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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Deuterium fractionation in formaldehyde photolysis: chamber experiments and RRKM theory" *by* E. J. K. Nilsson et al.

Anonymous Referee #1

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General Comments: This paper shows the results of relative dissociation rate determinations of the photolysis of D2CO with respect to H2CO and compares these results with previous determinations of HDCO basically of the same group of authors. The observed pressure dependence of the molecular channel of this photolysis is analyzed with means of the RRKM theory. It seems be predominantly caused be the unimolecular decomposition lifetime of the respective transition states. The results are of importance for the determination of global budgets of atmospheric species like methane, formaldehyde and hydrogen. The paper is well written and the experimental results seem to be reliable. The interpretation with help of the RRKM theory has some shortcomings. There seem to be a few interesting points the paper has missed to discuss.

Specific comments: The missing of information for the quantum yield of the radical

channel of D2CO is briefly mentioned in page 10312 in the context of a possible correction of the experimental results to account for the overlap of the lamp spectrum with the radical channel. Nilsson et al., 2010, is cited for a discussion of the sensitivity of the HDCO results to this parameter. First of all, the effect for D2CO might be larger. Second, the results of the RRKM calculations depend on this parameter as well (see Eq. 6 and 7). This should be discussed in more detail since the dissociation barriers given in Fig.3 might suggest a shift in the wavelength dependence of the quantum yield.

Is it possible to plot two curves for DH-CO and HD-CO dissociation rates instead of one for HDCO in Fig.3? Is one of them (HD-CO) near H2CO and the other (DH-CO) near D2CO like the dissociation barriers suggest? Are the respective transition states populated equally? Would that give new insight?

A simple consideration might be the following. DH-CO dissociates like D2CO, HD-CO like H2CO. The measured isotope effect of HDCO is the average of both. Then k(H2CO)/k(HDCO) = 1.75 = k(H2CO)/(0.5*k(HD-CO)+ 0.5*k(DH-CO)) and k(D2CO)=0.14*k(H2CO). k(H2CO)/k(D2CO) would be 7 in the high pressure limit. Would this be consistent to the data points in Fig.4?

The comparison of observation and RRKM theory in Fig.4 shows to features: the results of the RRKM theory at 100mabar are significantly smaller than the observations. This is interpreted as an indication of the presence of additional processes. The second feature is at the low pressure side. RRKM theory extrapolates to 1.1 and 1.2 for HDCO and D2CO. Both observational data sets seem to extrapolate to 1.0 which means no isotope effect at all. Does this have a meaning?

Table 2: The error for the k(H2CO)/k(D2CO) is stated to be the error of the slopes in Fig. 2 plus 3%. Actually, the errors stated are 3%. But Fig.2 shows a significant upward curvature of the data points used to calculate the slopes and Fig.4 shows significant differences of the results for 50, 200, and 600 mbar. The reproducibility of the slopes for D2CO seems to be like 10%. This should be reconsidered and included in Table 2

and Fig.4. Is there a reason for the curvature in Fig.2? Is it real?

Can a dissociation following the roaming reaction channel be described by the same RRKM theory? The yield of this channel is 10-20% of the total yield. It should be mentioned when the RRKM results are discussed.

Technical corrections: Fig. 1: Quantum yields and emission spectrum should be labeled in Fig. 1, for example by drawing an additional axis at the right of the plot going from 0 to 1 for quantum yield and arbitrary units for the emission spectrum of the lamp.

Fig. 3: The origin of the dissociation barriers should be given.

Eq6 and 7: Just for completeness. The meaning of sigma(Eph) and I(Eph) should be given in the text or in the caption of Fig. 1.

Fig.3: Is the log(kdis) plotted or kdis with a logarithmic axis?

Fig.1: It should be noted in the caption that the quantum yield for the molecular channel relates to 1013 mbar

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