

Theoretical kinetic study of the formation reactions of methanol and methyl hypohalites in the gas phase

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Abstract CH₃OX molecules (X = H, F, Cl and Br) can be formed in the atmosphere by the CH₃ + OX and CH₃O + X recombination reactions. In the present study the results of a theoretical analysis of the kinetics and thermochemistry of this class of reactions are presented. The molecular properties of the reactants and products were derived from *ab initio* calculations. The high-pressure limiting rate constants for the recombination reactions were evaluated using a version of the statistical adiabatic channel model. The kinetic equations derived in this study allow a description of the kinetics of the reactions under investigation in the temperature range of 200–500 K.

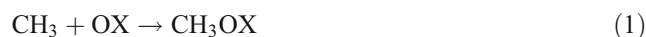
Keywords Hypohalites · Kinetics · Radicals · Recombination

Introduction

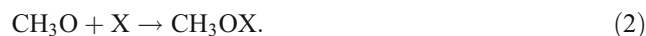
Methane is a major organic compound occurring in the natural troposphere with a background concentration approaching 2 ppm [1]. Methyl CH₃ radicals are formed in the polluted atmosphere by the reaction of CH₄ with hydroxyl OH radicals. The only significant atmospheric fate of CH₃ radicals is its reaction with molecular oxygen to form methylperoxy radicals CH₃O₂, which then react with nitric oxide, generating methoxy CH₃O radicals. The most important subsequent atmospheric paths of CH₃O are

related to reactions with molecular oxygen as well as the nitrogen oxides NO and NO₂ [1, 2].

The halogen oxides and atoms are common constituents of the atmosphere as they are efficiently produced by a variety of both natural and anthropogenic sources [2]. The recombination reactions of CH₃ and CH₃O radicals with halogen oxides/atoms lead to the formation of methyl hypohalites. In this study we present our theoretical investigations on the kinetics of the recombination reactions leading to the formation of the respective methyl hypohalites and methanol:



where: X = H, F, Cl and Br



The reaction products formed, i.e., the methyl hypohalites CH₃OX, are an interesting class of atmospheric organics and have become the subject of several experimental [3–7] and theoretical [8–14] investigations to examine their molecular structure and reactivity. Results of theoretical studies show methyl hypohalites as kinetically stable with respect to thermal and radical decomposition channels, able to act as temporary halogen reservoir species.

With the present study we want to extend our previous investigations on the recombination reactions leading to the formation of the respective fluorinated, chlorinated, and brominated methyl hypohalites and alcohols [15, 16]. Our theoretical analysis of the reaction kinetics was based on the molecular properties of the reactants obtained from *ab initio* calculations at the G2 level. The molecular data obtained from these calculations provide the necessary information for the computational methods used to evaluate the high-pressure limiting rate constants, $k_{\text{rec},\infty}$, for the studied recombination reactions over a wide range of temperatures.

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Computational details

The alkyl hypohalites were studied theoretically using quantum mechanical *ab initio* methods at various levels of theory [8–17]. Results of these calculations show that the G2 method [18] reproduces the structural parameters and molecular properties of a wide group of organic hypohalites very well. The reliable values of the thermochemical properties and vibrational frequencies obtained by G2 methodology for the trifluoro-, trichloro-, and tribromo-methyl hypohalites [15, 16] also favor the use of this level of theory for a description of the structural parameters of the investigated molecular systems. All quantum mechanical *ab initio* calculations were carried out using the Gaussian 03 program package [19]. The geometrical parameters of the structures studied were fully optimized at both the SCF and the second-order Møller-Plesset (MP2) level of theory with the 6–31G(d) basis set. The standard frozen-core approximation was kept throughout. Relative total energies were examined using G2 methodology [18]. Temperature corrections to the total energies and the ideal-gas thermodynamic functions were calculated (assuming no free and internal rotations) in the classical rigid-rotor and harmonic-oscillator approximation using the vibrational frequencies obtained in (U)HF/6–31G* calculations and scaled by a factor of 0.8929.

