金属羰基化合物M(CO)6(M=Cr, Mo, W)氧原子转移反应动力学与机理

师彦龙,高忆慈,史启祯,BASOLO, F.

兰州大学化学系;美国西北大学化学系

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摘要 本文研究了PPh3存在与不存在的情况下, M(CO)6(M=Cr, Mo, W)与三甲胺氧化物me3NO在CH2Cl2中的氧原子转移反应动力学. 反应速率遵循: r=k[M(CO)6][Me3NO], 并且rW>rMo>rCr,

并根据实验结果提出了反应机理, 讨论了溶剂对反应速率的影响.

 关键词
 反应机理
 反应动力学
 羰基络合物
 钼络合物
 金属络合物
 氧原子
 反应速度
 转移反应

 铬络合物
 钨络合物
 三甲胺 P
 N-氧化物

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A study of kinetics and mechanism of oxygen atom transfer reaction of M(CO)6(M=Cr, Mo, W)

SHI YANLONG,GAO YICI,SHI QIZHEN,BASOLO, F.

Abstract The kinetics for the reactions of M(CO)6 (M = Cr, Mo, W) with Me3NO were studied in the absence and the presence of PPh3. The rates are 1st-order in concns. of M(CO)6 and Me3NO, but zero order in PPh3 concentration The rates of reaction decrease in the order W > Mo? Cr. The rate increases with increasing dielec. strength of the solvent. A mechanism is proposed which involves attack on a carbonyl C with the formation of coordinatively unsatd. intermediates of the type M(CO)5, which then rapidly react with an entering ligand. Compared with other nucleophiles reported to react by CO attack in M(CO)6 substrates, Me3NO is a strong nucleophile.

Key wordsREACTION MECHANISMREACTION KINETICSCARBONYL COMPLEXMOLYBDENUMCOMPLEXMETAL COMPLEXOXYGEN ATOMREACTION RATETRANSFER REACTIONSCHROMIUM COMPLEXTUNGSTEN COMPLEXTRIMETHYLAMINE PAMINE OXIDE

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