

Impacts of acidity on multiphase chemistry in aqueous particles and clouds

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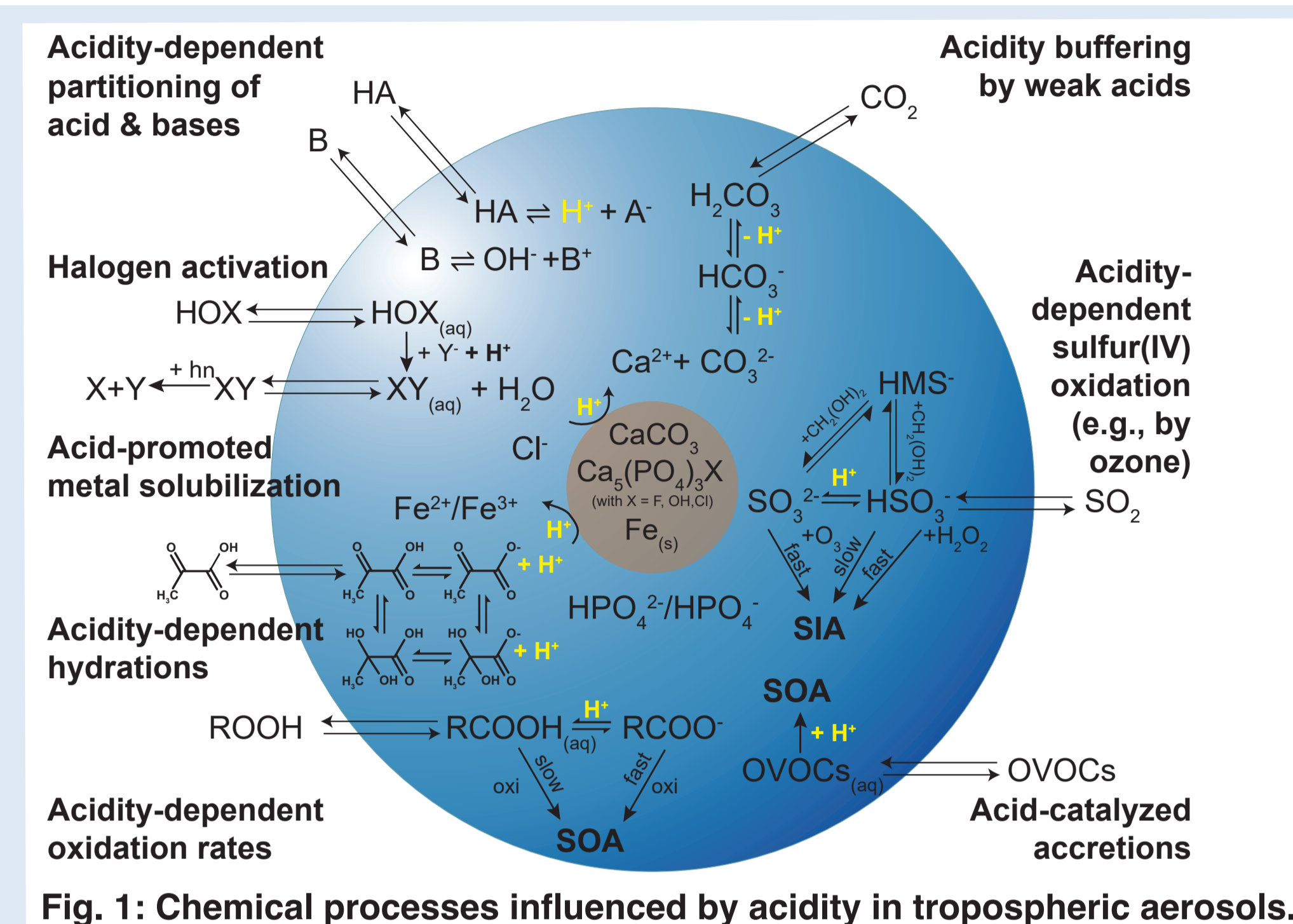
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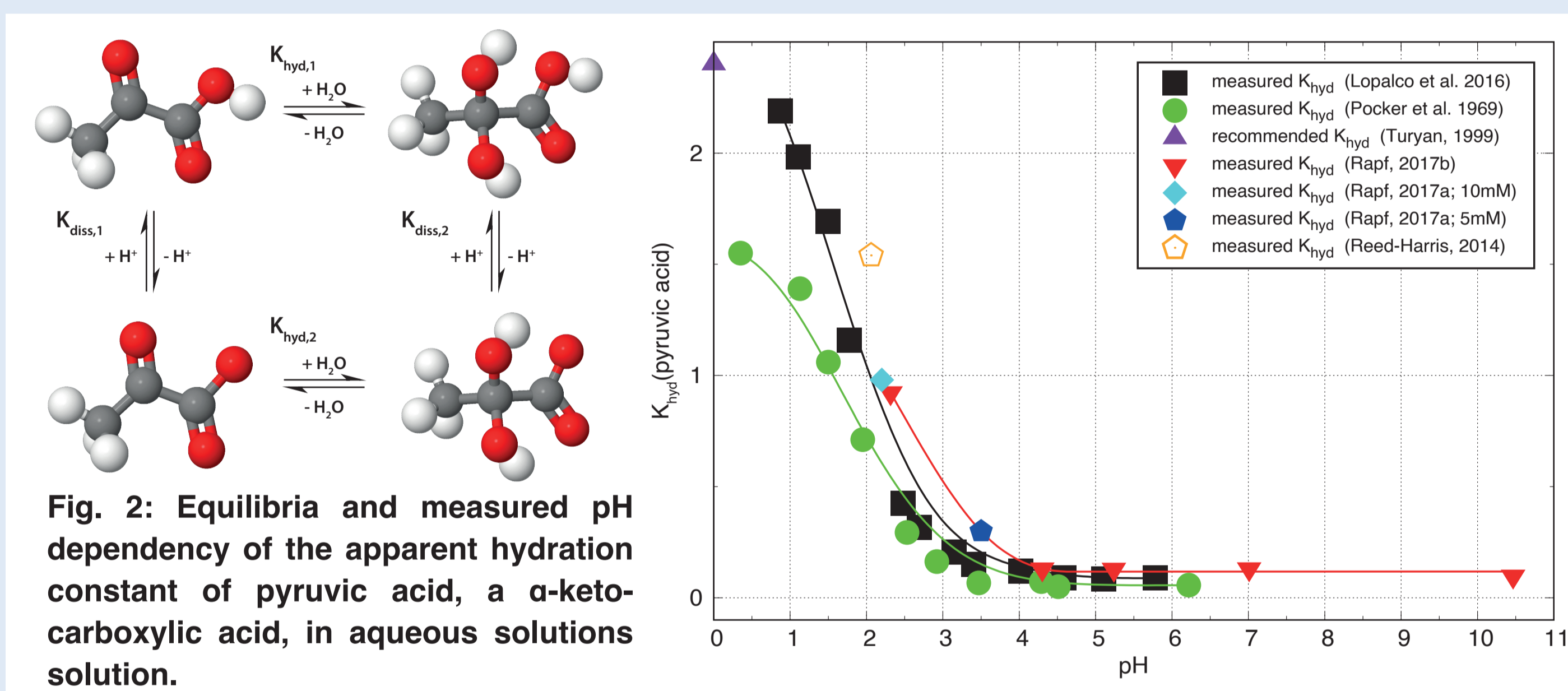
Introduction

