

Syntheses of some Thiolacetic Acid Derivatives

I. Trichlorothiolacetic Acid

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The trichlorothiolacetic acid has been synthesised by addition of hydrogen sulfide to trichloroacetic acid anhydride. The infra-red spectrum of the trichlorothiolacetic acid has been recorded and compared with the corresponding spectra of trichloroacetic acid and trichloroacetyl chloride.

Thiolacetic acid reacts easily with many olefins giving thiolacetates, from which by hydrolysis thiols in good yield can be obtained¹⁻³. Cunneen⁴ has shown that the chloro-substituted thiolacetic acids have still more additive activity depending on their higher acidity. From rubber and chlorinated thiolacetic acids Cunneen easily obtained adducts, but the reaction was difficult to bring about with thiolacetic acid.

Cunneen prepared the chlorinated thiolacetic acids by reacting the corresponding acetyl chlorides with hydrogen sulfide in the presence of aluminium chloride.

Trichlorothiolacetic acid, the most reactive of these acids, was conveniently prepared in this laboratory through addition of hydrogen sulfide to trichloroacetic acid anhydride:



In a similar way we had earlier prepared thiolacetic acid from hydrogen sulfide and acetic anhydride⁵.

The necessary trichloroacetic acid anhydride was obtained by dehydration of trichloroacetic acid with phosphoric anhydride and was purified by distillation in vacuum.

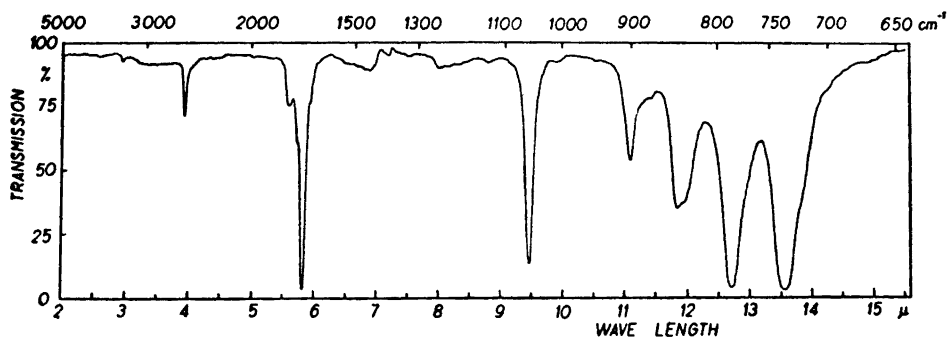
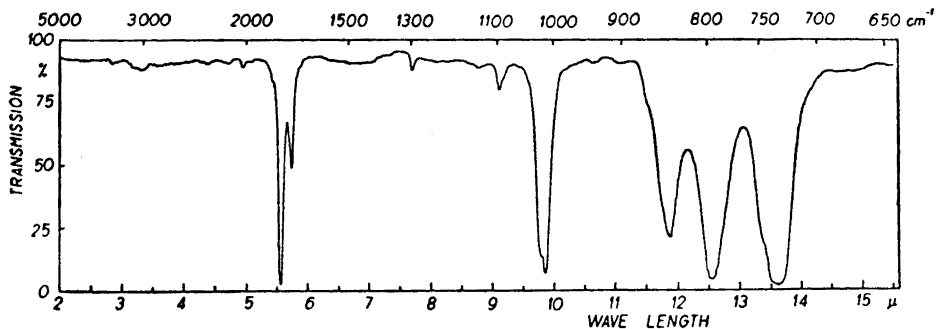
The addition of hydrogen sulfide to the trichloroacetic acid anhydride was carried out at room temperature. As a catalyst a small amount of pyridine was added. From the reaction mixture trichlorothiolacetic acid was isolated and purified. Physical data for trichloroacetic anhydride and trichlorothiolacetic acid do not seem to be reported in literature. Some data obtained are therefore given in Table 1.

Table 1. Physical data.

Compound	Boiling point °C/mm Hg	d_4^{20}	n_D^{20}	MR_D	AR_D of S
Trichloroacetic anhydride	105/12	1.6900	1.4857	52.43	—
Trichlorothioloacetic acid	40/4	1.6136	1.5300	34.36	8.31

In Table 1 the molar refraction MR_D is calculated from the physical data, using the Lorentz-Lorenz formula. According to the values given by Eisenlohr⁶ for the atomic refractions the molar refraction of the trichloroacetic acid anhydride ought to be only 51.54. The higher value we have found indicates a considerable exaltation.

