

## **Physical Chemistry Chemical Physics**

### **Examination of the chemical behavior of the quercetin radical cation towards some bases**

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**ELECTRONIC SUPPLEMENTARY INFORMATION**

**Table S1** Experimental and calculated bond and dihedral angles of quercetin (Q).  
 Experimental and calculated data refer to the solid and gaseous phases, respectively

Bond angle (°)	Q <sub>exp</sub> <sup>1</sup>	Q <sub>calc</sub>				
		a	b	c	d	e
A(C3'-O3'-H3')	112.6	108.6	108.6	108.2	108.3	108.3
A(C4'-O4'-H4')	101.8	110.8	110.7	110.6	110.5	110.3
A(C3'-C4'-C5')	120.8	120.2	120.0	120.1	120.0	120.2
A(C4'-C5'-C6')	118.8	120.3	120.5	120.5	120.5	120.4
A(C5'-C6'-C1')	121.0	119.9	120.2	117.0	120.0	119.9
A(C6'-C1'-C2')	119.3	119.4	118.7	119.0	118.9	119.3
A(C1'-C2'-C3')	119.8	120.5	120.9	120.8	120.9	120.6
A(C6'-C1'-C2)	121.3	121.7	121.9	121.8	121.8	121.6
A(O1-C2-C3)	121.3	119.9	119.1	119.3	119.5	119.9
A(C2-C3-C4)	120.3	121.1	121.5	121.2	121.2	121.1
A(C2-C3-O3)	122.3	123.4	123.7	124.2	124.2	124.1
A(C3-O3-H3)	110.3	105.0	104.5	103.9	104.0	104.5
A(C3-C4-O4)	120.3	118.9	118.8	118.6	118.7	118.8
A(C3-C4-C10)	116.8	116.7	116.9	117.0	116.9	116.7
A(C4-C10-C9)	120.2	119.3	119.2	119.3	119.3	119.4
A(C10-C9-O1)	120.4	120.5	120.4	120.4	120.4	120.5
A(C10-C5-O5)	118.5	120.7	120.5	120.1	120.3	120.2
A(C5-O5-H5)	101.9	108.2	107.7	107.2	107.3	107.5
A(C10-C5-C6)	122.1	119.8	119.7	119.6	119.6	119.8
A(C5-C6-C7)	118.6	119.4	119.6	119.5	119.6	119.4
A(C6-C7-O7)	119.8	121.0	121.3	121.2	121.2	120.9
A(C6-C7-C8)	122.4	122.3	122.1	122.2	122.2	122.3
A(C7-C8-C9)	117.1	117.5	117.7	117.6	117.7	117.5
A(C8-C9-C10)	122.8	122.2	122.2	122.0	122.1	122.1
Mean relative error (%)		1.59	1.71	1.80	1.70	1.58
<b>Torsion angle (°)</b>						
τ(C3-C2-C1'-C2')	7.0	11.7	0.0	0.0	0.0	14.0

- a: M052X/6-311+G(d,p)  
 b: B3LYP/6-311+G(d,p)  
 c: B3P86/6-311+G(d,p)  
 d: PBE1PBE/6-311+G(d,p)  
 e: M052X/cc-pvtz

1 M. Rossi, L. F. Rickles and W. A. Halpin, *Bioorg. Chem.* 1986, **14**, 55–69.

**Table S2** Experimental and calculated bond distances of quercetin (Q). Experimental and calculated data refer to the solid and gaseous phases, respectively

Bond distance (pm)	$Q_{\text{exp}}^1$	$Q_{\text{calc}}$				
		a	b	c	d	e
D(C1'-C2')	139.7	140.1	140.8	140.4	140.4	139.8
D(C2'-C3')	139.6	138.0	138.4	138.1	138.1	137.6
D(C3'-C4')	137.6	139.7	140.3	140.0	140.0	139.4
D(C4'-C5')	139.3	138.3	138.8	138.5	138.5	137.9
D(C5'-C6')	139.1	138.9	139.1	138.8	138.8	138.5
D(C1'-C6')	138.8	139.8	140.6	140.2	140.1	139.3
D(C3'-O3')	137.3	135.7	136.3	135.4	135.3	135.7
D(C4'-O4')	139.6	136.8	137.3	136.5	136.2	136.8
D(O3'-H3')	99.0	96.3	96.6	96.5	96.3	96.2
D(O4'-H4')	97.5	95.9	96.3	96.1	96.0	95.9
D(C1'-C2)	147.9	146.5	146.5	145.8	145.9	146.2
D(C2-O1)	136.5	136.5	137.3	136.5	136.2	136.4
D(C2-C3)	135.7	135.7	136.8	136.6	136.5	135.3
D(C3-C4)	144.9	144.9	145.0	144.3	144.4	144.5
D(C4-C10)	141.8	143.2	143.3	142.6	142.7	142.7
D(C10-C5)	142.0	141.6	142.2	141.7	141.7	141.3
D(C5-C6)	135.5	138.2	138.7	138.4	138.4	137.8
D(C6-C7)	140.3	139.8	140.2	139.9	139.9	139.5
D(C7-C8)	138.6	138.8	139.4	139.1	139.0	138.5
D(C8-C9)	139.7	138.4	138.8	138.5	138.5	138.1
D(C9-C10)	139.2	139.9	140.5	140.1	140.1	139.5
D(C9-O1)	137.0	135.2	135.8	135.2	134.9	135.0
D(C4-O4)	126.7	124.5	125.7	125.5	125.2	124.6
D(C3-O3)	135.1	135.2	135.6	134.8	134.6	135.2
D(C5-O5)	137.5	133.5	134.1	133.3	133.1	133.4
D(C7-O7)	135.8	135.3	136.0	135.2	135.0	135.3
D(O3-H3)	90.6	97.1	97.7	97.8	97.5	97.2
D(O5-H5)	94.8	98.0	98.7	99.0	98.6	98.4
D(O7-H7)	91.4	96.0	96.3	96.2	96.0	96.0
Mean relative error (%)		1.29	1.33	1.39	1.41	1.30

As expected, the solid-phase and gaseous-phase geometries of Q are not identical, due to intermolecular interactions in the solid state. Tables S1 and S2 show that the experimental geometry of Q is best reproduced with the M052X/6-311+G(d,p) level of theory. All further results were obtained using this theoretical model.

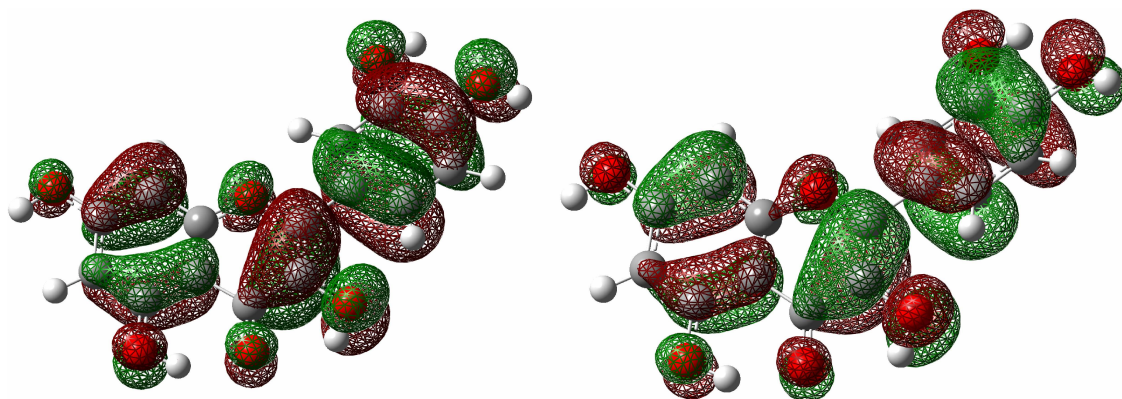
**Table S3** Calculated bond and dihedral angles of quercetin (Q) in the aqueous solution, and of the quercetin radical cation (Q<sup>•+</sup>) in the gaseous and aqueous phases

<b>Bond angle (°)</b>	<b>Q<sub>calc</sub></b>	<b>Q<sup>•+</sup><sub>calc</sub></b>	
	aqueous solution	gaseous phase	aqueous solution
A(C3'-O3'-H3')	109.1	111.0	110.4
A(C4'-O4'-H4')	110.7	113.3	112.4
A(C3'-C4'-C5')	120.0	120.9	120.6
A(C4'-C5'-C6')	120.2	119.8	119.7
A(C5'-C6'-C1')	120.0	120.1	120.3
A(C6'-C1'-C2')	119.7	119.6	119.5
A(C1'-C2'-C3')	120.1	120.4	120.1
A(C6'-C1'-C2)	121.5	121.9	121.9
A(O1-C2-C3)	120.5	118.0	127.4
A(C2-C3-C4)	121.1	121.5	121.1
A(C2-C3-O3)	122.3	124.2	123.0
A(C3-O3-H3)	106.5	105.9	107.9
A(C3-C4-O4)	119.5	116.3	117.5
A(C3-C4-C10)	116.5	116.3	116.4
A(C4-C10-C9)	119.5	119.7	119.6
A(C10-C9-O1)	120.4	120.6	120.8
A(C10-C5-O5)	120.3	121.1	120.6
A(C5-O5-H5)	107.8	110.7	109.2
A(C10-C5-C6)	120.5	119.8	120.3
A(C5-C6-C7)	119.2	119.4	119.1
A(C6-C7-O7)	120.9	122.3	121.3
A(C6-C7-C8)	122.2	122.2	122.3
A(C7-C8-C9)	117.5	117.5	117.5
A(C8-C9-C10)	122.6	122.5	122.7
<b>Torsion angle (°)</b>			
$\tau$ (C3-C2-C1'-C2')	29.0	0.1	10.8

