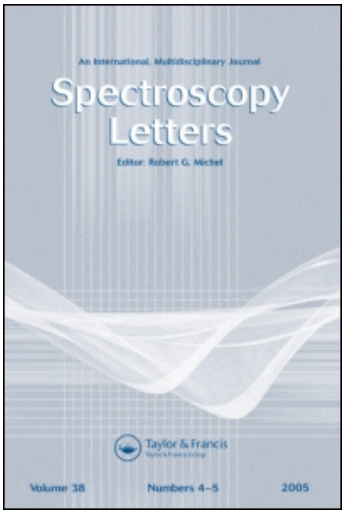

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THE ELECTRONIC ABSORPTION SPECTRUM OF METHANESULPHENYL CHLORIDE IN THE ULTRAVIOLET REGION *

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Methanesulfenyl chloride (CH_3SCl) has been used frequently as a reactant, especially in the study of its addition across carbon-carbon double bonds.[1-4] In the course of preliminary chemical kinetic investigations of the gas phase chlorination of small sulfur containing molecules, quantitative ultraviolet spectra data for CH_3SCl were needed to calculate the rate of formation of reaction products. We report here the extinction coefficients for CH_3SCl in the wavelength region 2000 Å to 4000 Å. To our knowledge these have not been reported previously.

Methanesulfenyl chloride was prepared in the gas phase at 25°C by two different methods (1) mixing equimolar amounts of CH_3SH and Cl_2 and (2) mixing equimolar amounts of CH_3SSCH_3 and Cl_2. Both methods gave identical extinction coefficients for CH_3SCl to within the overall precision of these experiments. A sample prepared by method (2) and then dissolved in CCl_4 showed a proton resonance spectrum consisting of a singlet at $\tau = 7.12$ using tetramethylsilane as a reference. This result compares well with $\tau = 7.09$ reported by Mueller and Butler[4] for a neat sample of CH_3SCl. We therefore concluded that both methods outlined above furnish the product CH_3SCl.

Reactants were prepared as follows: (1) Chlorine, J. T. Baker, was thoroughly degassed at -130°C (n-pentane slush) and then distilled from a trap at -78°C to another at -196°C, the middle fraction being retained. (2) Methanethiol, J. T. Baker, was degassed at -130°C prior to use. (3) Methyl Disulfide, Matheson, Coleman, and Bell, was degassed at -78°C and then distilled from a trap at 0°C to another at -196°C, the middle fraction being retained.

Ultraviolet absorption spectra of the purified reagents showed no detectable impurities and gave extinction coefficients within 3% of those reported elsewhere.[5]

Reactant pressures were measured in a constant volume using a Texas Instruments quartz spiral gauge after which they were transferred to a two-chamber reaction vessel. One chamber (40 cm^3) was a 10 cm long fused silica absorption cell, the other was a Pyrex sidearm (3 cm^3) separated from the absorption cell by a Teflon plug stopcock. A similar stopcock separated the sidearm from the vacuum line. The reactants were mixed at 25°C with the absorption cell in the sample compartment of a Cary 14 spectrophotometer. On mixing the spectra showed a strong time dependence due to reaction and diffusion for about 2 minutes after which the optical densities changed by less than 2% in an eight hour period.

When preparative method (1) was used the spectrum was taken after mixing; then the products were separated by distillation at low temperatures. The only products detectable were HCl and CH_3SCl. HCl was determined using vapor pressure measurements and infrared analysis. The total amount of HCl produced was equal to within 4% the amount of CH_3SCl produced. As expected, the absorption spectrum between 2000 Å and 4000 Å was the same before and after the HCl was removed since HCl absorbs only weakly above 2000 Å. When preparative method (2) was used the only detectable product was CH_3SCl.

TABLE I

Extinction Coefficients of CH_3SCl

λ (Å)	ε (M^{-1} cm^{-1})	λ (Å)	ε (M^{-1} cm^{-1})
4000	7.36 ± 0.63		
3950	9.36 ± 0.75	2950	3.43
3900	11.13 ± 0.48	2900	3.52
3850	14.07 ± 0.99	2850	4.33
3800	16.32 ± 0.76	2800	4.87
3750	19.10 ± 0.33	2750	5.77
3700	21.18 ± 0.24	2700	6.67
3650	23.12 ± 0.46	2650	8.12
3600	24.03 ± 0.37	2600	10.47 ± 0.92
3550	24.51 ± 0.46	2550	15.57 ± 0.05
3500	23.59 ± 0.13	2500	25.8 ± 1.9
3450	22.27 ± 0.26	2450	46.2 ± 5.0
3400	20.18 ± 0.37	2400	77.0 ± 3.2
3350	17.52 ± 0.40	2350	128.0 ± 6.2
3300	15.17 ± 0.65	2300	189 ± 10
3250	12.12 ± 0.63	2250	263 ± 15
3200	9.22 ± 0.36	2200	334 ± 19
3150	7.61 ± 0.82	2150	376 ± 20
3100	5.59	2100	446 ± 22
3050	4.33	2050	628 ± 25
3000	3.61	2000	510 ± 24

Spectra were recorded for concentrations in the range 1.2×10^{-4} M to 1.1×10^{-3} M. The resulting data shown in Table I are averages of three or four separate measurements at each wavelength except in the region 2650 Å to 3100 Å where the absorption is very small and was not accurately determined. The values reported for this region were taken from the 1.1×10^{-3} M experiment. The uncertainties given in Table I are average deviations.

The resulting spectrum shows distinct maxima at two wavelengths, 3550 Å ($\epsilon = 24.5\ M^{-1}\ cm^{-1}$) and 2055 Å ($\epsilon = 671\ M^{-1}\ cm^{-1}$) and a minimum at 2950 Å . These results may be compared with those obtained by Hazeldine and Kidd[6] for CF_3SCl which showed maxima at 3330 Å ($\epsilon = 25\ M^{-1}\ cm^{-1}$) and 2140 Å ($\epsilon = 235\ M^{-1}\ cm^{-1}$) in the gas phase. These same authors obtained spectra for CCl_3SCl in light petroleum and $CHCl_3$ solvents. Maxima occurred at 3220 Å ($\epsilon = 10.0\ M^{-1}\ cm^{-1}$) and 3240 Å ($\epsilon = 12.0\ M^{-1}\ cm^{-1}$) respectively. No data were reported for the 2100 Å region. Comparison of the spectra for CH_3SCl and CF_3SCl suggests that the nature of the electronic transitions is similar. Between 2000 Å and 2100 Å the spectrum of CH_3SCl shows some structure which is only partially resolved so that a meaningful vibrational spacing cannot be determined.

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