

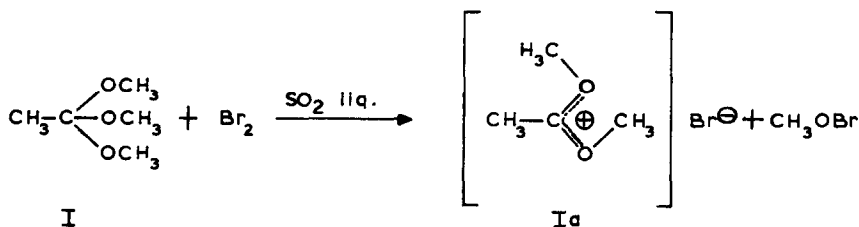
ALKOXYCARBONIUM IONS FROM ACETALS AND ORTHO ESTERS WITH BROMINE.

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Alkoxy-carbonium ions can be generated by reaction of  $\text{BF}_3$  with ortho esters and acetals (1,2). Well resolved NMR-spectra of these ions are obtained in solvents like  $\text{H}_2\text{SO}_4$ ,  $\text{SO}_2$ ,  $\text{SbF}_5$  and  $\text{CH}_3\text{NO}_2\text{-CH}_2\text{Cl}_2$  (3-6). Primary and secondary alkoxy-carbonium ions are formed by ionisation of  $\alpha$ -chloro ethers in  $\text{SbF}_5\text{-SO}_2$  (7,8).

We wish to report the formation of alkoxy-carbonium ions by reaction of ortho esters and acetals with bromine in  $\text{SO}_2$  according to:



This reaction, which is very rapid even at  $-80^\circ$ , demonstrates the stability of alkoxy-carbonium ions in this medium.

Methyl orthoacetate I reacts with one equivalent of bromine to give  $\text{CH}_3\text{OBr}$  and dimethoxymethylcarbonium ion Ia, as shown by NMR (Fig. 1).

The singlet at  $\delta = 4.25$  ppm originates from methyl hypobromite, as shown by independent synthesis from methanol and bromine.

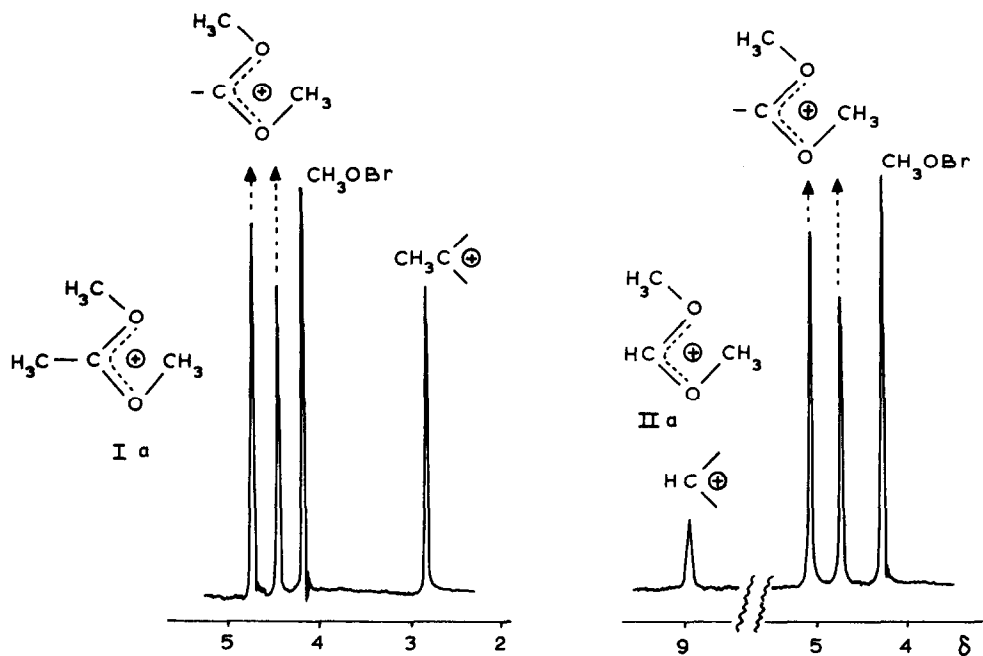


Fig. 1 NMR-spectra of alkoxy carbonium ions Ia and IIa in  $\text{SO}_2$  at  $-60^\circ$ . Shifts in ppm downfield from TMS. The relative intensities of the proton absorptions are consistent with the proposed structures.

The presence of two absorptions for the methoxy groups of Ia indicates the rotational "cis, trans" isomer as the only one at low temperatures, in accordance with earlier observations by Borch (3).

