



Maleic Anhydride in Industrial Plumes in the Arctic ?

Guest contribution

J.L. Jaffrezo, R. Hillamo and V.M. Kerminen

LGGE, Rue Molière, 38 402 St Martin d'Hères, Cedex, France

Intensive field experiments took place at Sevettijarvi (69° 35' N, 28° 50' E, 130 m. a.s.l.) in Finnish Lapland between July 4th and August 8th, 1997 in the course of the programme EAAS (European Arctic Aerosol Study). The programme focuses on interactions between the gas phase and aerosols, and on the impact of aerosols on radiative properties of the boundary layer. The permanent equipment at the station includes a DOAS (OPSIS AR 500, SO₂, O₃ and H₂O_v), a nephelometer (TSI 3563), particle counters (TSI: 3760/7610 CPC ; 7430 LPC). Basic ancillary meteorological measurements, automatic radon and black carbon analyses are also maintained. Additional equipment set up during the intensive period particularly concerned aerosol (total filter and impactors) and gas sampling (with mist chambers) for chemical analysis by Ionic Chromatography (inorganic, mono and dicarboxylic acids ; major cations).

During that summer campaign, we sampled several plumes originating from the industrial area of Nikel/Zapolyarnyi (Russia), 60 km away from the site, which is a major source of SO₂ in the Arctic. All these episodes are characterised by a systematic and very large increase of maleic acid (C₄H₄O₄) concentration in the mist chamber samples (up to 5ppb above a background about 1ppt) in phase with SO₂ increases (Fig. 1). Other results on the gas phase indicate no major changes for the concentrations of HCl, HNO₃, HCOOH and CH₃COOH during the episodes. The only other species significantly affected during the industrial plumes is nitrite (which testifies to the presence of NO_y in the atmosphere): 41.8 ± 32.9 ppt (calculated as HONO), compared to 8.8 ± 9.5 ppt in background conditions. Aerosol concentrations show large increases for sulfate during the episodes, and some moderate increases for nitrate and nitrite concentrations (Fig. 2). Conversely, the concentrations for particulate maleate, oxalate, acetate, glycolate, propionate, formate glycolate, glutarate, succinate and MSA are, at best, marginally affected during the episodes.

Proceedings of EUROTRAC Symposium '98

Editors: P.M. Borrell and P. Borrell

© 1999: WITPRESS, Southampton

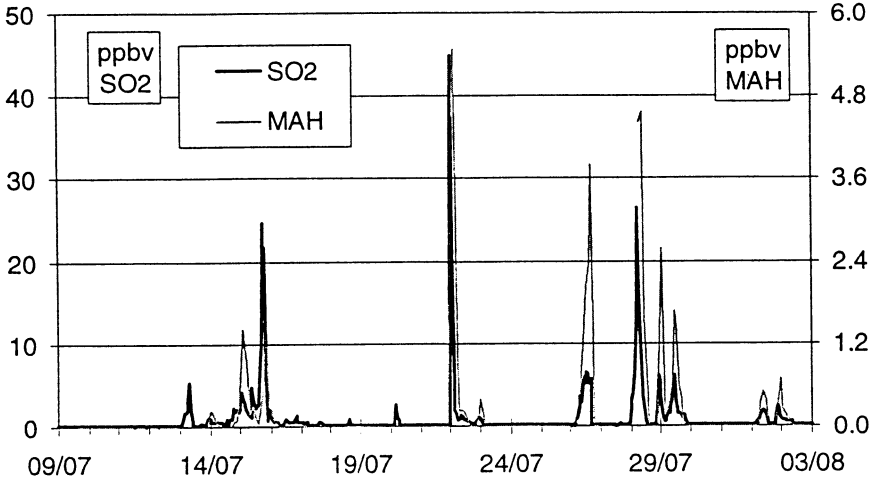


Fig. 1: Atmospheric concentrations of SO₂ (measured by DOAS) and maleic anhydride (MAH) (deduced from maleic acid measured by mist chambers).

