Acetanilide and para-substituted acetanilides were tritiated by heating with HTO in the presence of RhCl₃·3H₂O as a catalyst in an N,N-dimethylformamide solution at 105-107 °C for 18 h. Under such conditions, tritium introduced into the anilide molecules was found at the adjacent ortho positions to the acetamido group with virtually 100% regioselectivity. The substituent effect on the rate of tritiation was observed.

INTRODUCTION

The hydrogen isotope exchange reaction of aromatic compounds by the single step with HTO or D₂O in the presence of a catalyst is not only important for labeling these compounds with tritium or deuterium but also interesting from the mechanistic viewpoint. Strong Brønsted and Lewis acids, heterogeneous metal catalysts, and homogeneous metal complexes are used as catalysts.
The reaction mechanism has been studied on the basis of the intramolecular distribution of the isotopic hydrogen in the aromatic ring and the kinetic data\textsuperscript{2-7}. Recently, Lockley reported that anilides, aromatic acids, amides, and benzylamines were labelled with D\textsubscript{2}O in the presence of RhCl\textsubscript{3}.3H\textsubscript{2}O at the ortho positions to the functional group with high regioselectivity, for example, at least 97\% in acetanilide\textsuperscript{8,9}. The location of deuterium was determined by NMR. He also labelled with HTO various aromatic acids and amides in a similar procedure and reported on the specific activity of T-labelled compounds\textsuperscript{10}. So far, however, high regioselectivity in rhodium/III/ chloride catalyzed T-for-H exchange was demonstrated only in the case of sodium bromoglycate\textsuperscript{11}. The present study was designated to give a clue to the mechanism of the homogeneous rhodium/III/ chloride catalyzed exchange reaction using HTO, and the intramolecular tritium distribution and the substituent effect on tritium uptake were examined. The intramolecular tritium distribution was determined by chemical degradation, that is, by comparing specific activities among the parent anilide and its derivatives.

EXPERIMENTAL

Reagent grade acetanilide/I/ was supplied from the Wako Pure Chemical Industries, Ltd. p-Acetotoluidide/II/, p-chloroacetanilide/III/, and p-bromoacetanilide/IV/ were prepared by reactions between acetic anhydride and the corresponding anilines of reagent grade, which were obtained from the same company or the Tokyo Kasei Kogyo Co. Ltd. The anilides were purified by repeated crystallization. Calcd for /I/: C: 71.09; H: 6.71; N: 10.36\%. Found: C: 71.06; H: 6.73; N: 10.37\%. Calcd for /II/: C: