

Kinetics of the Reaction between Methoxyl Radicals and Hydrogen Atoms

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The kinetics of the reaction of CH_3O with H have been studied under pseudo-first-order conditions with an excess of H using an isothermal discharge-flow reactor. Three different CH_3O sources were used and the decay of $[\text{CH}_3\text{O}]$ was monitored by laser-induced fluorescence (LIF) as a function of $[\text{H}]$. A second-order rate coefficient of $(2.0 \pm 0.6) \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ was determined for reaction $\text{CH}_3\text{O} + \text{H} \rightarrow \text{products}$ at room temperature and a slight positive temperature dependence was observed between 298 and 490 K. Formaldehyde formation was found to be the dominant reaction path ($81 \pm 12\%$). Further identified products were OH ($7 \pm 3\%$) and methanol (a few percent) which were produced by the decomposition and stabilization, respectively, of the initially formed bound adduct.

Methanol has a considerable significance because of its possible role as an alternative fuel.¹ The intermediate species formed in the combustion of methanol, for instance the isomeric radicals CH_3O and CH_2OH , also play a significant role in the combustion of other alcohols and hydrocarbons.² Therefore the knowledge of the kinetics of reactions of CH_3O and CH_2OH radicals with other transient or stable species of the combustion systems are of particular interest.

The significance of accurate rate measurements can be well illustrated by referring to the controversy which arose on the origin of CH_3 formation in methanol pyrolysis and oxidation.³ In the light of recent direct studies⁴ of the $\text{OH} + \text{CH}_3\text{OH}$ reaction, which predict that CH_3O and CH_2OH radicals are formed with comparable rates at high temperatures, the reactions of $\text{CH}_3\text{O} + \text{H} \rightarrow \text{CH}_3 + \text{OH}$ and $\text{CH}_2\text{OH} + \text{H} \rightarrow \text{CH}_3 + \text{OH}$ must now be considered as significant sources of methyl radical in methanol combustion.

In this paper we report on the direct kinetic investigations of the reaction



in the temperature range 298–490 K and on the study of the branching behaviour of the various product channels. Only one previous study of reaction of methoxyl radicals with hydrogen atoms has been carried out⁵ which used the fast flow technique combined with mass-spectrometric analysis. In the present work we studied reaction (1) in an isothermal discharge-flow reactor and monitored the CH_3O concentration decay by LIF. Product channels and branching ratios were investigated using LIF (and in one case GC) for the identification and the build-up of the reaction products.

Experimental

The main part of the discharge flow–LIF apparatus was the flow reactor with a movable inlet (Fig. 1). The electrically heated tubular reactor was made of fused silica with a Teflon surface coating in order to reduce the loss of radicals on the reactor walls. Flow tubes of 26 and 40 mm internal diameter were used. The main carrier gas was helium, and flow rates for all gases were regulated by calibrated Tylan mass-flow controllers.

Hydrogen atoms were generated in a microwave discharge and the H-atom flow entered the reactor through a side-arm. Methoxyl radicals were produced inside the movable coaxial

double injector tube. In this way a constant initial methoxyl concentration could be used in a series of experiments, independent of the position of the movable inlet.

In order to check the reliability of the kinetic results, three different methoxyl radical sources were used. In most experiments the well known $\text{F} + \text{CH}_3\text{OH}$ reaction served to produce the methoxyl radicals. The F atoms were generated in a microwave discharge of F_2 in an excess of He in an Al_2O_3 discharge tube. Often the reaction $\text{CH}_3 + \text{NO}_2 \rightarrow \text{CH}_3\text{O} + \text{NO}$ was applied as the methoxyl source (this case is indicated in Fig. 1). The F atoms obtained in a microwave discharge reacted in the middle tube with CH_4 to give CH_3 radicals, which were subsequently oxidized by NO_2 in the outer jacket of the movable inlet. Finally, the third methoxyl radical source was the fast reaction between F

