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Probing Reacting Systems with Diffusion NMR

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NMR diffusion measurements continue to grow in application and importance [1-3] including providing much of the diagnostic power of MRI. Translational diffusion is intimately related to molecular size and consequently provides a direct link to chemical reactions. Moreover, it is generally through diffusion that reactants come together and how reaction products disperse. Consequently, NMR diffusion measurements are a powerful technique for studying reacting systems since it affords simultaneous measurement of the diffusion of each species and the kinetics of the reaction thereby providing deep insight into the reaction process. Indeed, it long been questioned as to whether energy released during a reaction propels the species in solution (Figure 1) [4, 5]. Recently NMR diffusion measurements have been applied to numerous reacting systems including the copper-catalyzed azide−alkyne cycloaddition (CuAAC) "click" reaction [4, 6] and polymerisation such as PET-RAFT polymerization [7].

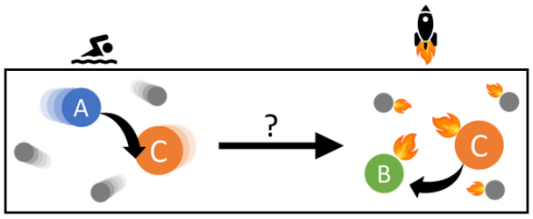

Fig. 1. Are species propelled by the energy released during a reaction?

Even in time-stationary systems it can be difficult to perform very accurate diffusion measurements, but the problems are exacerbated in reacting systems. Indeed, the measurement procedure is far from straightforward when the timescale of the reaction is of the order of the NMR diffusion measurement time [8, 9]. There can be a number of challenges including (i) if the populations of the species change during the measurement then this must be separated from the diffusive attenuation in the measurement, (ii) convection can result if the reaction causes temperature changes and convection can be confused with increased diffusion (e.g., [10, 11]), (iii) reaction products may alter NMR relaxation behaviour which will also influence the measured signal intensities. To avoid misinterpretation of the NMR diffusion data, great care must be taken to avoid the presence of experimental artifacts [4-6, 12-14].

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