

# N.M.R. AND I.R. STUDIES OF 1, 1, 1 TRIFLUOROACETONE IN PROTON DONOR SOLVENTS

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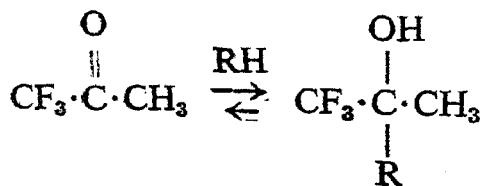
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## ABSTRACT

Interactions of 1, 1, 1 trifluoroacetone with proton donor solvents of the type RH [where R = HO, CH<sub>3</sub>S, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>S, CH<sub>3</sub>O, (CH<sub>3</sub>)<sub>2</sub>N, (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>N] have been investigated using NMR and infra-red techniques. Evidence of the formation of addition products of the type CF<sub>3</sub>.C(OH)R.CH<sub>3</sub> where OH group is hydrogen-bonded with the fluorine of the CF<sub>3</sub> group has been obtained.

## INTRODUCTION

A VERY significant reaction of polyfluoro compounds containing a keto group in the  $\alpha$  position is the instantaneous addition of a molecule of the type RH to the carbonyl group. Even a very weak nucleophile like water attacks 1, 1, 1 trifluoroacetone rapidly. This is because of the enhanced electropositivity of the carbonyl carbon atom due to the strong electron withdrawing power of the polyfluoro alkyl group. In trifluoroacetone, therefore, the equilibrium



lies far to the right [Albert *et al.* (1950); Donald *et al.* (1952); Harold *et al.* (1950), Haszeldine *et al.* (1951, 1952, 1953); Hudlicky *et al.* (1961); Murray *et al.* (1955); Nobukazu *et al.* (1941), Stacey *et al.* (1963)].

The present paper reports NMR and infra-red studies of the reactions of 1, 1, 1 trifluoroacetone with water, methylalcohol, *n*-butanethiol and dimethyl and diethyl amines with special reference to the structure of the product formed.

### EXPERIMENTAL

(1) *Chemicals.*—Trifluoroacetone was obtained from Aldrich Chem. Co. All other samples were commercially available and used after distillation.

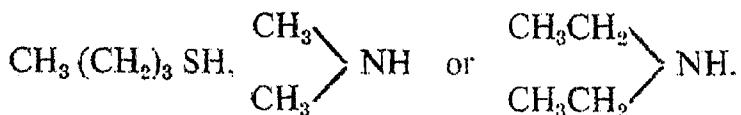
(2) *NMR Measurements.*—Trifluoroacetone was dissolved in different solvents in various proportions and the F<sup>19</sup> and H<sup>1</sup> spectra were recorded on a Varian high resolution NMR spectrometer operating at 56.445 Mc/s. The F<sup>19</sup> and the H<sup>1</sup> chemical shifts were measured relative to the corresponding lines in trifluoroacetic acid and cyclohexane respectively, used as external standards. Proton chemical shifts were finally converted to TMS standard.

(3) *Infra-red studies.*—Infra-red spectra were recorded on a Perkin-Elmer, Model-21 spectrometer with NaCl prism. 5% (V/V) solution of trifluoroacetone in CCl<sub>4</sub> was used with the required proton donor and the spectra were recorded in the region 4,000 cm.<sup>-1</sup>–1,000 cm.<sup>-1</sup> using a cell of 0.1 mm. thickness. Compensation for the solvent CCl<sub>4</sub> was obtained by a variable thickness cell in the reference beam.

### RESULTS AND DISCUSSION

*NMR work.*—F<sup>19</sup> spectrum of pure 1, 1, 1 trifluoroacetone gives a single sharp line at 4 ppm. relative to trifluoroacetic acid. The line shifts towards lower fields by about 2 ppm. on dilution with carbon tetrachloride.