- Acidity of aqueous atmospheric solutions is a key parameter
- Drives the partitioning of semi-volatile acidic or basic trace gases and their linked aqueous-phase chemistry
- Aqueous-phase chemistry affects the acidity of atmospheric aqueous phases, e.g. deliquesced aerosol particles, cloud and fog droplets
- Figure 1 illustrates the most important processes where acidity plays a role
- Feedbacks in acidity and chemistry have crucial implications: (i) tropospheric lifetime of air pollutants, hence air quality and atmospheric aerosol composition, (ii) deposition input into other terrestrial and oceanic ecosystems, (iii) the visibility, (iv) climate and (v) human health
- The present study outlines impacts of acidity (i) on the hydration of organic carbonyl compounds and (ii) multiphase chemistry of dissociating organic compounds in aqueous particles and clouds
- A comprehensive literature survey presents the current state of knowledge of acidity dependencies



Influence of acidity on hydration constants

- Hydration processes are typically acid- or base-catalyzed
- Equilibrium constant K_{hyd} describes the ratio of the diol and carbonyl fraction of the aldehyde or ketone
- Hydration of simple aldehydes and ketones and dicarbonyls is unaffected by pH
- Multifunctional carbonyl compounds that contain pH sensitive moieties, such as α -oxocarboxylic acids, are highly influenced by the pH



O₃ studies on aqueous-phase chemistry

- Ozone is an electrophilic and very selective oxidant for organic compounds
- Rather high acidity dependencies exist for phenolic compounds and hydroxylated benzoic acids

