# Notizen

## The Heats of Adsorption of the Trichloroethanes on Porous Alumina

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The trichloroethanes undergo rapid dehydrochlorination in the presence of porous transitional aluminas, at temperatures as low as 80 °C. Attempts to measure their heats of adsorption on these solids above 80 °C are therefore unsuccessful. Silica gel is an inactive dehydrochlorination catalyst, and the heat of adsorption of 1,1,2-trichloroethane measured for this material is reported.

In this note, we wish to make the following comments on the paper entitled "The heats of adsorption of some chlorinated hydrocarbons on porous $\gamma$-alumina" by Sanesi[1], published in this Journal. The author ascribes the two peaks observed in the chromatogram of 1,1,2-trichloroethane to adsorption of the chlorocarbon in two modes – (i) two H's and two Cl's and (ii) two Cl's and one H, adjacent to the surface.

We consider that the two peaks are in fact the result of chemical reaction on the column. We have investigated the solid catalyzed elimination of hydrogen chloride from a variety of chlorocarbons, and have found transitional aluminas to be active catalysts at temperatures above about 80 °C. The reactions of the trichloroethanes are particularly rapid. Thus, we find that both undergo quantitative dehydrochlorination on the first few centimeters of an alumina column at 80 °C, at a carrier gas flowrate of 60 mls/min. Using a 1 metre column, we found that two reaction product peaks were produced by 1,1,2-trichloroethane. Vinylidene chloride (VDC) and trans-dichloroethylene formed a single, unresolved peak (the major component of which was VDC), and cis-dichloroethylene formed the second peak. A single peak, vinylidene chloride, was given by 1,1,1-trichloroethane.

We have measured the heats of adsorption of these products on alumina by a method identical to that of Sanesi, and found the following:

- vinylidene chloride 34.0 kJ/mole (8.1 kcals/mole),
- trans-dichloroethylene 35.6 kJ/mole (8.5 kcals/mole),
- cis-dichloroethylene 37.8 kJ/mole (9.0 kcals/mole).

Our injection samples were about 0.1 $\mu$ mole in size, so these values should be compared with the $\overline{Q}$a,o values of Sanesi- i. e. 34.3 kJ/mole for 1,1,1-trichloroethane and 1,1,2-trichloroethane (first peak) and 40.6 kJ/mole (1,1,2 isomer, second peak). Sanesi's figure of 34.3 kJ/mole is consistent with our interpretation that dehydrochlorination has occurred on the column, giving VDC either as the exclusive, or the major product (1,1,1-trichloroethane and 1,1,2-trichloroethane, first peak, respectively). The agreement between Sanesi's second value for 1,1,2-trichloroethane and our heat of adsorption of cis-dichloroethylene is less convincing, but we consider that the discrepancy is within the possible experimental error. The standard deviation in our measured value could be as much as ± 2 kJ/mole. We note that Sanesi states that the standard deviation in his results could also be ± 2 kJ/mole in some cases.

We have measured the heats of adsorption of a number of chlorocarbons on silica gel (Porasil B), and find that to a reasonable approximation, heats of adsorption on alumina are equal to the corresponding heats of adsorption on silica, plus 4 kJ/mole. Silica gel is a relatively inactive dehydrochlorination catalyst, and we have been able to measure the heat of adsorption of 1,1,2-trichloroethane. We found a value of 46.0 kJ/mole, suggesting that the heat of adsorption on alumina is of the order of 50 kJ/mole.

We consider that two chromatographic peaks could arise from the adsorption of 1,1,2-trichloroethane in two modes, as suggested by Sanesi, only if the two modes are kinetically distinguishable – i. e. if a given molecule of 1,1,2-trichloroethane were always re-adsorbed in the same mode as it passes along the column. We can think of no mechanism for such a "memory" effect.

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[1] M. Sanesi, Z. Naturforsch. **29 a,** 1097 [1974].