



Thermodynamic Data

$$\Delta H_{298}^{\circ}(1\text{a}) \approx -682 \text{ kJ mol}^{-1}$$

$$\Delta H_{298}^{\circ}(1\text{b}) \approx -509 \text{ kJ mol}^{-1}$$

$$\Delta H_{298}^{\circ}(1\text{c}) \approx -623 \text{ kJ mol}^{-1}$$

$$\Delta H_{298}^{\circ}(1\text{d}) \approx -1059 \text{ kJ mol}^{-1}$$

$$\Delta H_{298}^{\circ}(1\text{e}) \approx -310 \text{ kJ mol}^{-1}$$

$$\Delta H_{298}^{\circ}(1\text{f}) \approx -470 \text{ kJ mol}^{-1}$$

$$\Delta H_{298}^{\circ}(1\text{g}) \approx -306 \text{ kJ mol}^{-1}$$

ΔH_{298}° of HOC was taken from an *ab initio* calculation [1]. All other thermodynamical data were taken from Ref. [2]. All reactions (1a-g) are enough exoergic to prevent small errors in the thermodynamic data to affect the viability of the processes.

Rate Coefficient Data k

$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T / K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
None			
<i>Rate Coefficient Reviews and Evaluations</i>			
$6 \times 10^{-7}(T/300)^{-0.5}$	10 – 300	UMIST database	
$6 \times 10^{-7}(T/300)^{-0.5}$		OSU website	
<i>Branching Fraction Measurements</i>			
None			

1(a) = 0.17

10 – 300

UMIST database and OSU website

1(b) = 0.00

1(c) = 0.83

1(d-f)=0.00

Comments

Rates and branching ratios of the CH_nO^+ ions have been measured [3-5] using storage rings, with the exception of CH_2O^+ . The reason why just this ion was exempted from such studies is the presence of two isomers with almost equal enthalpy of formation (CH_2O^+ and HCOH^+) [2], which would render a pure production of one of the isomers impossible. Also, both isomers might be present in the interstellar medium, like in the case of HCO^+ and HOC^+ . For the following deliberations, we consider the more stable CH_2O^+ isomer.

In the dissociative recombination of both HCO^+ and CH_2OH^+ the carbon-oxygen bond stays almost completely intact. We therefore assume the same to be true for CH_2O^+ . This, however, does not hold for the more hydrogenated CH_nO^+ like CH_3OH_2^+ , where channels involving break-up of the C-O bond dominate [5]. Like in HCO^+ and CH_2OH^+ , we allocate 90% of the dissociative recombination events to processes preserving the bond between the heavy atoms. Since dissociative recombinations of many hydrogen-containing ions have shown to proceed under preferable ejection of two hydrogen atoms (due to the formation of highly excited intermediates in the first step leading to emission of the first H-atom), we assume a branching fraction of 0.50 of reaction (1c). The respective figure for reaction (1a) we predict to be around 0.25, for (1d) we assume 0.15. For (1b), which involves a hydrogen migration, we expect only a branching fraction of 0.05. The rest of the dissociative recombination events should follow pathway (1g), the only channel leading to a break-up of the C-O bond without hydrogen migration. These predictions are restricted to CH_2O^+ , since the isomer could show a different behaviour.

Regarding the rate constant, there seems to be a tendency for them to increase for CH_nO^+ ions with ascending n. Therefore we would place the one for CH_2O^+ , somewhat in the middle between the ones for HCO^+ and CH_2OH^+ , namely at $5.0 \times 10^{-7}(\text{T}/300)^{-0.7} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Also, since dissociative recombination rate constants of

nitriles tend to have a higher temperature dependence, we propose an exponential factor of -0.7. The UMIST model also includes a radiative recombination of CH_2O^+ , leading to H_2CO with a rate constant of $1.1 \times 10^{-10}(\text{T}/300)^{-0.7} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Since the velocity of this process is far too low to allow it to compete with the dissociative recombination, it has been disregarded in our deliberations.

Recommended rate constant:

$$k = 5.0 \times 10^{-7}(\text{T}/300)^{-0.7} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

Recommended branching fractions:

(1a) = 0.25

(1b) = 0.05

(1c) = 0.50

(1d) = 0.15

(1e) = 0.00

(1f) = 0.00

(1g) = 0.05

Comments on Preferred Values

As can be seen, we assume a somewhat higher branching fraction of (1c) than the present models use. We also include 2 additional minor processes (1b) and (1f). The rate is very similar to that applied in both the UMIST and OSU models, so very dramatic effects of our new recommended values on their predictions are not anticipated.

References

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