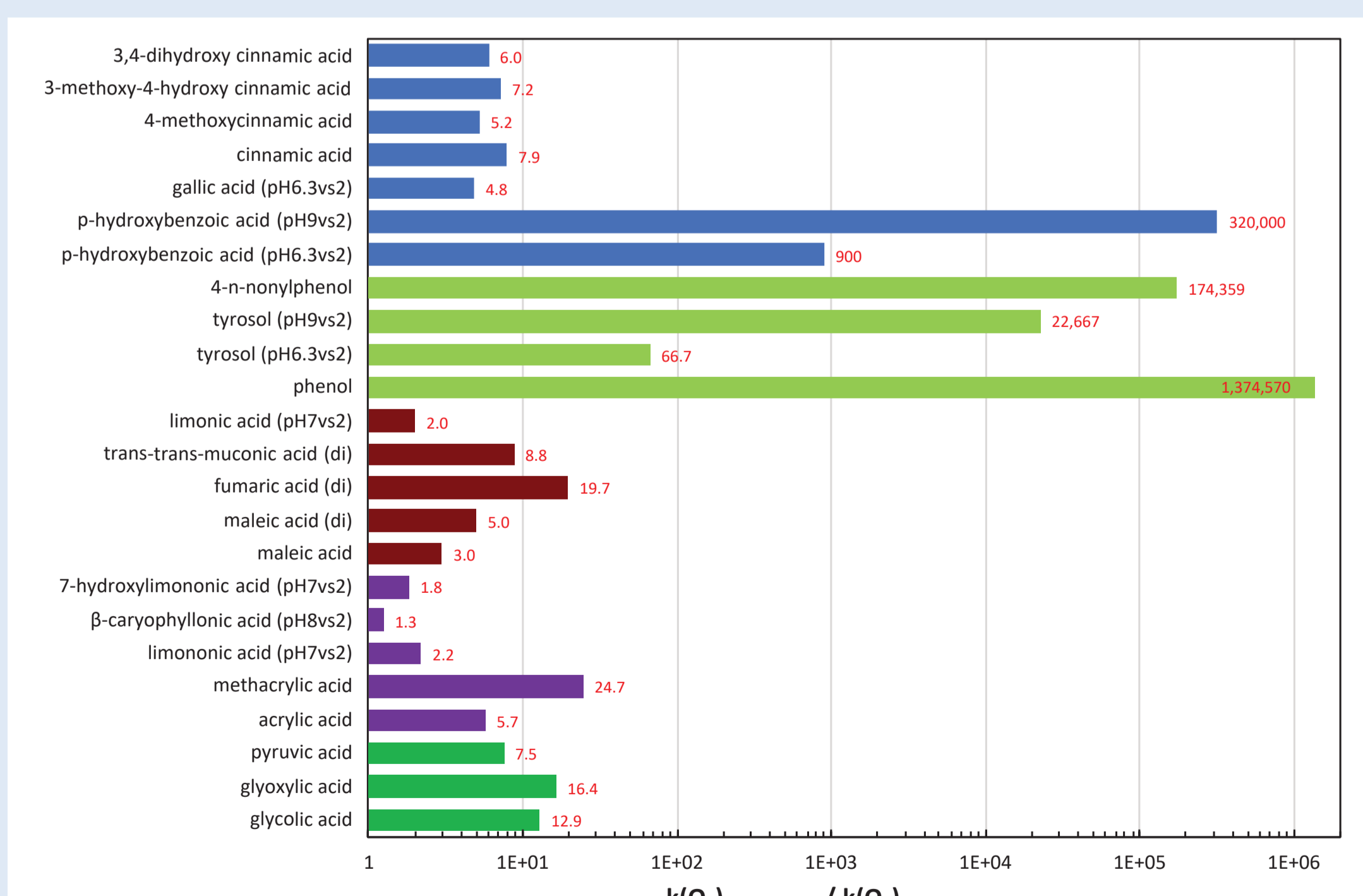


Fig. 3: Ratio of ozone reaction rate constants of deprotonated and protonated organics in aqueous solution.

