

# Structure Activity Relationships for Carbonyl Photolysis

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Carbonyls are among the most abundant and photoactive volatile organic compounds (VOCs) in the atmosphere. Their varied, complex structures pose a challenge to atmospheric chemistry models. Experimental photolysis parameters are available for small prototypical molecules [1], however this data does not cover all reaction channels and is missing larger abundant species.

Atmospheric models circumvent this lack of data by applying the same photolysis parameters from one molecule to all other molecules of that type, *e.g.* the photolysis rate of butanal is used for all linear aldehydes [2]. Such approaches do not fully account for the complex photochemistry of the carbonyl moiety, where small structural changes can alter photolysis rates, accessible electronic surfaces, or even which products are formed.

In this work theoretical chemistry is used to explore the photophysics of the carbonyl moiety as a whole, on all relevant electronic states ( $S_1$ ,  $T_1$ , &  $S_0$ ), and derive fundamental structure activity relationships (SARs) to rationalise the photochemistry of the diverse carbonyl species shown in Figure 1. This is accomplished with combined TD-DFT and coupled cluster methods [3], which are found to predict photochemical quantities with mean absolute deviations of 5-7 kJ/mol in comparison to experimental data.

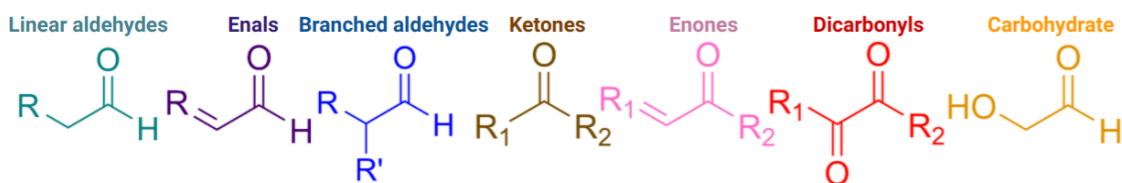


Figure 1: SARs arising from carbonyl classes are computed for 20 representative species.

Intrinsic barriers and photolysis thresholds are obtained, and energetic trends based on SARs are apparent, such as the propensity of  $\alpha$ -bonds to break based on structural branching or conjugation. The data obtained are the quantities required for calculating theoretical photolysis rates, which could supplement photolysis parameters missing from atmospheric models, and provide a chemically rationalised framework to modify existing photolysis data to more appropriately model the diversity of carbonyls in the atmosphere.

## References

1. R. Atkinson, *et al.*, *Atmospheric Chem. Phys.*, **6** (2006), 3625–4055.
2. M. Jenkin, S. Saunders, M. Pilling, *Atmospheric Environ.*, **31**, 1997, 81–104.
3. B. Organti, Fang C., Durbeej B., *Mol. Phys.*, **144**, (2016), 3448–3463.