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Trifluoromethyl Fluoroformate

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LOW-TEMPERATURE fractionation of the products of the photochemical reaction between trifluoromethoxyl fluoride[1] and a slight excess of carbon monoxide gave high yields (86%) of a new substance with the analytical and molecular-weight properties expected for trifluoromethyl fluoroformate. The irradiations were performed at 35° in a quartz vessel with u.v. light from a Q 700 lamp (Quarzlampen Gesellschaft m.b.H., Hanau, Germany), filtered through the Pyrex wall of a water bath. The pressure decrease during the reaction was slightly less than the initial pressure of trifluoromethoxyl fluoride.

Minor products were carbonyl fluoride, carbon dioxide, silicon tetrafluoride, and a substance (M, 310), not yet identified, but apparently containing six fluorine atoms per molecule and showing in the infrared spectrum (gas) carbonyl stretching (maxima at 1842 and 1828 cm.$^{-1}$) and other bands assignable to C–F and C–O stretching vibrations and deformations.

Trifluoromethyl fluoroformate melts near $-120°$; its vapour pressure obeys the equation: $\log p$ (mm.) $= 8{\cdot}701 - 1380/T$ (°K) between -50 and -100 °c. The extrapolated boiling point is $-36°$ and latent heat of vaporization 6·3 kcal./mole.

The infrared spectrum of the gaseous substance at low pressure (NaCl optics) shows strong absorption maxima in the carbonyl (1906 and 1901 cm.$^{-1}$), C–F (1296, 1260, and 1174 cm.$^{-1}$) and C–O (1026 and 1021 cm.$^{-1}$) stretching regions, in addition to other weaker peaks at lower frequencies (768, 677, 672, and 655 cm.$^{-1}$), assignable to deformations. The spectrum appears as a combination of those of trifluoromethoxyl fluoride,[2] bistrifluoromethyl peroxide,[3] and bisfluoroformyl peroxide.[3]

Trifluoromethyl fluoroformate decomposes on strong heating in a quartz vessel producing carbonyl fluoride, silicon tetrafluoride, carbon dioxide, and carbon tetrafluoride.

Experiments with trifluoromethoxyl fluoride alone or mixed with carbonyl fluoride [main reaction product: bistrifluoromethyl peroxide] under the same experimental conditions show that the photodissociation of trifluoromethoxyl fluoride is a slow reaction. Therefore, the formation of trifluoromethyl fluoroformate, which is faster than the former reaction, should be a chain reaction involving $F_3C{\cdot}O{\cdot}CO{\bullet}$ radicals.

Interaction between trifluoromethoxyl fluoride and carbon monoxide did not take place in the dark at 35° but at 90°, for instance, an equimolecular mixture (total pressure 400 mm.) reacts with maximal rate of pressure decrease of 1·3 mm./min.

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[3] A. J. Arvía and P. J. Aymonino, *Spectrochim. Acta*, 1962, **18**, 1299.