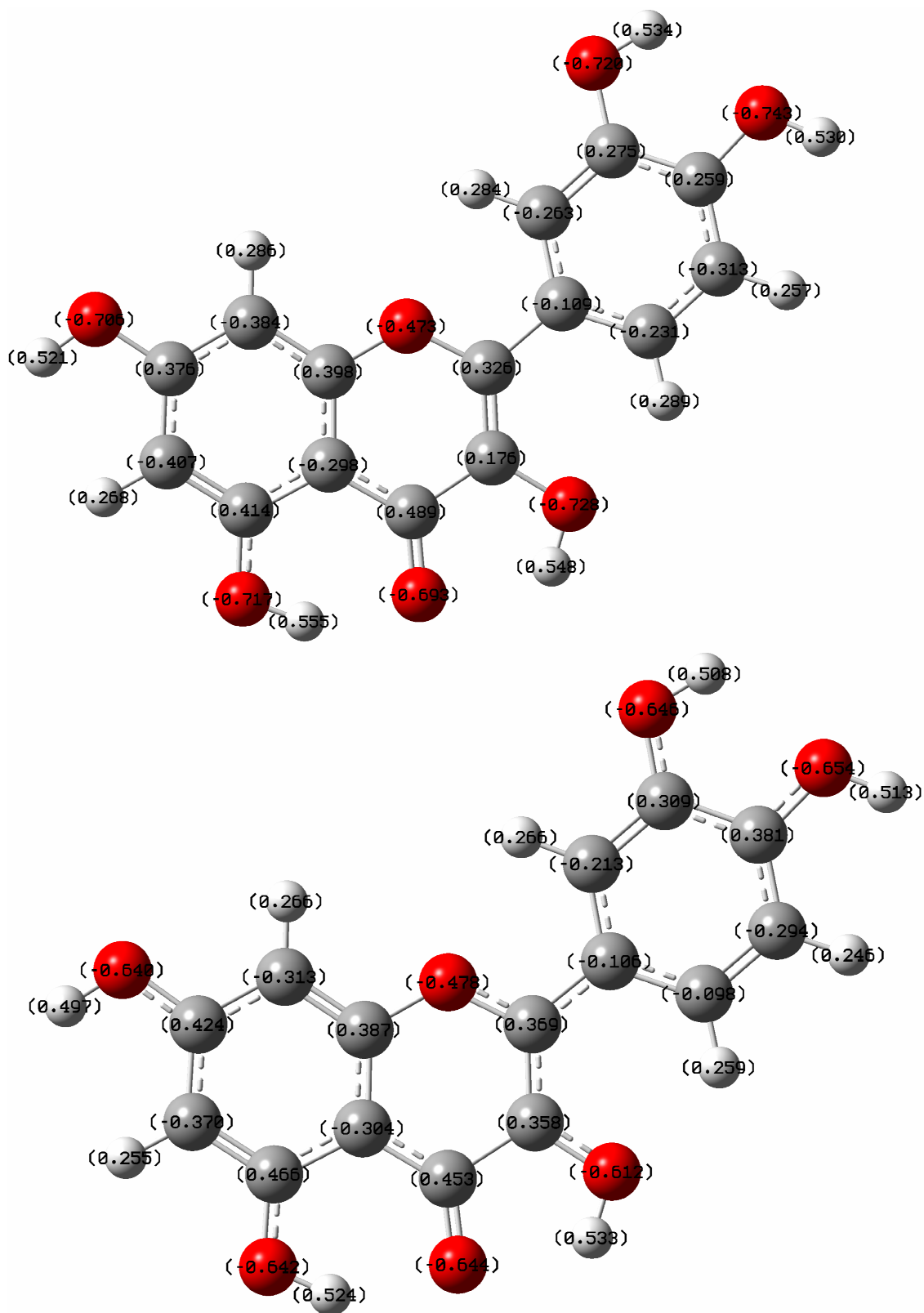


**Table S4** Calculated bond distances of quercetin (Q) in the aqueous solution, and of the quercetin radical cation ( $Q^{+\bullet}$ ) in the gaseous and aqueous phases

<b>Bond distance</b> (pm)	<b>Q<sub>calc</sub></b>		<b>Q<sup>+•</sup><sub>calc</sub></b>	
	aqueous solution	gaseous phase	gaseous phase	aqueous solution
D(C1'–C2')	140.1	141.3	141.3	141.6
D(C2'–C3')	138.0	136.9	136.9	136.6
D(C3'–C4')	139.8	142.3	142.3	142.6
D(C4'–C5')	138.6	139.5	139.5	140.0
D(C1'–C6')	139.6	142.3	142.3	142.6
D(C3'–O3')	137.0	133.5	133.5	134.9
D(C4'–O4')	136.5	133.1	133.1	132.3
D(O3'–H3')	96.6	96.5	96.5	96.7
D(O4'–H4')	96.4	96.3	96.3	96.8
D(C1'–C2)	146.4	142.5	142.5	142.0
D(C2–O1)	136.3	134.3	134.3	134.9
D(C2–C3)	135.6	140.1	140.1	139.9
D(C3–C4)	144.4	147.9	147.9	147.4
D(C4–C10)	143.4	141.4	141.4	142.1
D(C10–C5)	141.6	142.3	142.3	141.9
D(C5–C6)	137.8	138.5	138.5	137.9
D(C6–C7)	139.9	139.2	139.2	139.6
D(C7–C8)	138.8	140.8	140.8	139.7
D(C8–C9)	138.4	136.6	136.6	137.3
D(C9–C10)	139.9	140.7	140.7	140.4
D(C9–O1)	135.6	137.1	137.1	136.5
D(C4–O4)	125.2	123.4	123.4	123.9
D(C3–O3)	136.1	130.7	130.7	131.0
D(C5–O5)	135.1	132.3	132.3	134.3
D(C7–O7)	135.8	133.4	133.4	134.8
D(O3–H3)	97.1	98.4	98.4	97.9
D(O5–H5)	98.0	97.4	97.4	97.6
D(O7–H7)	96.5	96.2	96.2	96.6



**Fig. S1** HOMO of quercetin in the gaseous (left) and aqueous (right) phase.



**Fig. S2** The NBO charge distribution in quercetin (top) and its radical cation (bottom).

## Results for the reactions of different OH groups of Q<sup>+</sup> with hydroxide anion in the gaseous phase

All reactant complexes spontaneously transformed into Q and hydroxyl radical, implying that the presented results relate to the H atom transfer from different positions of Q to the hydroxyl radical.

### Results of the IRC calculations (Figs S3 – S6)

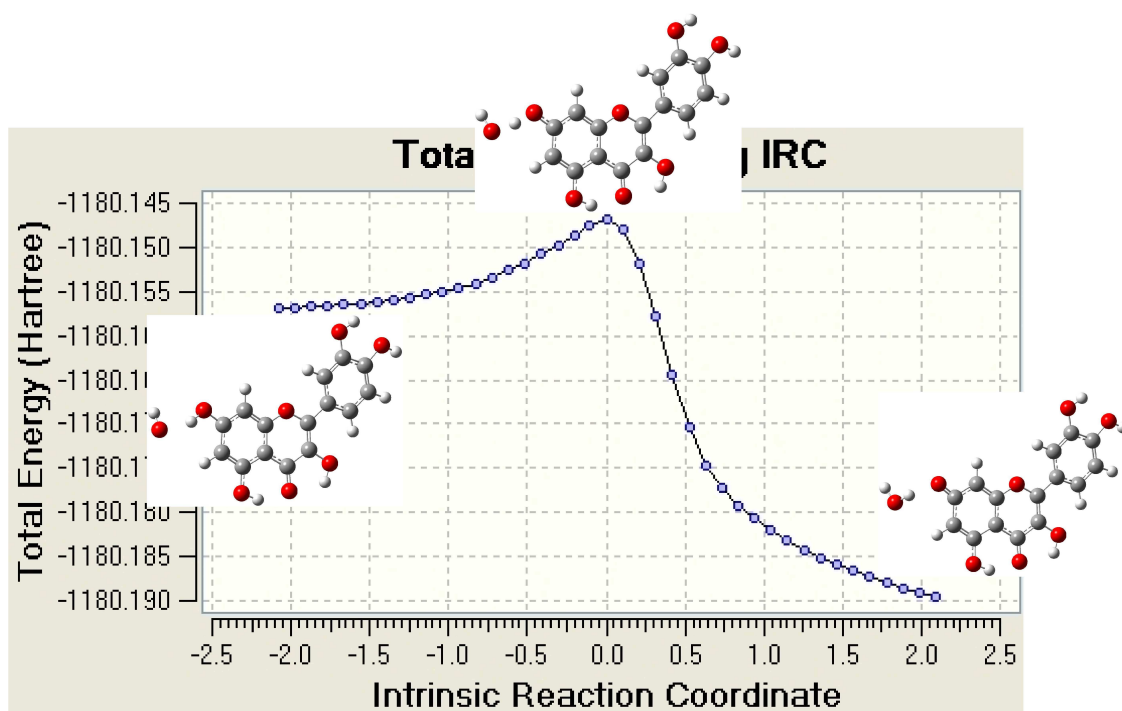


Fig. S3 Reaction in the position 7 of Q in the gaseous state.

