

Inhibition of Radical Chlorination by Chlorine Dioxide in Non-polar Media

PETER S. FREDRICKS, BENGT O. LINDGREN and OLOF THEANDER

Swedish Forest Products Research Laboratory, Box 5604, S-114 86 Stockholm, Sweden

In a previous paper¹ we have presented evidence for the inhibition by chlorine dioxide of the radical chlorination of carbohydrates in aqueous acid solution. It became therefore of interest to investigate if chlorine dioxide inhibits radical chlorinations in non-polar media.

Poutsma² has made a very thorough study of chlorination in non-polar media and has shown that olefins in darkness are chlorinated by two competing pathways, ionic and radical, the latter being initiated by molecule induced homolysis and inhibited by radical scavengers such as oxygen. Poutsma² has shown that if the chlorination of cyclohexene is carried out in the absence of oxygen and light three major products are obtained: *trans*-1,2-dichlorocyclohexane, 3-chlorocyclohexene, and 4-chlorocyclohexene. In the presence of oxygen, the 4-chloro-derivative was not formed showing that it was a product of the radical pathway.

In the present study we have chosen to study the effect of small quantities of chlorine dioxide on the chlorination of cyclohexene. A carbon tetrachloride solution of chlorine containing a small amount of chlorine dioxide was rapidly run into the stirred cyclohexene under a nitrogen atmosphere and in the dark. The products were analysed by GLC and the results compared with those obtained from chlorination in the absence of chlorine dioxide (Table 1). Clearly the formation of 4-chlorocyclohexene is practically eliminated, in agreement with an inhibition of the radical reaction by chlorine dioxide.

Experimental. Materials. The cyclohexene (Schuchardt) was distilled from sodium before use. The chlorine dioxide was prepared by oxidising sodium chlorite with chlorine in aqueous solution.

Chlorination method. Cyclohexene (20 ml) was placed in a blacked-out conical flask fitted with a central capillary gas inlet, a dropping funnel, and a magnetic stirrer. The

Table 1. Results from the chlorination of cyclohexene.

Reactant ratio ^a ClO ₂ /Cl ₂ /C ₆ H ₁₀	Product ratio ^b Dichlorocyclohexane/ 3-chlorocyclohexene/ 4-chlorocyclohexene
nil/0.095/1.00	2.23/1.00/0.24
nil/0.102/1.00	2.57/1.00/0.22
0.0018/0.092/1.00	2.18/1.00/0.00
0.0017/0.095/1.00	1.94/1.00/0.00

^a Mole ratio. ^b The ratio of the peak areas from the gas-liquid chromatogram.

apparatus was thermostated at 25°C and nitrogen passed through for 10 min to remove air. Chlorine and, when required, chlorine dioxide were dissolved in carbon tetrachloride at the required concentrations and 20 ml of the solution was added rapidly to the stirred cyclohexene by way of the dropping funnel. Nitrogen was then passed through the mixture for a further 10 min in order to remove any hydrogen chloride formed.

Analysis of the products. The analysis of the products was carried out by GLC on polypropylene columns (15 % on Chromosorb W) (Table 1) as described by Poutsma.² Identification of the peaks was accomplished by isolating samples from the gas chromatography column and determining their IR spectra on films between sodium chloride plates. The IR spectrum of the fraction identified as *trans*-1,2-dichlorocyclohexane was identical with that of this compound published earlier.³ The spectrum of 3-chlorocyclohexene fraction had strong peaks at 745, 869, 1223, and 1440; and that of 4-chlorocyclohexene fraction at 670, 680, 849, 1240, 1263, and 1440 cm⁻¹ and the spectra were identical with those of authentic compounds. IR spectra of the 3- and 4-chlorocyclohexene were kindly provided by Dr. M. L. Poutsma.

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