Clay Catalysis of the Non-Aqueous Diels-Alder Reaction and the Importance of Humidity Control

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Abstract: Unmodified kaolin clays are a simple and viable alternative to ferric ion-exchanged montmorillonites as catalysts for the normal electron demand Diels-Alder reaction. Water is the enemy : at 1 - 2 % levels, the stereoselectivity drops by a factor two or three.

Aqueous Diels-Alder cycloadditions, as pioneered by Breslow¹, provide very high stereoselectivities under mild conditions. Our contribution was to show that such excellent results could be achieved as well in organic solvents, methylene chloride for instance, in the presence of a montmorillonite clay catalyst 2^{-4} . The present study shows that (i) kaolinite clays are also effective ; and that (ii) it is important to control the water content of the clay, for which we submit (iii) an easy procedure to implement.

The test reaction is again addition of cyclopentadiene (60 mmol) onto methylvinylketone (5 mmol); in the presence of *n*-decane (0.1 g) as an internal standard for GC, and of variable amounts of the clay catalyst in methylene chloride [10 (A) or 100 (B) mL] at 20°C. GC was used to monitor the pseudo first-order kinetics in each run.

Kaolinite clays differ considerably in structure from montmorillonite clays. The latter are 2:1 aluminosilicates in which an octahedral aluminate layer is sandwiched in-between two tetrahedral silicate layers. Because of isomorphous substitution [a divalent cation instead of Al (III), a trivalent cation instead of Si (IV)], the silicate sheets bear dispersed negative charges, compensated with counterions. Stacking of the platelets (two to five typically) occurs, due to the Coulombic attraction of the charged planes and of the interlamellar counterions⁵. Kaolinites ε re 1:1 clays, associating one octahedral (AlO₆)_n and one tetrahedral

 $(SiO_4)_p$ layer. They exist also as stacks of platelets. The vertical cohesive force, however, is a strong network of hydrogen bonds between the alanol groups (as H-bond donors) and the surface silyloxy oxygens (as H-bond acceptors). Highly polar intercalates can nest in this hydrogen-bonded array⁶. Yet another difference between the two classes of clay minerals is their specific surface area. Values for the montmorillonites in the hundreds of m² per g endow them with high general worth as catalysts and supports. Values for kaolinites are more modest, typically in the range 5 - 20 m². g⁻¹.

Despite this apparent inferiority, we found that kaolinites serve also as excellent catalysts of the Diels-Alder reaction : accelerations by factors 10 - 50 result from use of kaolinites in amounts comparable to those of our earlier results with montmorillonites that made possible reactions at room temperature or below²⁻⁴. The rationale for turning to a kaolin clay is that its network of hydrogen bonds is reminiscent of that in liquid water. Accordingly, in like manner as the hydrophobic effect of water pushes together the diene and the dienophile¹, one may expect the reaction partners to be brought together by the hydrogen bond environment between the kaolin lamellae. We have opted for a kaolinite with a BET specific surface of $19 \text{ m}^2.\text{g}^{-1}$, more than twice that of the kaolinite that we had used to direct an aromatic nitration⁷. As befits heterogeneous catalysis, the rate constants are linear with the amount of the catalyst (Fig. 1).



Figure 1 - Pseudo first-order rate constants plotted against relative amounts of the kaolinite catalyst and of the dienophile.

Turning to the stereoselectivity, it increases (significantly, a factor two) with the reaction rate - putting once again the lie to the so-called "reactivity - selectivity principle" (Fig. 2).



Figure 2 - Plot of the (endo/exo) ratio for the cycloadducts as a function of the pseudo first-order rate constants.

The third and operationally most significant conclusion is the importance of firm control on the humidity of the clay that it may pick up, subsequent to its **dehydrative activation for 18 h in an oven at 110°C**. For this purpose, we deliberately reintroduced water : the clay is locked in a chamber together with a salt of well-defined hydration for 24 h. For instance, a saturated solution of ammonium chloride at 20°C is in equilibrium with its 79.4 % humid atmosphere ; while a saturated solution of calcium chloride at the same temperature has a 32.3 % humid atmosphere.

In the former case, the kaolinite acquires 1.9 % residual water, and the Diels-Alder addition proceeds in > 75% yield with a stereoselectivity of 11 (0.2 g kaolin/mmol MVK). In the latter case, with 0.9 % humid kaolin, at also 0.2 g/mmol, the yield is better than 80 % but the endo preference drops to 7. From these experiments, one can conclude to achieve stereoselectivities above a value 18, humidity of the kaolin must be kept well below 0.5 %.

To sum-up : recourse to a well-dried kaolin clay allows one to dispense with exchange of a montmorillonite into a homoionic Fe (III) clay ; but one has to be careful, for optimum results, that dehydration be sufficient.

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