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Temperature dependent rate coefficients for the reactions of Criegee biradicals with selected alcohols and sulphides

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The reactions of Criegee biradicals have received much attention in recent years, yet few reactive systems have undergone direct experimental measurement, and fewer still have been measured as a function of temperature.
In this study, absolute temperature-dependent rate coefficients for the gas-phase reactions of a suite of alcohols and sulphides with both formaldehyde oxide (CH_2OO) and acetone oxide ($(CH_3)_2COO$) are determined experimentally between 254 and 328 K using cavity ringdown spectroscopy for detecting Criegee biradicals. Major differences in reactivity and temperature dependence are observed both in terms of the functionality (between alcohols and sulphides) and also the degree of alkyl substitution about the Criegee biradical.
This diverse behaviour represents a uniquely challenging problem for atmospheric chemistry since the atmosphere contains a large variety of both functionalized compounds and Criegee biradicals, leading to a formidable parameter space which may be impossible to cover experimentally. Notwithstanding, new experimental data such as these are vital for understanding the general behaviour of Criegee biradicals in the atmosphere.