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Response to Comment on “An Ecofriendly Catalytic Route for the Preparation of Perfumery Grade Methyl Anthranilate from Anthranilic Acid and Methanol”

To the Editor:

Dr. Turner has made interesting comments on our work. We appreciate his views, to which most of the scientists working with liquid acid catalysis would subscribe. However, the major advantage of solid catalysts is that the reaction rates and selectivities can be modified by designing proper catalysts. In fact, he has complimented us on our work. The following points are sufficient to remove the apprehensions Dr. Turner has.

(1) In the laboratory experiments for reaction of anthranilic acid with methanol in the liquid phase, wherein the catalyst loading was 0.0248 g/cm^3 of liquid phase, no formation of dimethyl ether (DME) was detected. Therefore, the volatile organic compound (VOC) generation problem does not arise. If vapour-phase experiments are done, then there would be substantial dehydration of methanol, and hence DME formation would result. It should be realised that in the presence of sulfuric acid as a homogeneous catalyst, which is also a dehydrating agent, the formation of ether takes place.

(2) The analytical section of our paper[1] clearly mentions that after the filtration of the catalyst the reaction mixture was analysed without any removal of methanol. The analysis was done by using high-performance liquid chromatography (Tosoh, UV-8010) at ambient temperature. The Merck 50983 column with a stationary phase of Lichrospher 100 RP-18, particle size 5 μm, prepacked on a 250-mm × 4-mm-i.d. column with a Tosoh UV-8010 detector set at 254 nm, was used. The eluent used for the analysis was 80:20 methanol−water mixture with a flow rate of 0.8 mL/min.

(3) It was observed from the analysis that there was only unreacted anthranilic acid and the product methyl anthranilate (100% selectivity towards the ester), and no other side products were found to exist in the reaction mixture. The conversion was based on the anthranilic acid, and the methanol was undetectable as the eluent used in HPLC itself was a methanol−water mixture. The reaction was conducted in an autoclave without any vent-off, and there was not much autogenous pressure developed. Had DME been generated in situ, then substantial pressure rise would have resulted. We admit that we have not done the vapour-phase analysis, because we used to cool the autoclave at the end of the reaction and the pressure was found to drop to the original atmospheric pressure. Had there been any DME (bp −24.8 °C), it would be still in the vapour phase, and it would have shown pressure on the autoclave even at room temperature. This is a convincing proof. There would be some solubility of DME, if generated, in the liquid reaction mixture. Since it was not detected by HPLC, we presume that there is no DME generation. Thus, we conclude that there was no DME formation, and the question of VOC formation is hypothetical. Whether any DME would form on a large plant-scale experiment is a matter of debate. We have not conducted any pilot experiments to ascertain this fact. It should also be mentioned here that alkylation reactions with alcohols do form ethers in the presence of both liquid and solid acid catalysts.

(4) The overall efficacy of the process and a cost analysis comparison with the use of sulfuric acid as the catalyst are already explained in the original paper itself in the Conclusion section. Plenty of work is available with H_2SO_4 as catalyst, and hence we did not perform these experiments.

(5) We agree with Dr. Turner that there is a typographical error, as the boiling point of methyl anthranilate should have been mentioned as 256 °C, and we regret that mistake.

In conclusion, we appreciate the positive comments made by Dr. Turner and believe that our rebuttal will satisfy his curiosity.

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