Quantum chemical calculations of bond dissociation energies for COOH scission and electronic structure in some acids*

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Quantum chemical calculations are performed to investigate the equilibrium C–COOH bond distances and the bond dissociation energies (BDEs) for 15 acids. These compounds are studied by utilizing the hybrid density functional theory (DFT) (B3LYP, B3PW91, B3P86, PBE1PBE) and the complete basis set (CBS–Q) method in conjunction with the 6-311G** basis as DFT methods have been found to have low basis sets sensitivity for small and medium molecules in our previous work. Comparisons between the computational results and the experimental values reveal that CBS–Q method, which can produce reasonable BDEs for some systems in our previous work, seems unable to predict accurate BDEs here. However, the B3P86 calculated results accord very well with the experimental values, within an average absolute error of 2.3 kcal/mol. Thus, B3P86 method is suitable for computing the reliable BDEs of C–COOH bond for carboxylic acid compounds. In addition, the energy gaps between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of studied compounds are estimated, based on which the relative thermal stabilities of the studied acids are also discussed.

Keywords: bond dissociation energy, density functional theory, CBS–Q method

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1. Introduction

Esters of carboxylic acids, such as acetic acid molecules, one of the simplest and most widely used carboxylic acids having many important chemical and industrial applications, are important in a variety of products, ranging from perfumes to biofuels, which are of particular significance due to the rising price of crude oil and environmental concerns.[1–3] Glycolic acid, or the simplest α-hydroxycarboxylic acid with the functional groups of OH and COOH bonded at neighboring carbon atoms, is a widely used chemical in skincare. It is used to reduce wrinkles, and to treat acne in many patients around the world. Glycolic acid is also a useful compound in organic synthesis reactions including long chain polymerization processes.[4,5] In preference to more common mineral acids, oxalic acid is widely used as a neutralizing and acidifying agent, when its properties justify its higher cost. It is also used in textile manufacture and processing, wood and metal treatment, and the manufacture of miscellaneous chemical derivatives. The acid and its salts are extensively used as reagents in chemical analysis.[6] Benzoic acid and its salt, since it is widely regarded as the most active against yeasts, moulds and the least active against bacteria, are extensively used as preservatives in foods, beverages, toothpastes, mouthwashes, dentifrices, cosmetics, and pharmaceuticals.[7–10] 2-phenylacetic acid, often used in some perfumes possessing a honey-like odour and penicillin production, is an organic compound containing a phenyl functional group and an acetic acid functional group. It is expected to play very competitive and complex roles in determining its ground state conformational stability. The phenylacetic acid may also be a potent inhibitor of nitric oxide synthesis, which is an important signaling molecule that mediates a variety of essential physiological processes including neurotransmission, vasodilatation, and host cell defense.[11–15] However, several previous papers only focused on the molecular structures and vibration frequencies. In particular, the details concerning the bond strength characteristics of carboxylic acid compounds, which are of fundamental importance for the radical chemistry and the synthesis of organic materials and can be obtained by calculating the bond dissociation energy (BDE), have not been examined.

Bond dissociation enthalpy, useful for the prediction or interpretation of reactivity and selectivity in free radical chemistry, is an important thermodynamic quantity that contributes to the understanding of a diversity of processes ranging from enzyme mechanisms to surface chemistry. The bond dissociation enthalpy is also called the bond dissociation energy (BDE), of which the magnitude is primarily determined by the natures of the atoms involved in the bond. Many organic molecules studied in this work are often used as radical and intermediate sources. For most small and medium sized carboxylic acids here, experimental BDEs are not always determined directly. They can be derived from $\Delta_f H^0$ as explained in Ref. [16], which shows that most of the experimental measurements are of standard enthalpies of combustion by bomb and

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by flame calorimetry and are generally of the high accuracy required to calculate standard enthalpies of formation within 1 kJ/mol accuracy. But for large molecules, especially those unstable molecules, it is very difficult to experimentally determine the carboxylic radical stabilities of these molecules to the best of our knowledge. So it is accordingly important to be able to determine computationally the BDEs for carboxylic acids, which means that quantum chemical methods may provide valuable solutions to obtain accurate BDEs for those unstable molecules.

