Epoxidation Kinetics

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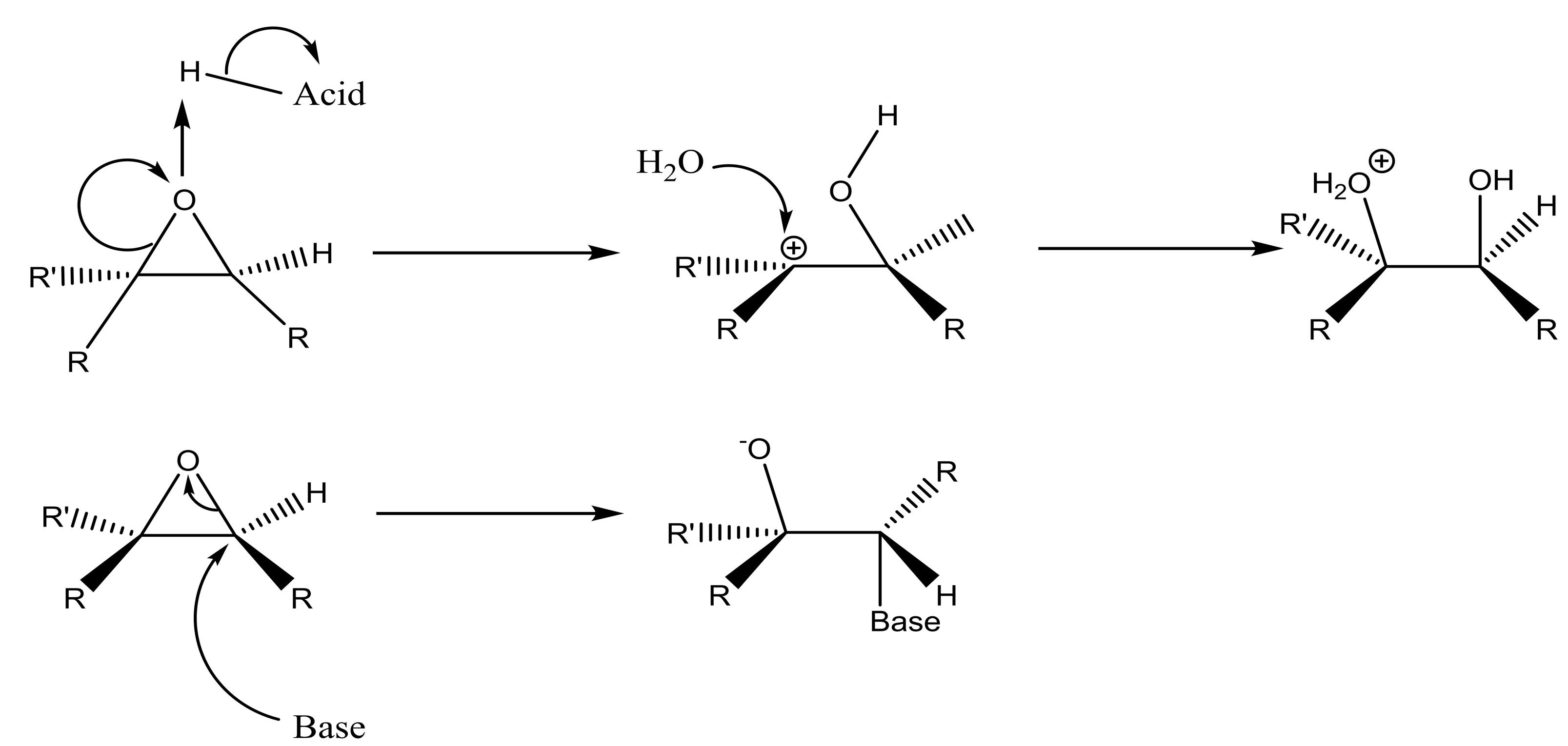
Abstract

The proposed mechanism for the epoxidation of cyclohexene was investigated by monitoring the following reactions using ATR IR: reaction of acetonitrile and hydrogen peroxide, the reaction between 2,2,2-trifluoroacetaphenone, hydrogen peroxide, and acetonitrile, and the entire epoxidation reaction.

