Gas-phase Kinetics of the Difluoroamino-radical

By A. J. White
UNIVERSITY OF WALES INSTITUTE OF SCIENCE AND TECHNOLOGY,
CARDIFF CF1 3NU

1 Introduction

Reviews of the fluorides of nitrogen,[1,2] in general, and the difluoroamino-radical,[3] in particular, appeared in the mid-1960s. At that time the gas-phase kinetic study of the reactions of the difluoroamino-radical was in its infancy – the only reactions studied being those of the hydrogen-abstraction reactions from alkanes[4] and acetone.[5] Since then various kinetic studies involving the difluoroamino-radical have been investigated by Trotman-Dickenson and his research school at the Edward Davies Chemical Laboratory, Aberystwyth. It is mainly the results of that research which form the basis of this review.

The difluoroamino-radical ($\cdot NF_2$) is a versatile radical which undergoes all the usual radical reactions of addition, abstraction, disproportionation, and combination. Furthermore, it acts as a radical trap, and because the difluoroamino-compounds so formed do not undergo further reaction, this often affords a simple method of studying organic radical decomposition reactions: the decomposition reactions of the propoxycarbonyl radical and the butoxyl radical and a whole range of acyl radical decomposition reactions have been studied in this way, although the results of these decomposition reactions are not considered in this review.

The difluoroamino-radical reactions have activation energies which are similar to those found for iodine reactions. The A factors, however, are usually on the low side – the only exception appears to be combination reactions with acyl and alkoxy-carbonyl radicals. This whole question is best viewed in the light of other nitrogen-containing radical kinetics and indeed the results seem to fit in quite well with these.

2 Tetrafluorohydrazine and the Difluoroamino-radical

A. General Properties.—Tetrafluorohydrazine (N_2F_4) is a colourless gas, but the liquid phase is often coloured purple, blue, or pink owing to nitric oxide impurity.[1] It melts at about 111 K and boils at about 200 K. The vapour pressure can be expressed[6] by the Clausius–Clapeyron equation (1):

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[1] C. B. Colburn, *Endeavour*, 1965, **24**, 138.
[2] J. K. Ruff, *Chem. Rev.*, 1967, **67**, 665.
[3] C. B. Colburn, *Chem. in Britain*, 1966, **2**, 336.
[4] J. Grzechowiak, J. A. Kerr, and A. F. Trotman-Dickenson, *Chem. Comm.*, 1965, 109.
[5] J. Grzechowiak, J. A. Kerr, and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1965, 5080.
[6] C. B. Colburn and A. Kennedy, *J. Amer. Chem. Soc.*, 1958, **80**, 5004.

$$\log P/\text{mmHg} = 6.33 - 692\,T^{-1} \quad (1)$$

The gas is toxic[7] and has an odour resembling that of fluorine. Light has been reported[8] to induce it to explode.

Tetrafluorohydrazine was first synthesized in 1958 by Colburn and Kennedy[6] by allowing nitrogen trifluoride to react with a fluorine acceptor, *e.g.* stainless steel, copper, arsenic, antimony, or bismuth, at 623—673 K. Although it was not realized at the time, this synthesis was actually the synthesis of the difluoroamino-radical ($\cdot NF_2$) which, on cooling, dimerized to form tetrafluorohydrazine.[3] The reaction proceeds according to equations (2) and (3) where M = Cu, As, Sb, Bi, or stainless steel:

$$NF_3 + M \rightarrow \cdot NF_2 + MF \quad (2)$$

$$2\cdot NF_2 \rightarrow N_2F_4 \quad (3)$$

B. Tetrafluorohydrazine–Difluoroamino-radical Equilibrium.—Even though the original synthesis of tetrafluorohydrazine was *via* the difluoroamino-radical, it was not until two years later that Colburn, Johnson, and their co-workers showed[9–11] the existence of the tetrafluorohydrazine–difluoroamino-radical equilibrium (4):

$$N_2F_4 \rightleftharpoons 2\,\cdot NF_2 \quad (4)$$

Table 1 summarizes their results, together with the mass spectral data given by Herron and Dibeler[12] and more recent measurements of pressure variation with temperature at constant volume.[13]

Table 1 *Tetrafluorohydrazine–difluoroamino-radical equilibrium*

Method	*Temperature range*/K	ΔH/ kJ mol^{-1}	ΔS/ J mol^{-1} K^{-1}	*Ref.*
$\left(\frac{\partial P}{\partial T}\right)_V$	373—423	83.3 ± 2.1	167 ± 8	10
	423—523	85.8 ± 0.8	—	13
U.v.	—	90.8 ± 8.4	188 ± 8	10
E.p.r.	340—435	80.8 ± 4.2	—	11
Mass Spectrometry	326—673	90.0 ± 6.7	—	12

The existence of this equilibrium is readily appreciated from thermochemical considerations. From the heats of formation of NF_3 (−132.8 kJ mol^{-1}),[14]

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[7] T. R. Carson and F. T. Wilinski, *Toxicol. Appl. Pharmacol.*, 1964, **6**, 447.

