Heterogeneous Chemistry of Acetone and Methanol in Liquid Sulfuric Acid

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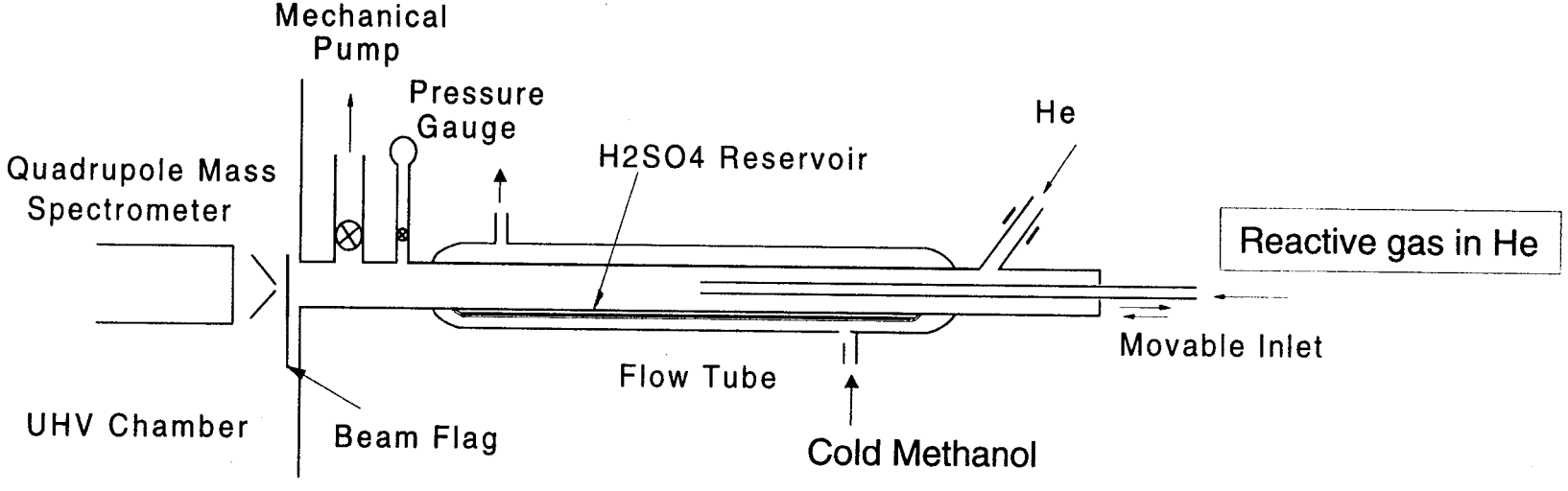
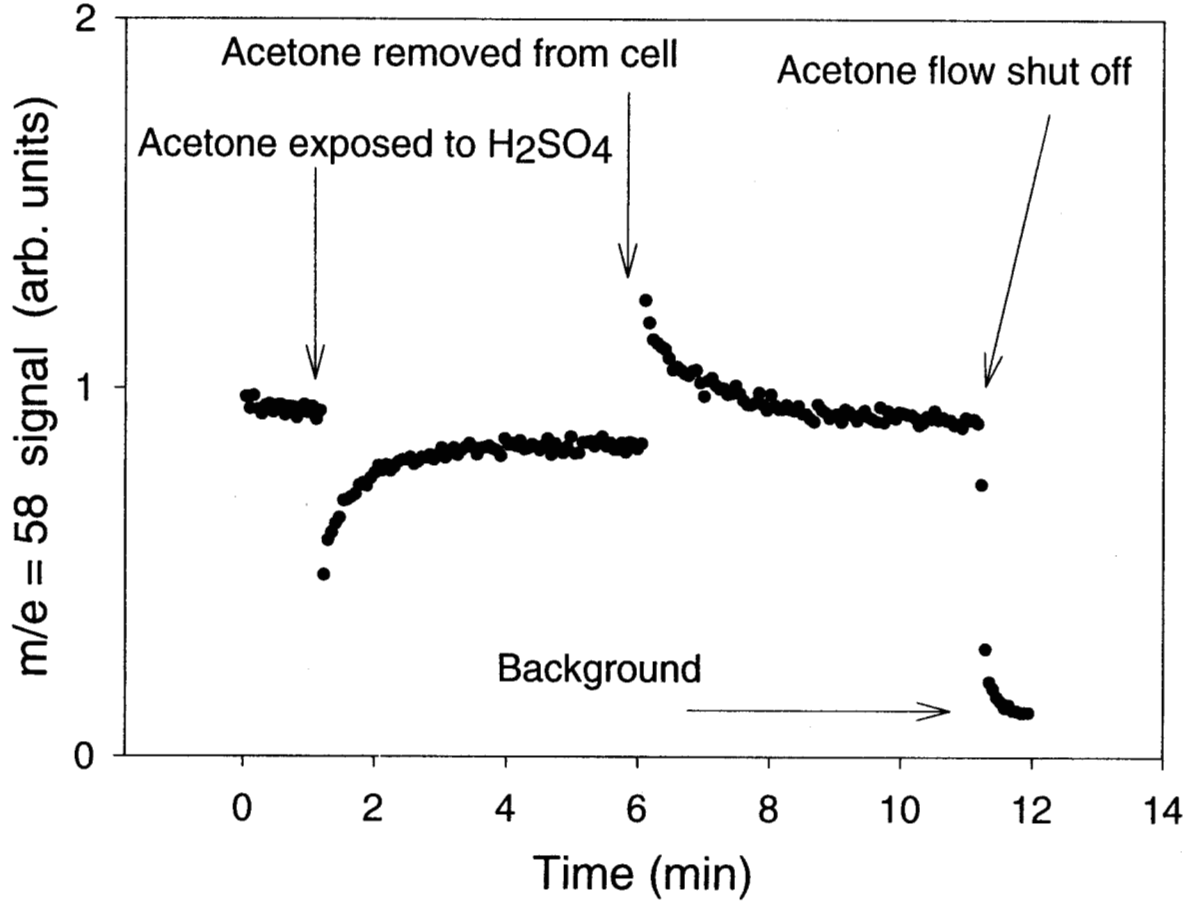
Abstract