To date, many study results have indicated that quantum chemical method, especially the density-functional theory (DFT), is a powerful method of predicting the geometry and harmonic vibrations of organic compounds.[17–25] The DFT is a useful method for investigating large molecules. For example, Jursic and Martin,[17] and Jursic[18] produced the reliable BDEs for H–O, O–O, and C–N bonds by hybrid B3LYP method and non-local BLYP method. Feng *et al*.[19] predicted the accurate BDEs of N–H bond for five- and six-membered ring aromatic compounds by CBSQ and G3 methods. Maung[20] evaluated the satisfactory BDEs for both RS–R and RS–H bond dissociations using BH and HLYP, B3P86, and B3LYP models. Shao *et al*.[21] investigated the reliable BDEs for C–NO_2 bond in some nitroaromatic molecules employing B3P86 method with 6-311G** basis set. In our previous work,[26–29] we have performed a series of systematic studies about the BDEs of C–NH_2, C–CN, C–SH, and C–OH in four different kinds of compounds. The B3P86 and CBS–Q methods have been found to be very accurate for computing the reliable BDEs for those compounds. Moreover, it seems that different quantum chemical computational methods are suitable for different molecular systems. To the best of our knowledge, for C–COOH bond in carboxylic acids, little attention has been paid to the information about the BDEs. Whether computational methods listed above are suitable to the production of the reliable results for carboxylic acids is still not known. If we can find out an accurate computational method to compute BDEs of C–COOH bond, it would be possible to use this method to predict those molecules whose experimental BDEs have not been available. These predictions will also be helpful for performing the organic synthesis and decomposition of carboxylic acids.

As a continuation of the interest in important carboxylic acids, we have addressed the important issues to deal with the systematic comparison of the BDEs for C–COOH bond dissociation in 15 title carboxylic acid compounds and to test whether the rule obtained in our previous work[26–29] is still suitable to the studied compounds. All the BDEs are calculated by employing the hybrid density functional theory (B3LYP, B3PW91, B3P86, and PBE1PBE) methods together with the 6-311G** basis set. For comparison, the complete basis set (CBS–Q) method is also utilized to estimate the C–COOH bond dissociation energies. By comparing the calculated results with the available experimental values, the suitabilities of four hybrid DFT methods and CBS–Q method of computing reliable bond dissociation energies of C–COOH bond for carboxylic acids are discussed. In addition, the energy gaps between the HOMO and LUMO of the title compounds are also investigated.

2. Computational methods

All calculations are performed by using the GAUSSIAN 03 program package.[30] For all studied compounds, geometry optimization is conducted. Each optimized structure is confirmed by the frequency calculation to be the real energy minimum with no imaginary vibration frequency. The equilibrium geometries and bond dissociation energies are obtained at the Becke-style three-parameter DFT[31] with the Lee–Yang–Parr correlation function (B3LYP),[32,33] the Perdew–Wang's 91 expression (B3PW91),[34] and Perdew's 86 (B3P86).[35] The 6-311G** basis set is employed for the four hybrid DFT methods. For its explanation see Ref. [36].

The complete basis set (CBS–Q) method,[37–47] which has been used to produce accurate BDE values in our previous work, is also utilized in the present study for comparison. More details about this method and basis set abbreviation can be found in Ref. [26]. Throughout the text, if the theory level is not specified then the discussed energies are obtained through CBS–Q (298.15 K) computational studies.

The C–COOH bond strength is obtained by calculating the BDE, defined here as the enthalpy change of the homolytic bond dissociation reaction:

$$R-X \rightarrow R\cdot + X\cdot . \tag{1}$$

Take acetic acid studied in this paper for example:

$$CH_3COOH \rightarrow CH_3\cdot + COOH\cdot .$$

The homolytic bond dissociation enthalpy (DH) of the *R*–*X* bond is computed from the heat of formation at 298.15 K of the species involved in the dissociation, i.e.,

$$E_{\mathrm{BDE}} = \Delta_{\mathrm{f}}H^0_{298.15,R} + \Delta_{\mathrm{f}}H^0_{298.15,X} - \Delta_{\mathrm{f}}H^0_{298.15,RX}. \tag{2}$$

For many organic molecules, BDE and DH are almost numerically equivalent, thus the terms "bond dissociation energy" and "bond dissociation enthalpy" often appear interchangeably in the literature.[48] Correspondingly, for carboxylic acids studied in this work, the homolytic bond dissociation energy of acetic acid (CH_3COOH) can be given as follows:

$$E_{\mathrm{BDE}} = E(CH_3) + E(COOH) - E(CH_3COOH). \tag{3}$$

The total energy E of each species includes electronic energy (E_e) and zero-point correction (ZPE) generated from a vibrational frequency calculation.