The high-pressure limiting rate constant for a recombination reaction, $k_{rec,\infty}$, was derived using a version of the statistical adiabatic channel model, i.e., the maximum free-energy method of Quack and Troe [20]. According to this version, $k_{rec,\infty}$ is given by the formula

$$k_{rec,\infty} = \frac{k_B T}{h} \frac{Q^\ddagger}{Q} K_{eq}, \quad (3)$$

where Q is the complete rovibrational partition function of CH_3OX , Q^\ddagger is the partition function of the activated complex, and K_{eq} denotes the equilibrium constant in the recombination direction. The partition function $Q^\ddagger(q^\ddagger)$ is taken as a minimum of the total partition function $Q^\ddagger(q)$ along the reaction coordinate q (q^\ddagger is identified with the location of the activated complex). The total partition function $Q^\ddagger(q)$ is expressed by an exponential interpolation of the complete rovibrational functions of the reactants and product, the electronic partition function, the zero-point energy function, and the centrifugal partition function.

Results and discussion

The definitions of the geometrical parameters of the CH_3OX structures are shown in Fig. 1. The structural parameters of all CH_3OX ($X = \text{H}, \text{F}, \text{Cl}, \text{and Br}$) molecules

as well as the CH_3 and CH_3O radicals were fully and independently optimized using analytical gradients at the SCF and MP2 levels with the 6–31G(d) basis set. The optimized geometrical parameters obtained at the MP2/6–31G(d) level, the harmonic vibrational frequencies (scaled by 0.8929) derived in the SCF/6–31G(d) calculations, and the total G2 energies for the CH_3OX molecules are gathered in Table 1. The molecular parameters of the other structures, such as CH_3 and CH_3O radicals and XO oxides, were published elsewhere [15, 16, 21].

The most stable molecular structure of CH_3OX appears to possess a staggered conformation with C_s molecular symmetry. The differences in the calculated C–O bond lengths of the CH_3OX molecules are very small, and r_{CO} varies from 1.420 Å to 1.436 Å for CF_3OH and CBr_3OH , respectively. These values are very close to the 1.427 ± 0.007 Å obtained from microwave studies by Venkateswarlu and Gordy [22] for methanol, $\text{H}_3\text{C–OH}$. The values of the C–H bond lengths derived at the MP2/6–31G(d) level in CH_3OX are also not sensitive to the kind of functional –OX group. The lengths of the C–H bonds in the methyl hypohalites are very close to each other and also to those obtained for methanol, CH_3OH . The same applies to the angular parameters of the CH_3OX structures. Only the O–X bond distance depends distinctly on the nature of the X atom, growing in the series O–H, O–F, O–Cl, and O–Br due to the increase in the halogen covalent radius.

The vibrational frequencies of the reactants and products can significantly contribute to the rate constant. Reliable values of the frequencies are then of crucial importance for the rate constant calculations. Except for CH_3OBr , the vibrational frequencies of CH_3OX molecules have been measured experimentally. In the G2 approach, the vibrational frequencies are calculated at the SCF/6–31G(d) level and scaled by 0.8929 to take into account their overestimation. Calculated in this way, the vibrational frequencies of CH_3OH , CH_3OF , and CH_3OCl reproduce well the frequencies derived experimentally. The greatest differences over 60 cm^{-1} correspond to the C–H modes of 3000 cm^{-1} , which only slightly contribute to the values of the vibrational partition functions at ambient temperatures.

