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Surface Catalyzed Hydrochlorination of 1,3-Butadiene.

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Abstract: The rates of disappearance of gaseous hydrogen chloride (-d[HCl]/dt) and 1,3-butadiene and appearance of the gaseous products 3-chloro-1-butene and *(E)*- and *(Z)*-1-chloro-2-butene (+d[products]/dt) in Pyrex IR cells at 295 K and total initial pressures of about 450 torr are found to be proportional to the surface-to-volume ratio (S/V) of the reaction vessel.

Qualitative aspects of surface effects during electrophilic addition to alkenes have a long history.[1] Most recently, surface effects have been implicated in the formation of product during the reaction of gaseous hydrogen chloride with various gaseous alkenes[2] and the effect of surface on the products of addition of hydrogen chloride to alkenes in solution has been reemphasized.[3] ***Quantifying*** these effects has proved more difficult.[4]

In this report we briefly describe both the technique which permits observation of the quantitative effect of the surface-to-volume ratio on the rates of the disappearance of starting materials and the appearance of products and our preliminary results with gaseous 1,3-butadiene, **[CAUTION]**[5] an alkene whose reaction with gaseous hydrogen chloride at fixed surface-to-volume ratio has recently been described.[6]

To evaluate the effects of the walls and added surface, the surface area of the reaction vessels was varied. Holes (5 mm dia.) were drilled through the center of a number of Pyrex fritted glass disks (ChemGlass, Vineland, NJ; 14 x 2 mm; coarse porosity) from which the organic impurities were then removed by (a) cycling the disks through a glass annealing oven and (b) sonication with chromic-sulfuric acids. After thorough washing (including further sonication) with distilled, deionized water, a further sonication with aqua regia followed by exhaustive washing and sonication with distilled, deionized water (no precipitate with acidic silver nitrate) was effected and two additional annealing oven treatments performed. Reproducible glass surface (*ca.* 3.3×10^2 cm^2/g)[7] could be obtained The disks were mounted in (nominally) 10 cm x 15 mm ID gas IR cells equipped with NaCl windows held in place over KELREZ (F&FP, Wilmington, DE) gaskets and a series of IR spectra were obtained as previously reported[6] on gaseous mixtures of purified hydrogen chloride and 1,3-butadiene. For initial pressures of hydrogen chloride and 1,3-butadiene in the range of 3×10^2 torr and 1.4×10^2 torr, respectively, **Figure** 1 demonstrates that, at 295 K, the initial rate of disappearance of hydrogen chloride (-d[HCl]/dt) is proportional to the surface-to-volume ratio of the cell. The same relationships apply to the initial rates of formation of the individual products, 3-chloro-1-butene and *(E)*- and *(Z)*-1-chloro-2-butene.

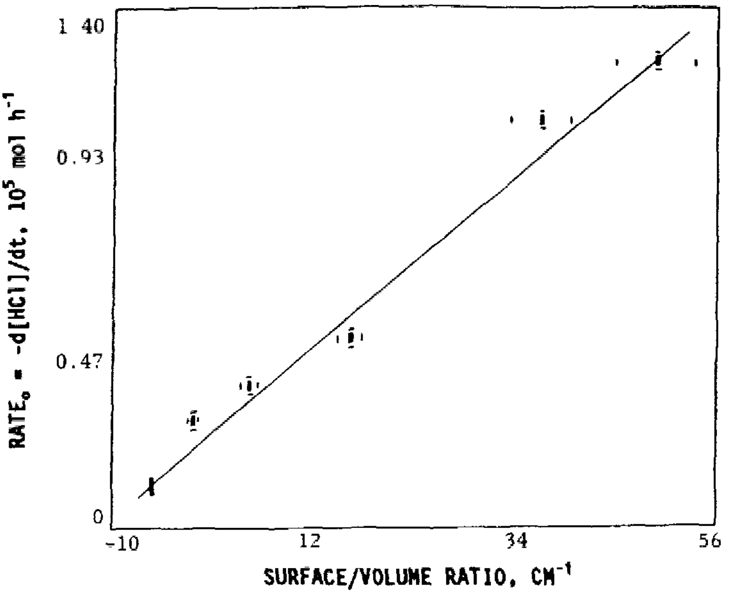

Figure 1. The variation in the initial rate of disappearance of hydrogen chloride (g) as a function of the surface-to-volume ratio (S/V) at 295 K. The initial concentrations of hydrogen chloride and 1,3-butadiene are 3.4×10^{-4} mol and 1.6×10^{-4} mol, respectively.