The average errors of the BDEs for the CBS–Q, B3LYP, B3P86, B3PW91, and PBE1PBE methods are determined by calculating the average absolute error (ε_{aae}) defined as

$$\varepsilon_{aae} = \frac{1}{N}\sum_{i=1}^{N}|x_i - c_i|, \quad (4)$$

where x_i represents the calculated data, c_i denotes experimental values, and N is the number of experimental or computational data.

3. Results and discussion

For R–COOH molecules, the BDEs can be obtained by calculating the total energies (including zero-point energies) of each parent carboxylic acid, the corresponding R fragment and COOH scission. The optimized CBS–Q and four hybrid density functional theory geometries and bond dissociation energies are presented in Tables 1 and 2. Because some experimental equilibrium bond distances are not available to the best of our knowledge, we only present 2 calculated equilibrium bond distances for CH_3–COOH and HOC(O)–COOH in Table 1 for comparison. Summarized in Table 3 are the calculated energy gaps between the HOMO and LUMO ($\Delta E = E_{LUMO} - E_{HOMO}$) of the carboxylic acids at various levels.

Table 1. Equilibrium C–COOH bond distances (Å, 1 Å=0.1 nm) for two acid compounds studied at various levels of theory and the experimental values.

	CH_3–COOH	HOC(O)–COOH
B3P86/6-311G**	1.412 (0.105)[b]	1.421 (0.123)
B3LYP/6-311G**	1.417 (0.100)	1.425 (0.119)
B3PW91/6-311G**	1.420 (0.097)	1.429 (0.115)
PBE1PBE/6-311G**	1.436 (0.081)	1.445 (0.099)
CBS–Q	1.359 (0.158)	1.367 (0.177)
Exp.[a]	1.517	1.544

[a]See Ref. [49]

[b]All the values in the parentheses correspond to the experimental results minus the theoretical results.

Table 2. The BDEs (kcal/mol) at 298.15 K for removal of the carboxyl group in the acid compounds at various levels of theory[a].

	B3P86 /6-311G**	B3LYP /6-311G**	B3PW91 /6-311G**	PBE1PBE /6-311G**	CBS–Q	Exp.[b] at 298.15 K
$HOCH_2$–COOH	86.6 (2.2)[c]	82.2 (6.6)	83.9 (4.9)	86.6 (2.2)	90.8 (–2.0)	88.8±1.3
HOC(O)–COOH	81.4 (–1.4)	76.5 (3.5)	78.5 (1.5)	81.2 (–1.2)	84.6 (–4.6)	80.0±1.5
CH_3–COOH	86.0 (6.0)	81.7 (10.3)	83.4 (8.6)	83.6 (8.4)	89.2 (2.8)	92.0±2.0
C_2H_3–COOH	105.0 (–1.0)	100.5 (3.5)	102.2 (1.8)	104.9 (–0.9)	107.8 (–3.8)	104.0±2.0
C_2H_5–COOH	88.7 (2.1)	84.1 (6.7)	85.9 (4.9)	88.7 (2.1)	93.4 (–2.6)	90.8±1.5
C_3H_7–COOH	89.5 (1.5)	84.9 (6.1)	86.7 (4.3)	89.6 (1.4)	94.9 (–3.9)	91.0±1.5
C_4H_9–COOH	89.1 (1.6)	84.4 (5.3)	86.2 (3.5)	89.2 (0.5)	95.2 (–5.5)	89.7±1.5
sC_4H_9–COOH	85.8 (5.8)	81.6 (10)	82.7 (8.9)	81.3 (10.3)	95.1 (–3.5)	91.6±3.0
tC_4H_9–COOH	83.2 (–0.7)	78.1 (4.4)	79.9 (2.6)	83.6 (–1.1)	93.3 (–10.8)	82.5±4.0
C_5H_{11}–COOH	90.7 (–1.9)	85.9 (2.9)	87.8 (1.0)	90.8 (–2.0)	–[d]	88.8±1.5
C_6H_{13}–COOH	87.8 (1.9)	83.3 (6.4)	85.0 (4.7)	87.9 (1.8)	–	89.7±1.5
C_6H_5–COOH	98.7 (4.0)	94.0 (8.7)	95.6 (7.1)	98.5 (4.2)	–	102.7±2.0
$C_6H_5CH_2$–COOH	71.1 (–4.1)	66.1 (0.9)	68.5 (–1.5)	71.5 (–4.5)	–	67.0±0.0
$C_{10}H_7$–1–COOH	103.0 (–0.2)	98.2 (4.6)	99.5 (3.3)	102.9 (–0.1)	–	102.8±2.0
$C_{10}H_7$–2–COOH	105.8 (–1.0)	101.3 (3.5)	102.6 (2.2)	106.1(–1.3)	–	104.8±2.0
Average absolute error	2.3	5.6	4.1	2.8	4.4	
Max. error	6.0	10.3	8.6	8.4	–10.8	