Using the values of Eisenlohr for the atomic refractions of carbon, hydrogen, chlorine and oxygen we have calculated the atomic refraction for the sulfur atom in the trichlorothioloacetic acid from the found molecular refraction.

Fig. 1. The infra-red spectrum of trichlorothioloacetic acid in CS_2 -solution.Fig. 2. The infra-red spectrum of trichloroacetyl chloride in CS_2 -solution.

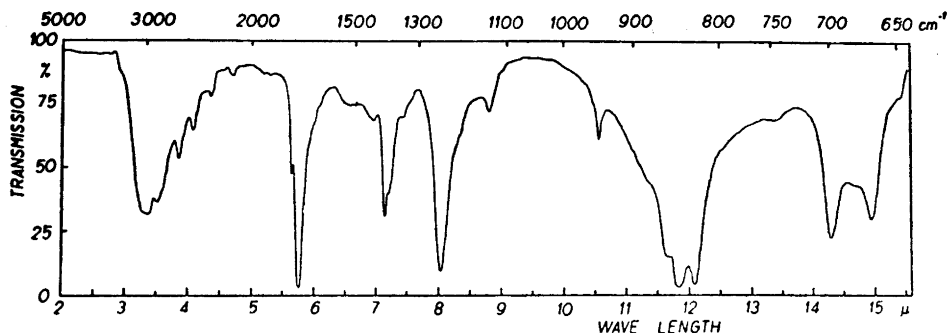


Fig. 3. The infra-red spectrum of trichloroacetic acid in CS_2 -solution.

tion. The calculated value 8.31 is in good agreement with the values we have found for other thiolacetic acids.

The infra-red spectrum of the trichlorothiolacetic acid has been recorded in a solution of carbon disulfide (Fig. 1). As a comparison the infra-red spectrum of the trichloroacetyl chloride (Fig. 2) and trichloroacetic acid (Fig. 3) are also given.

It is apparent from the spectra that the trichlorothiolacetic acid is free from trichloroacetic acid. The similarity of the spectra of trichlorothiolacetic acid and trichloroacetyl chloride is striking. The same relation between thiolacetic acid and acetyl chloride has been pointed out by Sheppard⁷. The absence of carbon-hydrogen bonds makes the spectrum of the trichlorothiolacetic acid comparatively simple, and the absorption bands in the region of the group-frequencies are very few. At 2554 cm^{-1} we find the weak S—H stretching band. At 1726 cm^{-1} the C=O stretching gives a strong absorption. The band at 1058 cm^{-1} seems to correspond to the trichloroacetyl chloride band at 1017 cm^{-1} , which has been assigned by Seewann-Albert⁸ to C—C stretching. The weak band of the trichlorothiolacetic acid at 903 cm^{-1} has no counterpart in the trichloroacetyl chloride spectrum and therefore seems to belong to the S—H deformation. The three absorption bands at the end of the spectrum

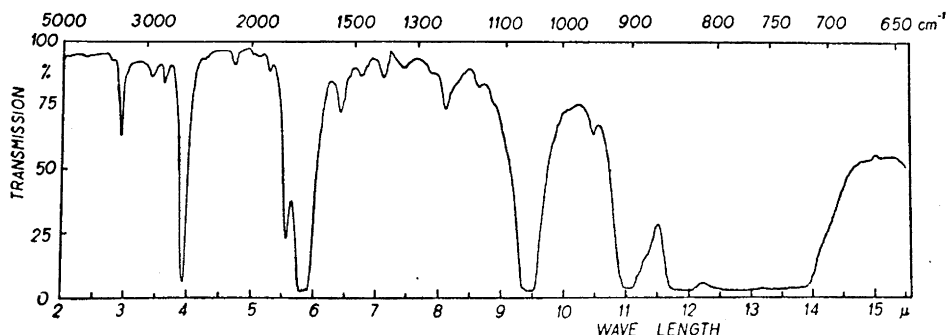


Fig. 4. The infra-red spectrum of liquid trichlorothiolacetic acid.

belong to chlorine stretching and skeletal vibrations and cannot safely be assigned without corresponding Raman-spectra.