It has been established that the use of G2 methodology leads to a realistic estimate of the total energy of a wide group of molecular structures. The enthalpy of formation,

Fig. 1 Definition of the geometrical parameters of CH_3OX ($X = \text{H}, \text{F}, \text{Cl}$ and Br)

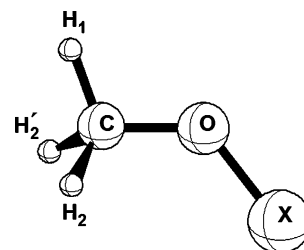


Table 1 Molecular properties of the methanol and methyl hypohalites ^{a)}

	CH ₃ OH	CH ₃ OF	CH ₃ OCl	CH ₃ OBr
CO	1.4244	1.4204	1.4339	1.4361
CH ₁	1.0899	1.0927	1.0913	1.0923
CH ₂	1.0971	1.0924	1.0937	1.0940
OX	0.9701	1.4512	1.7184	1.8680
H ₁ CO	106.2815	103.1373	103.4257	103.4551
H ₂ CO	112.2953	110.8767	111.3440	111.5698
COX	107.3393	103.1833	109.3898	110.0036
H ₂ COX	61.4911	61.8276	61.6644	61.7278
ν_1	311 (295)	244	230	221
ν_2	1040 (1034)	437	360	312
ν_3	1061 (1075)	922 (824)	703 (680)	599
ν_4	1151 (1145)	1090 (994)	1038 (1002)	1034
ν_5	1346 (1336)	1154	1150 (1150)	1150
ν_6	1462 (1455)	1206 (1188)	1181 (1170)	1172
ν_7	1475 (1465)	1433 (1418)	1440 (1424)	1440
ν_8	1485 (1478)	1445 (1476)	1454 (1456)	1456
ν_9	2844 (2844)	1484 (1479)	1478 (1471)	1479
ν_{10}	2885 (2970)	2891 (2803)	2880 (2820)	2875
ν_{11}	2951 (2999)	2971 (2914)	2951 (2904)	2943
ν_{12}	3676 (3680)	2976 (2991)	2970 (2920)	2957
E ₀ (G2)	-115.53488	-214.57354	-574.62301	-2687.47092

^{a)}G2 molecular parameters: geometrical structure optimized at the MP2/6-31G(d) level, (bond lengths in Å, valence and dihedral angles in degrees), the SCF/6-31G(d) vibrational frequencies ν_i (cm⁻¹) scaled by 0.8929 and the total G2-energies in a.u. at 0 K (ZPE included). Experimental frequencies for CH₃OH [23], CH₃OF [4] and CH₃OCl [6] in parenthesis.

$\Delta H_{f,298}^0$, can be directly evaluated as the G2 enthalpy at room temperature for the reaction in which the relevant molecule is formed from the gas-phase elements, such as C_(g), H_{2(g)}, O_{2(g)}, F_{2(g)}, Cl_{2(g)}, and Br_{2(g)}, and using the well-established values of enthalpy of formation at 298 K of gaseous carbon atom C_(g) and Br_{2(g)} of 715.0 kJ mol⁻¹ and 30.9 kJ mol⁻¹ [23, 24], respectively. The calculated values of the enthalpy of formation $\Delta H_{f,298}^0$ of CH₃OX molecules derived from G2 energies are given in Table 2. For CH₃OH and CH₃OF the calculated values of $\Delta H_{f,298}^0$ are in excellent agreement with those found experimentally [23, 24]. Slightly worse is the comparison of the calculated and experimental values of $\Delta H_{f,298}^0$ for CH₃OCl due to the low accuracy of the experimental value. However, the calculated value of $\Delta H_{f,298}^0(\text{CH}_3\text{OCl}) = -70.7$ kJmol⁻¹ lies within the range -64.5 ± 6.2 kJ mol⁻¹ [24] limited by the experimental error bounds. The value of $\Delta H_{f,298}^0(\text{CH}_3\text{OBr}) = -50.9$ kJmol⁻¹ is obtained theoretically in this study. To the best of our knowledge there is no experimental estimation of the enthalpy of formation for CH₃OBr. The energetics of the reactions under investigation at 0 K is shown in Fig. 2. All the reactions studied are exothermic. The formation of methanol in the recombination reaction CH₃O + H → CH₃OH appears to be the most

Table 2 Comparison of the experimental $\Delta H_{f,298}^0(\text{exp.})$ and theoretical $\Delta H_{f,298}^0(\text{calc.})$ values of the enthalpy of formation of CH₃OX molecules calculated from the total energies of the molecules obtained at the G2 level

