

PHOTOABSORPTION SPECTRA OF SOME HALOGEN-SUBSTITUTED METHYL NITROGEN OXIDES

T. D. Allston, M. L. Fedyk and G. A. Takacs

Department of Chemistry, Rochester Institute of Technology, Rochester,

N.Y. 14623 (U.S.A.)

INTRODUCTION

Trace amounts of halogen-substituted methyl nitrogen oxides may be produced in the atmosphere by termolecular reactions of NO and NO₂ with CXYZ, CXYZO, and CXYZO₂ (where X, Y, and Z may represent such atoms as Cl, F, or H). Sources of CXYZ, CXYZO, and CXYZO₂ include photodecomposition of halogenated methane molecules and reaction of CXYZ with O₃ and O₂, respectively. We report here the photoabsorption spectra and atmospheric photodissociation rate coefficients for gaseous CF₃NO, CCl₃NO, and CCl₃NO₂ at 295°K.

EXPERIMENTAL

Absorption measurements were made with a Perkin Elmer 450 uv-vis spectrophotometer and a Perkin Elmer 621 ir spectrophotometer. Twenty-four, thirty-one, and nineteen spectra were run over the 190-400nm region for CF₃NO, CCl₃NO, and CCl₃NO₂ for which the product of optical path length and pressure varied over a factor of 102, 205, and 183 respectively. Two samples each of CF₃NO (116 and 210 torr, 2-cm path length) and CCl₃NO (84 and 120 torr, 10 cm-path length) were scanned from 400 to 750 nm. IR absorption was measured using a 10-cm path length cell having NaCl windows.

The ir spectrum of CF₃NO (50 torr, Penninsular Chem Research, Inc.), which had been degassed at -196°C, agreed with that reported in the literature (1) and therefore the gas was used without further purification. Sample preparation was carried out both in the presence and near total absence of room light because CF₃NO is a deep blue gas which on exposure to visible light changes in color through green to yellow as a result of dimer formation (2). These samples gave the same photoabsorption cross-sections and showed no evidence for absorption by the dimer (2b).

Trichloronitrosomethane was prepared from the reaction of CCl₃SO₂Na with ClNO and purified by the method described by Sutcliffe (3). Infrared analysis showed traces of ClNO (4) in the CCl₃NO(5) and quantitative determination of the purified samples placed the ClNO impurity levels between 0.17 to 0.93% by volume. Corrections were made for the uv-vis absorption by ClNO (6).

Chloropicrin (CCl₃NO₂, Eastman Organic) was degassed at -196°C and the middle fraction of a bulb to bulb distillation from -63.5°C to -196°C was collected and used. This distillation was necessary in order to remove a faint yellow color in the liquid that was probably caused by Cl₂. The ir spectrum was in agreement with that reported in the literature (7).

RESULTS AND DISCUSSION

Photoabsorption cross-sections were calculated at each wavelength using the relationship $\sigma = 1/(CL) \ln(I_0/I)$ where C, L, I₀, and I are the concentration in molecules/cm³, optical path length in cm, incident and transmitted intensities, respectively.

CF₃NO absorbs in the visible region from 500 to 750 nm (8) and shows considerable fine structure due to excited vibrational modes in the n-π* transition of a nitrogen non-bonding electron (8b). Our visible cross-sections were in good agreement with the previously reported values (8). Photoabsorption cross-sections were obtained from 190 to 340 nm where CF₃NO shows two absorption bands with a maximum occurring at 268-2nm. The only previous reports of uv cross-sections have been at the wavelengths of maximum and minimum absorption between the two bands. Jander and Haszeldine (8a), Mason (8b), and this work cite the following values for the cross-section at the maximum: 7.64x10⁻²⁰, 6.88x10⁻²¹, and (7.38±0.14)x10⁻²¹cm², respectively.

CCl₃NO absorbs weakly from 380 to 660 nm with a maximum absorption occurring at about 560nm ((8.2±0.5)x10⁻²¹cm²). For wavelengths less than 380nm, absorption increases monotonically up to (5.5±0.4)x10⁻¹⁸cm² at 190nm.