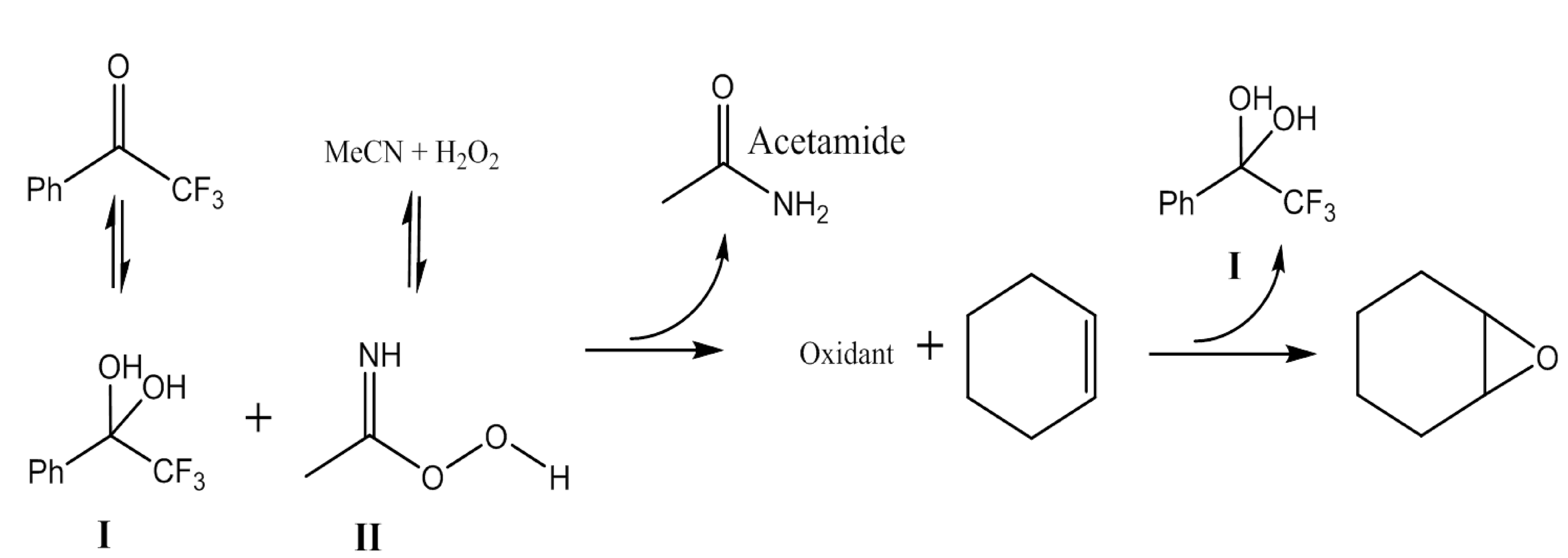
Introduction

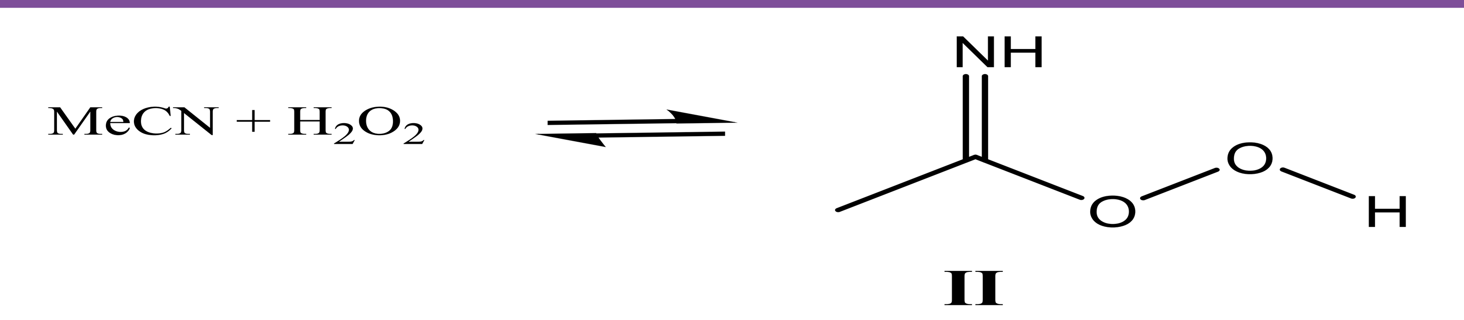
It has been reported that hydrogen peroxide can be used as an oxidant in an epoxidation reaction. The hydrogen peroxide is not strong enough on it's own to oxidize