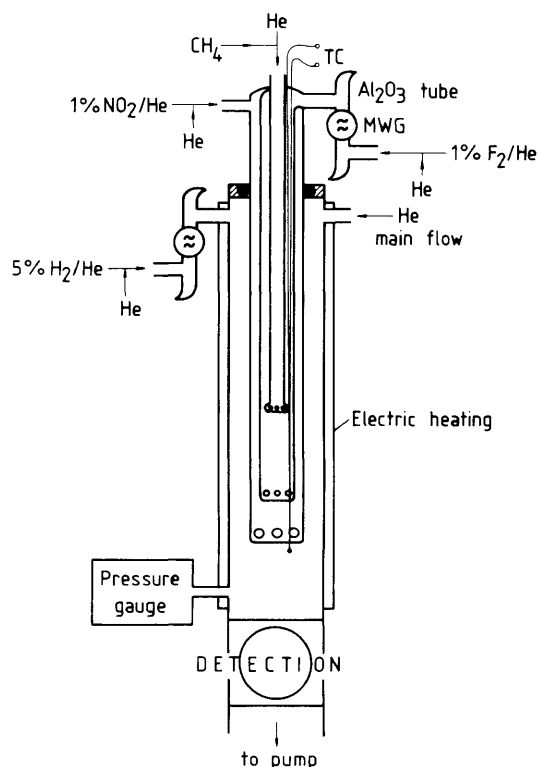


Fig. 1 Schematic representation of the fast-flow system

atom and CH_3ONO which we found to be a convenient clean source of CH_3O . (A more detailed description and comparison of the CH_3O radical sources will be published elsewhere.⁶)

The kinetics of reaction (1) were studied by monitoring $[\text{CH}_3\text{O}]$ decay in excess of H by means of fluorescence spectroscopy. The fluorescence excitation spectrum of CH_3O as obtained in the $\text{F} + \text{CH}_3\text{OH}$ reaction is shown in Fig. 2 and similar CH_3O spectra were recorded with the two other radical sources. The excitation wavelength of 292.8 nm obtained from a Lambda Physik EMG 101 excimer laser pumped frequency-doubled dye laser is assigned⁷ to the $\text{A}^2\text{A}_1(v_3 = 4) \leftarrow \text{X}^2\text{E}(v_3 = 0)$ transition. LIF was used also for the detection and for monitoring of product formation (i.e. for OH and CH_2O formation). Fluorescence of OH was excited at 308.2 nm in the P_1^1 line of the $\text{A}^2\Sigma^+ \leftarrow \text{X}^2\Pi$ transition.⁸ Moreover, CH_2O fluorescence was excited at 353.2 nm (DMQ dye) in the 4_0^1 band of the $\tilde{\text{A}}^1\text{A}_2 \leftarrow \tilde{\text{X}}^1\text{A}_1$ transition.⁹

A scheme of the detection system is shown in Fig. 3. In the detection of CH_3O , the induced fluorescence was collected via a filter system (consisting of a 290 nm cut-off filter and a broad bandpass filter UG 11) onto a XP-2020Q photomultiplier. The multiplier signal was preamplified and measured by means of a gated boxcar integrator. When monitoring LIF from the product species, different filter combinations were used: a 307 nm interference filter for OH, a 370 nm cut-off filter and a combination of BG 12 + WG 2 glass filters for CH_2O .

Absolute calibration of the LIF intensities had to be carried out in order to determine product yields. These were done before and after each experiment. Absolute calibration for OH had been carried out by producing known hydroxyl radical concentration via reaction $\text{H} + \text{NO}_2$ in a system where known $[\text{NO}_2]$ was created in the presence of an excess of H. Absolute calibration for CH_3O had been obtained by producing a known CH_3O concentration via reaction $\text{CH}_3 + \text{NO}_2$ in a system with known $[\text{NO}_2]$ and excess of CH_3 . In case of formaldehyde, calibration had been made with fresh gas mixtures containing 1% CH_2O in He. The mixture was prepared manometrically and the CH_2O content was checked by the chromotropic acid method. The H-atom concentration was determined by observing the equivalence point in the H-atom titration with NO_2 .

