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NITRATION OF 1,1-DICHLORODIFLUOROETHYLENE WITH NITROGEN DIOXIDE. THE INFRARED SPECTRA OF DIFLUORONITROACETYL CHLORIDE AND 1,1-DICHLORODIFLUORO-1,2-DINITROETHANE

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SUMMARY

Gas-phase nitration of CF_2CCl_2 with NO_2 at 323-353 K gave difluoronitroacetyl chloride, $O_2NCF_2C(O)Cl$, and 1,1-dichlorodifluoro-1,2-dinitroethane, $O_2NCF_2CCl_2NO_2$, which were isolated by fractional condensation and characterized by molecular weight determinations and infrared spectra. $[O_2NCF_2C(O)Cl]/[O_2NCF_2CCl_2NO_2] = [k'([CF_2CCl_2] + \gamma_{NO_2}[NO_2] + \gamma_P[P] + \gamma_X[X])]^{-1}$, where $k' = 3.3\pm0.7\times10^{-2}$ torr^{-1}, P is the sum of the products, X = C_2F_5Cl, CCl_3F, CF_4 or N_2 and γ are the relative collisional efficiency coefficients of each gas.

RESULTS AND DISCUSSION

Three compounds I, II and III were formed as products in the gas-phase reaction between NO_2 and 1,1-dichlorodifluoroethylene (CF_2CCl_2), whose kinetics has been investigated between 323 and 353 K [1]. The pressure of NO_2 was varied between 5 and 273 torr and that of CF_2CCl_2 between 5 and 150 torr. The reaction mixtures for analysis were condensed in the reaction vessel at liquid air temperature, following by fractional condensation in a vacuum system at 183 and 213 K respectively.

The compound I, that distilled together with CF_2CCl_2 at 183 K, was identified by its infrared spectrum as ClNO [2].

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The compound II, that distilled together with NO_2, was separated as volatile at 213 K in the experiments carried out until all NO_2 was consumed. The compound III remained as residue at 213 K.

The infrared spectra of the gaseous compounds II and III have been recorded on a Perkin-Elmer 221 spectrometer, using 10 cm gas cell with sodium chloride windows and are illustrated in Fig. 1. Their comparison is presented in Table 1. The infrared spectra suggested that II and III are difluoronitroacetyl chloride ($O_2NCF_2C(O)Cl$) and 1,1-dichlorodifluoro-1,2-dinitroethane ($O_2NCF_2CCl_2NO_2$) respectively [3]. To the best of my knowledge their infrared spectra have not been previously reported.

TABLE 1

The comparison of the infrared absorption spectra of gaseous $O_2NCF_2C(O)Cl$ and $O_2NCF_2CCl_2NO_2$

$O_2NCF_2C(O)Cl$ Frequency cm^{-1} [a]	$O_2NCF_2CCl_2NO_2$ Frequency cm^{-1} [a]	Tentative Assignment
1808 (vs)		CO str.
1619 (vvs)	1619 (vvs)	NO_2 antisym.str.
1349 (s)	1341 (m)	NO_2 sym. str.
1300 (m)	1306 (s)	C-N
1254 (vvs)	1257 (s)	
	1225 (s)	
1170 (w)	1166 (w)	C-F
1146 (w)		
1055 (m)	1060 (w)	
908 (vs)	952 (s)	C-C
	844 (w)	
811 (vs)	811 (s)	
	766 (m)	C-Cl
685 (w)	672 (w)	

[a] s-strong, m-medium, w-weak, v-very

Molecular weights for both compounds were determined by vapor-density measurements with a calibrated Pyrex bulb. The obtained values were 160 ± 3 for II and 227 ± 5 for III. The theoretical molecular weights of $O_2NCF_2C(O)Cl$ and of $O_2NCF_2CCl_2NO_2$ are 159.5 and 225 respectively.

