

Quantitative Measurement of Methyl Hydroperoxide in the Acetaldehyde Cool Flame

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Summary Methyl hydroperoxide concentrations have been measured in an acetaldehyde cool flame using a direct mass-spectrometric technique.

METHYL hydroperoxide (MHP), MeOOH , has been postulated to be an intermediate in the cool flame of acetaldehyde.¹ The presence of organic peroxides in such a cool flame has been established by wet chemical techniques, yet the chemical composition and concentrations are uncertain.²

We have measured directly the concentrations of MHP in acetaldehyde cool flames produced in a flow reactor operated at 1 atm. pressure. Our reactor is a 30-mm O.D. Vycor tube which passes through the ion-source region of a modified Bendix 12-107 time-of-flight mass spectrometer.³ The generation of cool flames in reactor tubes similar to the one used here has been described by Williams and Sheinson.⁴ The temperature profile of the reactor tube was measured with a Chromel-Alumel thermocouple placed in a 1-mm O.D. quartz tube. Molecules inside the reactor tube effuse through a laser-drilled orifice in the wall of the tube into the ion-source region of the mass spectrometer. The orifice is 1 cm from the point of ionization and the time from effusion to detection is *ca.* $10 \mu\text{s}$. Thus, a large fraction of the effusing molecules enter the ionization zone without suffering collisions with the mass spectrometer's metal walls. This sampling system has been shown to have little effect upon the medium being sampled and the ion intensity of a species has been found to be proportional to its partial pressure in the reactor tube (assuming constant total pressure).³

With the exception of MeOH , molecular ions of the cool flame species were used to monitor constituents of the flame. Since O_2 and MeOH have the same molecular weight,

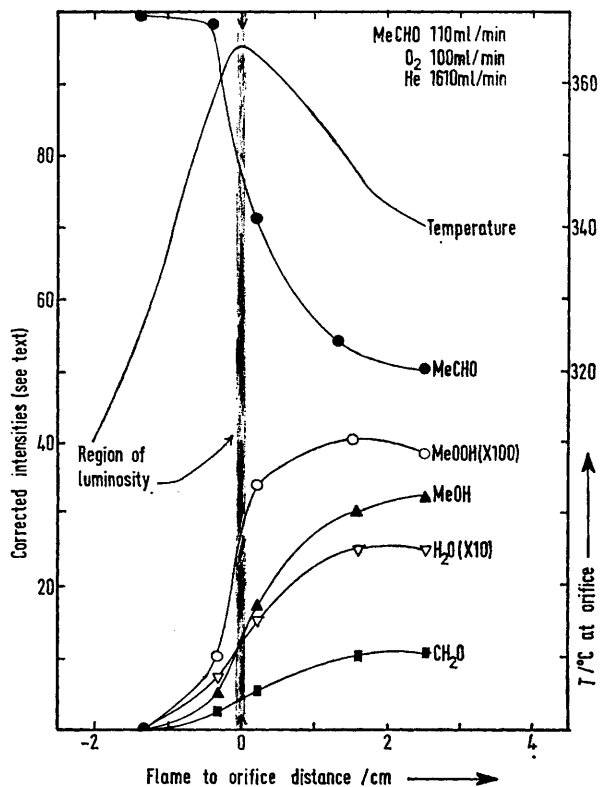


FIGURE. Corrected ion intensities vs. position of the cool flame relative to the orifice.

MeO^+ (m/e 31) was used as a monitor for MeOH. Fragmentation patterns for the species observed in the cool flame were determined using pure compounds as standards and correcting the measured ion-current intensities for fragmentation at the electron energy (14 eV) used. The ion intensities were normalized using Ar^+ as a standard, a known concentration of which was added to the system. The mass spectrometer was assumed to have the same sensitivity to all the monitored species. This assumption could result in a 50% error in the concentration values reported.

The mass spectrum of the post-flame region of acetaldehyde cool flames was observed to have peaks with m/e ratios of 48 and 47. A reasonable assumption is that these peaks are due to the P^+ and $(P - H)^+$ produced from MHP upon electron impact, *i.e.* to CH_4O_2^+ and CH_3O_2^+ . For confirmation, MHP was synthesized by the method of Rieche and Hitz,⁵ and its mass spectrum measured in our system. The measured spectrum agreed with the spectrum of MHP

reported by Shortridge and Hecklen⁶ and had peaks at m/e 47 and 48 with the same relative intensities as those observed in the flame study. Therefore, we conclude that MHP is produced in an acetaldehyde cool flame.

The dependence of the ion intensities of various species on the position of the acetaldehyde cool flame relative to the orifice in the reactor tube is shown in the Figure. The temperature profile of the flame is also shown. These data imply that for each mol of MeCHO consumed, *ca.* 0.1 mol of H_2O , 0.2 mol of CH_2O , 0.6 mol of MeOH, and 0.01 mol of MeOOH are produced. It is interesting that the concentration of MHP does not change significantly beyond the cool flame front. In this system the temperature decreases after the cool flame. The existence of MHP at these temperatures is consistent with estimates of 0.2–30 s for its half life at *ca.* 400 °C⁷ and supports the postulate¹ that it is an intermediate in the cool flame.

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⁶ R. Shortridge and J. Hecklen, *Canad. J. Chem.*, 1973, **51**, 2251.

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