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Kinetics, Energetics and OH Product Yield of the Reaction $CH_3O + O(^{3}P) \rightarrow CH_3O_2^* \rightarrow Products$

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Chemical Kinetics / Elementary Reactions / Laser Induced Fluorescence / Reactions with Bound Intermediates / Radicals

The rate constant for the reaction (1) CH₃O + O \rightarrow products at 298 K has been determined using 248 nm laser co-photolysis of CH₃ONO/O₃ mixtures for the generation of CH₃O radicals and O atoms combined with LIF for time resolved detection of CH₃O and product OH. k_1 is found to be (2.5 ± 0.7) 10⁻¹¹ cm³/s with a relative yield of OH of $\varphi = -\Delta[OH]/\Delta[CH_3O] = 0.12^{\pm0.08}_{-0.08}$. The results are shown to be consistent with a primary capture mechanism on an electronically adiabatic surface forming highly vibrationally excited CH₃O[‡] and followed by rapid subsequent decomposition or isomerization, viz.

$$CH_{3}O + O \rightarrow CH_{3}O_{2}^{*} \rightarrow CH_{3} + O_{2}$$
(1a)

$$\rightarrow CH_2OOH^* \rightarrow CH_2O + OH \tag{1b}$$

From modelling of the OH yield using RRKM theory the isomerization barrier between CH_3O_2 and CH_2OOH is placed near 160 kJ/ mol in good agreement with recent ab initio calculations. As a consequence the $CH_3 + O_2$ combustion reaction is predicted to proceed primarily via the low energy $CH_2O + OH$ channel, in contrast to most previous suggestions.

I. Introduction

In conventional terms bimolecular reactions are characterized by the existence of more or less pronounced potential energy barriers between reactants and products. Some of them, however, occur on purely attractive potentials like termolecular recombination processes and gain their bimolecular nature via the strong forward flux caused by the unimolecular fragmentation of the excited adducts. A notable example is the reaction

$$OH + O \rightarrow HO_2^* \rightarrow H + O_2$$
 (i)

which in a number of experimental [1-3] and theoretical [3-5] studies has been shown to bear all properties of a recombination reaction in the high pressure limit.

In the present paper we report an experimental and computational study of the reaction

$$CH_3O + O \rightarrow CH_3O_2^* \rightarrow CH_3 + O_2$$
 (1a)

$$\rightarrow CH_2OOH^* \rightarrow CH_2O + OH.$$
(1b)

This reaction is the simplest hydrocarbon analogue of reaction (i). Moreover, both reactions have strong energetic similarities through the intermediate formation of the peroxy species. As a consequence one may hope that similarities or differences between the rate coefficients of (i) and (1) can be extracted and be rationalized on the basis of current rate theory. An application of this approach to the reverse reactions, $(-i) H + O_2 \rightleftharpoons HO_2^* \rightarrow OH + O$ and $(-1a) CH_3$ $+ O_2 \rightleftharpoons CH_3O_2^* \rightarrow CH_3O + O$, has recently been published by Cobos et al. [5, 6].

The hydrocarbon reaction (1) differs from reaction (i) through the existence of at least one additional exothermic reaction channel, i.e. the isomerization of $CH_3O_2^*$ to CH_2OOH^* via 1.4-H-atom migration followed by subsequent decomposition of CH_2OOH to yield $CH_2O + OH$ (channel 1 b). The branching ratio of this channel is a function of the height of the isomerization barrier ΔE_{iso} . This quantity is also of fundamental importance to the $CH_3 + O_2$ chain branching reaction at high temperatures, viz.

$$\begin{array}{c} \mathrm{CH}_3 + \mathrm{O}_2 \rightleftharpoons \mathrm{CH}_3 \mathrm{O}_2^* \to \mathrm{CH}_3 \mathrm{O} + \mathrm{O} \\ \to \mathrm{CH}_2 \mathrm{OOH}^* \to \mathrm{CH}_2 \mathrm{O} + \mathrm{OH}. \end{array} \tag{-1a}$$

Although there is a large amount of experimental data on reaction (-1a) (for a summary see Ref. [7]) there is still conflicting evidence as to the branching ratio into the CH₂O + OH channel. Arrhenius expressions for this channel with

Ber. Bunsenges. Phys. Chem. 91, 708-717 (1987) – © VCH Verlagsgesellschaft mbH, D-6940 Weinheim, 1987. 0005-9021/87/0707-0708 \$ 02.50/0 activation energies differing by almost 100 kJ/mol [7, 8] have been reported.

It will be shown that from the present experimental study of the CH₃O + O reaction, together with RRKM modelling, and with the assumption that both reactions, CH₃ + O₂ and CH₃O + O, proceed through a common intermediate (CH₃O^{*}) an independent determination of ΔE_{iso} and hence the activation energy for the reaction CH₃ + O₂ \rightarrow CH₂O + OH can be made.

The present work has both applied and fundamental aspects. As has been mentioned reaction (1) is the low temperature complement of the $CH_3 + O_2$ combustion reaction. Therefore valuable insight into the molecular datails of a typical combustion reaction is provided from a study of a low temperature radical-radical reaction. Moreover, reaction (1) is a bimolecular reaction over a complex potential energy surface. As a consequence its details (overall rate coefficient for the formation of the excited $CH_3O_2^*$ adduct, branching ratios for fragmentation of $CH_3O_2^*$) can be predicted from current rate theory.

To our knowledge the present work is the first one to report an experimental and computational study of the $CH_3O + O$ reaction. A short note on our results has been published [9].

II. Experimental

The reaction between CH₃O radicals and O atoms has been studied using a combined laser photolysis/LIF technique. A schematic representation of the experimental set-up is provided in Fig. 1. Its major aspects have previously been described [10-12] and hence only a summary as well as modifications relevant to the present study will be given here.



