol)	ΔS (cal/Kmol)	ΔG (kcal/mol)	No	Type	ΔH (kcal/mol)	C (cal/Kmol)	ΔS (cal/Kmol)	ΔG (kcal/mol)
1	S	2.3741	8.0685	45.1274	-11.0738	25	S	4.2824	21.0518	73.0530	-17.4874
	SH^+	2.3963	8.4957	46.4224	-11.4375		SH^+	4.0825	21.8695	72.2212	-17.4395
2	S	3.6241	17.0149	71.2019	-17.5941	26	S	3.7279	20.4616	67.4154	-16.3619
	SH^+	4.8293	23.0429	78.0636	-18.4336		SH^+	4.1175	21.9709	71.7679	-17.2693
3	S	3.4746	18.8734	66.0267	-16.2014	27	S	2.7088	11.9150	60.0868	-15.1971
	SH^+	3.8954	21.7265	69.8863	-16.9308		SH^+	2.8725	13.4048	61.2132	-15.3690
4	S	2.8612	13.0990	58.2257	-14.4901	28	S	2.6447	11.1974	59.6899	-15.1429
	SH^+	3.4008	16.2952	61.7438	-14.9989		SH^+	2.7772	12.6956	59.2861	-14.8900
5	S	2.3806	8.2131	45.8722	-11.2893	29	S	4.5489	25.6633	79.9070	-19.2634
	SH^+	2.3807	8.2508	49.3120	-12.3143		SH^+	5.0441	29.1961	80.7449	-19.0179
6	S	4.3540	25.2488	74.9254	-17.9738	30	S	10.1573	61.8394	119.1064	-25.3364
	SH^+	4.1904	23.9007	76.5765	-18.6294		SH^+	9.0521	57.3759	110.1792	-23.7813
7	S	3.4101	19.0266	64.5194	-15.8167	31	S	5.7229	31.6004	85.7103	-19.8187
	SH^+	3.5913	20.5129	69.2343	-17.0405		SH^+	6.3620	34.7709	92.0889	-21.0805
8	S	5.2038	28.8248	86.2347	-20.4941	32	S	2.6640	10.4639	55.3725	-13.8371
	SH^+	6.0152	34.1723	90.2555	-20.8809		SH^+	2.7183	12.0258	55.6332	-13.8604
9	S	4.3606	18.6350	87.2930	-21.6527	33	S	2.9144	13.2942	56.3554	-13.8795
	SH^+	4.1044	18.5801	83.1918	-20.6868		SH^+	2.5078	9.8268	56.0536	-14.1961
10	S	4.7775	25.3288	78.6870	-18.6712	34	S	4.8272	23.6702	81.4584	-19.4474
	SH^+	5.2144	27.0959	85.0218	-20.1221		SH^+	4.7207	25.4865	77.7683	-18.4543

(*Contd.*)

Table 2 — Thermodynamic values of S and SH^+ forms in PM7 semi-empirical quantum chemical methods at 298 K (*Contd*.)

No	Type	ΔH (kcal/mol)	C (cal/Kmol)	ΔS (cal/Kmol)	ΔG (kcal/mol)	No	Type	ΔH (kcal/mol)	C (cal/Kmol)	ΔS (cal/Kmol)	ΔG (kcal/mol)
11	S	6.0290	29.6520	92.7323	-21.6053	35	S	3.1402	14.5567	65.8096	-16.4711
	SH^+	6.4885	33.8590	93.3174	-21.3201		SH^+	3.3929	16.0997	68.6829	-17.0746
12	S	6.9425	31.3737	105.4886	-24.4931	36	S	3.5076	18.0499	67.4578	-16.5949
	SH^+	6.8218	33.2474	96.6133	-21.9690		SH^+	3.6545	19.5761	68.4673	-16.7488
13	S	2.5506	10.9835	56.7532	-14.3618	37	S	5.2068	27.7072	84.6704	-20.0250
	SH^+	2.8966	12.5866	63.6322	-16.0658		SH^+	5.2119	29.2902	83.2376	-19.5929
14	S	4.4607	21.6474	77.1335	-18.5251	38	S	5.1979	28.2956	86.6556	-20.6254
	SH^+	5.2810	22.0835	95.6099	-23.2107		SH^+	5.0992	29.4368	84.0824	-19.9574
15	S	3.1492	15.2935	68.8602	-17.3711	39	S	3.1518	15.9795	63.9376	-15.9016
	SH^+	3.5085	17.3987	70.9040	-17.6209		SH^+	3.2820	17.0841	66.2536	-16.4616
16	S	5.3017	31.6257	76.2954	-17.4343	40	S	4.7679	23.2189	82.9288	-19.9449
	SH^+	4.8064	29.3361	78.3663	-18.5468		SH^+	4.7900	23.9650	82.8808	-19.9085
17	S	4.7798	27.2414	80.6221	-19.2456	41	S	4.4066	24.5871	72.9962	-17.3462
	SH^+	4.9768	28.7152	82.6037	-19.6391		SH^+	4.3738	24.9282	72.8710	-17.3417
18	S	4.8002	26.5276	81.9987	-19.6354	42	S	3.3154	18.1162	68.9475	-17.2310
	SH^+	4.8132	27.4379	83.1997	-19.9803		SH^+	3.3741	18.8897	67.9631	-16.8789
19	S	5.1861	25.4478	83.5478	-19.7111	43	S	4.9611	28.6092	82.3660	-19.5839
	SH^+	5.2595	31.6635	78.3675	-18.0940		SH^+	5.2397	29.6957	84.8835	-20.0556
20	S	4.0156	22.2171	72.6410	-17.6315	44	S	3.7124	18.9933	71.9036	-17.7149
	SH^+	5.1597	30.2394	78.5110	-18.2365		SH^+	3.9136	21.2627	71.8628	-17.5015
21	S	4.8487	22.8850	82.5188	-19.7419	45	S	4.5171	25.1294	79.1273	-19.0628
	SH^+	4.4982	26.4658	75.1175	-17.8868		SH^+	4.3704	26.7332	76.3726	-18.3887
22	S	4.0583	21.1790	72.8636	-17.6551	46	S	6.2063	35.4861	90.1886	-20.6699
	SH^+	4.8179	24.8913	78.6164	-18.6098		SH^+	6.8989	37.1900	98.2031	-22.3656
23	S	3.7938	19.2334	65.4766	-15.7182	47	S	4.9128	24.2359	83.8886	-20.0860
	SH^+	3.7532	19.9873	66.5597	-16.0815		SH^+	4.5768	25.5632	78.9129	-18.9392
24	S	5.0894	29.4912	80.1617	-18.7988						
	SH^+	5.6504	33.0915	84.5046	-19.5319						

Table 3 — Thermodynamic values of S and SH^+ forms in PM6 semi-empirical quantum chemical methods at 298 K

