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EXCHANGE OF π-VINYL ALCOHOL OF PLATINUM(II) COMPLEX WITH ACETALDEHYDE

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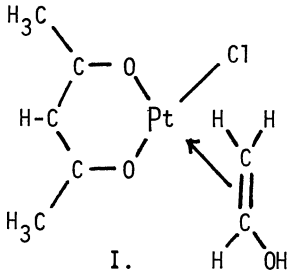
Exchange reaction of π-vinyl alcohol group on acetylacetonatochloroplatinum(II) with C^{14} labeled acetaldehyde was observed. If the exchange proceeds by attack of free vinyl alcohol, the sluggish reaction is attributable to the very small amount of vinyl alcohol in equilibrium with acetaldehyde.

We have recently described[1,2] a platinum complex which contains a π-bound vinyl alcohol moiety.



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We wished to determine whether free acetaldehyde, the stable tautaumeric form of vinyl alcohol, would undergo exchange with the complex and have carried out experiments with C^{14} labeled acetaldehyde.

A 250 microcuriesample of C^{14} paraldehyde (2.5 mg) was diluted with 2.0 ml of cold paraldehyde, cracked to acetaldehyde, and mixed with 10 ml of dioxane for ease in handling. The resulting 2.9 M solution had a specific activity of 23,500 cpm/μ mole. All activities were determined on a Beckman LS-250 scintillation counter in a dioxane-naphthalene-PPO-POPOP solution, using five minute counting periods.

A 50 mg sample of acetylacetonatochloro (π-vinyl alcohol)platinum(II), I., 163 m mole was dissolved in 11 ml of a dioxane solution 0.27 M in labeled acetaldehyde. After 45 hours at room temperature the solution was reduced to dryness, the residue dissolved in 0.1N NaOH, and extracted several times with chloroform. The aqueous solution was acidified and the complex extracted into chloroform, from which it was crystallized by concentration and addition of hexane. After a final recrystallization from aqueous NaOH/HCl 30 mg of material was obtained with a specific activity of 751 cpm/mg. The infrared spectrum of the recovered sample was identical to that of the starting material. Repeating the entire purification sequence with the 30 mg sample yielded 7.6 mg of material with an activity of 220 cpm/mg, which corresponds to 0.35% exchange.

In view of this small amount of exchange, the experiment was repeated, comparing samples of complex which were let stand in the labeled acetaldehyde solution for 45 hours and 1/2 hour. The purification sequence was carried out only once. The sample held for 45 hours had an activity of 331 cpm/mg; the one held for 1/2 hour, 24 cpm/mg for a net activity of 288 cpm/mg, corresponding to 0.46% exchange. Higher temperatures could not be used because of extensive decomposition.

We believe this small amount of exchange is, none the less, real. If the exchange proceeds by attack of free vinyl alcohol, the sluggish reaction is attributable to the very small amount of vinyl alcohol in equilibrium with acetaldehyde. Gero[3] has recently set an upper limit of 10^{-7} on the vinyl alcohol/acetaldehyde ratio, which with our data sets a lower limit of 1 M^{-1} sec^{-1} on the second order rate constant for exchange of $Pt(C_5H_7O_2)(Cl)$-$(CH_2{=}CHOH)$ with vinyl alcohol. The rate may be considerably higher; in a similar case Cramer's work[4] indicates that the exchange of ethylene with Zeise's salt has a rate constant of at least 170 M^{-1} sec^{-1} at -75°C. Further studies on the exchange of enols with this platinum compound will be published later.

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