The uptake of acetone vapor and methanol by liquid sulfuric acid has been investigated over a range of H_2SO_4 compositions and temperatures. Studies were performed with a flow-tube reactor, using a quadrupole mass spectrometer for detection. At most concentrations studied (40 to 75 wt. %), acetone was physically absorbed by sulfuric acid without undergoing irreversible reaction. However, at acid concentrations at or above 80 wt. %, reactive uptake of acetone was observed, leading to products such as mesityl oxide and/or mesitylene. The solubility of acetone in liquid sulfuric acid was found to increase with increasing acid concentration and decreasing temperature. In the 75 wt. % and 230 K range, the value for H* was found to be ~ $2x10^6$ M/atm, suggesting that acetone primarily remains in the gas under atmospheric conditions. Methanol, in contrast, shows reversible uptake at low acid concentrations but irreversible low temperature reaction between methanol and sulfuric acid at all concentrations. Above 65 wt % H_2SO_4, more than 90 % of uptake was found to be reactive. The product of the effective Henry's law constant, H*, and the square root of the overall liquid-phase reaction rate, k_{rxn}, was calculated as a function of acid concentration and temperature. Methanol reaction with sulfuric acid appears to be a dominant loss mechanism under volcanic-perturbed conditions.

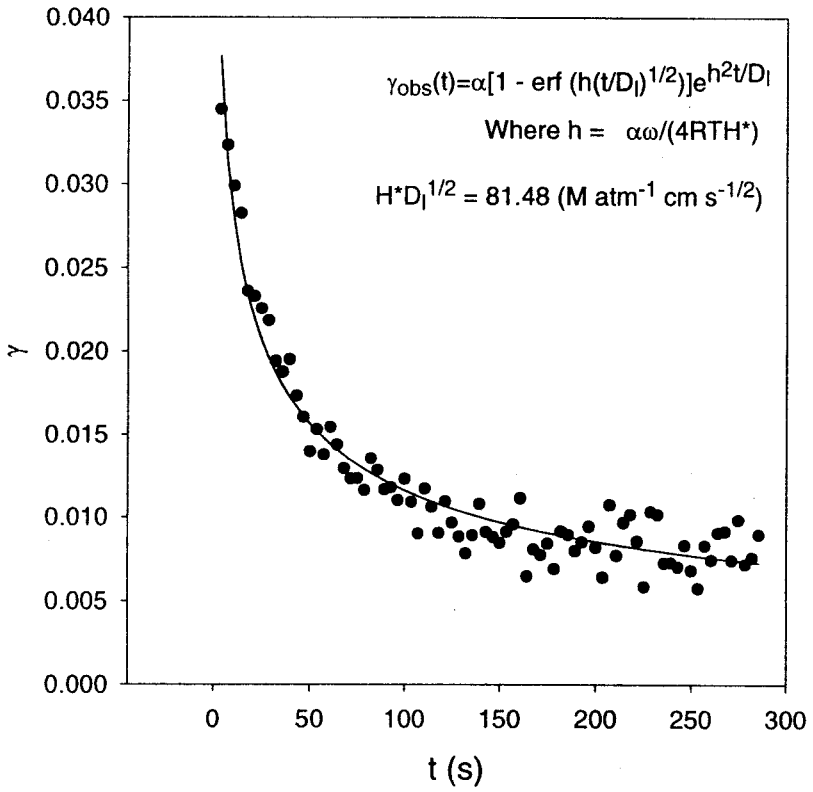
Experimental Setup

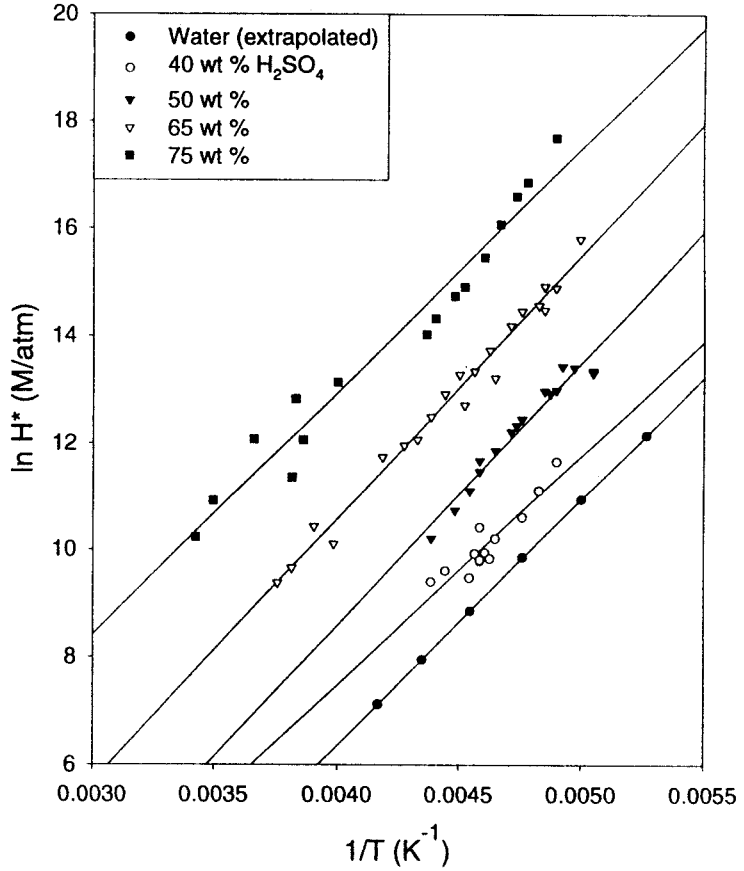


Reversible Uptake of Acetone by Sulfuric Acid

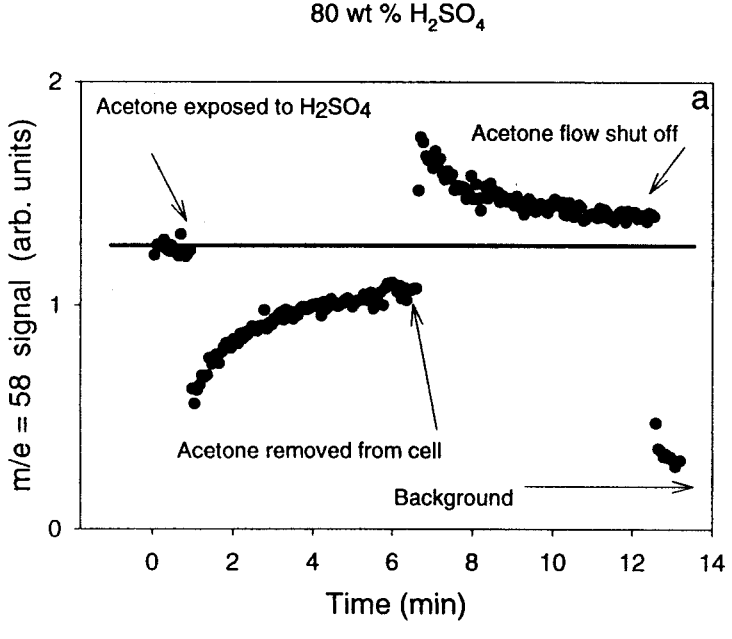


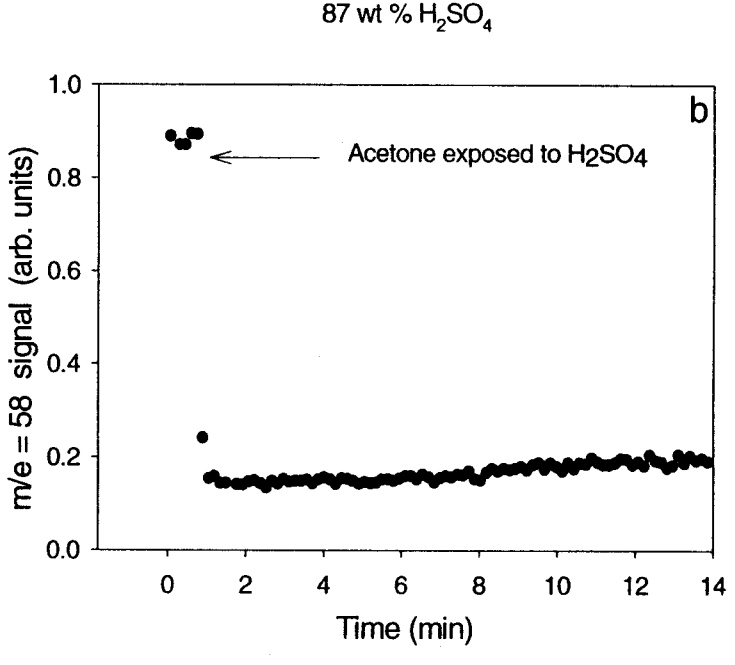
H* Determination for Acetone (40-75 wt. % H_2SO_4)



