The Co-C Bond in the Gas Phase

F. Fleckenstein[1], P. Chen[1]*

[1]Laboratorium für Organische Chemie, ETH Zürich

The Co-C bond in adenosylcobalamin (AdoCbl) is considered to be a weak bond. The homolytic bond cleavage is measured to be at most 16 kcal/mol in an enzymatic environment and 34 kcal/mol in aqueous media.[1] Threshold collision-induced dissociation (T-CID) is a method used to measure reactive cross-sections in the gas phase. From the reactive cross-sections, bond dissociation energies (BDEs) are deconvoluted using ligand collision-induced dissociation (L-CID)[2], a program written in-house. Our group previously measured the Co-C bond of the structurally similar adenosylcobinamid (AdoCbi) with T-CID/L-CID and obtained a BDE value of 41 kcal/mol.[3] When changing the adenosyl to a phenyl, *i.e.* changing a sp^3-hybridized carbon to a sp^2 one, we would expect the bond strength to increase. However, T-CID measurements of PhCbi reveal a decrease of the bond strength – from 41 kcal/mol to 38 kcal/mol.[4] To rationalize this observation, we hypothesize that the bond strength is modulated significantly through London dispersion by the presence of the sidechains on Cbl/Cbi. To test this hypothesis, Costa[5] complexes, which feature a similar chemical environment around cobalt but no such sidechains, are employed to obtain the unmodulated Co-C bond-strengths in the gas phase using T-CID/L-CID. The measurements reveal the BDE of sp^3-hybridized carbons to be 38 kcal/mol and 35 kcal/mol for methyl- and ethyl-Costa complexes, respectively, compared to 45 kcal/mol for the phenyl complex, which is in line with the expectation that the sp^3-hybridized carbons should be bound weaker to cobalt than the sp^2 ones. However, the trend appeared, at first, to be broken when we reach sp-hybridized carbons, as they go through a different dissociation and thus end up having similar BDEs to sp^3-hybridized ones. The BDEs for sp^3 and sp^2-hybridized carbons bound to cobalt compare favorably to calculations at the DFT level, while the gas phase structure of the sp Costa complexes remains unclear.

[1] Benjamin P. Hay, Richard G. Finke, *J. Am. Chem. Soc.* **1987**, *109*, 8012.
[2] Sanja Narancic, Andreas Bach, Peter Chen, *J. Phys. Chem. A* **2007**, *111*, 7006.
[3] Ilia J. Kobylianskii, Florian J. Widner, Bernhard Kräutler, Peter Chen*J. Am. Chem. Soc.* **2013**, *135*, 13648.
[4] Alexandra Tsybizova, Christopher Brenig, Christoph Kieninger, Bernhard Kräutler, Peter Chen, *Chemistry – A European Journal* **2021**, *27*, 7252.
[5] G. Costa, G. Mestroni, E. de Savorgnani, *Inorganica Chimica Acta* **1969**, *3*, 323.