Carbon Capture via Tetraperoxovanadates

Jacob Hirschi, Zhiwei Mao, Eduard Ribo, May Nyman, Tim Zuehlsdorff

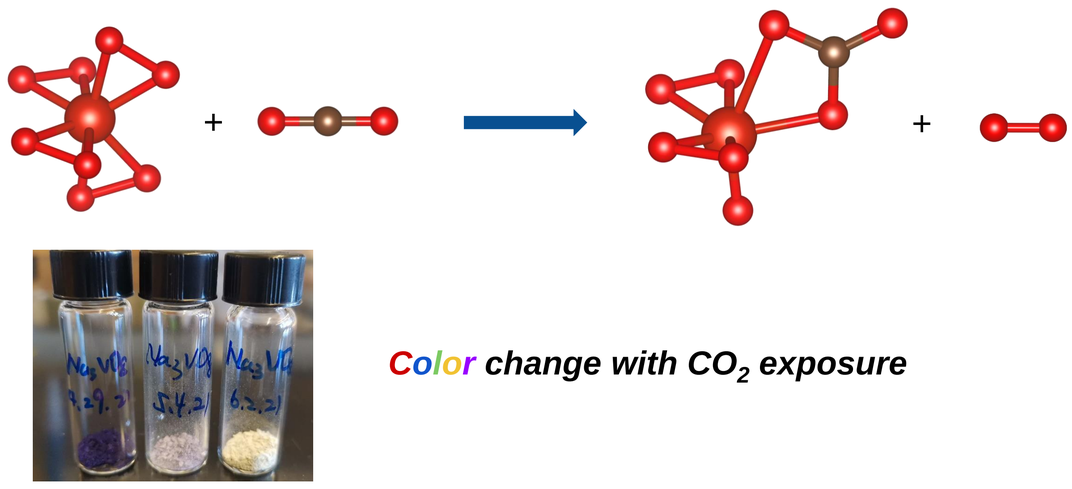
Oregon State University • Department of Chemistry • Corvallis, Oregon 97331

Scan me for PDF!

Introduction

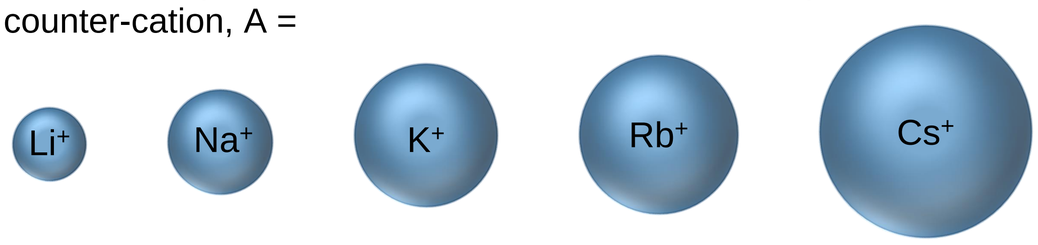
- Solid tetraperoxovanadates [1], $A_3[V(O_2)_4]$, have been shown to convert gaseous CO_2 to carbonate under ambient laboratory conditions via the reaction

$$A_3V(O_2)_4 + CO_2 \rightarrow A_3VO(O_2)_2(CO_3) + O_2$$



Color change with CO_2 exposure

- The efficiency of this reaction has been shown to depend on the counter-cation, A =



