

Kinetics of the reaction of OH with di-*n*-butoxymethane (DBM) in the range 298–710 K

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Abstract

The gas-phase reaction of OH($X^2\Pi$) radicals with di-*n*-butoxymethane (DBM) has been studied in the temperature range 298–710 K at total pressures between 50 and 100 Torr argon. OH radicals have been generated by excimer laser photolysis of H₂O₂ at 248 nm and have been detected by laser-induced fluorescence. Within the investigated ranges, the reaction has been found to be independent of temperature and total pressure. The bimolecular rate coefficient is $k_{\text{OH+DBM}} = (3.21 \pm 0.79) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$. The rate coefficient is compared with the results from an estimation using structure–activity relationships. Over the whole temperature range, the calculated results are somewhat higher than the experimental rate coefficients. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

The growing use of oxygenated organic compounds such as ethers, esters and alcohols as fuel additives, alternative fuels or solvents during the last years will lead to an increasing influence of these species on tropospheric chemistry. Volatile oxygen organic compounds (VOCs) are removed from the troposphere by reaction with OH radicals. The estimation of the influence of new VOCs on photochemical formation requires detailed information about their atmospheric degradation pathways. Besides mechanistic studies, determination of the rate coefficients for the reactions with OH are necessary. The rate coefficients for the reactions of OH with oxygenates which are in use for industrial applications, e.g.

methanol, ethanol or MTBE (methyl *t*-butyl ether), are well known [1]. However, the possible application of a large number of new oxygenated compounds such as diethers or esters is currently under discussion [2]. For these classes of compounds, the knowledge about their kinetic and mechanistic behaviour in the troposphere is generally poor.

Di-*n*-butoxymethane (DBM) is expected to find extended industrial application in the near future. DBM is used as a solvent and is under consideration as an alternative diesel fuel. In the present work, the reaction of OH radicals with DBM has been studied for the first time. The bimolecular rate coefficient $k_{\text{OH+DBM}}$ has been measured in the temperature range 298–710 K. All experiments have been carried out using the well-established pulsed excimer laser photolysis (ELP)/laser-induced fluorescence (LIF) technique. From the results, the tropospheric lifetime of DBM has been estimated. In addition, the rate

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coefficient $k_{\text{OH}+\text{DBM}}$ has been calculated by using the structure activity relationship (SAR) method developed by Atkinson and co-workers [3–5]. Experimental and estimated values have been compared and discussed.

2. Experiment

The ELP/LIF experimental set-up used in the present work is described elsewhere [6]. Briefly, the focused 248 nm radiation of a Lambda Physik Compex 102 excimer laser with a pulse energy of 20–30 mJ operating at 10 Hz was used to generate OH radicals by photodissociation of H_2O_2 which was evaporated in Ar. Relative $\text{OH}(\text{X}^2\Pi)$ concentrations were monitored by LIF using the Q_1 -branch of the $\text{A}^2\Sigma^+(v'=1) \leftarrow \text{X}^2\Pi(v''=0)$ transition at 282 nm and off-resonant detection of the $\text{A}^2\Sigma^+(v'=0) \rightarrow \text{X}^2\Pi(v''=0)$ transition at 308 nm. The probe laser was a Lambda Physik system comprising a Scanmate 1 dye laser with an SHG crystal pumped by an LPX 202 excimer laser. For monitoring OH radicals the frequency-doubled dye laser was operated with Coumarin 153 (Radiant Dyes Chemie) in methanol, yielding typical pulse energies of ~ 0.5 mJ.

The reaction cell used in the present work consisted of a stainless-steel cylinder with an inner ceramic cylinder. The ceramic cylinder was heated by means of a tantalum resistive wire. The temperature in the reaction cell was measured by shielded, calibrated thermocouples and kept constant during the experiments to better than ± 1.5 K. A detailed description of the reaction cell has been given elsewhere [7,8].

The OH fluorescence was observed at right angles to the laser beam through a lens system and an interference filter with a photomultiplier (EMI 9635QB). The output signal of the photomultiplier was integrated by a boxcar averager (SRS model SR 250), digitised and analysed by an ATARI MegaST microcomputer. The time delay between the photolysis laser and the probe dye laser was varied from zero to several milliseconds by means of a digital delay generator (BNC 7010). The time resolution used was 1 μs .

The reaction of OH radicals with DBM has been investigated under pseudo-first-order conditions with

DBM concentrations at least a hundred times larger than the OH precursor H_2O_2 . All measurements were carried out in slowly flowing gas mixtures with flow rates of < 0.5 m s^{-1} . The concentrations of the gases were determined from their partial flows measured with calibrated flowmeters (Tylan FM 360). In all experiments argon has been used as bath gas. DBM was diluted in argon with a ratio of $\sim 1:1000$ and stored in stainless-steel cylinders. The exact mixing ratio of the DBM/Ar mixtures was determined by means of Fourier-transform infrared spectroscopy.

