Kinetic Evidence of Synergistic Catalysis by Zinc Chloride and Phosphoryl Chloride in the Anionotropy of 1-Phenylprop-2-en-1-ol

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A MIXTURE of zinc chloride and phosphoryl chloride used as a catalyst in Friedel–Crafts acylations has been reported[1] to give better yields than either component alone. Recent electrolysis studies in acetonitrile solution have indicated that a 1 : 1 complex, $ZnCl_2,POCl_3$, is probably formed.[2]

We have found evidence that zinc chloride and phosphoryl chloride can interact synergistically to give a powerful Lewis acid. Phosphoryl chloride alone efficiently catalyses the anionotropic rearrangement of 1-phenylprop-2-en-1-ol to cinnamyl alcohol; this rearrangement is followed by a slow conversion to cinnamyl chloride. In tetrahydrothiophen 1,1-dioxide solution the rate, determined spectrophotometrically, is first-order in alcohol, and directly proportional to the concentration of the catalyst within the range 0·5—3·3 $\times$ 10^{-4}M. One set of data at varying temperatures (Table 1) leads to the expression $k_1 = 3{\cdot}5 \times 10^7 \exp(-11{,}600/RT)$. Zinc chloride alone, on the other hand, catalyses the rearrangement only very slowly ($k_1^{36\cdot6} = 1{\cdot}4 \times 10^{-4}$ min.$^{-1}$) even at much higher concentrations ($c = 9 \times 10^{-2}$M). With added amounts of zinc chloride, however, the rate with a constant concentration of phosphoryl chloride rises sharply, and then levels off at about 10 times the original rate (Table 2). It was not feasible to determine Arrhenius data for this system. Analysis of the data, according to the method of Job plots,[3] reveals that the highly active catalyst species corresponds to the 1 : 1 molecular complex. The nature of this interaction is not further disclosed by the present study.

TABLE 1

Rates of rearrangement of 1-*phenylprop*-2-*en*-1-*ol* (1·5 × 10^{-4}M) *with phosphoryl chloride* (5·3 × 10^{-5}M) *in tetrahydrothiophen* 1,1-*dioxide*

Temp. . .	36·1°	44·0°	49·3°	55·7°	61·0°
k_1 (min.$^{-1}$)	0·21	0·32	0·44	0·64	0·85

TABLE 2

Rates of rearrangement (*at* 36·7°) *of* 1-*phenylprop*-2-*en*-1-*ol* (1·5 × 10^{-4}M) *with phosphoryl chloride* (5·3 × 10^{-5}M), *with added zinc chloride, in tetrahydrothiophen* 1,1-*dioxide*

$ZnCl_2$ (× 10^5 M)	0	1·9	3·5	5·4	7·4	14
k_1 (min.$^{-1}$)	0·22	1·43	1·81	2·2	2·1	2·5

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