

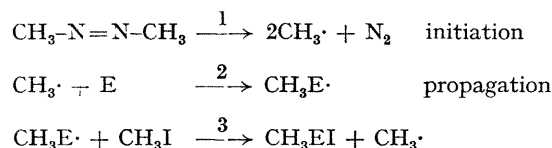
The Orientation of Methyl Radical Addition to Fluoroethylenes

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Summary The orientation of methyl radical addition to three fluoroethylenes in the gas phase has been determined; the results show substantial differences from the orientations previously observed for the addition of the electrophilic radicals trichloromethyl and heptafluoropropyl to the same olefins.

THERE have been a number of studies in which the rate of methyl radical addition to olefins has been measured.¹⁻³ All these studies have, however, only given the total rate of methyl radical addition; no data are available concerning the relative rates at each end of unsymmetrical olefins. In order to do this it is necessary to be able to isolate and characterise actual adducts. We have developed a technique we originally used with rather limited success in radical transfer reactions.⁴ Azomethane has been photolysed in the presence of the olefin under study and in the presence of a large excess of methyl iodide. The hoped-for reaction sequence was as follows (where E stands for ethylene):



Reaction 3 is approximately thermoneutral and would be expected to be reversible. There is a danger therefore that when the olefin is unsymmetrical and two adducts are formed CH_3EI and $\text{CH}_3\text{E'I}$ that the ratio of these two products instead of representing the ratio of the two rate constants k_2/k_2' we wish to measure, might represent a complex ratio of rate constants. Changing the methyl iodide concentration by an order of magnitude had no effect on the product ratio when 1,1-difluoroethylene was the olefin. Since this is the olefin in which $\text{CH}_3\text{E}\cdot$ and $\text{CH}_3\text{E}'\cdot$ differ most significantly we believe that this possibility can be discounted.

In a typical run azomethane (7.3×10^{-5} moles) was irradiated with a medium-pressure mercury arc in a "Pyrex" reaction vessel. The other reactants were the olefin (2.8×10^{-4} moles) and methyl iodide (7.3×10^{-4}

moles). The reaction vessel was surrounded by a furnace and the temperature maintained constant ($\pm 2^\circ$) throughout the run. The two propyl iodides (CH_3EI and $\text{CH}_3\text{E'I}$) were estimated by quantitative gas chromatography using a gas density balance. There were no other major products. Experiments were carried out with vinyl fluoride, 1,1-difluoroethylene and trifluoroethylene, and competitively with ethylene and vinyl fluoride, ethylene and 1,1-difluoroethylene, and trifluoroethylene and tetrafluoroethylene.

TABLE

Adding radical	Orientation ratio: ratios at 150°			Ref.
	$\text{CH}_2=\text{CFH}$	$\text{CH}_2=\text{CF}_2$	$\text{CFH}=\text{CF}_2$	
$\text{CCl}_3\cdot$	1:0.077	1:0.012	1:0.29	5
$\text{C}_3\text{F}_7\cdot$	1:0.050	1:0.009	1:0.25	6
$\text{CH}_3\cdot$	1:0.588	1:0.179	1:7.26	This work

The Table shows the relative orientation for the addition of methyl radicals compared with the electrophilic trichloromethyl⁵ and heptafluoropropyl⁶ radicals. For trifluoroethylene the actual orientation is reversed, while for difluoroethylene and for vinyl fluoride the relative rate of attack at the carbon atom bonded to fluorine is greater than for the two electrophilic radicals. The ratio of the rate of attack at $\text{CHF}=\text{}$ or $\text{CF}_2=\text{}$ over the rate of attack at $\text{CH}_2=\text{}$ is more than ten times greater for methyl than for the electrophilic radicals. The ratio of the rate of attack at $\text{CF}_2=\text{}$ over the rate of attack at $\text{CHF}=\text{}$ is more than twenty times greater bringing about the observed reversal of orientation in trifluoroethylene. The trend however is consistent for all three olefins. The total rate of addition of methyl radicals to ethylene³ and tetrafluoroethylene⁷ has been measured. In conformity with the present results the rate of addition to tetrafluoroethylene was ten times greater than the addition to ethylene. The explanation must be that polar forces are greater than has heretofore been believed.

The studies are being extended over a range of temperatures and from the competitive experiments it is hoped it will be possible to calculate Arrhenius parameters for attack at each end of the olefin using the literature values for the rate of addition of methyl radicals to ethylene³ and tetrafluoroethylene.⁷ Details of the identification of the products together with the full kinetic data will be sub-

mitted for publication with the competitive data. The present results show that the currently accepted ideas concerning directive effects in free radical additions need major revision, and must have a profound influence on our ideas concerning the importance of polar forces in homolytic processes.

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