an alkene to an epoxide but in the presence of acetonitrile and a 2,2,2-trifluoroacetaphenone catalyst an even more reactive oxidant can be formed to oxidize the olefin. This reaction is of interest because water is the only by product, making it a very environmentally friendly reaction. The reactants are also very inexpensive which is also beneficial.

Epoxides can be a very useful intermediate



The proposed reaction mechanism





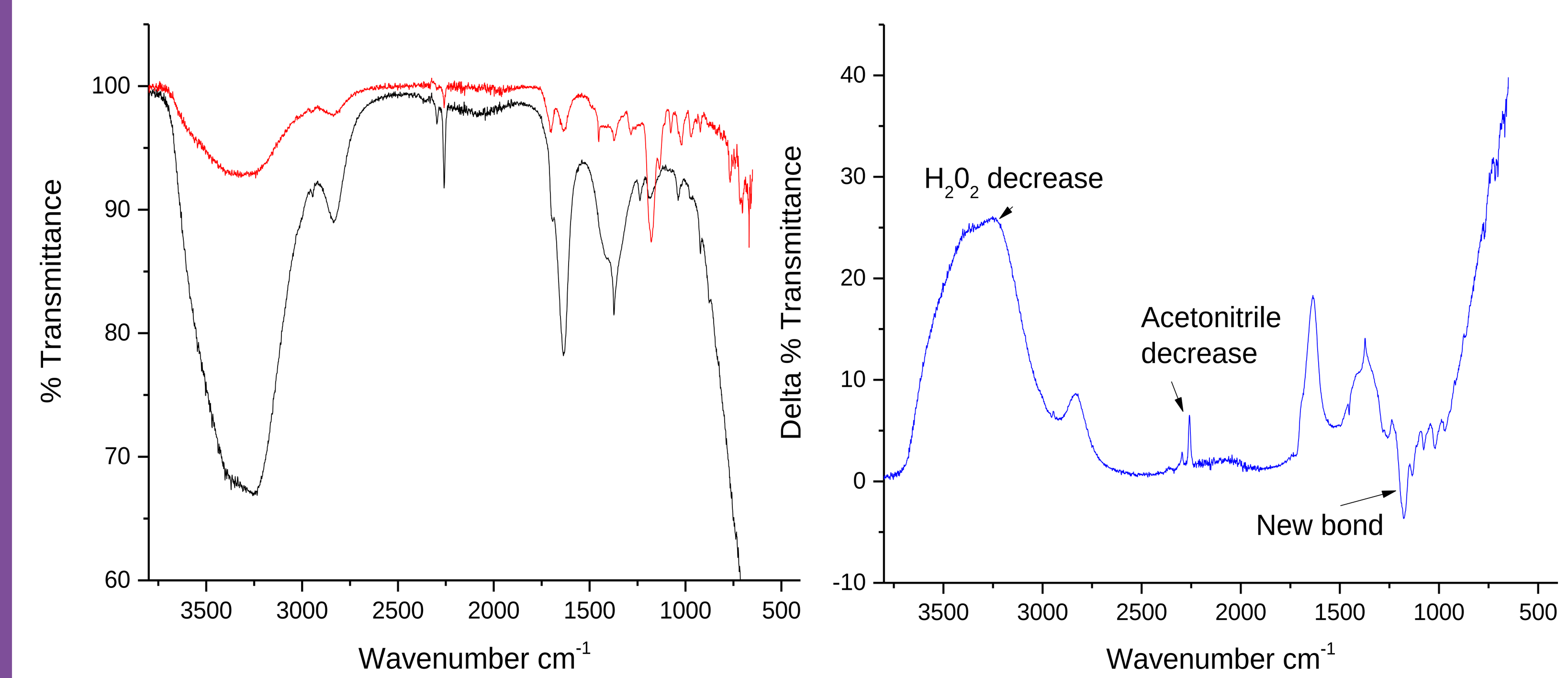
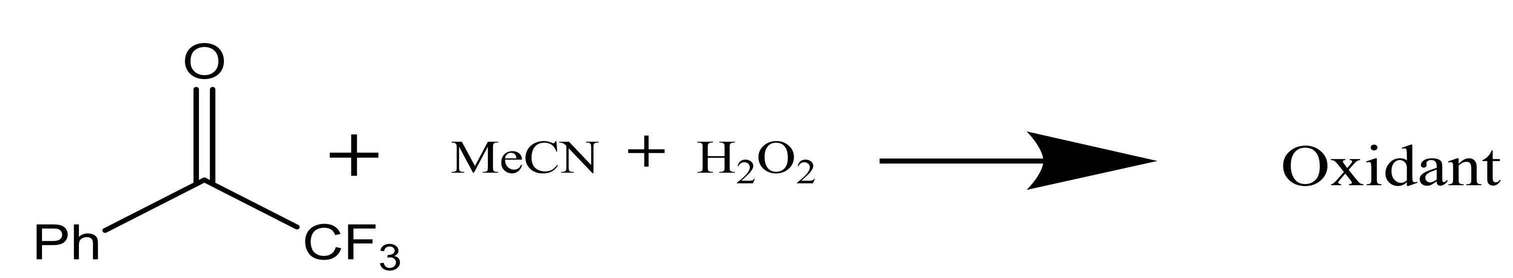


