

## ACTIVATED CARBON-MEDIATED ALKALINE HYDROLYSIS OF METHYL BROMIDE

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Activated carbon (AC) is commonly used to remove organic contaminants from waste streams by adsorption. Previous research has shown that ACs can effectively adsorb MB from quarantine and pre-shipment (QPS) fumigation chamber vent streams up to several percent by weight, even at high humidity. Efforts have been made on ways to remove or destroy adsorbed MeBr in order to regenerate the AC, including thermal desorption, wet degradation, and electrolysis. MB is susceptible to nucleophilic attack. Studies have been conducted on water or thiosulfate as the nucleophile. Water hydrolysis is slow even at elevated temperature (80 °C) and generates hydrobromic acid which is corrosive. While reaction with thiosulfate is rapid, it produces methyl thiosulfate, which is of questionable hazard.

In this study we considered a strategy of trapping MB by AC and then degrading it *in situ* (without a separate desorption step) in an aqueous sodium hydroxide bath, which would hydrolyze MB to relatively non-hazardous products, methanol and bromide ion. Hydroxide ion is a much stronger nucleophile than water. Conventional wisdom holds that in aqueous systems AC acts merely as an inert adsorptive sink by passively sequestering contaminants from reactions occurring in the bulk aqueous phase. According to this view, reaction of MB would be limited by its diffusion from the solid into the aqueous phase. We were surprised, however, to find that the rate was nearly independent of the percent of MB adsorbed, suggesting that AC itself was participating in hydrolysis. Here we investigated the role of AC in mediating alkaline hydrolysis of MB.

The complete decay of pre-sorbed MB in 1M NaOH in the presence of powdered or granular AC was complete in 2-3 h at 55 °C. The rate followed a two-term rate law corresponding to reactions occurring in both the aqueous and adsorbed states. The reaction in each state produced methanol and bromide, and had identical activation energies, consistent with a common mechanism, S<sub>N</sub>2 displacement by hydroxide. A small amount of dimethyl ether was produced by nucleophilic attack of methoxide ion formed as methanol built up in the reaction mixture. Direct involvement of surface of functional groups (e.g., hydroxyl groups) in the reaction was ruled out. The observed first order rate constant for reaction in the adsorbed state was 13% that in aqueous solution, but under conditions where >90%

of MB is adsorbed (most practical situations) hydrolysis occurs overwhelmingly in the adsorbed state. The dependence of adsorbed-state hydrolysis on aqueous hydroxide ion concentration, (0.83 order) suggested that adsorbed MB is attacked by adsorbed hydroxide ion.

The adsorbed-state reaction was accelerated by sorption or grafting of quaternary ammonium ( $\text{NR}_4^+$ ) compounds and the activation energy was reduced. Moreover, the adsorbed-state reaction was inhibited by added bromide, nitrate, or perchlorate salt following the classical chromatographic elution order in those anions ( $\text{Br}^- < \text{NO}_3^- < \text{ClO}_4^-$ ) on Type I and Type II quaternary ammonium anion exchange resins. This indicates that those ions are competing for hydroxide ion on the AC.

Two plausible mechanisms may be proposed that are consistent with the results. *i)* Ion Pair Partitioning (IPP) of  $\text{Na}^+\text{OH}^-$  ion pairs into the liquid-like phase of MB that condenses in the mesopores of AC upon adsorption. Non-aqueous hydroxide ion is expected to have enhanced nucleophilicity. *ii)* Anion Exchange (AE) of hydroxide ion at positively-charged sites on the AC surface. While the AC surface is net negatively charged due to ionizable acidic groups, there may be a low density of positively charged sites (heterocyclic nitrogen?) that offer anion exchange sites for  $\text{OH}^-$ . The adsorption of quaternary ammonium salts serves to neutralize repulsive negative surface charge, and to provide additional positive charges via the formation of hemimicelles.

A number of practical concerns were also addressed. The rate was essentially unaffected after four cycles. The buildup of bromide ion apparently did not seriously inhibit the rate. Methanol significantly increased the rate of degradation, however, presumably because methoxide ion is a stronger nucleophile than hydroxide, even though present at lower concentration. Four different ACs showed qualitatively similar behavior. Hydrolysis of MB can be carried out even in the adsorbed state meaning that capture and degradation can take place simultaneously and not limited by desorption from the solid. Research is ongoing to tailor AC in order to lower the temperature requirement.