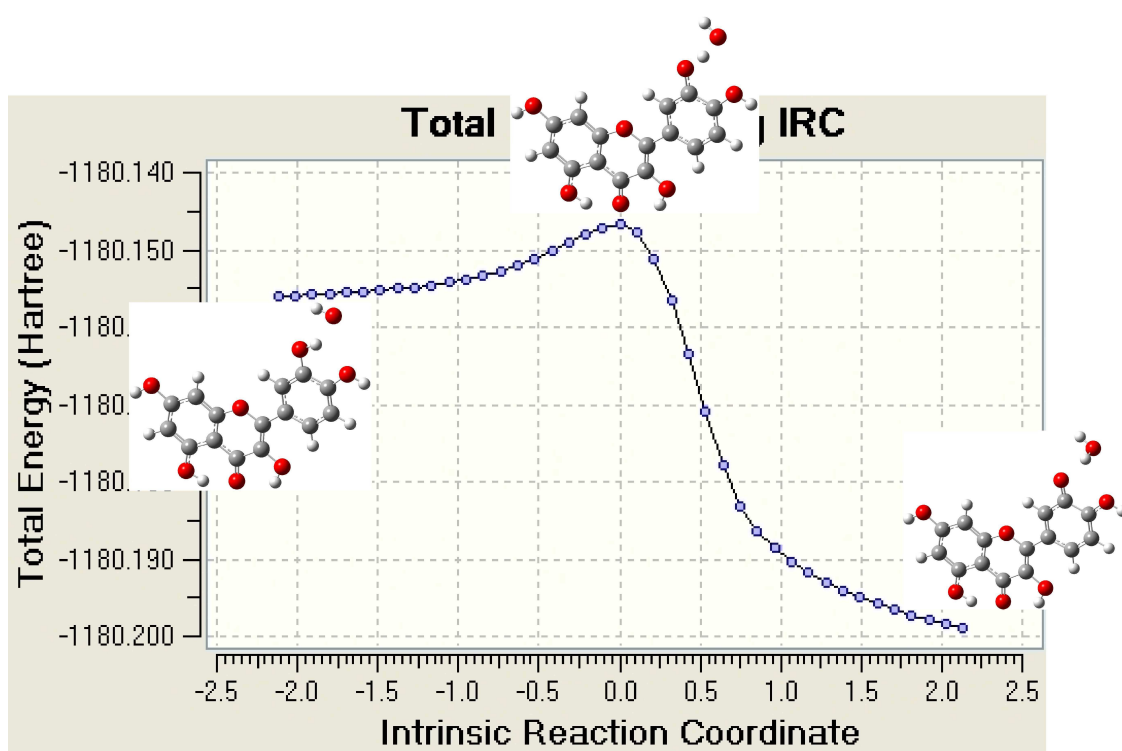


Fig. S4 Reaction in the position 3' of Q in the gaseous state.

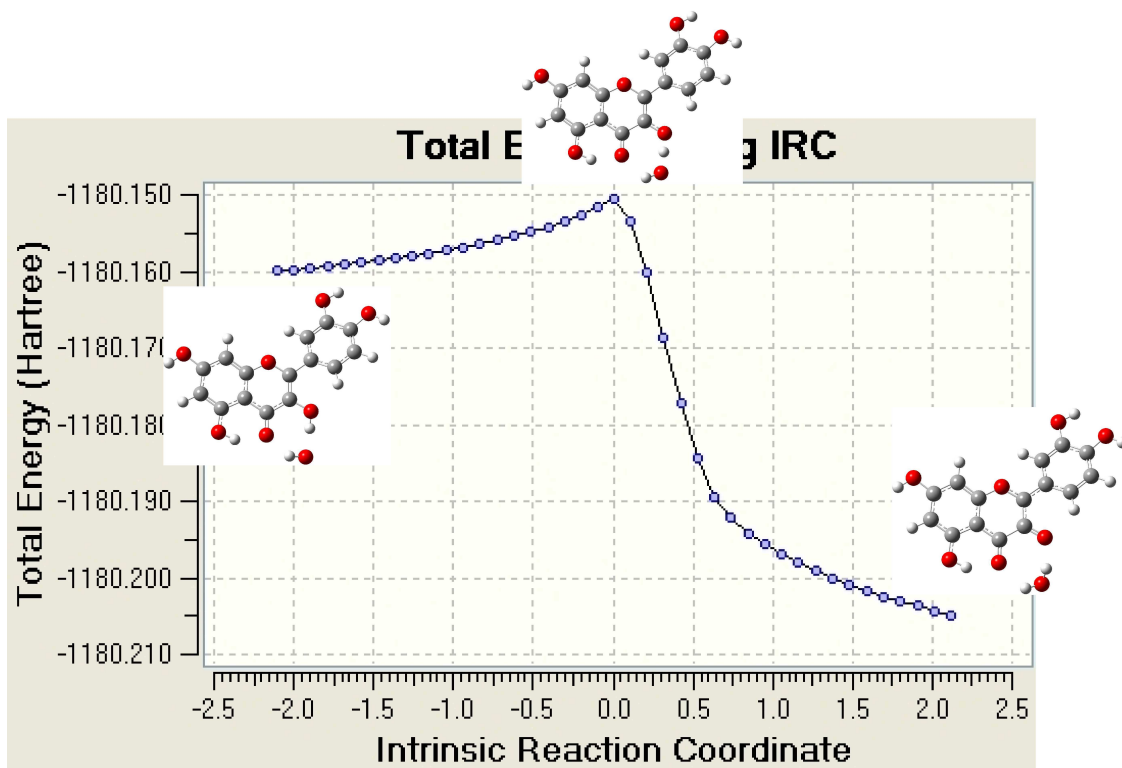
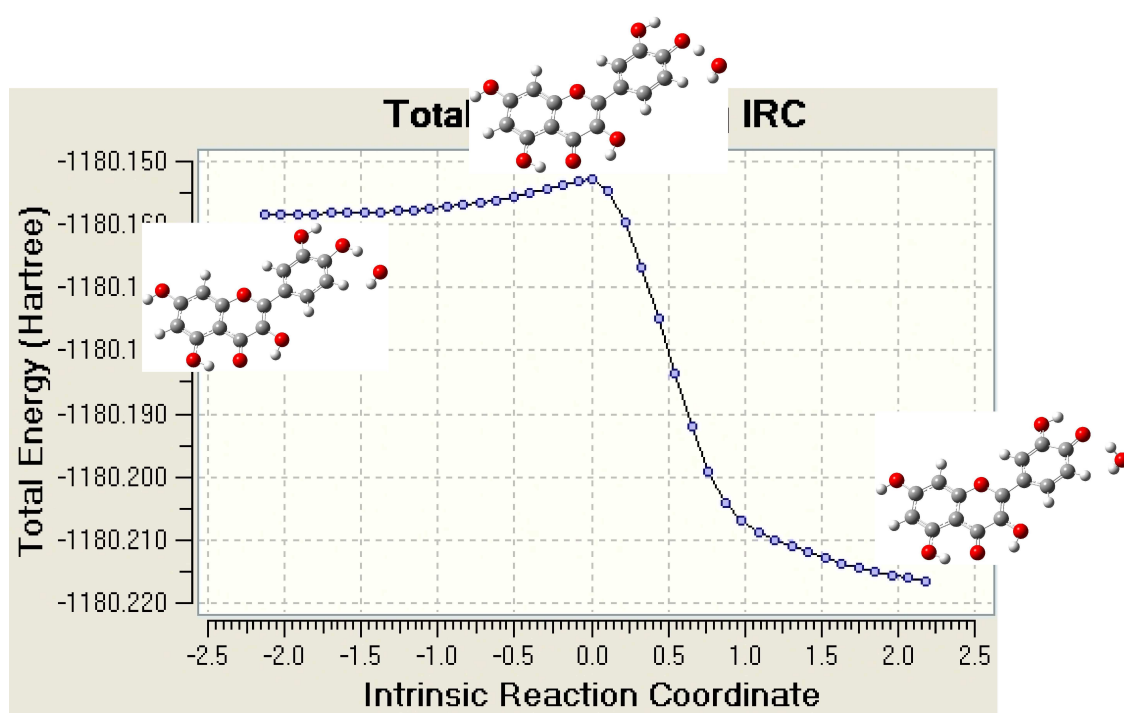


Fig. S5 Reaction in the position 3 of Q in the gaseous state.