The detection limits (defined as the species concentration corresponding to a signal-to-noise ratio of 1) were: 1×10^9

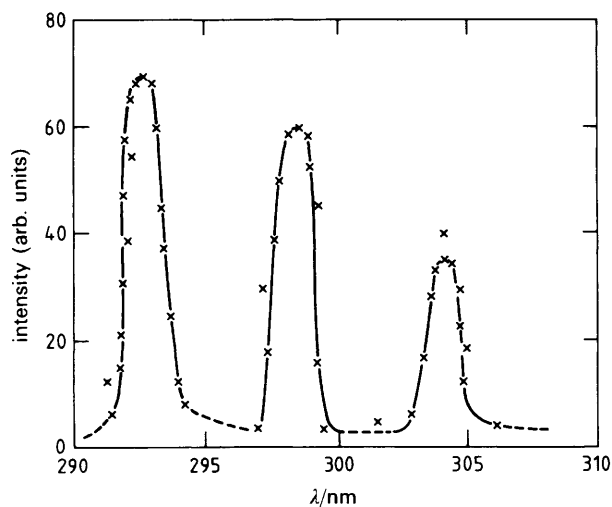


Fig. 2 Fluorescence excitation spectrum of CH_3O radical as obtained in the $\text{F} + \text{CH}_3\text{OH}$ reaction

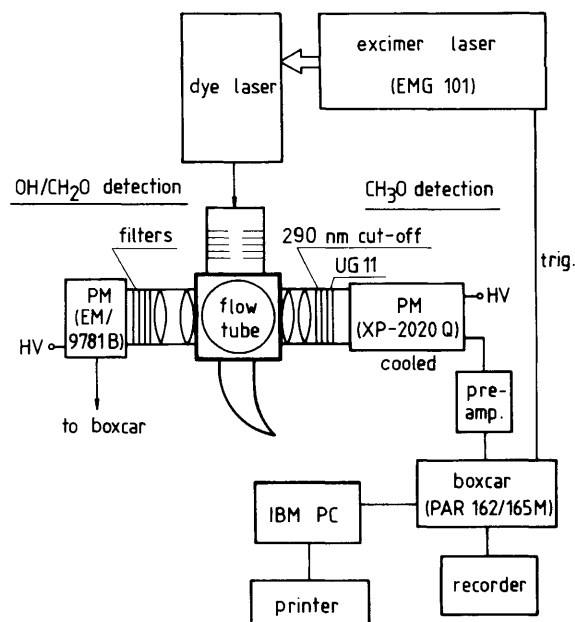


Fig. 3 Diagram of the detection system

cm^{-3} for CH_3O , $3 \times 10^7 \text{ cm}^{-3}$ for OH and $5 \times 10^{10} \text{ cm}^{-3}$ for CH_2O .

For methanol yield determination, condensable gases were trapped from 1% of the gas stream at liquid-nitrogen temperature; the trap was located between the detector and the pump. CH_3OH determination was made by GC.

The helium carrier gas was of Linde 4.6 quality and entered the reactor through silica gel traps cooled to liquid-nitrogen temperature. Methyl nitrite was obtained from methanol with nitrous acid. Gases were purified by sending them through cooled adsorbents, while purification of liquids was made by trap-to-trap vacuum distillation.

Results and Discussion

This study was carried out with two major objectives. First, experiments were performed to obtain the overall rate coefficient for reaction (1) as a function of temperature. Secondly, product formation was studied in order to identify the various reaction channels in reaction $\text{CH}_3\text{O} + \text{H}$ and to obtain the corresponding branching ratios.

Rate Coefficient of the Overall Reaction

The kinetics of reaction (1) was studied under pseudo-first-order conditions with at least nine-times excess of $[\text{H}]$. The methoxyl radical concentration was *ca.* $8 \times 10^{-13} \text{ mol cm}^{-3}$. The overall pressure in the reactor was between 1.7 and 4.0 mbar and the flow velocity of the helium carrier gas varied from 10 to 50 m s^{-1} .