CCl₃NO₂ is transparent to visible radiation but absorbs continuously from 190 to 375 nm. Absorption maxima appear at 272-2nm and 202-1nm with cross-sections of (1.64±0.03)x10⁻¹⁹cm² and (9.66±0.50)x10⁻¹⁸cm², respectively. Our results are approximately a factor of two higher than the previously reported cross-sections between 225 and 320nm (9).

Photodissociation of CF₃NO (2b), CCl₃NO (10), and CCl₃NO₂ (11) most probably occur by C-N bond breakage. Assuming a unit quantum yield for photodecomposition of these molecules, the atmospheric photodissociation coefficients, J (Table I), were calculated as a function of altitude from the product of the photoabsorption cross-section and the solar flux intensities. The photodissociation lifetimes of CF₃NO and CCl₃NO are approximately independent of altitude and are roughly 2 and 12 min., respectively, while the lifetime of CCl₃NO₂ varies significantly with altitude because it has no visible absorption spectrum.

TABLE I

Variation of Photodissociation Coefficients, J, with Altitude^a

Altitude, nm	Photodissociation Coefficients, J, sec ⁻¹		
	CF ₃ NO	CCl ₃ NO	CCl ₃ NO ₂
0	5.6(-3) ^b	1.2(-3)	5.7(-5)
10	5.7(-3)	1.3(-3)	8.3(-5)
20	5.8(-3)	1.3(-3)	8.9(-5)
30	5.9(-3)	1.3(-3)	1.2(-4)
40	6.2(-3)	1.4(-3)	4.3(-4)
50	6.6(-3)	1.5(-3)	8.0(-4)

^aCalculated from solar flux intensities at a zenith angle of 45°

^b5.6(-3) means 5.6x10⁻³

REFERENCES

- (a) H. F. Shurvell, S. C. Dass and R. D. Gordon, Can. J. Chem. **52**, 3149 (1974).
(b) R. Demuth, H. Burger, G. Pawelke, and H. Willner, Spectrochim. Acta, **34A**, 113 (1978).
- (a) B. K. Hunter, private communication reported in H. F. Shurvell, S. C. Dass, and R. D. Gordon, Can. J. Chem. **52**, 3149 (1974).
(b) R. N. Haszeldine and B. J. H. Mattinson, J. Chem. Soc. 1741 (1957); J. Jander and R. N. Haszeldine, ibid. 696 (1954); R. N. Haszeldine and J. Jander, ibid. 691 (1954).

3. (a) H. Sutcliffe, J. Org. Chem. **30**, 322 (1965).
(b) V. Astley and H. Sutcliffe, J.C.S. Perkin II 197 (1972).
4. (a) L. H. Jones, R. R. Ryan, and L. B. Asprey, J. Chem. Phys. **49**, 581 (1968).
(b) W. G. Burns and H. J. Bernstein, J. Chem. Phys. **18**, 1669 (1950).
5. A. R. Briden, D. Price, and H. Sutcliffe, J. Chem. Soc. (B) 387 (1968)
6. (a) A. J. Illies and G. A. Takacs, J. Photochem. **6**, 35 (1976).
(b) C. F. Goodeve and S. Katz, Proc. Roy. Soc. (London) **A172**, 432 (1932).
7. (a) J. G. Grasselli, "Atlas of Spectral Data and Physical Constants for Organic Compounds", p. B-653 (1973).
(b) R. N. Haszeldine, J. Chem. Soc. 2525 (1953).
8. (a) J. Jander and R. N. Haszeldine, J. Chem. Soc. 912 (1954).
(b) J. Mason, J. Chem. Soc. 3904 (1957).
9. J. Jander and R. N. Haszeldine, J. Chem. Soc. 919 (1954).
10. B. G. Gowenlock, J. Pfab, and G. Kresze, J.C.S. Perkin II 511 (1974)
11. J. G. Calvert and J. N. Pitts, Jr., "Photochemistry", John Wiley and Sons, N.Y. (1966).