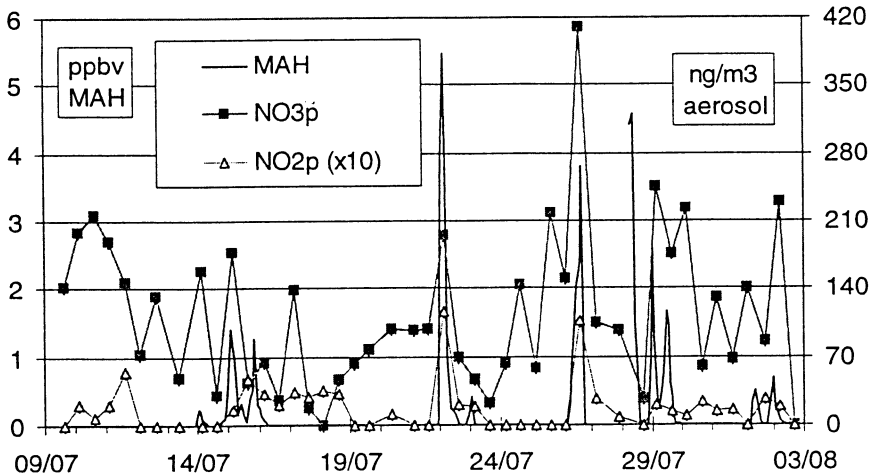


Fig. 2: Atmospheric concentrations of MAH and particulate nitrate and nitrite.

Considering the low vapour pressure of maleic acid (3.6×10^{-5} mm Hg) and its air-water equilibrium constant (10^9 M.atm⁻¹), it is extremely unlikely that maleic acid is partitioned towards the gas phase in the atmosphere. We propose that the maleate collected in the liquid phase of the mist chambers comes from the dissolution and hydratation of maleic anhydride (MAH):

$$\text{OC}-\underset{\text{O}}{\text{CH}=\text{CH}}-\text{CO}.$$

Bandow *et al.* (1985) identified MAH in FTIR products studies of the OH-initiated oxidation of toluene, benzene and xylene isomers. They postulated that the unsaturated 1,4-dicarbonyl butenedial (OHC-CH=CH-CHO) was the precursor of MAH, after ring cleavage of the aromatics by OH addition. Subsequent studies showed that unsaturated 1,4-dicarbonyls were important products in the oxidation of many aromatics (Yu *et al.*, 1997). Bierbach *et al.* (1994) calculated the tropospheric lifetimes for the unsaturated dicarbonyls they studied, and concluded that MAH was surprisingly stable under most conditions, with a lifetime of 4.5 days (for OH concentrations of 1.6×10^6 molecules.cm⁻³), the reaction with OH being the major atmospheric removal process in the gas phase.

Yield of formic acid (as a secondary product), HCHO and glyoxal ((CHO)₂) are higher than that of MAH during at least the first 2 hours of irradiation of toluene and benzene (Bandow *et al.*, 1985). It is therefore of note that we do not see any significant perturbation of the concentrations of formic and glyoxylic acids during the episodes, nor variations for other compounds like oxalate, which are believed to be end products of oxidation of many organics in the atmosphere (Kawamura and Ikushima, 1993). At present, we cannot present a satisfactory hypothesis explaining these observations.

We investigated the fate of maleate in aqueous phase, with successive reanalyses over a period of 9 days of one mist chamber sample collected during one episode. This sample was kept at room temperature in the dark, and no oxidant was added to the air-tight bottles. The first analyses took place within 1 hour of the end of the collection. Fig. 3 indicates an increase in sulfate concentration, implying the availability of oxidants for the oxidation of SO₂. It also indicates consistent decrease in maleate concentrations, without production of any other species analysed in our conditions. The concentrations of formate and acetate are slowly decreasing in the meantime. The general lack of degradation products of maleate may indicate that it does not undergo direct oxidation giving smaller compounds in the conditions of our liquid phase, but reacts leading to products undetected with our technique. Further tests on a synthetic solution of maleate (500 ppb) and H₂O₂ (1500 ppb) show that maleate is not oxidised in these conditions over a period of 10 days. Further laboratory experiments are necessary in order to try to elucidate several inconsistent

observations, including the slow rate of oxidation of SO_2 , and the seemingly 1:1 molar rate of reaction of maleate and sulfate in the natural samples.