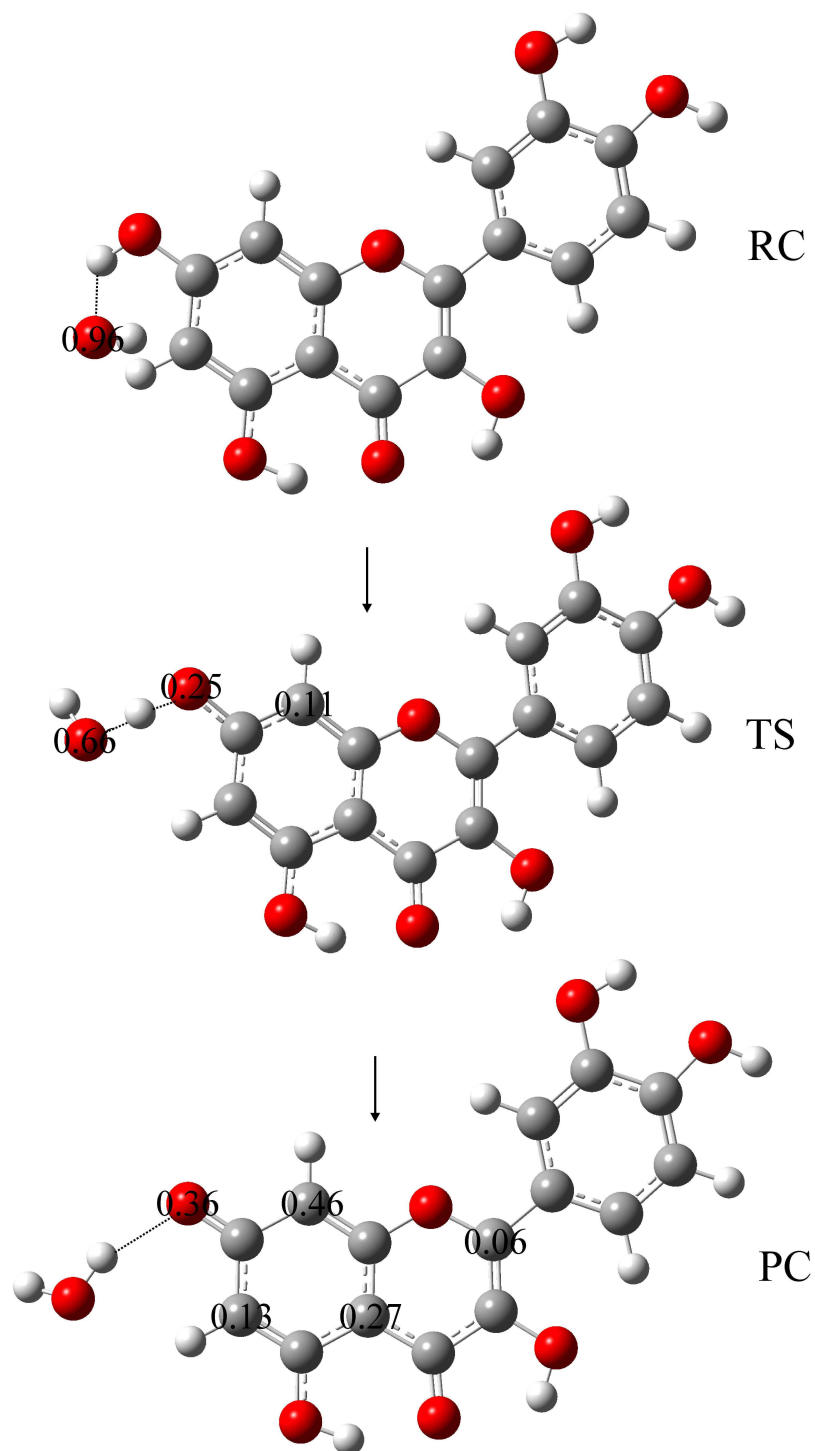


**Fig. S6** Reaction in the position 4' of Q in the gaseous state.

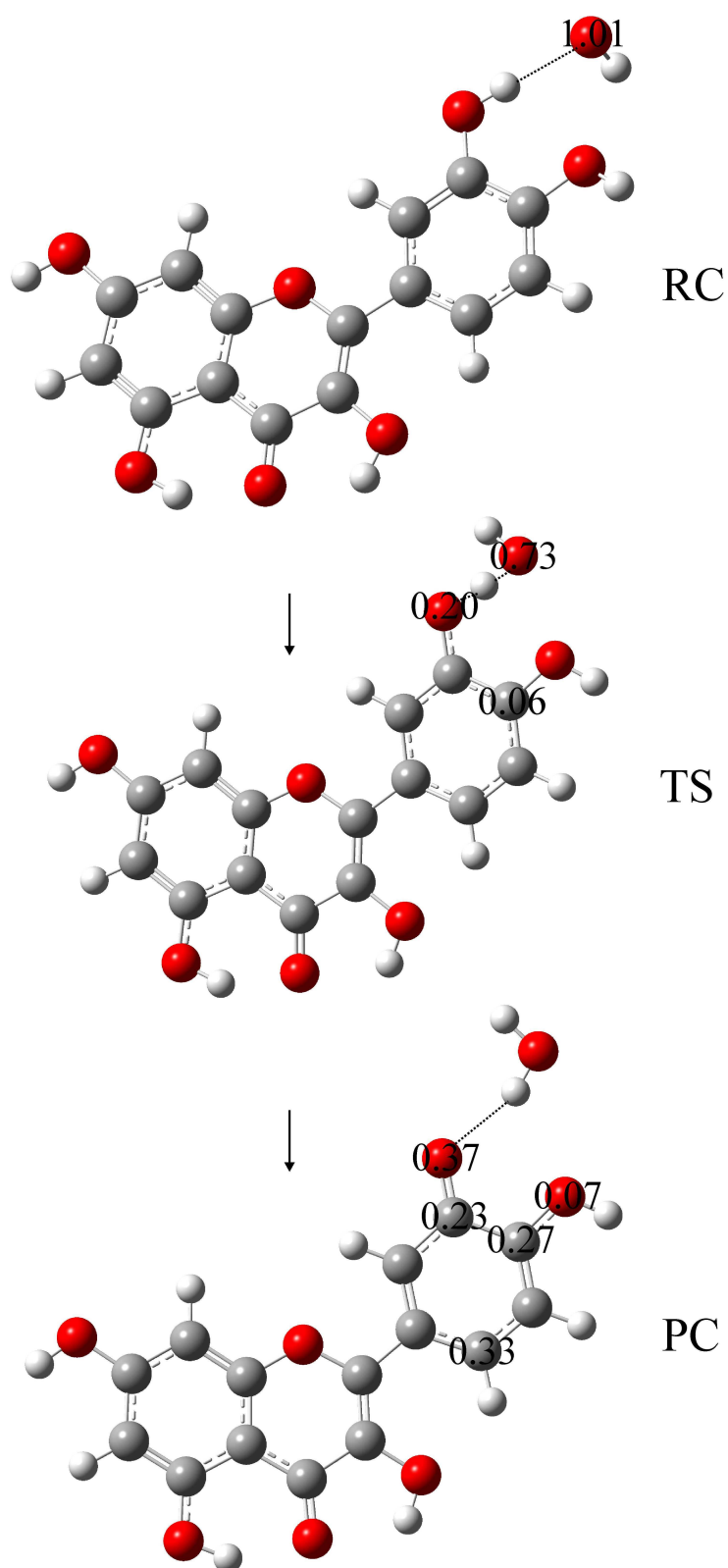
**Table S5** Crucial bond distances in the participants in the reactions of hydroxyl radical with different OH groups of Q in the gaseous phase

Species	Bond distances (pm)				
RC7		210.0		96.6	134.7
TS7	O11 – H7	131.4	H7 – O7	106.1	O7 – C7
PC7		96.6		193.9	124.5
RC3'		195.7		96.8	135.1
TS3'	O11 – H3'	139.2	H3' – O3'	103.7	O3' – C3'
PC3'		96.4		206.2	124.1
RC3		196.3		97.2	134.9
TS3	O11 – H3	130.9	H3 – O3	108.3	O3 – C3
PC3		96.3		202.6	123.3
RC4'		209.8		96.5	136.5
TS4'	O11 – H4'	144.6	H4' – O4'	102.0	O4' – C4'
PC4'		96.7		192.9	124.5