No	Type	ΔH (kcal/mol)	C (cal/Kmol)	ΔS (cal/Kmol)	ΔG (kcal/mol)	No	Type	ΔH (kcal/mol)	C (cal/Kmol)	ΔS (cal/Kmol)	ΔG (kcal/mol)
1	S	2.3732	8.0524	45.1079	-11.0689	25	S	4.4156	21.7413	75.1273	-17.9724
	SH^+	2.4165	8.7228	44.5931	-10.8723		SH^+	4.0835	22.2152	72.0656	-17.3921
2	S	3.4798	17.8811	67.4398	-16.6173	26	S	4.4439	23.2422	73.3379	-17.4108
	SH^+	4.1961	20.7138	73.5001	-17.7069		SH^+	4.5387	24.1362	74.5490	-17.6769
3	S	3.8163	20.6429	68.0534	-16.4636	27	S	2.7651	12.2963	60.4100	-15.2371
	SH^+	4.1267	20.8256	73.2728	-17.7085		SH^+	3.0787	14.4602	62.4265	-15.5244
4	S	2.9315	13.6134	59.9745	-14.9409	28	S	2.6547	11.2879	59.7875	-15.1619
	SH^+	3.5159	16.4974	63.3261	-15.3552		SH^+	2.7903	12.7230	59.3890	-14.9076
5	S	2.3816	8.2317	45.9273	-11.3047	29	S	5.3631	31.4671	82.0159	-19.0777
	SH^+	2.3826	8.2910	49.3342	-12.3189		SH^+	5.0994	29.5389	80.7343	-18.9595
6	S	4.3952	25.7465	75.2510	-18.0295	30	S	10.6335	65.4450	119.2760	-24.9107
	SH^+	4.0788	24.1146	74.9478	-18.2557		SH^+	9.9707	62.4778	114.4787	-24.1440
7	S	3.4066	19.3569	64.4480	-15.7990	31	S	5.6074	31.1931	84.1838	-19.4793
	SH^+	3.6829	21.2420	69.7674	-17.1078		SH^+	6.4644	36.9868	92.3398	-21.0528
8	S	5.1688	29.4762	84.5631	-20.0310	32	S	2.8379	10.8695	56.9540	-14.1344
	SH^+	6.1290	34.8116	90.8026	-20.9302		SH^+	3.1664	12.7975	65.0874	-16.2296

(*Contd*.)

Table 3 — Thermodynamic values of S and SH^+ forms in PM6 semi-empirical quantum chemical methods at 298 K (*Contd*.)

No	Type	ΔH (kcal/mol)	C (cal/Kmol)	ΔS (cal/Kmol)	ΔG (kcal/mol)	No	Type	ΔH (kcal/mol)	C (cal/Kmol)	ΔS (cal/Kmol)	ΔG (kcal/mol)
9	S	3.8406	17.1136	79.4372	-19.8316	33	S	3.1238	13.4455	58.0898	-14.1870
	SH^+	4.3354	19.2597	85.8156	-21.2376		SH^+	3.5364	15.7213	63.3611	-15.3452
10	S	5.1785	26.3430	82.9562	-19.5424	34	S	4.8730	24.0830	82.0409	-19.5752
	SH^+	5.0292	26.9594	81.0274	-19.1170		SH^+	5.0483	26.1284	83.2012	-19.7456
11	S	5.9969	31.5178	88.8030	-20.4664	35	S	3.1133	14.1183	65.2251	-16.3238
	SH^+	6.3036	33.6970	91.7582	-21.0403		SH^+	2.6580	11.2601	64.6495	-16.6076
12	S	6.7998	31.7777	100.8623	-23.2571	36	S	3.8234	17.6840	74.3398	-18.3298
	SH^+	6.7262	33.3835	95.4786	-21.7264		SH^+	3.8403	20.3476	69.5984	-16.9000
13	S	2.5952	11.1254	57.0514	-14.4061	37	S	5.3372	28.4254	86.0271	-20.2988
	SH^+	2.8984	12.7927	62.7259	-15.7939		SH^+	5.4281	30.3984	85.3704	-20.0122
14	S	4.2484	21.0059	75.6978	-18.3095	38	S	5.1000	28.6777	83.4820	-19.7777
	SH^+	5.2294	21.9813	95.5351	-23.2401		SH^+	5.0407	29.7392	83.2947	-19.7811
15	S	3.3428	16.0157	70.0934	-17.5450	39	S	3.3331	16.6153	65.1075	-16.0689
	SH^+	3.5213	16.7493	71.3755	-17.7486		SH^+	3.3101	16.9347	66.5571	-16.5239
16	S	5.2974	32.7814	75.7085	-17.2637	40	S	5.2330	24.4575	87.2059	-20.7543
	SH^+	5.1567	30.8448	81.9501	-19.2644		SH^+	5.4507	26.8637	88.2018	-20.8334
17	S	4.6677	27.1050	79.8040	-19.1139	41	S	4.6084	25.2490	74.4699	-17.5836
	SH^+	5.1686	30.0996	83.9852	-19.8590		SH^+	4.6323	26.5542	74.3556	-17.5257
18	S	4.8367	26.9380	82.2914	-19.6861	42	S	3.3472	18.6372	69.0840	-17.2399
	SH^+	5.2091	29.3143	85.9009	-20.3893		SH^+	3.4348	19.5911	68.2590	-16.9064
19	S	5.1033	26.0783	82.2006	-19.3925	43	S	4.9684	28.8382	82.3612	-19.5752
	SH^+	6.7114	37.6437	89.0438	-19.8236		SH^+	5.7020	31.4628	89.3814	-20.9337
20	S	4.1032	22.9723	73.1432	-17.6935	44	S	3.7848	19.5718	72.7418	-17.8923
	SH^+	5.9204	33.7668	84.5547	-19.2769		SH^+	3.7988	21.3972	70.2021	-17.1214
21	S	4.8001	23.3625	80.2577	-19.1167	45	S	4.5302	25.8212	78.5558	-18.8794
	SH^+	4.8830	25.0795	80.1210	-18.9931		SH^+	4.8582	28.9213	79.9044	-18.9533
22	S	4.4560	21.8794	77.4426	-18.6219	46	S	6.3418	36.4238	90.9605	-20.7644
	SH^+	4.6728	24.1113	77.9260	-18.5491		SH^+	6.7228	37.5308	95.1372	-21.6281
23	S	3.8954	19.7448	66.0748	-15.7948	47	S	4.5905	24.3991	79.7222	-19.1667
	SH^+	4.3377	20.8633	73.8949	-17.6830		SH^+	4.6425	25.8910	79.4091	-19.0214
24	S	5.3139	30.3176	81.8125	-19.0662						
	SH^+	5.8404	32.8606	87.4996	-20.2345						

Table 4 — Thermodynamic values of S and SH^+ forms in PM6-DH2 semi-empirical quantum chemical methods at 298 K

No	Type	ΔH (kcal/mol)	C (cal/Kmol)	ΔS (cal/Kmol)	ΔG (kcal/mol)	No	Type	ΔH (kcal/mol)	C (cal/Kmol)	ΔS (cal/Kmol)	ΔG (kcal/mol)
1	S	2.3732	8.0524	45.1079	-11.0689	25	S	4.4489	21.7944	75.5211	-18.0564
	SH^+	2.4165	8.7228	44.5931	-10.8723		SH^+	4.0829	22.2099	72.0629	-17.3918
2	S	3.6597	18.3234	69.1396	-16.9439	26	S	4.4431	23.2383	73.3185	-17.4058
	SH^+	3.9884	20.1370	71.2772	-17.2522		SH^+	4.5161	24.1030	74.3350	-17.6357
3	S	3.8065	20.6424	67.9550	-16.4441	27	S	2.7654	12.2974	60.4114	-15.2372
	SH^+	4.0288	21.0746	71.5113	-17.2815		SH^+	3.0685	14.4596	62.3482	-15.5112
4	S	3.0206	14.0859	60.4496	-14.9934	28	S	2.6549	11.2892	59.7884	-15.1620
	SH^+	3.4963	16.3366	63.4512	-15.4122		SH^+	2.7899	12.7202	59.3874	-14.9075
5	S	2.3816	8.2317	45.9274	-11.3048	29	S	5.0068	29.0797	80.1834	-18.8878
	SH^+	2.3850	8.3410	44.3971	-10.8453		SH^+	5.0993	29.5363	80.7359	-18.9600
6	S	4.3877	25.6773	75.2274	-18.0300	30	S	10.6743	65.7565	119.7385	-25.0077
	SH^+	4.1803	24.7519	75.4671	-18.3089		SH^+	9.9163	62.3559	114.0797	-24.0795

(*Contd*.)

