

Kinetic Study of α -Bromo-*o*-toluic Acid Using Raman Spectroscopy

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Raman technique has been utilized to demonstrate its feasibility for studying the kinetics of organic reactions in aqueous solution. The solvolytic reaction of α -bromo-*o*-toluic acid in 80% aqueous ethanol has been selected as a model system. Due to a moderate reaction rate and a detection possibility of Raman signal, the solvolytic reaction of α -bromo-*o*-toluic acid¹ is considered as a very good model system for the present Raman study. The major problem in measuring reactions with Raman spectroscopy consists in extracting small vibrational peaks of reactant or product from the strong Raman backgrounds of solvent.² In this work, we have successfully monitored the disappearance of the C-Br stretching peak for the reactant, α -bromo-*o*-toluic acid, and the appearance of the vibrational peak for the product, phthalide. The solvolysis rates of α -bromo-*o*-toluic acid in 80% aqueous ethanol have been determined by measuring the disappearance rate of the C-Br stretching Raman peak at 619 cm⁻¹ normalized to a C-H stretching peak at 2978 cm⁻¹ as an internal standard. Here we report the kinetic analysis for the solvolytic reaction of α -bromo-*o*-toluic acid using Raman spectroscopy.

Experimental and Computational Section

Raman measurements were performed with a Kaiser Holoprobe Raman system. A cavity stabilized diode laser at 785 nm was used as the excitation source. The laser power was approximately 40 mW. A macro-sample chamber equipped with a filtered fiber optic probe-head was used to collect the scattered light.³ Rayleigh line was removed from the collected Raman scattering by a holographic notch filter in the collection path.⁴ Raman scattering was detected with a CCD camera and spectral resolution was 4 cm⁻¹. Mid-infrared spectra were recorded with a Bio-Rad FTS-6000 interferometer operating at a resolution of 2 cm⁻¹. A cryogenic MCT detector and KBr windows were used for the infrared measurements.

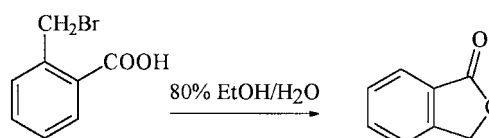
α -Bromo-*o*-toluic acid was prepared by the published method.⁵ Phthalide, which was used for the product identification, was purchased from Aldrich Chemical and used without further purification. The reaction product was identified using FT-IR and NMR spectroscopy. Solvolysis of α -bromo-*o*-toluic acid for kinetic measurements was accomplished in a 50 mL volumetric flask in a temperature-controlled water bath. About 1 mL of sample was periodically transferred to a quartz cell and quenched for the Raman measurements. All spectral manipulations were performed using GRAMS/32

software from Galactic Industries Corporation.

The vibrational frequencies for both the reactant, α -bromo-*o*-toluic acid, and the product, phthalide, were calculated using the B3LYP method.⁶ The C-Br stretching mode of α -bromo-*o*-toluic acid and the vibrational mode of phthalide have been assigned on the basis of the calculated results of each normal mode. All the calculations were performed using the GAUSSIAN98 program package implemented on an alpha-cluster computer system.⁷ The GAUSSVIEW program was also used to visualize the vibrational modes assisting the assignment of spectra.

Results and Discussion

Model reaction under investigation is the solvolytic reaction of α -bromo-*o*-toluic acid in 80% aqueous ethanol. Figure 1 shows the Raman spectra of (a) 80% aqueous ethanol only, (b) the reactant, α -bromo-*o*-toluic acid, in 80% aqueous ethanol, and (c) the fully converted product, phthalide, in 80% aqueous ethanol at 35 °C.



As mentioned above, the most difficult problem in measuring the reaction using Raman spectroscopy is extracting

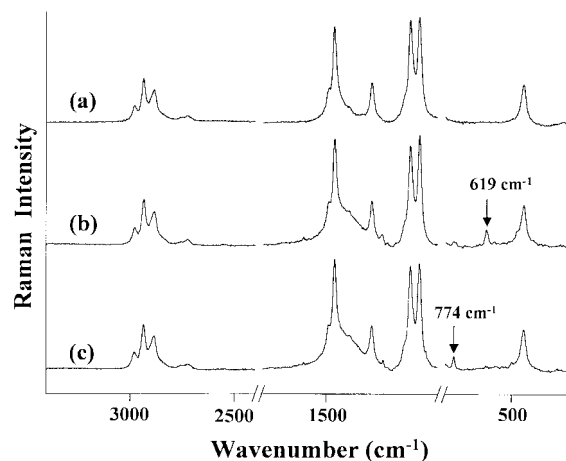


Figure 1. Raman spectra of (a) 80% aqueous ethanol only, (b) reactant (α -bromo-*o*-toluic acid) in 80% aqueous ethanol, and (c) fully converted product (phthalide) in 80% aqueous ethanol.

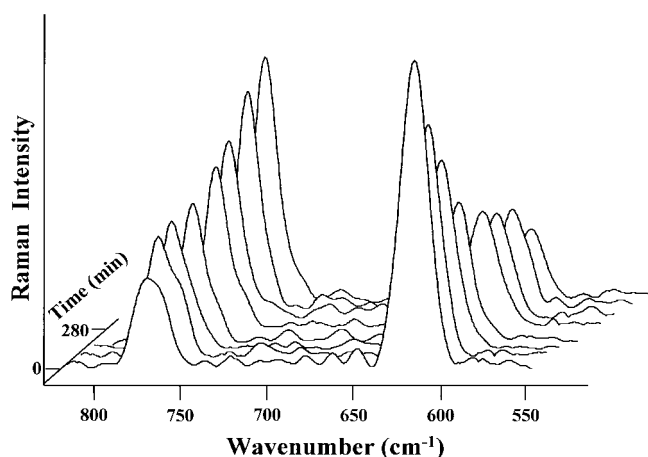


Figure 2. Time-dependent Raman spectra of α -bromo-*o*-toluic acid, showing loss of the 619 cm^{-1} peak and gain of the 774 cm^{-1} peak, in 80% aqueous ethanol. Reaction temperature is $35\text{ }^{\circ}\text{C}$ and time interval for each spectrum is 40 min.

the small Raman peaks of reactant or product from the large backgrounds of solvent. In our Raman spectra, however, the disappearance of the C-Br stretching peak for the reactant and the appearance of vibrational peak for the product have been clearly monitored at 619 cm^{-1} in Figure 1(b) and at 774 cm^{-1} in Figure 1(c), respectively.