Molecular system	$\Delta H_{f,298}^0(\text{calc.})$ (kJ mol ⁻¹)	$\Delta H_{f,298}^0(\text{exp.})^{\text{a)}$ (kJ mol ⁻¹)
CH ₃ OH	-202.6	-201.6±0.2
CH ₃ OF	-96.2	-96.0±3.0
CH ₃ OCl	-70.7	-64.5±6.2
CH ₃ OBr	-50.9	

^{a)} from Refs. [23, 24]

exothermic process, with a reaction enthalpy of -439 kJ mol⁻¹. The recombination reactions of the methyl radicals CH₃ with OX are also strongly exothermic, with reaction enthalpies of -383 , -347 , -326 , and -320 kJ mol⁻¹ for CH₃ + OH, CH₃ + FO, CH₃ + BrO, and CH₃ + ClO, respectively. The recombination reactions of the methoxy radicals with the halogen atoms are distinctly less exothermic because the dissociation bond energies of the O–X oxygen halides are considerably lower than those of the C–O and O–H bonds.

The comparison with experiments shows that the vibrational frequencies and G2 total energies of the molecular structures derived in this study are realistic and can then be considered as credible input data for the rate constant calculations. The high-pressure limiting rate constants $k_{\text{rec},\infty}$ for the recombination reactions (1,2) and $k_{\text{diss},\infty}$ for the inverse dissociation (–1,–2) reactions:



where: X = H, F, Cl, and Br



were calculated using the maximum free-energy method [20]. The calculated rate constant k_∞ in this model depends on the values of two empirical parameters: a “looseness”

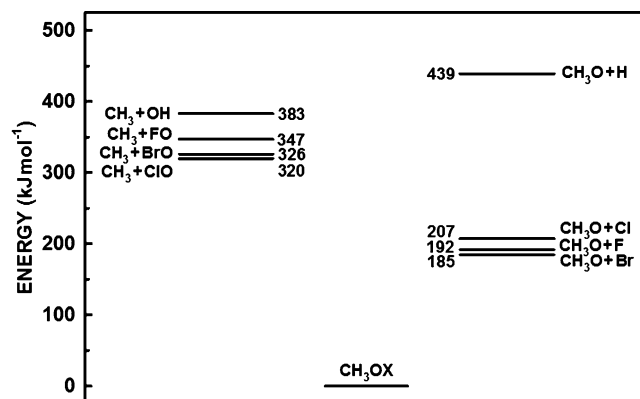
**Fig. 2** Relative G2 energies of the reactants and products of reactions (1) and (2) at 0 K (ZPE included)

Table 3 Values of the calculated high-pressure limiting rate constants $k_{\text{rec},\infty}$ for the recombination reactions (1) and (2)^{a)}

T (K)	CH ₃ +OH	CH ₃ +FO	CH ₃ +ClO	CH ₃ +BrO	CH ₃ O+H	CH ₃ O+F	CH ₃ O+Cl	CH ₃ O+Br
200	6.6	4.8	4.1	3.7	29.1	3.6	4.5	3.9
250	8.4	5.8	5.0	4.6	31.6	4.0	5.0	4.3
300	10.0	6.6	5.7	5.2	33.7	4.3	5.4	4.6
350	11.2	7.3	6.2	5.7	35.4	4.6	5.7	4.9
400	12.2	7.8	6.7	6.1	36.9	4.8	5.9	5.1
450	13.1	8.2	7.0	6.5	38.2	5.0	6.2	5.3
500	13.8	8.5	7.3	6.7	39.3	5.1	6.4	5.5
$\alpha/\text{\AA}^{-1}$	0.90	1.11	1.16	1.21	1.02	1.35	1.18	1.24
$\beta/\text{\AA}^{-1}$	1.95	2.42	2.52	2.63	2.22	2.93	2.57	2.69