Table 4 — Thermodynamic values of S and SH^+ forms in PM6-DH2 semi-empirical quantum chemical methods at 298 K (*Contd.*)

No	Type	ΔH (kcal/mol)	C (cal/Kmol)	ΔS (cal/Kmol)	ΔG (kcal/mol)	No	Type	ΔH (kcal/mol)	C (cal/Kmol)	ΔS (cal/Kmol)	ΔG (kcal/mol)
7	S	3.4240	19.4645	64.5436	-15.8100	31	S	5.5969	31.1654	84.2751	-19.5171
	SH^+	3.8693	22.6398	70.6390	-17.1811		SH^+	6.4583	36.4015	92.1119	-20.9910
8	S	5.2414	29.6320	85.0036	-20.0897	32	S	2.7428	10.7241	55.9829	-13.9401
	SH^+	6.1831	35.0819	91.1410	-20.9769		SH^+	3.1000	12.7849	59.7188	-14.6962
9	S	3.8439	17.1221	79.4715	-19.8386	33	S	3.1235	13.4455	58.0878	-14.1866
	SH^+	4.3516	18.8836	87.0291	-21.5831		SH^+	2.8991	13.6673	58.1749	-14.4371
10	S	4.9526	26.0069	80.3913	-19.0040	34	S	4.8428	24.0713	81.3198	-19.3905
	SH^+	5.0395	27.0706	82.4729	-19.5374		SH^+	4.9492	25.8522	81.0836	-19.2138
11	S	5.9120	31.2843	88.5749	-20.4833	35	S	3.1123	14.1153	65.2187	-16.3228
	SH^+	6.3305	33.1143	93.2960	-21.4717		SH^+	2.7896	11.5130	65.4857	-16.7251
12	S	6.7471	31.8066	98.4703	-22.5970	36	S	3.8987	17.9170	72.9766	-17.8483
	SH^+	6.6730	33.2521	94.6547	-21.5341		SH^+	3.9866	19.2589	74.3070	-18.1569
13	S	2.5951	11.1257	57.0507	-14.4060	37	S	5.2049	28.3265	83.9163	-19.8022
	SH^+	2.8989	12.7960	62.7281	-15.7940		SH^+	5.2839	30.0690	84.1399	-19.7898
14	S	4.2523	21.0139	75.7333	-18.3162	38	S	5.1078	28.7006	83.5594	-19.7929
	SH^+	5.2014	21.9863	93.8549	-22.7674		SH^+	5.0411	29.7641	83.2859	-19.7781
15	S	3.3400	16.0142	70.0698	-17.5408	39	S	3.3336	16.6220	65.1067	-16.0682
	SH^+	3.5277	16.7621	71.4404	-17.7616		SH^+	3.3144	16.9284	66.5944	-16.5308
16	S	6.2248	38.8559	80.3825	-17.7292	40	S	5.2332	24.4598	87.1561	-20.7393
	SH^+	5.1691	30.8540	82.3139	-19.3605		SH^+	5.4752	27.1395	87.6339	-20.6397
17	S	4.5808	26.9069	78.8236	-18.9086	41	S	4.6068	25.2463	74.4555	-17.5809
	SH^+	5.2117	30.1138	84.4807	-19.9635		SH^+	4.6293	26.5453	74.3283	-17.5206
18	S	4.8809	27.0382	82.7354	-19.7742	42	S	3.3623	18.7090	69.1693	-17.2502
	SH^+	5.0424	28.5090	85.0603	-20.3056		SH^+	3.4340	19.5911	68.2545	-16.9059
19	S	5.0297	25.8382	81.4153	-19.2321	43	S	5.3227	31.0549	84.1509	-19.7543
	SH^+	6.3310	36.3693	85.4813	-19.1424		SH^+	4.8741	28.4702	81.2477	-19.3377
20	S	4.0923	22.9558	73.0494	-17.6764	44	S	3.7916	21.3967	70.1017	-17.0987
	SH^+	5.9380	33.7880	84.8238	-19.3395		SH^+	3.8667	18.9322	75.2038	-18.5440
21	S	4.8300	23.3746	80.9296	-19.2871	45	S	4.8315	28.7849	79.7931	-18.9469
	SH^+	4.5653	24.3763	76.6702	-18.2824		SH^+	4.5094	25.2478	79.8144	-19.2753
22	S	4.2954	21.7529	74.9578	-18.0420	46	S	7.2120	38.2392	101.9504	-23.1692
	SH^+	4.6875	24.5390	77.2623	-18.3367		SH^+	6.3322	35.7634	96.2273	-22.3436
23	S	3.8834	19.7477	66.0110	-15.7879	47	S	4.6429	25.8919	79.4128	-19.0221
	SH^+	4.3275	20.8344	73.8195	-17.6707		SH^+	4.0970	22.2204	76.4833	-18.6950
24	S	5.4799	27.6760	87.5991	-20.6247						
	SH^+	5.7557	32.8004	86.0092	-19.8750						

Table 5 — Thermodynamic values of S and SH^+ forms in RM1 semi-empirical quantum chemical methods at 298 K

No	Type	ΔH (kcal/mol)	C (cal/Kmol)	ΔS (cal/Kmol)	ΔG (kcal/mol)	No	Type	ΔH (kcal/mol)	C (cal/Kmol)	ΔS (cal/Kmol)	ΔG (kcal/mol)
1	S	2.3697	7.9764	45.0660	-11.0600	25	S	4.3077	23.3160	72.2337	-17.2180
	SH^+	2.3960	8.4410	44.5858	-10.8905		SH^+	3.8834	20.9635	71.0495	-17.2893
2	S	3.5467	16.5984	70.0132	-17.3172	26	S	4.2831	22.1561	71.3159	-16.9691
	SH^+	3.7907	20.3984	69.1424	-16.8138		SH^+	3.9155	20.5950	70.8783	-17.2063
3	S	3.9855	19.2536	70.7649	-17.1025	27	S	2.6787	11.7494	59.9699	-15.1924
	SH^+	3.9628	20.2811	71.6416	-17.3864		SH^+	2.8679	13.2794	61.2213	-15.3761

(*Contd.*)

Table 5 — Thermodynamic values of *S* and SH^+ forms in RM1 semi-empirical quantum chemical methods at 298 K (*Contd*.)