[8] A. P. Modica and D. F. Hornig, Princeton University, Report No. 357-275, October 1963.

[9] C. B. Colburn and F. A. Johnson, *J. Chem. Phys.*, 1960, **33**, 1869.

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

[11] L. H. Piette, F. A. Johnson, K. A. Booman, and C. B. Colburn, *J. Chem. Phys.*, 1961, **35**, 1481.

[12] J. T. Herron and V. H. Dibeler, *J. Chem. Phys.*, 1961, **35**, 747.

[13] G. von Ellenreider, E. Castellano, and H. J. Schumacher, *Z. phys. Chem.*, 1967, **55**, 144.

[14] L. C. Walker, *J. Phys. Chem.*, 1967, **71**, 361.

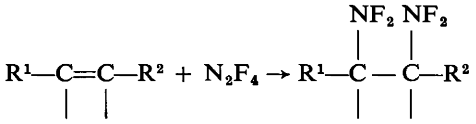
$\cdot NF_2$ (35.6 kJ mol^{-1}),[14] and $\cdot F$ (78.9 kJ mol^{-1}),[15] the strength of the first N—F bond in nitrogen trifluoride can be calculated to be 247.3 kJ mol^{-1}. This value can be compared with the average N—F bond energy of 280.7 kJ mol^{-1} in nitrogen trifluoride.[16] This indicates that the strength of the two remaining N—F bonds in the difluoroamino-radical must average 297.4 kJ mol^{-1}. Thus it is energetically unfavourable for the difluoroamino-radical to abstract a fluorine atom from tetrafluorohydrazine to form nitrogen trifluoride. This is in contrast to ammonia, where the first N—H bond is the strongest.[3]

C. Structure of Tetrafluorohydrazine and the Difluoroamino-radical.—The microwave spectrum[17] of tetrafluorohydrazine shows that there are two 'most probable' configurations of tetrafluorohydrazine: one, the planar form, in which the angle between the two NF_2 groups is 180° and the other, the non-planar form, in which the angle of rotation of one NF_2 group with respect to the other is 65°. Electron-diffraction[18] and infrared[19] studies, however, indicate that the tetrafluorohydrazine molecule exists in the twisted configuration, as predicted by molecular orbital calculations.[20]

Electron diffraction[18] yielded a value of 139 pm for the N—F bond distance and 104° for the F—N—F angle in the NF_2 group in tetrafluorohydrazine, and 136 pm and 103° in the difluoroamino-radical.

3 Addition Reactions

The kinetics of the addition of tetrafluorohydrazine to olefins have been extensively studied.[21–23] The overall reaction may be written as:



$$R^1{-}\underset{|}{C}{=}\underset{|}{C}{-}R^2 + N_2F_4 \rightarrow R^1{-}\underset{|}{\overset{NF_2}{\overset{|}{C}}}{-}\underset{|}{\overset{NF_2}{\overset{|}{C}}}{-}R^2$$

and the proposed mechanism as in equations (5)—(10):

$$N_2F_4 \rightleftharpoons 2\cdot NF_2 \tag{5}$$

$$Ol + \cdot NF_2 \rightarrow \cdot OlNF_2{}^* \tag{6}$$

$$\cdot OlNF_2{}^* \rightarrow Ol + \cdot NF_2 \tag{7}$$

$$\cdot OlNF_2{}^* + M \rightarrow \cdot OlNF_2 + M \tag{8}$$

[15] H. A. Skinner and G. Pilcher, *Quart. Rev.*, 1963, **17**, 264.

[16] Y. N. Inel, Ph.D. Thesis, University of Wales, 1968.

[17] D. R. Lide and D. E. Mann, *J. Chem. Phys.*, 1959, **31**, 1129.

[18] R. K. Bohn and S. H. Bauer, *Inorg. Chem.*, 1967, **6**, 304.

[19] M. D. Harmony, R. J. Myers, L. J. Schoen, D. R. Lide, jun., and D. E. Mann, *J. Chem. Phys.*, 1961, **35**, 1129.

[20] J. P. Simons, *J. Chem. Soc.*, 1965, 5406.

[21] A. J. Dijkstra, J. A. Kerr, and A. F. Trotman-Dickenson, *J. Chem. Soc.* (*A*), 1966, 582.