[a]Zero-point energies are taken into account.
[b]The data are from Ref. [50].
[c]All the values in the parentheses correspond to the experimental results minus the theoretical results.
[d]Impossible to evaluate with current computational facilities.

Initially, we examine the C–COOH bond lengths of carboxylic acid compounds by various DFT methods. From Table 1, the theoretically predicted structure of carboxylic acids reveals that the bond lengths of 2 acids produced by B3P86 functional with 6-311G** basis set are the worst, with the C–COOH bond lengths for CH_3–COOH and HOC(O)–COOH being 1.412 Å and 1.421 Å respectively. B3LYP functional and B3PW91 functional combined with 6-311G** basis set produce slightly better results than B3P86 functional. It can be seen that the errors of the bond distances for two molecules, calculated with B3LYP method and B3PW91 method, are all smaller than those in B3P86 method, which means the B3LYP and B3PW91 computations are closer to the experimental values.[49] PBE1PBE/6-311G** method produces the

best results for CH_3–COOH (1.436 Å) and HOC(O)–COOH (1.445 Å), with the deviations from the experimental values for C–COOH bond length being 0.081 Å and 0.099 Å, respectively. It is noteworthy that the bond distances produced by four functionals are all shorter than the corresponding experiment values, which means that the four functional methods all underestimate the C–COOH bond lengths for the title compounds.

Take CBS–Q calculations for example. For CBS–Q computation, which can yield very good bond distances in amino compounds,[26] the calculated bond distances in carboxylic acid compounds are not very accurate. For instance, the C–COOH bond distance for CH_3–COOH is 1.359 Å, even 0.158 Å shorter than the experimental value (1.517 Å),[49] and it is worse than that obtained by any DFT method discussed above. Although the bond distance for HOC(O)–COOH produced by CBS–Q method is slightly better than those by B3P86 functional and B3LYP functional, the bond length 1.367 Å is not very accurate.

Then the BDEs of C–COOH bond for all the carboxylic acids should be evaluated. Listed in Table 2 are the bond dissociation energies for 15 title compounds predicted by employing B3LYP, B3P86, B3PW91, and PBE1PBE hybrid DFT theory and CBS–Q method in conjunction with 6-311G** basis set. All of the experimental values in Table 2 are taken from Ref. [50]. From Table 2, it can be noted that although the hybrid B3LYP method is a popular computational tool, which was shown to work remarkably well and give an extraordinary agreement between computed and experimental energies for small polar molecules in Ref. [51], for the 15 carboxylic acid compounds, BDEs are rather poorly calculated by the B3LYP/6-311G** method, with an average absolute error of 5.6 kcal/mol and a maximum error of 10.3 kcal/mol for CH_3–COOH. It is obvious that these computational results are beyond the desirable accuracy of order for quantum thermochemical methods. Two other systems, C_6H_5–COOH and sC_4H_9–COOH, both have errors larger than 8.0 kcal/mol. Thus, it is clear that this method is not suitable for predicting the excellent bond dissociation energies for carboxylic acids. From Table 2, we can also see that all the B3LYP calculated results tend to underestimate the BDEs for 15 title compounds.

