Syntrophic Propionate Oxidation via Butyrate: a Novel Window of Opportunity under Methanogenic Conditions

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Gan and colleagues (1) recently observed that upon the application of [^{13}C]propionate to anoxic paddy soil, label was concurrently incorporated in *Smithella* spp. and *Syntrophomonas* spp. *Smithella* spp. utilize propionate in a nonrandomizing pathway in which propionate is first dismutated to acetate and butyrate before being degraded via β -oxidation (2, 3), while *Syntrophomonadaceae* are known butyrate degraders (4). This led the authors to raise the possibility of a trophic interaction between propionate- and butyrate-oxidizing syntrophs in the degradation of propionate in methanogenic ecosystems: when cultivated on propionate, *Smithella propionica* indeed produces (small amounts of) butyrate (2, 3).

What the authors did not discuss though are the intriguing thermodynamic and energetic consequences of the *Smithella* pathway, consequences that may be of practical importance as propionate degradation is often a critical step in methanogenic bioreactors (5, 6). In the classical propionate degradation route, 3 mol of hydrogen (or formate) is produced per mol of substrate degraded (7, 8); for the alternative route via the *Smithella* pathway, the analogous ratio is 1. Consequently the windows of opportunity of the two pathways are different: there is a significant range of conditions under which propionate oxidation via the *Smithella* route is exergonic, whereas the classical pathway would be endergonic (Fig. 1A). Figure 1B illustrates this for the prevalent concentrations in the experiments of Gan and colleagues (1), where propionate and acetate are in the range of 10 mM and 1 mM, respectively. Unfortunately the authors did not provide data for

H_2 . However, there is an intriguing report on propionate degradation in the literature that provides such data. Krylova and Conrad (9) reported apparently endergonic propionate oxidation in a methanogenic paddy soil, which they explained by assuming that propionate was degraded within microbial aggregates in which syntrophic propionate degraders were shielded from thermodynamically unfavorable H_2 by methanogenic bacteria consuming H_2 . Figure 1C offers an alternative explanation and illustrates that propionate degradation via the *Smithella* pathway would be exergonic in this soil. This line of thinking has potential biotechnological applications, as the low thermodynamic sensitivity toward H_2 of the *Smithella* pathway may lead to strategies to improve the precarious stability of propionate degradation in methanogenic waste treatment systems. Whether butyrate will be an important extracellular intermediate in such strategies remains to be seen.

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FIG 1 Thermodynamic constraints (A) and effect of hydrogen (B and C) on propionate degradation in methanogenic ecosystems. (A) The classical propionate degradation pathway is exergonic below the line with the closed circles, while propionate degradation via butyrate is exergonic below the line with the open circles; H_2 -based methanogenesis is exergonic at hydrogen partial pressures above $10^{-5.94}$ atm; H_2 -based acetogenesis is exergonic above the dotted line. (B) The effect of H_2 on the energetics of propionate degradation via the classical route ($\text{CH}_3\text{CH}_2\text{COO}^- + 3\text{H}_2\text{O} \rightarrow \text{CH}_3\text{COO}^- + \text{HCO}_3^- + 3\text{H}_2 + \text{H}^+$; $\Delta G^{\circ'} = 76.5$ kJ/reaction [closed circles]) and via the *Smithella* pathway ($2\text{CH}_3\text{CH}_2\text{COO}^- + 2\text{H}_2\text{O} \rightarrow 3\text{CH}_3\text{COO}^- + \text{H}^+ + 2\text{H}_2$; $\Delta G^{\circ'} = 48.4$ kJ/reaction [open circles]). (C) Thermodynamics of propionate degradation in methanogenic paddy soil via the classical route (closed circles) and via the *Smithella* pathway (open circles), based on data from Krylova and Conrad (8) (for details, see the supplemental material), with calculations after Dolfing et al. (10) and Thauer et al. (11).

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