

865. Preparation of Bis(trifluoromethyl) Peroxide and its Reaction with Hexafluoropropene.

By H. L. ROBERTS.

Bis(trifluoromethyl) peroxide was prepared by the reaction of trifluoromethyl hypofluorite with carbonyl fluoride at approximately 100 atmospheres and 275°. Its reaction with hexafluoropropene was studied.

BIS(TRIFLUOROMETHYL) PEROXIDE was first prepared by Swarts¹ who obtained it in trace quantities in the electrolysis of aqueous solutions containing trifluoroacetate ion. A better preparative method is described by Porter and Cady² who employed the reaction of trifluoromethyl hypofluorite with carbonyl fluoride.



This reaction is, however, reversible and at atmospheric pressure only a 20—30% conversion of the reagents to the peroxide is possible. Despite the great reactivity of trifluoromethyl hypofluorite it was found possible to react it with carbonyl fluoride in a nickel autoclave at pressures of up to 200 atm. without any difficulty, and under these conditions over 90% conversion of the trifluoromethyl hypofluorite and carbonyl fluoride to bis(trifluoromethyl) peroxide was possible, the reaction going to its equilibrium in about 30 minutes at 275°.

Bis(trifluoromethyl) disulphide³ has been shown by Eleuterio to react with hexafluoropropene to form a high-polymer suggesting that the reaction may proceed via the formation of $\text{CF}_3\text{S}\cdot$ radicals. The reaction of bis(trifluoromethyl) peroxide with hexafluoropropene would be expected to give similar results to those obtained with the disulphide. In a preliminary experiment, in which a mixture of bis(trifluoromethyl) peroxide and hexafluoropropene was irradiated by Hg 2537 Å radiation, a heavy oil was formed. This was followed by a more detailed study of the thermal reaction between the two molecules. When 0.5 mole of bis(trifluoromethyl) peroxide was heated with one mole of hexafluoropropene reaction commenced at 225° and was complete within three hours. The product was distilled to give a series of telomers $\text{CF}_3\text{O}[\text{C}_3\text{F}_6]_n\cdot\text{OCF}_3$, where $n \geq 2$. The compounds were isolated and characterised for $n = 2, 3$, and 4 (see Table).

¹ Swarts, *Bull. Soc. chim. belges*, 1933, **42**, 102.

² Porter and Cady, *J. Amer. Chem. Soc.*, 1957, **79**, 5628.

³ Eleuterio, U.S.P. 2,958,685.

It was observed that no $\text{CF}_3 \cdot [\text{C}_3\text{F}_6] \cdot \text{OCF}_3$ was isolated. At this relative concentration of reactants a substantial quantity of $n = 1$ compound would be expected if $n = 2, 3$, and 4 compounds were obtained. As a further check that the $n = 1$ compound was not formed, another experiment was carried out in which the olefin was injected into excess of the peroxide at 250°. Here the higher temperature and high relative concentration of the olefin⁴ would favour the formation of the telomer of lowest molecular weight. Although some compounds boiling below 106°, the boiling point of $\text{CF}_3\text{O} \cdot [\text{C}_3\text{F}_6]_2 \cdot \text{OCF}_3$, were obtained, they were shown not to be $\text{CF}_3\text{O} \cdot [\text{C}_3\text{F}_6] \cdot \text{OCF}_3$ which, if formed at all, could not have exceeded 0.1% of the products formed. This absence of a 1 : 1 addition product was also observed by Case and Pass in the reaction of hexafluoropropene with bis(pentafluorosulphur) peroxide and pentafluorosulphur hypofluorite.⁵

By reversing the injection procedure and reacting the peroxide with excess of olefin a solid product was obtained.

The telomers produced in this reaction gave single peaks when examined by gas chromatography. Nuclear magnetic resonance spectra⁶ revealed the presence of CF_3O , CF_3 , CF_2 , and C-F groups but it was not possible to state definitely if addition was head to head, head to tail, or random.

Experimental.—Apparatus and procedure. Autoclave reactions were carried out in a stainless-steel autoclave of 250 c.c. capacity and a nickel-lined autoclave of 500 c.c. capacity. They were fitted with a bursting disc (usually 500 atm.) close to the head of the vessel. The autoclaves could be heated by means of a copper-block electric furnace and the temperatures measured were those of the outer wall of the autoclave adjacent to the furnace.

The autoclave was charged with gaseous reagents by cooling it in liquid air and distilling in the reagent from a weighed cylinder; liquid reagents were added before cooling. After the reaction the autoclave was cooled to room temperature and any gas pressure remaining was released through a system of traps cooled in liquid air. The traps were allowed to warm slowly to room temperature and their residual contents were combined with the contents of the autoclave. The gaseous products were examined separately.

The columns used for gas-chromatographic analysis were packed with "Chromosorb" on which "dinonyl phthalate" had been deposited.

Infrared spectra were recorded on a Perkin-Elmer Infracord spectrophotometer.

