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MINI-REVIEW

Alasdair M. Cook · Karin Denger

Dissimilation of the C_2 sulfonates

Abstract Organosulfonates are widespread in the environment, both as natural products and as xenobiotics; and they generally share the property of chemical stability. A wide range of phenomena has evolved in microorganisms able to utilize the sulfur or the carbon moiety of these compounds; and recent work has centered on bacteria. This Mini-Review centers on bacterial catabolism of the carbon moiety in the C_2-sulfonates and the fate of the sulfonate group. Five of the six compounds examined are subject to catabolism, but information on the molecular nature of transport and regulation is based solely on sequencing data. Two mechanisms of desulfonation have been established. First, there is the specific monooxygenation of ethanesulfonate or ethane-1,2-disulfonate. Second, the oxidative, reductive and fermentative modes of catabolism tend to yield the intermediate sulfoacetaldehyde, which is now known to be desulfonated to acetyl phosphate by a thiamin-diphosphate-dependent acetyltransferase. This enzyme is widespread and at least three subgroups can be recognized, some of them in genomic sequencing projects. These data emphasize the importance of acetyl phosphate in bacterial metabolism. A third mechanism of desulfonation is suggested: the hydrolysis of sulfoacetate.

Keywords Ethanesulfonate · Taurine · Isethionate · Sulfoacetate · Ethanedisulfonate · Coenzyme M · Sulfoacetaldehyde · Sulfoacetaldehyde acetyltransferase · Acetyl phosphate

Introduction

Organosulfonates are widespread compounds. The ground we walk on, or rather, the humic material in it is sulfonated. The atmosphere we live in contains methanesulfonate (Fig. 1) and presumably ethanesulfonate (Fig. 1), as well as methane, whose formation involves coenzyme M (Fig. 1). The plants we eat contain substituted sulfoquinovose, a glucose derivative (Fig. 1), in the thylakoid membrane and the compound is degraded via sulfoacetate (Fig. 1). The meat we eat contains taurine (Fig. 1), our digestive process involves taurocholate (Fig. 1) and many natural taurine derivatives are known. Taurine is also involved in the nutrition of microbial mats. Isethionate (Fig. 1) is found in nervous tissue and macroalgae. Our woollen clothes contain cysteate (Fig. 1) and some bacterial spores contain sulfolactate (Fig. 1). Sulfonated aromatic com-

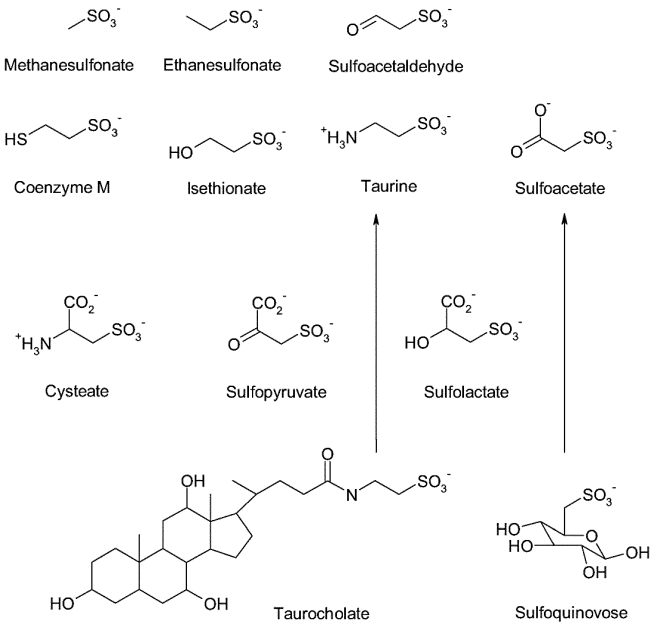

Fig. 1 Some naturally occurring organosulfonates. *The arrows* leading to taurine (EC 3.5.1.24) and sulfoacetate (cf. Cook et al. 1999) indicate degradative pathways in which the sulfonate moiety is retained. Semi-synthetic surfactants based on taurine, isethionate and sulfoacetate and analogous to taurocholate (cited in Cook et al. 1999) are presumably also degraded via these C_2-sulfonates

