

Studies on Oxygenated Fuel Additives: Ethers and Acetals

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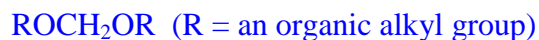
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Ever increasing political pressure for a cleaner environment has triggered large research efforts over the past decade within the automobile and solvent industries to develop new, oxygenated, low atmospheric reactivity fuels and solvents, respectively. The main stimulus for the interest in such compounds in Europe is existing or pending legislation demanding the regulation of the reactivity of the anthropogenic VOC emissions to the atmosphere, in particular from solvents and motorised vehicles. Obviously to assess the environmental acceptability of alternative oxygenated solvents or fuel additives a comprehensive understanding of their gas-phase oxidation mechanism is required, preferably prior to deployment of the compounds.

Within the EU INFORMATEX project and also the German TFS/LT3 project much effort has been directed towards investigation of the atmospheric photo-oxidation mechanisms of organic compounds used (or under consideration) as fuel additives. The INFORMATEX and TFS projects concentrated on investigating the atmospheric photo-oxidation mechanisms of ether compounds already in use for gasoline reformulation, i.e. MTBE, ETBE and TAME. Since this material is well documented this abstract will focus on the acetals which are not so commonly known

Acetals are a group of oxygenated organic compounds with the general diether structure,



These substances have excellent solvent properties and also good toxicological and ecotoxicological profiles which makes them suitable as potential replacements for many of the chlorinated and aromatic solvents currently in widespread use. Recent research has also shown that addition of acetals to diesel fuel greatly improves the environmental properties of the engine exhaust. Tests on methylal ($\text{CH}_3\text{OCH}_2\text{OCH}_3$) and n-butylal ($\text{C}_4\text{H}_9\text{OCH}_2\text{OC}_4\text{H}_9$), for example, have shown that:

- the engine particle emissions are greatly reduced
- the NO_x emissions are substantially reduced
- butylal improves the cetane number

Since the widespread of such compounds will lead to release of large amounts of these substances to the atmosphere it is obviously desirable to assess the potential environmental implications of such releases prior to deployment. Reported here are exploratory investigations on the atmospheric fate of a series of acetals performed in the laboratory and also in the large outdoor EUPHORE simulation chamber in Valencia in Spain. The data is used to assess the ozone forming potential of this class of compound and their primary oxidation products and their likely influence on atmospheric reactivity on local and larger scales.

Experimental

The atmospheric behavior of the acetals has been investigated in laboratory photoreactors and also in the large outdoor simulation chamber EUPHORE in Valencia Spain.

The laboratory experiments were performed in Wuppertal in a 1080 l quartz reaction chamber at 298 K and a total pressure of 1000 mbar using synthetic air as the bath gas. The photolysis ($\lambda_{\max} = 360$ nm) of $\text{CH}_3\text{ONO/NO}$ was used as the OH radical source. FT-IR spectroscopy was the main analytical method used for the analysis of reactants and products.

The experiments in the large-scale (200 m^3) EUPHORE photoreactor were performed at 1000 mbar total pressure and between 284 and 290 K using purified air as the matrix gas. The principle analytical techniques employed were *in situ* FTIR and GC.

Atmospheric Gas Phase Reactivity

The acetals currently under investigation are listed in Table 1.

- With the exception of methylal ($\text{CH}_2\text{OCH}_2\text{OCH}_2$) all the acetals investigated react relatively quickly with OH radicals (k between 2 and $5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$; see Table 1).
- This corresponds to atmospheric OH-lifetimes of approx. 60 h for methylal and between 1.4 and 6 h for the other acetals (calculated with $[\text{OH}] = 1 \times 10^6 \text{ molecule cm}^{-3}$).
- Reactions with O_2 and NO_2 are negligibly slow.
- The acetals do not absorb in the atmospheric actinic region therefore photolysis does not occur.

Ozone Forming Potential

Tests have been performed in the EUPHORE chamber to assess the ozone formation potential of the acetals. Two different types of “classical“ smog-type experiment have been performed; one series of experiments with the pure acetal and another with additional reactive hydrocarbons. Examples of the ozone formation are shown in Figure 1.