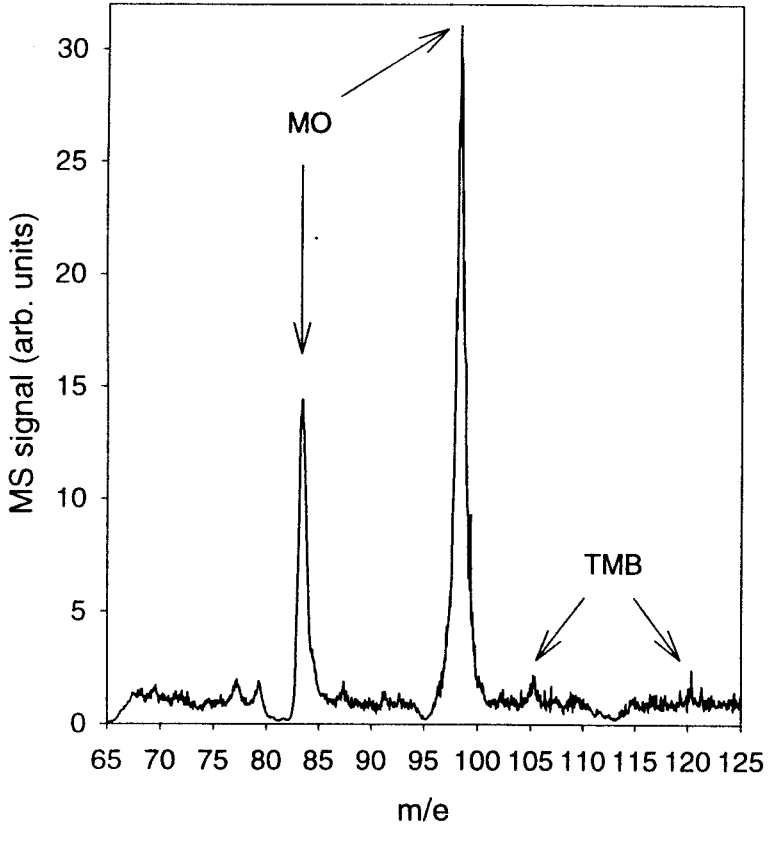


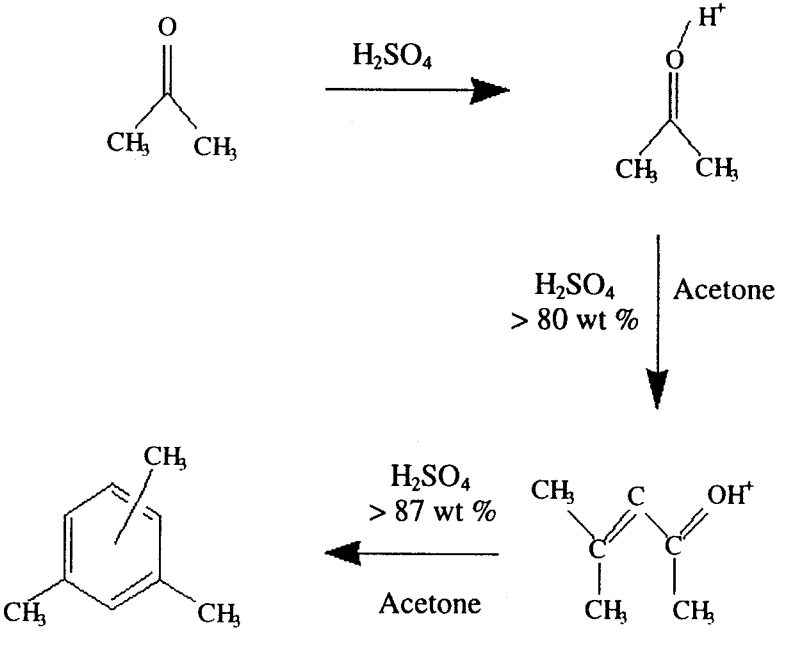
Reactive Uptake of Acetone (> 80 wt. % H_2SO_4)





