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GAS PHASE REACTION OF CF_3CN AND OTHER NITRILES WITH CHLORINE ATOMS

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SUMMARY

The photolytically induced reaction of Cl_2 with some nitriles was investigated in the gas phase at room temperature. The reaction with CF_3CN produced $CF_3CCl{=}NCl$, $CF_3CCl{=}N{-}N{=}CClCF_3$ and CF_3CCl_3 as well as minor quantities of $CF_3(Cl)C{=}N{-}CCl_2CF_3$, $CF_3CCl_2(CF_3)C{=}N{-}N{=}C(Cl)CF_3$, $CF_3CCl_2{-}N{=}N{-}CCl_2CF_3$, $CF_3CCl_2(CF_3)C{=}N{-}CCl_2CF_3$ and $CF_3CCl_2(CF_3)C{=}N{-}N{=}C(CF_3)CCl_2CF_3$. ClCN reacted in a similar way giving $CCl_2{=}NCl$, $CCl_2{=}N{-}N{=}CCl_2$ and CCl_4 as principal products.

On the other hand, when HCN was allowed to react with chlorine atoms, only ClCN, $CCl_2{=}NCl$ and CCl_4 were obtained. No compounds containing C-H bonds were found.

Possible reaction schemes taking into account the products obtained are discussed.

INTRODUCTION

The reactions of fluorine atoms and trifluoromethyl radicals with ClCN[1,2] have been studied in this laboratory. This paper deals with the results obtained for chlorine atom reactions with CF_3CN, ClCN and HCN. Chlorination, fluorination and chlorofluori-

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nation of trifluoroacetonitrile have been described in various papers. These are qualitative studies of addition to the triple bond, i.e., thermal [3], photochemical[4]reactions or in the presence of catalysts at either high pressures[5] or low temperatures [6] and in flow systems[7].

With regard to the chlorination of cyanogen chloride, it is known that the reaction between chlorine and ClCN in the presence of activated charcoal[8] leads to the formation of $CCl_2=NCl$. This product can also be obtained by irradiating ClCN saturated with Cl_2[9].

Gas phase contact chlorinations of HCN give ClCN, HCl and small amounts of cyanuric chloride with various catalysts such as coke [10], activated charcoal[11] or Zeolite 13X [12]. ClCN is also produced from aqueous or liquid HCN and chlorine in a partitioned bubble-column reactor [13].

RESULTS

Reaction of CF_3CN with chlorine

In a standard synthesis, 46 mmol Cl_2 and 57 mmol CF_3CN were photolyzed in a glass vessel (3 l) for 25 minutes, producing about 2.5 g of yellow liquid. A distillation at -100° allowed the separation of N_2 as well as of the unreacted Cl_2 and CF_3CN. A later distillation at -30° led to two fractions which were further analyzed as follows.

Chromatographic analyses of the volatile fraction at -30°C showed three different peaks. A good separation of these three products was very hard to achieve; an acceptable separation was possible by operating the column at 25°C with lower gas carrier flow (20 ml/min). The first peak isolated had a molecular weight of 185 ± 5, calc. 187.5, a boiling point of 46 ± 3°C, its IR spectrum showed absorptions at 717 (s), 723 (m), 797 (m), 835 (w), 862 (vs), 911 (s), 1194 (m), 1232 (vs), 1257 (vs), 1280 (m), 1340 (w) cm^{-1} in accordance with those already published for CF_3CCl_3[14]. The mass spectrum (Table 1) agreed with these results. The substance corresponding to the second peak had a molecular weight of 163 ± 5, calc. 166, and IR absorptions at 785 (w), 986 (m), 1189 (vs), 1230 (vs), 1237 (m), 1290 (m), 1311 (m) and 1615 (m) cm^{-1}. These results and the mass spectrum (Table 1) suggested the structure $CF_3CCl=NCl$. This substance has not been described in the literature yet. The third peak corresponded to a substance with a molecular weight of 260 ± 7, calc. 261, showed IR absorption at 746 (w), 758 (m), 994 (s), 1010 (m), 1188 (vs), 1192 (vs), 1237 (vs), 1292 (vs), 1648 (m) cm^{-1} in accord with published IR absorptions[15] for $CF_3CCl = N-N=CCl-CF_3$ (III). The mass spectrum (Table 1) is in accordance with this structure.

