



Cite this: *Phys. Chem. Chem. Phys.*, 2015, 17, 32571

Correction: Acid-catalyzed carboxylic acid esterification and ester hydrolysis mechanism: acylium ion as a sharing active intermediate *via* a spontaneous trimolecular reaction based on density functional theory calculation and supported by electrospray ionization-mass spectrometry

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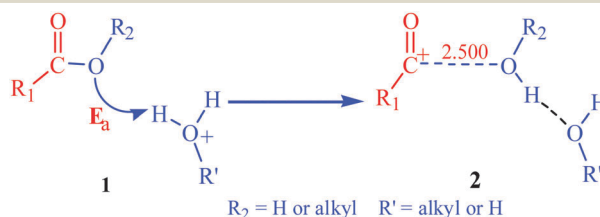
Correction for 'Acid-catalyzed carboxylic acid esterification and ester hydrolysis mechanism: acylium ion as a sharing active intermediate *via* a spontaneous trimolecular reaction based on density functional theory calculation and supported by electrospray ionization-mass spectrometry' by Hongchang Shi *et al.*, *Phys. Chem. Chem. Phys.*, 2015, DOI: 10.1039/c5cp02914g.

DOI: 10.1039/c5cp90203g

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In the published article, the activation energy E_a in Table 1 is incorrect. The E_a data actually are the activation energies that the proton (H^+) transfers to hydroxyl-oxygen or alkyl-oxygen, not those of generating acylium ions. For example, the C–O bond distance is 1.527 and 1.538 Å in the Fig. 1 (2) and Fig. 2 (2), respectively. The bond has been partly, but not completely disconnected, so the E_a (9.0 and 3.4 kcal mol^{−1}) cannot lead to the formation of the corresponding acylium ions. The E_a that can generate acylium ions must be recalculated in accordance with a new scheme.

Scheme 5 (1) shows that an initial bimolecular system of $RCOOR_2 + R'OH_2^+$ goes through an effective Lewis collision to complete the hydroxyl-oxygen or alkyl-oxygen protonation. Because the water or alcohol molecule is a good leaving group, this collision caused the C–OR₂ bond disconnection, which generates an acylium ion and a water or an alcohol molecule, as shown in Scheme 5 (2).



Scheme 5 1 is the initial bimolecular system, 2 is the system after an effective Lewis collision. The bond distance is in angstroms.

In the optimization of system 2, the $R-C^+(O)-O(H)R_2$ bond distance set here is equal to 2.500 Å. In this spacing, the interaction between the acylium ion and $O(H)R_2$ molecule is slight, that is, the C–OR₂ bond is completely disconnected. The 2.500 Å is frozen in the optimization. The E_2 of system 2 is higher than the E_1 of 1. The elevated energy is the E_a of the hydroxyl-oxygen or alkyl-oxygen protonation: $E_a = E_2 - E_1$.



For the protonation of $\text{CH}_3\text{COOH} + \text{CH}_3\text{OH}_2^+$ (configuration A), the calculation result is shown as Fig. 1.

$$E_a = E_2 - E_1 = -345.192684 - (-345.218981) = 0.026297 \text{ a.u.} = 16.5 \text{ kcal mol}^{-1}.$$

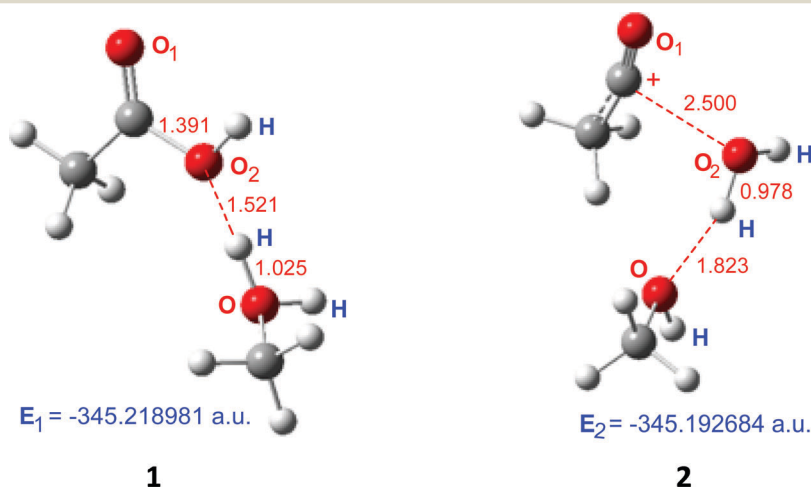


Fig. 1 The optimized initial bimolecular system **1** and the energy E_1 of $\text{CH}_3\text{COOH} + \text{CH}_3\text{OH}_2^+$ (configuration A); the optimized system **2** and the energy E_2 of $\text{CH}_3\text{C}^+\text{O} + \text{H}_2\text{O} + \text{CH}_3\text{OH}$. The bond distance is in angstroms.

