

C–C Bond Formation from Dimethyl Ether *via* a Radical Mechanism in the Presence of Strong Acid

Henri Choukroun, Daniel Brunel, and Alain Germain

Laboratoire de Chimie Organique, UA-CNRS 1097, Université des Sciences et Techniques du Languedoc, 34060 Montpellier Cédex, France

The selective radical dimerization of dimethyl ether by peroxodisulphuryl difluoride in fluorosulphuric acid, suggests that a radical intermediate for initial C–C bond formation in the conversion of methanol into hydrocarbons is a possibility.

The conversion of methanol into hydrocarbons over acidic catalysts has received increasing attention in recent years. Nevertheless, the mechanism is still not really understood.¹ While the reversible formation of dimethyl ether as a preliminary step is generally accepted, the mechanism of the formation of the initial C–C bond, the crucial step of the process, is still the subject of debate. The hypothesis involving an oxonium ylide intermediate, which has recently received experimental attention,^{2,3} appears attractive. However, the formation of such an ylide by deprotonation of the trimethyl-oxonium ion requires basic but non-nucleophilic sites which have never been detected on acidic zeolites.⁴ Furthermore, a carbenoid-type mechanism, which is the oldest hypothesis,⁵ cannot be definitively eliminated.⁶ The occurrence of a radical mechanism has already been postulated⁷ but has not received any support so far.

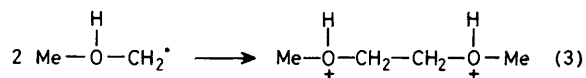
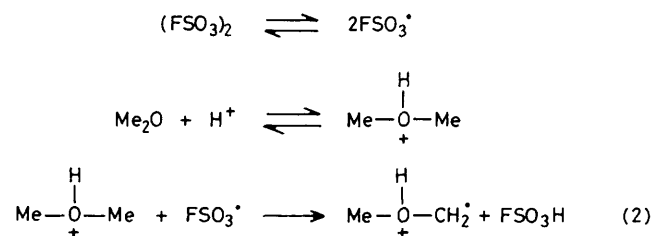
In previous work concerning the isomerization of alkanes,⁸ we have demonstrated that radical activation can be effective in perfluorinated sulphonic acids, showing that radical reactions are not incompatible with strongly acidic media. We describe here the selective radical-initiated dimerization of dimethyl ether in fluorosulphuric acid which demonstrates that a combination of radical and acidic activations can promote the C–C bond formation.

In the present work we have found that, protonation excepted, dimethyl ether does not react in fluorosulphuric acid at room temperature. Under these conditions, the ether is also not electroactive. However, a reaction does occur with the peroxodisulphuryl difluoride generated by electro-oxidation of the acid. Two processes have been used: either the pure peroxide is synthesized and isolated according to Dudley,⁹ then added to a solution of dimethyl ether in fluorosulphuric acid, or the peroxide is generated *in situ* by

electrolysis of a solution of dimethyl ether in fluorosulphuric acid as we previously described.¹⁰ Both methods give dimethoxyethane as the sole product in 50 to 60% coulombic yield, equation (1).



Unlike the reaction of methane¹¹ or 1*H*-perfluoroalkanes,¹⁰ fluorosulphate ($\text{FSO}_3\text{CH}_2\text{OMe}$) is not produced, equation (4). This difference is probably the result of the protonation of the ether, since methane and hydrogenoperfluoroalkanes are not protonated under the same conditions. Likewise the good selectivity for dimer formation can be explained by the



stabilization of the methoxymethyl radical by *O*-protonation, equation (2). In this way, bimolecular dimerization, equation (3) can occur rather than monomolecular decomposition of the radical, equation (5).

These results show that formation of a C–C bond *via* a radical mechanism can occur from dimethyl ether in the presence of strong acid. In our opinion, this could revive the hypothesis of a radical process for the conversion of methanol into hydrocarbons. At present, radical reactions of dimethyl ether are regarded as sources of methane and carbonyl compounds only.^{2,12} Our results suggest that C–C bond formation could occur as well. Furthermore, the detection of radical cations as a result of the adsorption of, for example, alkenes and aromatics on zeolites¹³ and the autocatalytic nature of methanol conversion into hydrocarbons,¹⁴ both argue in favour of a radical mechanism for the latter reaction.

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