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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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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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, until 0.31 g in 125 ml absorbed 3.74 Mrad. 2-Hydroxyestrone (13 percent) was isolated, as well as recovered estrone (50 percent). No other products could be identified by gas chromatography. Estradiol similarly gave 2-hydroxyestradiol (9 percent), and recovered starting material (54 percent), with an absorbed dose of 3.38 Mrad. The $G_{(-M)}$ values (molecules reacted per 100 ev absorbed) were 1.14 and 1.54, for estrone and estradiol, respectively. No estrolactone was detected, although a trace (1 percent) of estrolactone acetate had been found in the radiolysis products of estrone in acetic acid (*2*).

The bromination (*3*) and nitration (*4*) of estrone lead to substitution at both carbon-2 and carbon-4. However, biological oxidation appears to occur at the carbon-2 rather than at the carbon-4, in that 2-methoxyestrone was isolated from the urinary metabolites of estradiol (*5*). Radiolytic hydroxylation often parallels biological hydroxylation (*6*).

The radiolysis of estrone and estradiol offers a simple method of preparing their 2-hydroxy derivatives, and it is a convenient alternative to chemical synthesis (*7*).

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Earth Tremors Generated by Old Faithful Geyser

Abstract. *Several types of earth tremors that could be associated with the eruption cycle of Old Faithful Geyser were registered by a seismograph placed a few meters from the geyser's orifice. Each tremor type was indicative of a specific geyser action. A totally unexpected result was an observed bimodal distribution in frequency of the interval between eruptions.*

During January 1965, I took advantage of a winter stay (*1*) in Yellowstone National Park to investigate the earth tremors generated by Old Faithful Geyser. Because of its predictability and repeatability, the geyser is especially convenient for study. Absence of tourists during the winter months insured that background noise would be low. Although geyser action would be expected to generate very small earth tremors, only one study seems to have been made of them, that of the Onikôbe Geyser in Japan (*2*) which showed the development of pulsative tremors of roughly 10 cy/sec in the neighborhood of the geyser, the tremors becoming particularly prevalent as eruption time approached.

In my study, a Hall-Sears model HS-10-1 geophone, placed on the geyserite cone of Old Faithful about 20 m from the geyser vent, was used to detect the tremors. This geophone senses particle velocity, and in this case was set up to measure the vertical particle velocity of the ground surface. The frequency response of the instrument is fairly flat from 30 to 1 cy/sec. Sensitivity of the instrument falls off rapidly at frequencies less than 1 cy/sec. Signals generated by the geophone were amplified and fed to a Sanborn strip recorder, located about 70 m from the geyser, which had recording speeds of 5 and 50 mm/sec.

In general, two somewhat different types of sequences were observed, one corresponding to a long interval between eruptions, and the other to a short interval. (The bimodal distribution of intervals is discussed later). The sequence shown in Fig. 1 is typical of that occurring during the long interval. Immediately after the eruption and for 20 to 30 minutes thereafter (trace A), there is a complete absence of any regular tremors. This quiescent period is followed first by a short series of substantial long-period movements (approximately 0.1 cy/sec; trace B) lasting for a minute or so. In some cases, these are repeated a few minutes later, but then cease entirely. The geophone is quite insensitive to this frequency, so that the record indicates very substantial earth movement, most likely extensive tilting. Occasionally this motion is accompanied by audible booming.

The large low-frequency movement seems to initiate, or be an indicator of, a subterranean change; for shortly after, the long-period motion ceases and a regular series of sharp signals, shown in trace C, begins. Since the geophone responds well to this frequency, each signal corresponds to only a relatively weak tremor which occurs at the rate of about one per second. In making this recording, heat input to the recording pen was kept low in order to obtain a fine-line trace. Under this condition, the pen does not record high-frequency components. Thus each signal in trace C which appears as a sawtooth pulse is in reality the short packet of wavelets evident in the more rapid recording, with higher heat input to the recording pen, shown in trace D. Each of these packets consists of two to four wavelets having a frequency of from 15 to 30 cy/sec.

At about the same time that the weak tremors begin, a series of much stronger but less frequently occurring pulses starts. The pulses are not exhibited in trace C since they would be way off scale. A rapid recording at much reduced (24 db) amplification of a series of three of these short-period strong pulses is reproduced in trace E. Each strong pulse lasts for about 0.1 second, a length of time similar to the duration of the weak signals; but the strong pulse does not have the same oscillatory character of the weak bursts. Generally, a strong pulse or a group of these heralded a violent ejection of steam which occurred 15 to 20 seconds after the pulse. The weak and strong signals continue in this fashion until eruption occurs, after which the sequence begins anew.

When the interval between eruptions is short, the above sequence is somewhat different: both weak tremors and strong pulses start immediately after cessation of the previous eruption. The introductory, long duration movements (trace B) may or may not occur.

The frequency and temporal distribution of strong pulse activity typical of short and long intervals between eruptions is shown in Fig. 2. This