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RARE-GAS MATRIX ISOLATION OF DICHLOROCARBENE FROM THE GAS PHASE

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Recently dichlorocarbene has been isolated after some photodecomposition and halomethanes-lithium atoms reactions in inert matrices at 15°K (1). However, the attempts (2) to observe the expected spectrum of CCl_2 in the frozen products of some pyrolitic gas reactions have failed.

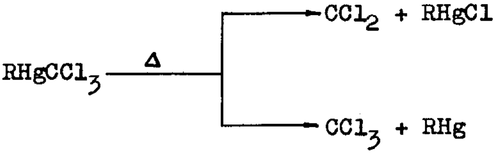
While investigating carbene reaction mechanisms by the rare-gas matrix-isolation method we have been able to stabilize CCl_2 from the gas phase and to observe its IR-spectrum (3). For the first time we have used a gas-phase pyrolysis of $RHgCCl_3$ compounds ($R = C_6H_5$, CCl_3, Cl) as a source of dichlorocarbene (4).

The experiments were carried out at the temperatures of 200-600°C in a high vacuum pyrolizer joined to a liquid helium optical cryostat (5). In each experiment a 4-5 mg sample of $RHgCCl_3$ was decomposed at a flow rate of 3-4 μmole/hr. The pyrolysis products and argon ($Ar:RHgCCl_3$ mole ratio being 1000) were simultaneously condensed on the KBr window at 8-10°K.

The temperature of decomposition was different for various $RHgCCl_3$. The $C_6H_5HgCCl_3$ pyrolysis was completed above 250°C. The amount of $Hg(CCl_3)_2$ converted varied from 20% up to 100% in the 200-600°C temperature range while CCl_3HgCl decomposition was not complete even at 600°C.

IR-spectra (400-1000 cm^{-1}) of the reactive intermediates and their stable dimers in Ar matrices have revealed the following absorption band frequencies (cm^{-1}) which were identical for all three compounds investigated: 720 (ν_1 CCl_2), 746 (ν_3 CCl_2), 898 (ν_3 CCl_3), and 779 (ν_{11} C_2Cl_4), 785 (ν_{10} C_2Cl_6), 915 (ν_9 C_2Cl_4). The absorption bands of RHgCl pyrolysis products were different for each compound (695 and 729 cm^{-1} for C_6H_5HgCl, 733 cm^{-1} for CCl_3HgCl and 403-413 cm^{-1} for $HgCl_2$). This assignment agrees with our spectra of matrix-isolated C_2Cl_4, C_2Cl_6, C_6H_5HgCl, CCl_3HgCl molecules (6) and the literature data for CCl_2, CCl_3 species (1) and $HgCl_2$ (7). The high-resolution IR-study of CCl_2 and CCl_3 has given additional evidence in favour of such an assignment (8). The warming of the matrix up to 35-40°K (with subsequent cooling to 10°K to record a spectrum) resulted in the disappearance of the 720, 746 and 898 cm^{-1} bands whereas the stable molecule absorptions remained. The ν_1 vibration band of CCl_3 was not found in the spectra after any of the $RHgCCl_3$ pyrolyses which supports the suggestion (9,8) that the radical is planar.

In each experiment the relative intensity ratio, $\nu_3(CCl_2)/\ \nu_3(CCl_3)$, was larger than 1.0 decreasing as the pyrolysis temperature rose. The ratio had the maximum value of about 4.0 in the case of $Hg(CCl_3)_2$ decomposition at 300°C and depended on the substituent R. This result suggests a simultaneous and independent CCl_2 and CCl_3 formation:



The CCl_3 formation (along with CCl_2) in $RHgCCl_3$ pyrolysis can be explained by weakening intermolecular mercury-chlorine atoms coordination (10) in the gas phase under high temperature conditions. This coordination is favour-able for CCl_2 elimination in solution (11).

The present results show that the matrix isolation technique is useful for the direct spectroscopic detection of unstable intermediates in gas phase reactions and for the study of reactions mechanisms.

Trichloromethyl- (and probably other halomethyl-) mercury compounds are found to be an effective source of carbenes in the gas phase. This conclusion is confirmed by $RHgCCl_3$ copyrolysis with some olefins and 1,3-dienes.

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