Methoxyl LIF signals were measured as a function of reaction time, using the so called 'on-off' technique. Typical first-order decay plots at room temperature and different hydrogen-atom concentrations are presented in Fig. 4. The slope obtained with the H flow off gave the rate coefficient of $k_w = 30 \text{ s}^{-1}$ for the wall reaction of CH_3O . The semilogarithmic plots of $\ln(S_{\text{H on}}/S_{\text{H off}})$ vs. reaction time provided the pseudo-first-order rate coefficient, $k'_1 = k_1[\text{H}]$. The k'_1 values were corrected¹⁰ for diffusion and Poiseuille flow and were converted into bimolecular rate coefficients by the known H-atom concentrations or k_1 values were obtained from plots of k'_1 vs. $[\text{H}]$ (Fig. 5). A good straight line with a zero intercept can be fitted to the experimental points. Second-order

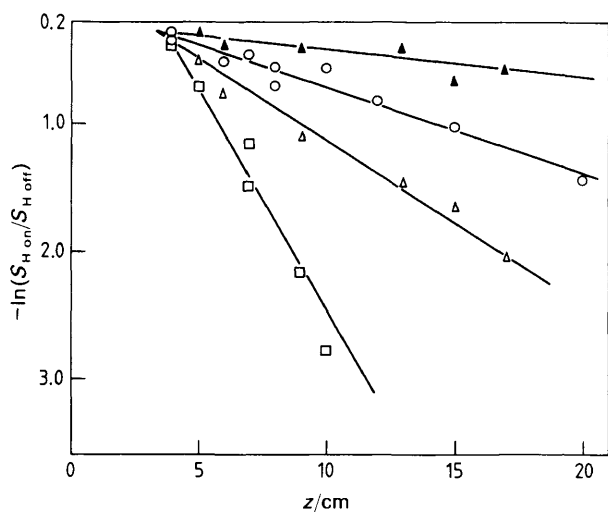


Fig. 4 CH_3O decay plots at room temperature. z is the length of the reaction zone, while S_{on} and S_{off} stand for the CH_3O LIF signals with H-atom flow on and off, respectively. \blacktriangle , H off; \circ , $[\text{H}] = 3.5 \times 10^{-12} \text{ mol cm}^{-3}$; \triangle , $[\text{H}] = 10.5 \times 10^{-12} \text{ mol cm}^{-3}$; \square , $[\text{H}] = 19.4 \times 10^{-12} \text{ mol cm}^{-3}$

rate coefficients derived from such plots are given in Table 1, together with other kinetic parameters for the overall reaction (1).

Surveying the results listed in Table 1, it should be noted that these data were obtained under wide experimental conditions. For instance, in the k_1 determinations indicated in the first four lines, three different methoxyl radical sources and two reactors with different internal diameters were used. The invariance of the k_1 values from the experimental conditions and reactant concentrations demonstrates the consistency of the kinetic results. The average value for the

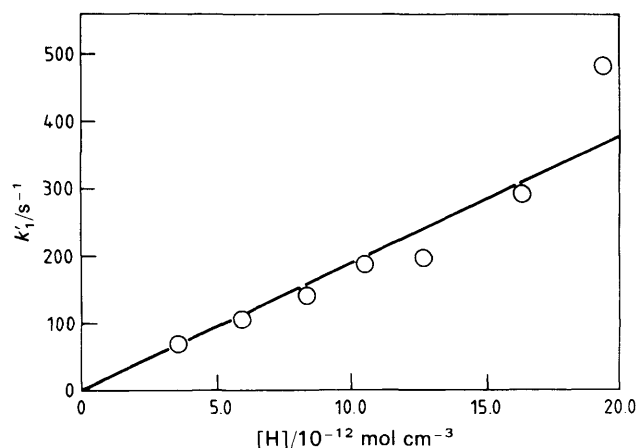


Fig. 5 Plot of pseudo-first-order rate coefficient, $k_1' = k_1[\text{H}]$, vs. H-atom concentration at room temperature

room-temperature second-order rate coefficients is

$$k_1 = (2.0 \pm 0.6) \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

This agrees with the only existing literature value for the reaction ($2 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) which was obtained by Hoyermann *et al.*⁵ also in fast-flow studies but using mass-spectrometric detection.

