Bond Strengths in Fluorinated Compounds: Decomposition of Chemically Activated 1,1,1-Trifluoropropane

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KNOWLEDGE of the dissociation energies (D) of the bonds in fluorinated compounds is restricted by lack of data on their heats of formation. In particular the effect of fluorine substitution on the strength of carbon–carbon bonds is uncertain in magnitude and even in direction. The study of the decomposition of chemically activated 1,1,1-trifluoropropane yields direct and precise information on the point. The compound can be formed by the combination of radicals in two ways:

$$\mathrm{Me} + \mathrm{CH_2CF_3} = \mathrm{MeCH_2{\cdot}CF_3}^{*}$$

$$\mathrm{MeCH_2} + \mathrm{CF_3} = \mathrm{MeCH_2{\cdot}CF_3}^{**}$$

The radicals for the first reaction were produced by the photolysis of a mixture of acetone and 1,1,1-trifluorobutan-3-one; those for the second from diethyl ketone and hexafluoroacetone. The activated molecules either eliminated hydrogen fluoride (k_e) or were deactivated by collision (k_S). The relative rates of these processes were determined by measurement of the yields of the propane and propene over a pressure range 2—57 torr.

The energy content of the propane depends on both the strength of the C–C bond formed (defined at 25°) and the heat content of the radicals. The heat content can be exactly calculated if the frequencies of the vibrations are known. Spectroscopic data on radicals are limited but satisfactory assignments can be based on known frequencies of normal molecules. The energy contents of the propane in the first part of the Table were calculated in this way on the assumption that $D(\mathrm{Me{-}CH_2CF_3}) = 85{\cdot}0$ kcal. mole^{-1}, which is the value for the bond in propane at 25°. In the second part, the energy contents are derived from the values of log k_e/k_S on the basis of the nearly linear relation between E and log k_e/k_S established in the first part. The first three rates are obtained by interpolation. The heat contents of the radicals can be found as before and hence the dissociation energy of the $\mathrm{CF_3{-}CH_2Me}$ bond. This proves to be $4{\cdot}5 \pm 0{\cdot}4$ kcal. mole greater than that for the first bond.

Although this method is of limited applicability, TABLE

CF_3CH_2–Me

T (°K)	D(C–C) + (kcal. mole^{-1})	(H^0–H^0_{298}) =	E	log k_e/k_s (torr^{-1})
405	85·0	3·5	88·5	−1·15
444	85·0	4·9	89·9	−1·00
492	85·0	6·7	91·7	−0·85
532	85·0	8·5	93·5	−0·70
578	85·0	10·5	95·5	−0·47
621	85·0	12·6	97·6	−0·23

CF_3–CH_2Me

T (°K)	log k_e/k_s (torr^{-1})	E =	(H^0–H^0_{298}) +	D(C–C) (kcal. mole^{-1})
423	−0·66	93·5	4·1	89·4
460	−0·54	94·7	5·4	89·3
514	−0·30	97·1	7·5	89·6
558	−0·10	99·2	9·3	89·9
575	−0·04	99·8	10·0	89·8
643	+0·15	101·9	12·7	89·2

$$D(CF_3\text{–}CH_2Me) - D(CF_3CH_2\text{–}Me) = 4{\cdot}5 \pm 0{\cdot}4$$

it yields unusually accurate values of differences in bond strengths. The present finding confirms the deduction made by other means that fluorine substitution increases the strength of carbon–carbon bonds;[1] considerable probable errors must be assigned to these earlier determinations.

(*Received, May 13th,* 1968; *Com.* 598.)

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[1] E. Tschuikow-Roux, *J. Phys. Chem.*, 1965, **69**, 1075; J. W. Coomber and E. Whittle, *Trans. Faraday Soc.*, 1967, **63**, 2656; C. A. Goy, A. Lord, and H. O. Pritchard, *J. Phys. Chem.*, 1967, **71**, 1086.