Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supplementary Material

A kinetic study of reactions of calcium-containing molecules with O and H atoms: implications for calcium chemistry in the upper atmosphere.

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The material presented here supplements the electronic structure calculations described in the main paper. All calculations were performed at the B3LYP/6-311+g(2d,p) level of theory using the Gaussian 03 suite of programs.[1]

Figures S1 – S4 illustrate the geometries of significant stationary points on the potential energy surfaces of the reactions studied experimentally. These stationary points are illustrated in Figures 11b and 12 (main text), and Figures S5 and S6.

Figures S5 and S6 are potential energy surfaces for the reactions $CaCO_3$ + O and CaO_2 + H, respectively.

Figure S1. Species involved in the reactions $CaCO_3$ + O (Figure S5) and $CaCO_3$ + H (Figure 12b). TS = transition state. Colour code: yellow = Ca; red = O; grey = C; white = H.

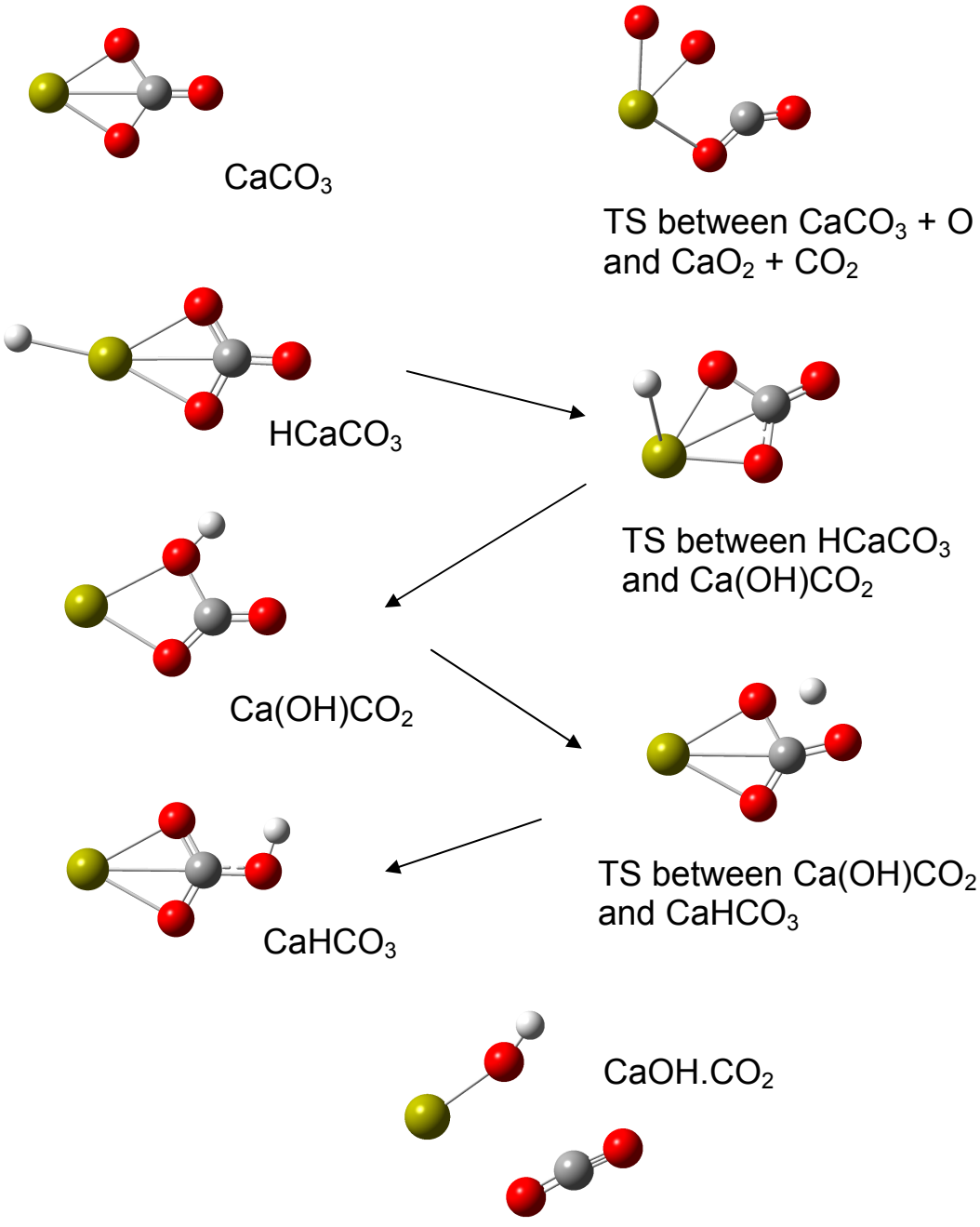


Figure S2. Species involved in the reactions CaO + H_2 (Figure S6), CaOH + H (Figure 11b) and $Ca(OH)_2$ + H.