No	Type	ΔH (kcal/mol)	C (cal/Kmol)	ΔS (cal/Kmol)	ΔG (kcal/mol)	No	Type	ΔH (kcal/mol)	C (cal/Kmol)	ΔS (cal/Kmol)	ΔG (kcal/mol)
4	S	2.7961	12.2706	57.5617	-14.3573	28	S	2.6777	11.2210	59.9134	-15.1765
	SH+	3.1239	14.5535	59.6205	-14.6430		SH+	2.7080	12.0625	58.9674	-14.8643
5	S	2.4508	8.9398	44.6661	-10.8597	29	S	4.7094	27.8660	78.6338	-18.7235
	SH+	2.3796	8.2268	49.3251	-12.3192		SH+	4.5460	26.1804	78.3270	-18.7955
6	S	4.3406	25.3809	74.9444	-17.9929	30	S	10.4780	65.4213	117.6853	-24.5923
	SH^+	4.0070	23.7699	74.4978	-18.1933		SH^+	10.1635	61.9867	118.0714	-25.0218
7	S	3.4051	19.2238	64.4395	-15.7979	31	S	5.6143	30.7904	86.5278	-20.1710
	SH^+	3.6425	21.3386	69.3635	-17.0278		SH^+	6.0065	34.0476	89.9305	-20.7927
8	S	5.0577	28.6812	84.2028	-20.0347	32	S	2.6504	11.0575	53.5943	-13.3207
	SH^+	6.3551	34.8753	93.9794	-21.6507		SH^+	2.6840	11.8520	55.4171	-13.8303
9	S	4.0410	17.8439	82.6282	-20.5822	33	S	2.7135	11.0907	57.0200	-14.2785
	SH^+	4.4976	20.7554	83.1356	-20.2768		SH^+	2.5156	9.6891	56.3579	-14.2791
10	S	4.7417	24.7563	79.5788	-18.9728	34	S	4.6679	23.3502	80.0152	-19.1767
	SH^+	4.7257	26.2299	77.7605	-18.4469		SH^+	4.6395	24.2942	79.8993	-19.1705
11	S	6.4086	31.7457	92.9218	-21.2821	35	S	2.9914	13.1970	65.6361	-16.5681
	SH^+	6.1049	31.9442	91.4076	-21.1346		SH^+	3.1166	15.0454	66.4969	-16.6995
12	S	6.9767	31.2892	106.5167	-24.7653	36	S	3.5442	17.1913	68.4155	-16.8436
	SH^+	7.0745	33.0349	102.0235	-23.3285		SH^+	3.9305	19.0862	71.6017	-17.4068
13	S	2.4544	10.4777	56.1244	-14.2707	37	S	5.2928	27.8240	86.5932	-20.5120
	SH^+	2.8110	12.0765	63.0191	-15.9687		SH^+	5.1717	29.1694	83.6834	-19.7660
14	S	4.6485	22.0879	78.6014	-18.7747	38	S	4.8956	27.5175	82.7132	-19.7529
	SH^+	4.9809	23.4591	86.7865	-20.8815		SH^+	4.9078	28.8200	82.5919	-19.7045
15	S	3.8462	17.6203	73.7510	-18.1316	39	S	3.1703	15.3971	64.3357	-16.0017
	SH^+	3.8287	18.5894	72.9490	-17.9101		SH^+	3.1441	16.0950	65.6045	-16.4060
16	S	5.4115	33.2697	76.3651	-17.3453	40	S	5.1838	24.6728	87.4300	-20.8704
	SH^+	4.8263	30.4034	78.2133	-18.4812		SH^+	5.3331	26.5011	88.2866	-20.9763
17	S	4.6023	26.4236	79.4771	-19.0819	41	S	4.0089	23.5437	70.4451	-16.9837
	SH^+	4.7838	28.6256	79.8251	-19.0041		SH^+	4.5206	25.5979	73.8805	-17.4958
18	S	4.9542	27.4450	82.9650	-19.7694	42	S	3.3058	18.3275	67.4691	-16.8000
	SH^+	5.3377	30.0465	86.5083	-20.4417		SH^+	3.3930	19.2569	68.0272	-16.8791
19	S	5.5796	31.4558	79.9615	-18.2489	43	S	4.8741	28.4702	81.2477	-19.3377
	SH^+	5.0698	30.5628	77.6459	-18.0686		SH^+	4.8640	28.1592	81.8568	-19.5294
20	S	4.5423	27.7680	72.9161	-17.1867	44	S	3.8667	18.9322	75.2038	-18.5440
	SH^+	4.6732	27.7175	75.7970	-17.9143		SH^+	3.4785	20.4649	68.9060	-17.0555
21	S	4.7874	23.1178	80.4849	-19.1971	45	S	4.5094	25.2478	79.8144	-19.2753
	SH^+	4.8427	24.6566	80.7657	-19.2255		SH^+	4.8305	29.5486	79.2852	-18.7965
22	S	4.1940	22.7069	71.6669	-17.1628	46	S	6.3322	35.7634	96.2273	-22.3436
	SH^+	4.5094	23.3876	76.6301	-18.3264		SH^+	7.1127	37.9034	100.7166	-22.9009
23	S	3.8750	20.4258	66.0663	-15.8128	47	S	4.0970	22.2204	76.4833	-18.6950
	SH^+	3.8365	21.2522	67.1015	-16.1598		SH^+	4.3102	23.6800	77.9645	-18.9232
24	S	5.1956	29.7585	81.2499	-19.0169						
	SH^+	5.9797	32.8713	88.2347	-20.3142						

Table 6 — Thermodynamic values of S and SH^+ forms in PM3 semi-empirical quantum chemical methods at 298 K