Concerning the B3PW91 calculations, it is also demonstrated that the average absolute errors between the B3PW91 results and experimental values for carboxylic acid compounds range from 1.0 kcal/mol to 8.6 kcal/mol, which are somewhat smaller than those found by the B3LYP method. But the average absolute error of 4.1 kcal/mol and the maximum error of 8.6 kcal/mol for CH_3–COOH are still not acceptable. From Table 2, we can see that all of the B3PW91 calculated results also underestimate the BDEs for carboxylic acids, except for the result of the $C_6H_5CH_2$–COOH, of which the computed BDE is 1.5 kcal/mol larger than the corresponding experimental BDE. Since it is inaccurate in predicting the bond dissociation energy, the B3PW91 method is not recommended to produce the BDEs of C–COOH bond.

As shown in Table 2, it is evident that the calculation quantities obtained with B3P86 functional are much closer to the experimental ones than with B3LYP and B3PW91 functional, with the absolute deviations between the B3P86 values and the experimental ones[46] ranging from 0.2 kcal/mol to 6.0 kcal/mol. For most molecules, excellent agreement exists between calculated results and experimental data. It can be noted that for $C_{10}H_7$–1–COOH, the B3P86 method in the 6-311G** yields the very accurate bond dissociation energy of 103.0 kcal/mol, with only 0.2 kcal/mol deviation from the experimental value. Moreover, the computed bond dissociation energies for tC_4H_9–COOH, C_2H_3–COOH, and $C_{10}H_7$–2–COOH are 83.2 kcal/mol, 105.0 kcal/mol, and 105.8 kcal/mol, respectively, with the experimental values of 82.5 kcal/mol, 104.0 kcal/mol, and 104.8 kcal/mol, respectively, in which the absolute discrepancies are all within 1.0 kcal/mol. It is interesting to point out that the B3P86 functional also gives the more accurate bond dissociation energies in our previous work.[27–29] From Table 2, we can also see that the difference in computational result between B3P86 and PBE1PBE functional is significant, with an average absolute error of 2.8 kcal/mol and a maximum error of 8.4 kcal/mol for the latter method. In addition, as for C_2H_3–COOH, C_4H_9–COOH, and $C_{10}H_7$–1–COOH, PBE1PBE method with 6-311G** basis set produces the most reliable bond dissociation energies in the four DFT calculations.

In our previous work,[26] the CBS–Q method is proved to be capable of predicting the reliable BDEs for amino compounds. In order to test whether this method will be still able to handle the BDEs much better than the DFT calculations for the carboxylic acid system, the CBS–Q method is also employed to predict the BDEs to give an extensive comparison. As can be seen in Table 2, although the C–NH_2 bond dissociation energies obtained by the CBS–Q method are in extraordinary agreement with the experimental values,[26] it is incapable of accurately computing the BDEs for C–COOH bond. Most of the CBS–Q calculated results overestimate the BDEs for carboxylic acid compounds. In the case of tC_4H_9–COOH, the calculated BDE is 93.3 kcal/mol, 10.8 kcal/mol larger than the experimental one, which is not acceptable in regard to the experimental error. Although the CBS–Q method cannot give the accurate BDEs for most title compounds, it should be mentioned that for CH_3–COOH, the C–COOH bond dissociation energy (89.2 kcal/mol) has better calculated values than those obtained by any other quantum chemical methods. Meanwhile, as the number of the atoms increases in each molecule, it is extremely time-consuming and requires

high–performance computational resources for larger systems. Therefore, the CBS–Q method is not an optional method to estimate the BDEs for carboxylic acid compounds.

Finally, we investigate the energy gaps between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the studied compounds. As is well known, HOMO and LUMO are of great importance in several chemical processes. The energy of the HOMO (E_{HOMO}) measures the electron donating characteristic of a compound and the energy of the LUMO (E_{LUMO}) measures its electron accepting characteristic.[48–54] The HOMO–LUMO gap, i.e., the difference in energy between the E_{HOMO} and E_{LUMO}, is an important stability index. In reactions of a nucleophile with an electrophile, the interaction between the HOMO of the nucleophile and the LUMO of the electrophile contributes to the attraction between the two reactants. Studying HOMO and LUMO is expected to show whether the reaction is feasible and the relative thermal stability of an individual molecule. A large HOMO–LUMO gap implies high stability for the molecule in the sense of its lower reactivity in chemical reactions.[55] Also, it is of great interest to discuss the compound thermal stability at an electron level.

