LOW TEMPERATURE THERMODYNAMIC EQUILIBRIUM OF CO_2 DIMER ANION SPECIES IN CRYOGENIC ARGON AND KRYPTON MATRICES

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The separated CO_2 dimer anion, $(CO_2)(CO_2{}^-)$, is observed by FTIR spectroscopy in matrix isolation experiments at 1652 cm^{-1} upon deposition of high energy argon ions into an argon matrix doped with 0.5% CO_2. It has previously been reported by Andrews that upon annealing the matrix to 25K, the separated species converts to an oxalate-like $C_2O_4{}^-$ species which appears at 1856 cm^{-1}.[a] We have observed that subsequently holding the matrix at 10K caused the $C_2O_4{}^-$ species to fully convert back to $(CO_2)(CO_2{}^-)$. Upon further investigation, we determined that the two species reversibly interconvert between 19K and 23K, suggesting the species are in thermodynamic equilibrium. The associated van't Hoff plot has a linear trend and indicates an endothermic reaction driven by a large increase in entropy. An analogous experiment in a krypton matrix was performed, and the equilibrium was found to occur between 26K and 31K. Interestingly, analysis revealed the reaction in krypton is more endothermic, but has nearly the same entropy value as was observed in the argon experiment.

[a]Zhou, M.; Andrews, L.; J. Chem. Phys. 110, 2414 (1999).