Theoretical study of the C? vs. O?Acylation of metal enolates. Frontier molecular orbital analysis including solvent effects

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An extended version of the Klopman?Salem equation of chemical reactivity, which incorporates the effect of an external electrostatic field in both charge and orbital contributions, has been applied to analyze the reactivity pattern of ambient metal enolates towards acylation reactions in different solvents. The results are consistent with the experimental observation that the proportion of C?acylation product is enhanced for solvents of low polarity where a relevant orbital control contribution is predicted. Comparison between the cis/trans proportion of C? and O?acylation products are also qualitatively accounted for by the FMO analysis. © 1993 John Wiley & Sons, Inc.