

THE AROMATIC NUCLEOPHILIC SUBSTITUTION REACTION. POSSIBLE AMINE CATALYSIS IN THE REACTION OF TETRABUTYLAMMONIUM HYDROXIDE WITH 2,4-DINITROCHLOROBENZENE^{1, 2}—

In connection with another problem, it was necessary to confirm the kinetic order and rate constants for the reaction of 2,4-dinitrochlorobenzene (abbreviated 2,4-DNCB) and tetrabutylammonium hydroxide (abbreviated TBAH). In a previous investigation, Reinheimer and Hostetler (1964) found that commercial TBAH gave erratic rate data. When the TBAH was prepared by the method of Fritz and Marple (1962), consistent rate data were obtained. The present investigation began with TBAH prepared by the method of Fritz and Marple, but erratic rate data were again obtained. The new rate constants were 1.5 to four times as large as those previously reported by Reinheimer and Hostetler. Further, when the molar ratio of 2,4-DNCB/TBAH was about 4, straight-line plots of $\log [(TBAH)/(2,4-DNCB)]$ vs. time were obtained. When the same molar ratio was 2 or less, curvature of the kinetic plot, indicating a more rapid reaction, was observed. When a less concentrated stock solution of TBAH was used, the curvature disappeared, but the rate constants were still quite high when compared with the previous results. Possible causes for this acceleration and curvature were: 1) impure solvent, 2) impure TBAH due to impure starting materials or to decomposition of the TBAH stock solution, or 3) impure 2,4-DNCB.

Several of the possible causes can be readily eliminated. Impure solvent cannot be the cause, for a similar-rate investigation was being carried out at the same time with the same dioxane-water solvent, and there were no complications in the concurrent experiments. A second support for the purity of the solvent lies in the fact that the reaction of 2,4-DNCB and NaOH in the dioxane-water solvent gave consistent rate constants as compared with the previous investigation. The rate constants are not precisely the same, but lie well within experimental error.

The purity of the 2,4-DNCB cannot be the cause of the acceleration on the basis of the reproducibility of the rate constants. The organic starting material for the preparation of TBAH is tetrabutyl ammonium bromide. Our sample melted at 111–111.5°C, and the literature value of 113°C is given by Fowler, Loebenstein, Pall, and Kraus (1940). Decomposition of the TBAH was discounted when standardization over a period of time showed no concentration change.

The erratic rates do not seem to be due to a concurrent reaction. Isolation of the reaction product from accelerated and non-accelerated reactions gave a single product. Analysis by thin-layer chromatography of the reaction product from kinetic experiments gave a single spot, which corresponds to the expected phenol. If methoxide ion were present, the 2,4-dinitroanisole would form a second spot with a much greater R_f value. The most likely impurity, tributylamine, when it is the only nucleophile, does not react rapidly enough to account for the rate increase.

Finally, a second sample of TBAH was prepared by the method of Fritz and Marple (1962). The removal of the methanol in the concentration step was accomplished in two ways, at steam-bath temperatures and also at room temperature. The high-temperature concentration gave a solution which had a dark orange color and a strong odor of amine, while the product of evaporation at lower temperature had a pale yellow color and a faint amine odor. The last traces of the amine were removed by treatment with activated charcoal, after which the solution was passed through an Amerlite IRA 900 macroporous resin on the

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hydroxide cycle. The purified TBAH gave consistent rate data and straight-line kinetic plots up to 70 percent reaction at both high- and low-concentration ratios. The reaction was found to be first order in 2,4-DNCB and first order in TBAH. The rate constants are consistent with the data previously obtained by Hostetler and Reinheimer.

We conclude that the salt effects observed by Hostetler and Reinheimer are real and not due to some unrecognized catalyst. The use of the tetraalkylammonium hydroxide data, in combination with the data for alkali metal hydroxides, to determine the rate constant at zero concentration is again affirmed. However, if one uses TBAH or another tetraalkylammonium hydroxide which is temperature sensitive, kinetic complications may result. We recommend that tetraalkylammonium hydroxides that do not readily undergo a Hofmann elimination be used; for example, tetramethyl- or benzyltrimethylammonium hydroxides. The acceleration that was observed is probably due to the tertiary amine, because the acceleration disappeared when the amine was removed.—JOHN D. REINHEIMER and WAYNE HOSTETLER, *Department of Chemistry, The College of Wooster*, and *Department of Science, Wooster High School, Wooster, Ohio*.

LITERATURE CITED

- Fritz, J. S. and L. W. Marple. 1962. Potentiometric titration of acids in t-butyl alcohol. *Anal. Chem.* 34: 921; 796.
- Fowler, D. L., W. V. Loebenstein, D. B. Pall and C. A. Kraus. 1940. Some unusual hydrates of quaternary ammonium salts. *J. Am. Chem. Soc.* 62: 1140.
- Reinheimer, J. D. and Wayne Hostetler. 1964. Aromatic nucleophilic substitution reaction. *Ohio J. Sci.* 64: 275.
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