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Comment on “Activation of methane to CH_3^+ : A selective industrial route to methanesulfonic acid”

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Díaz-Urrutia and Ott (Reports, 22 March 2019, p. 1326) report a selective conversion of methane to methanesulfonic acid that is proposed to occur by a cationic chain reaction in which CH_3^+ adds to sulfur trioxide (SO_3) to form $\text{CH}_3\text{-S(O)}_2\text{O}^+$. This mechanism is not plausible because of the solvent reactivity of CH_3^+ , the non-nucleophilicity of the sulfur atom of SO_3 , and the high energy of $\text{CH}_3\text{-S(O)}_2\text{O}^+$.

The direct synthesis of methanesulfonic acid (MSA) from methane and sulfur trioxide (SO_3) is a potentially high-value but challenging transformation. Older approaches to this conversion involved either metal-catalyzed reactions or catalysis by peroxy salts, generally in fuming sulfuric acid (oleum) solutions, in reactions that are thought to occur by free-radical chain mechanisms (1, 2). Recently, Díaz-Urrutia and Ott reported the highly selective formation of MSA from methane in oleum catalyzed by sulfonyl peroxide derivatives, and it was proposed that the high yields and selectivity observed were the result of a novel mechanism involving CH_3^+ in a cationic chain reaction (3). In the proposed mechanism (Fig. 1), the protonated catalyst (1) carries out a hydride abstraction from methane to give the chain-carrying CH_3^+ . The CH_3^+ is then proposed to add to an S=O bond of SO_3 at the sulfur (as in 2) to produce $\text{CH}_3\text{-S(O)}_2\text{O}^+$ (3). The $\text{CH}_3\text{-S(O)}_2\text{O}^+$ would then abstract a hydride from methane to afford the MSA and CH_3^+ to continue the chain. Notably, no methyl bisulfate (MBS; $\text{CH}_3\text{OSO}_3\text{H}$) could be observed in this reaction, and the success of as little as 0.1% catalyst was indicative of very long chains.

We describe here why this mechanism is unreasonable in a series of ways based on literature precedent and standard chemical precepts. To add quantitative insight into the energetic infeasibility of the process, computational studies were carried out on the key structures in CCSD(T)/aug-cc-pVTZ//M06-2X/6-31+G(d,p) calculations including an SMD implicit solvent correction, supplemented by CAS(10,10)-NEVPT2 for open-shell structures of 3 (4).

A first concern is that CH_3^+ would be too reactive with the solvent to be an intermediate in a chain reaction. Strongly stabilized carbocations have long been directly observed in sulfuric acid solutions, but the range of observable cations is limited by the basicity and nucleophilicity of sul-

furic acid. At an extreme, the marginally observable cumyl cation $\text{PhC}^+(\text{CH}_3)_2$ requires 30% oleum (5). CH_3^+ is in contrast an intrinsically high-energy structure; gas-phase hydride affinities place CH_3^+ at 94 kcal/mol above the cumyl cation (6–8). This high energy fits with solution observations. Olah *et al.* were unable to observe CH_3^+ under the most stringently non-nucleophilic superacid conditions (9). From an extrapolated $\text{p}K_{\text{R}}$ value, CH_3^+ is less favorable to form in solution than the cumyl cation by ~30 orders of magnitude (10). If CH_3^+ were formed in an oleum solution, its reaction with the sulfuric acid to form $\text{CH}_3\text{OS(O)(OH)}_2^+$ (4, Fig. 2) is computationally predicted by the CCSD(T)/SMD//M06-2X calculations to be barrierless in potential energy and downhill in free energy by 29.5 kcal/mol. Proton transfer from $\text{CH}_3\text{OS(O)(OH)}_2^+$ to solvent would afford MBS, an unreactive thermodynamic sink in these reactions. For a successful chain reaction requiring little catalyst, the CH_3^+ would have to react $\gg 100$ times faster with the less-basic SO_3 than it undergoes the barrierless reaction with solvent.

A second concern is that SO_3 is not nucleophilic at its sulfur atom. Although SO_3 reacts widely with nucleophiles and free radicals, the literature does not contain any examples of SO_3 reacting with electrophiles at the sulfur atom. The non-nucleophilicity of the sulfur atom is readily understandable from simple resonance considerations, as significant contributing resonance structures (Fig. 1) place a positive charge on the sulfur but no valid resonance structure places either a negative charge or a lone pair of electrons on the sulfur.