A.M. Cook (✉) · K. Denger
Department of Biology, University of Konstanz,
78457 Konstanz, Germany
e-mail: Alasdair.Cook@uni-konstanz.de,
Tel.: +49-7531-884247, Fax: +49-7531-882966

pounds seem to be rare natural products, but they are widespread in laundry powders and dyestuffs. We formulate some of our pharmaceuticals with sulfonates. This information is drawn from the literature (Budzikiewicz et al. 1998; Cook et al. 1999; Huxtable 1992; Kelly and Murrell 1999; Lie et al. 1998; O'Neil 2001; Visscher et al. 1999). The biosynthesis of aliphatic sulfonates involves either oxidation of thiol groups or addition of sulfite groups (Graham et al. 2002; Huxtable 1992). Many processes are involved in the desulfonation of these compounds (Cook et al. 1999; Kelly and Murrell 1999; Kertesz 2000; Lie et al. 1998; van der Ploeg et al. 2001), but this review is focused on the dissimilation of C_2-sulfonates, where the reaction product of the longest-known desulfonative enzyme has just been correctly identified.

Growth physiology

Ethanesulfonate is the simplest C_2-sulfonate and it demonstrates the key characteristic of many organosulfonates, namely chemical inertness. The C–SO_3^- bond-strength rivals that of the C–C bond (Cook et al. 1999) and is correspondingly difficult to cleave. Ethanesulfonate, possibly derived from the natural product ethanethiol (Paramasigamani 1984) by oxidation in the atmosphere (cf. Kelly and Murrell 1999), is subject to quantitative dissimilation under oxic conditions by at least one bacterium, *Achromobacter xylosoxidans* AE4 (Erdlenbruch et al. 2001).

Taurine is a phylogenetically ancient entity, long known as a source of sulfur for microorganisms (Huxtable 1992): this aspect of sulfonate metabolism is dealt with elsewhere (Kertesz 2000; Kertesz and Kahnert 2001; Masepohl et al. 2001; van der Ploeg et al. 2001). The compound is an amino acid and is utilized as a source of nitrogen: this phenomenon will not be dealt with here. Taurine has been recognized for many years as a sole source of carbon and energy for aerobic bacterial growth, with the release of sulfate (Ikeda et al. 1963; Stapley and Starkey 1970). Kondo's group established that the aerobic, bacterial catabolism of taurine by *A. xylosoxidans* NCIMB 10751 (Kondo et al. 1971) involves sulfoacetaldehyde (Fig. 1). Support for this idea was obtained from *Pseudomonas aeruginosa* TAU5 (Shimamoto and Berk 1979, 1980), *Ralstonia* sp. strain EDS1 (Denger and Cook 2001) and *Rhodococcus* spp (Chien et al. 1999; Ruff et al. 2002).

Anaerobic bacteria have developed a wide range of dissimilatory phenomena involving taurine. The compound represents an electron acceptor in a respiration in *Bilophila wadsworthia* RZATAU to yield sulfide, ammonia and acetate (Laue et al. 1997b), an electron donor in a respiration in *Alcaligenes defragrans* NKNTAU, *Paracoccus denitrificans* NKNIS and *P. pantotrophus* NKNCYSA to yield sulfate, ammonia and CO_2 (Denger et al. 1997a; Mikosch et al. 1999) and a fermentative substrate in *Desulfonispora thiosulfatigenes* GKNTAU to yield thiosulfate, ammonia and acetate (Denger et al. 1997b). Sulfoacetaldehyde is an intermediate in the dissimilatory process in each of these organisms (Denger et al. 2001; Laue and Cook 2000a; Ruff et al. 2002). A fermentation in *D. singaporensis* yields sulfide, ammonia and acetate (Lie et al. 1999a).

Isethionate was shown to be degraded via sulfoacetaldehyde in *Achromobacter xylosoxidans* NCIMB 10751 (Kondo et al. 1977), and both *Burkholderia* sp. strain ICD (King et al. 1997; Ruff et al. 2002) and *Ralstonia* sp. strain EDS1 (Denger and Cook 2001) are also presumed to do so. As with taurine, anaerobic bacteria have evolved a range of dissimilatory phenomena for isethionate. The compound represents an electron acceptor in *Desulfovibrio desulfuricans* IC1, *Desulfitobacterium* spp, *Desulfomicrobium norvegicum* and *B. wadsworthia*, to yield sulfide and acetate (Laue et al. 1997b; Lie et al. 1996,. 1999b). The compound can be oxidized under denitrifying conditions by e.g. *Alcaligenes defragrans*, *P. denitrificans* and *P. pantotrophus* (Denger et al. 1997a; Mikosch et al. 1999; Ruff et al. 2002); and it also supports fermentation in *Desulfovibrio* sp. strain GRZCYSA and two other isolates, to sulfate plus sulfide and acetate (Denger et al. 1999; Laue et al. 1997a).

