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## 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

Hongchang Shi,\* Yilei Wang and Ruimao Hua

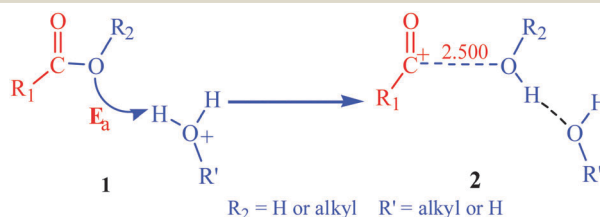
Correction for 'Acid-catalyzed carboxylic acid esterification and ester hydrolysis mechanism: acylium ion as a sharing active intermediate *via* a spontaneous trimolecular reaction based on density functional theory calculation and supported by electrospray ionization-mass spectrometry' by Hongchang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

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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<sup>-1</sup>) 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–OR<sub>2</sub> 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–OR<sub>2</sub> 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.

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

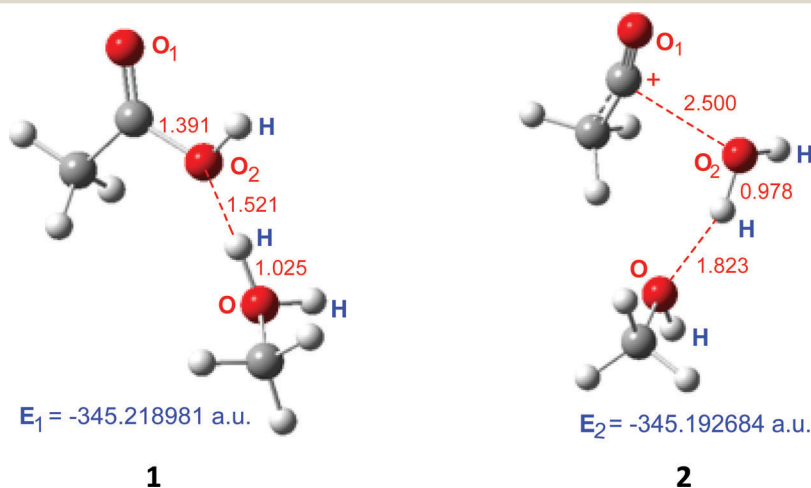


Fig. 1 The optimized initial bimolecular system **1** and the energy  $E_1$  of  $\text{CH}_3\text{COOH} + \text{CH}_3\text{OH}_2^+$  (configuration A); the optimized system **2** and the energy  $E_2$  of  $\text{CH}_3\text{C}^+\text{O} + \text{H}_2\text{O} + \text{CH}_3\text{OH}$ . The bond distance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

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

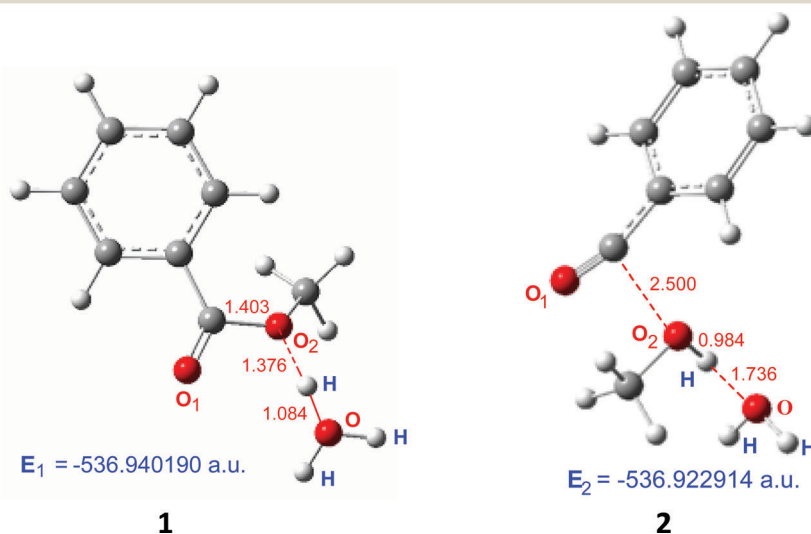


Fig. 2 The optimized initial bimolecular system **1** and the energy  $E_1$  of  $\text{C}_6\text{H}_5\text{COOCH}_3 + \text{H}_3\text{O}^+$  (configuration B); the optimized system **2** and the energy  $E_2$  of  $\text{C}_6\text{H}_5\text{C}^+\text{O} + \text{CH}_3\text{OH} + \text{H}_2\text{O}$ . 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.	$E_1/a.u.$	$E_2/a.u.$	$E_a$
CH <sub>3</sub> COOH + CH <sub>3</sub> OH <sub>2</sub> <sup>+</sup>	A	-345.218981	-345.192684	16.5
	B	-345.217477	-345.190683	16.8
CH <sub>3</sub> COOCH <sub>3</sub> + H <sub>3</sub> O <sup>+</sup>	A	-345.220936	-345.196416	15.4
	B	-345.217162	-345.192777	15.3
C <sub>6</sub> H <sub>5</sub> COOH + CH <sub>3</sub> OH <sub>2</sub> <sup>+</sup>	A	-536.945912	-536.919611	16.5
	B	-536.944778	-536.920010	15.5
C <sub>6</sub> H <sub>5</sub> COOCH <sub>3</sub> + H <sub>3</sub> O <sup>+</sup>	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-OR<sub>2</sub> 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<sub>3</sub>OH<sub>2</sub><sup>+</sup> or H<sub>3</sub>O<sup>+</sup> in 2,4,6-trimethylbenzoic acid and its methyl ester

Molecular system	Config.	$E_1/a.u.$	$E_2/a.u.$	$E_a/kcal\ mol^{-1}$
(CH <sub>3</sub> ) <sub>3</sub> C <sub>6</sub> H <sub>2</sub> COOH + CH <sub>3</sub> OH <sub>2</sub> <sup>+</sup>	A	-654.839323	-654.827446	7.4
	B	-654.839660	-654.827455	7.7
(CH <sub>3</sub> ) <sub>3</sub> C <sub>6</sub> H <sub>2</sub> COOCH <sub>3</sub> + H <sub>3</sub> O <sup>+</sup>	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.