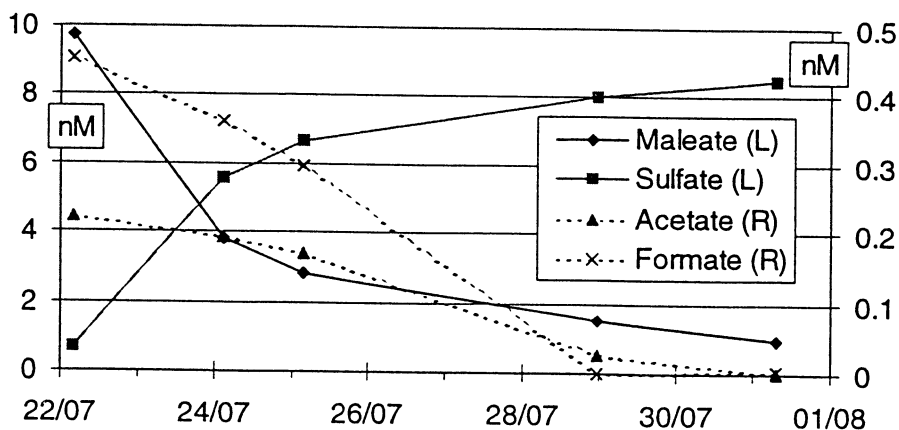


Fig. 3: Evolution of the concentrations of maleate, sulfate (left axis), acetate and formate (right axis) in a mist chamber sample collected during an industrial episode.

Our results present several implications for atmospheric chemistry and atmospheric cycling of hydrocarbons. If our hypothesis, that the maleate seen in our samples results from incorporation of MAH from the atmosphere, is valid, implications are that the ring cleavage may be an important pathway in the oxidation of light arenes, and represents a significant sink for OH radicals. The formation of very high concentrations of MAH, together with its high stability in the gas phase would create favorable conditions for long range transport and dispersion of point source emissions of organics over large areas. In turn, this could also have an impact on the budget of OH radicals far from sources, the main gaseous sink of MAH being the reaction with OH. It should be noted that these reactions may not be specific to the Arctic nor to the industries in the Kola Peninsula, with low molecular weight arenes being major products of many anthropogenic emissions. Indeed, high concentrations of maleate in mist chamber samples have been measured in central France and at Sevetijarvi in winter 1997 to 1998 in airmasses coming from central Europe.



References

- Bandow H., N. Washida, H. Akimoto; Ring-cleavage reactions of aromatic hydrocarbons studied by FTIR spectroscopy. I: photo-oxidation of toluene and benzene in the NO_x-air system, *Bull. Chem. Soc. Japan* **58** (1985) 2531–2540.
- Bierbach A., I. Barnes, K.H. Becker, E. Wiesen; Atmospheric chemistry of unsaturated carbonyls: butenedial, 4-oxo-2-pentenal, 3-hexene-2,5-dione, maleic anhydride, 3H-furan-2-one, and 5-methyl-3H-furan-2-one, *Environ. Sci. Technol.* **28** (1994) 715–729.
- Kawamura K., K. Ikushima; Seasonal changes in the distribution of dicarboxylic acids in the urban atmosphere, *Environ. Sci. Technol.* **27** (1993) 2227–2235.
- Yu J., H.E. Jeffries, K.G. Sexton; Atmospheric photo-oxidation of alkylbenzenes-I: carbonyl product analyses, *Atmos. Environ.* **31** (1997) 2261–2280.