### Spin density distribution in the participants in the reactions of Q with hydroxyl radical (Figs S7 – S10)

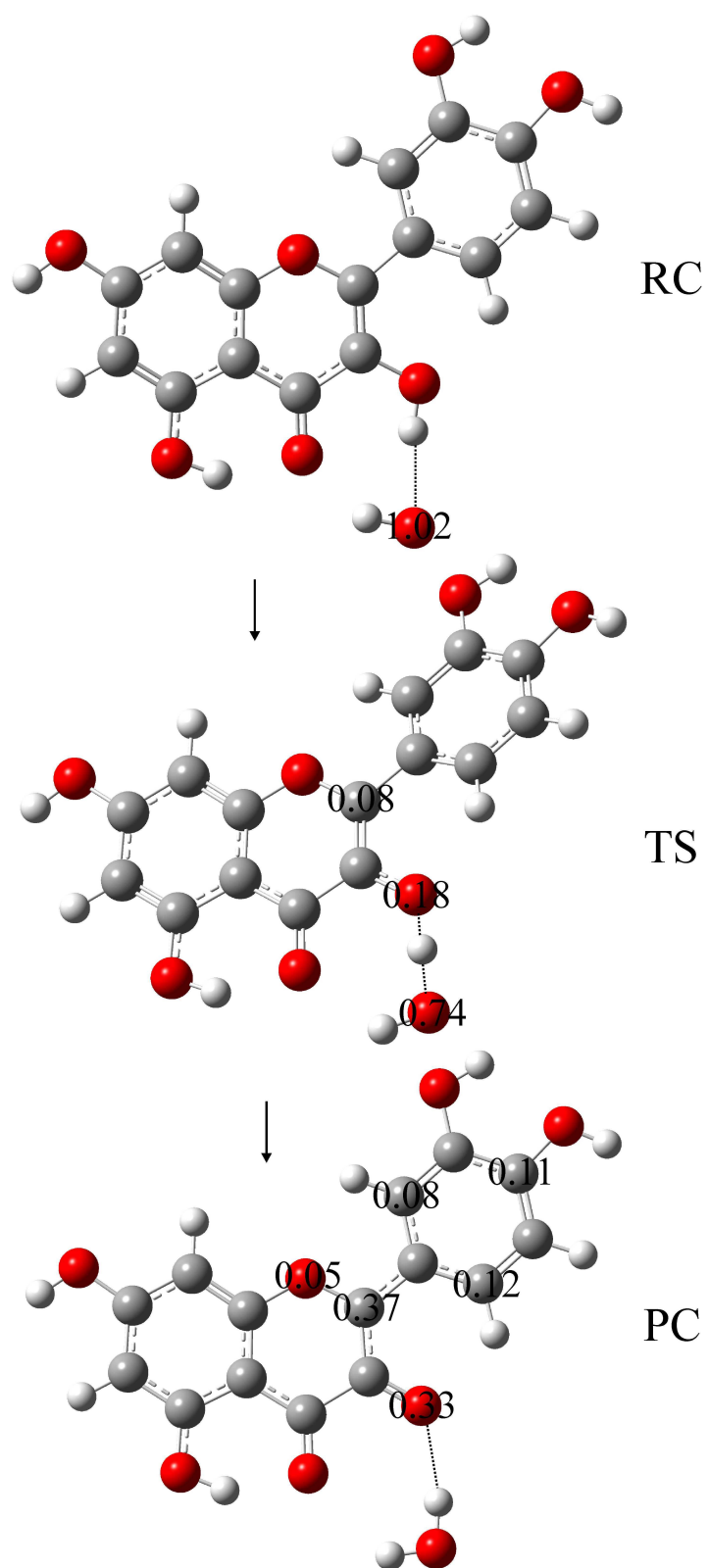


**Fig. S7** Reaction in the position 7 of Q in the gaseous phase.

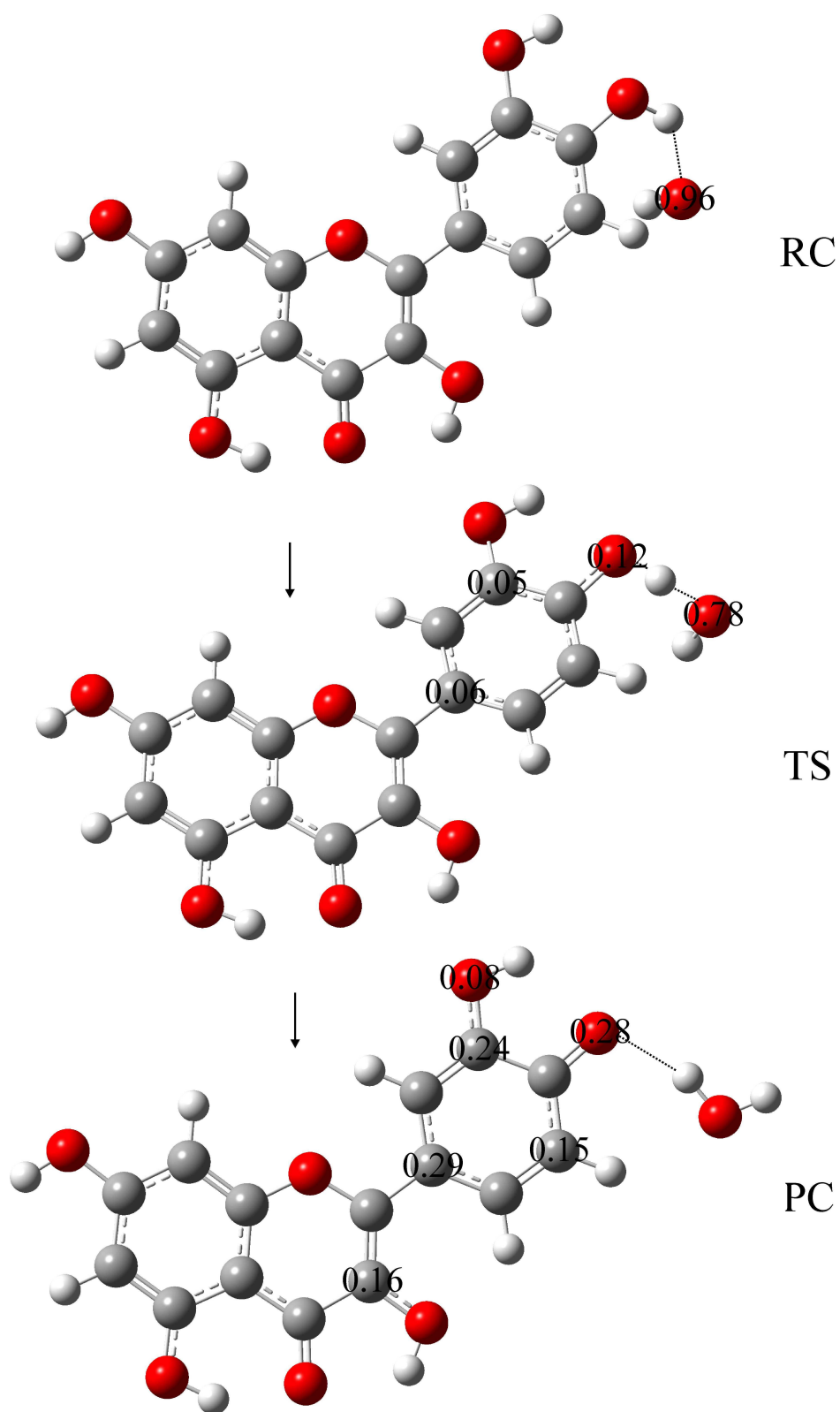


**Fig. S8** Reaction in the position 3' of Q in the gaseous phase.

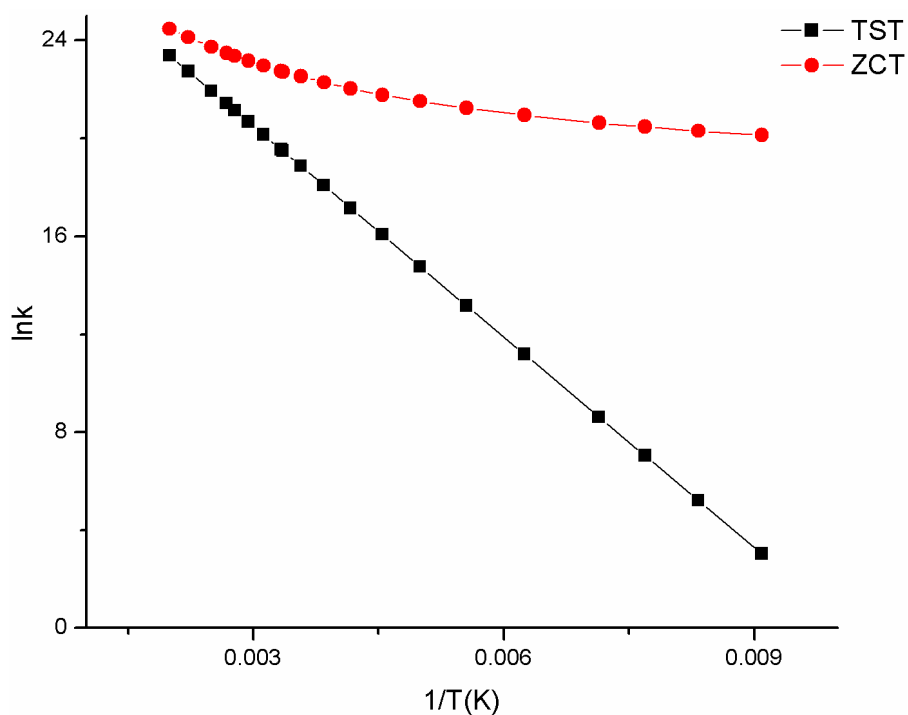




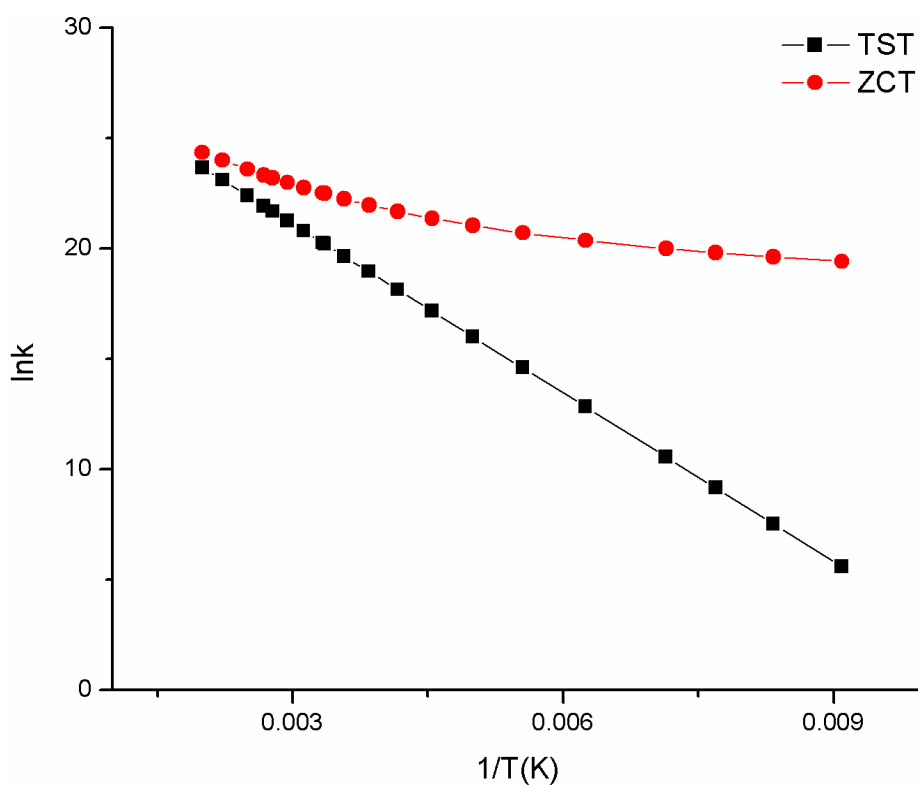
**Fig. S9** Reaction in the position 3 of Q in the gaseous phase.



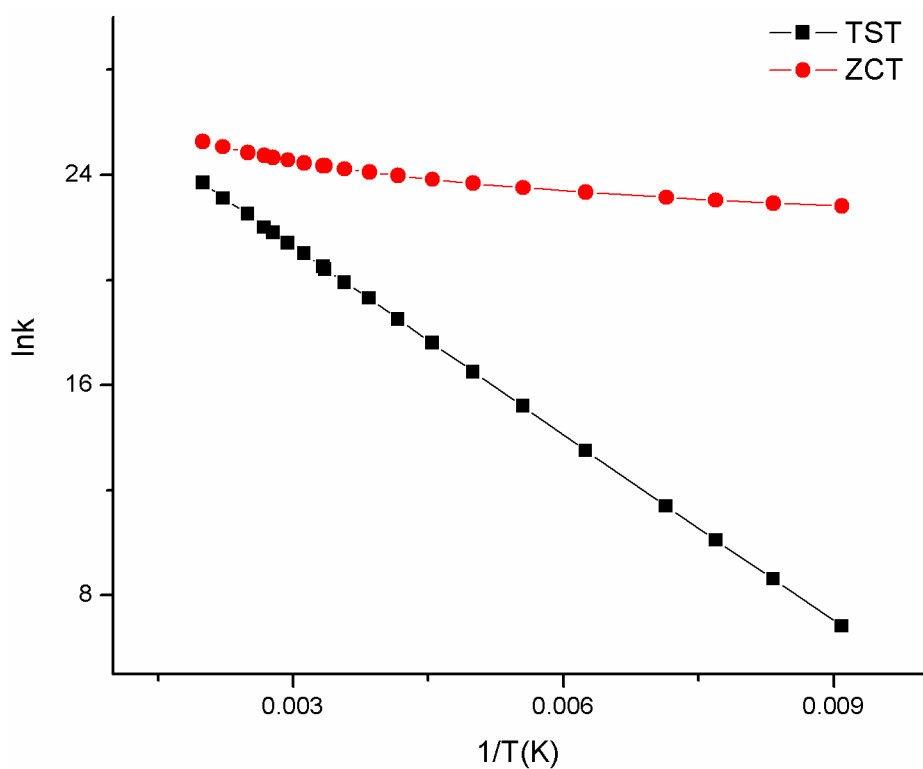
**Fig. S10** Reaction in the position 4' of Q in the gaseous phase.