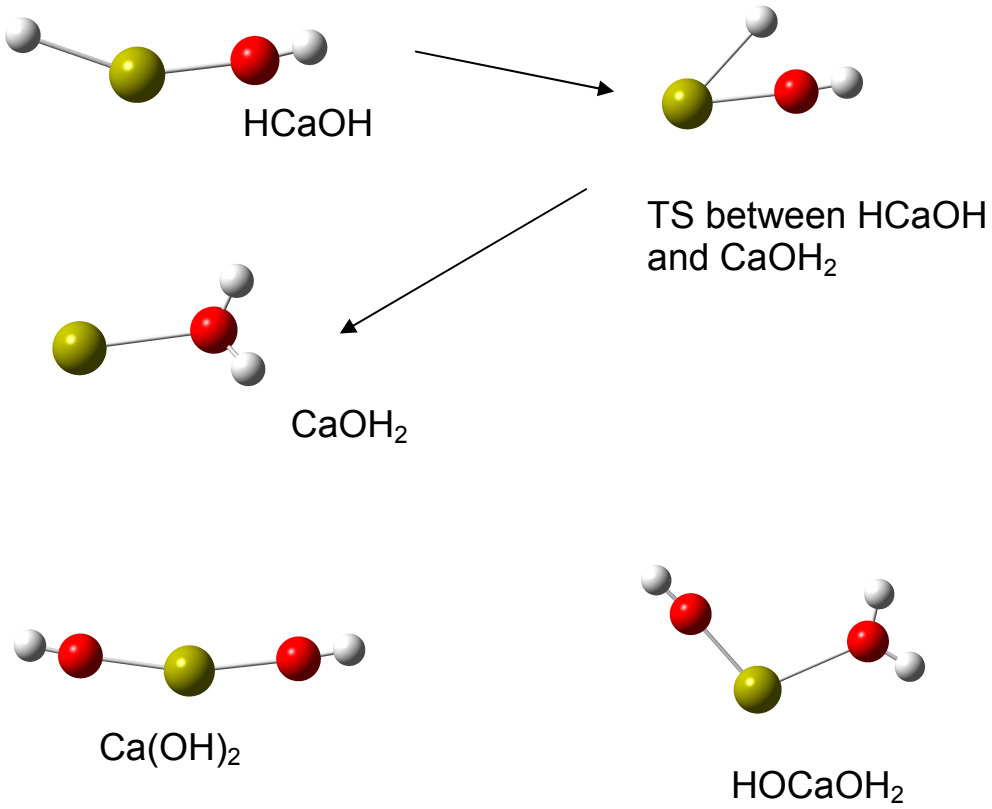


Figure S3. Species involved in the reaction CaO_2 + H (Figure 13a)

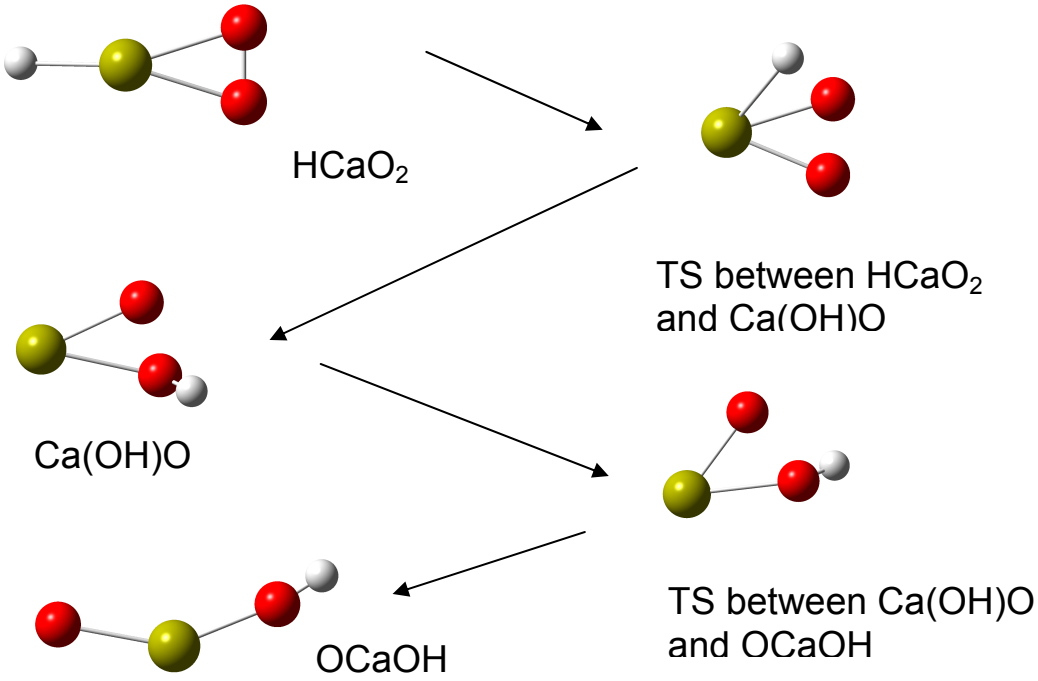
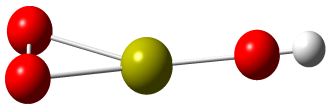
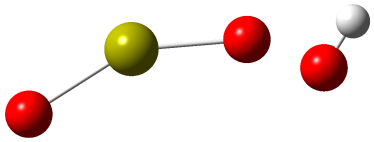


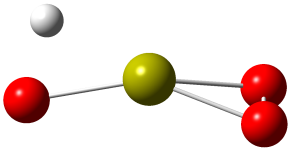
Figure S4. Species involved in the reaction CaO_3 + H (Figure 12a).