Preparation of bis(trifluoromethyl) peroxide. Carbonyl fluoride (64 g.) and trifluoromethyl hypofluorite (68 g.) were distilled into the 500 c.c. nickel-lined autoclave. The autoclave was heated to 275° during 3 hr., the pressure reaching a steady value of 780 lb./sq. in. after 4½ hr., showing reaction to be complete. When the autoclave was cooled to room temperature the pressure was 300 lb./sq. in. The products were removed from the autoclave and distilled on a Podbielniak column. There was a forerun consisting mostly of carbonyl fluoride; the main fraction, b. p. -37° (102 g., 93%), was bis(trifluoromethyl) peroxide (Found: M , 169. $\text{C}_2\text{F}_6\text{O}_2$ requires M , 170). The infrared spectrum of the product was identical with that reported by Porter and Cady.²

Reaction of bis(trifluoromethyl) peroxide with hexafluoropropene. Bis(trifluoromethyl) peroxide (85 g., 0.5 mole) and hexafluoropropene (150 g., 1 mole) were distilled into the 250 c.c. autoclave and heated to 225°. From the gaseous products, trifluoromethyl peroxide (34 g., 0.2 mole) was recovered along with traces of hexafluoropropene and carbonyl fluoride, identification being by gas chromatography and infrared absorption spectra. The liquid products were distilled and the products characterised as indicated in the Table.

Injection of bis(trifluoromethyl) peroxide into excess of hexafluoropropene. Hexafluoropropene was heated to 200° in the 250 c.c. autoclave, the final pressure being kept below 400 atm. by venting. Bis(trifluoromethyl) peroxide was injected in 0.23 c.c. quantities every 15 min. for 1½ hr. during which time the pressure dropped 30 atm. When the autoclave had been cooled and vented a white solid product (10 g.) was obtained the infrared spectrum of which showed broad intense bands at 1240 and 980 cm^{-1} similar to those of compound (III) (Found:

⁴ Krespan, *J. Amer. Chem. Soc.*, 1961, **83**, 3424.

⁵ Case and Pass, *J.*, 1963, 6047.

⁶ Dr. D. W. A. Sharp, personal communication.

Compound	Analysis (%)				B. p.	V. p., $\log_{10} p_m = A - [B/T (^{\circ}\text{K})]$		$\Delta H_{\text{vap.}}$ kcal./mole	<i>d</i> (g./c.c.)	Principal infrared bands (cm. ⁻¹)
	Calc. C	Calc. F	Found C	Found F		A	B			
CF ₃ O·[C ₃ F ₆] ₂ ·OCF ₃ (I)	20.4	72.8	20.5	73.0	106°	7.487	1755	8.03	1.821— 0.0026t (°C)	1310, 1250vs, 1140, 980
CF ₃ O·[C ₂ F ₆] ₃ ·OCF ₃ (II)	21.3	73.5	21.7	71.1	154	8.045	2246	10.28	1.903— 0.0024t	1310, 1250vs, 1140, 980
CF ₃ O·[C ₃ F ₆] ₄ ·OCF ₃ (III)	21.8	74.0	27.2	73.7	197	8.879	2819	12.90	1.990— 0.0026t	1240 (broad) 980

C, 23.0; F, 74.1%; C : F 1 : 2.04, indicating that the compound was CF₃O·[C₃F₆]_{*n*}·OCF₃, where *n* was approximately 20).

Injection of hexafluoropropene into excess of bis(trifluoromethyl) peroxide. Bis(trifluoromethyl) peroxide (154 g.) was heated to 250° in the 250 c.c. autoclave. Hexafluoropropene (169 g.) was injected during 1 hr. at such a rate that the temperature did not rise more than 10° above the original value. The vessel was allowed to cool and the pressure reduced to atmospheric by venting through a trap cooled in liquid air. There was obtained 85 g. of gas in the trap and 190 g. of residual liquid in the autoclave. A loss of 48 g. was presumably due to poor trapping out of the gaseous products.

The gaseous product was shown by infrared spectroscopy and gas chromatography to contain carbonyl fluoride and bis(trifluoromethyl) peroxide in a ratio of approximately 1 : 3.5 by weight.

The liquid product slowly evolved hexafluoropropene (i.r. spectroscopy and gas chromatography) (34 g.) at room temperature and in the first stages of its distillation.

The degassed liquid on distillation gave fraction (1), b. p. 26—106° (25 g.). There was no sign of any separation of components, the boiling point rise being continuous. Fraction (2), b. p. 106—107° (75 g.), was compound (I). The residue (54 g.) was examined by gas chromatography and shown to be a mixture of compounds I, II, and III.

The first fraction was re-examined by gas chromatography and was shown to contain the following components in order of elution: (i) hexafluoropropene, (ii) perfluoropentane, (iii) perfluoro-*cis*-1,2-dimethylcyclobutane, (iv) an unidentified component, (v) compound (I). The approximate ratio of abundance of these compounds was 10 : 100 : 10 : 1 : 20.

The products were identified by their infrared spectra in the case of hexafluoropropene, perfluoro-*cis*-1,2-dimethylcyclobutane⁷ and compound (I), and by analysis for perfluoropentane (Found: C, 20.8; F, 78.4%; *M*, 290. Calc. for C₅H₁₂: C, 20.9; F, 79.1%; *M*, 288). The infrared spectrum obtained for this component suggested that it was a mixture of three possible isomers. The fourth component was present in such small amount that it was impossible to obtain an analysis. Its infrared spectrum showed bands similar to that of compound (I) and it may be that it is CF₃O·[C₃F₆]_{*n*}·OCF₃.

IMPERIAL CHEMICAL INDUSTRIES LIMITED, MOND DIVISION,
THE HEATH, RUNCORN, CHESHIRE.

[Received, February 1st, 1964.]

⁷ Hauptschein, Fainberg, and Baird, *J. Amer. Chem. Soc.*, 1958, **80**, 842.