For the alkyl-oxygen protonation of $\text{C}_6\text{H}_5\text{COOCH}_3 + \text{H}_3\text{O}^+$, the calculation result is shown as Fig. 2.

$$E_a = E_2 - E_1 = 0.017276 \text{ a.u.} = 10.8 \text{ kcal mol}^{-1}.$$

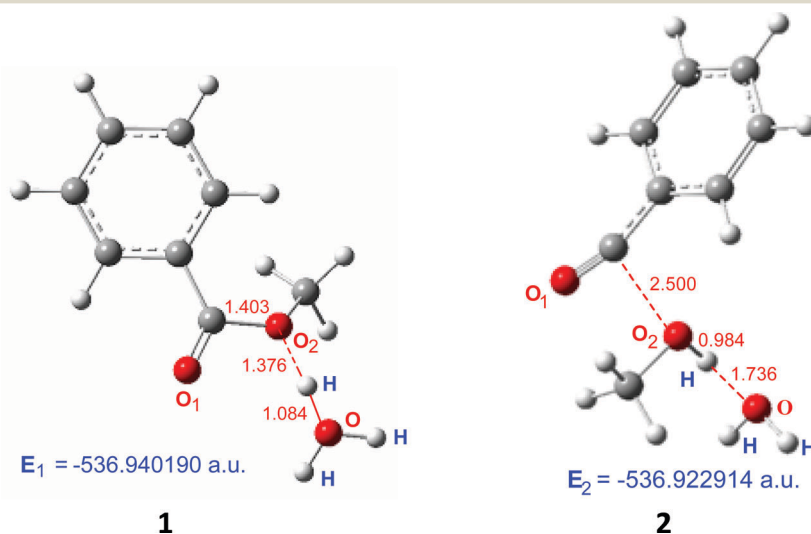


Fig. 2 The optimized initial bimolecular system **1** and the energy E_1 of $\text{C}_6\text{H}_5\text{COOCH}_3 + \text{H}_3\text{O}^+$ (configuration B); the optimized system **2** and the energy E_2 of $\text{C}_6\text{H}_5\text{C}^+\text{O} + \text{CH}_3\text{OH} + \text{H}_2\text{O}$. The bond distance is in angstroms.



For acetic acid, benzoic acid and their methyl ester, the E_a of their hydroxyl-oxygen and alkyl-oxygen protonations are changed as in the following Table 1.

Table 1 The hydroxyl-oxygen and alkyl-oxygen protonation E_a of acetic acid, benzoic acid and their methyl esters

| System | Config. | $E_1/\text{a.u.}$ | $E_2/\text{a.u.}$ | E_a |
|--|---------|-------------------|-------------------|-------|
| $\text{CH}_3\text{COOH} + \text{CH}_3\text{OH}_2^+$ | A | -345.218981 | -345.192684 | 16.5 |
| | B | -345.217477 | -345.190683 | 16.8 |
| $\text{CH}_3\text{COOCH}_3 + \text{H}_3\text{O}^+$ | A | -345.220936 | -345.196416 | 15.4 |
| | B | -345.217162 | -345.192777 | 15.3 |
| $\text{C}_6\text{H}_5\text{COOH} + \text{CH}_3\text{OH}_2^+$ | A | -536.945912 | -536.919611 | 16.5 |
| | B | -536.944778 | -536.920010 | 15.5 |
| $\text{C}_6\text{H}_5\text{COOCH}_3 + \text{H}_3\text{O}^+$ | A | -536.946688 | -536.922924 | 14.9 |
| | B | -536.940190 | -536.922914 | 10.8 |

The E_a in Table 1 are much higher than that in the Table 1 of the published article, which is reasonable because the C-OR₂ bond is completely disconnected, and this requires more energy.

The E_a values of the hydroxyl-oxygen and alkyl-oxygen protonation in the Abstract, Introduction, Scheme 7 and Scheme 8 should be accordingly changed in accordance with Table 1.

The Table 5 in the published article has been changed as following Table 5. It is also the E_a calculations of hydroxyl-oxygen or alkyl-oxygen protonation.

Table 5 E_a of hydroxyl-oxygen or alkyl-oxygen protonation by CH_3OH_2^+ or H_3O^+ in 2,4,6-trimethylbenzoic acid and its methyl ester

| Molecular system | Config. | $E_1/\text{a.u.}$ | $E_2/\text{a.u.}$ | $E_a/\text{kcal mol}^{-1}$ |
|---|---------|-------------------|-------------------|----------------------------|
| $(\text{CH}_3)_3\text{C}_6\text{H}_2\text{COOH} + \text{CH}_3\text{OH}_2^+$ | A | -654.839323 | -654.827446 | 7.4 |
| | B | -654.839660 | -654.827455 | 7.7 |
| $(\text{CH}_3)_3\text{C}_6\text{H}_2\text{COOCH}_3 + \text{H}_3\text{O}^+$ | A | -654.842084 | -654.830307 | 7.4 |
| | B | -654.837079 | -654.829814 | 4.6 |

For the E_a calculation of carbonyl-oxygen protonation in the published article, the calculation scheme and result (Table 2) are correct because the protonation is a simple proton transfer.

The change mentioned above not only does not affect the conclusions in the published article, but also helps to support these conclusions.

The Royal Society of Chemistry apologises for these errors and any consequent inconvenience to authors and readers.