Rate coefficients obtained in the 298–490 K temperature range are presented as a function of temperature in Fig. 6. The points with error bars indicate multiple determinations and the lengths of the bars represent 2σ errors. Circles, squares and triangles refer to the $\text{F} + \text{CH}_3\text{OH}$, $\text{CH}_3 + \text{NO}_2$ and $\text{F} + \text{CH}_3\text{ONO}$ methoxyl sources, respectively. It is clear that the rate parameters do not depend on the experimental conditions in the temperature range studied. Although there is considerable uncertainty in the data, a small increase of k_1 with increasing temperature can be observed. If this temperature dependence is expressed in the form of the n th power of T , i.e. $k \propto T^n$, then a value of $n = 0.7 \pm 0.4$ corresponding to an activation energy of $E = 2.5 \pm 1.5 \text{ kJ mol}^{-1}$ can be estimated.

Product Channels and Branching Ratios

Detection of primary products of CH_3O reaction has been attempted by searching for LIF signals emitted by possible reaction products. As an additional check of the identification the laser-excitation spectra of the species detected were compared with literature data. Identification of the primary products and determination of the product branching ratios were made at room temperature under the same experimental conditions as those used in the determination of the k_1 rate parameters (see above).

In the study of CH_2O formation, reactions $\text{F} + \text{CH}_3\text{ONO}$ and $\text{CH}_3 + \text{NO}_2$ were used as methoxyl radical sources.

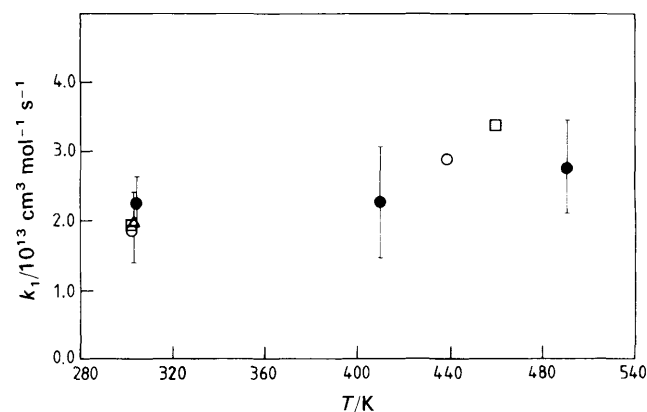


Fig. 6 Temperature dependence of the overall rate coefficient k_1 . CH_3O sources: $\text{F} + \text{CH}_3\text{OH}$ (\circ), $\text{CH}_3 + \text{NO}_2$ (\square) and $\text{F} + \text{CH}_3\text{ONO}$ (\triangle). Empty and filled symbols refer to the 40 mm and 26 mm i.d. reactors, respectively

Table 1 Kinetic results for reaction $\text{CH}_3\text{O} + \text{H} \rightarrow \text{products}$

T/K	CH_3O source	reactor i.d./mm	no. of runs	$[\text{H}]/10^{-12} \text{ mol cm}^{-3}$	$k_1/10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
303 ± 3	$\text{F} + \text{CH}_3\text{OH}$	40	7	3.5 – 19.4	1.9 ± 0.5
303 ± 3	$\text{F} + \text{CH}_3\text{OH}$	26	5	9.1 – 26.5	2.3 ± 0.4
299	$\text{CH}_3 + \text{NO}_2$	40	1	5.2	1.9
300	$\text{F} + \text{CH}_3\text{ONO}$	40	1	6.1	1.9
410 ± 4	$\text{F} + \text{CH}_3\text{OH}$	26	4	5.4 – 11.1	2.3 ± 0.8
438	$\text{F} + \text{CH}_3\text{OH}$	40	1	4.0	2.9
458	$\text{CH}_3 + \text{NO}_2$	40	1	3.6	3.4
490 ± 4	$\text{F} + \text{CH}_3\text{OH}$	26	4	2.3 – 23.1	2.8 ± 0.7

Reaction $F + CH_3OH$ was not used because of the possibility of an additional CH_2O production route *via* CH_2OH radicals. The LIF signal observed with 353.2 nm excitation (≥ 2 mJ per flash) was identified as induced CH_2O fluorescence. The excitation LIF spectrum taken in the 350–359 nm range was in accordance with that reported for CH_2O by Miller and Lee.⁹ Thus, it can be concluded that one reaction channel leads to $CH_2O + H_2$ formation.

