

PT4 Gas phase synthesis and reactivity of the Ivanoff reagent anion, $[\text{CH}_2\text{CO}_2\text{Li}]^-$.

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$[\text{CH}_2\text{CO}_2\text{Li}]^-$ reacts with neutrals via addition/elimination and/or LiO^- transfer.

Dianions are versatile reagents in organic synthesis [1]. Doubly deprotonation of carboxylic acids possessing α -hydrogens was observed over a hundred years ago by Grignard [2] and the resultant salts were subsequently exploited by Ivanoff as reagent nucleophiles in stereospecific reactions with carbonyl compounds [3]. Despite their widespread use, surprisingly little is known about the fundamental properties of these salts. Decarboxylation of the lithium complex of doubly deprotonated malonic acid, $[\text{CH}_2(\text{CO}_2)_2\text{Li}]^-$, yields the hitherto unknown *gas phase* Ivanoff reagent anion $[\text{CH}_2\text{CO}_2\text{Li}]^-$, **1**. The gas phase ion-molecule reactions of **1** with a wide range of substrates were examined using mass spectrometry experiments. $[\text{CH}_2\text{CO}_2\text{Li}]^-$ is a stronger base than the acetic acid enolate $[\text{CH}_2\text{CO}_2\text{H}]^-$ [4] by nearly 20 kcal mol⁻¹ and reacts with neutral reagents via a number of pathways including addition/elimination and LiO^- transfer. For example, the products of the reaction of **1** with CS_2 are $[\text{CH}_2\text{CS}_2\text{Li}]^-$ and $[\text{LiOCS}_2]^-$. Detailed thermochemical data of **1** derived from experiments and DFT calculations will also be presented.

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