Fig.	1
0-	

Schematic representation of excimer laser photolysis/LIF experimental arrangement. The length of the reaction cell, excluding side arms, is 20 cm. The actual width of the photolysis laser beam is 1 cm

Briefly, this technique uses excimer laser photolysis to generate radical species. Whereas, however, in former applications in studies of radical-stable reagent reactions it was only necessary to generate one kind of radical (i.e. OH, CH₃O) we have now extended this method to the study of radical-radical reactions by using the cophotolysis of two different precursors for the generation of two different radical species. In the present study CH₃O radicals and O(³P) atoms were simultaneously formed in the 248 nm (KrF) cophotolysis of CH₃ONO/O₃ mixtures diluted in 20 mbar of N₂, viz.

$$\begin{array}{rcl} \mathrm{CH_3ONO} + h\nu & \rightarrow & \mathrm{CH_3O}(\tilde{X}\,^2\mathrm{E}) + \,\mathrm{NO}\\ \mathrm{O_3} + h\nu & & \rightarrow & \mathrm{O}(^1\mathrm{D}) + \,\mathrm{O_2}(\mathrm{a}\,^1\Delta_{\mathrm{g}})\\ & & \rightarrow & \mathrm{O}(^3\mathrm{P}) + \,\mathrm{O_2}(\mathrm{X}\,^3\Sigma_{\mathrm{g}}^-)\\ \mathrm{O}(^1\mathrm{D}) + \,\mathrm{N_2} & & \rightarrow & \mathrm{O}(^3\mathrm{P}) + \,\mathrm{N_2}. \end{array}$$

Under these conditions $O({}^{1}D)$ atoms are quantitatively quenched to $O({}^{3}P)$ atoms on the sub-µs time scale [13], such that i) formation of OH in the reaction $O({}^{1}D) + CH_{3}ONO \rightarrow OH + CH_{2}ONO$ is avoided and ii) the initial concentration of $O({}^{3}P)$ can be calculated from the extent of O₃ photodissociation. The deactivation of O₂ (a ${}^{1}\Delta_{g})$ on the other hand by N₂ is slow ($k = 1.4 \cdot 10^{-19}$ cm³/s [14]) such that this species survives the time scale of the experiment. Also, its reaction with O₃ ($k = (3 \pm 1) \ 10^{-15}$ cm³/s [14]) which would generate additional O({}^{3}P) atoms, viz.

$$O_2 (a^1 \Delta_g) + O_3 \rightarrow O(^3P) + 2 O_2$$

occurs on a long time ($\Delta t \ge 0.3$ s) and hence with negligible relevance to the present study.

In the present experiments the precursor concentration of CH₃ONO was fixed at $1.5 \cdot 10^{13}$ cm⁻³, giving rise to an initial CH₃O concentration of ~ 10^{12} cm⁻³. Ozone, on the other hand, was in large excess and was varied between $(0.1 - 1.7) \ 10^{15}$ cm⁻³, with the result that initial [0] ranged between $(0.4 - 6.0) \ 10^{13}$ cm⁻³. These concentrations were calculated from the photophysical properties of the precursors ($\sigma_{CH_3ONO}^{248} = 1.2 \cdot 10^{-17}$ cm² [17]), their concentrations and the number of incident laser photons per unit area (N_p) according to the low optical density approximation of the Beer-Lambert law [10, 18]:

$$[\mathbf{R}] = N_{\mathbf{p}} \cdot [\mathbf{R}\mathbf{P}] \cdot \sigma_{\mathbf{R}\mathbf{P}} \cdot \phi_{\mathbf{R}} . \tag{*}$$

In here, N_p is determined from laser pulse energy measurements. Using a calibrated pyroelectric detector (laser precision RJ) this quantity can be determined with an accuracy of $\pm 10\%$. Assuming the same error limit for [RP] and σ_{RP} the calculated initial concentration of radicals is estimated to be accurate to $\pm 30\%$. The concentrations of the radical precursors CH₃ONO and O₃ were determined by absorption measurements at 200 nm (Xe-arc) and 253.7 nm (Hg low pressure lamp), respectively, prior to entering the reaction cell. In order to avoid unnecessary accumulation of products between subsequent laser pulses the gas mixture is slowly flown through the reaction cell (linear flow rate typically 10 cm/s).

The technique of laser photolysis reagent generation in radicalradical reactions has previously been applied by Ravishankara et al. [18] for studies of the reaction $HO_2 + O(^{3}P)$. These authors claim that spacial uniformity of the laser beam is strongly required in order to avoid different rates of reaction in different parts of the beam. A sequented aperture optical integrator was used [19] to achieve uniformity of their 3 cm diameter beam. In the present study no such device deemed essential since we only use the very center (1 cm diameter) of the excimer laser beam where the spacial intensity distribution is uniform to within 10%. A much smaller cross section of illumination can be afforded here since the radical detection is made by a spacially narrow dye-laser compared to conventional resonance light source used by Ravishankara et al.

The kinetics of reaction (1) was primarily followed by monitoring the decay of CH₃O. For this purpose the output of an excimer laser pumped frequency doubled dye laser (EMG 102/FL 2002, Lambda Physik) operating with Sulforhodamin B was tuned to the 3.0 (298.4 nm) or 2.0 (304.2 nm) band of the CH₃O ($\tilde{X}^2E - \tilde{A}^2A_1$) transition [20] and passed into the reaction cell coaxially with the photolysis laser beam. The resulting fluorescence was collected via a $\lambda \ge 320$ nm cut-off filter onto a photomultiplier and measured in analogue mode by means of a gated boxcar integrator [10]. In this arrangement the fluorescence intensity of CH₃O is determined at a fixed time Δt , the pre-selected delay between photolysis and analysis laser beam. In order to obtain the full time dependent concentration profile of CH₃O the delay time is correspondingly varied. For the detection of OH the dye-laser is tuned to 307.97 nm. At this wavelength the Q₁2-line of the $X^2\Pi - A^2\Sigma^+$ – (0,0 band)transition is selectively excited without overlap with the CH₃O bands. Fluorescence of OH is collected and measured via the same optical and electronic components except that the cut-off filter is replaced by a 308 nm IF-filter. In order to determine the branching ratio of OH formation the OH fluorescence intensity had to be calibrated. This was done by replacing CH₃ONO/O₃ of the gas mixture by HNO₃ under otherwise identical conditions. Through generation of OH by 248 nm HNO₃ photolysis a fluorescence intensity signal is obtained which is self-calibrated via the OH concentration as calculated from Eq. (*). The detection sensitivity for OH in the present experiments is estimated to be ~ 1 · 10⁸ cm⁻³; the corresponding value for CH₃O is ~ 1 · 10¹⁰ cm⁻³.