Sulfoacetate catabolism is widespread in aerobic bacteria, e.g. *Aureobacterium* sp. strain SFCD2, *Comamonas* sp. strain SFCD1 and *Ralstonia* sp. strain EDS1 (Denger and Cook 2001; King and Quinn 1997; Martelli and Sousa 1970). The compound serves as an electron acceptor for growth of *B. wadsworthia* and *Desulfovibrio* sp. strain RZACYSA and as a source of electrons for nitrate respi-

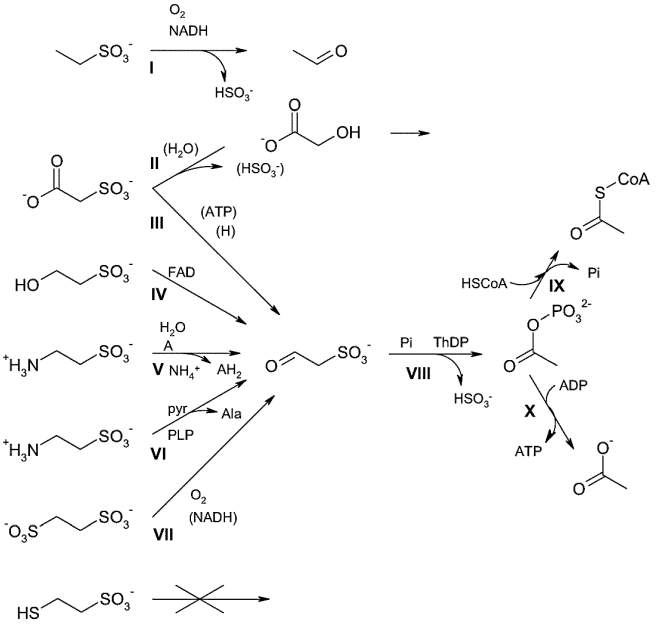

Fig. 2 Summary of the dissimilatory, desulfonative pathways discussed in the text. The *roman numerals I–X* refer to enzyme activities which are discussed in the text. Reactants *in parentheses* are presumptive. *The letter A in path V* represents an unidentified, oxidized electron carrier. *Ala* L-alanine, *PLP* pyridoxal 5′-phosphate, *pyr* pyruvate, *ThDP* thiamin diphosphate

ration during growth of *P. pantotrophus* NKNCYSA (Rein and Cook, unpublished data).

Sulfoacetaldehyde is a common intermediate (Fig. 2), but is not often examined as a growth substrate. Lie et al. (1996) observed that *D. desulfuricans* IC1 utilizes the compound as an electron acceptor.

Coenzyme M has not been reported to be degraded (Denger et al. 1997a, 1999; Laue et al. 1997b; Lie et al. 1996), and more enrichment cultures failed while this review was prepared. Desulfonation of the compound under sulfur-limited conditions is known (Schleheck and Cook, unpublished data).

Ethane-1,2-disulfonate is catabolized by aerobic bacteria (Fig. 2), e.g. *Ralstonia* sp. strain EDS1, but no enrichment culture grew under anoxic conditions (Denger and Cook 2001).

Enzymes and genes

Transport systems are poorly understood. It is axiomatic that ionic organosulfonates require transport systems to cross the cell membrane (Graham et al. 2002). Direct evidence for saturable transport systems in intact microorganisms is available (Huxtable 1992). Genetic evidence for ATP-binding cassette (ABC) transporters involved in the assimilation of sulfur from taurine and ethanesulfonate is now available (Kertesz 2000; Masepohl et al. 2001; van der Ploeg et al. 2001) and ABC transporters can now be hypothesized in taurine catabolism (Ruff et al. 2002).

