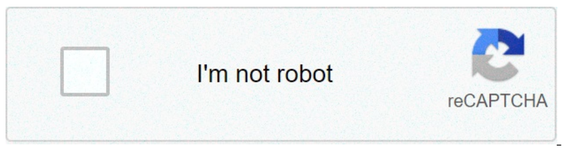

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Ligand substitution reaction in octahedral complexes

Transition metal complexes can exchange a ligand for another, and these reactions are important in their synthesis, stereochemistry and catalytic chemistry. The mechanisms of chemical reactions are intimately connected to the reaction kinetics. As in organic chemistry, the mechanisms of transition metal reactions are typically deducted from experiments that examine the addiction of the concentration of incoming and outgoing ligands on the reaction rate, the detection of intermediate and the stereochemistry of reagents and products. Thermodynamic vs kinetics. When we think of the reactions of transition metal complexes, it is important to remember the distinction between their thermodynamics and kinetics. Take for example the formation of the Tetracyanonickelate Square Planate Square: [CE {^ {2 +} _ {(AQ)} + 4CN ^ {-} _ {(AQ)} = [NI (CN) 4] ^ {2 -} _ {(AQ)}}} :: k _ {(EQ)} About 10 ^ {30} m ^ {- 4}} m ^ {- 4} thermodynamically, [ni (NI (CN) 4] 2- Very stable, which means that the balance above is very far to the right. Claratically, however, the complex is lable, which means that it can quickly exchange its ligands. For example The exchange between a cn-ion labeled 13c and a cn-ligand bound occurs on the timing of dozens of milliseconds: [ce {[ni (cn) 4] ^ {2 -} _ {(AQ)} + * cn ^ {-} _ {(AQ)} -> [Ni (Ni (CN) 3 (* CN)] ^ {2-} + CN ^ {2-} + {(AQ)}}} :: k_ { Exchange} About 10 ^ {2} m ^ {- 1} s ^ {- 1}} s, a compound can be thermodynamically unstable but cinetically inert, which means it requires a relatively long time to react. For example, the [CO (NH3) 6] 3+ ion is unstable in acid, but the His hydrolysis reaction with concentrated HCL takes about a week to go to room temperature: [CE {[CO (NH3) 6] ^ {3 +} _ {(AQ)} + 6H3O ^ {+} _ { (AQ)} -> [CO (H2O) 6] ^ {3 +} _ {(AQ)} + 6NH4 ^ {+} _ {(AQ)}}: K_ {EQ} A. 10 ^ {30}} 50 ^ {30}} Henry Taube, which studied the mechanisms of ligand exchange reactions in simple test tube experiments, transition metal complexes classified as a labile if their reaction half-pitch was a minute Or not, and inert if it took more time to react. The dynamic range of ligand replacement rates is enormous, which covers at least 15 sizes orders. On the timing of most laboratory experiments, the definition of the labilities taube is useful for classifying reactions in those that have low and high activation energies. As we will see, the crystal field stabilization energy (CFSE) plays a key role in determining the activation energy and therefore the replacement rate of the ligand. Henry Taube (Stanford University) received the 1983 Nobel Prize for his work on the transfer of electron and the reactions of ligand exchange of the transition complexes of crystal metal complexes of crystal field stabilization and exchange rates of the Ligando. Consider a very commentary and simple ligand exchange reaction, which is the replacement of a water molecule for another in an octahedral complex [M (M (H2O) 6] N + complex. Since the products (With the exception of the label) they are the same as the reagents, we know it ÃŻ "gÃ ¢ â ° = 0 and keq = 1 for this reaction. The progress of the reaction can be monitored by NMR using water with a label isotopically (typically containing 17o or 18O): The most surprising thing about this reaction (otherwise boring) is the vast difference in rates constant - about 14 sizes orders - for several metal ions and oxidation states: MN + Log K (sec-1) CR3 + -6 V2 + -2 CR3 + 8 CU2 + 8 While at the beginning it may seem strange that the same ion in two different states of different oxidation (CR3 + Vs. CR2 +) would be inert or labile, respectively, we can To rationalize the difference by drawing diagrams of d-orbital split for complexes. What we find is that the Ottahedrus complexes that have high CFSE (CR3 +, V2 +) tend to be inert. Vice versa, ions with high energy electrons, such as orbital (CR2 +, CU2 +) tend to be labile. In the case of CR3 + and V2 +, the energy penalty to distort the complex away from the octahedral symmetry - to make, for example, an intermediate of coordinates at 5 or 7 - is particularly high. This activation energy for The replacement is lower for CR2 + and CU2 +, which has already electrons in the anti-band for example orbital. Based on the rules we have developed for the calculation of the CFSE of the transition metal complexes, we can now include trends in the replacement rates of the Ligand: Ottahedrus complexes with configurations D3 and D6 (low spin), such as CR3 + (D3), CO3 + (D6), RH3 + (D6), RU2 + (D6) and OS2 + (D6) tend to be replacement-inert due to their high CFSE. The D8 glider complexes, especially those in the 4D and 5D series, are also replacement-inerts. Examples are complexes of PD2 +, PT2 + and AU3 +. The intermediate cases are complexes of FE3 +, V3 +, V2 +, NI2 + and of the main group ions (BE2 â € AL3 +), since the strength of acid Lewis decreases