III. Results and Discussion

1. Decay Measurements of CH₃O

The rate coefficient k_1 has been determined by observing the decay of CH₃O in the presence of excess O atoms using pseudo-first order kinetics. A typical experimental profile of the CH₃O fluorescence intensity as observed in analogue mode with the boxcar averager (gate delay 3 μ s, gate width 0.5 μ s) for different delay times between photolysis and analysis laser is shown in Fig. 2. The fluorescence intensity decays exponentially (Fig. 3); the corresponding pseudo-first



Fig. 2

Recorder traces of CH₃O fluorescence intensity signals as obtained with the boxcar averager for different delay times (in ms) between photolysis and analysis laser. Each signal is the average of ~100 individual analysis laser pulses. $[CH_3O]_0 = 1.5 \cdot 10^{12} \text{ cm}^{-3}$; $[O]_0 = 2.7 \cdot 10^{13} \text{ cm}^{-3}$



Fig. 3

Logarithmic representation of CH₃O fluorescence internsities against reaction time for different initial oxygen atom concentrations

order rate coefficients, $k_{1st} = -\Delta \ln I_F / \Delta t$, are linearly dependent on the initial oxygen atom concentration (Fig. 4). Both these observations are confirming evidence that for the given experimental conditions ([CH₃O]₀ ~ 10¹² cm⁻³, [O]₀ = (0.4-6.0) 10¹³ cm⁻³) the system is kinetically well behaving and that reaction (1) has indeed been studied in isolation. From the plot of Fig. 4 we obtain for the second order rate coefficient, $k_1 = k_{1st}/[O]_0$,

$$k_1 = (2.5 \pm 0.7) \cdot 10^{-11} \text{ cm}^3/\text{s}.$$



First-order rate coefficients for the decay of CH₃O as a function of the initial oxygen atom concentration

The observed decay of CH₃O in the absence of O₃ and O atoms of $\sim 200 \text{ s}^{-1}$ is merely attributed to a loss out of the excitation volume by diffusion and flow. Potential loss of CH₃O in reaction with CH₃ONO, NO and by disproportionation, viz.

$$CH_3O + CH_3ONO \rightarrow \text{products}$$
 (2)

$$CH_3O + NO(+M) \rightarrow CH_3ONO(+M)$$
 (3)

$$CH_3O + CH_3O \rightarrow CH_3OH + CH_2O$$
 (4)

is too slow ($k_2 = 5.6 \cdot 10^{-14} \text{ cm}^3/\text{s}$ [21], $k_3 = 1.3 \cdot 10^{-11} \text{ cm}^3/\text{s}$ at 20 mbar [21] and $k_4 = (7 \pm 4) \cdot 10^{-12} \text{ cm}^3/\text{s}$ [22]) to create significant additional CH₃O consumption.

The question, however, arises whether there are potential CH₃O loss processes the rates of which vary linearly with $[O]_0$ and which hence could pretend an O atom reaction. In the present experiments the variation of [O] has been made by variation of initial $[O_3]$ and is hence associated with a variation of O₂ (³ Σ) (an unavoidable impurity of O₃) and O₂ (¹ Δ_g) (formed in O₃ photolysis). As a consequence these species could in principle also account for the acceleration of the CH₃O decay. However, the reactions with O₃ and O₂(³ Σ), viz.

$$CH_{3}O + O_{3} \rightarrow CH_{3}O_{2} + O_{2}$$
(5)

$$CH_3O + O_2(^3\Sigma) \rightarrow CH_2O + HO_2$$
 (6)

can easily be ruled out due to their small rate coefficients $(k_5 \le 3 \cdot 10^{-15} \text{ cm}^3/\text{s} [21], k_6 = 2.0 \cdot 10^{-15} [12])$. Moreover,

reactions of $O_2({}^{1}\Delta_g)$ with radicals are generally known not to be significantly enhanced compared to the reactions of ground state O_2 [23, 24]. Since $O_2({}^{1}\Delta_g) \leq [O]_0 \leq 6 \cdot 10^{13}$ cm⁻³, we therefore assume that $O_2({}^{1}\Delta_g)$ does not compete with O atoms for the consumption of CH₃O.

In the present experiments we have monitored CH₃O radicals over the time scale of ≤ 1 ms where their decay is exponential and solely attributable to a consumption by O atoms. For longer reaction times (≥ 2 ms), however, nonexponential CH₃O decays with strong curvature of the ln I_F vs. t plot were observed. In fact, in some experiments the CH₃O concentration, after the initial exponential decay, appeared to almost reach a steady state value. In our view this effect is due to consecutive reactions arising from the radical products of the primary step (OH, CH₃). These are expected to lead i) to rapid oxygen atom consumption via the closed chain

$$OH + O \rightarrow O_2 + H$$
 (i)

 $CH_3 + O \rightarrow CH_2O + H$ (7)

$$H + O_3 \rightarrow OH + O_2 \tag{8}$$

and ii) to - in lesser extent - CH₃O re-formation via

$$CH_3 + O_3 \rightarrow CH_3O + O_2. \tag{9}$$

Both effects diminish the actual CH₃O decay constant. Modelling studies of CH₃O profiles using this chemistry and their associated rate coefficients ($k_i = (3.3 \pm 0.4) \ 10^{-11} \text{ cm}^3/\text{s}$ [1-3], $k_7 = 1.4 \cdot 10^{-10} \text{ cm}^3/\text{s}$ [25], $k_8 = 2.9 \cdot 10^{-11} \text{ cm}^3/\text{s}$ [13] and $k_9 = (2.5 \pm 0.5) \ 10^{-12} \text{ cm}^3/\text{s}$ [26]) were in good agreement with the experimental observations.

2. Rate and Branching Ratio of OH Formation

In addition to CH₃O decay measurements we have also performed experiments on the product distribution by in-



Laser induced fluorescence profiles of OH product formation. T = 298 K, p = 20 mbar (N₂). The concentrations of CH₃O and O atoms (in units of 10^{-13} cm⁻³) for the individual curves are ①: 3.1/ 12.0; ②: 2.9/6.7 and ③: 0.27/12.2. The horizontal lines indicate the calculated OH fluorescence intensities for infinite reaction times (see text)

vestigation of OH formation. The result of typical LIF OH profiles as obtained for different initial reagent concentrations is shown in Fig. 5.

As can be seen OH is formed very rapidly, passes through a maximum and decays on a slower time scale. Its rate of formation increases with $[O]_0$, whereas the concentration at maximum increases with $[CH_3O]_0$. Both these observations indicate that OH is a product of the reaction between CH₃O and O. In order to extract quantitative information from these profiles with regard to the rate and branching ratio of OH formation we have chosen to assign them to a sequence of two pseudo-first order reactions, viz.

$$CH_3O + O \rightarrow CH_2O + OH$$
 (1b)

$$OH + R \rightarrow products.$$
 (ω)

In here reaction (ω) describes the effective loss of OH from a steady-state value, established by the sequence of reactions (i) OH + O \rightarrow O₂ + H and (8) H + O₃ \rightarrow OH + O₂, with a first order rate coefficient (as obtained from the profiles of Fig. 5) of k_{ω} [**R**] = 110 ± 10 s⁻¹.