Ethanesulfonate is activated by an inducible, specific, presumably NADH-dependent, multi-component monooxygenase (Fig. 2, I) to generate the unstable, transient bisulfite-addition complex of formaldehyde, which is converted by loss of the good leaving group sulfite into acetaldehyde (Fig. 3; Erdlenbruch et al. 2001). The enzymology of this powerful oxidation has not yet been worked up to the level attained with the mononuclear-iron methanesulfonate monooxygenase (cf. Kelly and Murrell 1999), with its similarities to the mononuclear-iron dioxygenases involved in the desulfonation of some aromatic sulfonates (cf. Cook et al. 1999).

Sulfoacetate is degraded by many bacteria, one of which was found to excrete glycolate transiently during growth (Martelli and Sousa 1970). Possibly a hydrolytic reaction was catalyzed in the simple reaction mixture used (Fig. 2, II), analogous to the haloacetate halidohydrolase (EC 3.8.1.3) referred to by the authors. This would surely yield sulfite, although only sulfate was determined (Martelli and Sousa 1970). However, a sensitive assay for sulfite was unavailable at that time (cf. Cook et al. 1999). The organisms have not been maintained (Martelli, unpublished data).

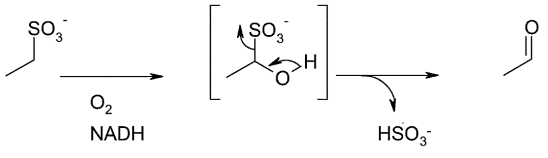

Fig. 3 Presumed mechanism of the oxygenative desulfonation of ethanesulfonate, derived from published data (Erdlenbruch et al. 2001; Kelly and Murrell 1999)

King and Quinn (1997) and Denger and Cook (2001) presented evidence that sulfoacetate is degraded via sulfoacetaldehyde (Fig. 2, III) in *Comamonas* sp. strain SFCD1 and *Ralstonia* sp. strain EDS1. The pathway to sulfoacetaldehyde is currently unknown, but it obviously involves the energetically expensive activation of the carboxylate and its reduction to sulfoacetaldehyde (Denger and Cook 2001).

Isethionate is converted into sulfoacetaldehyde in an FAD-dependent reaction (Fig. 2, IV) by a particulate fraction from *Achromobacter xylosoxidans* (Kondo et al. 1977). *Burkholderia* sp. strain ICD and *Ralstonia* sp. strain EDS1 are also considered to degrade isethionate via sulfoacetaldehyde (Denger and Cook 2001; King et al. 1997).

Lie et al. (1996) suggested that isethionate might be degraded via ethanol in some sulfate-reducing bacteria, but additional data indicate dissimilation via sulfoacetaldehyde (Leadbetter and Gritzer, personal communication). The metabolism of isethionate in some of these organisms involves an inducible 97-kDa protein, which is seen by SDS-PAGE (Lie et al. 1999b), but it is unclear which function the native protein fulfils.

Taurine is a substrate for at least four enzymes that yield sulfoacetaldehyde, but only two of these enzymes are specifically induced during growth with taurine. Kondo's group discovered taurine dehydrogenase (EC 1.4.99.2; Fig. 2, V), an inducible, large, membrane-bound enzyme (Kondo and Ishimoto 1987; Kondo et al. 1971, 1973), which is currently known only in *A. xylosoxidans* NCIMB 10751. The second reaction found inducibly in many aerobes and anaerobes is taurine:pyruvate aminotransferase (Tpa; EC 2.6.1.–; Fig. 2, VI), which is soluble. The enzyme was discovered in *Pseudomonas aeruginosa* TAU5, partially purified and shown genetically to be essential for growth with taurine (Shimamoto and Berk 1979); but this organism was not maintained (Berk, personal communication). The enzyme was detected in *D. thiosulfatigenes* GKNTAU (Denger et al. 2001), *Alcaligenes defragrans* NKNTAU (Ruff et al. 2002) and *B. wadsworthia* (Laue et al. 1997b), from which it was purified (Laue and Cook 2000a). Tpa is a homomultimer with a subunit of 51 kDa. Tetramers are the most common species, but other aggregates are present. The cofactor is pyridoxal 5′-phosphate. Three major donors of an amino group are known: taurine [(apparent K_m) K_m^{app} 7.1 mM; rate 100%], hypotaurine (K_m^{app} 0.8 mM; rate 218%] and β-alanine (rate 38%). The major acceptor of amino groups is pyruvate (K_m^{app} 8.1 mM) and the reaction is stoichiometric. The *tpa* gene shares ≤38% identity with the most closely related transaminase in the NCBI database (as at August 2002) and this dissimilarity has been used for PCR identification of isolates from the gut canal of many carnivores and omnivores, such as *B. wadsworthia*, which seem to be absent from the herbivore gut canal (Laue, in preparation).

