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SUPPORTING INFORMATION

GAS PHASE KINETICS OF THE OH+CH_3CH_2OH REACTION AT TEMPERATURES OF THE INTERSTELLAR MEDIUM (T = 21-107 K)

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Determination of ethanol concentrations by UV spectroscopy at 185 nm

Diluted mixtures of ethanol (in He, Ar or N_2) were prepared in two 20-L storage bulbs connected in series or in a 50-L glass bulb. Partial pressures (5-20 mbar) of ethanol were introduced in the bulbs and the total pressure ranged from 1000 to 1200 mbar. The concentration of ethanol in the jet, $[CH_3CH_2OH]_{jet}$, is usually calculated as its proportion in the total mass flow (F_{Total}). This proportion is given by the total gas density n corrected with the fractional flow of ethanol:

$$[\mathrm{CH3CH2OH}]jet = n \times f \times \frac{F(\mathrm{CH3CH2OH})}{F\mathrm{Total}} \tag{S1}$$

The dilution factor f is the mixing ratio of ethanol in the storage bulb, i.e. the ratio of the partial pressure of ethanol ($P_{CH_3CH_2OH}$) to the total pressure in the bulb (P_{Total}). In order to check for any loss of the reactant during the course of an experiment, the value of f was determined by UV spectroscopy at 185 nm before and/or after the kinetic measurements. For this, a known pressure from the storage bulb ($P_{T,UVcell}$ = 10-100 Torr of diluted ethanol) was introduced in a 107-cm absorption cell. The cell either empty or filled with the absorber was irradiated with a Hg-Ar lamp. The transmitted light intensities I and I_0, respectively, were detected by a filtered solar blind phototube.[1] The change in the transmitted intensity is related to the partial concentration of ethanol (and hence the dilution factor f in the storage bulb) according to the Beer-Lambert's law:

$$[\mathrm{CH3CH2OH}]UV\ cell = \frac{-\log(\mathrm{I/I0}))}{\sigma_{185\mathrm{nm}} \times l} \tag{S2}$$

where σ_{185nm} is the absorption cross section at 185 nm and l is the optical path length (107 cm). Several groups determined σ_{185nm}, but the most recent ones are those reported by Orkin et al.[2], who recorded the UV spectrum of ethanol between 160 and 220 nm with a resolution of 0.16 nm and Dillon et al.[3], who performed a single wavelength determination. A difference of 7% was found in Dillon et al.'s value with respect to that of Orkin et al. In the present work we used the absorption cross section reported by Orkin et al. ($\sigma_{185nm} = 1.106\times10^{-18}$ cm^2 molecule^{-1}) to derive the concentration of ethanol in the absorption cell. The election of this absorption cross section is based on the comprehensive study performed by these authors to clarify the discrepancy with Dillon et al.'s value near the ethanol absorption maximum. Knowing the ethanol concentration in the absorption cell from Equation S2, the value of f was, then, derived from the following expression:

$$f = [\mathrm{CH3CH2OH}]UV\ cell \quad \times \quad \frac{RT}{PT,UV\ cell} \qquad \text{(S3)}$$

$[CH_3CH_2OH]_{jet}$ ranged from 2×10^{12} molecule cm^{-3} to 1.1×10^{14} molecule cm^{-3} (Table 3 of the manuscript), which is low enough to avoid dimerization of ethanol in the timescale of the experiment. The obtained f values from the optical measurements and the pressure measurements were in good agreement within ±3%, leading confidence to the determination of the ethanol concentration on the jet from equation (S1) using the f values obtained from pressure measurements. Conservatively, a ±10% σ_{sys} was added to σ_{stat} in the rate coefficients in order to obtain the total uncertainty σ_{tot}, as the square root of the sum of the systematic and statistical errors squared.

References

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