Correction to "Ab Initio Reaction Kinetics of Hydrogen Abstraction from Methyl Formate by Hydrogen, Methyl, Oxygen, Hydroxyl, and Hydroperoxy Radicals"

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Due to a bug temporarily introduced into our TigerCI code concerning the treatment of triplet states, the energies predicted by MRACPF theory for the MF + O(^{3}P) reaction were incorrect, which led to incorrect rate constants. The entries in Tables 3 and 6 for MF + O(^{3}P) should be updated as given below. The largest difference between the old and updated relative energies is 1.5 kcal/mol. Additionally, when the CASSCF space is increased by including more electrons on the oxygen atom, the calculated MRACPF barrier heights increase by up to 2.6 kcal/mol instead of the previously reported maximum increase of 1.5 kcal/mol. The trends and conclusions made in the original paper are unaffected by these corrections.

Page 8436. Table 3 should be replaced by the following, where the changes are shown in boldface.

Page 8440. Table 6 should be replaced by the following, where the changes are shown in boldface.

Table 3. Comparison of Barrier Heights (E_a) and Reaction Enthalpies (ΔH) (kcal mol^{-1}) of MF Hydrogen Abstraction by O (^{3}P), Obtained at the MRSDCI+DS(MRACPF)/cc-pV∞Z//DFT-B3LYP/cc-pVTZ Level[a]

methods	E_a-A	ΔH^{0K}-A	ΔH^{298K}-A	E_a-B	ΔH^{0K}-B	ΔH^{298K}-B
experiment[b]	10.2			10.5		
MRSDCI+DS/cc-pV∞Z						
CAS(4e,4o)[c]	11.0	−2.5	−1.7	11.9	−1.5	−0.9
CAS(6e,5o)[d]	10.9	−2.4	−1.6	10.9	−1.4	−0.8
CAS(8e,6o)[e]	10.3	−3.1	−2.4	10.8	−1.4	−0.8
MRACPF/cc-pV∞Z						
CAS(4e,4o)[c]	**10.6**	**−3.6**	**−2.8**	**10.0**	**−3.3**	**−2.7**
CAS(6e,5o)[d]	**11.5**	**−3.2**	**−2.4**	**11.2**	**−3.0**	**−2.4**
CAS(8e,6o)[e]	**10.7**	**−4.7**	**−3.9**	**12.6**	**−2.9**	**−2.3**

[a]All energies are relative to the total energies of reactants. Increasing the CASSCF active space changes E_a by up to **2.6** kcal/mol. [b]Reference 14. [c]Active space: CAS(4e,4o), including the σ and σ^* of the breaking C−H and the two $2p$ singly occupied orbitals of the abstracting oxygen atom. [d]Active space: CAS(6e,5o), including the σ and σ^* of the breaking C−H and three $2p$ orbitals of the abstracting oxygen atom. [e]Active space: CAS(8e,6o), including the σ and σ^* of the breaking C−H and all the valence orbitals of the abstracting oxygen atom.

Table 6. Comparison of Modified Arrhenius ($k = AT^n \exp(-E_a/RT)$) Parameters for Methyl Formate Hydrogen Abstraction by H, CH$_3$, O, HO$_2$, and OH Radicals, Obtained by Transition State Theory within the Separable Hindered Rotor Approximation for Torsional Motion[a]

reaction	A (cm^3 mol^{-1} s^{-1})	n	E_A (kcal/mol)
HC(=O)OCH$_3$ + H → HC(=O)OCH$_2^\bullet$ + H$_2$	5.17×10^3	3.11	8.00
HC(=O)OCH$_3$ + H → $^\bullet$C(=O)OCH$_3$ + H$_2$	3.60×10^3	3.05	7.61
HC(=O)OCH$_3$ + CH$_3$ → HC(=O)OCH$_2^\bullet$ + CH$_4$	2.48×10^{-7}	5.70	8.68
HC(=O)OCH$_3$ + CH$_3$ → $^\bullet$C(=O)OCH$_3$ + CH$_4$	9.54×10^{-5}	5.02	8.03
HC(=O)OCH$_3$ + O → HC(=O)OCH$_2^\bullet$ + OH	$\mathbf{2.18 \times 10^{-1}}$	**4.22**	**6.86**
HC(=O)OCH$_3$ + O → $^\bullet$C(=O)OCH$_3$ + OH	$\mathbf{2.88 \times 10^2}$	**3.32**	**7.28**
HC(=O)OCH$_3$ + HO$_2$ → HC(=O)OCH$_2^\bullet$ + H$_2$O$_2$	1.75×10^{-3}	4.81	15.72
HC(=O)OCH$_3$ + HO$_2$ → $^\bullet$C(=O)OCH$_3$ + H$_2$O$_2$	4.06	3.68	15.76
HC(=O)OCH$_3$ + OH → HC(=O)OCH$_2^\bullet$ + H$_2$O	8.74	3.64	0.64
HC(=O)OCH$_3$ + OH → $^\bullet$C(=O)OCH$_3$ + H$_2$O	1.29×10^6	2.06	2.75

[a]The parameters are fitted to rate constants calculated from 300 to 1500 K. OH abstraction dominates all pathways.