The first of these enzymes, the taurine dehydrogenase, releases ammonium ion from the taurine, and this is ex-

creted into the medium. The transaminase, however, simply transfers the amino group into alanine. From this, it can be released as the ammonium ion by the action of alanine dehydrogenase (EC 1.4.1.4), which has been purified from *B. wadsworthia* (Laue and Cook 2000b).

Toyama et al. (1973) claimed a third enzyme in *P. putida*, again a pyruvate-dependent transamination of taurine, but the authors renamed it ω-amino acid:pyruvate aminotransferase (e.g. Yonaha et al. 1992), which is synonymous with β-alanine:pyruvate aminotransferase (EC 2.6.1.18; SWISS-PROT OAPT_PSEPU) and which has 31% sequence similarity with Tpa (Laue and Cook 2000a). The fourth enzyme has been termed taurine:2-oxoglutarate transaminase (EC 2.6.1.55). It is found in "*Achromobacter superficialis*". Since it also acts on β-alanine, which induces its formation, and taurine does not support growth of this organism, we suspect that its physiological function is the transamination of β-alanine.

Ethane-1,2-disulfonate is subject to initial oxygenation (Fig. 2, VII), presumably by a multi-component monooxygenase (cf. ethanesulfonate, above), which could not be assayed in cell extracts of *Ralstonia* sp. (Denger and Cook 2001). The product of this reaction is presumably sulfoacetaldehyde (Fig. 2).

Sulfoacetaldehyde was considered for 30 years to be cleaved to acetate and sulfite (Denger et al. 2001; King and Quinn 1997; King et al. 1997; Kondo and Ishimoto 1972, 1974, 1975; Shimamoto and Berk 1980). Whereas there is no concern about the identification of sulfite, it is now clear that the extensive care taken to identify acetate was invested after the real product had been destroyed:

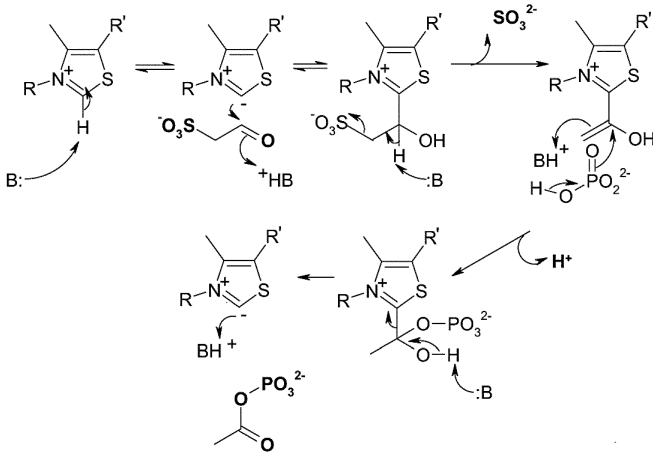

Fig. 4 Presumed mechanism of ThDP-dependent sulfoacetaldehyde acetyltransferase (Xsc), adapted from the generation of active aldehyde in a typical ThDP-linked enzyme (Metzler 2001). The binding domain for the diphosphate moiety of ThDP is present (Ruff et al. 2002) In the pyrimidine domain, we presume that the base (*B:*) which activates C2 in the thiazole ring of ThDP, is the amino group of the aminopyrimidyl moiety of the cofactor. This is due in turn to interaction of the pyrimidyl N1′ with glutamate E53 in Xsc_{Dt} or E61 in Xsc_{Ad} (Ruff et al. 2002), analogous to acetohydroxyacid synthase, where the highly conserved glutamate is E47 (Bar-Ilan et al. 2001). We do not know whether the aminopyrimidyl group is responsible for other transfers of protons in the reaction

