Water-promoted formation of methyl formate from methanol via methoxymethanol on ice

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Methyl formate (MF; $HCOOCH_3$) is abundantly found in various astronomical objects, including cold molecular clouds [1]. Because of a good correlation with MF in observations, methanol, which is a primordial organic molecule on interstellar dust, is thought to be parent molecule. However, the results of laboratory experiments on the photolysis of pure methanol solid did not to explain the MF abundances astronomically observed [2, 3]. Recently, laboratory observation of ice dust analogue indicated that methanol would contact water ice at the dust surface rather than being as pure solid [4]. Therefore, the effect of H_2O on the MF formation should be considered as well as the photolysis of methanol. To study the details of the MF formation mechanism, small amounts of products and those radical precursors on the ice surface need to be monitored, which is difficult with conventional methods, such as FT-IR. Therefore, we newly developed highly sensitive nondestructive detection method, so-called Cs^+ ion pickup method [5], to monitor products and radicals, and performed the experiments for the photolysis of methanol (0.3 ML) on ice [6].

Analysis of the reaction products from the photolysis showed the formation of methoxymethanol (MM; CH_3OCH_2OH) and MF as the main components. This result was different from the UV photolysis of pure methanol solids, in which CH_2OH-derived molecules such as ethylene glycol (EG; $HOCH_2CH_2OH$) and ethanol were mainly produced. This MF generation is well consistent with cosmic MF observations. To clarify the reaction process of MM and MF, the irradiation time dependence of the signal intensities of trace reaction products such as CH_3O and/or CH_2OH, MM, MF, and OH was measured (Figure 1). A sequential behavior such as $CH_3OH \rightarrow CH_3O$ and/or $CH_2OH \rightarrow MM \rightarrow MF$ was observed, indicating found that MF was efficiently generated by photodissociation of MM. In addition, from the fact that MM is the main product on ice among the $C_2H_6O_2$ isomers, it is considered that the formation of CH_3O was promoted by the abstraction reaction from methanol by the OH radical generated by the photolysis of H_2O.

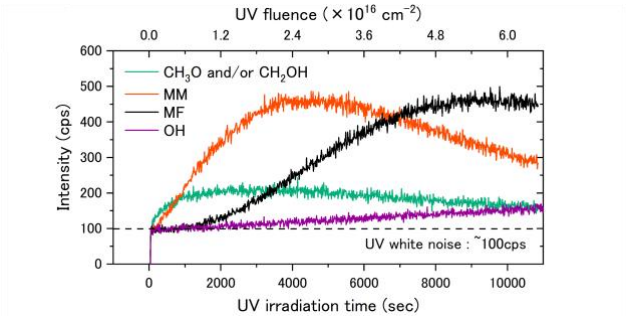

Figure 1: Variations in the signal intensities of surface species generated during UV irradiation to the sample of CH_3OH (0.3 ML) on ASW (10 ML) at 10 K. Pickup signals of MF, MM, CH_3O and/or CH_2OH, and OH which are photoproducts.

References

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