Figure (1). IR spectra on the right: (0.011 mL, 0.43 mmol) Hydrogen Peroxide and (0.025 mL, 0.43 mmol) acetonitrile, black line is the initial spectrum and red is the final spectrum. The delta spectrum on the right shows the subtraction of the black line from the red line.



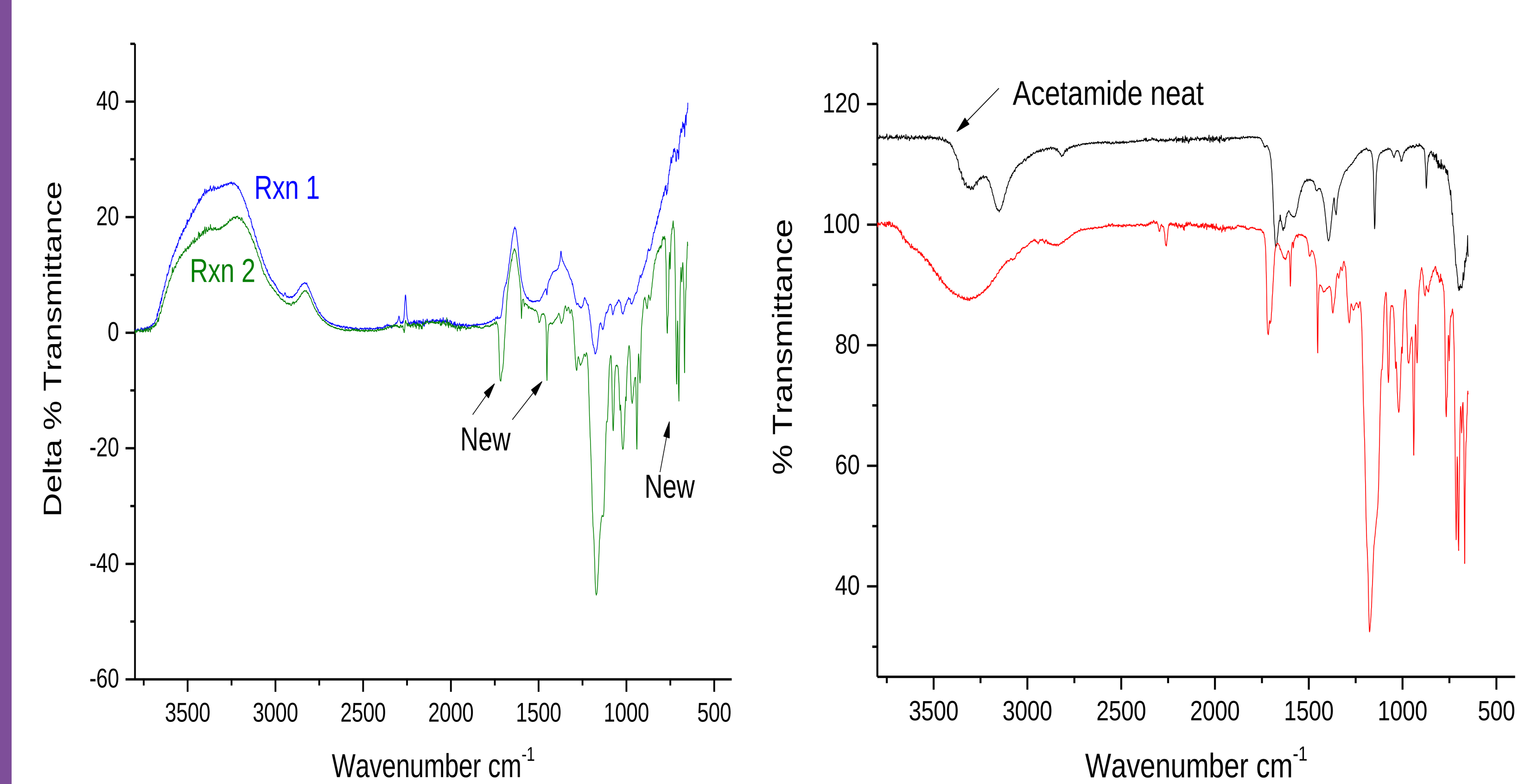
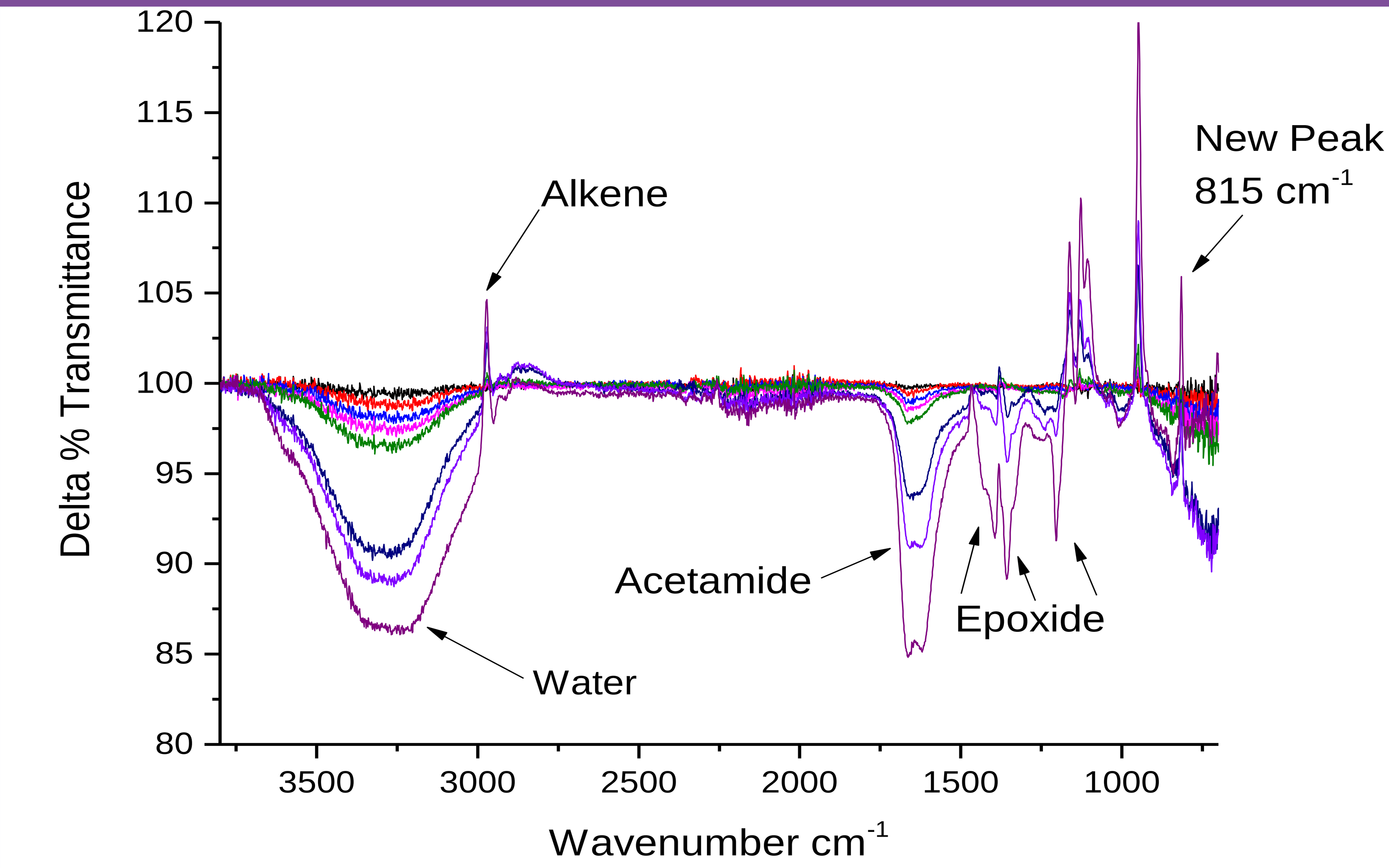