The branching ratio for the reaction channel of formaldehyde production has been derived from sets of experiments in which the time profiles of $[CH_3O]$ decay and $[CH_2O]$ build-up were determined (Fig. 7). As expected, the CH_3O concentration decreased and the CH_2O concentration increased, at least up to *ca.* 10 ms. In this series of experiments, as well as in other similar experiments, formaldehyde concentration appeared to decrease at longer reaction times. The decrease may be the result of secondary reactions which occurred between CH_2O and the reactants. Nevertheless, from the first part of the profile one can obtain an initial rate of CH_2O formation and from the comparison of this rate with the initial consumption rate of CH_3O one can estimate the branching ratio for CH_2O production. From the results presented in Fig. 7 and from four other similar sets of experiments one obtains that $CH_2O + H_2$ formation is the major reaction route which accounts for $81 \pm 12\%$ of the reaction between CH_3O and H at room temperature. This conclusion is in good agreement with the results of the Göttingen group,⁵ who estimated the contribution of CH_2O formation to be *ca.* 75% in the reaction of H with CH_3O/CH_2OH .

Similar investigations of the OH-formation route were carried out using $F + CH_3ONO$ and $F + CH_3OH$ as the CH_3O source. The OH radical was detected by the LIF signal generated with 308.2 nm laser flash excitation (≤ 0.1 mJ per flash). A check of the identification was obtained from the excitation LIF spectrum taken in the 307.5–308.5 nm range which agreed with that reported⁸ for OH. Identification of OH as a reaction product can be taken as an evidence that there is a reaction channel which leads to $CH_3 + OH$ formation. One part of CH_3 is expected to be converted into CH_4 , although attempts to detect the small methane quantities by GC were unsuccessful.

The branching ratio for the $CH_3 + OH$ channel was again derived from the concentration *vs.* time profiles of the CH_3O reactant decay and of the product OH build-up. Such profiles

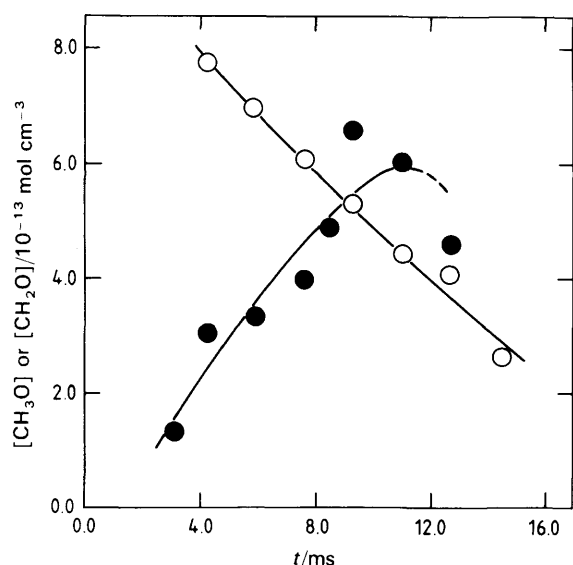


Fig. 7 Time profiles of $[CH_3O]$ decay and $[CH_2O]$ build-up. CH_3O source: $F + CH_3ONO$. O, CH_3O ; ●, CH_2O

obtained with $F + CH_3ONO$ radical source at room temperature are presented in Fig. 8. The OH concentration is seen to increase with increasing reaction time in the first time-period of the reaction, however, this tendency changes and a decrease of $[OH]$ occurs after *ca.* 7 ms. This decrease of $[OH]$ is obviously caused by secondary reactions, probably by the reaction of the reactive OH radical with the CH_3ONO radical source. From the OH concentration profile measured at longer reaction times, an empirical correction for the perturbation caused by secondary reactions can be estimated. Correcting in this way the first part of the curve, an initial rate for the OH-radical formation is obtained which compared with the initial rate of CH_3O consumption yields the required branching ratio for OH formation. Thus, we determined $7 \pm 3\%$ for the contribution of the $CH_3 + OH$ channel in the $CH_3O + H$ reaction. There is no experimental value available in the literature for comparison.