The non-volatile fraction at -30°C was a yellow oily liquid with a vapour pressure less than 10 Torr at room temperature. It was analyzed by gas chromatography - mass spectrometry using an QB17 column at 20°C. According to the mass spectra (Table 1), five other products were characterized: $CF_3(Cl)C=N-CCl_2CF_3$, $CF_3CCl_2(CF_3)C=N-N=C(Cl)CF_3$, $CF_3CCl_2-N=N-CCl_2CF_3$, $CF_3CCl_2(CF_3)C=N-CCl_2CF_3$ and $CF_3CCl_2(CF_3)C=N-N=C(CF_3)CCl_2CF_3$. However, it is worth mentioning that in those syntheses where the Cl_2/CF_3CN ratio was higher than two, this yellow oily liquid was not formed being CF_3CCl_3, $CF_3CCl=NCl$ and $(CF_3CCl=N)_2$ the only products detected.

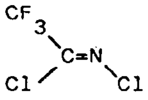
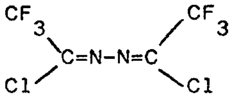
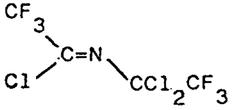
In order to get more information about the mechanism, some quantitative runs were performed in a quartz cylinder of 180 cc, with the U.V. light filtered by a 436nm Schott plate. The results are summarized in Table 2.

Reaction of ClCN with chlorine

In a typical run, chlorine (17.5 mm) and ClCN (24.6 mm) were introduced into a glass vessel (3 l) and irradiated during

TABLE 1

Mass spectra of the products for the $CF_3CN + Cl_2$ reaction.

Retention time(s)	Compound	Major peaks
16	CF_3-CCl_3 (I)	$C_2Cl_3F_2$(3%), $C_2Cl_2F_3$(100%), $C_2Cl_2F_2$(6%), CCl_3(81%), $CFCl_2$(43%), C_2ClF_2(6%), CCl_2(32%), CF_3(70%), CF_2(10%), CCl(22%), Cl(28%), CF(11%).
17	 (II)	C_2ClF_3N(20%), C_2F_3N(2%), C_2F_2N(8%), CF_3(100%), CClN(3%), CF_2(6%), CCl(2%), Cl(3%).
19	 (III)	$C_4Cl_2F_6N_2$(6%), $C_4Cl_2F_5N_2$(1%), $C_4ClF_6N_2$(10%), $C_3Cl_2F_3N_2$(8%), C_2ClF_3N(1%), C_2ClF_3(5%), CCl_2N(4%), CF_2Cl(9%), C_2F_2N(9%), CF_3(100%), CClF(3%), CClN(2%), CF_2(6%), Cl(2%).
24	 (IV)	$C_4Cl_2F_6N$(13%), $C_3Cl_3F_3N$(4%), $C_2Cl_2F_3$(8%), C_2ClF_3(3%), CCl_2F(5%), CF_2Cl(10%), CF_3(100%), CFCl(3%), CCl(4%), Cl(6%).