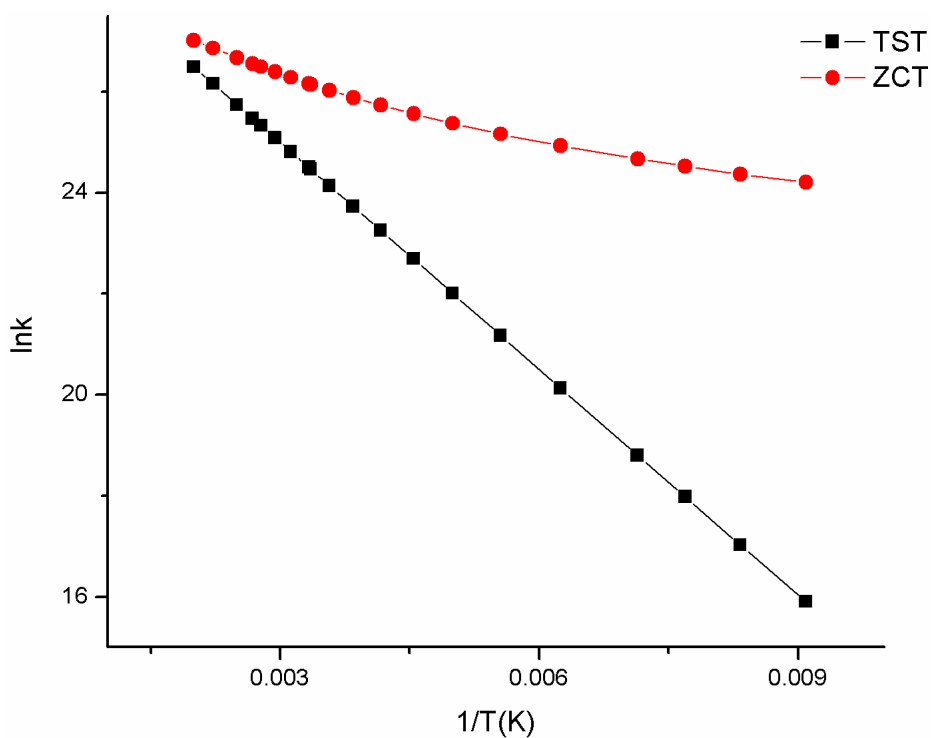
**Fig. S11** Plot of  $\ln k$  ( $k^{TST}$  and  $k^{ZCT}$ ) versus  $1/T$  for the reaction in the position 7 of Q in the gaseous phase.



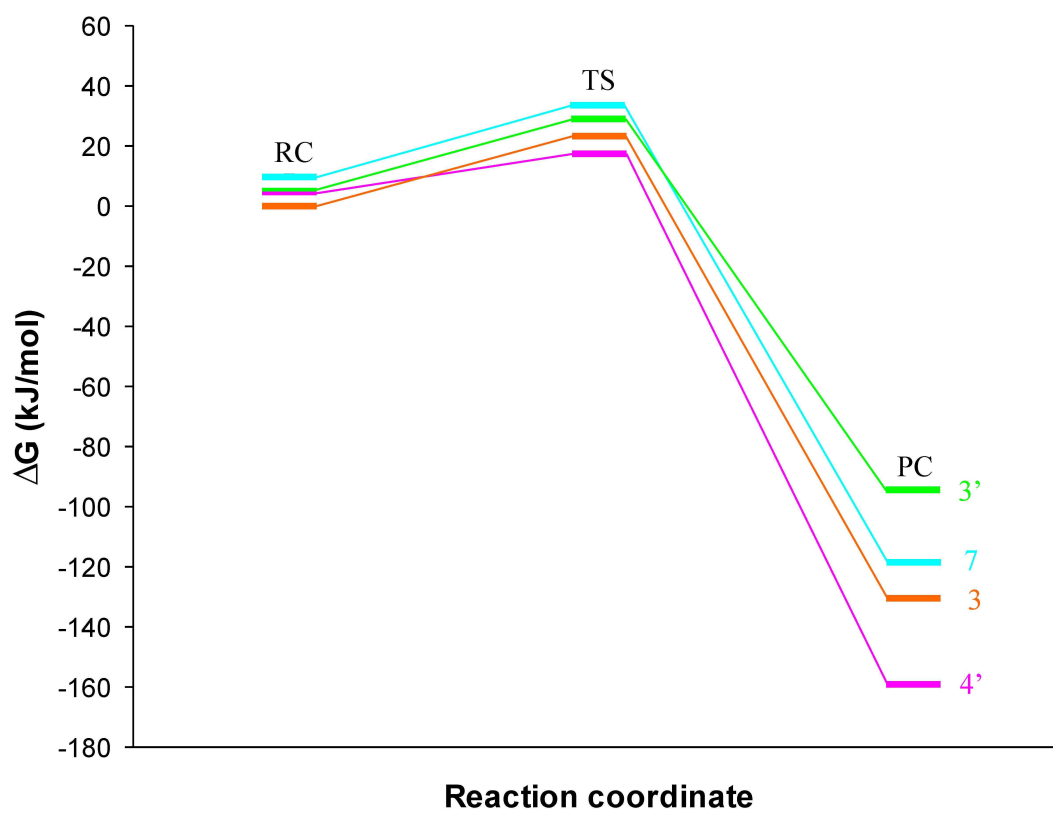
**Fig. S12** Plot of  $\ln k$  ( $k^{TST}$  and  $k^{ZCT}$ ) versus  $1/T$  for the reaction in the position 3' of Q in the gaseous phase.



**Fig. S13** Plot of  $\ln k$  ( $k^{TST}$  and  $k^{ZCT}$ ) versus  $1/T$  for the reaction in the position 3 of Q in the gaseous phase.



**Fig. S14** Plot of  $\ln k$  ( $k^{TST}$  and  $k^{ZCT}$ ) versus  $1/T$  for the reaction in the position 4' of Q in the gaseous phase.



**Fig. S15** Energy profile for the reactions of hydroxyl radical with different OH groups of Q in the gaseous phase

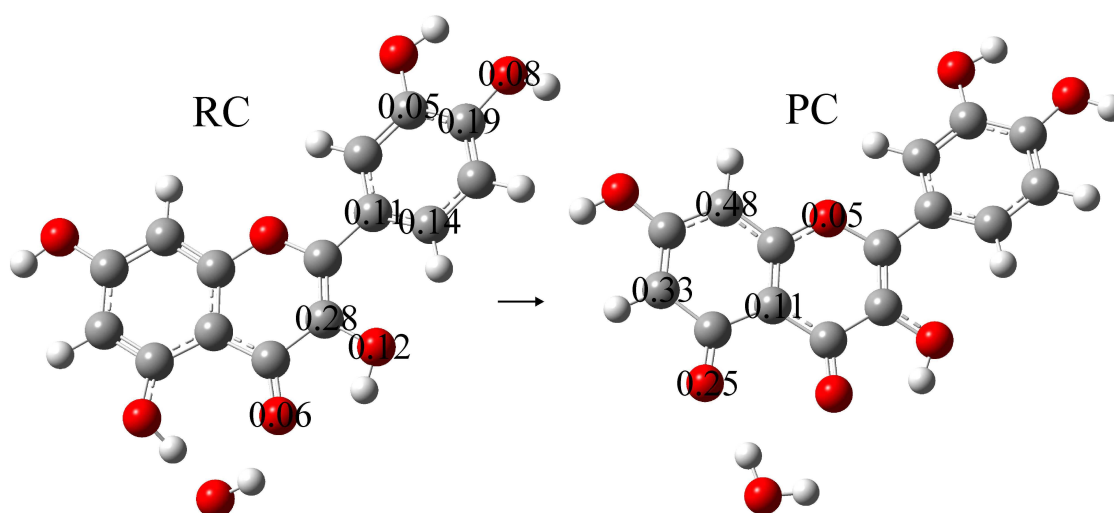
## Results for the reactions of different OH groups of $Q^{+\bullet}$ with hydroxide anion in the aqueous phase

In each reaction of  $Q^{+\bullet}$  with hydroxide anion in the aqueous phase, an electron is not spontaneously transferred from the hydroxide anion to  $Q^{+\bullet}$ , implying that phenolic hydrogen is transferred as a proton, i.e., that  $Q^{+\bullet}$  undergoes the SET-PT mechanism.

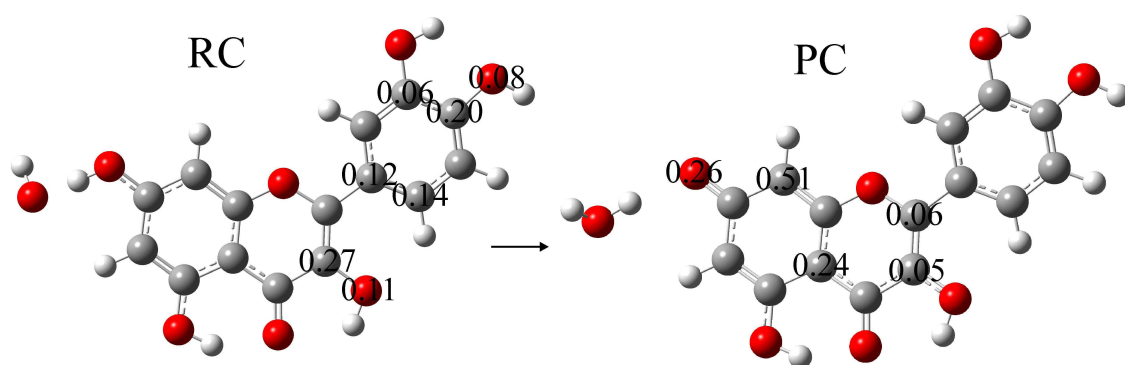
**Table S6** Crucial bond distances in the product complexes of the reactions of  $Q^{+\bullet}$  with hydroxide anion in the aqueous solution

Species	Bond distances (pm)					
PC5	O11 – H5	96.9	H5 – O5	189.6	O5 – C5	123.7
PC7	O11 – H7	97.0	H7 – O7	187.0	O7 – C7	124.6
PC3'	O11 – H3'	97.0	H3' – O3'	187.5	O3' – C3'	124.7
PC3	O11 – H3	96.9	H3 – O3	189.6	O3 – C3	124.1
PC4'	O11 – H4'	97.0	H4' – O4'	186.8	O4' – C4'	124.8

