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TO WHOM IT MAY CONCERN

The present work emphasizes the potential of photocatalysis in chemical utilization of carbon dioxide. The photocatalytic approach has been investigated as a route to achieve:

- i) carboxylation of organic substrates;
- ii) CO₂ reduction to C₁ molecules;
- iii) photocatalytic reduction of NAD⁺ to NADH, a research topic which is relevant to enzymatic CO₂ reduction.

The materials used as photocatalysts have been well characterized through a variety of techniques.

Chapter 4 describes some examples of photocatalyzed carboxylation of a few organic substrates, such as acetylacetone and 2,3-dihydrofuran.

In principle, carboxylation of acetylacetone may occur at the internal methylene or a terminal methyl group. The author reports the formation of both the carboxylation products, 2-acetyl-3-oxobutanoic acid and 3,5-dioxohexanoic acid. This conclusion is based on the analysis of NMR spectra and the comparison with the calculated spectra. However, both 2-acetyl-3-oxobutanoic acid and 3,5-dioxohexanoic acid may exist under a variety of tautomeric forms, which are not considered in the NMR analysis. This feature may complicate somewhat the interpretation of the NMR spectra and the assignment of resonances on the basis of calculated spectra may not be so straightforward as reported and may require more prudence. Let me note, for instance, that the calculated spectrum [ADC/C+H NMRPredictors and DB(v. 12.01)] for (*E*)-2-acetyl-3-hydroxybut-2-enoic acid (the tautomeric enol form of 2-acetyl-3-oxobutanoic acid) shows signals at 181 and 174 ppm (well comparing with the experimental signals at 181 and 171 ppm, respectively assigned to 2-acetyl-3-oxobutanoic acid and 3,5-dioxohexanoic acid). In my opinion, the comparison of the NMR spectra of the reaction mixture with those of authentic samples of both the carboxylic acids (2-acetyl-3-oxobutanoic acid and 3,5-dioxohexanoic acid) would be of greater help.

When 2,3-dihydrofuran was used as the substrate, spectroscopic evidences supported the formation of 2,3-dihydrofuran-3-carboxylic acid. The latter species formed with low yield and selectivity, because of formation of several side-products. Nevertheless, the carboxylation reaction of the dihydrofuran ring was regioselective as no evidence for the formation of 2,5-dihydrofuran-2-carboxylic acid was obtained. The reasons of so a high regioselectivity are not clear and have not been discussed.

Chapter 5 focuses on the photocatalytic reduction of carbon dioxide. In addition to the new photocatalysts investigated, an interesting element of novelty of this study (as also stressed by the author in the Introduction of Chapter 5) is the use of relatively cheap *i*-PrOH as electron/proton donor. Unfortunately, no attempt has been made (at least for the most efficient photocatalytic system) to compare the use of *i*-PrOH in this typology of process with that of more conventional *e*-donors, such as TEA, TEOA, EDTA, under otherwise analogous reaction conditions.

Chapter 6 is relevant to the field of enzymatic reduction of CO₂ and focuses on photocatalytic regeneration of NADH under visible light irradiation. This is a challenging research area. The present work describes a few encouraging results which have been obtained using [Cp*(bpy)Rh]Cl₂ as a suitable electron mediator.

As a whole, my assessment of the overall thesis work is positive and I consider Dr. T. Baran worthy of receiving the degree of Doctor of Philosophy.

Yours faithfully
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