For the sequence (1 b) and (ω) the rate of OH formation is given by

$$\frac{d[OH]}{dt} = k_{1b}[O]_0[CH_3O]_0$$
$$\cdot \exp(-k_1[O]_0t) - k_{\omega}[OH][R]$$

where k_1 is total rate coefficient for CH₃O consumption $(k_1 = k_{1a} + k_{1b})$ and from which upon integration the expression

$$[OH] = \frac{k_{1b}[O]_0[CH_3O]_0}{k_{\omega}[R] - k_1[O]_0} + \{\exp(-k_1[O]_0t) - \exp(-k_{\omega}[R]t)\}$$

is obtained for the temporal behaviour of OH. For the present conditions $(k_1[O]_0 \gg k_{\omega}[R])$ and for reaction times $t \ge t_{\max}$ this expression can be approximated by

$$[OH]_{t>t_{max}} \simeq (k_{1b}/k_1) [CH_3O]_0 \exp\left(-k_{\omega}[\mathbf{R}]t\right).$$

As a consequence the OH concentration at maximum $([OH]_{max})$ and its deviation from the [OH] value at infinite reaction time and in the absence of reaction (ω) $([OH]_{\infty} = (k_{1b}/k_1)$ [CH₃O]₀)

$$[OH]_{max}/[OH]_{\infty} \simeq \exp(-k_{\omega}[R]t_{max})$$

can be calculated from the experimental t_{max} value without prior assumption of $k_1[O]_0$. We obtain $[OH]_{\text{max}}/[OH]_{\infty} = 0.89$ and 0.83 for $t_{\text{max}} = 1.0$ and 1.7 ms, respectively.

The correction for $[OH]_{max}$ (I_{Fmax}^{OH}) to obtain $[OH]_{\infty}$ $(I_{F_{\infty}}^{OH})$ can now be used to derive the first-order rate coefficients for OH formation $(k_{1st} = k_1[O]_0)$ from plots of $-\ln(I_{F_{\infty}}^{OH} - I_{F}^{OH}(t))$ vs. t for reaction times $t \le t_{max}$. The results are shown in Fig. 6a. As can be seen the rise of OH is exponential; the corresponding time constants are propor-

tional to the initial O atom concentration (Fig. 6b). For the rate coefficient k_1 we obtain

$$k_1 = (1.9 \pm 0.7) \cdot 10^{-11} \text{ cm}^3/\text{s}.$$

This value is somewhat lower than the corresponding value derived from the CH₃O decay measurements. Generally, however, the agreement is very satisfactory and the results from the OH measurements may be taken as an independent confirmation of k_1 .



Fig. 6

a) Logarithmic representation of OH fluorescence intensity rise for short reaction times. The numbers refer to the curves of Fig. 5.
b) Dependence of k_{1st} on the initial O atom concentration

The question may be raised though whether OH might have been generated by a completely different reaction which i) bears all the above properties (i.e. rate of formation of OH α [O]₀, OH-yield α [CH₃O]) and which ii) fortuitously has a bimolecular rate coefficient in the order of k_1 . Considering all possibilities the first requirement can only be met by the reaction

$$O + HNO \rightarrow OH + NO \quad \Delta H_R = -217 \text{ kJ/mol}$$
 (10)

where HNO is assumed to arise from the 248 nm photolysis of CH₃ONO at a yield of 12 \pm 4%. This information is inferred from direct measurements of the photolysis coproduct CH_2O [16, 27]. Unfortunately there appears to be no direct measurement in the literature for the rate coefficient k_{10} . Only an estimate of $k_{10} = 8 \cdot 10^{-13} T^{0.5} \exp(-1000$ K/T) cm³/s, corresponding to a value of $k_{10} = 5 \cdot 10^{-13}$ cm³/s at 298 K has recently been reported [28]. Although source and reliability of this data remain unclear this value appears to be sufficiently small to exclude the likelihood of reaction (10). Moreover, we also exclude the possibility that OH is formed in a reaction of H atoms with O_3 , (8) H + $O_3 \rightarrow OH + O_2$, since H atoms in our system are only generated consecutively, i.e. via the reaction (7) $CH_3 + O$ \rightarrow CH₂O + H, and hence cannot account for the fast initial rise of OH as observed experimentally.

The measurements of OH profiles as associated with reaction (1) can also be used to derive the branching ratio of OH formation, $\varphi_{OH} = -\Delta[OH]/\Delta[CH_3O]$, via a calibration of the fluorescence intensity I_F^{OH} . This was done by replacing CH₃ONO/O₃ of the reagent mixture by HNO₃ under otherwise identical conditions whereupon a known amount (cf. Eq. (*)) of OH is generated. Its associated fluorescence intensity can be directly compared with that observed in the $CH_3O + O$ reaction without additional quenching corrections [29]. The result of OH yields relative to initial CH_3O for the experiments of Fig. 5 is shown in Fig. 7. We obtain

$$\varphi_{\rm OH} = k_{\rm 1b}/k_{\rm 1} = 0.12 \, \frac{+0.08}{-0.04}.$$

Hence, OH formation is a minor channel of reaction (1). The dominant reaction products therefore must be assumed to be $CH_3 + O_2$, completely analogous to reaction (i), OH + $O \rightarrow H + O_2$.



Absolute yield of OH (extrapolated to infinite reaction times) for different initial CH₁O concentrations

3. Energy Correlations Between CH₃O₂ Species

The present results reflect the kinetics of a reaction over a complex energy surface. We assume that reaction (1) starts with the scavenging of an oxygen atom by CH₃O forming a highly vibrationally excited CH₃O^{*}/₂ radical. The subsequent fate of CH₃O^{*}/₂ is either decomposition to CH₃ + O₂ or isomerization to CH₂OOH⁺ followed by immediate fragmentation to yield CH₂O + OH. Collisional deactivation of CH₃O^{*}/₂ does not occur.

Whereas this picture explains the gross features of the reaction, any theoretical interpretation of e.g. the OH product yield requires more quantitative information on the variation of the potential energy along the reaction coordinate. Electronic ground state enthalpies of formation for reagents, intermediates, and products are summarized in Table 1, together with the values accepted here. Fig. 8 provides a corresponding graphical representation.

Whereas the thermochemistry of reagents and products and hence ΔH_R^0 of the overall reaction are well defined, there is considerable uncertainty as to ΔH_f^0 for CH₂OOH and the corresponding transition state of its formation from CH₃O₂. The latter is of extreme importance to the interpretation of the OH yield measurements. Based on an activation energy for the high temperature reaction

$$CH_3 + O_2 \rightarrow CH_2O + OH$$



Fig. 8 Energy correlation between reagents, intermediates and products for the reaction CH₃O + O. Absolute values and differences refer to standard enthalpies of formation at 298 K

Table 1 Summary of enthalpies of formation for hydrocarbon radical species and transition states and reaction enthalpies relevant to the reaction $CH_3O + O$ products

	$\Delta H_{1,298}^{0}/\text{kJ mol}^{-1}$		
Species	literature values	value accepted here	
CH ₃	146.9 [30]	146.9	
CH ₃ O	17.6 [31]	16.5	
	15.9 ± 0.8 [32]		
	16.7 ± 0.8 [33]		
	3 ± 4 [34]		
CH ₃ O ₂	17.6 [35]	17.6	
	23.8 [36]		
CH ₂ OOH	54 ± 10^{a})	65	
	69.8 [36]		
$\Delta H^{\ddagger}(CH_{3}O_{2} \rightarrow CH_{2}OOH)$	164 ± 20^{b})	180	
	205 [36]		
$CH_3O + O \rightarrow CH_3O_2$	$\Delta H_{\rm R, 298}$: -248.1 kJ/mol		
\rightarrow CH ₁ + O ₂	-119.0kJ/mol		
\rightarrow CH ₂ O + OH	- 335.3 kJ/mol		

^a) Estimated from group additivity rules [37].