Table 3 displays the calculated energy gaps. As shown in Table 3, the calculated values of energy gaps ΔE have the same trends at various levels and the ΔE results obtained from DFT methods are similar to each other. Take the energy gap ΔE obtained by the B3P86/6-311G** method for example. The molecule $HOCH_2$–COOH has the biggest value of the energy gap between the HOMO and LUMO, 0.29030 a.u. (a.u. is the abbreviation for atomic unit), which shows that the $HOCH_2$–COOH molecule is the most stable compound in the carboxylic acids. The compound which has the smallest value of the energy gap in the B3P86 method is the $C_{10}H_7$–1–COOH molecule and the energy gap value is about 0.16024 a.u., which indicates that $C_{10}H_7$–1–COOH compound is the least stable molecule.

Table 3. Calculated values of energy gap ΔE (10^{-3} a.u.) between the HOMO and LUMO of the carboxylic acid compounds at various levels of theory[a].

	B3P86 /6-311G**	B3LYP /6-311G**	B3PW91 /6-311G**	PBE1PBE /6-311G**	CBS–Q
$HOCH_2$–COOH	290.30	288.76	289.44	310.69	497.18
HOC(O)–COOH	218.78	218.69	218.33	238.29	430.25
CH_3–COOH	284.81	283.37	284.05	305.19	483.40
C_2H_3–COOH	227.02	226.89	226.53	246.09	440.72
C_2H_5–COOH	282.45	280.05	281.65	302.04	489.42
C_3H_7–COOH	282.58	281.01	281.98	302.70	486.96
C_4H_9–COOH	282.46	280.15	281.24	302.53	485.92
sC_4H_9–COOH	280.72	281.59	281.90	297.09	485.84
tC_4H_9–COOH	282.63	281.24	282.12	302.78	485.37
C_5H_{11}–COOH	289.06	287.42	288.30	309.42	–[b]
C_6H_{13}–COOH	281.21	279.91	280.71	301.26	–
C_6H_5–COOH	215.01	213.89	214.72	230.57	–
$C_6H_5CH_2$–COOH	239.66	237.25	239.26	253.71	–
$C_{10}H_7$–1–COOH	160.24	159.20	160.23	173.16	–
$C_{10}H_7$–2–COOH	165.75	164.63	165.71	178.72	–

[a]Zero-point energies are taken into account.

[b]Impossible to evaluate with current computational facilities.

Because a large HOMO–LUMO gap implies high stability for the molecule in the sense of its lower reactivity in chemical reactions, $HOCH_2$–COOH has the highest stability and lowest reactivity among the studied compounds when it is attacked by a free group and $C_{10}H_7$–1–COOH has lower stability and higher reactivity.

4. Conclusion

In the present study, we tested the *ab initio* CBS–Q method and four hybrid DFT B3P86, B3LYP, B3PW91, and PBE1PBE methods to compute the equilibrium bond distances and the bond dissociation energies of the C–COOH bond for 15 carboxylic acid compounds. By comparing the computed results with the available experimental ones, it is indicated that although the C–NH_2 bond dissociation energies calculated by the CBS–Q method are in extraordinary agreement with the experimental values in our previous work,[26] the CBS–Q calculations are inadequate to obtain the reliable bond dissociation energies for C–COOH bond. However, the B3P86/6-31G** method can still yield the accurate BDEs of the C–COOH bond, with an average absolute error of 2.3 kcal/mol and a maximum error of 6.0 kcal/mol. This conclusion is consistent with that we have drawn in our previous work.[27–29]

Hence, the B3P86 method is recommended to be the best option to calculate the BDEs of C–COOH bond for carboxylic acid compounds. In addition, we also discussed the energy gaps between the HOMO and LUMO of 15 title compounds and estimate the relative thermal stability. It is noted that $HOCH_2$–COOH is the most stable compound and the $C_{10}H_7$–1–COOH is the least stable compound.

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