^{a)} all values of the rate constants in units $10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

parameter α and the Morse parameter β , which describe the intermediate part of the potential energy surface. The value of the parameter β is usually derived from the force constant and the dissociation energy of the breaking bond of the adduct. The parameter α is a typical fitting parameter with a value chosen to get the best agreement between the values of the calculated and experimental rate constants. The “standard” choice of α is that corresponding to a ratio of $\alpha/\beta \approx 0.5$, since the comparative study by Cobos and Troe [25] shows, for many reactions studied, that the best agreement between theoretical and experimental values of k_{∞} is reached at an α/β of 0.46 ± 0.09 . This relation can be employed to estimate the magnitude of k_{∞} when there is no experimental kinetic information on the reaction kinetics.

The calculated values of the rate constants $k_{\text{rec},\infty}$ for reactions (1) and (2) are gathered in Table 3. The values of α used in our calculations were always taken as equal to 0.46β to check the reliability of the α value choice recommended by Cobos and Troe [25]. The rate of the $\text{CH}_3 + \text{OX}$ recombination reactions (1) is described by the rate constant $k_{1,\infty}$, within the range $(5.2 - 10.0) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 300 K. The fastest is $\text{CH}_3 + \text{OH}$ recombination, which is also the most exothermic process from among the reactions (1). This reaction has been the subject of several experimental studies [26–29] and values of the rate constant $k_{\text{rec},\infty}$ of $(0.9-1.7) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ were measured. These results are in line with our calculated value of $k_{\text{rec},\infty}(\text{CH}_3 + \text{OH}) = 1.0 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, which is equal to the value recommended by kinetic data evaluation [28]. The lowest values of $k_{1,\infty}$ of 5.7×10^{-11} and $5.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, were calculated for the $\text{CH}_3 + \text{ClO}$ and $\text{CH}_3 + \text{BrO}$ reactions, respectively. The experimental kinetic data related to these reactions are very limited. A value of the overall rate constant of $(1.3 \pm 0.4) \times 10^{-10}$ for the reaction $\text{CH}_3 + \text{ClO} \rightarrow \text{Products}$ has been estimated by Biggs et al. [30]. If we take into account that the reactants of this reaction can also decay in the reaction $\text{CH}_3 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_6$ ($k_{\text{rec},\infty} \approx 5 \times 10^{-11} \text{ cm}^3$

$\text{molecule}^{-1} \text{ s}^{-1}$ [28]), the value estimated theoretically seems realistic.

Recombination of the methoxy radical with the hydrogen atom reaction is characterized by the highest value of the rate constant, i.e., a $k_{2,\infty}(\text{CH}_3\text{O} + \text{H})$ of $3.4 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 300 K. Unfortunately there are no experimental data on the kinetics of this reaction. The rate constants for the other methoxy radical and halogen atom combination reactions are considerably lower and cover the range $(4.3-5.4) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$; the lowest one is $k_{2,\infty}$ of $4.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the reaction $\text{CH}_3\text{O} + \text{F}$. Experimental information on the reaction kinetics is uncertain and very limited. An overall rate constant of $(1.5 \pm 0.5) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 300 K [31] was measured for the $\text{CH}_3\text{O} + \text{F} \rightarrow \text{Products}$ reaction.

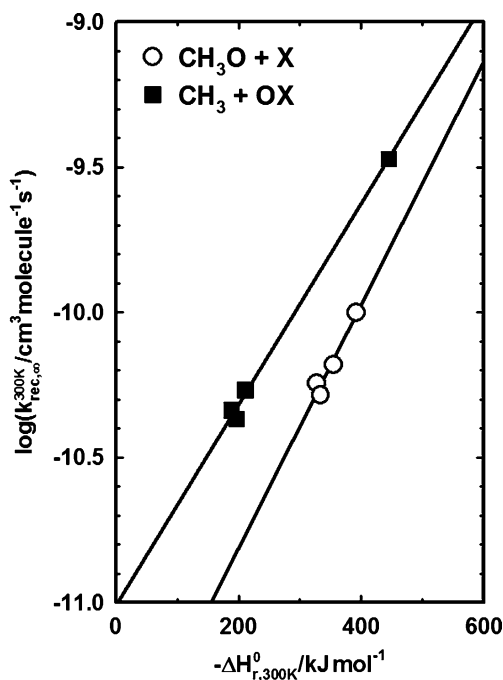


Fig. 3 The dependence of $\log k_{\text{rec},\infty}$ on the reaction enthalpy calculated at 300 K