Another possible reaction channel may supply products $^1CH_2 + H_2O$. In principle, the detection of this reaction route could be carried out by observing the singlet methylene LIF at 590.7 nm excitation wavelength. This has, however, not been attempted because the consumption of 1CH_2 in secondary reactions (first of all by inter-system crossing to 3CH_2) is very rapid which makes the study of 1CH_2 formation by the fast-flow technique impossible. Thus, we are confined to estimate the branching ratio for the $^1CH_2 + H_2O$ channel on the basis of mass-balance considerations (see below).

Finally, the reaction route that yields the combination product CH_3OH has to be considered. As mentioned in the Experimental section, CH_3OH yields were determined from samples trapped out from the gas stream behind the detector block. GC analyses showed definitely the formation of CH_3OH , with no indication of other reaction products. An accurate CH_3OH yield could not, however, be determined for a number of reasons: (i) the small amount of CH_3OH to be analysed; (ii) possible trapping loss; (iii) the relatively high background correction, determined under identical conditions but with the H_2 flow turned off. On the basis of the results of three runs (two with $CH_3 + NO_2$ and one with $F + CH_3ONO$ radical sources) one may assess that 1–7% of the $CH_3O + H$ reaction gives the stabilization product CH_3OH at 3 mbar overall pressure. This yield compares favourably with the 4% estimated by Hoyermann *et al.*⁵ for the formation of CH_3OH in the reaction of H with CH_3O/CH_2OH .

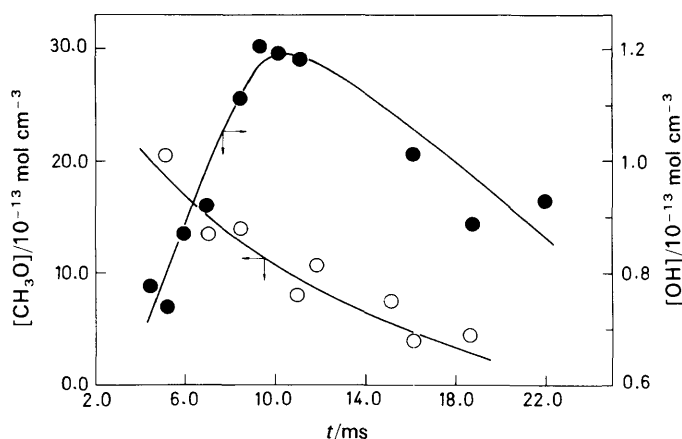


Fig. 8 Time profiles of $[CH_3O]$ decay and $[OH]$ build-up. CH_3O source: $F + CH_3ONO$. O, CH_3O ; ●, OH

Table 2 Reaction channels for CH₃O + H together with reaction enthalpies and branching ratios

no.	reaction	$\Delta H_{298}^{\circ}/\text{kJ mol}^{-1}$	ρ
(2)	CH ₃ O + H → CH ₂ O + H ₂	-344	0.81 ± 0.12
(3a)	→ CH ₃ OH* \xrightarrow{M} CH ₃ OH	-437	0.04 ± 0.03
(3b)	→ CH ₃ OH* → CH ₃ + OH	-51	0.07 ± 0.03
(3c)	→ CH ₃ OH* → CH ₂ OH + H	-44	ca. 0.02 ^a
(3d)	→ CH ₃ OH* → CH ₃ O + H	0	ca. 0.01 ^a
(3e)	→ CH ₃ OH* → ¹ CH ₂ + H ₂ O	-47	≤ 0.05
(3f)	→ CH ₃ OH* → CH ₂ O + H ₂	-344	< 0.01 ^a

^a For source see text.

Reaction Mechanism

Methoxyl radicals and hydrogen atoms may react in a number of ways; the more probable ones are summarized in Table 2, together with literature data¹¹ for the reaction enthalpies (ΔH_{298}°) and branching ratios ($\rho_i = k_i/\Sigma k_i$). The latter were obtained in this work except where otherwise indicated. The errors shown for ρ are estimated values selected basically on the ground of the experimentally determined statistical errors.

