Hydrogen Abstraction by Difluoroamino-radicals and the Strengths of C–H Bonds

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WHEN a mixture of tetrafluorohydrazine and an alkane is heated the alkane is consumed at a rate that is consistent with its removal by reaction (1), presumably followed by reaction (2).

$$NF_2 + RH = NF_2H + R \quad .. \quad (1)$$

$$R + NF_2 = RNF_2 \quad .. \quad .. \quad (2)$$

The difluoroamine is not stable at convenient temperatures and a complex mixture of products is ultimately formed. The second-order rate constants for reaction (1) can be found from measurements of the consumption of the alkane in mixtures in which the hydrazine is in great excess. The concentration of difluoroamino-radicals can be calculated from the accurate determination of the dissociation constant of the hydrazine by Johnson and Colburn.[1] Above 180° and below 40 mm. pressure over 90% of the hydrazine is dissociated, small errors in the dissociation constant are then unimportant and the overall activation

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[1] F. A. Johnson and C. B. Colburn, *J. Amer. Chem. Soc.*, 1961, **83**, 3043.

energy for the consumption depends very little on the heat of the dissociation. The conditions are particularly favourable for the determination of k_1 and E_1. The values listed in Table 1 were found over a wide range of conditions. Values for the dissociation energies of C–H bonds in alkanes have been found by electron impact, iodine reactions, and brominations. From these determinations the mean values in Table 2 can be selected. The activation energies for the attack of methyl radicals on alkanes are then given by the Polanyi relation

$$E(\mathrm{Me}) = 0{\cdot}49\ [D(\mathrm{C{-}H}) - 74{\cdot}3],$$

as can be seen from the comparison of values, found and calculated. Similarly good agreement is found between the values for bromination and those calculated from the equation

$$E(\mathrm{Br}) = 0{\cdot}86[D(\mathrm{C{-}H}) - 82{\cdot}5].$$

These two relations can be used in conjunction with the activation energy for the attack of methyl radicals on cyclopentane (9·1 kcal. mole^{-1}) and of bromine atoms on neopentane (14·3 kcal. mole^{-1}) to give for the strengths of the bonds 92·9 [10] and 99·2 [9] kcal. mole^{-1}. From these values and those for n-butane and isobutane it is found that:

$$E(\mathrm{NF_2}) = 1{\cdot}00[D(\mathrm{C{-}H}) - 72{\cdot}5].$$

As is shown in Table 1, this equation fits the results very well. The proportionality factor has the value of unity that should be expected for attack by an unreactive radical. The equation also sets a minimum value of 72·5 kcal. mole^{-1} for the strength of the NF_2–H bond; this minimum is probably close to the actual value.

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TABLE 1. *Hydrogen abstraction by difluoroamino-radicals*

Alkane	Temp.	log A (mole^{-1} c.c. sec.$^{-1}$)	E (kcal. mole^{-1}) Found	E (kcal. mole^{-1}) Polanyi
Isobutane	155—282°	10·49 ± 0·04	18·49 ± 0·10	18·4
Cyclopentane	180—282	10·93 ± 0·05	19·91 ± 0·11	20·3
n-Butane	180—282	11·83 ± 0·04	22·20 ± 0·08	22·1
Neopentane	180—282	13·22 ± 0·03	26·68 ± 0·07	26·7

TABLE 2. *Polanyi relations for hydrogen abstractions*

Alkyl group	D(C–H) (kcal. mole^{-1} at 25°)				Activation energy			
	Electron impact[2]	Iodine reaction	Bromination	Weighted mean	Methyl		Bromine atom	
					Found[8]	Polanyi	Found[9]	Polanyi
Methyl ..	103·4	103·8[3]	103·9[7]	103·8	14·5	14·5	18·3	18·3
Ethyl	98·3	97·7[4]	98·3[7]	98·0	11·9	11·7	13·4	13·3
Isopropyl ..	95·3	94·5[5]	—	94·5	10·3†	9·9	10·1	10·3
s-Butyl ..	—	—	—	94·6*	9·7†	9·9	10·2	10·4
t-Butyl ..	91·0	91·4[6]	—	91·0	8·2	8·2	7·5	7·3

* Bromination results used to interpolate this value.

† Parallel work by the same authors on abstraction of secondary deuterium atoms indicates that activation energies for these reactions are nearly equal.

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[2] Results of D. P. Stevenson as collated for 0° K in T. L. Cottrell, "The Strengths of Chemical Bonds," Butterworths, London, 1960.

[3] M. C. Flowers and S. W. Benson, *J. Chem. Phys.*, 1963, **38**, 882, with thermodynamic data of A. S. Carson, W. Carter, and J. B. Pedley, *Proc. Roy. Soc.*, 1961, *A*, **260**, 550.

[4] D. B. Hartley and S. W. Benson, *J. Chem. Phys.*, 1963, **39**, 132.

[5] P. S. Nangia and S. W. Benson, *J. Amer. Chem. Soc.*, 1964, **86**, 2773.

[6] H. Teranishi and S. W. Benson, *J. Amer. Chem. Soc.*, 1963, **85**, 2887.

[7] G. C. Fettis and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1961, 3037.

[8] W. M. Jackson, J. R. McNesby, and B. de B. Darwent, *J. Chem. Phys.*, 1962, **37**, 1610.

[9] G. C. Fettis, J. H. Knox, and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1960, 4177.

[10] A. S. Gordon and S. R. Smith, *J. Phys. Chem.*, 1962, **66**, 521.