Radical Addition to Alkene–Metal Cation Complexes

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MP2/6–31G* calculations reveal a significant kinetic acceleration of methyl radical addition to ethylene on complexation of the alkene with the lithium cation, an effect which should be general for alkyl radical addition to alkene–metal cation complexes.

Radical addition to alkenes is a technically important reaction which has received much theoretical[1] and experimental[2] attention. Recently, Münger and Fischer[3] demonstrated that the rates of addition of t-butyl radicals to alkenes are dependent on the alkene electron affinities, in accord with the notion[1] that the initial interaction between nucleophilic alkyl radicals and alkenes involves predominantly a one-electron interaction involving the radical singly occupied molecular orbital (SOMO) and the π^* alkene LUMO. If this is the case, the initial radical–alkene interaction can be strengthened, and
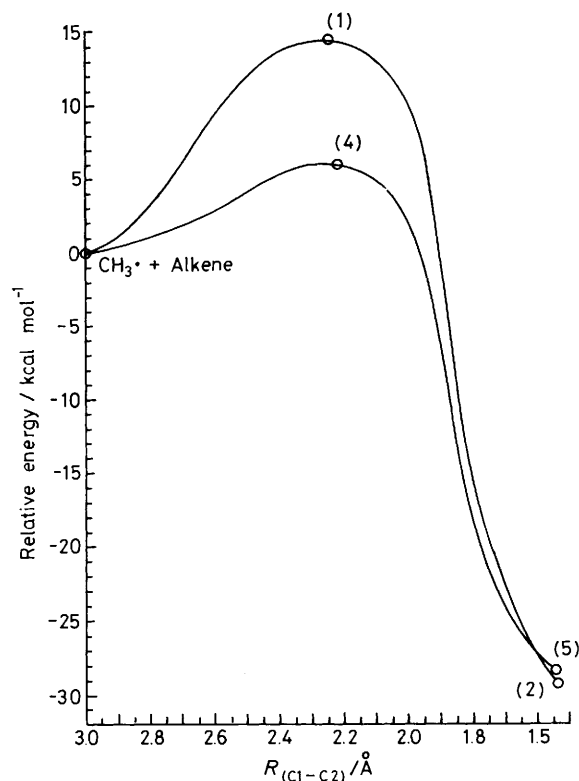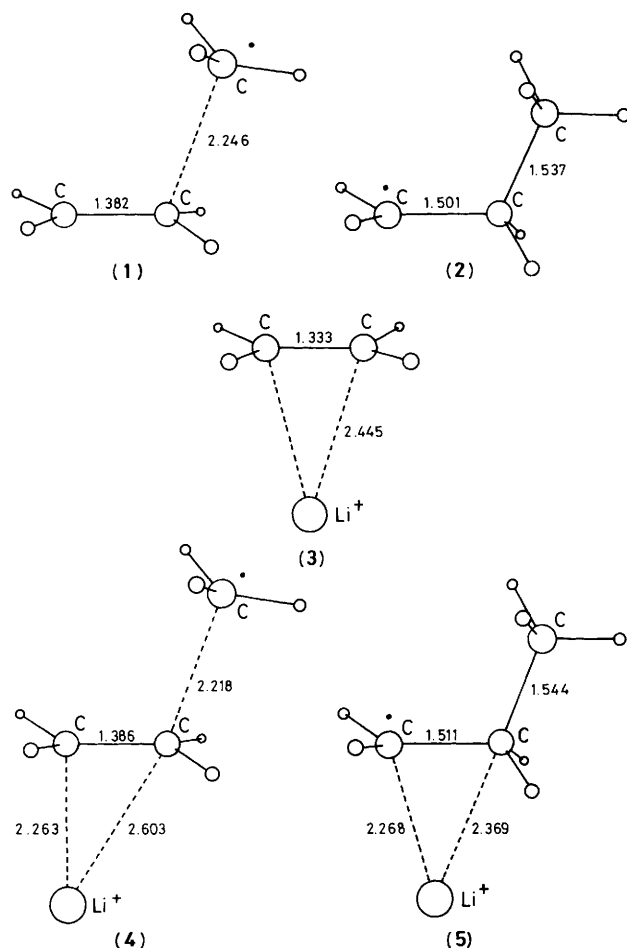
Figure 1. Schematic reaction profiles for the addition of methyl radical to ethylene (upper curve) and (3). $R_{(C1-C2)}$ is the length of the developing C–C bond, and the reactants have been arbitrarily placed at $R_{(C1-C2)} = 3$ Å and defined as having zero energy.

hence the activation energy for addition lowered, if the electron affinity of the alkene is increased by complexation to a metal cation. This communication reports *ab initio* calculations† designed to test this hypothesis for a model system; methyl radical addition to ethylene and its complex with Li⁺.

The calculated (MP2/6–31G*) activation energy for the prototype reaction, the addition of $CH_3\cdot$ to ethylene *via* transition state (1) is 14.4 kcal mol⁻¹, and the length of the

forming C–C bond is 2.246 Å. The n-propyl radical (2) is calculated to lie 29.3 kcal mol⁻¹ lower in energy than the reactants. Figure 1 shows a comparison of the potential curve for this reaction with that for the corresponding addition to the ethylene–Li⁺ adduct, (3).[4] This adduct is bound by 24.3 kcal mol⁻¹ relative to C_2H_4 + Li⁺ at MP2/6–31G*, and should therefore have an electron affinity about 1 eV lower than the ionisation potential of Li·. The transition state (4) for methyl addition to (3) lies only 6.0 kcal mol⁻¹ higher in energy than the reactants and exhibits a shorter (2.218 Å) bond distance for the new C–C bond than (1). The lithium cation, which symmetrically bridges the double bond in (3), moves towards the developing radical centre. The carbon–carbon double bond is, however, scarcely longer than in (1). The product of this reaction, the n-propyl-lithium radical cation (5), also has an unsymmetrically bridging lithium cation, but the distance between the central carbon atom and lithium is shorter than in either (3) or (4). Radical cation (5) is calculated to be bound by 23.3 kcal mol⁻¹ relative to (2) and Li⁺, so that the heats of reaction for the two radical additions are very similar, as shown in Figure 1. The net result is a strong kinetic acceleration of the radical addition without any significant thermodynamic change.

The above results should be considered in relation to the discrepancy between the calculated (14.4 kcal mol⁻¹) and experimental (7.7 kcal mol⁻¹)[5] activation energies for $CH_3\cdot$ addition to ethylene. Unusually, the MP2 correction results in

a larger deviation from experiment than that obtained at UHF/6–31G*, where the activation energy is calculated to be 9.4 kcal mol⁻¹. At this level the lowering of the barrier to addition to (3) is much less (from 9.4 to 6.7 kcal mol⁻¹) than at MP2/6–31G*. Assuming a constant overestimation of the activation energy at MP2/6–31G* suggests that methyl addition to (3) may occur without a barrier.

The kinetic acceleration of radical addition found here should be general for all nucleophilic radicals and for a variety of metal cations, especially those, like Ag⁺, which form stable alkene complexes. As these complexes are most stable for alkenes which are unreactive to nucleophilic radicals, complexation with metal cations may be a useful method of extending the utility of radical additions.

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References

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