An interrelated third concern is that the $\text{CH}_3\text{-S(O)}_2\text{O}^+$ product of the proposed electrophilic addition of CH_3^+ to the sulfur atom is an oxylium ion (a monovalent oxygen cation). Oxylium ions are exceedingly high-energy structures; hydride affinities place HO^+ 98 kcal/mol above the high-energy

CH₃⁺ (**6**). From this, it would be expected that the CH₃-S(O)₂O⁺ would be higher in energy than the separate CH₃⁺ and SO₃. Calculations support this expectation. Figure 2 shows the calculated energetics for a series of relevant structures. The closed-shell symmetrical **3-C₃V** structure for CH₃-S(O)₂O⁺ is not a minimum on the potential energy surface, and it is predicted to be 61.6 kcal/mol above the starting CH₃⁺ / SO₃. An asymmetric open-shell form of **3** (**3-open shell**) was an energy minimum but remained extremely high in energy in both CCSD(T) and CAS(10,10)-NEVPT2 calculations. The lowest-energy structure arising from CH₃⁺ binding at the sulfur of SO₃ is one in which two oxygens have bonded to form a strained dioxathirane (**3-C_s**). This structure avoids placing a formal positive charge on an oxygen, but it is still a prohibitive 37.6 kcal/mol above the CH₃⁺ / SO₃. The only thermodynamically feasible reaction of CH₃⁺ with SO₃ is bond formation with an oxygen atom to afford **5**. Díaz-Urrutia and Ott noted that bond formation at the oxygen atom could not account for the formation of MSA (**3**), and the formation of **5** is in any case predicted to be less favorable than reaction of CH₃⁺ with the sulfuric acid to form **4**, by 15.5 kcal/mol. The preferred methylation of the solvent fits with the known 27 kcal/mol greater proton affinity of H₂SO₄ over SO₃ (**7**).

These considerations preclude any possibility of the MSA being formed by the proposed chain process involving CH₃⁺ and CH₃-S(O)₂O⁺. The actual mechanism for this impressive transformation remains unknown. Díaz-Urrutia and Ott excluded a free-radical mechanism based largely on observations in the presence of free-radical inhibitors, but we note that a uniquely rapid free-radical step may potentially complicate experimental observations. In part because of a favorable quadrupolar interaction of a methyl radical (CH₃•) with SO₃, the two are predicted to form a free energy-favored face-to-face complex (at -2.0 kcal/mol versus the separate CH₃• / SO₃). The barrier for the subsequent addition via transition state **6** is then minimal. As a result, the CH₃• / SO₃ reaction would occur at approximately a diffusion-controlled rate and, most notably, as quickly as CH₃• could react with any free-radical inhibitor. Under such circumstances, the interpretation of observations in the presence of inhibitors requires great care.

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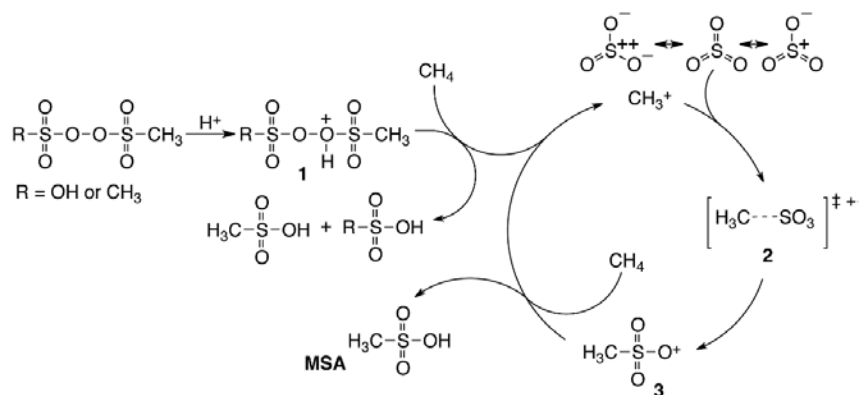


Fig. 1. Mechanistic proposal of Díaz-Urrutia and Ott. The proposed mechanism is supplemented here by three of the resonance structures for SO_3 .

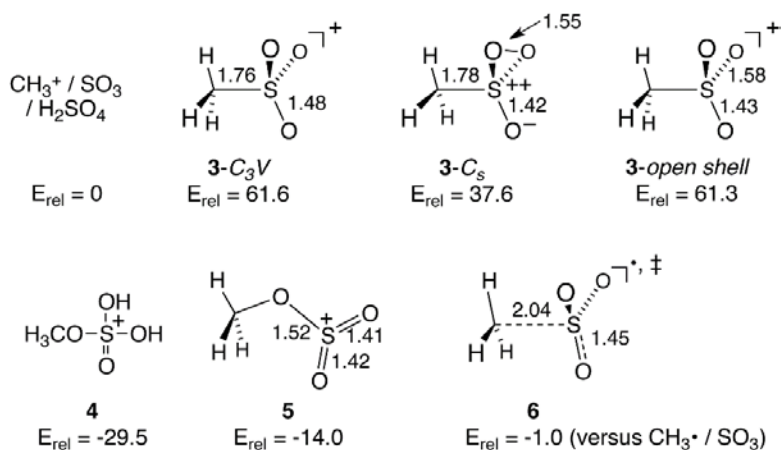


Fig. 2. Calculated energies for key structures. The free energies shown are based on CCSD(T)/aug-cc-pVTZ single-point energies and SMD explicit solvent corrections for gas-phase structures optimized in M06-2X/6-31+G** calculations, with a standard state of 1 M and 25°C. An unrestricted broken-symmetry basis was used for **3-open shell**. CAS(10,10)-NEVPT2 calculations place **3-open shell** at 25.1 kcal/mol above **3-Cs**.

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