No	Type	ΔH (kcal/mol)	C (cal/Kmol)	ΔS (cal/Kmol)	ΔG (kcal/mol)	No	Type	ΔH (kcal/mol)	C (cal/Kmol)	ΔS (cal/Kmol)	ΔG (kcal/mol)
1	S	2.3700	7.9831	45.0021	-11.0406	25	S	4.5213	22.6983	74.7334	-17.7493
	SH^+	2.3765	8.1326	46.0139	-11.3356		SH^+	4.3045	22.6170	73.6062	-17.6302
2	S	3.4198	17.6185	67.0478	-16.5605	26	S	3.8962	21.6114	68.6422	-16.5591
	SH^+	3.9992	21.1972	70.5036	-17.0109		SH^+	3.8416	19.7533	71.2219	-17.3825
3	S	3.8631	18.6697	69.8090	-16.9399	27	S	2.7998	12.5174	60.5760	-15.2519
	SH^+	3.7884	20.4525	69.4184	-16.8983		SH^+	2.9299	13.7744	61.4830	-15.3920
4	S	2.8255	12.3483	57.7358	-14.3797	28	S	2.6681	11.2854	59.8156	-15.1569
	SH^+	4.1989	18.9658	68.6057	-16.2456		SH^+	2.7522	12.3855	59.1417	-14.8720
5	S	2.3745	8.0955	45.8229	-11.2807	29	S	5.0252	29.5066	80.5799	-18.9876
	SH^+	2.4805	9.3442	49.6830	-12.3250		SH^+	4.5315	27.3010	77.5923	-18.5910
6	S	4.2036	24.5831	75.5664	-18.3152	30	S	9.7217	60.4154	114.5527	-24.4150
	SH^+	4.0629	23.8804	74.9616	-18.2757		SH^+	9.3901	59.1957	111.2861	-23.7732
7	S	3.4323	19.4683	64.5814	-15.8129	31	S	5.4003	30.2713	83.3864	-19.4488
	SH^+	3.7604	22.7000	69.8452	-17.0534		SH^+	6.2051	34.4531	92.4585	-21.3475
8	S	4.9524	28.7500	82.2355	-19.5537	32	S	2.8580	11.4386	56.7587	-14.0561
	SH^+	6.1443	34.1248	92.9303	-21.5490		SH^+	2.7645	11.4675	57.7476	-14.4443
9	S	3.9406	17.6353	79.9780	-19.8929	33	S	2.7488	11.1841	57.2578	-14.3140
	SH^+	4.5723	20.8237	86.8735	-21.3160		SH^+	3.4895	14.9507	62.6789	-15.1888
10	S	4.8955	25.0730	81.4662	-19.3814	34	S	4.6872	23.3776	80.7769	-19.3843
	SH^+	4.9619	26.5770	80.1797	-18.9317		SH^+	4.6870	24.8708	78.2601	-18.6345
11	S	6.5509	31.7728	94.5293	-21.6188	35	S	2.9736	13.5982	66.4694	-16.8343
	SH^+	6.3813	32.7895	92.9440	-21.3160		SH^+	3.1658	14.7533	66.9256	-16.7780
12	S	6.7782	30.8120	101.5574	-23.4859	36	S	3.6242	17.7398	68.8029	-16.8791
	SH^+	6.6058	32.1914	96.6439	-22.1941		SH^+	3.6611	18.3778	69.4759	-17.0427
13	S	2.4557	10.6065	56.0987	-14.2617	37	S	5.2266	27.9886	85.2277	-20.1713
	SH^+	2.8068	12.0209	61.8941	-15.6376		SH^+	5.3612	29.6921	84.9725	-19.9606
14	S	4.8817	20.7982	88.9020	-21.6111	38	S	4.9125	27.8392	82.1581	-19.5706
	SH^+	5.1477	21.9620	92.2468	-22.3418		SH^+	4.8658	28.7157	82.2360	-19.6405
15	S	3.4969	16.4964	71.1960	-17.7195	39	S	3.0765	15.2510	63.6346	-15.8867
	SH^+	3.6572	16.5133	73.3269	-18.1942		SH^+	3.3828	17.5224	66.9414	-16.5657
16	S	4.8502	33.7863	72.0352	-16.6162	40	S	5.1906	24.3039	88.5539	-21.1984
	SH^+	4.8584	30.2499	78.6325	-18.5740		SH^+	5.4140	26.6238	88.5815	-20.9833
17	S	4.6414	26.7843	79.6609	-19.0975	41	S	4.2731	23.8233	72.3339	-17.2824
	SH^+	4.8696	28.3627	81.1228	-19.3050		SH^+	4.7697	25.7666	76.6495	-18.0719
18	S	4.8831	27.0574	82.5743	-19.7240	42	S	3.3626	18.7402	67.7683	-16.8323
	SH^+	4.8076	27.7558	82.9958	-19.9251		SH^+	3.4005	19.3659	68.0568	-16.8805
19	S	5.5899	31.5227	79.9024	-18.2210	43	S	5.1587	29.6561	83.7802	-19.8078
	SH^+	5.2386	30.4685	79.3682	-18.4131		SH^+	5.4955	31.1996	87.4792	-20.5733
20	S	4.1902	24.4788	71.5422	-17.1294	44	S	3.9062	19.4611	73.8352	-18.0967
	SH^+	4.1291	24.3848	74.3868	-18.0382		SH^+	3.7110	21.2278	70.7828	-17.3822
21	S	4.8041	23.5970	80.3330	-19.1351	45	S	4.2248	24.7546	75.7322	-18.3434
	SH^+	5.0738	28.0356	80.7467	-18.9887		SH^+	4.4186	26.5949	75.7269	-18.1480
22	S	3.5629	19.6884	69.5693	-17.1688	46	S	6.4589	36.0216	94.1001	-21.5829
	SH^+	4.3605	22.7521	75.2823	-18.0736		SH^+	6.8199	38.1608	95.6876	-21.6950
23	S	3.8155	19.7807	65.5939	-15.7314	47	S	4.1906	22.4735	77.0572	-18.7724
	SH^+	3.8810	20.4128	68.0763	-16.4057		SH^+	4.3008	23.3498	77.8382	-18.8950
24	S	4.9063	27.7631	83.0263	-19.8355						
	SH^+	5.5187	31.7164	83.9730	-19.5052						

Table 7 —Thermodynamic values of S and SH^+ forms forms in AM1 semi-empirical quantum chemical methods at 298 K

No	Type	ΔH (kcal/mol)	C (cal/Kmol)	ΔS (cal/Kmol)	ΔG (kcal/mol)	No	Type	ΔH (kcal/mol)	C (cal/Kmol)	ΔS (cal/Kmol)	ΔG (kcal/mol)
1	S	2.3694	7.9697	45.0980	-11.0698	25	S	4.4403	21.4552	76.3155	-18.3017
	SH^+	2.3804	8.2144	44.6458	-10.9241		SH^+	3.7397	20.2436	70.1909	-17.1772
2	S	3.4923	16.1857	69.3972	-17.1881	26	S	4.0208	21.1470	69.6972	-16.7490
	SH^+	3.9556	18.8795	72.1307	-17.5394		SH^+	3.8773	20.0676	70.9617	-17.2693
3	S	3.5770	18.7543	68.2684	-16.7669	27	S	2.7245	11.9401	60.2016	-15.2156
	SH^+	3.7305	20.0946	69.2352	-16.9016		SH^+	2.8030	12.8437	60.8883	-15.3417
4	S	2.7731	11.9186	57.5211	-14.3682	28	S	2.5992	10.6978	59.5546	-15.1481
	SH^+	4.1426	18.4630	68.4318	-16.2501		SH^+	2.7081	11.9070	59.0209	-14.8801
5	S	2.3783	8.1638	45.8341	-11.2803	29	S	4.6298	27.3169	77.9471	-18.5984
	SH^+	2.3777	8.1847	49.2933	-12.3117		SH^+	4.4019	26.0670	76.9407	-18.5264
6	S	4.2908	24.4602	76.4333	-18.4864	30	S	9.7077	60.2524	113.3552	-24.0721
	SH^+	4.0359	23.4665	74.7593	-18.2424		SH^+	9.4050	58.2340	112.6431	-24.1626
7	S	3.2689	18.3009	63.7444	-15.7270	31	S	5.4337	29.5942	84.0704	-19.6193
	SH^+	3.5344	20.0456	68.9545	-17.0140		SH^+	6.4335	34.5591	95.3466	-21.9798
8	S	4.9140	27.7820	82.3414	-19.6237	32	S	2.6924	10.3806	55.4137	-13.8209
	SH^+	6.3475	34.3367	94.6064	-21.8453		SH^+	2.7457	12.0628	55.7515	-13.8682
9	S	4.2161	18.3841	84.0987	-20.8453	33	S	2.6904	10.6189	57.0264	-14.3035
	SH^+	4.8537	20.2798	94.7756	-23.3894		SH^+	2.7339	12.2423	57.8009	-14.4908
10	S	4.8134	24.1009	81.4685	-19.4642	34	S	4.5767	22.6873	78.2359	-18.7376
	SH^+	4.8878	25.6123	79.6693	-18.8537		SH^+	4.5263	23.9143	77.1818	-18.4739
11	S	6.4644	30.8945	94.4647	-21.6861	35	S	2.7919	12.1069	64.2652	-16.3591
	SH^+	6.5564	33.0363	95.8989	-22.0215		SH^+	3.1730	14.3834	67.4676	-16.9324
12	S	6.8897	30.5487	103.5202	-23.9593	36	S	3.7056	16.7781	72.4434	-17.8825
	SH^+	6.9382	31.4650	103.0092	-23.7585		SH^+	3.7176	17.7849	71.1026	-17.4709
13	S	2.4361	10.4719	55.9379	-14.2334	37	S	4.8371	26.0223	81.8655	-19.5588
	SH^+	2.7729	11.9356	62.7547	-15.9280		SH^+	5.1137	27.8407	83.8133	-19.8627
14	S	4.3068	21.0823	76.2788	-18.4243	38	S	4.8175	26.9958	81.2414	-19.3925
	SH^+	4.7540	22.4336	84.8521	-20.5319		SH^+	4.6580	27.4662	80.9066	-19.4522
15	S	3.4777	16.3553	72.2864	-18.0637	39	S	2.9065	13.1737	64.3718	-16.2763
	SH^+	3.9960	19.6147	73.8925	-18.0240		SH^+	3.0437	15.3460	64.9697	-16.3172
16	S	4.7889	30.9992	72.1866	-16.7227	40	S	4.8203	22.6562	85.1724	-20.5611
	SH^+	4.7377	29.4761	77.7181	-18.4223		SH^+	5.4241	25.3516	90.3496	-21.5001
17	S	4.6271	25.7945	80.1638	-19.2617	41	S	3.8818	22.8704	69.8433	-16.9315
	SH^+	4.9187	27.1734	87.1712	-21.0583		SH^+	4.5134	25.1885	73.9814	-17.5330
18	S	4.7065	25.9363	81.6987	-19.6397	42	S	3.2390	17.6986	67.1714	-16.7781
	SH^+	5.0079	28.4039	84.3102	-20.1165		SH^+	3.3059	18.5026	67.6152	-16.8434
19	S	5.4927	31.7901	78.4776	-17.8937	43	S	5.3237	30.7317	85.0818	-20.0307
	SH^+	4.8536	28.4055	77.1182	-18.1277		SH^+	5.4428	30.6597	86.0420	-20.1977
20	S	5.0776	28.9706	79.5175	-18.6187	44	S	3.6873	17.9674	72.4290	-17.8965
	SH^+	5.1500	30.7782	78.7669	-18.3226		SH^+	3.6183	20.6369	69.7663	-17.1720
21	S	4.3633	23.0009	75.8138	-18.2292	45	S	4.1557	23.9665	75.4824	-18.3380
	SH^+	4.6055	23.1302	78.9095	-18.9095		SH^+	4.5132	27.2134	77.6070	-18.6137
22	S	4.1702	21.2431	73.7372	-17.8035	46	S	5.9104	33.5615	88.1110	-20.3467
	SH^+	4.5540	23.3814	76.5803	-18.2670		SH^+	6.6692	35.4242	96.9332	-22.2169
23	S	3.3841	17.9920	62.9309	-15.3693	47	S	4.6625	23.0496	81.5586	-19.6420
	SH^+	3.7571	19.5049	67.1981	-16.2680		SH^+	4.6049	24.1842	80.8889	-19.4999
24	S	5.1202	29.1256	80.9968	-19.0169						
	SH^+	5.4191	30.5130	84.5700	-19.7827						