Mechanism for Reactive Uptake

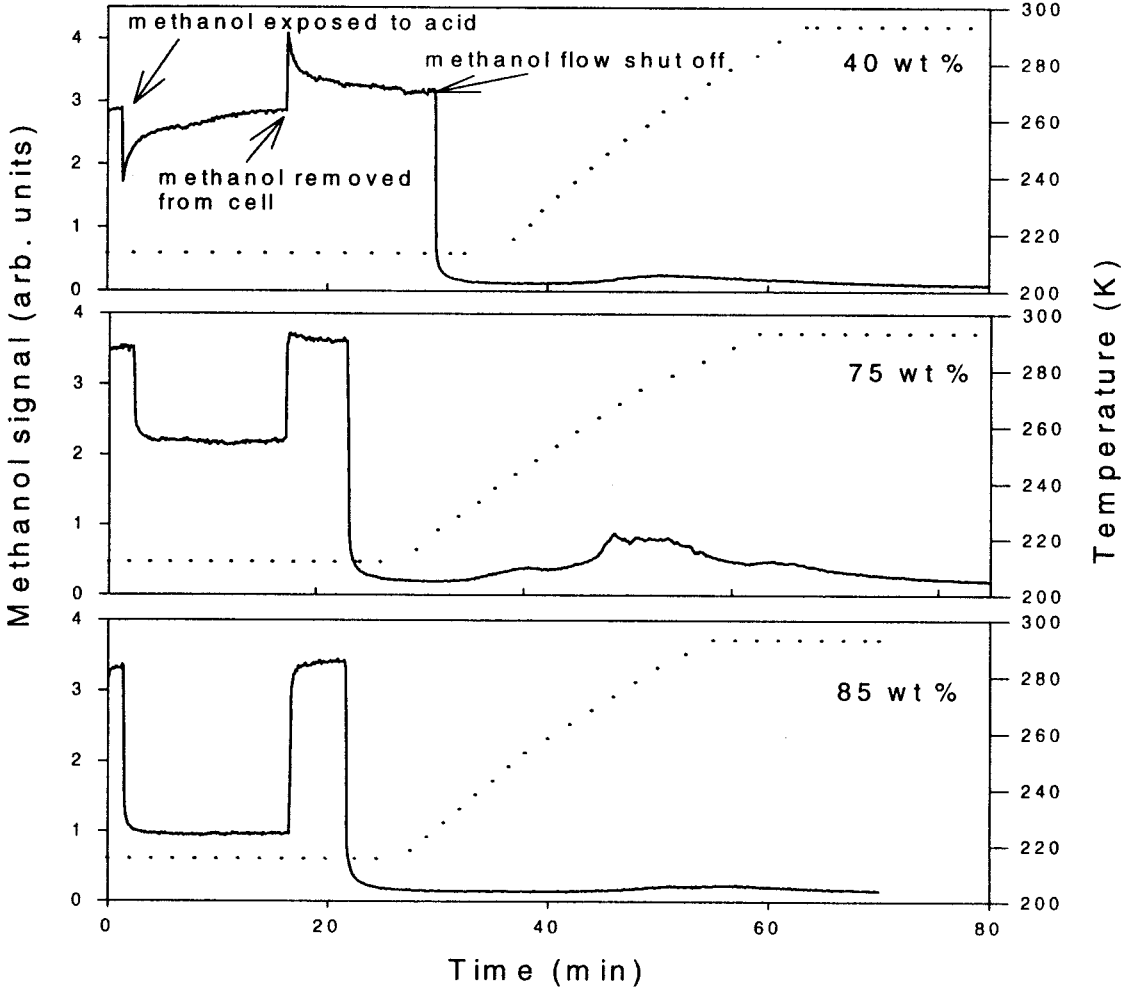




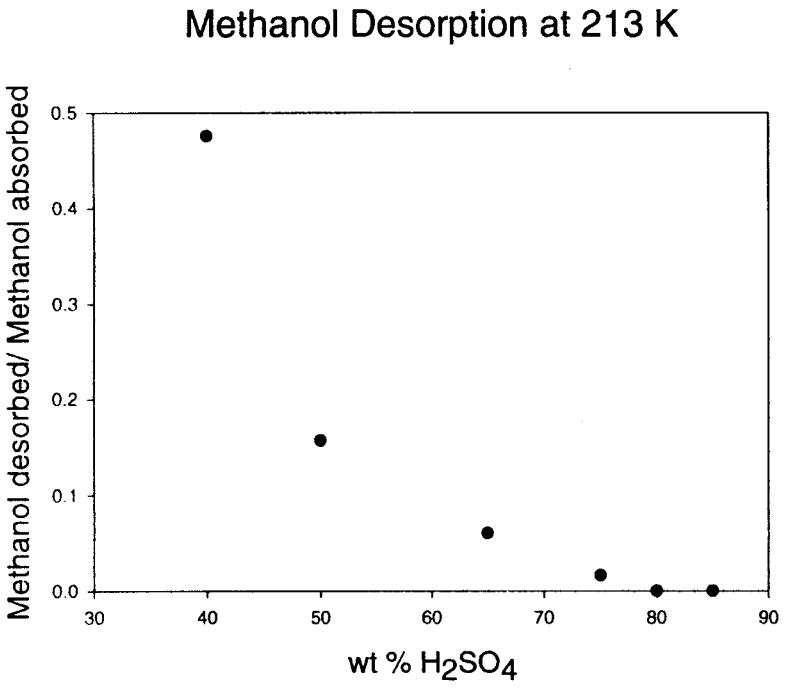
Atmospheric Implications for Acetone

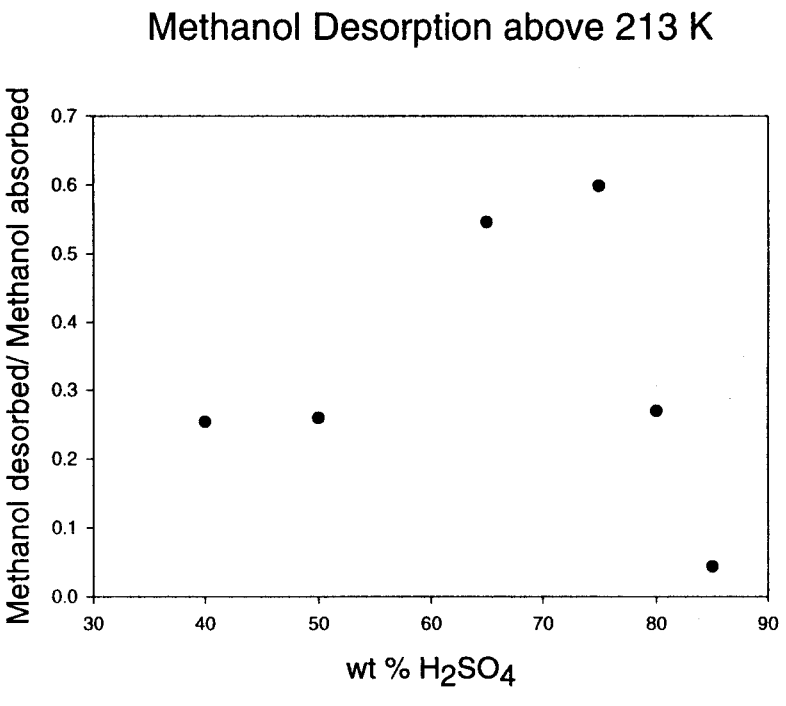
- Solubility of acetone at typical upper tropospheric conditions (75 wt % H_2SO_4 at 230 K) is ~2 x10^6 M/atm
- Assuming volume fractions of sulfate are 10^{-14} and 10^{-10} for quiescent and volcanic-perturbed conditions, the uptake accounts for 10^{-6} and 10^{-2} of tropospheric acetone, respectively
- Uptake by sulfate is not a significant sink for tropospheric acetone