with the size of the increasing time . The ion CU2 + (D9), as an ionic Jahn-Teller, is already distorted from the octahedral symmetry and is therefore quite labile, exchanging water ligands at a rate of about 108 S-1. Ligand replacement mechanisms. For a complex MLN subjected to replacement of Ligand, there are essentially three different reaction mechanisms: in the dissociative mechanism, an MLN complex first loses a ligand to form an intermediate of MLN-1, and the incoming ligand reacts with the mln- fragment 1: [ce {l_ {n-1} ml [- l, k_ {1}] [+ l, k _ {- 1}] l _ {n-1} m- box -> [+ Y, K_ {2}] L _ {N-1} My} This mechanism is illustrated below for replacing the Ligand on an octahedral ML6 complex. The intermediate state in this example involves a fragment of bobpraramidal trigonal and free ligand ligand. If the rate of determination of the rate is the dissociation of l from the complex, the concentration of y does not affect the reaction rate, which leads to the law of the first order rate: Ã, illustration of the mechanism of replacement of the dissociative ligand for a complex ML6. The reaction energy profile is shown to the right. [TASSO = k_ {1} [ml_ {n}] In the case of an octahedral complex, this reaction would be the first order in ML6 and Zero order in Y, but only if the highest energy transition status is that That is that precedes the formation of the intermediate ML5. If the two transition states are close to energy (as in the case of the right-hand animation), the rate law becomes more complicated. In this case, we can simplify the problem by assuming a low steady state concentration of intermediate MLN. The resulting rate law is: [rate = frac {k_ {1} k_ {2} [y] [ml_ {n}]} {k _ {- 1} [l] + k_ {2} [y]} which reduces the simplest rate of the first order rate when K2 [Y] >> K-1 [L]. Because the formation of the transition state involves the dissociation of a ligand, the entropy of activation is always positive in the dissociative mechanism. In the associative mechanism, the incoming ligand attacks the MLN complex, forming transiently mlny intermediate and the intermediate therefore loses a ligand that forming MLN-1Y product complexes that undergo a membership replacement are generally coordinally unsaturated or containing a Ligando that can change its bond to metal, to example change in the apocenza or the decrease of a nitric oxide ligand In homogeneous catalysis, the associative path is desirable because the binding event, and therefore the selectivity of the reaction, depends not only on the nature of the metal catalyst but also on the molecule that is involved in the catalytic cycle. The pseudorotation mechanisms of the berries examples of membership mechanisms are Found in chemistry of plaid metallic complexes D8 square, eg. The Vaska complex (IRCL (CO) [P (C6H5) 3] 2) and tetracloroplatinato (II). These compounds (ML4) bind the incoming ligand (replacement) Y to form the ML4Y pentacoordinate intermediates, which in a later passage dissociate one of their ligands. Although the incoming ligand is initially linked to an equatorial site, the pseudorotation of the berry provides a low energy consumption path for all ligands to taste both equatorial and axial sites. The dissociation of the ligand must occur from an equatorial site based on the principle of microscopic reversibility. The dissociation of Y results in no reaction, but the dissociation of L provokes net replacement, producing the D8 ML3Y complex. The first step is typically rate of determining. Therefore, the activation entropy is negative, which indicates an increase in the order in the transition state. The membership reactions follow the kinetics of the second order: the rate of the product appears depends on the concentration of ML4 and Y. The trans effect, which is connected to the associative mechanism, controls the stereochemistry of certain replacement reactions of the ligand. The trans effect refers to the labilization (making it reactive) of the ligands that are transmitted to certain other ligands, the latter named transitorial ligands. The labilization of the trans ligandi is attributed to the electronic effects and is more remarkable in the square planar complexes, but it can also be observed with octahedrus complexes. [18] The CIS effect is more often observed in the ointedrus complexes. In addition to the Kinetic Trans effect, Trans Ligandi also have an influence on the state of land of the molecule, the most remarkable are the lengths and the stability of the bond. Some authors prefer the term trans influence to distinguish this from the kinetic effect, [19] while others use more specific terms as a transural trans effect or thermodynamic trans effect. [18] The discovery of the Trans effect is attributed to Ilya Ilich Chernyaev, [20] which recognized him and gave a name in 1926. [21] The intensity of the Trans effect (measured by the increase in the rate of Replacement of the Trans Ligand) follows this sequence: FÃ ¢ ', H2O, OHÃ,'

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