Kinetic Acidity of Methane

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Summary The rate of deuterium exchange of methane with caesium cyclohexylamide in cyclohexylamine at 50° is $3{\cdot}1 \times 10^{-2}$ that of cyclopropane, on a per-hydrogen-atom basis.

THE relative acidity of the simplest hydrocarbon, methane, has only been approximately estimated, using equilibrium data for organometallic exchange reactions,[1,2] polarographic reduction potentials,[2,3] or extrapolations from more acidic compounds.[4] We report the directly-measured kinetic acidity of methane, by caesium cyclohexylamide (CsCHA) catalysed deuterium incorporation from *NN*-dideuteriocyclohexylamine. The previously described kinetic reactor[5] was modified to permit its construction in stainless steel with suitable greaseless valves, as a precaution against the overpressure of undissolved methane. Cyclopropane was used as a rate standard; its rate of tritiodeprotonation relative to cyclohexane in this system has previously been reported.[6] Kinetic aliquots of the mixed gaseous hydrocarbons over the solution phase were analysed by mass spectrometry, suitably calibrated with authentic deuteriomethanes. The solubilities of methane and cyclopropane in cyclohexylamine were determined separately; in this kinetic experiment 96·5% of the cyclopropane and 33·2% of the methane were in the solution phase. The kinetic aliquots taken were small compared to the total so that these numbers do not change significantly during the run. The first order rate constants for loss of undeuteriated substrate corrected for the amounts actually in solution are: cyclopropane, $(7{\cdot}7 \pm 0{\cdot}7) \times 10^{-4}\,\mathrm{s}^{-1}$; methane, $(1{\cdot}60 \pm 0{\cdot}08) \times 10^{-5}\,\mathrm{s}^{-1}$. Thus methane is $3{\cdot}1 \times 10^{-2}$ as reactive as cyclopropane (per hydrogen) or $2{\cdot}2 \times 10^{3}$ as reactive as cyclohexane.[6]

Preliminary results indicate that the exchange rates of hydrocarbons with primary C–H bonds (ethane, neopentane, hexamethylethane) are 10^{2}—10^{3} slower than methane; hence, the kinetic acidity order for alkanes is established as: $CH_4 >$ primary C–H $>$ secondary C–H.

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