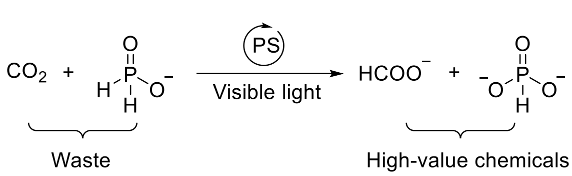
日本化学会 第105春季年会 (2025)

Metal-free reduction of CO_2 to formate using phosphinates as an electron donor

([1]*Graduate School of Science, Kobe University*) ○Jiasheng Xu,[1] Tatsuhiro Harada,[1] Suguru Murakami,[1] Weibin Xie,[1] Yuto Nakagawa,[1] Masahiko Hayashi,[1] Ryosuke Matsubara[1]
Keywords: Carbon dioxide; Organocatalyst; Sodium phosphinate; Photosensitizer

The increase in carbon dioxide concentration on Earth has led to global warming, which has become an urgent problem that society needs to solve. On the other hand, with the increase of human activities, fossil fuels on Earth are gradually decreasing. In order to simultaneously address these two issues, how to convert carbon dioxide into fossil fuels at a low cost has attracted widespread attention from researchers around the world. The currently reported methods have limited the large-scale application of carbon dioxide reduction due to the use of expensive metal catalysts, high-energy sources such as electricity or hydrogen. Our previous studies have shown that under visible light irradiation, using carbazole and benzimidazole as catalysts can efficiently reduce carbon dioxide to formate[1]. Unfortunately, the sacrificial electron donor used in this reaction system is ascorbic acid, which also consumes energy during the production process, and after oxidation, the by-products generated are waste, which also imposes a certain burden on the environment. On the other hand, phosphinates, as byproduct of phosphoric acid synthesis, have the characteristics of non-toxicity, stability, environmental friendliness, and can be produced in large quantities. Previous studies have shown that phosphinates can be used as a sacrificial electron donor in reductive amination reactions.

Based on the above findings, we developed a carbon dioxide reduction system using phosphinates as a sacrificial electron donor. This study aims to simultaneously address the aforementioned issues by developing a "two birds with one stone" reaction that converts CO_2 into energy while upcycling waste under illumination conditions. The developed system in this study uses dibenzothiophene as a photosensitizer to efficiently reduce carbon dioxide to formate, with turn over number of 74. The control experiment shows that light and photosensitizer are indispensable for the reaction progress. ^{13}C-labeled carbon dioxide experiment result shows that the carbon of formate comes from carbon dioxide, which was determined by ^{1}H, ^{13}C NMR analysis. ^{31}P NMR indicates that phosphinates is oxidized by carbon dioxide to trivalent phosphate salts, which are a reusable co-product.



1) W. Xie, J. Xu, U. Md Idros, J. Katsuhira, M. Fuki, M. Hayashi, M. Yamanaka, Y. Kobori, R. Matsubara, *Nat. Chem.* **2023**, *15*, 794-802.