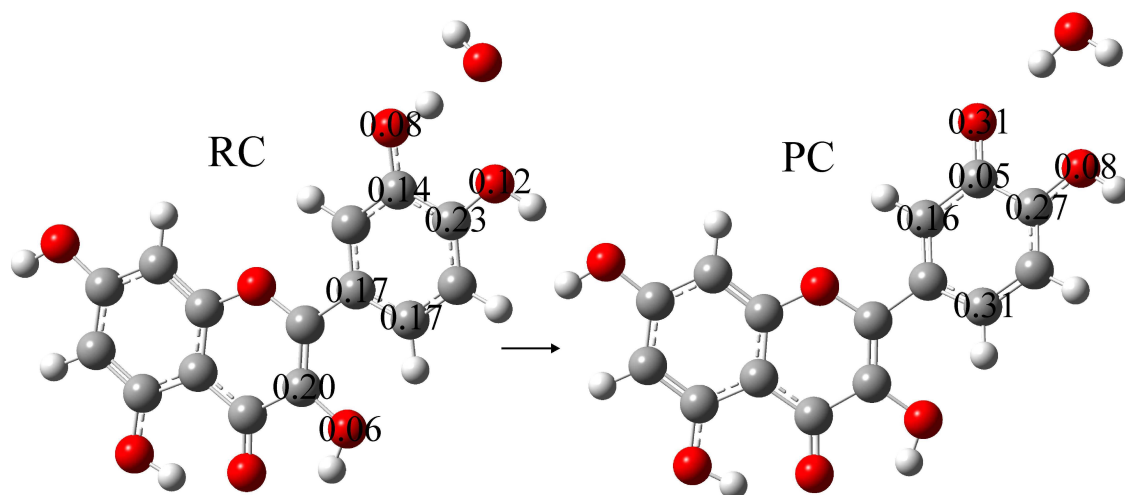
### Spin density distribution in the hypothetical reactant complexes and product complexes (Figs S16 – S20)



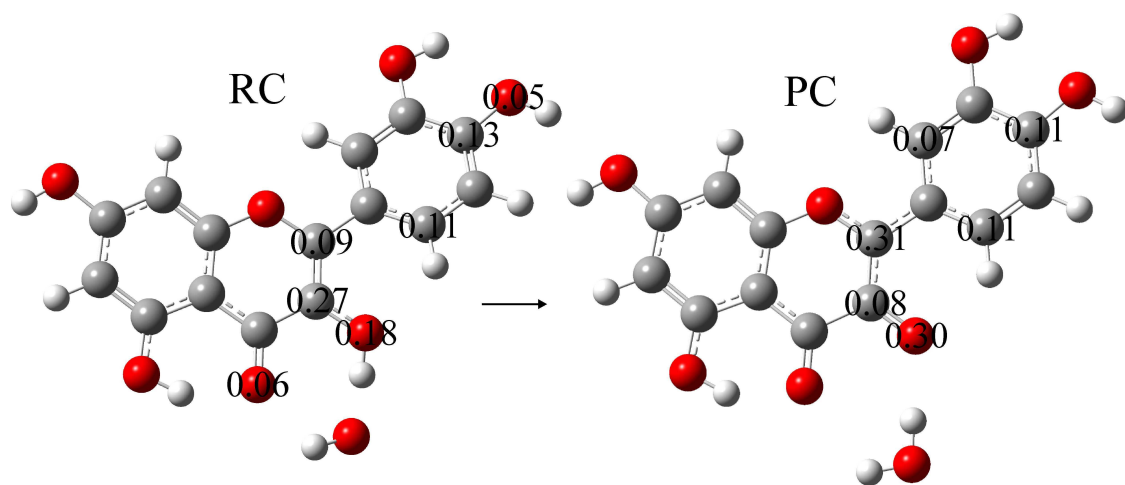
**Fig. S16** Reaction in the position 5 of  $Q^{+\bullet}$  in the aqueous solution.



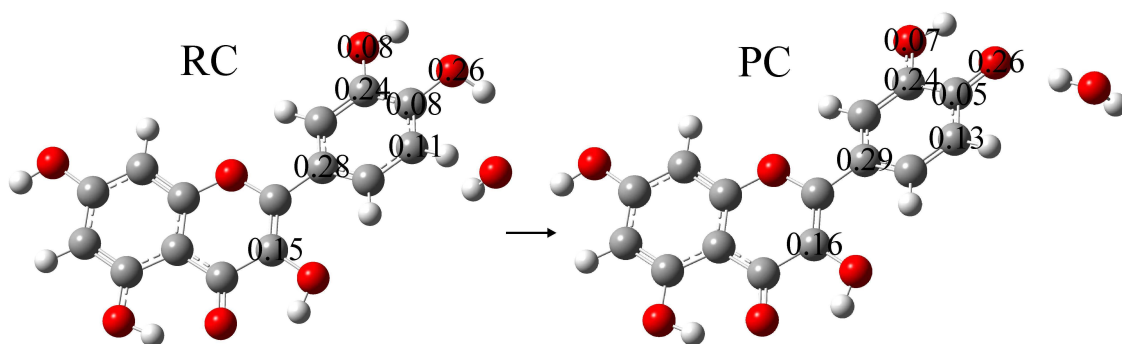
**Fig. S17** Reaction in the position 7 of  $Q^{+\bullet}$  in the aqueous solution.



**Fig. S18** Reaction in the position 3' of  $Q^{+\bullet}$  in the aqueous solution.



**Fig. S19** Reaction in the position 3 of  $Q^{+\bullet}$  in the aqueous solution.

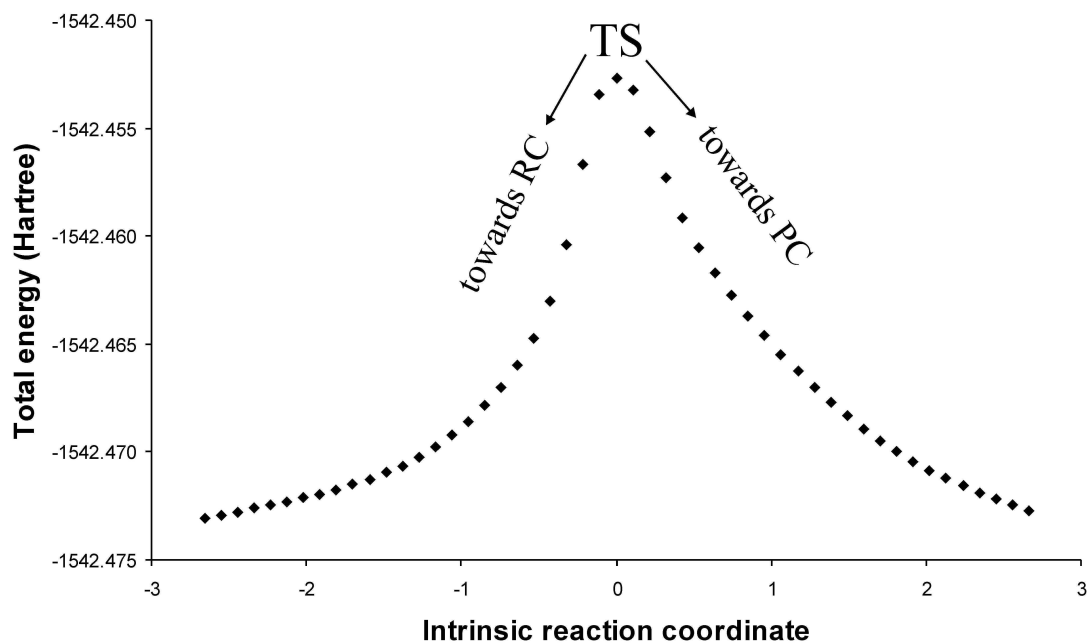


**Fig. S20** Reaction in the position 4' of  $Q^{+\bullet}$  in the aqueous solution.

### Results for the reaction of $Q^{+\bullet}$ with the MeS anion in the gaseous and aqueous phases

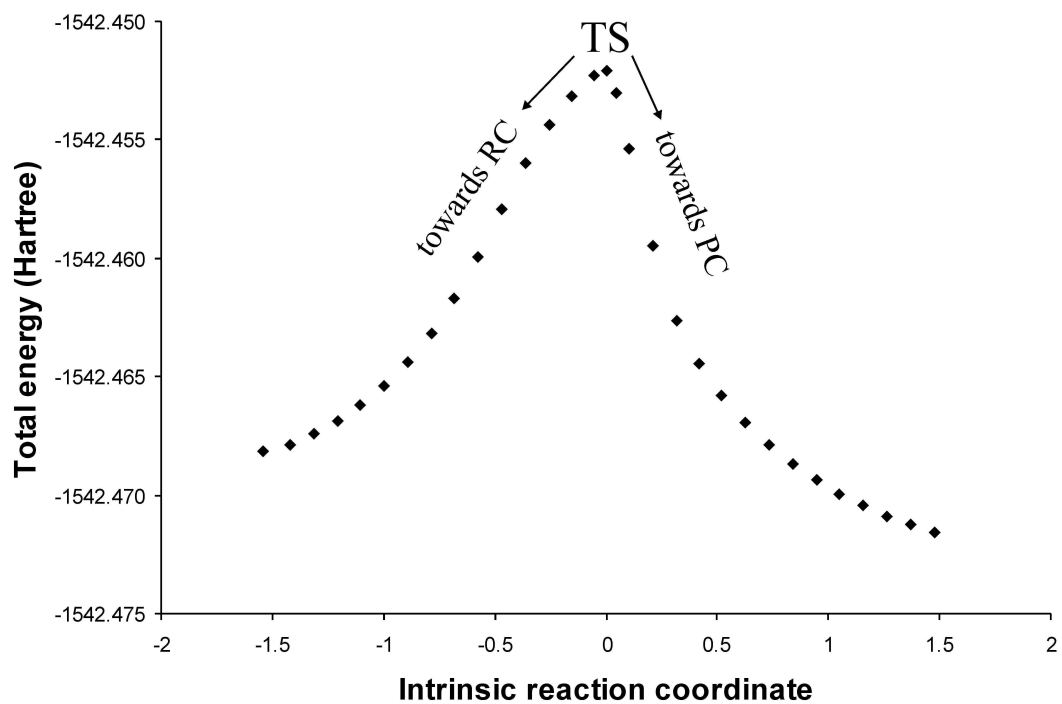
In the reaction of  $Q^{+\bullet}$  with the MeS anion in both gaseous and aqueous phases, an electron is spontaneously transferred from the anion to  $Q^{+\bullet}$ , implying that the results below relate to a transfer of phenolic hydrogen atom from Q to the  $CH_3S^\bullet$  radical, where Q undergoes the HAT mechanism.