- the ozone production decreases along the series ethylal-propylal-butylal
- in mixtures with ethene they reduce ozone formation on a short-term irradiation basis (5-6 h)

- none of the acetals is very efficient in the production of ozone on the basis of short term irradiation experiments acetals, which give relatively high HCHO yields show the highest ozone production
- in mixtures with ethene they reduce the ozone formation compared to pure ethene

Products and Oxidation Mechanism

For the straight chain acetals the major products from the OH initiated oxidation are alkoxy-methyl formates ($C_nH_{(2n+1)}OCH_2OCHO$) and aldehydes ($C_nH_{(2n+1)}CHO$) in equi-molar yield. In addition di-alkyl carbonates ($C_nH_{(2n+1)}OC(O)OC_nH_{(2n+1)}$) are also formed in low yields. For the branched acetals ketones are major products. The pathways leading to the above products are illustrated for the reaction of OH radicals are illustrated for butylal in Figure 1.

Conclusions/Possible Atmospheric Implications

- acetals will be degraded quickly in the atmosphere producing mainly aldehydes and alkoxy-methyl formates
- the ozone formation tests suggest that acetals will not contribute to ozone formation on a local scale and may even lead to a reduction, however, 2 to 3 day scenarios are needed to assess the long-term impacts
- the aldehydic products will certainly contribute to ozone formation over a longer time scale: photolysis will lead to the formation of highly reactive alkenes and thermally stable PAN-like compounds which can transport NO_x
- the formates will be oxidised only slowly, mainly to diformates, and will probably be removed by deposition - more work is needed on the fate of these compounds

Although the addition of acetals to diesel will certainly be beneficial with respect to particle and NO_x formation and also ozone production on a local scale the results suggest that on the long term their use may result in the spread of reactivity over wider scales. The best environmental option with regards to the use of alternative solvents / fuel additives may eventually, in many cases, boil down to a choice between „the lesser of two evils“.

References

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Table 1: Summary of the recommended rate coefficients for the reaction of OH radicals with acetals obtained in this work and reported in the literature.

Compound	$10^{11} k_{\text{OH}}$ $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Technique ⁱ	Temperature K	Reference
dimethoxy methane (DMM)	0.49 ± 0.02	RR	300 ± 1	this work
	0.53 ± 0.05	RR	295 ± 2	Wallington et al. [1]
	0.46 ± 0.16	PR-UV	346 ± 3	Wallington et al. [1]
	0.49 ± 0.08	RR	298 ± 2	Porter <i>et al.</i> [2]
	0.46 ± 0.01	PLP-LIF	298 ± 2	Porter <i>et al.</i> [2]
diethoxy methane (DEM)	1.84 ± 0.18	RR	298 ± 2	this work
	2.04 ± 0.14	RR	298 ± 2	Porter <i>et al.</i> [2]
	2.06 ± 0.01	PLP-LIF	298 ± 2	Porter <i>et al.</i> [2]
	1.68 ± 0.16	FP-RF	$298 \pm$	Dagaut <i>et al.</i> [3]
di- <i>n</i> -propoxy methane (DNPM)	2.63 ± 0.49	RR	296 ± 4	this work
di- <i>iso</i> -propoxy methane (DIPM)	3.93 ± 0.48	RR	295 ± 4	this work
di- <i>n</i> -butoxy methane (DNBM)	3.47 ± 0.42	RR	298 ± 2	this work
	3.21 ± 0.79	ELP-LIF	$298 - 710^{\text{ii}}$	Becker et al. [4]
di- <i>iso</i> -butoxy methane (DIBM)	3.68 ± 0.57	RR	299 ± 3	this work
di- <i>sec</i> -butoxy methane (DSBM)	4.68 ± 0.05	RR	299 ± 4	this work

i) RR = relative kinetic technique; PR-UV = pulsed radiolysis - transient UV absorption; PLP-LIF = pulsed laser photolysis - laser induced fluorescence; FP-RF = flash photolysis - resonance fluorescence; ELP-LIF = eximer laser photolysis - resonance fluorescence.

ii) Rate coefficient was reported to be independent of temperature over the temperature range investigated.