The argon with a stated purity of 99.998% employed in this work was supplied by Messer-Griesheim. DBM (Lambiotte & Cie.) has been distilled twice for purification and carefully degassed before use. H_2O_2 (Peroxid-Chemie, 85 wt%, stabilised) has been used without further purification.

3. Results and discussion

From the LIF measurements, relative $\text{OH}(\text{X}^2\Pi)$ radical concentrations have been measured as a function of the reaction time. As shown in Fig. 1, the LIF signal decayed exponentially for all DBM concentrations. In the absence of DBM, the OH decay was mainly caused by reaction with H_2O_2 . This is supported by the fact that the measured decay constants were strongly dependent on the H_2O_2 concentration.

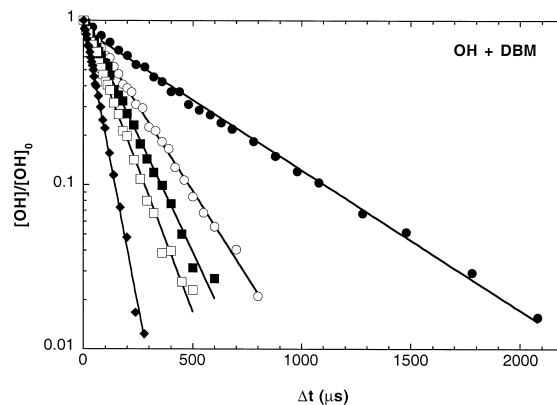


Fig. 1. Semi-logarithmic plot of the OH decay after laser photolysis of H_2O_2 in 100 Torr Ar in the presence of different DBM concentrations (10^{13} cm^{-3}): (●) 0; (○) 3.06; (■) 5.37; (□) 7.77; (◆) 19.37.

The OH decay could be monitored over at least 4 lifetimes. The addition of DBM caused a more rapid decay of OH radicals. By plotting the natural logarithm of the relative OH concentration as a function of reaction time, pseudo-first-order decay constants k' were calculated from the slope of the individual straight line plots which were obtained for different concentrations of DBM. The k' values increased proportionally with the concentration of added DBM, as illustrated in Fig. 1.

The bimolecular rate coefficients $k_{\text{OH}+\text{DBM}}$ for a given temperature were then obtained by plotting corrected pseudo-first-order decay constants $k'_{\text{corr.}}$ as a function of the DBM concentration, as shown as an example in Fig. 2. The $k'_{\text{corr.}}$ values have been obtained by subtracting the decay constants, which were measured in the absence of DBM, from the corresponding k' values.

Almost all experiments were carried out at a total pressure of 50 Torr. A few additional experiments at a total pressure of 100 Torr at room temperature yielded similar results, indicating that the reaction of OH radicals with DBM is pressure independent within this range.

The bimolecular rate coefficients for the reaction OH + DBM have been measured in the temperature range 298–710 K. The rate coefficients obtained are summarised in Table 1. The error limits represent a 90% confidence interval and reflect the statistical precision only. The given rate coefficients are weighted means of at least five k -values which were determined in independent experiments using at least

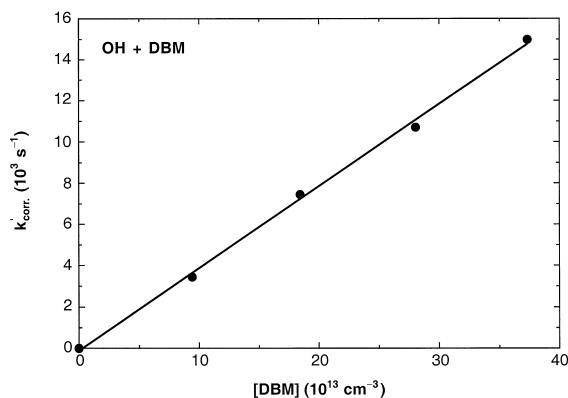


Fig. 2. Plot of pseudo-first-order decay constants $k'_{\text{corr.}}$ vs. the concentration of DBM for 298 K at 100 Torr total pressure.

Table 1

Bimolecular rate coefficients for the reaction OH + DBM

<i>T</i> (K)	<i>k</i> _{exp} ($10^{-11} \text{ cm}^3 \text{ s}^{-1}$)	<i>k</i> _{SAR} ($10^{-11} \text{ cm}^3 \text{ s}^{-1}$)
298	3.39 ± 0.46	9.0
400	2.57 ± 0.30	5.5
500	3.85 ± 0.52	4.9
600	2.94 ± 0.62	5.0
710	3.31 ± 0.69	5.4

k_{exp} = data measured in the present work (errors reflect 90% confidence interval); k_{SAR} = data obtained by structure activity relationship [3–5].