From the spectrum of the trichlorothiolacetic acid and the similarity of this spectrum with that of the trichloroacetyl chloride, it can be concluded that trichlorothiolacetic acid predominantly must exist in form of CCl_3COSH . Earlier Sheppard⁷ and later Mecke and Spiesscke⁹ have stated the same relation for the thiolacetic acid. In the thiolacetic acid, however, a small percentage of the isomeric thionform CH_3CSOH was found. This isomer could be identified by a weak band at $1\,225\text{ cm}^{-1}$ belonging to the $\text{C}=\text{S}$ stretching. The two isomeric forms are in equilibrium and the amount of the thionform increases at higher temperature.

In order to further investigate the spectrum of the trichlorothiolacetic acid we made a recording of the liquid acid in a thin layer (Fig. 4).

The absorption at the higher wave lengths is too strong but in the shorter wave length region there are interesting absorption bands. The absorption band at $3\,431\text{ cm}^{-1}$ most probably can be assigned to the $\text{O}-\text{H}$ group. Since there is also a distinct band at $1\,232\text{ cm}^{-1}$, which can be attributed to the $\text{C}=\text{S}$ stretching, the existence of a small quantity of the thionform CCl_3CSOH must be assumed.

EXPERIMENTAL

Preparation of trichloroacetic acid anhydride: 300 g pure trichloroacetic acid was heated in an oil bath with 130 g phosphoric anhydride (the theoretical amount) at 210°C for 10 h. After cooling to room temperature the liquid layer was decanted from the viscous phosphoric acid and distilled in vacuum. At $93-97^\circ\text{C}$ and 8 mm Hg 207 g trichloroacetic acid anhydride was obtained (yield 73 %). This product was redistilled in vacuum in a fractionation column according to Todd¹⁰ with about 40 theoretical plates. The main fraction boiled at 105°C and 12 mm Hg. (Found: Cl 68.5. Calc. for $\text{C}_2\text{O}_3\text{Cl}_3$: Cl 68.9).

Preparation of trichlorothiolacetic acid: Hydrogen sulfide was dispersed through a fritted glass disc into 183 g trichloroacetic anhydride and 1 ml pyridine at room temperature. To get a sufficient absorption height a narrow glass tube was used for the mixture. The rate of absorption was followed by weighing the reaction tube and titrating the reaction product with iodine (*cf.* the preparation of thiolacetic acid⁵). The reaction velocity was comparatively low and came to a stop after 40 h. Vacuum distillation gave 60 g trichlorothiolacetic acid (yield 56 %). The acid was purified by vacuum distillation with a Widmer-column, b. p. 40°C at 4 mm Hg. (Found: Cl 59.4; S 17.73; equiv. wt. 180.5. Calc. for C_2HOSCl_3 : Cl 59.3; S 17.87; equiv. wt. 179.45).

The infra-red spectra

The infra-red spectra were recorded with a *Perkin-Elmer* double-beam spectrometer Model 21 a with rock-salt prism. Slit schedule 927, corresponding to program 4. Speed: 3 min/ μ . The frequencies of the absorption bands are given below.

Trichlorothiolacetic acid (Fig. 1). 100 g/l CS_2 -solution. Cell: 0.1 mm 2 554 (w), 1 787(w), 1 726(s), 1 058(s), 903(m), 846(s), 788(s), and 738(s).

Trichloroacetyl chloride (Fig. 2). 26.4 g/l CS_2 -solution. Cell: 0.459 mm 1 803(s), 1 750(w), 1 023(m), 1 017(s), 844(s), 797(s), and 736(s).

Trichloroacetic acid (Fig. 3). 99.9 g/l CS_2 -solution. Cell: 0.1 mm. At 3 008 broad band with small peaks at 2 878, 2 628, 2 478, and 2 323. 1 787(w), 1 747(s), 1 407(s), 1 252(s), 1 141(w), 951(w), 847(s), 830(s), 701(s), and 671(s).

Trichlorothiolacetic acid, liquid. Cell: 0.052 mm. 3 431(m), 2 937(w), 2 782(w), 2 554(s), 2 112(w), 1 803(m), 1 690-1 730(vs), 1 559(w), 1 483(w), 1 404(w), 1 340(w), 1 232(w), 1 050-1 070(vs), 956(w), 900-915(vs), and 720-860(vs).

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