

Investigation of gas phase kinetics of atmospherically relevant reactions of aromatic, non-aromatic and inorganic radicals with C₁-C₂ esters and alcohols in the conditions relevant to the Earth's troposphere

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The atmosphere consists of a vast pool of trace gases and the effect of these trace species on the atmosphere is disproportionate to their abundances as they are responsible for various phenomenon ranging from urban photochemical smog, acid deposition, ozone depletion and formation in stratosphere and troposphere respectively, to potential climate change. The high reactivity of trace species like, radicals make them one of the most important chemical species in the Earth's atmosphere as they react with various types of pollutants those are released into the atmosphere mainly because of man-made activities. These pollutants are majorly constituted by polycyclic aromatic hydrocarbons (PAHs) and ultimately forms various secondary organic aerosols (SOAs) when oxidation products of the volatile organic compounds (VOCs) deposit onto these pollutant species or form new particles. These SOAs accounts for a major fraction of the global atmospheric sources of aerosols that are considered to be highly detrimental to both the environment and human health. In addition, the formed SOAs can also act as cloud condensation nuclei affecting cloud properties as well as the hydrological cycle of the atmosphere¹. Thus, kinetic investigations involving atmospherically relevant radicals are essential to not only assess the environmental impact of anthropogenic activities, but also will help us in mitigating the global menace of air pollution and its subsequent impacts in the near future.

The rate coefficients for the reactions of phenyl (C₆H₅), formyl (HCO) and iodine oxide (IO) radicals with ethyl formate (HCO₂Et), ethyl acetate (CH₃CO₂Et), methanol (MeOH) and ethanol (EtOH) were investigated experimentally in the gas phase using laser based in-built cavity ring-down spectroscopy (CRDS), in the temperature and pressure range of 258-362 K and 45-65 Torr respectively using N₂ as the bath gas. The simplest aromatic radical, phenyl was generated in-situ via the photolysis of nitrosobenzene at 248 nm by a KrF excimer laser and the generated radicals were probed at 504.8 nm using a Nd:YAG pumped dye laser²⁻³. HCO radicals were generated by the photolysis of a mixture of (Cl+HCHO+N₂) at 248 nm and thereby probed at 614.5 nm. IO radicals were generated in the CRDS reaction zone by photolyzing a mixture of (CH₃I+O₃+N₂) at 248 nm and the generated radicals were probed at 445.04 nm. In order to perform the kinetic investigations, the time delay between the photolysis and probe lasers were varied within a particular range at a slow-flow pseudo-1st order condition and 2 Hz. The dependency of the kinetics on experimental pressures and laser fluences were verified. To complement our experimental findings, kinetics for the title reactions were investigated theoretically using Canonical Variational Transition State Theory (CVT) with Small Curvature Tunnelling (SCT) corrections at coupled cluster level of theory. In addition, thermochemical parameters as well as branching ratio contribution for the individual respective pathways were also calculated.

References

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- [3] Mondal, K.; Kaipara, R.; Rajakumar, B. *J. Phys Chem A* **2019**, *123*(45), 9682-9692.

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