

## **A Computational Investigation into the Structure and Energetics of Acyclic Alpha Keto Cations**

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Alpha keto cations have been implicated as reaction intermediates as far back as 1910. Access to these unusual intermediates has been through the solvolysis of chloro epoxides, alpha keto mesylates, triflates or similar leaving groups. Computational work on acyclic alpha keto cations by Houk and coworkers in the 1980's supported a planar structure that delocalized charge onto the carbonyl oxygen. Isodesmic reactions showed that increasing methyl group substitution at the cationic center decreased the stability of the cation, opposite the expected result based on hyperconjugation. Our work stands in direct contradiction of this earlier work. Using DFT methods, we have found that acyclic alpha keto cations are non-planar and do not exhibit any resonance delocalization of positive charge onto the carbonyl. Using a combination of Weinhold's NBO theory and Bader's Atoms in Molecules (AIM) theory, stabilization of the alpha keto cation in acyclic systems is due to bond formation between the carbonyl oxygen and the cationic center. Isodesmic reactions at the DFT level reveal that groups capable of stabilizing a positive charge *increase* the stability of the cation. For methyl groups, NBO analysis revealed that the hyperconjugative effect is quite pronounced, reflecting the strong destabilization of the cationic center.