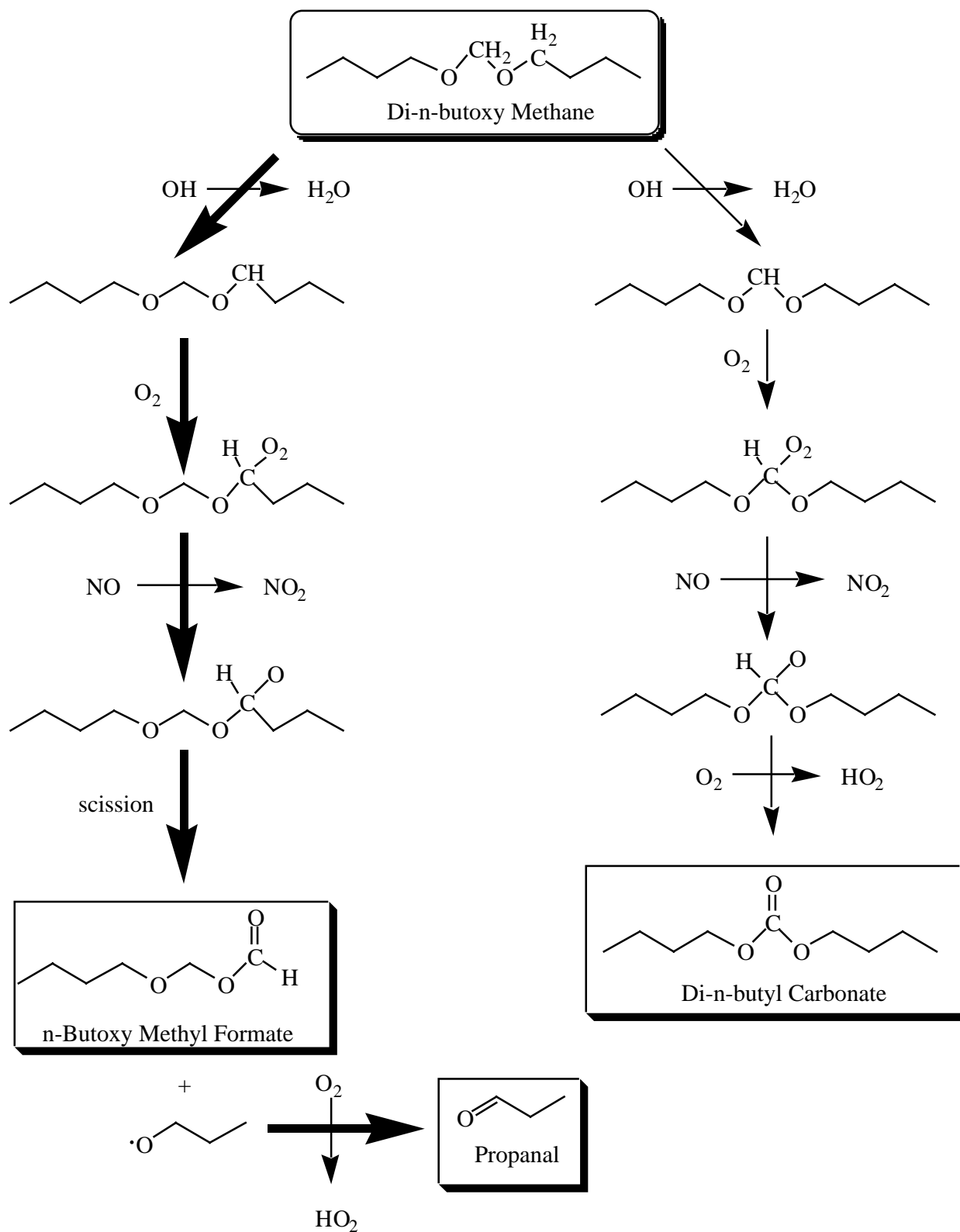


Figure 1: Mechanism for the OH radical initiated oxidation of n-butylal.