Methanol Uptake and Desorption

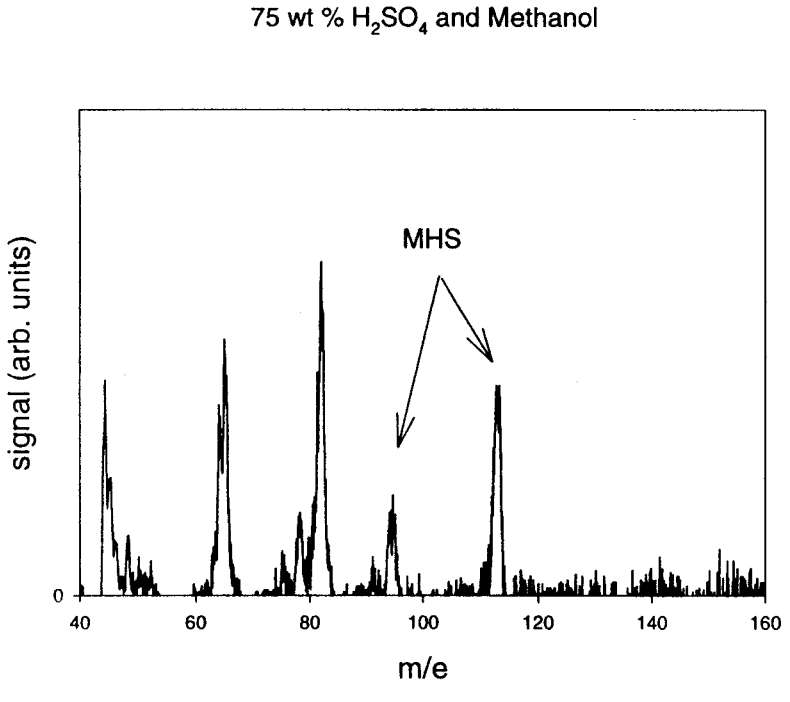


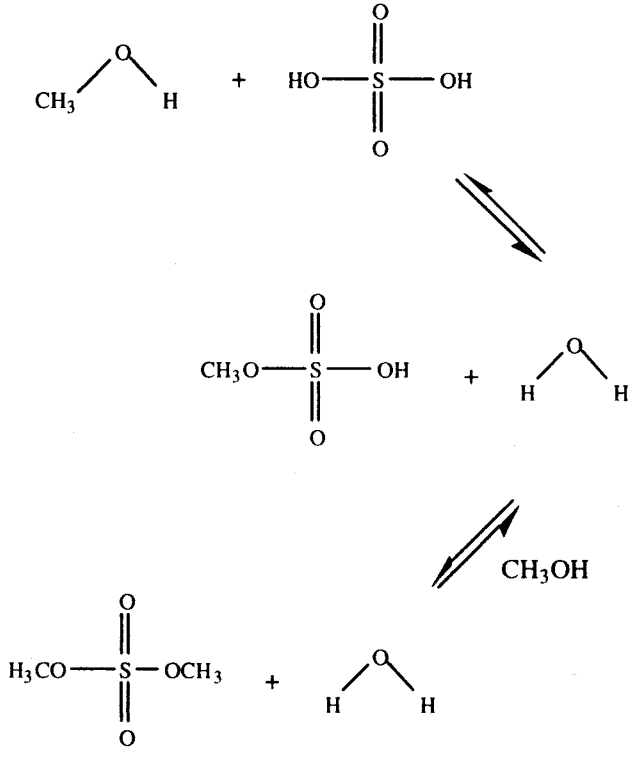
Desorbing Fractions of Methanol





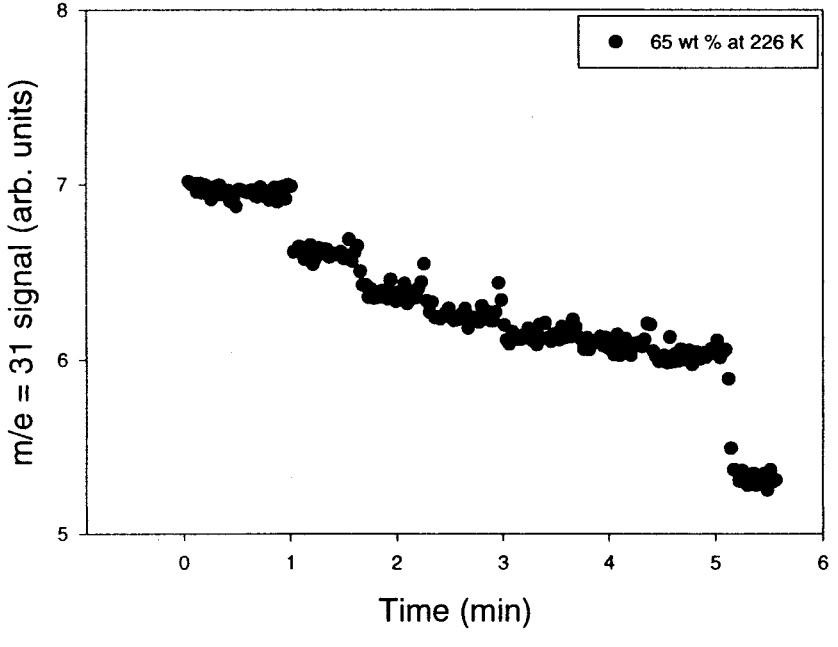
Mechanism for Methanol Uptake



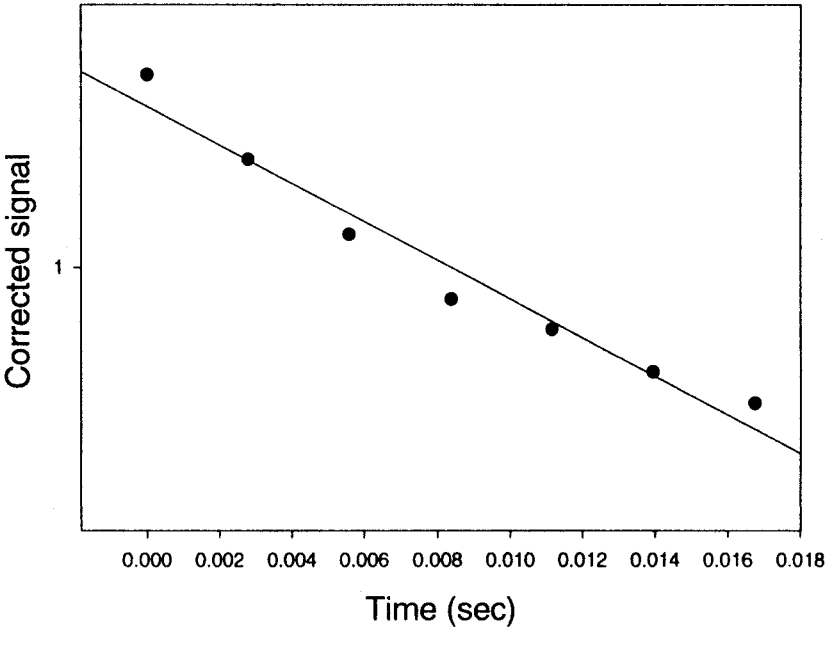


Methanol Reactive Uptake Measurement

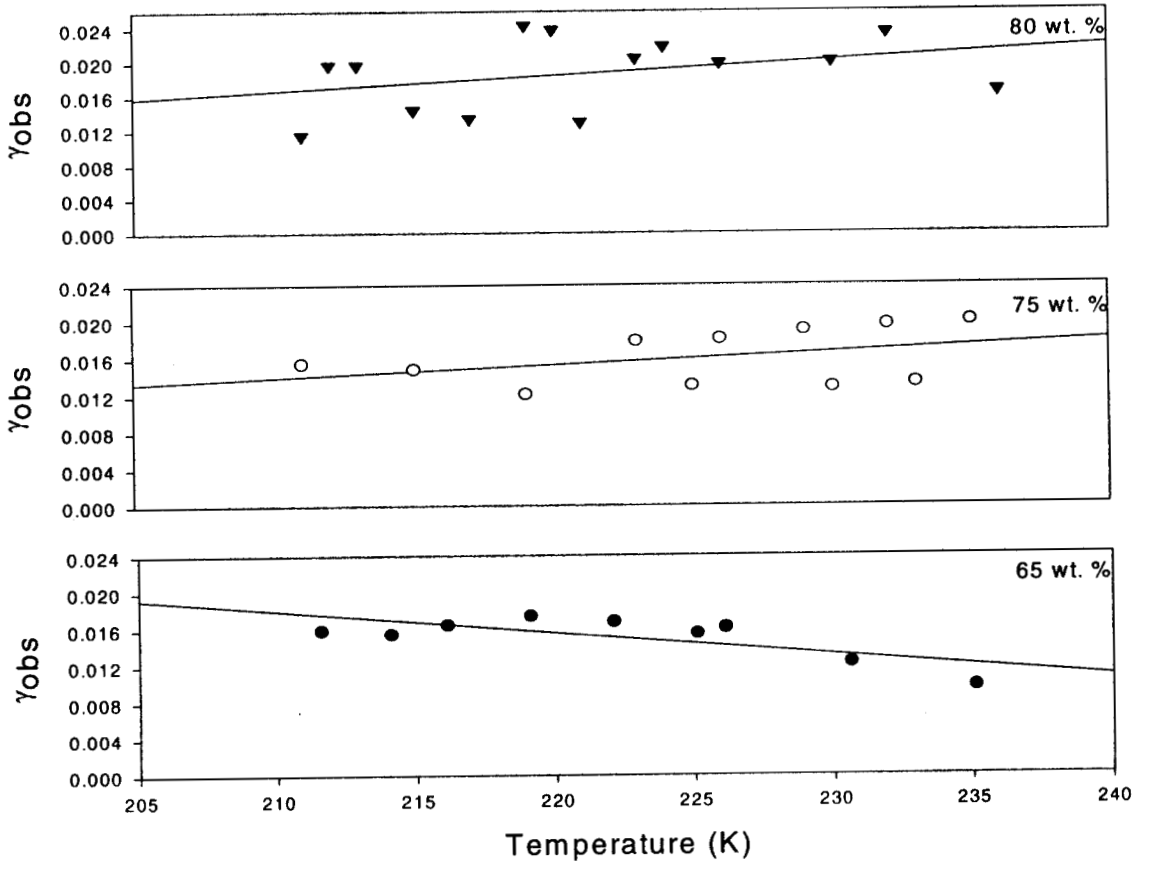
Stepwise increase in injector position



Slope gives observed uptake rate, for calculating γ