Table 8 — Thermodynamic values S and SH^+ forms in MNDO semi-empirical quantum chemical methods at 298 K

No	Type	ΔH (kcal/mol)	C (cal/Kmol)	ΔS (cal/Kmol)	ΔG (kcal/mol)	No	Type	ΔH (kcal/mol)	C (cal/Kmol)	ΔS (cal/Kmol)	ΔG (kcal/mol)
1	S	2.3692	7.9631	44.9461	-11.0247	25	S	4.7109	23.1407	76.0154	-17.9417
	SH^+	2.3964	8.4129	44.5459	-10.8783		SH^+	3.6851	19.2855	70.5448	-17.3373
2	S	3.2278	16.2683	66.0930	-16.4679	26	S	3.8698	18.6388	69.6966	-16.8998
	SH^+	3.5500	18.6162	67.9760	-16.7069		SH^+	3.6988	19.2906	69.2922	-16.9503
3	S	3.3754	18.2032	65.5093	-16.1464	27	S	2.7436	11.8920	60.3462	-15.2396
	SH^+	3.7574	20.1449	69.3804	-16.9180		SH^+	2.8122	12.9140	60.9089	-15.3386
4	S	2.7588	11.7844	57.4457	-14.3600	28	S	2.5882	10.5510	59.4936	-15.1408
	SH^+	3.1339	14.3438	59.7657	-14.6763		SH^+	2.8254	12.2902	59.6908	-14.9624
5	S	2.3729	8.0590	45.8533	-11.2914	29	S	4.7191	26.8193	79.4180	-18.9474
	SH^+	2.3767	8.1594	49.2903	-12.3118		SH^+	4.8460	26.1304	84.1886	-20.2422
6	S	3.9511	23.0003	74.1594	-18.1484	30	S	9.4858	59.5405	114.1987	-24.5454
	SH^+	3.9756	23.1769	74.4552	-18.2120		SH^+	9.4627	59.0997	111.2772	-23.6979
7	S	3.3959	18.8952	64.5046	-15.8265	31	S	5.7353	29.7232	87.6827	-20.3942
	SH^+	3.7079	20.5426	71.6350	-17.6393		SH^+	6.2510	34.0321	91.4348	-20.9965
8	S	4.8457	27.3734	82.2366	-19.6608	32	S	2.8201	10.4835	56.7531	-14.0923
	SH^+	5.0487	28.6621	84.5619	-20.1508		SH^+	2.7529	12.4251	55.8343	-13.8858
9	S	3.7015	16.0714	78.4713	-19.6829	33	S	2.5494	10.3921	54.3430	-13.6448
	SH^+	4.7800	19.6871	97.7422	-24.3472		SH^+	2.8436	12.7564	58.0995	-14.4701
10	S	4.9455	24.2698	82.5042	-19.6408	34	S	4.5768	22.3744	79.2618	-19.0432
	SH^+	4.7858	24.3833	82.1294	-19.6887		SH^+	4.7107	23.6741	79.7737	-19.0619
11	S	5.9819	27.8809	93.0131	-21.7360	35	S	2.7948	11.8218	64.5210	-16.4324
	SH^+	6.7271	32.5409	98.9764	-22.7679		SH^+	3.1740	14.0767	68.2382	-17.1610
12	S	6.3404	31.2729	93.3540	-21.4791	36	S	3.5629	16.6302	68.7381	-16.9210
	SH^+	6.1142	30.1829	91.8196	-21.2480		SH^+	2.5997	17.5593	68.9786	-17.9559
13	S	2.4538	10.3672	56.1589	-14.2815	37	S	5.0564	26.0936	83.9689	-19.9663
	SH^+	2.8189	12.0035	63.1115	-15.9883		SH^+	4.8666	27.3425	80.8930	-19.2395
14	S	4.0966	19.8852	74.7858	-18.1896	38	S	4.8146	27.0342	81.5795	-19.4961
	SH^+	4.0684	18.9840	80.6019	-19.9510		SH^+	5.2042	29.0014	87.4036	-20.8421
15	S	3.7498	17.4241	73.7232	-18.2198	39	S	2.8700	13.5794	62.6393	-15.7966
	SH^+	3.4732	15.8755	71.5727	-17.8555		SH^+	3.0533	15.2137	65.1144	-16.3508
16	S	5.2347	32.2963	75.8018	-17.3542	40	S	5.0993	24.4489	85.4727	-20.3716
	SH^+	4.5738	27.8747	77.1150	-18.4065		SH^+	5.3000	25.2944	89.3222	-21.3181
17	S	4.6231	25.4680	80.5507	-19.3811	41	S	3.9562	21.9949	70.5559	-17.0695
	SH^+	4.9207	26.7709	85.5240	-20.5654		SH^+	4.6026	24.8597	76.0007	-18.0456
18	S	4.6987	25.7932	81.6815	-19.6424	42	S	3.2694	17.7571	68.7445	-17.2164
	SH^+	5.0358	28.3968	84.7428	-20.2175		SH^+	3.3259	18.5192	67.7569	-16.8657
19	S	5.1932	29.9510	76.4474	-17.5881	43	S	5.2978	29.6246	84.3347	-19.8340
	SH^+	5.1896	29.4787	79.5325	-18.5111		SH^+	5.5672	30.4408	87.5162	-20.5127
20	S	4.0588	24.4070	70.4826	-16.9450	44	S	3.5759	17.7156	69.5438	-17.1482
	SH^+	4.1776	24.5862	72.6583	-17.4745		SH^+	3.7742	19.2771	70.5774	-17.2579
21	S	4.3550	23.3582	74.9284	-17.9736	45	S	4.4137	24.3774	78.7258	-19.0466
	SH^+	4.4734	24.2952	75.7969	-18.1140		SH^+	4.3111	25.6146	76.5699	-18.5067
22	S	4.6200	22.6598	78.7556	-18.8491	46	S	6.1111	33.7884	90.1745	-20.7609
	SH^+	4.7953	24.5772	78.2916	-18.5356		SH^+	6.1214	34.4555	89.8675	-20.6592
23	S	3.3675	17.3226	62.9389	-15.3882	47	S	4.4214	22.3033	79.9486	-19.4033
	SH^+	3.8190	19.8585	67.4508	-16.2813		SH^+	4.3165	22.5419	79.8755	-19.4864
24	S	5.1419	27.2310	83.4208	-19.7175						
	SH^+	5.0391	29.6704	80.1763	-18.8534						