### Results of the IRC calculations (Figs S21, S22)

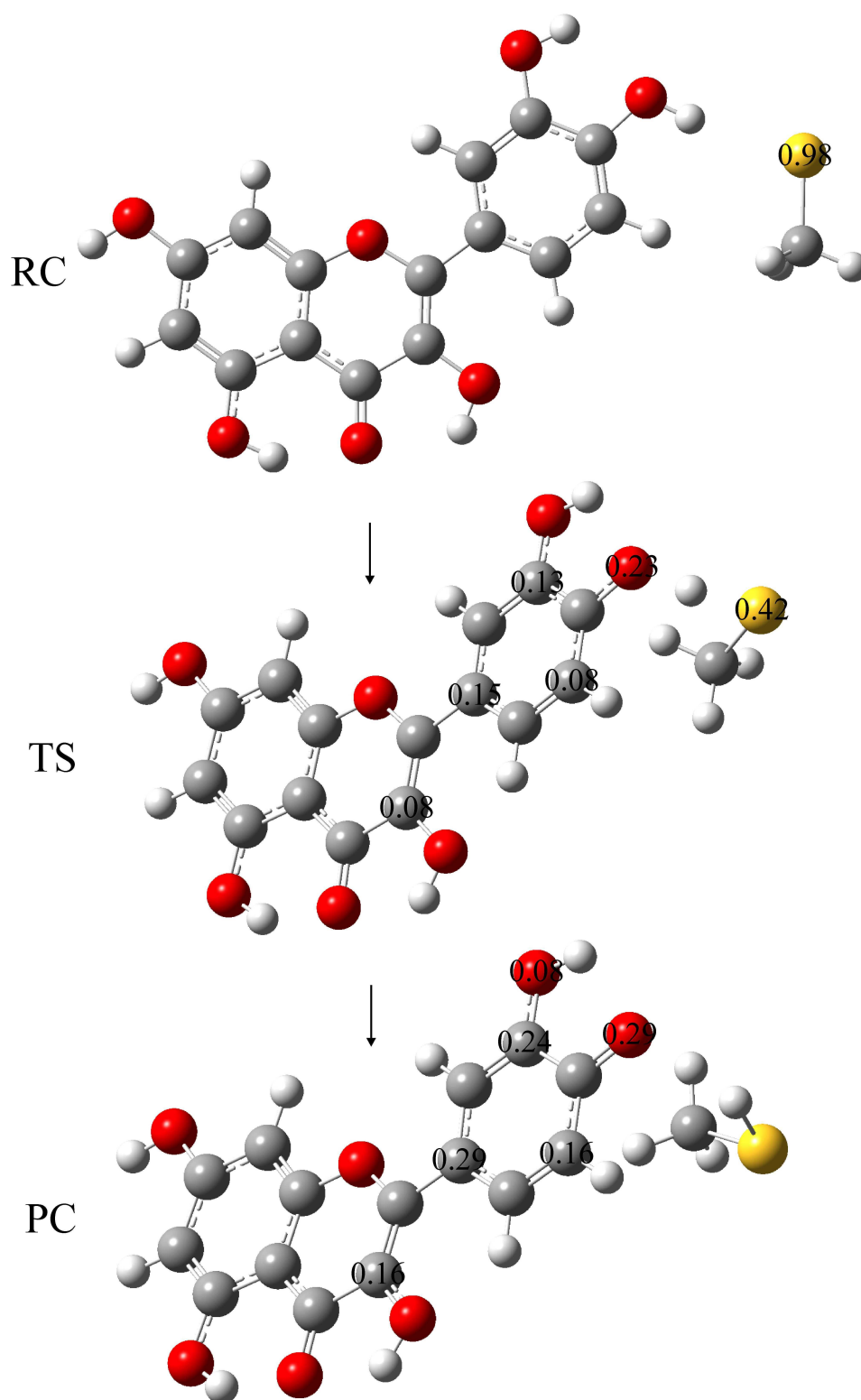


**Fig. S21** Reaction in the position 4' of Q in the gaseous phase.

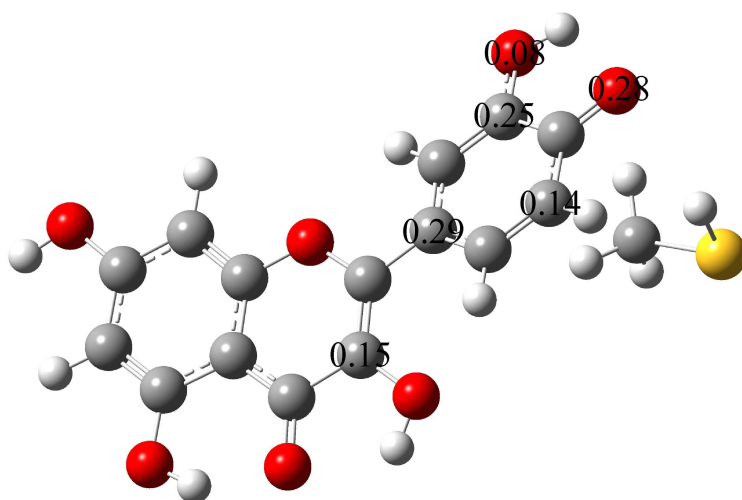




**Fig. S22** Reaction in the position 4' of Q in the aqueous solution.



**Fig. S23** Reaction in the position 4' of Q with  $\text{CH}_3\text{S}^\bullet$  radical in the gaseous phase. Spin density distribution in the participants in the reaction.



**Fig. S24** Spin density distribution in the product complex of the reaction in the position 4' of Q with  $\text{CH}_3\text{S}^\bullet$  radical in the aqueous solution.

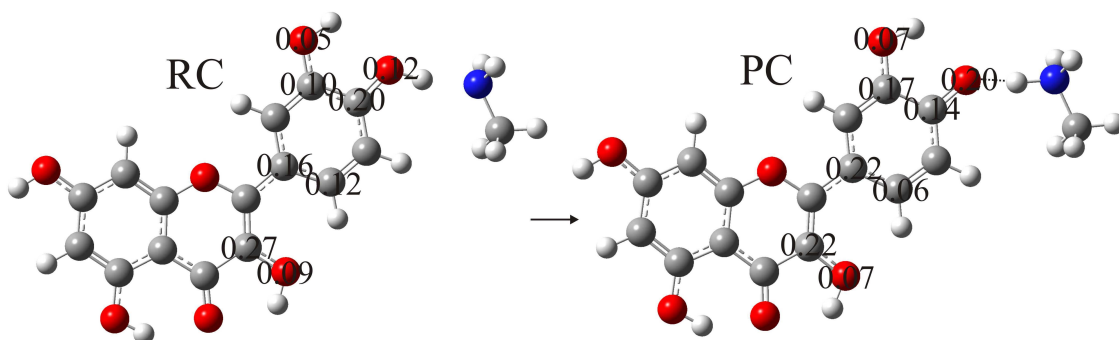
### Results for the reaction of $\text{Q}^{+\bullet}$ with methylamine in the gaseous and aqueous phases

In the reaction of  $\text{Q}^{+\bullet}$  with methylamine in both gaseous and aqueous phases, an electron is not spontaneously transferred from methylamine to  $\text{Q}^{+\bullet}$ , implying that phenolic hydrogen is transferred as a proton, i.e., that  $\text{Q}^{+\bullet}$  conforms to the SET-PT mechanism.

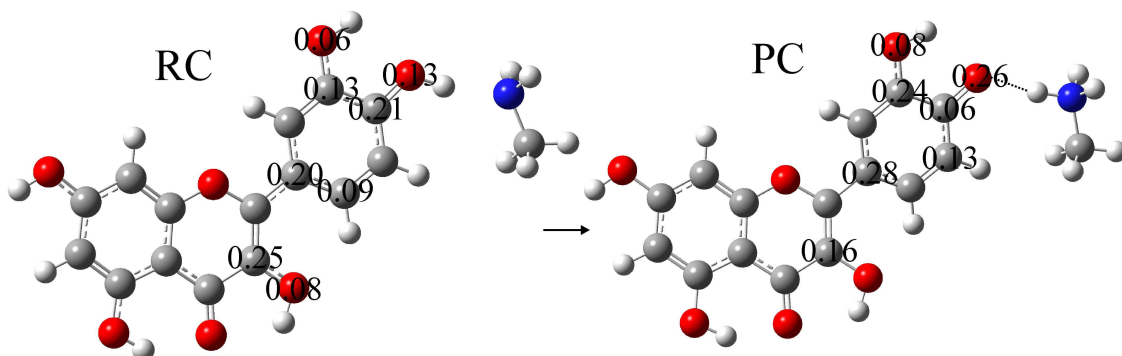
**Table S7** Crucial bond distances in the product complex of the reaction in the 4' position of  $\text{Q}^{+\bullet}$  with methylamine in the gaseous and aqueous phases

Product complex	Bond distances (pm)		
	N11 – H4'	H4' – O4'	O4' – C4'
PC4'	<b>Gaseous phase</b>		
	109.7	147.1	126.9
PC4'	<b>Aqueous solution</b>		
	103.4	184.2	125.2

### Spin density distribution in the hypothetical reactant complexes and product complexes (Figs S25, S26)



**Fig. S25** Reaction in the position 4' of  $Q^{+\bullet}$  in the gaseous phase.



**Fig. S26** Reaction in the position 4' of  $Q^{+\bullet}$  in the aqueous solution.