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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 stoiciometries 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^o 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^{o} 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 D_2O at CA 0^{o} in a vacuum line. The volatile products of hydrolysis were separated by vacuum line fractionation. The materials passing a -95^{o} trap and stopping in a -196^{o} trap (C_2 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:

$$Na_nC_mH_p + D_2O \longrightarrow D_nC_mH_p + nNaOD$$

It should be noted that identical results were obtained from when the hydrolysis of the solid was carried out either immediatedly 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 D_2O hydrolysis of the solid product from CCl_4 and sodium vapor gave a 51% yield (based on CCl_4) of hydrocarbons consisting of 80% C_2D_4, 15% C_2D_6. There was no evidence of any CD_4 (hydrolysis being carried out in a closed system) indicating that the polymeric "CNa_4" might not have been formed in this reaction, in contrast to CLi_4 in the reaction of lithium vapor with CCl_4. (1) In the latter case, deuterolysis of the solid reaction product gave a 14% yield of CD_4. The other products were the same in both sodium and lithium reactions. The apparent absence of "CNa_4" 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% C_2H_5D, 30% C_2H_4 and 50% C_2D_2. The preferential formation of C_2H_5Na indicates that both the vapor phase and the well-known solution phase reaction of sodium with C_2H_5Cl 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 C_2H_5Na 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 C_2Li_6, C_2Li_4, and small amounts of CLi_4. (5)

A 14% yield of hydrocarbons consisting of 50% C_2D_6, 30% C_2D_4 and 20% C_2D_2 were obtained when the reaction product from HCl_2C - CCl_2H and Na vapor was hydrolyzed with D_2O. There was no partially deuterated C_2 species present. The observation that C_2Na_6 is produced in this reaction indicates that the C - H bond in an ethane becomes vibrationally excited for reaction and substituion by sodium if a sufficient number of chlorine substituents are present.

After the above distintive results from C_2H_5Cl and $C_2H_5Cl_4$had been obtained, the reactions of H_2ClC - $CClH_2$ and H_2ClC - CCl_2H 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 C_2D_6 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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