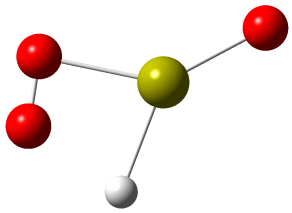
$HOCaO_2$ (^2A)



$OCaOOH$ (^2A)



$O(H)CaO_2$ (^4A)



$OCa(H)O_2$ (^4A)

OCaH

Figure S5. Potential energy surface (triplet spin multiplicity) for $CaCO_3$ + O

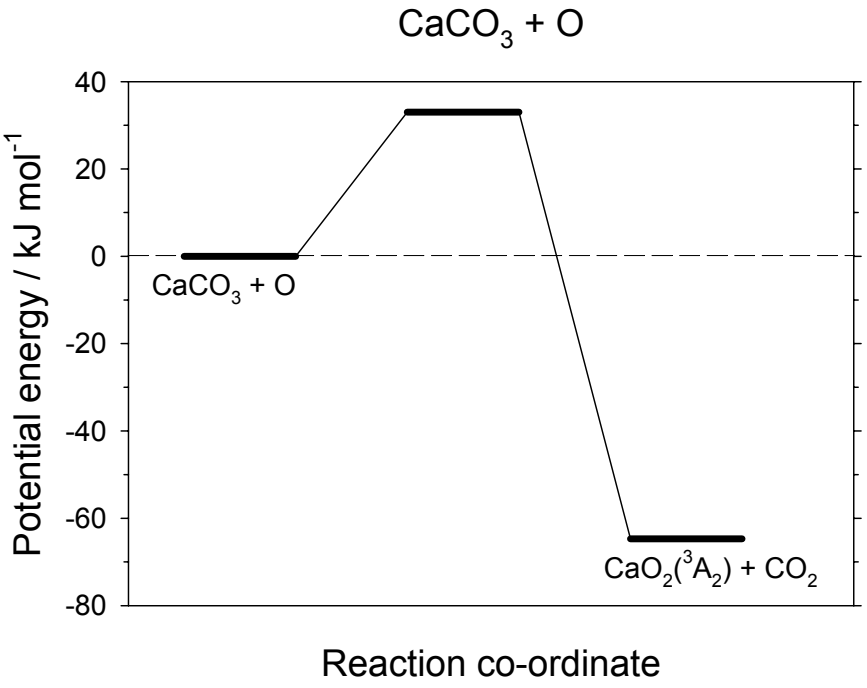
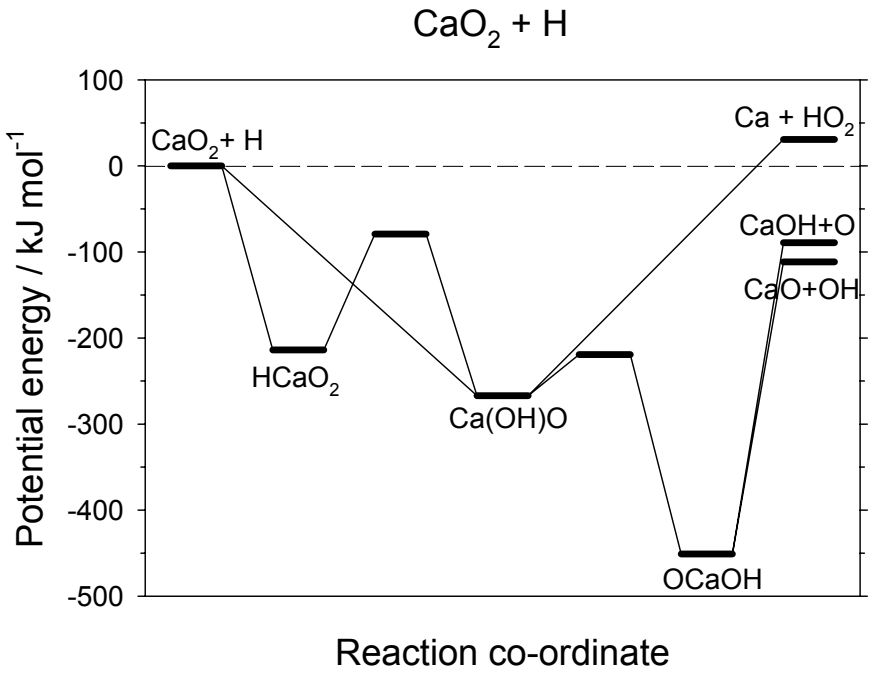


Figure S6. Potential energy surface (doublet spin multiplicity) for CaO_2 + H



1 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. J. A. Montgomery, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, *Gaussian 03, Revision B.03*, Gaussian Inc., Pittsburgh PA, 2003.