When the trifluoroacetone is dissolved in HOH, CH<sub>3</sub>OH, CH<sub>3</sub>SH,



in addition to the line for the pure solute one obtains a line at a higher field (7 ± 2 ppm.) which can be ascribed to the F<sup>19</sup> in the addition product. It may be pointed out that the intensity of the line due to the unreacted solute decreases with increase in the concentration of the solvent until most of the solute gives the addition product. The chemical shift of the hydroxyl proton in the addition product in a concentrated solution (98% V/V) of trifluoroacetone in various solvents is about – 5.5 ppm. relative to TMS. This value

is less than that for the OH proton even in pure water and methyl alcohol for which the values are  $-5.1$  and  $-4.8$  ppm. respectively. Therefore, it shows that the OH proton in the addition product is hydrogen-bonded and that the strength of the hydrogen bonding is more than that in pure water or methyl alcohol. This shows that the hydrogen bonding involves a more electronegative atom such as F. This is also indicated by the  $F^{19}$  resonance studies in the addition product in which the  $F^{19}$  line occurs at a higher field. It is difficult to find out exactly whether hydrogen bonds are inter and/or intramolecular because the OH line is fairly weak and broad even at the concentrations studied and any further dilution of the solution with carbon-tetrachloride makes it difficult to record the line.

*Infra-red work.*—The bands corresponding to stretching frequencies of C—F and C = O in the infra-red spectra of 1, 1, 1 trifluoroacetone are shown in Fig. 1. Typical spectra of the products obtained with some of the solvents are also shown in the same figure.

In the trifluoroacetone, the three strong bands in the region  $1250\text{ cm.}^{-1}$ — $1100\text{ cm.}^{-1}$  correspond to C—F stretching frequencies [Haszeldine and Leedham (1962)] and a strong band at about  $1760\text{ cm.}^{-1}$  to the C = O region. The very weak bands observed in the region  $3500$ — $3600\text{ cm.}^{-1}$  are due to the overtones and the combination bands; the first overtone of the C = O band falls in this region.

The significant changes observed in the spectrum on addition of solvents are as follows:

(1) The strong C = O absorption at  $1760\text{ cm.}^{-1}$  decreases in intensity considerably with the increase in the concentration of the solvent and finally disappears with excess of the solvent (Fig. 1).

(2) A medium strong broad band appears at  $3400\text{ cm.}^{-1}$  This indicates the presence of a hydrogen-bonded OH group in the product. This is shown in Fig. 1 for butanethiol solvent.

(3) In the C—F stretching region at  $1200\text{ cm.}^{-1}$  the three strong C—F bands are considerably altered. As the concentration of the proton donor is increased, the C—F stretching bands decrease in intensity and new bands appear in the neighbourhood. In the case of methanol and the thiol, there is a decrease of about  $(10\text{--}20)\text{ cm.}^{-1}$  for the three C—F absorption frequencies indicating that the C—F bond is weakened and it can be attributed to the formation of  $\text{F}\cdots\text{H}\cdots\text{O}$  bond.

(4) In addition to the three bands due to the changed C-F absorptions, one observes a band at about  $1170\text{ cm}^{-1}$  which can be ascribed to C-(OH).