With less than one equivalent of bromine added to the ortho acetate  $\text{CH}_3\text{C}(\text{OCH}_3)_3$ , the same pattern for ion Ia (Fig. 1) is found, in addition to absorptions of the starting material.

A similar reaction takes place if methyl orthoformate II,  $\text{HC}(\text{OCH}_3)_3$ , is treated with an equivalent amount of bromine in  $\text{SO}_2$ , yielding the corresponding carbonium ion IIa (Fig. 1).

However, with half an equivalent of bromine added, only one broad absorption is found for the methoxy groups of both the ion IIa and the starting material II, indicative of a relatively slow exchange between the ion and the orthoformate.

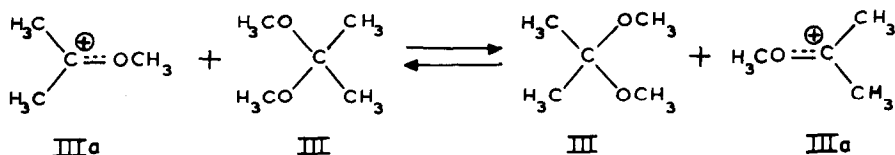
A more rapid exchange is apparent in the case of the dimethyl methoxy carbonium ion IIIa, obtained from 2,2-dimethoxypropane III and bromine. This ion

shows absorption at  $\delta = 5.00$  ( $\text{OCH}_3$ , 3H) and  $\delta = 3.20$  ( $\text{CH}_3$ , 6H).

If less than one equivalent of bromine is used to generate the carbonium ion IIIa, sharp singlets are found for the methyl and methoxy groups at positions intermediate between those for the acetal and the ion.

In fact, the shifts of the methyl and methoxy groups are approximately linearly dependent on the added amount of bromine (Fig. 2).

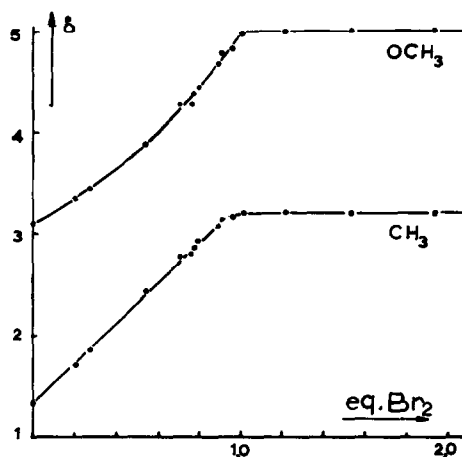
This demonstrates clearly that even at  $-60^\circ$  a rapid and reversible intermolecular exchange exists:



Addition of 2,2-dimethoxypropane III to the alkoxy-carbonium ion IIIa shifts the position of the methyl and methoxy groups in the direction of the corresponding signals for the pure acetal.

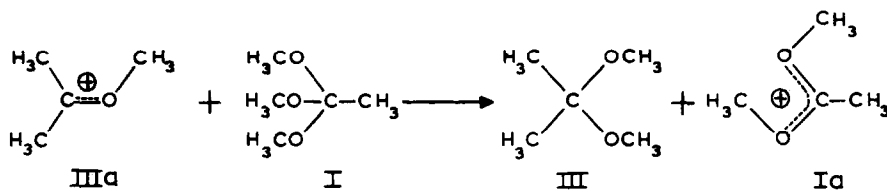
Fig. 2

Shifts of methyl and methoxy groups of III-IIIa as a function of the molar ratio bromine/acetal.



Because replacement of one methyl group in IIIa by a methoxy group leads to a more stable dimethoxymethylcarbonium ion Ia, it can be understood that the latter is less reactive in similar exchange processes.

When the dimethylmethoxycarbonium ion IIIa is further treated with an equivalent amount of methyl orthoacetate I, the more stable dimethoxymethylcarbonium ion Ia is formed, together with 2,2-dimethoxypropane III:



A similar exchange phenomenon between triphenylfluoroborate and methyl ortho-carbonate has been described by Meerwein (2) and by Ramsey and Taft (6).

At  $-30^\circ$  the carbonium ions Ia and IIa each react with the bromine ion to yield methyl bromide, and methyl acetate and (more rapidly) methyl formate respectively, as shown by NMR.

The thermal decomposition of IIIa is much more complex.

The described ortho esters I and II, and the acetal III also react with hydrobromic acid in  $\text{SO}_2$ , to give the same carbonium ions Ia, IIa and IIIa, together with protonated  $\text{CH}_3\text{OH}$ .

More detailed information about the bromination of acetals and ortho esters will be given elsewhere.

#### Acknowledgement

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