

THE REACTIONS OF SODIUM VAPOR WITH CHLOROCARBONS

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Recent studies have shown that reactions of lithium vapor with halocarbons, (1) halogen substituted hydrocarbons, (2) or unsaturated (3) hydrocarbons lead to extremely reactive new polylithium organic compounds having stoichiometries such as CLi_4 , C_2Li_6 , C_2Li_4 , etc.

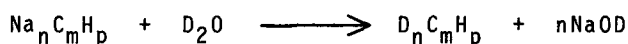
Reactions of chlorocarbons with sodium atoms were investigated as an extension to the previously reported lithium work. Such reactions of sodium vapor, although predictably exhibiting some similarities, surprisingly have been found to be very different when studied in detail.

Both types of compounds, multiply sodium substituted hydrocarbons and polylithium organic compounds, are of substantial current interest due to the likelihood of their bonding and geometry proving to be unprecedented both as in the solid state and as isolated gas phase species in high temperature vapors. This latter area has been elegantly illustrated by the ab initio calculations of Schleyer, Pople and coworkers. (4)

We report here some reactions of excess sodium vapor produced at 440-460° in vacuum (10 - 5 torr) with carbontetrachloride and partially chlorinated ethanes, $C_2H_{6-x}Cl_x$, where $x = 1$ to 4. The apparatus and experimental procedure have been described previously. (3)

In a representative reaction, 15 grams of sodium, vaporized in vacuum at

440-460° during 25 - 30 minutes, was allowed to react with about 1.2 grams of the chlorocarbon and the products were collected on a liquid nitrogen cooled cold finger. Thereafter, the reaction vessel was warmed to room temperature under vacuum and any volatile materials were removed by pumping. The reaction vessel was then opened under argon and the extremely reactive brittle gray - brown solid product was hydrolyzed with D₂O at CA 0° in a vacuum line. The volatile products of hydrolysis were separated by vacuum line fractionation. The materials passing a -95° trap and stopping in a -196° trap (C₂ hydrocarbons) were analyzed by g.l.c. using 10 m x ¼" durapak phenyl isocyanate on Porasil C column. The individual deuterated hydrocarbons were identified by comparison of their retention times with those of known samples as well as by both low and high resolution mass spectra. Since deuterolysis of a C - Na bond results in selective formation of a C - D bond to produce a deuterium substituted hydrocarbon, it was thus possible to characterize the sodium compounds obtained in each reaction:



It should be noted that identical results were obtained from when the hydrolysis of the solid was carried out either immediately after the reaction or after having kept the solid for over twenty four hours at room temperature. A "blank" study of the deposition of chlorocarbons and sodium at single intervals where no co-condensation was possible gave only extremely small amounts of totally different products (i.e. mainly coupling reactions). Furthermore, there was no visible reaction in the solid phase during its transfer under argon into the hydrolysis vessel. These observations suggest that the sodium compounds were in fact formed from the reaction of sodium vapor with the chlorocarbons. The polysodium organic compounds prepared must be stored in vacuum or under argon and react violently with water.

The careful D₂O hydrolysis of the solid product from CCl₄ and sodium vapor gave a 51% yield (based on CCl₄) of hydrocarbons consisting of 80% C₂D₄, 15% C₂D₆. There was no evidence of any CD₄ (hydrolysis being carried out in a closed system) indicating that the polymeric "CNa₄" might not have been formed in this reaction, in contrast to CLi₄ in the reaction of lithium vapor with CCl₄. (1) In the latter case, deuterolysis of the solid reaction product gave a 14% yield of CD₄. The

other products were the same in both sodium and lithium reactions. The apparent absence of "CNa₄" in the sodium reaction may be attributable to steric factors. These multisubstituted sodium compounds, like the previously reported lithium compounds, (1) react with substances such as chlorotrimethylsilane to give analogous carbon methylsilanes. However, the conversion is low due to the insoluble nature of the sodium compounds and the product amounts are sufficient for mass spectral characterization only.

Since it was known (2) that partially halogenated propanes gave rise to perlithiated products upon their reaction with lithium vapor, probably as a result of vibrational - excitation of carbon - hydrogen bonds, a study of the reactions of sodium vapor with partially chlorinated ethanes was undertaken.

Thus, ethylchloride gave, after deuterolysis, a 36% yield of hydrocarbons consisting of 60% C₂H₅D, 30% C₂H₄ and 50% C₂D₂. The preferential formation of C₂H₅Na indicates that both the vapor phase and the well-known solution phase reaction of sodium with C₂H₅Cl are analogous. The same products were obtained in the reaction of sodium vapor with ethylbromide. Since the ethylene is undeuterated, it seems probable that it may have been produced by the elimination of NaH from C₂H₅Na by energy from the hydrolysis reaction, or by dehydrohalogenation by RNA intermediates. In striking contrast, the reaction of lithium vapor with chloroethane is known to produce C₂Li₆, C₂Li₄, and small amounts of CLi₄. (5)

A 14% yield of hydrocarbons consisting of 50% C₂D₆, 30% C₂D₄ and 20% C₂D₂ were obtained when the reaction product from HCl₂C - CCl₂H and Na vapor was hydrolyzed with D₂O. There was no partially deuterated C₂ species present. The observation that C₂Na₆ is produced in this reaction indicates that the C - H bond in an ethane becomes vibrationally excited for reaction and substitution by sodium if a sufficient number of chlorine substituents are present.

After the above distinctive results from C₂H₅Cl and C₂H₅Cl₄ had been obtained, the reactions of H₂C1C - CClH₂ and H₂C1C - CCl₂H with Na vapor were also studied. In each case the hydrolysis product consisted of ethane, ethylene and acetylene. However, the ethane consisted of a mixture of small amounts of C₂D₆ and other partially deuterated species with the minimum number deuterium atoms corresponding to the number of chlorine atoms present in the chlorocarbons. Similarly, the ethylene

also was a mixture of C_2D_4 and other partially deuterium substituted species.

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