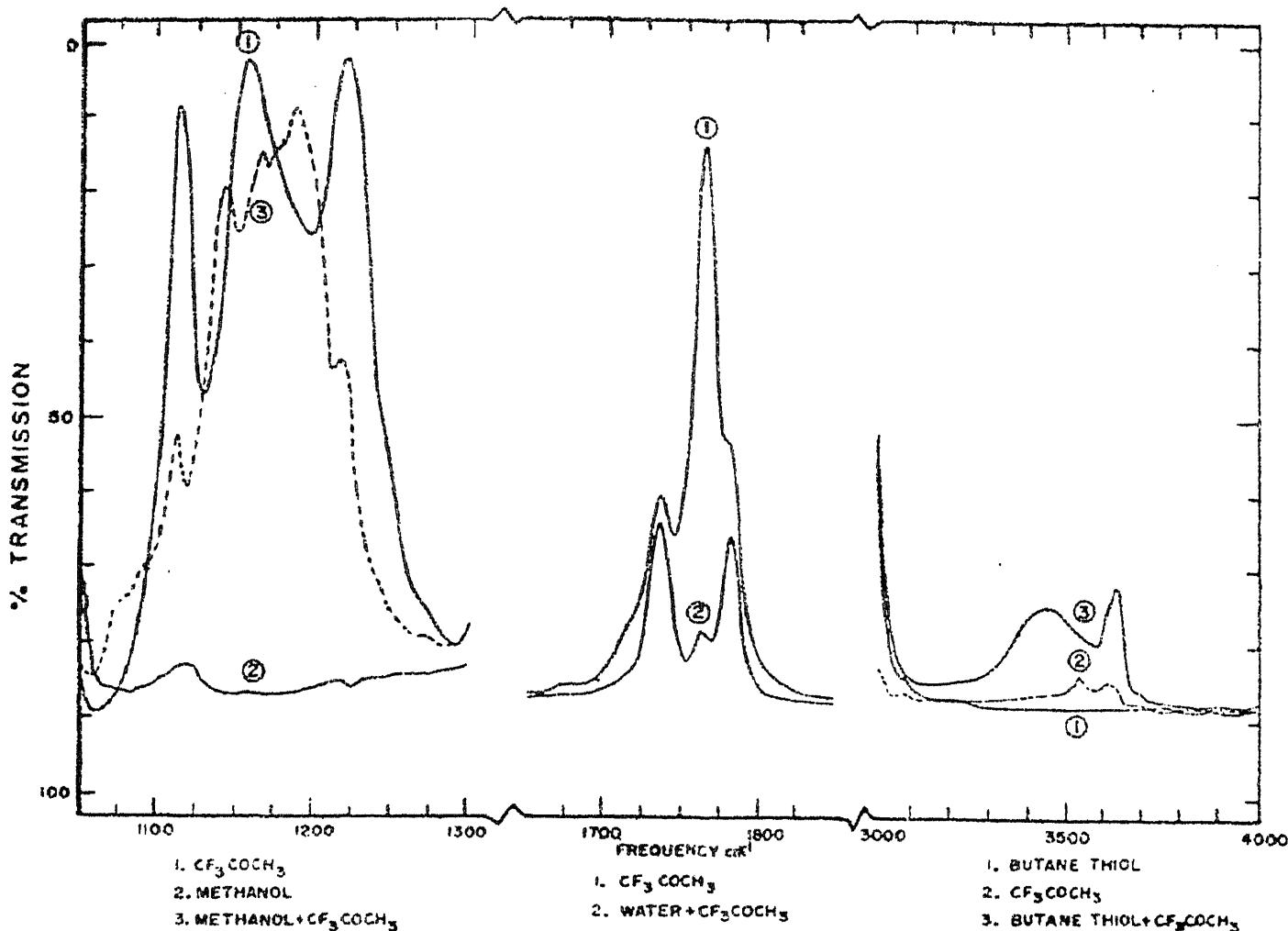


Fig. 1

### CONCLUSION

It can be concluded from the NMR and infra-red studies that addition products are formed in 1, 1, 1 trifluoroacetone-proton donor mixtures. The OH of the addition product forms hydrogen bond with fluorine of the CF<sub>3</sub> group.

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### REFERENCES

Albert, L. Henne, John, W. Sheppard and Even J. Young *J. Am. Chem. Soc.*, 1950, **72**, 3577.

Donald, R. Husted and Arthur H. Ahlbrecht *J. Am. Chem. Soc.*, 1952, **74**, 5422.

Harold Shechter and Franklin Conrad *Ibid.*, 1950, **72**, 3371.

Haszeldine, R. N., *et al.* .. *J. Chem. Soc.*, 1951, 609; 1952, 3483; 1953, 1748.

Hudlicky, M. .. *Chemistry of Organic Fluorine Compounds*, Pergamon Press, 1961, p. 262.

Murray Hauptschein and Robert A. Braun *J. Am. Chem. Soc.*, 1955, **77**, 4930.

Nobukazu Fukuhara and Lucius A. Bigelow *Ibid.*, 1941, **63**, 788.

Stacey, M., Tatlow, J. C. and Sharpe, A. G. *Advances in Fluorine Chemistry*. Butterworths, Publishers, London, 1963, **3**, 2.