7. The fallout trays were low-sided flat pans covered to a depth of about 1.3 cm with polyethylene spheres 0.63 cm in diameter. Because most of the particles are traveling at extremely low angles at the moment of collection, orientation of the tray and the micrometeorology of its vicinity are very important; it is unlikely that the geometric area of the tray is equivalent to that of the ground. Moreover, the polyethylene balls complicate the chemistry by making difficult the removal of the collected material. We shall not use this type of collector again.
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9. J. Knox, private communication, 1964.
10. Sponsored by the AEC.

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Exchange of Carbon-Bound Hydrogen Atoms ortho to the Hydroxyl Group in Tyrosine

Abstract. *The carbon-bound hydrogen atoms of tyrosine that exchange with solvent protons in strongly acid solutions at about 100°C are not the methylene hydrogen atoms but a pair on the aromatic ring. Of the two pairs of protons on the aromatic ring, observed in the proton magnetic resonance spectra, the pair at higher field undergoes exchange in 2.4*N *DCl at 100°C. Other hydrogen atoms, attached either to aliphatic or aromatic carbon atoms, exhibit no noticeable exchange under the same conditions. From a chemical-shift analysis the exchanging protons are assigned as those* ortho *to the hydroxyl group on the aromatic ring.*

Study of hydrogen-isotope exchange has been used to acquire information concerning the secondary structure of proteins. In small model compounds and peptides, hydrogen atoms bound to carbon exchange very slowly or not at all at reasonable temperatures and *p*H, whereas hydrogens bound to oxygen or nitrogen exchange rapidly with hydrogen in the solvent. Peptide hydrogen atoms bound to nitrogen in proteins frequently exhibit a slower rate of exchange with solvent hydrogens than small peptides. This slower rate is ascribed to hydrogen bonding of the hydrogens or to their inaccessibility in a hydrophobic core of proteins (*1*).

Under more extreme conditions of temperature and acidity, carbon-bound hydrogens may also exchange with solvent protons. In a study of tritium exchange of proteins and amino acids in 6*N* HCl at 105°C for about 24 hours, up to two carbon-bound hydrogens of tyrosine exchanged with solvent protons (*2*). These investigators assigned the exchangeable hydrogens to the methylene group of tyrosine. Though this assignment is that expected for base-catalyzed exchange, it seemed unlikely for acid-catalyzed exchange. For this reason we studied the exchange of tyrosine hydrogens in DCl solutions at 100°C by proton-magnetic-resonance spectroscopy. In 18 hours we found no noticeable exchange of the methylene hydrogens but observed exchange of one of the two pairs of hydrogens attached to the aromatic carbons.

The proton-magnetic-resonance spectra were recorded on a Varian A60 spectrometer at room temperature. Chemical shifts are recorded as τ values with tetramethylsilane as an external standard. Tau values are obtained by subtracting the chemical shift in parts per million from the value of 10.0 assigned to tetramethylsilane. Higher τ values correspond to higher fields, and all tyrosine peaks appear toward the low-field side of the tetramethylsilane peak. No magnetic susceptibility corrections have been applied.

The spectrum of 0.3*M* tyrosine in 2.4*N* DCl consists of an apparent doublet centered at 6.7 τ, a triplet centered at 5.6 τ, and a complex A_2B_2 pattern with centers at 3.0 and 2.7 τ. From their position and spin-spin splitting patterns, the two high-field bands are assigned to aliphatic CH_2 and CH groups, respectively. On expanded scale these two high-field bands appear as a deceptively simple three-spin system (*3*) with an average coupling constant of 7.0 cy/sec.

By analogy with other results (*4*), the aromatic hydrogens at 3.0 τ are assigned to the pair *ortho* and those at 2.7 τ (lowest field) to the pair *meta* to the hydroxyl group on the benzene ring of tyrosine. These last two groups of protons are spin-spin coupled, and they give rise to the A_2B_2 pattern.

After heating the DCl solution of tyrosine for about 18 hours at 100°C, the proton-magnetic-resonance spectrum at room temperature was similar to that recorded above, except that the peaks centered at 3.0 τ had disappeared. Only a singlet appeared at 2.7 τ for the pair of aromatic hydrogens in the *meta* position to the hydroxyl group. No other changes due to heating were observed in the spectrum.

The results indicate that neither the aliphatic CH_2 or CH protons undergo exchange, after about 18 hours at 100°C, with deuterium in the acidic solvent. Disappearance of the complex A_2B_2 pattern and appearance of a sharp singlet at the lowest-field position after heating demonstrates that the high-field pair of aromatic protons has undergone exchange. From the chemical-shift analysis the pair of hydrogens that exchanged with deuterium of the solvent is in a position *ortho* to the hydroxyl group of tyrosine.

Hydrogen isotope exchange of *p*-cresol in aqueous sulfuric acid solutions has been determined gravimetrically by Gold and Satchell (*5*), who stated, "it seems legitimate to assume that the two nuclear positions concerned in the exchange are those *ortho* to the hydroxyl group." The chemical-shift analysis of our proton-magnetic-resonance study permits separate identification of each type of hydrogen environment and establishes that exchange does indeed occur predominantly in positions *ortho* to the hydroxyl group in *p*-substituted phenols. Possible mechanisms for the acid-catalyzed exchange have been discussed (*5*, *6*).

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References and Notes

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Radiolysis of Estrone and Estradiol

Abstract. *Gamma irradiation of estrone and estradiol in 1*N *aqueous sodium hydroxide results in the formation of 2-hydroxyestrone and 2-hydroxyestradiol, respectively. Estrolactone (16a-oxa-D-homoestrone) was not encountered.*

Keller and Weiss (*1*) reported that the only product formed in the x-ray radiolysis of estrone in aqueous sodium hydroxide was a low (2-percent) yield of estrolactone. The radiolysis of aromatic compounds in aqueous solution usually leads to the formation of phenols.

Estrone was irradiated in 1*N* sodium hydroxide with cobalt-60 γ rays,