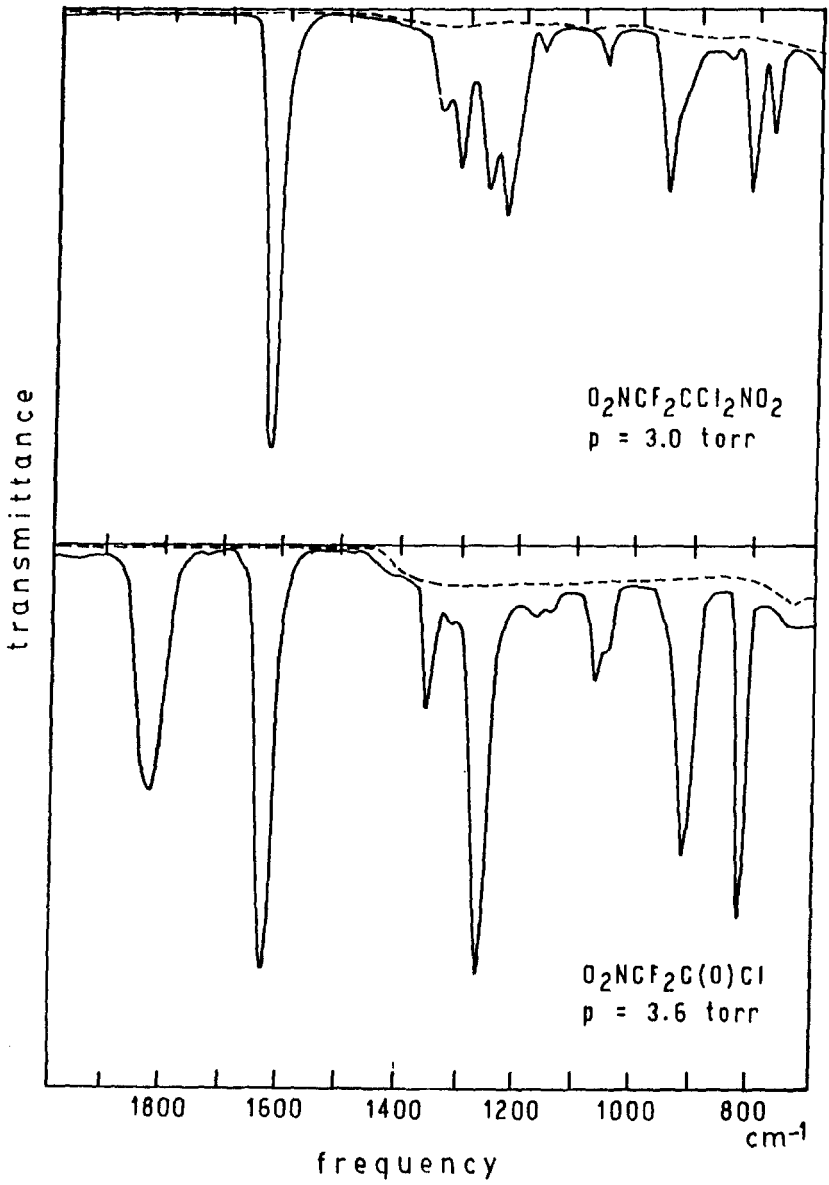

Fig. 1. The infrared spectra of $O_2NCF_2C(O)Cl$ and $O_2NF_2CCl_2NO_2$.

Additional identification of II was made comparing its infrared spectrum with that of $O_2NCF_2C(O)Cl$ prepared according to the method described by Fokin et al. [4], condensing the substance distilling between 163 and 193 K after difluoronitroacetic acid had reacted with phosphorus pentachloride.

The formation of $O_2NCF_2CCl_2NO_2$ in the reaction of NO_2 with CF_2CCl_2 reported previously by Haszeldine [5], supports the identification of III as $O_2NCF_2CCl_2NO_2$.

The ratio of the products, $[O_2NCF_2C(O)Cl]/[O_2NCF_2CCl_2NO_2]$, was influenced by the pressure of the gases present in the reaction system and could be well represented by the following expression:

$$\frac{[O_2NCF_2C(O)Cl]}{[O_2NCF_2CCl_2NO_2]} = [k'([CF_2CCl_2] + \gamma_{NO_2}[NO_2] + \gamma_P[P] + \gamma_X[X])]^{-1}$$

where k' is equal to $3.3\pm0.7\times10^{-2}$ $torr^{-1}$, P is the sum of the products and X is the inert gas added to the reaction system (N_2, CF_4, CCl_3F or C_2F_5Cl). γ are the corresponding efficiency coefficients, assuming that those of the products are similar.

The values obtained for the relative efficiency coefficients were:

$$\gamma_{CF_2CCl_2} : \gamma_P : \gamma_{C_2F_5Cl} : \gamma_{CCl_3F} : \gamma_{CF_4} : \gamma_{N_2} : \gamma_{NO_2} =$$

1 : 0.22 : 0.15 : 0.14 : 0.054 : 0.015 : <0.01.

The values of k' and γ are practically independent of the temperature in the temperature range of the experiments, 323 - 353 K. γ depends on the relative collisional frequency and k' on the relation between the collisional frequency and the excited molecule decomposition rate constant, both being almost constant over this small temperature range. $O_2NCF_2C(O)Cl$ and ClNO were formed in equimolecular amounts.

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