This is more than two times higher than our calculated value; however, the recombination $\text{CH}_3\text{O} + \text{F} \rightarrow \text{CH}_3\text{OF}$ is only one of several fast processes responsible for the decay of the reactants, such as $\text{CH}_3\text{O} + \text{CH}_3\text{O} \rightarrow \text{Products}$ (with a rate constant of $1.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) [31], $\text{CH}_3\text{O} + \text{F} \rightarrow \text{CH}_2\text{O} + \text{HF}$ (1.3×10^{-11}) [31], $\text{F} + \text{CH}_2\text{O} \rightarrow \text{HCO} + \text{HF}$ (6.6×10^{-11}) [32], and $\text{CH}_3\text{O} + \text{HCO} \rightarrow \text{CH}_3\text{OH} + \text{CO}$ (1.5×10^{-10}) [33]. The calculated value of the rate constant of $5.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 300 K for the $\text{CH}_3\text{O} + \text{Cl} \rightarrow \text{CH}_3\text{OCl}$ reaction is in line with the experimental value of $(7.6 \pm 1.4) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [34] of the overall rate constant for $\text{CH}_3\text{O} + \text{Cl} \rightarrow \text{Products}$, which describes an upper limit of the high-pressure limiting rate constant $k_{2,\infty}(\text{CH}_3\text{O} + \text{Cl})$. The rate constant calculated for the recombination of methoxy radicals with bromine atoms of $4.6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at room temperature is in very good agreement with the $(5.3 \pm 0.9) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ measured by Shah et al. [34]. Hence there is no calculated rate constant for the reactions under investigation whose magnitude conflicts with available experimental measurements. As shown in Fig. 3, the calculated rate constant is strongly correlated with the heat of reaction. The dependence of $\log k_{\text{rec},\infty}$ on reaction enthalpy appears linear for both types of reactions, $\text{CH}_3 + \text{OX}$ and $\text{CH}_3\text{O} + \text{X}$.

The recombination of the methyl and hydroxyl radicals shows the most significant temperature dependence, i.e., $\sim T^{0.5}$. The temperature dependence of the rate constants $k_{\text{rec},\infty}$ for the other recombination reactions proved to be weak, but they are still stronger than one would expect for typical recombination reactions, which seldom exceed $T^{0.2}$. However, a similar dependence of $k_{\text{rec},\infty}$ on temperature was derived for analogous recombination reactions of halogenated methyl and methoxy radicals [15, 16, 35]. In the temperature range of 200–500 K, the values of $k_{\text{rec},\infty}/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the recombination reactions (1) and (2) can be expressed in the form:

$$\begin{aligned} k_{\text{rec},\infty}(\text{CH}_3 + \text{OH}) &= (1.0 \pm 0.4) \times 10^{-10} \times (T/300)^{0.53} \\ k_{\text{rec},\infty}(\text{CH}_3 + \text{FO}) &= (6.6 \pm 2.5) \times 10^{-11} \times (T/300)^{0.35} \\ k_{\text{rec},\infty}(\text{CH}_3 + \text{ClO}) &= (5.7 \pm 1.9) \times 10^{-11} \times (T/300)^{0.35} \\ k_{\text{rec},\infty}(\text{CH}_3 + \text{BrO}) &= (5.2 \pm 1.8) \times 10^{-11} \times (T/300)^{0.36} \end{aligned}$$