^b) Estimated from intrinsic atom metathesis activation energy (42 kJ/mol) plus ring strain energy (104 kJ/mol) [35].

of $E_a \simeq 145 \text{ kJ/mol}$ the CH₃O₂ \rightarrow CH₂OOH isomerization barrier (ΔE_{iso}) was previously assumed to be ~ 250 kJ/mol [39] making OH formation essentially inaccessible from $CH_3O + O$. A recent re-determination of E_a , however, led to a much smaller value (41 kJ/mol [7]), inferring $\Delta E_{\rm iso} \sim$ 160 kJ/mol and $\Delta H_i^* \sim 177$ kJ/mol. This lower value is also expected from a simple estimate of ΔE_{iso} using the sum rule: intrinsic activation energy for H atom transfer ($\sim 42 \text{ kJ}/$ mol) + 4-member ring strain energy (104 kJ/mol) [38]. More importantly, independent confirmation of a low ΔH^{*}_{+} value came from two recent ab initio calculations [36, 37]. Whereas Melius [36], based on bond-additivity-corrected Moller-Plesset fourth order perturbation theory (BAC-MP4) obtained 205 kJ/mol for ΔH^* of the CH₃O₂ \rightarrow CH₂OOH transition state, a value of 223 kJ/mol was predicted by Kamiya et al. [37] using a lower order (MP3)

perturbation method. Due to unknown contributions of configuration interaction in a tight transition state the value of [37] was assumed to be an upper limit. For the present considerations a value for ΔH ^{*} of 180 kJ/mol, corresponding to an isomerization barrier of ~ 160 kJ/mol was adopted.

The reaction

$$CH_3O(^{2}E) + O(^{3}P) \rightarrow CH_3(^{2}A'') + O_2(^{3}\Sigma_g^{-})$$
(1 a)

is both spin and orbital symmetry allowed. The connecting adiabatic surface in C_s geometry is of character ²A" which is also the character of the electronic ground state of CH₃O₂. This surface does not, however, correlate with the products of channel (1 b) CH₂O(¹A₁) + OH(²\Pi). Since however the interaction of CH₃O(²E) + O(³P) in C_s geometry also gives rise to a surface of character A', there is an additional orbital symmetry allowed pathway for the reaction

$$CH_3O(^{2}E) + O(^{3}P) \rightarrow CH_2O(^{1}A_1) + OH(^{2}\Pi).$$
 (1b)

The intermediate CH_3O_2 state connecting with this surface is the excited ²A' state [37]. The $CH_3O_2 \rightarrow CH_2OOH$ cyclic transition state is of the same character [37]. As a consequence there is no orbital symmetry or spin restriction to either of these product channels. Moreover, since both surfaces (A' and A'') are probably strongly mixed at the high energies at which CH_3O_2 species are populated from CH_3O + O, we will for the following discussion neglect their separate existence and will treat both channels as to proceed adiabatically on one surface corresponding to ground state CH_3O_2 .

4. Theoretical Kinetic Considerations

As has been mentioned before reaction (1) can be assumed to be a barrierless scavenging process followed by unimolecular fragmentation or isomerization of the excited adduct. As a consequence the overall rate coefficient as well as the branching ratio should be predictable from statistical unimolecular rate theory.

Specific rate coefficients k(E, J) for the unimolecular dissociation of CH₃O₂ into the two channels CH₃ + O₂ and CH₃O + O were recently calculated by Cobos et al. [6] based on a simplified statistical adiabatic channel (SAC) model [40]. Although a slightly different looseness of the interaction in the vicinity of the two exits of the CH₃O₂ potential was assumed it was found that due to the energy difference k(E, J) for the CH₃ + O₂ channel is at least a factor of 100 larger than for the CH₃O + O channel. As a consequence the reaction CH₃O + O \rightarrow CH₃O^{*}₂ \rightarrow CH₃ + O₂ was predicted to proceed i) without appreciable redissociation of CH₃O^{*}₂ and ii) with a rate coefficient identical with the high pressure recombination rate coefficient for CH₃O + O \rightarrow CH₃O₂. An isomerization of CH₃O^{*}₂ to yield CH₂OOH was not considered.

The occurrence of the isomerization channel was however taken into account in two previous RRKM calculations [39, 41], designed to predict the branching ratio of the CH₃ + O₂ reaction at high temperatures. Whereas the results for the thermal rate coefficient of the CH₃O + O channel were in reasonable agreement, the grossly different assumptions made for the barrier height to isomerization between CH₃O₂ and CH₂OOH ($\Delta E_{iso} = 250$ kJ/mol; Hsu et al. [39]; $\Delta E_{iso} = 150$ kJ/mol; Reitelboim et al. [41]) led to correspondingly large differences in the prediction of the importance of the CH₂O + OH channel.

In view of this situation and because our studies are the first ones to provide quantitative measurements of the branching ratio for the reverse reaction at low temperatures RRKM-calculations with the aim i) to test the consistency with the above energy scheme and ii) to re-predict the high temperature branching ratio for $CH_3 + O_2$ deemed essential. For the following discussion the notation

$$CH_{3}O + O \xrightarrow[k_{-1}]{k_{1}} CH_{3}O_{2}^{*} \xrightarrow{k_{a}} CH_{3} + O_{2}$$
$$\xrightarrow{k_{b}} CH_{2}OOH^{*} \rightarrow CH_{2}O + OH$$

is used.

4.1. Specific Rate Coefficients:

Specific rate coefficients $k_i(E)$ for the fragmentation and isomerization of CH₃O^{*} into the various channels (i = -1, a, b) have been calculated from the usual expression [42]

 $k_{i}(E) = N_{i}^{+}(E_{i}^{+})/h \cdot \varrho(E)$

where $N_i^+(E_i^+)$ is the number of active states of the activated complex and $\varrho(E)$ is the density of states of the dissociating molecule.

