Carboxylation Reactions Studied Using *Caged* CO_2

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The use of *caged* compounds, i.e. compounds which release a desired effector molecule upon photolytic cleavage, has greatly advanced our understanding of enzymes and their mechanisms. Among other things, they permit the tracking of fast reactions without the need for rapid mixing techniques.

We introduce here the use of "*caged* CO_2" for the study of carboxylation reactions. CO_2 is released from a precursor compound via a laser flash, and its reactions can be observed directly via the strong infrared absorption signal of CO_2 at 2343 cm^{-1} that is associated with the molecule's stretching mode. Several compounds with different photolytically cleavable protecting groups have been tested; they differ with respect to quantum yield, the rate of CO_2 release and the potentially adverse reactivities of their byproducts.

In subsequent experiments the photolytically triggered CO_2 release was used to monitor the hydration of CO_2 in aqueous solutions of different pH values and their rate increase upon addition of carbonic anhydrase, as well as the formation of carbamates during the reaction of CO_2 with various amines.

Here we report on the photolytically triggered IR difference spectra of the *caged* CO_2 compounds, and the results of *rapid-scan* IR spectroscopy that was employed to monitor the reactions mentioned above.

The ultimate goal of this study will be to use these new tools for the observation of enzymatic carboxylation reactions, namely those carried out by the important class of biotin-dependent carboxylases, and by the most abundant carboxylating enzyme on earth, the plant's Ribulose-1,5-bisphosphatcarboxylase (Rubisco).