CHEMISTRY LETTERS, pp. 393-394, 1974. Published by the Chemical Society of Japan

AN OXYGEN ADDUCT OF POLY-4-VINYLPYRIDINE-BOUND TRICHLOROTITANIUM(III)

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E.s.r. spectroscopic studies indicate the formation of a novel oxygen adduct of poly-4-vinylpyridine-bound $TiCl_3$, whose electronic structure should be formally described as $Ti(IV)-O_2^-$.

Although the properties of oxygen adducts of low valent transition-metal complexes of the group VIII have been well defined, only a few and preliminary papers have been reported on oxygen adducts of high valent transition-metal complexes.$^{1)}$ Instability of these oxygen adducts is probably due to their high reactivities toward original complexes. This paper shows that polymeric ligands suppressed the high reactivity of an oxygen adduct of $TiCl_3$, which was detected by e.s.r.

Poly-4-vinylpyridine cross-linked with 18 % divinylbenzene was chosen as the polymer. Powders of the polymer were mixed with $TiCl_3$ in ethanol ($TiCl_3$/vinylpyridine unit = 1/10), and were stirred for several hours. After rinsing with ethanol, they were dried in vacuum. Resulting reddish-yellow powders were transferred to an e.s.r. sample tube. All were operated under nitrogen at room temperature. E.s.r. spectra were measured at room temperature.

Without oxygen the powders showed a singlet peak with $g = 1.960$ and $\Delta H_{msl} = 22$ G, which was attributed to $TiCl_3$ bound to the polymer. After admission of oxygen, a new peak with three principal g values(2.004, 2.010, 2.022) appeared, and the $TiCl_3$ peak came to have a shoulder in the region of low magnetic field, as shown in Figure. The amounts of the new species(1) and $TiCl_3$$^{2)}$ varied with time, and this variation also depended upon atmosphere. By admission of atmospheric oxygen, the amount of $TiCl_3$ decreased at first rapidly and then gradually (45 % of original $TiCl_3$ after 25 min and 23 % after 2.4 hr). The amount of (1) increased rapidly to 19 % of original $TiCl_3$ after 25 min, and then remained almost constant. After 2.6 hr the sample was evacuated and nitrogen was added. By this operation the amount of (1) decreased gradually, while $TiCl_3$ kept an almost constant amount. Reevacuation and admission of atmospheric oxygen again resulted in the rapid increase of (1). The sum of the amounts of these two species decreased monotonously with time under any atmosphere. The line-shape of the signal of (1) was independent of oxygen pressure.

Many investigators have reported on O_2^- radicals on the surface of titanium dioxide, whose principal g values are 2.002-2.004, 2.009-2.011,and 2.019-2.024.[3)]

The principal g values of (1) are nearly identical with those in the above reports. From this fact and the behavior of (1) with the change of atmosphere, (1) is reasonably concluded to be an oxygen adduct of poly-4-vinylpyridine-bound $TiCl_3$. Its electronic structure should be formally described as $Ti(IV)-O_2^-$.

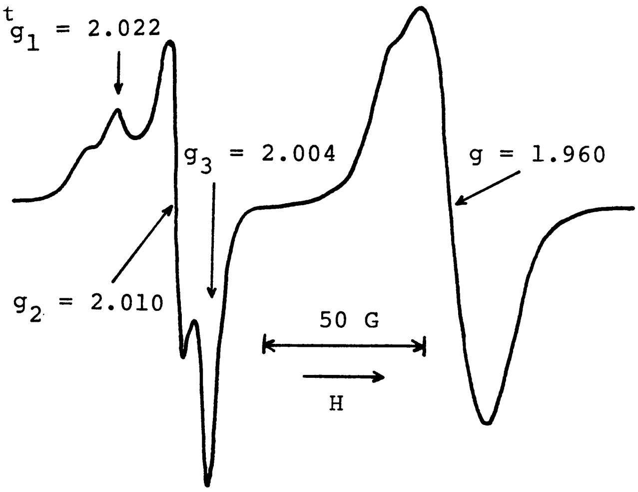

Figure. X-band e.s.r. spectrum of poly-4-vinylpyridine-bound $TiCl_3$ after addition of oxygen.

Studies on the structure and the reactivity of this oxygen adduct are in progress.

The author wishes to thank Drs. Y. Imanishi and S. Yoshida for helpfull discussions, and Dr. T. Suzuki for providing kindly $TiCl_3$.

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(2) The ratio of the amounts of these two species was assumed to be equal to the ratio of the areas of integrated e.s.r. spectrum of these two species.

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(Received March 11, 1974)