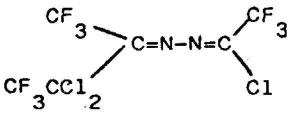
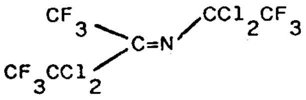
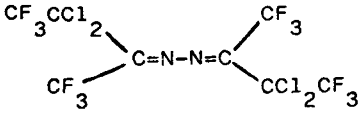
32	 (V)	$C_6Cl_2F_9N_2$(38%), $C_5Cl_3F_6N_2$(3%), $C_4Cl_2F_6N$(4%), C_4ClF_6N(6%), $C_2Cl_2F_3$(100%), CCl_2F(3%), CF_2Cl(3%), CF_3(10%), CN_2(6%).
45	$CF_3CCl_2-N{=}N-CCl_2CF_3$ (VI)	$C_4Cl_3F_6N_2$(0,2%), $C_4Cl_2F_6N_2$(0,5%), $C_4ClF_6N_2$(0,9%), $C_3Cl_2F_3N_2$(1,7%), $C_2Cl_2F_3N_2$(1%), $C_2Cl_2F_3$(100%), C_2ClF_3(12%), CCl_2F(12%), $CClF_2$(6%), CF_3(22%).
88	 (VII)	$C_6Cl_3F_9N$(7%), $C_6Cl_2F_9N$(2%), C_6ClF_9N(1%), $C_5Cl_2F_6N$(3%), $C_4Cl_2F_6N$(86%), C_4ClF_6N(24%), C_4ClF_6N(1%), $C_3Cl_3F_2$(4%), $C_3Cl_2F_3$(5%), $C_2Cl_2F_3$(13%), C_4ClF_2N(4%), C_3ClF_2(6%), CCl_2F(8%), C_3F_3(11%), C_3ClN, CF_2Cl(24%), CF_3(100%), CF_2(3%), Cl(3%).
178	 (VIII)	$C_4Cl_2F_6N$(45%), $C_2Cl_2F_3$(25%), C_4ClF_2N(11%), C_2ClF_3(4%), CCl_2F(6%), C_4F_2N(6%), C_3F_3(10%), $CClF_2$(24%), C_2F_2N(3%), CF_3(100%), $CClF$(1%), CF_2(1%), Cl(2%), CF(2%).

TABLE 2

Experimental results for $CF_3CN + Cl_2$ reaction.

Run	Light Intensity	Cl_2 (mmol)	CF_3CN (mmol)	Photolysis time min	CF_3CCl_3 (mol)	$CF_3CCl=NCl$ (mol)	$(CF_3CClN)_2$ (mol)
1	I_o	0.35	0.048	120	0.095	1.94	0.175
2	I_o	0.35	0.048	60	0.020	1.34	0.105
3	$I_o/2$	0.35	0.048	60	0.005	0.66	0.050
4	I_o	0.70	0.048	60	0.005	2.82	0.230
5	I_o	1.05	0.048	60	0.005	3.26	0.310
6	I_o	0.35	0.087	60	0.015	1.47	0.310
7	I_o	0.35	0.087	60	0.015	1.51	0.380

30 minutes. After separation of unreacted material by means of distillation at -50°, the gas chromatographic analysis showed three products: the first peak was identified by IR spectroscopy as Cl_4C [16]; the second peak corresponds to a substance with a molecular weight of 135 ± 5, calc. 132.5; boiling point of 90°C (by extrapolation) and its IR shows absorption in the vapour phase at 750 (m), 980 (s) and 1850 (m). This is in agreement with previous reports [17]for $CCl_2=NCl$. The third substance has very low vapour pressure at room temperature. Its vapour shows absorptions in the IR at 975 (m) and at 1592 (m), which are compatible with those obtained in the liquid phase for $Cl_2C=N-N=CCl_2$ [18]. A non-volatile fraction at -10°C was not analyzed.

Reaction of HCN with chlorine

A mixture of 0.18 mmol HCN and 0.73 mmol Cl_2 contained in a 170 cc quartz cylinder was photolyzed at 32°C for 10 hours. Afterwards, the mixture was transferred to a cell and analyzed by

IR-spectroscopy. Besides HCN, only absorptions corresponding to ClCN and CCl_4 were observed. Some CCl_2=NCl was observed for photolysis times less than an hour and for lower Cl_2/HCN ratios. However, when the mixture was analyzed by gas chromatography, more ClCN than expected appeared.