In a first approximation we have used a fixed transition state configuration containing only vibrations as active modes. This is appropriate for tight activated complexes across strongly curved potential barriers, as for instance TS:b. For the two dissociating channels (TS: -1 and TS:a) we have also included angular momentum conservation on a rotational adiabatic potential of the form [42] $V_{\text{eff}}(J) = J(J+1) \hbar^2/2 \mu r^2 - Cr^{-6}$ for which the location of the potential maximum, $r^+ = (6 \ \mu C/J(J+1) \ \hbar^2)^{0.25}$, and hence of the transition state becomes J dependent. The effect of J conservation is to allow the flow of additional energy of the amount $\Delta E_J = J(J+1) \hbar^2/2\mu \left[(1/r^{+2}) - (1/r_0^2) \right]$ from adiabatic rotations into active modes upon expansion of the dissociating bond. As a consequence k(E, J) values are always larger than k(E) values for which angular momentum constraints are neglected. The number of states at active energy, $N_i^+(E_i^+)$, was obtained by direct counting at low energies, or else by the Whitten-Rabinovitch approximation. The vibrational frequencies of the activated complexes were mostly those of Hsu et al. [39]. All parameters used in this calculation are summarized in Table 2.

 Table 2

 Summary of parameters used in RRKM calculations for the fragmentation and isomerization channels of CH₃O₂

E _{oi} *)/ kJ mol ⁻¹	r^{+}/r_{0}^{b})	v(v ⁺)/cm ⁻¹ 2990, 2950, 2900, 1400(2), 1350, 1100, 960, 900(2), 450, 300°)		
_	_			
243	2.4 (J = 20) 1.7 (J = 36)	2950(3), 1380(3), 1200(2), 960, 100, 50 ⁴)		
122	2.3 (J = 20) 1.7 (J = 36)	2946(3), 1500, 1383(3), 960, 900, 270, 185°)		
160	-	2970(2), 2200, 1400(2), 1350, 1300, 960, 166(2)°)		
	E _{ol} *)/ kJ mol ⁻¹ - 243 122 160	$ \begin{array}{cccc} E_{oi}^{a}/r & r^{+}/r_{0}^{b} \\ \hline & & & r^{+}/r_{0}^{b} \\ \hline & & & & - \\ 243 & 2.4 & (J = 20) \\ & & & 1.7 & (J = 36) \\ 122 & 2.3 & (J = 20) \\ & & & 1.7 & (J = 36) \\ 160 & - \\ \end{array} $		

^a) The energy barrier between the ground state of CH_3O_2 and the activated complex of the designated channel (threshold energy) at 0 K.

^b) This is the relative expansion of the dissociating bond at potential maximum.

^c) These frequencies were obtained by Snelson, cited in Ref. [39].

⁽⁴⁾ The first 9 of these frequencies correspond approximately to the free CH₃O radical [20, 43]. They have been used in the RRKM calculation by Hsu et al. [39] in combination with two free internal rotations. For the present calculations two low frequencies (100 and 50 cm⁻¹) were added.

^e) Taken from Hsu et al. [39].

The results of calculated k(E) and k(E, J) curves for the various dissociation and isomerization channels of CH₃O₂ are presented in Fig. 9. Energies are counted relative to ΔH_{10}^0 of CH₃O₂. The difference between k(E) and k(E, J) curves is largest at low energies. With regard to the specific branching ratio $k_a(E)/k_b(E)$ for CH₃O²

at energies \geq 248 kJ/mol it can probably be entirely neglected in view of other (i.e. energetic) uncertainties.



Specific rate coefficients k(E) and k(E, J) for dissociation and isomerization of CH₃O₂ into the designated channels. The k(E, J) curves for J = 20 and 36 correspond to the maximum of the rotational populations at 298 K and 1000 K. E_{oi} = threshold energies at 0 K

4.2. Thermally Averaged Rate Coefficients:

a) Re-dissociation of CH₃O^{*}₂ and Branching Ratio for OH Formation

The scavenging of O atoms by CH_3O forms a chemically activated $CH_3O_2^*$ radical with an energy distribution function of [44]

$$f^*(E) = k_{-1}(E)\varrho(E)\exp(-E/RT)/\int_0^\infty k_{-1}(E)\varrho(E)\exp(-E/RT)dE.$$

From this the thermal rate coefficients for dissociation and isomerization $k_1^{(T)}$ can be obtained via

$$k_i^{(T)} = \int_0^\infty k_i(E) f^*(E) dE.$$

Using the k(E)-curves derived above we obtain at 298 K: $k_{-1} = 3.0 \cdot 10^7 \text{ s}^{-1}$, $k_a = 2.9 \cdot 10^{11} \text{ s}^{-1}$, and $k_b = 5.1 \cdot 10^{10} \text{ s}^{-1}$. This result infers that there is indeed a strong reactive flux from CH₃O^{*} in the forward direction; re-dissociation of CH₃O^{*} is comparatively unimportant. The branching ratio for OH formation is calculated to be

$$\varphi_{\rm OH} = k_{\rm b}/(k_{\rm a} + k_{\rm b}) = 0.15$$

in good agreement with the experimental result. As a consequence, the potential barrier of $\Delta E_{iso} = 160 \text{ kJ/mol}$ must be considered to be consistent with the present findings. Moreover, the absolute values of $k_{\rm a}$ and $k_{\rm b}$ indicate that for pressures up to ~ 10 bar collisional deactivation of CH₃O[‡] will be unimportant. These conclusions remain essentially unchanged even if J-conservative k(E, J) curves instead of simple k(E) curves are being used.

b) The Total Scavenging Rate Coefficient k_1

The rate coefficient for the overall scavenging process, k_1 , can be calculated from the thermal rate constant for the reverse dissociation of CH₃O₂ in the high pressure limit and involving the equilibrium constant; viz.

$$k_1(T) = K_1(T) \cdot \int_0^\infty k_{-1}(E) f(E) dE.$$

In here, f(E) in the distribution function for thermal CH₃O₂ given by $f(E) = \varrho(E) \cdot \exp(-E/RT)/Q_v$. Using the $k_{-1}(E)$ curve of Fig. 9 we obtain at 298 K $k_1 = 2.7 \cdot 10^{-11}$ cm³/s, in very satisfactory agreement with the experimental value, $k_1 = (2.5 \pm 0.7) \ 10^{-11} \ \text{cm}^3/\text{s}$. The quality of the computed k_1 -value, however, must not be overestimated since it is derived on the basis of a set of a "chosen" transition state properties. In fact if we improve the physical model by allowing for angular momentum conservation through calculation of $k_{-1}(T)$ from the expression

$$k_{-1}^{J}(T) = \int_{0}^{\infty} \sum_{J=0}^{\infty} k_{-1}(E,J) f(E,J) dE$$

which in a thermalized system reduces to $(Q_R^*/Q_R)k_-^{T}$, where Q_R^* and Q_R are the partition functions of the adiabatic rotations of the activated complex and the dissociating molecule, we obtain at 298 K $k_1^1 = 1.5 \cdot 10^{-10}$ cm³/s, a factor of five larger than obtained with the simple k(E)-curve. As a consequence the "vibrational looseness" of the activated complex would have to be reduced in order to obtain agreement of k_1^* with the experimental data.