Figure (2). Delta spectra for the reaction between the hydrogen peroxide and acetonitrile (blue line) and the reaction between 2,2,2-trifluoroacetaphenone, hydrogen peroxide, and acetonitrile (green). The spectra on the right shows on overlay of the neat acetaamide spectrum in black on top of the subtraction spectrum of the reaction of the catalyst, acetonitrile and peroxide.



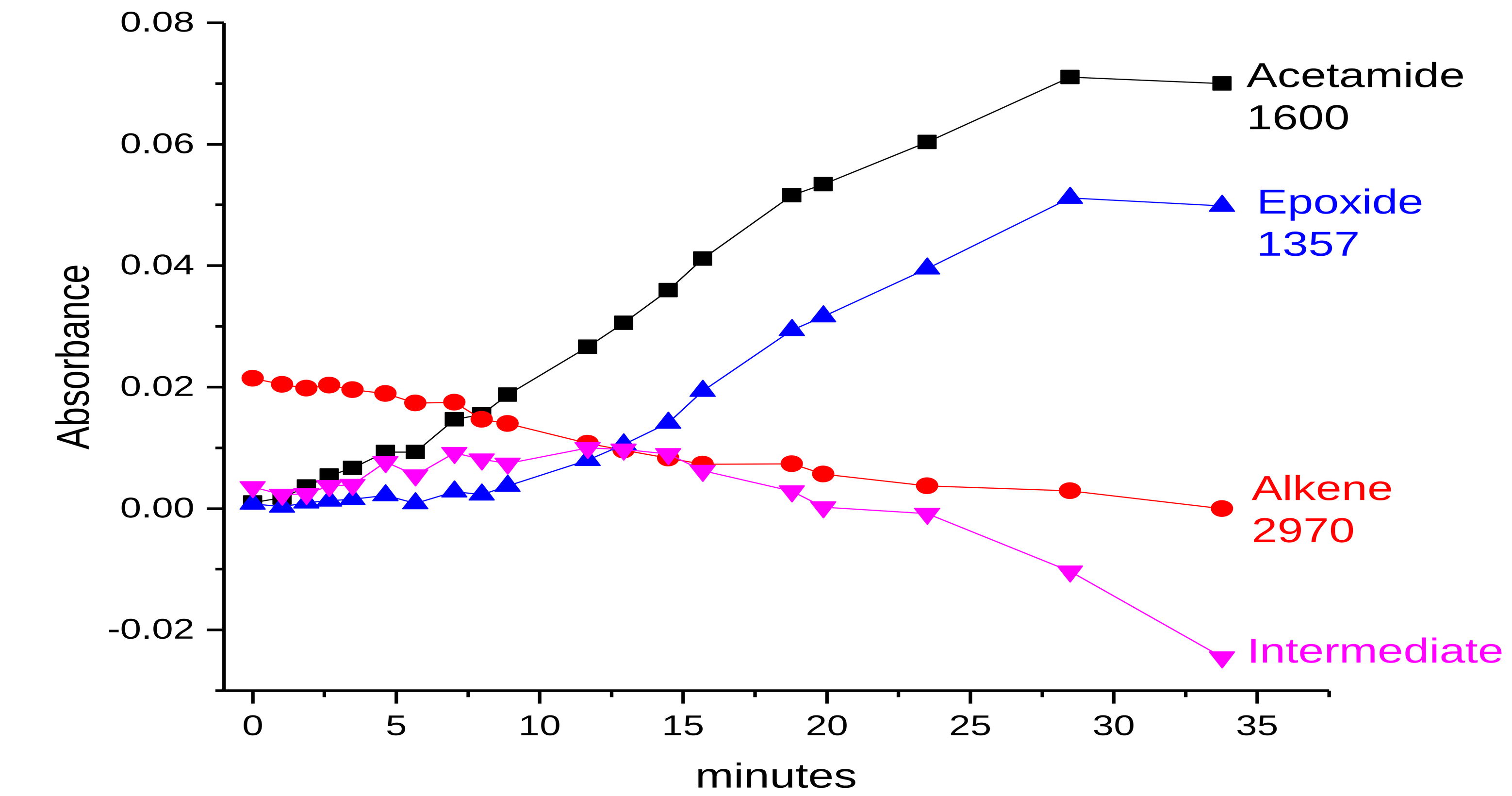


Figure (3). Delta spectra for the reaction of cyclohexene (1 equiv), catalyst, hydrogen peroxide (2equiv) and acetonitrile (2 equiv) in a isopropyl/ EDTA buffered solution (pH 11). The bottom graph is the absorbance versus time for the peaks at 2970 (red), 1357 (blue), 1600 (black), and 815 (magenta).

Conclusion

The IR spectra for the individual reactions suggest there are three distinct reactions happening. The absorbance versus time for the peak at 2970 is due to the alkene and it is linear suggesting the rate of epoxidation is zeroth order in respect to the alkene.

Reference

Limnios, D.; Kokotos C. G. 2,2,2-Trifluoroacetophenone: An organocatalyst for an Environmentally Friendly Epoxidation of Alkenes. *J. Organic Chem.*