6 different DBM concentrations. Within the experimental errors, the reaction OH + DBM shows no temperature dependence. The averaged rate coefficient $k_{\text{OH}+\text{DBM}}$ has been determined to be

$$k_{\text{OH}+\text{DBM}} = (3.21 \pm 0.79) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}.$$

The result can be compared with data from literature for other diethers which are summarised in Table 2. All rate coefficients are of the same order of magnitude. The experimental results exhibit that ethers with the general structure ROCH_2OR show increasing rate coefficients with increasing carbon number of R.

The observed temperature independence of $k_{\text{OH}+\text{DBM}}$ is in agreement with other experimental studies on comparable oxygenates. Dagaut et al. [12] investigated the reactions of OH with 2,2-dimethoxypropane and 2,2-diethoxypropane. For both reactions, no significant temperature dependence was observed in the range 240–440 K. Porter and co-workers [9] investigated the reactions of a couple of diethers with the general structure of $\text{RO}(\text{CH}_2)_n\text{OR}$ with OH radicals in the range 230–370 K. All rate coefficients show only weak temperature dependencies with small activation energies of $\sim 10 \text{ kJ/mol}$. From all the literature data it can be assumed, that the reactions of OH with diethers of the type $\text{RO}(\text{CH}_2)_n\text{OR}$ generally show weak temperature dependencies.

From the bimolecular rate coefficient $k_{\text{OH}+\text{DBM}}$ obtained in this work, the atmospheric lifetime of DBM has been estimated. It can be assumed that the only significant sink of DBM in the troposphere is reaction with OH radicals. Hence, at an OH daytime concentration of $5 \times 10^6 \text{ cm}^{-3}$ [13] for a summer

Table 2

Comparison of bimolecular rate coefficients for the reactions of OH radicals with selected aliphatic and cyclic diethers at room temperature (k_{exp} = experimental data; k_{SAR} = data obtained by structure activity relationship [3–5])

Compound	k_{SAR} ($10^{-12} \text{ cm}^3 \text{ s}^{-1}$)	k_{exp} ($10^{-12} \text{ cm}^3 \text{ s}^{-1}$)	Refs. (k_{exp})
Dimethoxymethane	68	4.9 ± 0.8	[9]
Diethoxymethane	82	20.4 ± 1.4	[9]
Di- <i>n</i> -propoxymethane	88	— ^a	
Di- <i>iso</i> -propoxymethane	99	— ^a	
Di- <i>n</i> -butoxymethane	90	3.21 ± 0.79	this work
1,3-Dioxolane	85	10.3 ± 1.4	[10]
1,4-Dioxane	35	10.9 ± 0.5	[11]

^aNo experimental data available.

day in a polluted region, the atmospheric lifetime, τ_{DBM} , will be 1.7 ± 0.3 h.

This relatively short lifetime indicates that DBM will be removed rapidly during daylight from the troposphere. As a consequence, the products of the OH-initiated oxidation of DBM could possibly contribute to local photochemical formation. Therefore, mechanistic and product studies on this compound should be carried out in the near future to assess the ozone forming potential of this compound.

Additionally, the rate coefficients measured in the present work have been compared with estimations obtained using the SAR algorithm by Atkinson and co-workers [3–5]. The results are summarised in Table 1. The data for the SAR calculation exhibit a weak temperature dependence of the rate coefficient. At ~ 500 K, the value of $k_{\text{OH} + \text{DBM}}$ shows a minimum. At higher and at lower temperatures, the rate coefficient slightly increases, which does not correlate with the experimentally observed temperature independence. However, except for room temperature, the calculated data are in agreement with the experimental results within the relatively high methodical errors of the SAR method.

As already shown by Atkinson [4], the SAR algorithm leads to higher deviations from experimental data for oxygenated VOCs. This has been confirmed in a recent study of Porter et al. [9]. Table 2 shows a comparison of experimental and calculated rate coefficients for a number of diethers. The values for k_{SAR} have been obtained in the present work. For all treated species, the application of the SAR method leads to significantly higher rate coefficients than the experimental results.

From the study of Atkinson [4], it can be concluded that especially the calculation of temperature-dependent rate coefficients for oxygenates leads to larger errors. However, in the present study the experimental data for $k_{\text{OH} + \text{DBM}}$ are covered by the confidence intervals of the corresponding SAR calculations for temperatures ≥ 400 K.

4. Summary

In conclusion, the reaction of $\text{OH}(\text{X}^2\Pi)$ with di-*n*-butoxymethane (DBM) has been studied over the temperature range 298–710 K by excimer laser photolysis/laser-induced fluorescence. Within the investigated range, no temperature dependence of the bimolecular rate coefficient, $k_{\text{OH} + \text{DBM}}$, has been observed. The rate coefficient was also found to be independent of total pressure in the range 50–100 Torr. From the obtained rate coefficient, the tropospheric lifetime of DBM has been derived.

The experimental data obtained in the present study have been compared with estimated rate coefficients calculated using an established structure–activity relationship algorithm. The estimated values are higher than the experimental data.

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