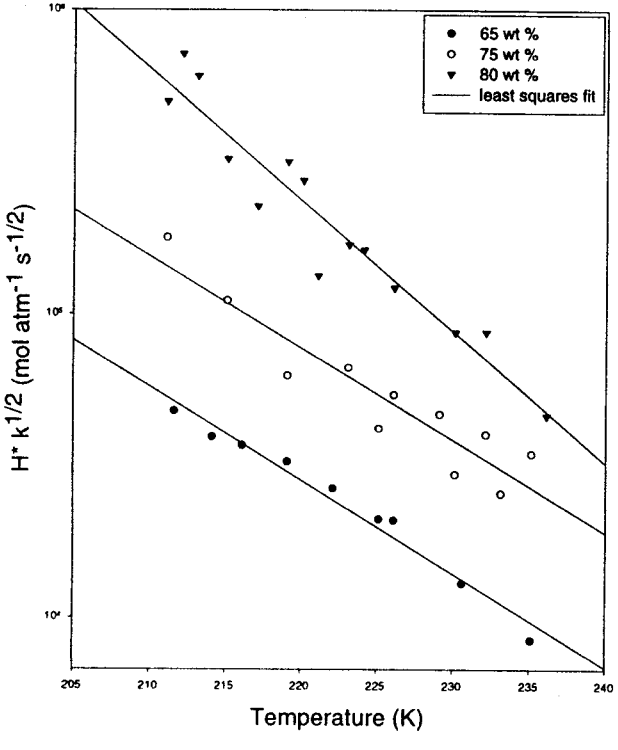


Reactive Uptake Coefficient for Methanol on Sulfuric Acid

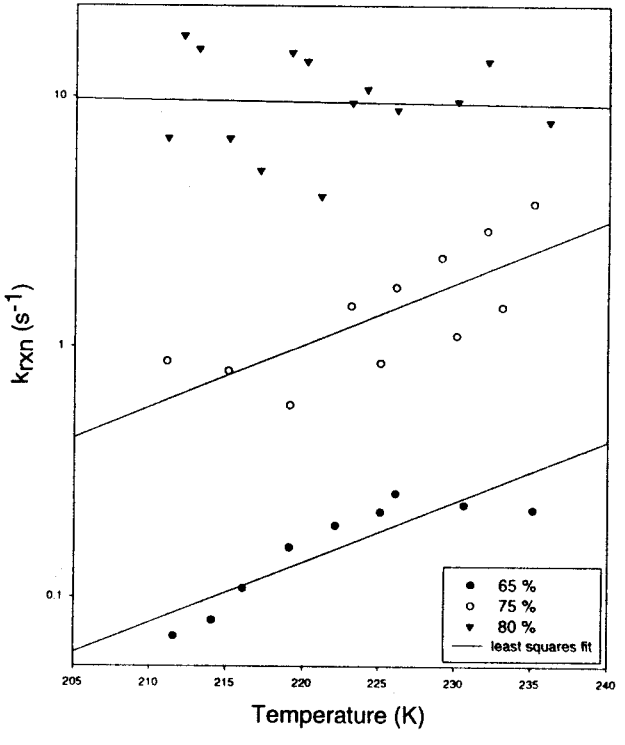


H* and K_{rxn} Determination

Calculation of $H^*k^{1/2}$ from γ_{obs}



K_{rxn} assuming H* of water



Atmospheric Implications for Methanol

- Photodissociation and reactions with water are not significant pathways for methanol loss under typical atmospheric conditions
- The loss rate of methanol with the OH radical is estimated at 10 km as $k(OH + CH_3OH) \times [OH] = 1.5 \times 10^{-7}\ s^{-1}$
- Using the data for 75 wt % H_2SO_4 the rate is estimated to be for $2 \times 10^{-5}\ s^{-1}$ under volcanic-perturbed conditions and $2 \times 10^{-7}\ s^{-1}$ for quiescent conditions
- Reaction with sulfuric acid is the dominant loss mechanism for methanol under volcanic conditions