The absolute value of k_1 has also recently been calculated by Cobos et al. [6] using the statistical-adiabatic-channel (SAC) model. This model makes rigorous account of rotational adiabaticity of various J states and uses no adjustable parameters except for a looseness parameter (α) of the CH₃O₂ potential surface near the exit to the dissociating channel. With $\alpha = 1.1$ Å⁻¹ $k_1 = 1.7 \cdot 10^{-11}$ cm³/s at 298 K was obtained, slightly lower than the present RRKM result but again in very satisfactory agreement with the experimental data.

The temperature dependence of k_1 can be derived in an analogeous way. The resulting values of k_1 , together with k_{-1} , K_1 from the present evaluation and the data calculated by Cobos et al. [6], are summarized in Table 3. As can be seen both methods predict a slight increase of k_1 with increasing temperature. The general agreement between the two approaches is maintained throughout the whole temperature region. It should be noted, however, that the present RRKM model also predicts a slight negative temperature dependence of k_1 below 500 K, corresponding to $E_A/R = -150$ K around 300 K.

Table 3 Calculated rate coefficients k_{-1} and k_1 for different temperatures

T/K k_{-1}/s^{-1} a)		<i>K</i> ₁ /cm ^{3 b})	$k_1/10^{-11} \text{ cm}^3 \text{ s}^{-1}$ SAC3 RRKM ^d		
-, ,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	,		(A)	(B)	
250	8.8 · 10 ⁻³⁷	3.4 · 10 ²⁵		3.0	
298	$1.3 \cdot 10^{-28}$	2.0 · 10 ¹⁷		2.7	15.0
300			1.7		
500	2.3 · 10 ⁻¹¹	1.1		2.6	
800			2.2		
1000	1.2 · 10 ²	$2.8 \cdot 10^{-13}$		3.3	10.0
1150	5.3 · 10 ³	$6.8 \cdot 10^{-15}$	2.6	3.6	
1300	1.0 · 10 ⁵	3.9 · 10 ⁻¹⁶	2.6	3.9	
1550	3.8 · 10 ⁶	$1.2 \cdot 10^{-17}$	2.9	4.4	
1800	5.2 · 107	9.6 · 10 ⁻¹⁹	3.0	5.0	
2300	1.8 · 10 ⁹	$3.4 \cdot 10^{-20}$	3.2	6.0	

^a) Thermal rate coefficient for the dissociation of CH₃O₂ into CH₃O + O.
 ^b) Equilibrium constant for CH₃O + O ⇒ CH₃O₂ as calculated on the basis of the thermochemical data of Burcat [45] but adjusted to give agreement with ΔH⁰_{1,298} (CH₃O₂) = 17.6 kJ/mol [35].

Statistical adiabatic channel model (Cobos et al. [6]) with α = 1.1 Å⁻¹.
 This work from simple k(E) curves (A) and for inclusion of J conservation, k(E, J), (B).

5. Comparison with Other Experimental Data and Implications for the High Temperature $CH_3 + O_2$ Reaction

The rate coefficient k_1 has to our knowledge not been determined before such that no data are available for direct comparison. However, the analogous reaction

$$OH + O \rightarrow HO_2^* \rightarrow H + O_2$$
 (i)

has been studied fairly extensively [1-3, 46] and some interesting comparison may be derived from these results.

At room temperature k_i has been determined as $(3.3 \pm 0.4) 10^{-11}$ cm³/s, only a factor of 1.3 larger than the rate coefficient for reaction (1). This must be considered as to be entirely consistent if we assume similar shapes of the HO/RO+O interaction potential. In this case the "loose rate constant" for recombination will be dominated by the term $k_{\rm rec}^{\rm cose} \simeq (kT/h) (h^2/2\pi\mu kT)^{3/2}$ [6, 47], i.e. show a reduced mass dependence of power -3/2, whereupon k_i/k_1 is predicted as 1.44. Moreover, temperature dependent studies of k_i at both low [2, 3] and high temperatures (as inferred from the reverse H + O₂ reaction [46]) indicate a negative temperature dependence, with $T^{-0.5}$ [3] near 300 K and decreasing by a factor of 2 up to 2000 K in accordance with the $k_{\rm res}^{\rm hose}$ expression. Surprisingly, however, the same does not seem to be the case for the CH₃O + O reaction.

Reaction (1) is the reverse of the high temperature combustion reaction

$$CH_3 + O_2 \rightleftharpoons CH_3O_2^* \rightarrow CH_3O + O.$$
 (-1a)

However a direct comparison with results from such studies is complicated since the interaction of CH_3 radicals with O_2 has a second channel, viz.

$$CH_3 + O_2 \rightleftharpoons CH_3O_2^* \rightarrow CH_2OOH^* \rightarrow CH_2O + OH$$

(-1b)

As a consequence rate measurements of either CH_3 decay or product rise can only provide the sum of both rate coefficients unless accompanied by branching ratio measurements.

There have been four shock tube studies in which measurements of k_{-1a} have been performed. From CO flame band emission studies in CH4 oxidation Brabbs and Brokaw [48] deduced $k_{-1a} = 4 \cdot 10^{-11} \exp(-14500 \text{ K/T}) \text{ cm}^3/\text{s}$, and concluded that channel (-1b) was unimportant. The same conclusion with regards to the relative importance of (-1b) was also drawn in two more recent studies using CO laser absorption $(k_{-1a} = 1.7 \cdot 10^{-10} \exp(-15500 \text{ K/T}) \text{ cm}^3/\text{s};$ Hsu et al. [39]) and atomic resonance absorption spectrometry $(k_{-1a} = 1.2 \cdot 10^{-11} \exp(-12910 \text{ K}/T) \text{ cm}^3/\text{s}, k_{-1b} =$ $8.3 \cdot 10^{-11} \exp(-17400 \text{ K/T})$; Bhaskaran et al. [8]), respectively. A value for k_{-1a} comparable with the former three $(k_{-1a} = 3.7 \cdot 10^{-10} \exp(-16960 \text{ K/T}) \text{ cm}^3/\text{s})$ was also reported in the most recent study by Saito et al. [7] using atomic and OH radical resonance absorption. However, in contrast to [8, 39, 48] the channel (-1b) was found to dominate in the $T \leq 1500$ K regime due to a relatively low activation barrier ($k_{-1b} = 5.3 \cdot 10^{-13} \exp(-4530 \text{ K/T}) \text{ cm}^3$ s^{-1} [7]) for this route.