and

$$\begin{aligned} k_{\text{rec},\infty}(\text{CH}_3\text{O} + \text{H}) &= (3.4 \pm 0.8) \times 10^{-10} \times (T/300)^{0.33} \\ k_{\text{rec},\infty}(\text{CH}_3\text{O} + \text{F}) &= (4.3 \pm 1.5) \times 10^{-11} \times (T/300)^{0.31} \\ k_{\text{rec},\infty}(\text{CH}_3\text{O} + \text{Cl}) &= (5.4 \pm 1.7) \times 10^{-11} \times (T/300)^{0.29} \\ k_{\text{rec},\infty}(\text{CH}_3\text{O} + \text{Br}) &= (4.6 \pm 1.3) \times 10^{-11} \times (T/300)^{0.28} \end{aligned}$$

The error limits were estimated from the values of $k_{\text{rec},\infty}$ corresponding to the lower and upper limits of the recommended ratio of $\alpha/\beta = 0.46 \pm 0.09$, i.e., for $\alpha = 0.37\beta$ and $\alpha = 0.55\beta$ [25].

The high-pressure limiting rate constants, $k_{\text{diss},\infty}/\text{s}^{-1}$ for the respective CH_3OX dissociation reactions (–1) and (–2) obtained *via* the theoretical equilibrium constants can be shown as

$$\begin{aligned} k_{\text{diss},\infty}(\text{CH}_3\text{OH} \rightarrow \text{CH}_3 + \text{OH}) &= (6.3 \pm 2.5) \times 10^{15} \times (T/300)^{1.6} \times \exp(-46550/T) \\ k_{\text{diss},\infty}(\text{CH}_3\text{OF} \rightarrow \text{CH}_3 + \text{FO}) &= (2.2 \pm 0.8) \times 10^{16} \times (T/300)^{0.85} \times \exp(-42230/T) \\ k_{\text{diss},\infty}(\text{CH}_3\text{OCl} \rightarrow \text{CH}_3 + \text{ClO}) &= (2.1 \pm 0.7) \times 10^{16} \times (T/300)^{0.77} \times \exp(-38950/T) \\ k_{\text{diss},\infty}(\text{CH}_3\text{OBr} \rightarrow \text{CH}_3 + \text{BrO}) &= (1.9 \pm 0.6) \times 10^{16} \times (T/300)^{0.87} \times \exp(-39700/T) \end{aligned}$$

and

$$\begin{aligned} k_{\text{diss},\infty}(\text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{O} + \text{H}) &= (1.3 \pm 0.3) \times 10^{15} \times (T/300)^{0.96} \times \exp(-53000/T) \\ k_{\text{diss},\infty}(\text{CH}_3\text{OF} \rightarrow \text{CH}_3\text{O} + \text{F}) &= (2.2 \pm 0.8) \times 10^{15} \times (T/300)^{0.08} \times \exp(-23420/T) \\ k_{\text{diss},\infty}(\text{CH}_3\text{OCl} \rightarrow \text{CH}_3\text{O} + \text{Cl}) &= (2.5 \pm 0.8) \times 10^{15} \times (T/300)^{-0.17} \times \exp(-25230/T) \\ k_{\text{diss},\infty}(\text{CH}_3\text{OBr} \rightarrow \text{CH}_3\text{O} + \text{Br}) &= (2.1 \pm 0.6) \times 10^{15} \times (T/300)^{-0.31} \times \exp(-23580/T) \end{aligned}$$

The above expressions complete the series of kinetic equations published in two previous papers [15, 16] which describe the kinetics of recombination reactions $\text{CX}_3/\text{CX}_3\text{O} + \text{OY}/\text{Y} \rightarrow \text{CX}_3\text{OY}$ ($\text{X}, \text{Y} = \text{H}, \text{F}, \text{Cl}, \text{and Br}$). The experimental information on the kinetics of these reactions is very limited and uncertain. Therefore it is very important to note that all the experimental values of the rate constants available in literature are in line with the corresponding calculated ones. This provides evidence in support of the reliability of the rate constants calculated for this class of reactions. This has significant importance for some practical applications, such as the kinetic modeling of atmospheric chemistry and combustion.

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