

THE REACTION OF TRIFLUOROMETHYL RADICALS WITH NEOPENTANE.
AN S_H2 REACTION AT A SATURATED ALIPHATIC CARBON ATOM.

by R.A. Jackson and M. Townson

School of Molecular Sciences, University Sussex, Brighton BN1 9QJ, Sussex.

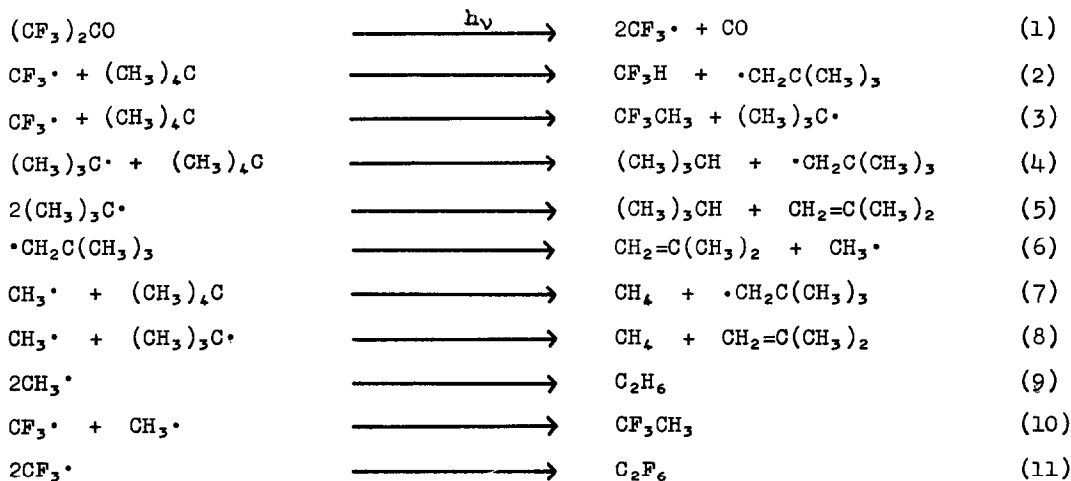
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Free radical substitution reactions of saturated organic compounds normally involve, as a first step, abstraction of a hydrogen or halogen atom. Direct displacement of one radical by another at a saturated aliphatic carbon atom (other than by "hot" radicals) has never been conclusively established,¹ though S_H2 reactions appear to occur in ring opening reactions of strained cyclopropane compounds.² S_H2 reactions at organometallic centres are well established.^{1,3}

We report evidence that trifluoromethyl radicals, produced by photolysis of hexafluoroacetone, react with neopentane at 300° in part by reaction (3), an S_H2 reaction at a methyl group which involves the displacement of a t-butyl radical.

At 200°, U.V. photolysis of a mixture of hexafluoroacetone and neopentane in a quartz vessel gives substantial quantities of trifluoromethane and only trace amounts of hexafluoroethane, which indicates that the initially formed trifluoromethyl radicals efficiently abstract hydrogen atoms from the neopentane (reaction 2). Ethane and 1,1,1-trifluoroethane were absent from the products, in agreement with the observations of Bell and Platt.⁴

At 300°, the products (identified by g.l.c. retention times and mass spectra) include methane, trifluoromethane, ethane, 1,1,1-trifluoroethane, hexafluoroethane, isobutene and isobutane. We propose scheme (1-11) to account for these products. (There is no reaction in the dark at this temperature).