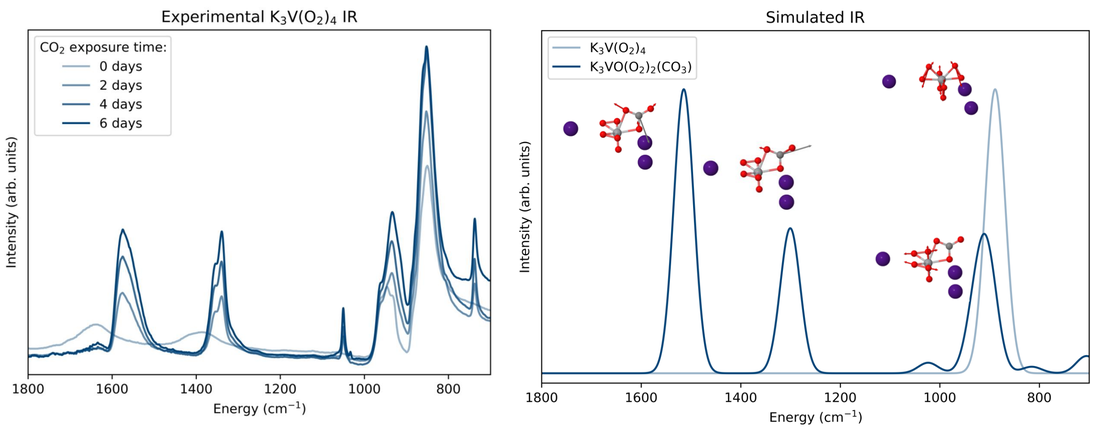
Increasing counterion size

Increasing reactivity

Solid-State Models

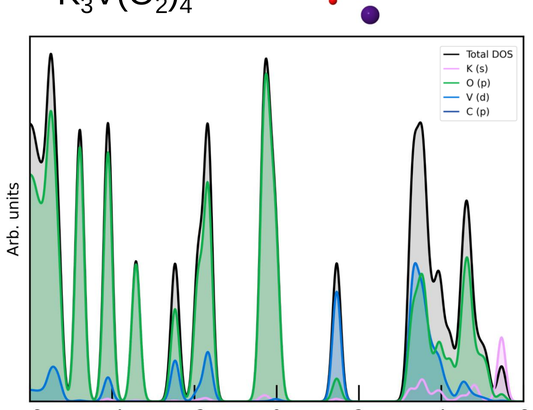
Phonons

- From available crystal structures of the starting material and product [2], DFT unit cell optimizations with periodic boundary conditions and phonon calculations were carried out to assist in experimental peak assignments
- PBE/850 eV cutoff, 2x2x2 k-grid in castep 20.11 [3]



Projected Density of States (PDOS)

