Stabilization of the Transition State of the HO_2^- H^+ Reaction by a Lone Pair on the β-Oxygen Atom

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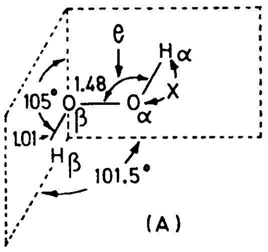
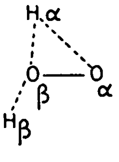
Summary Calculations of the change of total energy of the system, $H^+ + HOO^-$ to form H_2O_2, caused by the shift of $\angle O_\beta O_\alpha H_\alpha$ and H_α–O_α bond length, have been performed; the results indicate a substantial stabilization of the transition state by the lone pairs on O_β in HOO^-.

SUPPORTING evidence for the participation of lone pairs adjacent to the nucleophilic centre in HOO^- in the transition state of an S_N2 reaction can be obtained by calculation of the total energy of the reaction system, electrophile



(A)



(B)

Calculated total energy of a hydrogen peroxide molecule (*eV*) *caused by the shift of* ∠OOH *and* H–O *bond length*

	X (Å)					
θ (°)	1·0	1·2	1·35	1·5	1·65	1·8
20				−1007·0	−1018·3	−1030·9
25				30·0	35·8	41·4
30			−1038·8	40·9	43·7	
35			44·4	45·6	46·6	47·1
40	−1045·3	−1046·4	46·8	47·0	46·9	46·4
50	47·2	47·6	46·8	45·7	44·5	42·0
60	47·9	47·4	45·8	43·8	41·9	40·1
80	48·8	47·8	45·9	43·7	41·8	
100	49·2[a]	48·1	46·1	44·0	42·0	40·4
120	48·9	47·7	45·8	43·7	41·7	40·1
150	47·2	46·1	44·2	42·2	40·4	39·0
180	45·7	44·4	42·4	39·3		37·1
210	47·2	46·1	44·2	42·2	40·5	38·9
240	48·8	47·7	45·8	43·7	41·7	40·1
260	49·1	48·1	46·1	44·0	42·0	40·3
280	48·7	47·8	45·8	43·7	41·7	
300	47·6	47·1	45·5	43·6	41·7	39·9
310	46·8	47·1	46·3	45·2	44·1	41·8
320	44·6	45·6	45·9	46·2	46·2	45·9
325			43·4	44·6	45·7	46·3
330			37·5	38·6	42·6	45·0
335				28·6	34·4	40·3
340					16·8	29·6

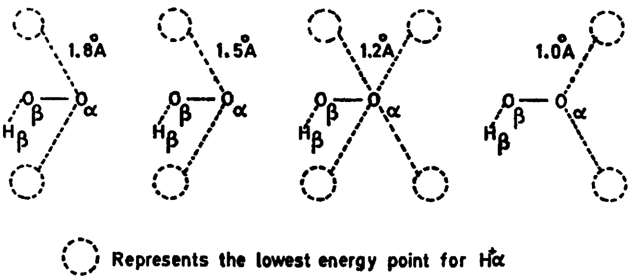
[a] Crystalline form (lowest energy form).

+ HOO^-, by shifting an electrophile around HOO^-. The following SCF calculations using CNDO/2 approximation were performed.

To simplify the calculation, we used H^+ instead of more normal electrophiles such as esters. The variation of the total energy changes in hydrogen peroxide due to the shifts of ∠OOH and H–O bond length was calculated considering the core-core repulsion. The configuration (A) of hydrogen peroxide was used for the calculations.

According to our calculations, h.o. levels in H_2O_2 and H_2O are −16·2 and −17·6 eV, respectively, while the observed ionization potentials for H_2O_2 and H_2O are 11·3[1] and 12·6 eV, respectively. The results in the Table show that the lowest energy point for hydrogen changes according to its O–H bond length, as indicated in the Figure.

This mode of reaction of HOO^- shows the importance of the O_β oxygen atom in lowering the activation energy. For example, when the H–O bond length is 1·5 Å, H^+_α approaches from the direction of O_β and the lowest total energy is −1047 eV which is 3 eV lower than when H^+ approaches from the direction of a hydrogen atom in the crystalline form of H_2O_2 (−1044 eV; ∠OOH 100°).



FIGURE

The reaction therefore proceeds *via* the intermediate (B).

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[1] K. Watanabe, *J. Chem. Phys.*, 1957, *26*, 542.