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Pressure Effects on Product Channels of Hydrocarbon Radical-Radical Reactions; Implications for Modelling of Planetary Atmospheres

A. Fahr, J. Halpern and M. N'Doumi
Department of Chemistry, Howard University, Washington D.C., U.S.A. (askar.fahr@gmail.com)

Abstract

Relatively large hydrocarbon molecules (C4, C6 and larger) have been observed in several planetary atmospheres. The mechanism for their formation and destruction are not well understood.

Previously we had studied the kinetics and product channels of small unsaturated hydrocarbon radical (C2 and C3s) reactions relevant to planetary atmospheric modelling. Reactions of C2 radicals (such as vinyl, H_2CCH and ethynyl C_2H) and C3 radicals (such as propargyl, $HCCCH_2$ and allyl, H_2CCCH_3) can affect the abundances of a large number of stable observable C3, C4, C5, C6 and larger molecules, including linear, aromatic and even poly aromatic molecules.

We have experimentally determined pressure-dependent product yields for self- and cross-radical reactions performed at 298 K and at selected pressures between ~4 Torr (0.5 kPa) and 760 Torr (101 kPa). Final products were determined by gas chromatograph with mass spectrometry/flame ionization detection (GC/MS/FID). In some cases complementary computational studies extended the pressure and temperature range of the observations and provided valuable information on complex reaction mechanisms. These studies provide a systematic framework so that important energetic and structural parameters for radical-radical reactions can be assessed.

Here we report a compilation of our earlier results relevant to planetary atmospheres in addition to recent ones for allyl radical (H_2CCCH_3) reactions.

In general, there are multiple lines of evidence that the chemically activated combination adduct, $R_1.R_2*$, is either stabilized by bimolecular collisions (at higher pressures) or can be subject to a variety of unimolecular reactions, including isomerization, cyclization and decomposition (at lower pressures and/or high temperatures). Therefore the "apparent" combination/disproportionation product ratios and the nature and yields of reaction products exhibit complex pressure dependences. Inclusion of pressure effects on product channels of radical-radical reactions can significantly affect the planetary atmospheric modelling predictions.