In an attempt to obtain some quantitative results, a mixture of 0.06 mmol HCN and 0.06 mmol Cl_2 was first analyzed by IR spectroscopy. No ClCN was detected, precluding a thermal reaction between HCN and chlorine at 32°C. The mixture was immediately injected in the gas chromatograph and analyzed with the dinonylphthalate column operated at 30°C. Approximately 40% HCN was converted to ClCN. In an experiment where Cl_2 was reduced to 0.01 mmol, only 4% HCN was converted. Similar results were obtained with a column of 15% halocarbon oil on Chromosorb. When the unreacted mixture was carefully distilled at -130°C and later gc-analyzed, only Cl_2 was found in the volatile fraction and only HCN in the non-volatile fraction. No ClCN could be detected in either fraction.

When a mixture of 0.06 mmol HCN and 0.06 mmol Cl_2 was photolyzed for 5 minutes, carefully distilled at -130°C and analyzed by gc, the only product observed was ClCN (2% of HCN).

DISCUSSION

As suggested by the compounds already characterized, chlorine atom reactions with CF_3CN (or ClCN) give not only addition but cleavage products. The first step could be certainly the addition of Cl-atom to the triple bond leading to CF_3CCl=N radical. Its reaction with Cl_2 could yield CF_3CCl=NCl. From results shown in Table 2, either CF_3CCl=NCl or CF_3CCl=N-N=$CClCF_3$ rates seem to decrease with time, but CF_3CCl_3 rates tend to increase. It is likely that CF_3CCl=NCl could readily undergo chlorine addition leading to an unstable radical CF_3CCl_2-NCl which breaks down giving CF_3CCl_2 radical. When the CF_3CN concentration was high enough, CF_3CCl_2 radicals reacted further, producing the imines $CF_3CCl_2(CF_3)C=N-N=C(CF_3)CCl_2CF_3$ or $CF_3CCl_2(CF_3)C=N-CCl_2CF_3$ as was found by mass spectrometry in the residue. For higher chlorine concentrations, however, CF_3CCl_2 radicals were mainly trapped by Cl_2 giving CF_3CCl_3. When the light intensity was reduced by one half, almost no CF_3CCl_3 was formed, giving further evidence for considering it as a by product. If the CF_3CN concentration was doubled, the amount of $CF_3CCl=N-N=CClCF_3$ was certainly increased, but that of $CF_3CCl=NCl$ remained about the same. This can be rationalized if $CF_3CCl=N-N=CClCF_3$ was formed by recombination of $CF_3CCl=N^\cdot$ radicals.

Although some qualitative deductions can be drawn from Table 2, the reaction mechanism is likely to be very complex. A reaction sequence taking into account the observed products could be:

$$Cl_2 + h\nu \longrightarrow 2\ Cl^\cdot \qquad (1)$$

$$Cl^\cdot + CF_3CN \longrightarrow \underset{(R_1)}{CF_3CCl=N^\cdot} \qquad (2)$$

$$R_1 + Cl_2 \longrightarrow CF_3CCl=NCl + Cl^\cdot \qquad (3)$$

$$2\ R_1 \longrightarrow CF_3CCl=N-N=CClCF_3 \qquad (4)$$

$$CF_3CCl=NCl + Cl^\cdot \longrightarrow CF_3CCl_2-\dot{N}Cl \longrightarrow \underset{(R_2)}{CF_3\dot{C}Cl_2} + NCl \qquad (5)$$

$$R_2 + Cl_2 \longrightarrow CF_3CCl_3 + Cl^\cdot \qquad (6)$$

$$R_2 + R_1 \longrightarrow CF_3CCl=N-CCl_2CF_3 \qquad (7)$$

$$R_2 + CF_3CN \longrightarrow \underset{(R_3)}{CF_3CCl_2(CF_3)C=N^\cdot} \qquad (8)$$