A comparison of all reported k_{-1a} measurements, after conversion to k_1 using a statistically derived expression for the equilibrium constant K_{1a} , with the result from the present work is shown in Fig. 10. As can be seen, the experimental high temperature data show a relatively large scatter, both in absolute values as well as the size and sign of their temperature dependence. Whereas, however, the data of Bhaskaran et al. [8] can be considered consistent with the present work and its theoretical extrapolation, all other results are larger by more than half an order of magnitude, clearly incompatible with the present findings. Since the reported k_{-1a} -data depend on both, the overall rate coefficient $(k_{-1a} + k_{-1b})$ and the branching ratio, too large k_{-1a} -values could in fact easily result from overestimating the relative importance of channel (-1a).



Fig. 10

Arrhenius representation of the rate coefficient k_1 . All high temperature results are from measurements of the reverse $CH_3 + O_2 \rightarrow CH_3O + O$ reaction (see text): SIKI: Saito et al. [7], HSCGL: Hsu et al. [39]. BB: Brabbs, Brokaw [48], BFJ: Bhaskaran et al. [8]. O: this work; the curves are theoretical predictions based on RRKM (this work) and SAC (Cobos et al. [6]) theory

As has been mentioned above there is considerable uncertainty in the literature with regards to the relative importance of channels (-1a) and (-1b) of the CH₃ + O₂ reaction at high temperatures due to the grossly varying assumptions of the CH₃O₂ \rightarrow CH₂OOH isomerization barrier (ΔE_{iso}). The result from the present work, in particular the OH yield measurements, have confined ΔE_{iso} to a value near 160 kJ/mol, which corresponds to an activation energy for reaction (-1b) of ~ 33 kJ/mol, consistent with the recent measurements of Saito et al. [7]. Moreover, by using the detailed mechanism

$$CH_3 + O_2 \rightleftharpoons CH_3O_2^* \rightarrow CH_3O + O$$
 (-1a)

$$\rightarrow CH_2OOH^* \rightarrow CH_2O + OH \qquad (-1b)$$

we can calculate the individual rate coefficients k_{-1a} and k_{-1b} from the expressions $k_{-1a}(T) = K_{-1}(T) \cdot k_{-1}(T)$ and $k_{-1b}(T) = K_{-1}(T) \cdot k_b(T)$. In here $K_{-1}(T)$ is the equilibrium constant for CH₃ + O₂ \rightleftharpoons CH₃O₂ and $k_{-1}(T)$ and $k_b(T)$ are the averaged rate coefficients for the dissociation and isomerization of thermal CH₃O₂. Using the thermochemical data of Burcat [45] to calculate $K_{-1}(T)$ and with $k_{-1}(T)$, $k_b(T)$ as obtained from the corresponding k(E) curves we obtain

$$k_{-1a}(T) = 1.0 \cdot 10^{-11} \exp(-14360 \text{ K/T}) \text{ cm}^3/\text{s}$$

and

$$k_{-1b}(T) = 5.6 \cdot 10^{-13} \exp(-4500 \text{ K/T}) \text{ cm}^3/\text{s}.$$

Hence, the $CH_2O + OH$ channel (-1b) is predicted to occur with low activation energy and, despite its small preexponential factor, to dominate over the $CH_3O + O$ channel (-1a) at all temperatures below 3000 K. This is in contrast to most previous conclusions except those of Saito et al. [7].

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The One-Dimensional Band Structure of (Tetrazaporphyrinato)iron(II)

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Chemical Bond / Materials Properties / Polymers / Quantum Mechanics / Wave Functions

The one-dimensional (1 D) band structure of (tetrazaporphyrinato)Fe(II) (Fe(tp)) has been investigated in the framework of a semiempirical Hartree-Fock (HF) self-consistent-field (SCF) crystal orbital (CO) approach. The calculated ground state of this 1D solid is of spatial B_{1g} symmetry. This configuration in the 3d⁶ material is determined by two half-filled bands of the insulating Mott-Hubbard-type where all CO microstates in the first Brillouin zone are singly occupied. Both Mott-Hubbard dispersions are strongly metal-centered, i.e. $3d_{z^2}$ and $3d_{xy}$. The width of the σ -type ($3d_{z^2}$) band amounts to ca. 0.21 eV while a nearly dispersionless band is predicted for the δ interaction ($3d_{xy}$). These two half-filled 3d bands lie below the Fermi energy, while the highest occupied states are of ligand π character. The band structure properties of the Mott-Hubbard insulator have been determined by means of a grand canonical (GC) averaging procedure which corresponds to an approximate spin-restricted mean-field description. The HF SCF energy of the "spin-paired" 3d⁶ configuration is predicted to have a higher energy. Therefore, an "aufbau" principle is not valid in the ground state of this 1D material. The implications of this ground state on the magnetic properties of Fe(tp) are also discussed.

I. Introduction

One-dimensional (1D) materials that are formed by metallomacrocycles have been studied extensively in the past years as a result of their interesting optical, magnetic and charge carrier properties [1-6]. The conductivities of partially oxidized modifications are highly anisotropic; the corresponding systems belong to the class of incoherent 1D solids [7]. In Ni(II) porphyrines a strong interrelation between the stacking geometry and important solid-state properties has been observed [8-10]. The injected charge carriers in Ni(II) metallomacrocycles with short interring separations are of a spatially uncorrelated Bloch-electron type. The atomic limit of the Hubbard Hamiltonian is realized in (porphyrinato)Ni(II) systems with larger separations between the molecular building units [10]. The primitive translation vectors in the Ni(II) metallomacrocycles are found in an interval between ca. 3.2 Å to 3.8 Å.

Porphyrines (p), phthalocyanines (pc), and tetrazaporphyrines (tp) are frequently employed π ligands in 1D organometallic systems. Several of the corresponding Ni(II) systems have been synthesized since the early eighties [8-10]. In the absence of partial oxidation these 1D solids are only weak semiconductors. The partial electron removal is a prerequisite for the formation of incompletely filled energy bands. The one-dimensional band structures of Ni(p), Ni(pc) and Ni(tp), respectively, have been studied in some detail:

- (i) by a semiempirical crystal orbital (CO) approach in the Hartree-Fock (HF) self-consistent-field (SCF) formalism [11-14], and
- (ii) by a simplified X_{α} multiple scattering model [15]. The effect of intermolecular coupling in the latter approach has been approximated via an estimated non-self-consistent model potential. Both numerical methods allowed for the reproduction and rationalization of experimental findings (i.e. classification of the nature of injected carriers, magnetic behaviour, strength of the electronic correlations, estimation of antiferromagnetic exchange interactions).

The solid-state properties of partially oxidized Co(pc) [16] and Fe(pc) [17] (see Fig. 1) have been reported in two recent contributions. Experimental observations in the Co

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