that product is acetyl phosphate (Ruff et al. 2002; Fig. 2, VIII; Fig. 4). Labile acetyl phosphate was identified by wet chemistry as Fe(III)acetylhydroxamate, by the specific reaction with phosphate acetyltransferase and by matrix-assisted laser desorption/ionization time-of-flight mass spectrometry. The yield of product from sulfoacetaldehyde is stoichiometric; correspondingly, negligible acetate is formed unless the sample is mistreated. The enzyme has been renamed sulfoacetaldehyde acetyltransferase (Xsc; EC 2.3.1.–) with the tentative formal name "acetylphosphate:sulfite acetyltransferase (isomerizing)".

Xsc has now been purified from three bacteria, *A. xylosoxidans* NCIMB 10751 (Kondo and Ishimoto 1975; Ruff et al. 2002), *D. thiosulfatigenes* (Denger et al. 2001) and *Alcaligenes defragrans* (Ruff et al. 2002). The enzyme seems to be a homodimer or a homotetramer with a subunit of about 64 kDa and it is inducible (in *D. thiosulfatigenes*, taurine is the only known growth substrate). The enzyme from *D. thiosulfatigenes* (Xsc_{Dt}) has a high affinity for sulfoacetaldehyde (K_m^{app} 0.2 mM), a low affinity for phosphate (K_m^{app} about 6 mM) and a tightly-bound cofactor, thiamin diphosphate (ThDP). The enzymes from *Achromobacter xylosoxidans* and *Alcaligenes defragrans* (Xsc_{Ax} and Xsc_{Ad}) have a low affinity for sulfoacetaldehyde (K_m^{app} 2–5 mM), a low affinity for phosphate (K_m^{app} 5–6 mM) and a requirement for ThDP in the reaction mixture (K_m^{app} 2–3 μM). An inducible, 64-kDa protein is associated with the dissimilation of taurine in a range of α-, β- and δ-proteobacteria (Ruff et al. 2002) and in the Gram-positive *D. thiosulfatigenes* (Denger et al. 2001) and *Rhodococcus opacus* (Ruff et al. 2002).

The sequence of the gene encoding Xsc_{Dt}, xsc_{Dt} (previously abbreviated as *sly*), revealed that the enzyme belongs to the family of the acetohydroxyacid synthases (about 30% identity at the amino acid level only; Denger et al. 2001), a group of ThDP-dependent enzymes. The sequence of xsc_{Ad} has no significant similarity with xsc_{Dt} at the nucleotide level, but about 45% identity of sequence at the amino-acid level (Ruff et al. 2002). Close homologues of xsc_{Ad} were found in several genomic databases and three of the organisms concerned, *Burkholderia fungorum* LB400, *Rhodococcus* sp. strain RHA1 and *Sinorhizobium meliloti* Rm1021, were found to dissimilate taurine. This was taken as preliminary evidence for the function of the gene products. Dendrograms indicated three sub-groups of *xsc* genes: (1) those similar to xsc_{Ax} and xsc_{Ad} [e.g. from two *Burkholderia* spp, two *Ralstonia* spp and *Comamonas* sp. (i.e. β-Proteobacteria) and from two *Rhodococcus* spp (Nocardiaceae)], (2) xsc_{Dt} and two genes from *Desulfitobacterium hafniense* and (3) from *S. meliloti*, *Rhodobacter capsulatus* and *R. sphaeroides*. Subgroups 1 and 2 correspond to different biochemical properties, whereas the enzymes of subgroup 3, though active, have not been examined in detail (Ruff et al. 2002; Ruff and Cook, unpublished data). We hypothesize a different group of Xsc, which is not active in current tests in vitro. *Bilophila wadsworthia* generates sulfoacetaldehyde from taurine (Laue and Cook 2000a), contains a sulfite reductase (Laue et al. 2001), which requires one product of

the reaction of the putative Xsc, and the organism excretes acetate (Laue et al. 1997b), presumably after the reaction of an acetate kinase (Fig. 2, X). The simplest explanation of the facts is a hypothetical acetyltransferase of different M_r from Xsc and inactive in crude extract.