$$R_3 + R_1 \longrightarrow CF_3CCl_2(CF_3)C=N-N=CClCF_3 \qquad (9)$$

$$R_3 + R_2 \longrightarrow CF_3CCl_2(CF_3)C{=}N{-}CCl_2CF_3 \qquad (10)$$

$$R_3 + R_3 \longrightarrow CF_3CCl_2(CF_3)C{=}N{-}N{=}C(CF_3)CCl_2CF_3 \qquad (11)$$

$$CF_3CCl{=}N{-}N{=}CClCF_3{+}Cl_2 \longrightarrow CF_3CCl_2{-}N{=}N{-}CCl_2CF_3 \qquad (12)$$

A reaction scheme similar to 1-6 might be followed when ClCN is allowed to react with chlorine. Actually, besides CCl_4, $CCl_2{=}NCl$ and $CCl_2{=}N{-}N{=}CCl_2$ were found to be the main products. Compounds like those formed in reactions 7, 9, 10, 11 and 12 could remain in the non-volatile fraction not analyzed.

In the case of the reaction Cl_2 + HCN, the difference between distilled and non-distilled mixtures led us to suspect the occurrence of an heterogeneous reaction between HCN and Cl_2 assisted by the chromatographic support. Actually, other authors have reported the effectiveness of catalysts such as charcoal or Zeolite 13X in HCN chlorinations[10-12]. Therefore, it was of fundamental importance to eliminate all Cl_2 from the mixture previous to the gc-analysis. Although a scrubber column of Carbosorb has been recommended[19], it proved to be unsuccessful because of the scrubber action on ClCN as well as on Cl_2. Because there is no certainty of eliminating all Cl_2 with the distillation at -130°C the quantity of ClCN could be estimated with a 10% error.

The most important feature for this reaction is the absence of the cleavage product (CCl_3H) as well as of the imine(CClH=NCl) demonstrating that the preferable route is replacement of H from HCN by Cl instead of chlorine addition. The way the H atom is replaced is not clear, but a direct abstraction leading to HCl and CN could be ruled out at room temperature due to the high endothermicity (*ca.* 20 kcal). Perhaps the reaction of Cl with HCN occurs via an addition; however, the radical CClH=N does not lead to the expected imine CClH=NCl, but to ClCN which could continue reacting, leading to $CCl_2{=}NCl$ and this in turn to CCl_4

and N_2 as by products, as it was found by IR spectroscopy in mixtures at higher conversions.

Unlike HCN, ClCN readily undergoes addition giving various unsaturated products. The polarization of CN bond by chlorine might account for the difference in reactivity.

EXPERIMENTAL

Commercially available Cl_2 was bubbled in traps with acidic $KMnO_4$ and concentrated H_2SO_4 and collected at -85°C. The CF_3CN was purchased, ClCN was synthesized following Klemenc's method [20]. To obtain HCN, concentrated H_2SO_4 was allowed to react with KCN. All these samples were purified by trap-to-trap distillation in vacuum. Purity was checked by IR, UV spectroscopy and/or gas chromatography.

General method

The gases were handled in a greaseless Pyrex vacuum system equipped with a quartz spiral used as null instrument with a mercury manometer. The syntheses were carried out in a Pyrex balloon maintained at room temperature by cooling air and illuminated by the full Hg arc lamp (Phillips 400 W).

After illumination, the gas mixture was transferred to a U-trap cooled with liquid nitrogen, distilled and then analyzed by gas chromatography, IR spectroscopy and/or mass spectrometry.

Apparatus

IR spectra were recorded in a Beckman IR 12. Chromatrographic analyses were performed on a dinonylphthalate column (30%, 3 m long) with a Varian Aerograph chromatograph, fitted with a thermal conductivity detector. U.V. spectra were recorded in a Cary 14 spectrometer, mass spectra were performed with a 3300 Finnigan mass spectrometer attached to an INCOS data system at

90 eV, and the molecular weights of gases were determined by vapour density measurements.

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