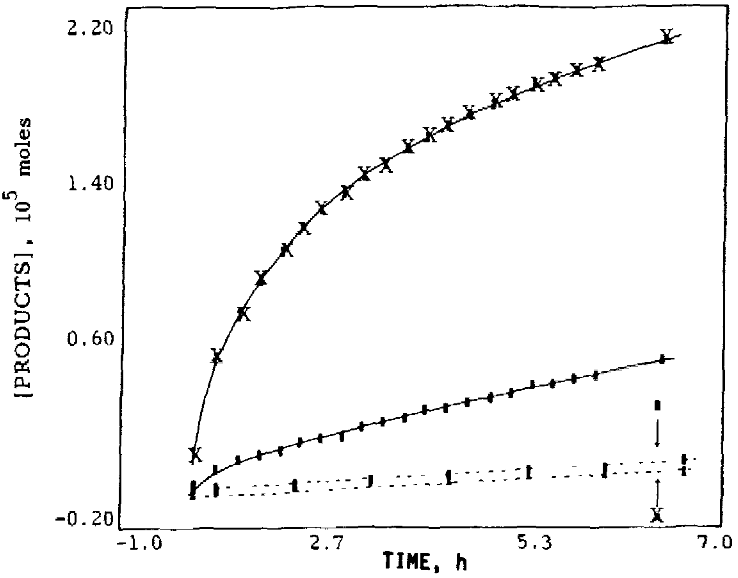

Figure 2. The variation in formation of the products 3-chloro-1-butene (X) and *(E)*-1-chloro-2-butene (•) as a function of surface-to-volume ratio (S/V) [S/V = 48 cm^{-1} (———); S/V = 2.3 cm^{-1} (- - - -)] at 295 K. The initial concentrations of hydrogen chloride and 1,3-butadiene are 3.4×10^{-4} mol and 1.6×10^{-4} mol, respectively.

As might be expected if there are at least some *different* catalytic sites giving rise to the *different* products [it having been shown[6] that the products are stable to the reaction conditions and (a) not only do not revert to starting materials but (b) also do not interconvert] the rates for the individual product formation also appear to depend upon the quantity of the surface. Thus, the product of "1,2-addition" (3-chloro-1-butene) initially lags behind those of "1,4-addition" (both *(E)*- and *(Z)*-1-chloro-2-butene) in a cell with no added surface. Eventually (i.e. at about 90 h) the ratio of "1,2-addition" to (total) "1,4-addition" products is about 1:1. However, *in proportion to added surface*, not only does the total rate of product formation increase but also there is a reversal in the initial ratio of products. That is, *in proportion to added surface*, the quantity of 3-chloro-1-butene initially forges ahead of that of *(E)*- and *(Z)*-1-chloro-2-butenes which, none-the-less, after a time dependent on the quantity of surface, again eventually reaches a 1:1 ratio which does not change as the reaction continues. **Figure 2** presents this information graphically for the two extrema of surface to volume ratios reported here. That the product ratio determined by infrared spectroscopy in the gas phase also reflects the ratio on the surface was demonstrated by gas chromatographic analysis[6] of the gases and, separately, removal and sonication of the disks in tetrachloroethylene,[8] and gas chromatographic analysis of the material found on the disks which, within experimental error, was identical to that found in the gas phase.

Although detailed analysis awaits examination of the reaction at different initial pressures and temperatures it is now clear that (a) at least some different sites give rise to the different products at different initial rates and that (b) there is little, if any, reaction between the gases hydrogen chloride and 1,3-butadiene in the "absence" of surface.

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(4) Discussions of the well known effect of varying the surface-to-volume ratio (S/V) in heterogeneous processes, albeit without specific inclusion of reference to electrophilic addition, can be found in (a) Kondratev, V. *Chemical Kinetics of Gas Reactions*; Pergamon: New York; **1964**; p 44 ff. (b) Melville, H.; Gowenlock, B. *Experimental Methods in Gas Reactions*; MacMillian: New York; **1964**; p 358 ff.

(5) It has recently been suggested that 1,3-butadiene may be a "super carcinogen". See Ames, B. N.; Gold, L. S. *Science* **1991** *251*, 12.

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(7) By actual measurement the Pyrex coarse porosity filters are prepared from granular glass of average diameter particle size between 75 and 105 μm. The density of an average disk is 2.01 g cm^{-3}, from which it follows that the average surface area is about 3.3 x 10^{2} cm^{2}/g. The horizontal error notation in **Figure 1** includes the uncertainty in particle size while the verticle error includes deviation from replicated experiments.

(8) In our initial experiments, disks from completed reactions were divided into two portions; half being extracted with ether and half with tetrachloroethylene (TCE). On the 6 ft x 1/4 in 0.19% picric acid on Carbopak C column used[6], TCE has a retention time of 13 min (column temperature = 90°C; injector temperature = 250°C; He flow = 3 cm^{3} min^{-1}) while the products reported are completely eluted within 2.5 min. In concert with our IR observations, no new products with retention times less than TCE were found. That no new products with retention times of the order of 13 min (i.e. containing more halogen and retained on the disks) were present was determined from the ether extract. The retention time of diethyl ether under the above specified conditions was 1.0 min.

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