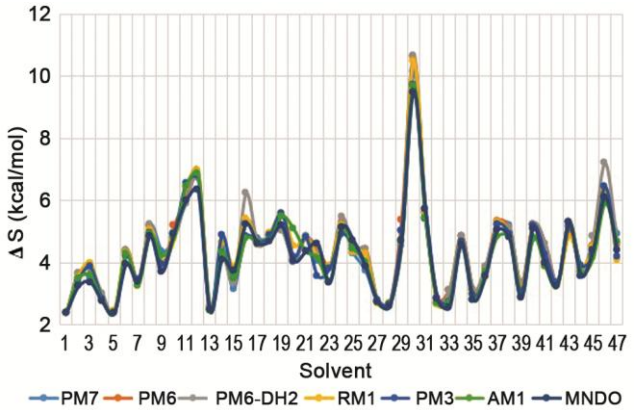

Fig. 1 — Thermodynamic values of ΔH (kcal/mol) is calculated with semi-empirical quantum chemical method for *S* form.

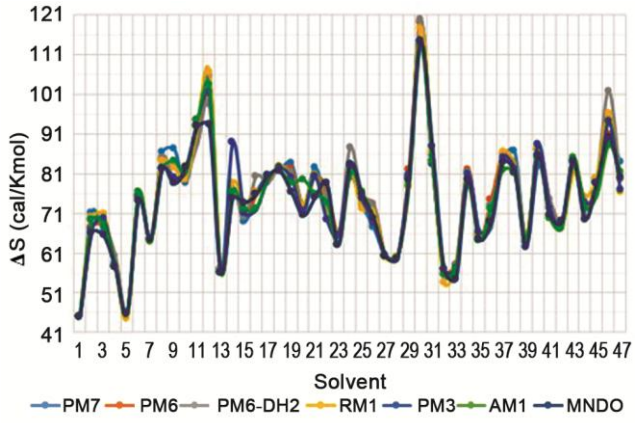

Fig. 2 — Thermodynamic values of ΔS (cal/Kmol) is calculated with semi-empirical quantum chemical method for *S* form.

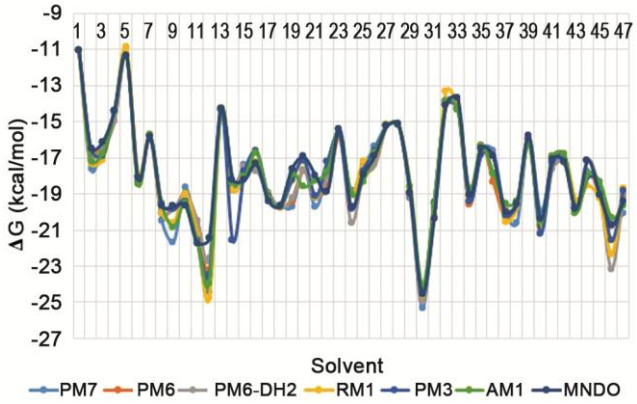

Fig. 3 — Thermodynamic values of ΔG (kcal/mol) is calculated with semi-empirical quantum chemical method for *S* form.

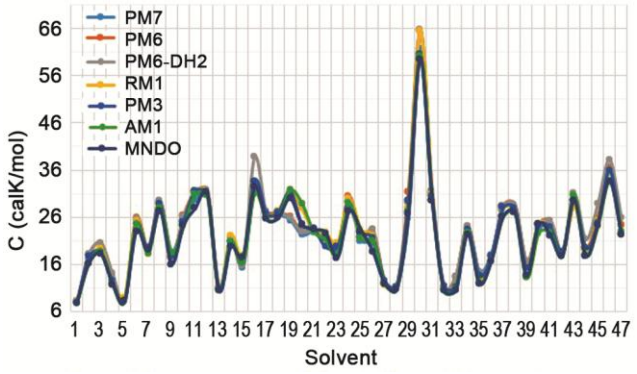

Fig. 4 — Thermodynamic values of C (calK/mol) is calculated with semi-empirical quantum chemical method for *S* form.

Results and Discussion

The enthalpy, H, is described as H = U + pV, where p is the pressure of the system, and V is its volume. Because U (internal energy), p, and V are all state functions, the enthalpy is a state function, too. As is true of any state function, the change in enthalpy, ΔH and between any pair of initial and final states is independent of the path between them. Although the definition of enthalpy may appear arbitrary, it has important implications for thermochemistry. An enthalpy change can be measured calorimetrically by monitoring the temperature change that accompanies a physical or chemical change occurring at constant pressure. A calorimeter for studying processes at constant pressure is called an isobaric calorimeter[19]. But, we theoretically calculated the enthalpy value in this study through semi-empirical quantum chemical methods (PM7, PM6, PM6-DH2, RM1, PM3, AM1, and MNDO) at 298 K in computational chemistry with MOPAC 2016 computer program. When the values are examined in Table 2 – 8, we see that the greatest values of enthalpy (ΔH, kcal/mol) are obtained in hexamethyl phosphoramide ($C_6H_{18}N_3OP$) for forms of S; 10.1573 kcal/mol for PM7, 10.6335 kcal/mol for PM6, 10.6743 kcal/mol for PM6-DH2, 10.4780 kcal/mol for RM1, 9.7217 kcal/mol for PM3, 9.7077 kcal/mol for AM1, 9.4858 kcal/mol for MNDO and for forms of SH^+; 9.0521 kcal/mol for PM7, 9.9707 kcal/mol for PM6, 9.9163 kcal/mol for PM6-DH2, 10.1635 kcal/mol for RM1, 9.3901 kcal/mol for PM3, 9.4050 kcal/mol for AM1, 9.4627 kcal/mol for MNDO. The lowest values of enthalpy are obtained in water (H_2O) for forms of S 2.3741 kcal/mol for PM7, 2.3732 kcal/mol for PM6, 2.3732 kcal/mol for PM6-DH2, 2.3697 kcal/mol for RM1, 2.3700 kcal/mol for PM3, 2.3694 kcal/mol for AM1 and 2.3692 kcal/mol for MNDO, for forms of SH^+ obtained in ammonia (NH_3) 2.3807 kcal/mol for PM7, 2.3826 kcal/mol for PM6, 2.3850 kcal/mol

for PM6-DH2, 2.3796 kcal/mol for RM1, 2.3777 kcal/mol for AM1, 2.3767 kcal/mol for MNDO and obtained in water (H_2O) 2.3765 kcal/mol for PM3.

