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| Book Name: | [Chemistry and Biochemistry: Research Progress](https://www.bookpi.org/bookstore/product/chemistry-and-biochemistry-research-progress-vol-1/) |
| Manuscript Number: | **Ms\_BPR\_5922** |
| Title of the Manuscript:  | **Marcus Cross-Relationship Probed by Time-Resolved CIDNP** |
| Type of the Article | **Book Chapter** |

**Special note:**

**A research paper already published in a journal can be published as a Book Chapter in an expanded form with proper copyright approval.**

**Source Article:**

**This chapter is an extended version of the article published by the same author(s) in the following journal.**

**Journal of International Journal of Molecular Sciences, 24: 13860, 2023.**

**DOI:** [**https://doi.org/10.3390/ijms241813860**](https://doi.org/10.3390/ijms241813860)

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| PART 1: Comments |
|  | Reviewer’s comment**Artificial Intelligence (AI) generated or assisted review comments are strictly prohibited during peer review.** | Author’s Feedback *(Please correct the manuscript and highlight that part in the manuscript. It is mandatory that authors should write his/her feedback here)* |
| **Please write a few sentences regarding the importance of this manuscript for the scientific community. A minimum of 3-4 sentences may be required for this part.** | The above manuscript presents a significant advancement in the field of physical chemistry and reaction kinetics by providing detailed experimental validation of the Marcus cross-relation for degenerate electron exchange (DEE) reactions involving short-lived radicals. By utilizing the time-resolved CIDNP technique, the study overcomes the limitations of traditional spectroscopic methods for such transient species. The systematic investigation of temperature-dependent DEE rate constants, reorganization energies, and nuclear relaxation times not only enriches the existing understanding of radical-based electron transfer mechanisms but also offers a valuable dataset for researchers working on biochemical redox processes, photochemical systems, and radical-mediated reactions in biological and environmental contexts.  |  |
| **Is the title of the article suitable?****(If not please suggest an alternative title)** | Yes |  |
| Is the abstract of the article comprehensive? Do you suggest the addition (or deletion) of some points in this section? Please write your suggestions here. | Yes |  |
| **Is the manuscript scientifically, correct? Please write here.**  | Yes |  |
| **Are the references sufficient and recent? If you have suggestions of additional references, please mention them in the review form.****-** | Yes |  |
| Is the language/English quality of the article suitable for scholarly communications? | Can be improved |  |
| Optional/General comments | 1. Why were the specific radical pairs (GMP(-H)•/GMP(-H)−, N-AcTyrO•/N-AcTyrO−, and TyrO•/TyrO−) chosen for this study?
2. Were control experiments conducted to confirm that the observed CIDNP effects arise solely from the described electron transfer processes and not from other side reactions?
3. Some proton signals were excluded from analysis due to poor signal-to-noise ratio. Can the authors discuss if any improvements in experimental setup or optimization of sample concentrations could help resolve these limitations in future work?
4. The study was conducted within a temperature range of 8–65°C. Was there any observable thermal degradation of reactants, or changes in solvent properties ?
5. The authors used the Fisher model for fitting CIDNP kinetics. Could they briefly explain why this model was chosen over others?
6. The Smoluchowski equation was used to estimate diffusion rate constants with corrections for charge interactions. Did the authors validate the chosen molecular radii and dielectric constants against experimental diffusion measurements ?
7. The paper mentions corrections for CIDNP decay during RF pulse duration (1–2 µs). Could the authors provide more quantitative validation on how critical this correction is for accurate kinetic fitting?
8. The study used D2O as a solvent. Could the authors comment on how using H2O instead might influence the observed DEE kinetics and CIDNP effects ?
9. Could the authors include additional comparison plots showing both the calculated rate constants from the Marcus cross-relation and the experimentally determined values, preferably over the studied temperature range?
10. How do the findings of this study validate, challenge, or refine existing understanding of the Marcus cross-relation when applied to systems involving short-lived radicals?
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| **PART 2:**  |
|  | **Reviewer’s comment** | **Author’s Feedback** (It is mandatory that authors should write his/her feedback here) |
| **Are there ethical issues in this manuscript?**  | *(If yes, Kindly please write down the ethical issues here in details)* |  |

**Reviewer details:**

**Hemaprobha Saikia, Bodoland University, India**