OH, NO₃ radical studies on aqueous-phase chemistry

- OH or NO₃ radicals can react either by H-atom abstraction, electron transfer or by addition to a double bond
- OH radicals usually react by H-atom abstraction with saturated compounds in the range of $k = 10^7 - 10^9 \text{ M}^{-1} \text{ s}^{-1}$
- Unsaturated and aromatic compounds react by OH radical addition in the range of $k = 10^9 - 10^{10} \text{ M}^{-1} \text{ s}^{-1}$
- Acidity effect on reactivity of OH with organics is generally small
- Exceptions are small organic acids such as formic, acetic, oxalic and malonic acids, which are more dependent on the acidity of the surrounding environment
- NO₃ reactions of protonated saturated aliphatic carboxylic acids are in the range of $k = 10^4 - 10^6 \text{ M}^{-1} \text{ s}^{-1}$

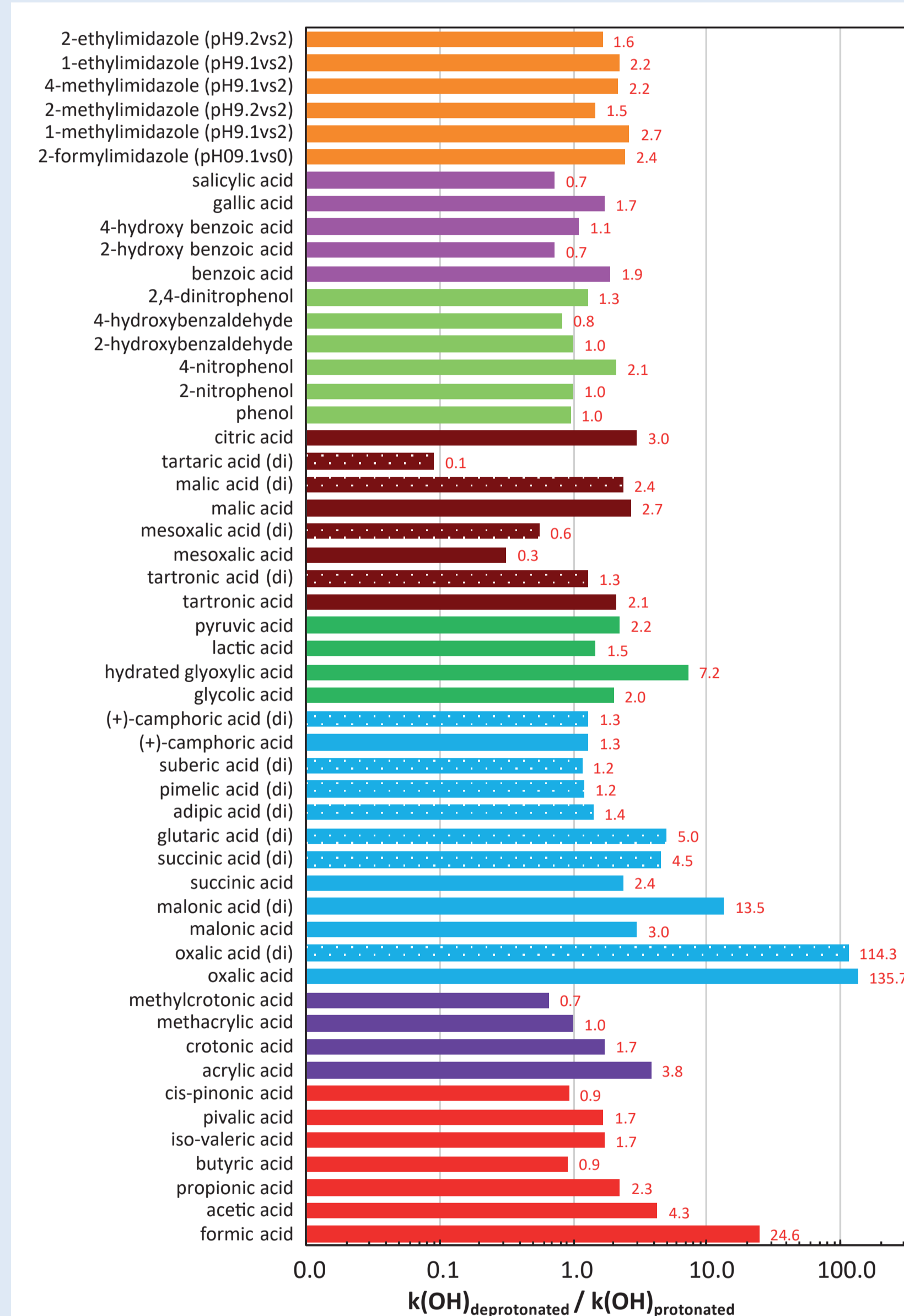


Fig. 4: Reactivity ratios of different dissociating organics. The ratio of the dianion and protonated dicarboxylic acid is indicated by (di).