Acetyl phosphate is considered to be an energy storage compound (Metzler 2001). Since it is an intermediate in a degradative pathway, it clearly has at least one other function (Fig. 2). The role of the acetyl phosphate from sulfonates varies in the different metabolic scenarios in which it is found. In aerobic metabolism and in nitrate reducers, acetyl phosphate is largely a precursor to acetyl CoA (Fig. 2, IX) and the tricarboxylic acid cycle with the glyoxylate bypass, with a possible role in phosphorylating two-component regulatory systems (Ruff et al. 2002). In fermentations or effective sulfite reduction, in contrast, acetyl phosphate is the point of divergence between acetyl CoA for anabolism (Fig. 2, IX) and conservation of energy via acetate kinase (Fig. 2, X). Phosphate acetyltransferase (EC 2.3.1.8; Fig. 2, IX) is a key enzyme in all these systems. Enzyme activity has been detected in sufficient activity in most organisms tested; and, in all but one of the organisms for which we have the necessary sequence data, a putative phosphate acetyltransferase gene is immediately downstream of the *xsc* gene or in the immediate neighborhood (Ruff et al. 2002). The substrate-level phosphorylation (Fig. 2, X), which is surely important to the fermentative and sulfite-reducing organisms, is only one aspect of energy conservation, where electron transport also plays roles (Denger et al. 1997b; Laue et al. 2001).

Fates of sulfite

We suspect that sulfite is always the product of enzymatic desulfonation, but the sulfite from these C_2-compounds is seldom found in significant amounts outside the cell under laboratory conditions (cf. the degradation of aromatic sulfonates; Cook et al. 1999). *Paracoccus denitrificans* NKNIS is a rare exception and excretes sulfite during the dissimilation of taurine under denitrifying conditions (Denger et al. 1997a; Ruff et al. 2002). Sulfite can be oxidized into sulfate (presumably by EC 1.8.2.1 or EC 1.8.3.1), dismutated into sulfate and sulfide, transformed into thiosulfate or reduced into sulfide, but only the latter reaction has been characterized at the protein level. This is the sulfite reductase (EC 1.8.99.3) from *B. wadsworthia*, which generates "sulfide", e.g. HS^- (Laue et al. 2001), and which is presumably representative of several of the sulfate-reducing bacteria cited.

A putative, regulated pathway for taurine in *S. meliloti*

The data on taurine:pyruvate aminotransferase, sulfoacetaldehyde acetyltransferase and phosphate acetyltransferase in *A. defragrans* NKNTAU allowed Ruff et al. (2002) to identify a region on the pSymB megaplasmid of *S. meliloti* in which they postulate a regulator gene, a catabolic TauABC transporter, a taurine dehydrogenase (Fig. 2, V), a sulfoacetaldehyde acetyltransferase (Fig. 2, VIII) and a phosphate acetyltransferase (Fig. 2, IX). A similar pathway, but with a different class of transporter, may be deduced from the genomic sequence of *Rhodobacter sphaeroides* (Ruff and Cook, unpublished data). Ruff et al. (2002) also postulated a regulated locus for the degradation of sulfoacetaldehyde in *B. fungorum*. So, a study of the biochemistry of one enzyme, Xsc, coupled with genomic sequencing, has allowed testable hypotheses to be generated on a range of previously inaccessible enzymes, transporters and regulators. The location, nature and regulation of sulfite oxidation should also become available.

Conclusions

There are only two established mechanisms of desulfonation in the dissimilation of C_2-sulfonates: (1) specific, inducible monooxygenases (e.g. Fig. 3) and (2) acetyl-phosphate:sulfite acetyltransferase (isomerizing; Fig. 4) at a point of convergence of several pathways (Fig. 2). One further mechanism is suspected: hydrolysis to glycolate. We can recognize that a presumably novel pathway exists to convert sulfoacetate to sulfoacetaldehyde. The first hypothetical access to transport systems for the entry of taurine into the cell, to regulatory mechanisms for the inducible catabolic enzymes and to a poorly understood enzyme is becoming available from genomic sequences.

The dissimilatory desulfonations discussed here are usually different from the desulfonation of the same compound involved in the assimilation of sulfonate sulfur (Cook et al. 1999; Kertesz 2000): one exception is now Xsc under anoxic conditions (Ruff et al. 2002). Desulfonation reactions and their control probably still hold many surprises and potential applications (Kertesz and Wietek 2001).

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