The main primary steps, which take place when CH₃O and H interact, are disproportionation yielding CH₂O + H₂ and combination producing an energized methanol molecule, CH₃OH*, with 437 kJ mol⁻¹ excess energy. The latter can subsequently undergo a number of reactions, as represented in Table 2. Competition between direct hydrogen-atom abstraction and indirect reaction *via* a complex which then rearranges to products is not unusual among gas-phase radical-radical processes.¹²

The study of product formation has shown CH₂O + H₂ formation to be the dominant reaction path. However, at least two possible mechanisms of CH₂O + H₂ formation have to be considered: one is direct disproportionation of CH₃O and H, while the other is an indirect way occurring through the energized complex CH₃OH*. On the basis of arguments enumerated below, we believe that disproportionation is the predominant mode of formaldehyde formation: (i) an *ab initio* study¹³ of the H₄CO potential-energy surface showed that elimination of molecular H₂ from CH₃OH occurs with large activation energy which makes this process slow compared to other reactions; (ii) a crossed molecular beam study¹⁴ of the reaction ¹O + CH₄ (which is known to proceed principally *via* CH₃OH* complex), indicated that molecular H₂ elimination from vibrationally excited methanol is of very minor importance compared to H-atom elimination; (iii) the small positive activation energy obtained in this work for the overall reaction CH₃O + H is in accordance with the suggestion that the formation of CH₂O (*i.e.* the major product) occurs by disproportionation. Thus, we conclude that CH₂O + H₂ are formed in the radical-radical process (2) rather than *via* CH₃OH* by molecular H₂ elimination [step (3f)].

Apart from disproportionation reaction (2), all other reactions occur *via* vibrationally excited CH₃OH. Recently, Dean and Westmoreland¹⁵ analysed the kinetics of chemically activated molecules (including CH₃OH*) formed by CH₃ radical reactions. The QRRK analysis concluded that the role of these reactions changes considerably with pressure. This is partly because of the collisional stabilization process. At the low pressures used in this study (1.7–4.0 mbar), collisional stabilization of CH₃OH* in reaction (3a) is relatively less important. We found C–O bond fission reaction (3b) to be the major reaction of CH₃OH*. Similar findings were made by Hack *et al.*¹⁶ in the investigation of the ¹CH₂ + H₂O reaction and by Satyapal *et al.*¹⁷ in the study of the

¹O + CH₄ reaction, both of which are believed to proceed mainly *via* CH₃OH* complexes.

We could not obtain experimental information on the H-atom elimination reactions (3c) and (3d). However, it has been found¹⁷ in the investigation of reaction ¹O + CH₄ that the yield of H elimination from CH₃OH* is 0.25. Since the contribution of other channels was assumed to be negligible, a yield of 0.75 was obtained for the dissociation of the complex into CH₃ + OH. On this basis we can estimate that H-atom elimination from CH₃OH* accounts for *ca.* 2–5% of reaction CH₃O + H in our system. Taking into account the thermochemistry of reactions (3c) and (3d), the branching ratios given in Table 2 for ρ_{3c} and ρ_{3d} were obtained.

Finally, a rough estimate for the yield of ¹CH₂ + H₂O formation can be made on the basis of mass-balance consideration. The 5% contribution is of course very uncertain because of accumulation of errors in our estimate. If one takes into account the possibility of any other reaction not included in our mechanism, then the 5% contribution for reaction (3e) should be considered as an upper limit.

After the survey of the mechanism and kinetic data on the CH₃O + H system one may address again the problem of origin of CH₃ formation in methanol oxidation, which was mentioned in the introduction. Our results on the CH₃O + H reaction seem to indicate that this reaction can account only for a small part of CH₃ production. Methyl formation in reaction CH₂OH + H is probably even less efficient since CH₃ formation in this system is almost thermoneutral. Thus, it is probably the reaction CH₃O + CO → CH₃ + CO₂ and unimolecular decomposition of CH₃OH which are the major CH₃ sources in CH₃OH decomposition and oxidation at higher temperatures. Further study of this problem is obviously required.

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Paper 1/00960E; Received 1st March, 1991