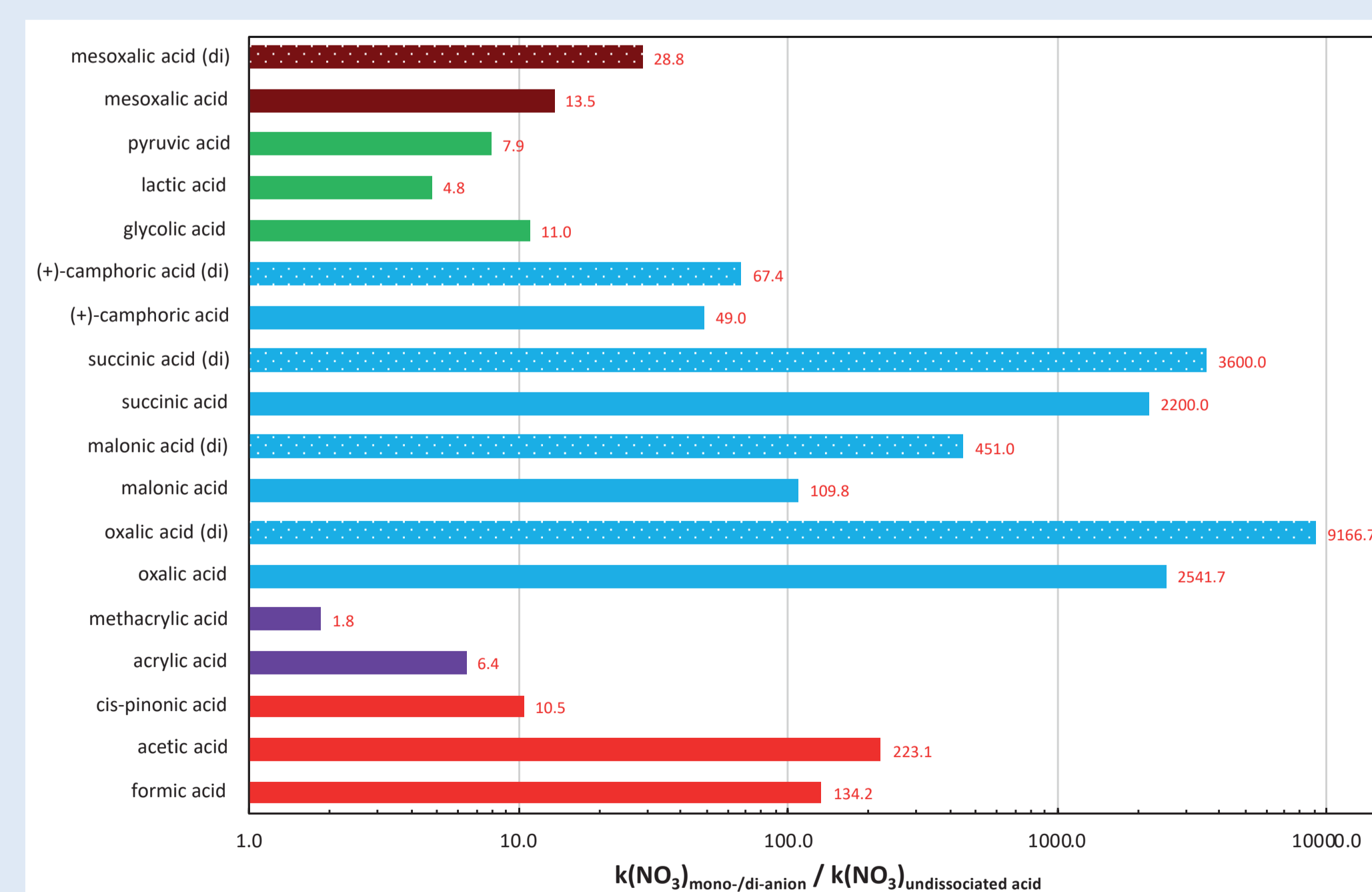


Fig. 5: NO₃ reactivity ratios of different carboxylic acids.

- Deprotonated acids react in a range of $k = 10^6 - 10^8 \text{ M}^{-1} \text{ s}^{-1}$ with NO₃ radicals
- NO₃ usually react by addition with unsaturated acids ($k = 10^7 - 10^8 \text{ M}^{-1} \text{ s}^{-1}$)
- Addition reaction on the C=C double bond is more important than the ETR

References

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Summary

- Hydration processes of multifunctional carbonyl compounds, such as α -oxocarboxylic acids, are highly influenced by the pH-value
- OH radical reaction are less affected by the pH, with exception of small carboxylic acids such as formic acid and oxalic acid
- NO₃ and O₃ reactions with organic acids, are highly affected by the acidity of the surrounding aqueous phase