The greatest values of heat capacity (C, cal/Kmol) are obtained in hexamethyl phosphoramide ($C_6H_{18}N_3OP$) for forms of S; 9.0521 cal/Kmol for PM7, 65.4450 cal/Kmol for PM6, 65.7565 cal/Kmol for PM6-DH2, 65.4213 cal/Kmol for RM1, 60.4154 cal/Kmol for PM3, 60.2524 cal/Kmol for AM1, 59.5405 cal/Kmol for MNDO and for forms of SH^+; 57.3759 cal/Kmol for PM7, 62.4778 cal/Kmol for PM6, 62.3559 cal/Kmol for PM6-DH2, 61.9867 cal/Kmol for RM1, 59.1957 cal/Kmol for PM3, 58.2340 cal/Kmol for AM1, 59.0997cal/Kmol for MNDO. The lowest values of heat capacity are obtained in water (H_2O) for forms of S 8.0685 cal/Kmol for PM7, 8.0524 cal/Kmol for PM6, 8.0524 cal/Kmol for PM6-DH2, 7.9764 cal/Kmol for RM1, 7.9831 cal/Kmol for PM3, 7.9697 cal/Kmol for AM1, 7.9631 cal/Kmolfor MNDO, for forms of SH^+ obtained in ammonia (NH_3) 8.2508 cal/Kmol for PM7, 8.2910 cal/Kmol for PM6, 8.3410 cal/Kmol for PM6-DH2, 8.2268 cal/Kmol for RM1, 8.1847 cal/Kmol for AM1, 8.1594 cal/Kmol for MNDO and obtained in H_2O 8.1326 cal/Kmol for PM3.

The greatest values of entropy (ΔS, cal/Kmol) are obtained in hexamethyl phosphoramide ($C_6H_{18}N_3OP$) for forms of S; 119.1064 cal/Kmol for PM7, 119.2760 cal/Kmol for PM6, 119.7385 cal/Kmol for PM6-DH2, 117.6853 cal/Kmol for RM1, 114.5527 cal/Kmol for PM3, 113.3552 cal/Kmol for AM1, 114.1987 cal/Kmol for MNDO and for forms of SH^+; 110.1792 cal/Kmol for PM7, 114.4787 cal/Kmol for PM6, 114.0797 cal/Kmol for PM6-DH2,118.0714 cal/Kmol for RM1, 111.2861 cal/Kmol for PM3, 112.6431 cal/Kmol for AM1, 111.2772 cal/Kmol for MNDO. The lowest values of entropy are obtained in water (H_2O) for forms of S 45.1274 cal/Kmol for PM7, 45.1079 cal/Kmol for PM6, 45.1079 cal/Kmol for PM6-DH2, 45.0021 cal/Kmol for PM3, 45.0980 cal/Kmol for AM1, 44.9461 cal/Kmol for MNDO and obtained in ammonia (NH_3) 44.6661 cal/Kmol for RM1, for forms of SH^+ obtained in water (H_2O) 46.4224 cal/Kmol for PM7, 44.5931 cal/Kmol for PM6, 44.5858 cal/Kmol for RM1, 46.0139 cal/Kmol for PM3, 44.6458 cal/Kmol for AM1, 44.5459 cal/Kmol for MNDO and obtained in ammonia (NH_3) 44.3971 cal/Kmol for PM6-DH2.

Finally, when we examine, we found that the greatest values of free energy (ΔG, kcal/mol) for forms of S are obtained in hexamethyl phosphoramide ($C_6H_{18}N_3OP$) -25.7813 kcal/mol for PM7, 24.9107 kcal/mol for PM6, -25.0077 kcal/mol for PM6-DH2, -24.4150 kcal/mol for PM3, -24.0721 kcal/mol for AM1, -24.5454 kcal/mol for MNDO, and are obtained in tert-butanol ($((CH_3)_3COH$) -24.7653 kcal/mol for RM1, for forms of SH^+; -23.7813 kcal/mol for PM7, -24.1440 kcal/mol for PM6, -24.0795 kcal/mol for PM6-DH2, -25.0218 kcal/mol for RM1, -23.7732 kcal/mol for PM3, -24.1626 kcal/mol for AM1, -23.6979 kcal/mol for MNDO. The lowest values of free energy are obtained in water (H_2O) for forms of S -11.0738 kcal/mol for PM7, -11.0689 kcal/mol for PM6, -11.0689 kcal/mol for PM6-DH2, -11.0406 kcal/mol for PM3, -11.0698 kcal/mol for AM1, 11.0247 kcal/mol for MNDO, and obtained 10.8597 kcal/mol for RM1 in ammonia (NH_3), for forms of SH^+ obtained 11.4375 kcal/mol for PM7, -10.8723 kcal/mol for PM6, -10.8905 kcal/mol for RM1, -11.3356 kcal/mol for PM3, -10.9241 kcal/mol for AM1, -10.8783 kcal/mol for MNDO in water (H_2O), and obtained -10.8453 kcal/mol for PM6-DH2 in ammonia.

When its temperature is increased, the internal energy of a substance increases as well. The increase depends on the conditions under which the heating takes place. So, we suppose that the sample is confined to a constant volume. If the internal energy is plotted against temperature, then a curve like the one in Fig. 5 may be obtained. The slope of the

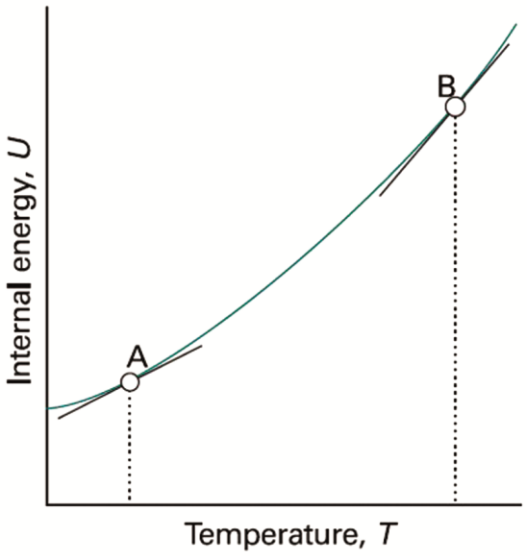

Fig. 5 — The internal energy of a system increases as the temperature is raised; this graphs ows its variation as the system is heated at constant volume. The slope of the tangent to the curve at any temperature is the heat capacity at constant volume at that temperature. Note that, for the system illustrated, the heat capacity is greater at B than at A[19].

tangent to the curve at any temperature is called the heat capacity of the system at that temperature. The heat capacity at constant volume is denoted C[19]. The second law of thermodynamics can be expressed in terms of the entropy, S. which is used to identify the spontaneous changes among those permissible changes. The entropy of an isolated system increases in the course of a spontaneous change: $\Delta S_{tot} > 0$ where S_{tot} is the total entropy of the system and its surroundings. Thermodynamically irreversible processes (like cooling to the temperature of the surroundings and the free expansion of gases) are spontaneous processes, and hence must be accompanied by an increase in total entropy[19]. When Table 2 – 8 are examined, it has been observed that the change of free energy has different values between solvents and models.

Conclusions

As a result, the pKa values of organic molecules which are synthesized or are thought to be synthesized can be calculated by using these obtained values. In short, a large data base for researchers has been created. Many researchers who want to work with these solvents can use these values to calculate the different quantitative properties of organic molecules. It is because these values are of importance for quantitative calculations.

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