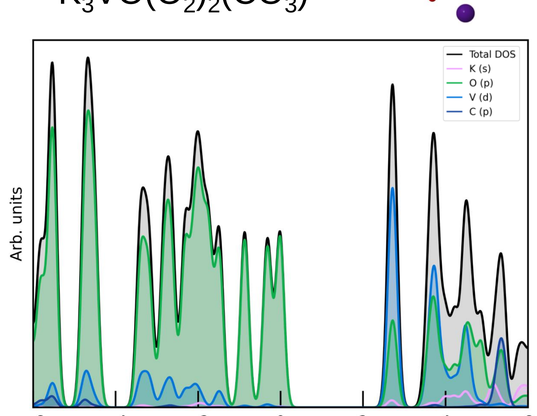
$K_3V(O_2)_4$



E_g ~ 1 eV

Purple

$K_3VO(O_2)_2(CO_3)$



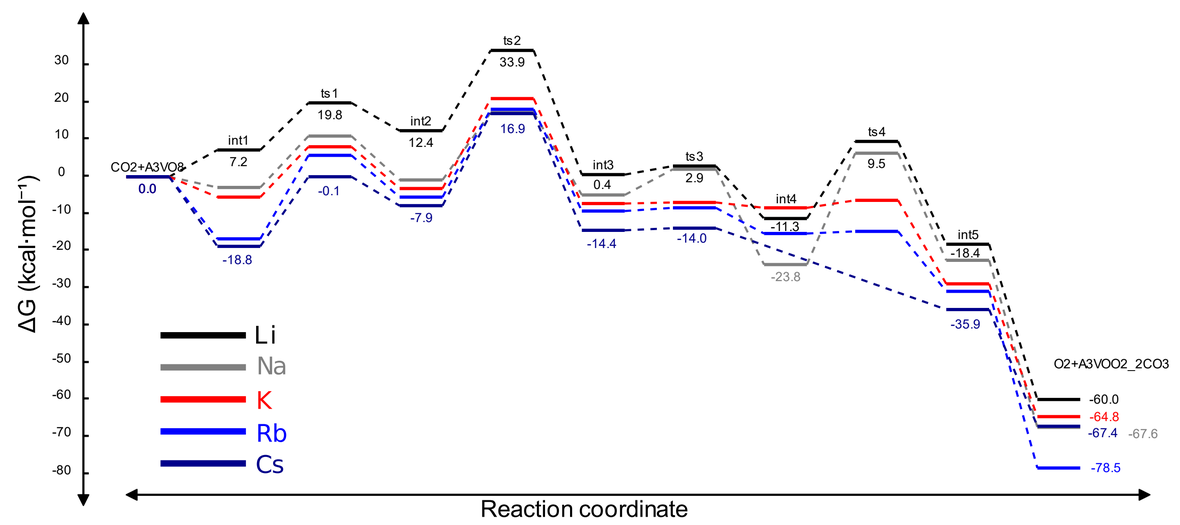
E_g ~ 2 eV

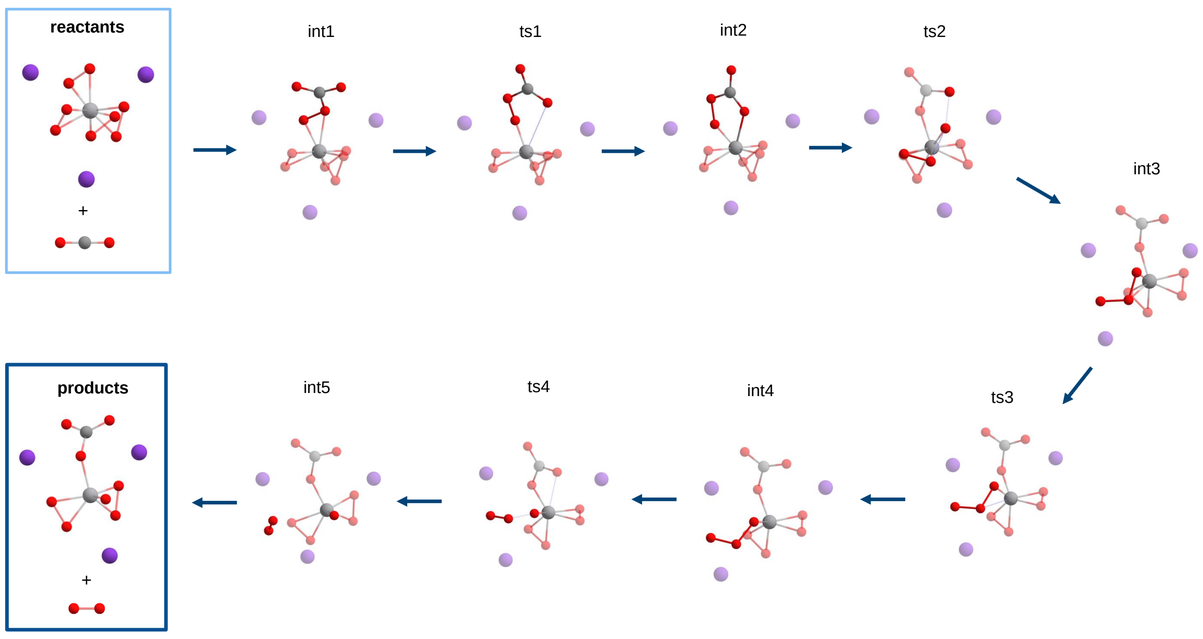
Yellow

Reaction Mechanism

Cluster Model

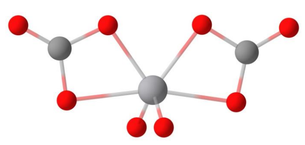
- By considering only one discrete gas-phase unit of $A_3V(O_2)_4$, insights into the thermodynamics and kinetics of the transformation can be gained by constructing a series of intermediates and transition states with molecular DFT calculations in Gaussian 16 Rev. A [4]
- The CAM-B3LYP functional with a mixed basis set of LANL2DZ ECP for the counterions and 6-31+G* for the rest of system was used

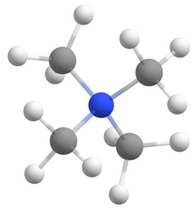




Conclusions/Future Directions

- Our work corroborates the formation of carbonate from carbon dioxide in the solid-state and explains the corresponding color change through phonon and PDOS calculations, respectively. Molecular DFT calculations demonstrate that the conversion plausibly proceeds through a four-step process involving peroxycarbonate and ozone intermediates. Larger alkali counterions are associated with lower barriers for O_2 detachment (int4 → ts4 → int5 above).
- Future work will include extension to larger counterions, e.g. ammonium and tetramethylammonium, larger metal centers, and assessing the feasibility of binding two equivalents of CO_2.





Acknowledgements

Nyman Group, Zuehlsdorff Group

Department of Energy Grant, DE-SC0022278

OSU Chemistry Department

References

[1] Haxhillazi, G. Preparation, Structure and Vibrational Spectroscopy of Tetraperoxo Complexes of Cr^{V+}, V^{V+}, Nb^{V+}, and Ta^{V+}; 2003.

[2] Zou, G.; Lin, Z.; Zeng, H.; Jo, H.; Lim, S.-J.; You, T.-S.; Ok, K. M. $Cs_3VO(O_2)_2CO_3$: An Exceptionally Thermostable Carbonatoperoxovanadate with an Extremely Large Second-Harmonic Generation Response. Chem. Sci. 2018, 9 (48), 8957–8961.

[3] Clark, S. J.; Segall, M. D.; Pickard, C. J.; Hasnip, P. J.; Probert, M. I.; Refson, K.; Payne, M. C.. First Principles Methods Using CASTEP. *Zeitschrift für Kristallographie - Crystalline Materials* 2005, *220* (5-6), 567–570

[4] Gaussian 16, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

hirschij@oregonstate.edu