Figure 2 shows the time-dependent Raman spectra at $35\text{ }^{\circ}\text{C}$, showing the intensity changes of the 619 and 774 cm^{-1} peaks with the extent of solvolysis. In order to confirm the normal mode for the 619 cm^{-1} peak of α -bromo-*o*-toluic acid and the mode for the 774 cm^{-1} peak of phthalide, the frequency calculations at the B3LYP/6-31G(d) level have been carried out. The calculated vibrational frequencies for each molecule agree well with the observed Raman frequencies. The Raman spectra in Figure 2 show that the 619 cm^{-1} peak disappears after long reaction time, demonstrating that complete conversion can be detected by the Raman technique.

The Raman peak due to the C-Br stretching mode of α -bromo-*o*-toluic acid at 619 cm^{-1} was used to monitor the extent of solvolysis. In order to correct the sample-to-sample fluctuations in Raman peak area, the 619 cm^{-1} peak was normalized for the peaks of the C-H vibrational modes ranging from 2800 cm^{-1} to 3200 cm^{-1} as an internal standard. To calculate the extent of solvolysis, the 619 cm^{-1} peak was integrated from 590 cm^{-1} to 640 cm^{-1} and the 2978 cm^{-1} peak was integrated from 2800 to 3200 cm^{-1} . Even though the Raman peaks in the 2800 - 3200 cm^{-1} region are composed of three Raman modes, it is apparent that they are suitable peaks to be used as an internal standard since the peak areas are very consistent regardless of the extent of solvolysis.

The general n th order model was applied and a reaction order of 2.0 was determined. The plots to determine the second order rate constants at 25 , 35 , 45 , and $55\text{ }^{\circ}\text{C}$ are shown in Figure 3. All the plots show very good linear correlation over 0.98. The second order rate constants at those temperatures are also shown in Table 1 with the

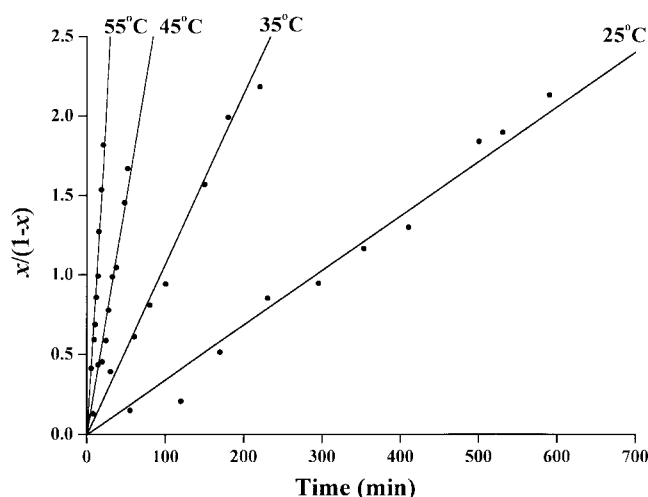


Figure 3. Plots of conversion ratio to determine the second order rate constants at various temperatures. Here x is the degree of solvolysis.

Table 1. Reaction temperatures, concentrations, and corresponding second order rate constants for the solvolysis of α -bromo-*o*-toluic acid in 80% aqueous ethanol

| Temperature ($^{\circ}\text{C}$) | Initial concentration (M) | Rate constant k ($\text{M}^{-1}\text{min}^{-1}$) | Correlation coefficient |
|------------------------------------|---------------------------|--|-------------------------|
| 25 | 0.081 | 3.432×10^{-3} | 0.993 |
| 35 | 0.070 | 1.073×10^{-2} | 0.993 |
| 45 | 0.070 | 2.987×10^{-2} | 0.991 |
| 55 | 0.070 | 8.100×10^{-2} | 0.986 |

correlation coefficient values for the straight-line fits. The fits are slightly better at lower temperatures where there is less relative error in the time of reaction due to the slower reaction rates. The rate constant data in Table 1 were also used to determine the Arrhenius behavior and activation energy of reaction. The Arrhenius plot also shows a very good linear correlation and the activation energy of the reaction is determined to be $19.8\text{ kcal mol}^{-1}$.

Conclusion

In this study, Raman technique has been applied to monitor the solvolytic reaction of α -bromo-*o*-toluic acid in 80% aqueous ethanol. The weak Raman peaks of the reactant and the product have been successfully extracted from the strong Raman backgrounds of solvent. The disappearance of the C-Br stretching Raman signal at 619 cm^{-1} for the reactant has been utilized to determine the second order rate constants for the reaction. This peak was normalized to a C-H stretching signal at 2978 cm^{-1} as an internal standard to normalize the sample-to-sample fluctuations. By monitoring the peak area change during the reaction, the second order rates at four different temperatures and activation energy have been determined. The Raman spectra presented in this paper clearly demonstrate the feasibility of using this technique for monitoring the solvolytic reactions at various temperatures.

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