USE OF FTIR IN THE EXAMINATION OF QUATERNIZATION REACTIONS USING DIMETHYL CARBONATE

Dianna Wineinger and Gary W. Earl
Department of Chemistry, Augustana College
Sioux Falls, SD 57197

ABSTRACT

The purpose of this research was to evaluate the quaternization reactions of tertiary amines and the alkylating agent dimethyl carbonate using FTIR (Fourier transform infrared spectroscopy).

Keywords

Dimethyl carbonate, methyl carbonate anion, quaternary ammonium compounds, FTIR

INTRODUCTION

Industry currently uses the highly toxic alkylating agents methyl chloride and dimethyl sulfate for the quaternization of tertiary amines. Although these alkylating agents do not survive in the final product, plant workers are at risk of accidental exposure. This research examines dimethyl carbonate as an alternative alkylating agent because of its very low toxicity rating. The original goal of this particular work was to find a means of following the quaternization reactions using FTIR. Various quaternary ammonium compounds and tertiary amines were examined. In addition, the FTIR of the methyl carbonate anion was identified.

The anion of methyl carbonate quaternaries can be replaced with the anions of various acids. A few preliminary reactions involving this conversion of the methyl carbonate anion were conducted using both weak and strong acids.

METHODS

A Parr pressure reactor was used for the quaternization reactions. Methyl alcohol was used as the reaction solvent and the headspace was purged with nitrogen gas to remove ambient oxygen. Materials used were reagent grade chemicals. Various tertiary amines were quaternized including tributylamine and tridodecylamine at reaction temperatures around 150 °C and pressures around 200 psi.

Prior to FTIR analysis the methyl alcohol solvent and excess dimethyl carbonate were evaporated using a Brickmann Büchi Rotavapor apparatus. An
IBM Instruments IR32 FTIR was used to collect spectral data. Neat liquid samples were analyzed between sodium chloride plates.

RESULTS AND DISCUSSION

An example FTIR spectrum (Fig. 1) of the amine reactant and the quaternary product shows the peak overlap. This prevents using FTIR for following the extent of quaternization.

An FTIR spectrum of the methyl carbonate anion was not found in the chemical literature; therefore, the methyl carbonate anion was acquired by reacting sodium methoxide with dimethyl carbonate to produce the desired anion and dimethyl ether. The carbonyl peak frequency in dimethyl carbonate (~1757 cm\(^{-1}\)) was expected to decrease due to resonance, and the carbon-oxygen bond (~1280 cm\(^{-1}\)) frequency was expected to increase.

An example FTIR spectrum (Fig. 3) of the sodium methyl carbonate anion shows that the predicted frequency changes were accurate.

The possibility of using the carbonyl peak of the methyl carbonate anion for calibration was considered; however, in our hands the methyl carbonate anion converts to hydrogen carbonate in the presence of water. An example FTIR spectrum (Fig. 4) of a methyl carbonate quaternary product after exposure to water shows peaks matching those of hydrogen carbonate (Fig. 5). Therefore, it was concluded that FTIR was not a feasible means of following the extent of reaction.
The next portion of the work involves making new quaternaries possessing different anions. The methyl carbonate quaternary was treated with various acids to form new compounds via the following reaction:

\[
\text{Quat'Anion} + H^+ \rightarrow \text{Quat'New Anion} + \text{New Anion} + CO_2 + \text{Methanol}
\]

Conversions with strong acids go to completion. An example of a strong acid product is the following sulfate quaternary (Fig. 6).

Conversions with weak acids are problematic in that the reaction does not go to completion. The methyl carbonate anion acts as a weak base which does not react well with a weak acid. Therefore, the methyl carbonate quaternary was converted to the hydroxide quaternary using calcium hydroxide. The basicity of the hydroxide anion (pH ~14) thus allows for a complete reaction using a weak acid. An example of this process for the lactate quaternary is shown in figures 7, 8, 9, and 10. A partial anion conversion resulted using only lactic acid (Fig. 7); however, complete conversion was achieved via the hydroxide quaternary intermediate (Fig. 9).

**CONCLUSION**

Infrared spectroscopy is not a good method for following quaternization reactions of tertiary amines and dimethyl carbonate. The conversion of methyl carbonate quaternaries to hydroxide quaternaries provides a means by which many new quaternaries can be made.
REFERENCES


ACKNOWLEDGMENTS

This material is based upon work supported by the NSF/EPA grant [CHE-9613052] provided to Gary W. Earl. This work was carried out in the Summer Science Institute during the Summer of 1997 at Augustana College.