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## The Thermal Decomposition of Ethyl Mercaptan and Ethyl Sulphide

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**I**N the first issue of this journal (Volume 1, page 77), in their paper with the above title, Trenner and Taylor make several references to our own work on a similar subject. We believe they have misrepresented us on a sufficiently large number of points to give a completely misleading impression of its nature to any one reading their article.

For example, according to Trenner and Taylor: "It has frequently been suggested that the aliphatic mercaptans behave thermally in a manner similar to the amines, and might therefore be suspected of decomposing in a unimolecular manner. In fact, that is the supposed finding of Malisoff and Marks recently for propyl, butyl, amyl and heptyl mercaptans, both iso and normal."

Here is what we say in our summary: "It is impossible with data of this order of accuracy to decide finally between a first and a second-order reaction. The trend is much closer to a first-order reaction and is confirmed by an approximate independence of the rate of decomposition of the concentration used and the simultaneous poor agreement with tests for bimolecularity." And in the body of our article we say "This leaves much room for vacillation in deciding between first and second-order reactions," and we express our doubts in some detail.

According to Trenner and Taylor: "... it is hardly surprising that Malisoff and Marks should find no effect from hydrogen and carbon dioxide."

What we said in our summary: "The decomposition of amyl mercaptan is to some extent depressed by the admixture of gases like hydrogen and carbon dioxide." And in the article itself: "It was found that gases like hydrogen and carbon dioxide have no marked effect on the order of magnitude of the amount decomposed."

Our conclusions are "hardly justifiable" because "the intermediate, as has been shown, reacts analytically as a mercaptan." Despite their impression to the contrary Trenner and Taylor have not *shown* the presence of an inter-

mediate; the compound they obtained might have been one, but it might just as well have been a secondary product. And concerning this compound, which is supposed to make the results of our analyses worthless, they themselves say that "as has been shown, a maximum concentration of the intermediate is found in the neighborhood of the point of inflection"—and in this neighborhood, working at pressures of the order of atmospheric, they obtained "small yields," because "its rate of formation is only slightly greater than its rate of decomposition." To secure enough product for an analysis to be made they worked at lower temperature and at *150 atmospheres*. The mercaptans in our experiments were at pressures of the order of 10 millimeters.

The difference between the temperature coefficients found by us and by Trenner and Taylor may be ascribable to other things than our "unjustifiable averaging of numerous erratic results." There is, for one thing, the difference in conditions of experiment, and, for another, the fact that Trenner and Taylor had first to assume that certain points on their curves were "comparable" and then to determine these points by inspection—a process of a rather subjective nature, as can be seen from their Table VI, which contains points of inflection read from Fig. 3. Our values were determined directly from the amount decomposed found by analysis.

Trenner and Taylor talk of our "conclusions that mercaptan decomposition involves a straight split into olefine and hydrogen sulfide in a manner satisfactorily accounted for by a single unimolecular rate." The "straight split" was a suggestion on our part, but was so far from being a conclusion that we spend about a quarter page in discussing a possible chain mechanism.

It is chiefly to this sort of reference by Trenner and Taylor that we object. We make a suggestion concerning the mechanism, a suggestion justified by the experimental results, with full knowledge of its nature as an assumption, and we state that

the evidence favors this rather than the other hypothesis so far advanced. We do not consider it a conclusion, in fact we advance still another hypothesis. But Trenner and Taylor speak of our "conclusions" and "finding," and having thus set up a straw man proceed to demolish him. This seems to us decided misrepresentation, especially as Trenner and Taylor proceed from their supposed refutation to cast doubt upon the validity of our experimental results.

As for the other details of criticism on the page which Trenner and Taylor devote to our results, it is well to realize that this article of theirs deals with the decomposition of ethyl mercaptan in the *absence* of solvents, by a static method, at pressures mostly of the order of several hundred mm,

with times of contact of the order of a half hour, at temperatures from  $386^{\circ}$ – $420^{\circ}$ . Our experiments were done with different mercaptans, in hydrocarbon diluents where the total mercaptan pressure in the gas was of the order of 10 mm, with times of contact from a few seconds to three minutes, at temperatures from  $300^{\circ}$  to  $475^{\circ}$ . We analyzed the products, they simply followed the pressure changes.

It is well to repeat that the title of our paper contains the words "in hydrocarbon solvents" and all our conclusions refer to decomposition under those conditions only. It is quite possible for some of them to diverge from results of Trenner and Taylor without our being entirely incorrect.