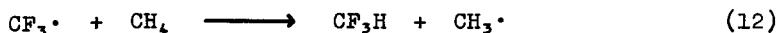
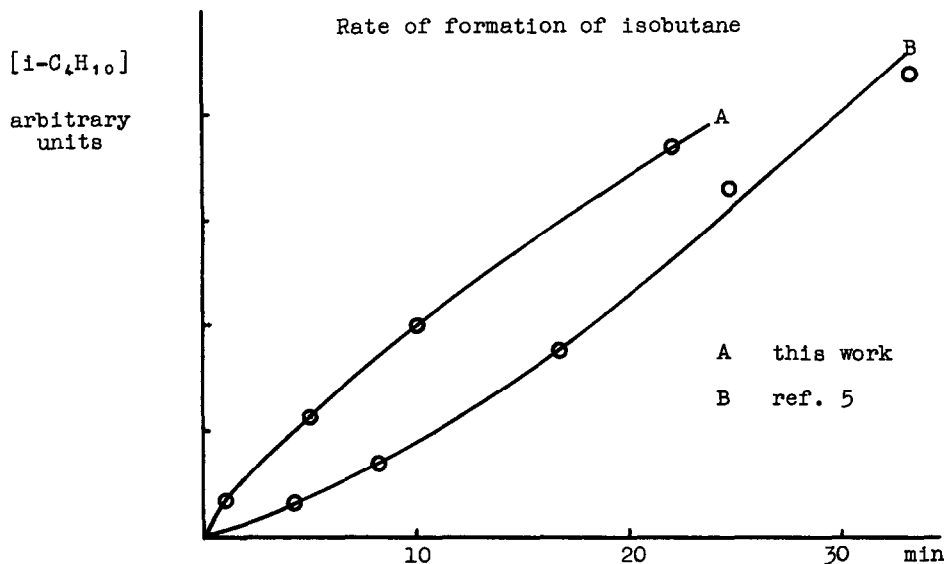


The occurrence of step (3), an $S_{\text{H}}2$ reaction by a trifluoromethyl radical at a methyl group of neopentane is supported by two lines of evidence:-

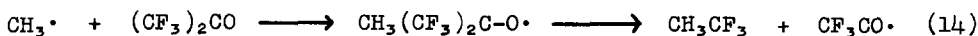
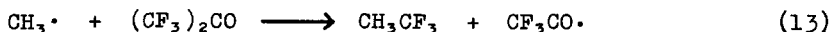
(1) Isobutane appears to be a primary product in the reaction at 300° as is shown by a plot of isobutane formed against time, which indicates a finite rate of production of isobutane at zero time, subsequently slowing down (see diagram). This contrasts with the mercury-photosensitized decomposition of neopentane⁵ where isobutane was also formed, but as a secondary product (rate of production increases with time - see curve B in the diagram).

Though isobutane can be produced by the fragmentation reaction (6), the only likely method of primary formation of isobutane is by hydrogen abstraction (4) [or disproportionation (5)] by a t-butyl radical. Since the direct break-age of a C-C bond in neopentane does not take place at an appreciable rate at 300° , the $S_{\text{H}}2$ reaction (3) seems to be the only feasible primary process which could give a t-butyl radical and thence isobutane.

(2) The amount of CF_3CH_3 produced (compared with that of C_2H_6 and C_2F_6) is much too great to be accounted for solely by reaction (10). [As a control experiment, hexafluoroacetone was photolysed in methane at 300° to produce methyl radicals by reactions (1) and (12), followed by the combination reactions (9), (10), and (11)]. This indicates that some process other than radical



combination is responsible for much of the CF_3CH_3 production in the hexafluoroacetone/neopentane experiment, strongly supporting reaction (3). Back reactions on the original ketone of type (13) or (14) which might give a greater proportion than statistical of CF_3CH_3 can be ruled out by our parallel experiments with methane and hexafluoroacetone, where such reactions should be equally feasible.



Thus the evidence strongly supports the occurrence of the $\text{S}_{\text{H}2}$ reaction (3) in this system. The past lack of success in identifying $\text{S}_{\text{H}2}$ reactions at saturated carbon suggests that such reactions have high activation energies. The rationale for choosing the present system and conditions was as follows:-

- (1) Lower activation energies will be expected with reactive radicals such as $\text{CF}_3\cdot$.
- (2) Activation energies should likewise be reduced if the leaving radical is stabilized (in this case t-butyl).
- (3) High temperatures should favour high activation energy reactions.

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