[22] A. J. Dijkstra, J. A. Kerr, and A. F. Trotman-Dickenson, *J. Chem. Soc.* (*A*), 1967, 105.

[23] A. J. Dijkstra, J. A. Kerr, and A. F. Trotman-Dickenson, *J. Chem. Soc.* (*A*), 1967, 864.

$$\cdot\text{OlNF}_2 \rightarrow \text{Ol} + \cdot\text{NF}_2 \tag{9}$$

$$\cdot\text{OlNF}_2 + \cdot\text{NF}_2 \rightarrow \text{Ol(NF}_2)_2 \tag{10}$$

where Ol represents the olefin, $\cdot\text{OlNF}_2{}^*$ is a vibrationally excited radical, and M is any molecule in the system capable of removing excess energy.

From steady-state considerations, the rate equation may be written as equation (11):

$$\frac{1}{k_{\text{obs}}} = \frac{t[\text{Ol}][\cdot\text{NF}_2]}{[\text{Product}]} = \frac{1}{k_6}\left(1 + \frac{k_7}{k_8[\text{M}]}\right)\left(1 + \frac{k_9}{k_{10}[\cdot\text{NF}_2]}\right) \tag{11}$$

where t = time. The Arrhenius parameters of reaction (6) are given in Table 2.

Table 2 *Addition of difluoroamino-radicals to olefins*

Olefin	*Temperature range*/K	E_6/ kJ mol^{-1}	log A_6/ ml mol^{-1} s^{-1}
Ethylene	351—428	64.9	10.6
Propene	334—391	57.3	10.2
But-1-ene	334—391	56.9	10.1
trans-But-2-ene	334—391	49.8	9.5
cis-But-2-ene	334—391	49.8	9.5
Isobutene	314—373	49.8	9.8
2-Methylbut-2-ene	314—373	42.3	9.0
2,3-Dimethylbut-2-ene	314—373	34.7	8.3
Cyclopentene	334—391	46.0	8.9
Vinyl bromide	351—405	55.2	9.6
Vinyl chloride	351—405	54.0	9.4

There was found to be a linear relationship between E_6, the activation energy of the first step, and the ionization potential of the olefin, showing that the olefin which produces the more stable free radical reacts faster. E_6 Values also show that substitution of a hydrogen atom by a methyl group in ethylene lowers the activation energy (E_6) by 7.5 kJ mol^{-1} per methyl group. This indicates that the difluoroamino-radical is an electropilic species. Butadiene was found to be more reactive than straight-chain olefins but halogen substitution reduces reactivity.

Pankratov *et al.*[24] studied the addition of tetrafluorohydrazine to isobutene and found the overall rate constant k was given by

$$k = 3.2 \times 10^9 \exp(-52\,300/RT) \text{ ml mol}^{-1} \text{ s}^{-1}$$

Dijkstra *et al.*[22] found the rate constant of the initial step (6) to be

$$k_6 = 9.0 \times 10^9 \exp(-49\,800/RT) \text{ ml mol}^{-1} \text{ s}^{-1}$$

[24] A. V. Pankratov, L. A. Akhanshchikova, and Yu. A. Adamova, *Russ. J. Inorg. Chem.*, 1968, **13**, 1513.

Although these rate constants agree fairly well with one another, Pankratov and his workers did not study the effect of constant [M] or constant [$\cdot NF_2$] on the rate constant as Dijkstra *et al.* had done, and their investigations into the mechanism of the addition were not as thorough as those of Dijkstra *et al.*

The values of k_6 can be compared with the rate constants for attack on olefins by other radicals given in refs. 23 and 24. The difluoroamino-radical behaves differently from both methyl and trifluoromethyl radicals. This is because the reactions of methyl and trifluoromethyl radicals with alkenes are largely determined by steric effects. The reactivity of hydrogen atoms with alkenes has been shown by Cvetanovic[25] to be correlated with atom-localization energies – these also follow a different pattern from that of the difluoroamino-radical. There is, however, quite good correspondence between the rate constant for the difluoroamino-radical addition to alkenes and the rate constants for the addition of oxygen[26] and bromine atoms.[27] The reactions of bromine atoms depend upon the establishment of a pre-equilibrium and special factors may determine the rates. Oxygen atoms are electrophilic species that directly attack the π-electrons of the double bond, as do probably the electrophilic difluoroamino-radicals. The issue regarding σ- or π-complexes between difluoroamino-radicals and olefins is not, however, so clear-cut. Additional important evidence concerns the addition of difluoroamino-radicals to *cis*- and *trans*-but-2-ene. The *cis*-isomer is found in the products of the addition of difluoroamino-radicals to *trans*-but-2-ene and *vice versa.* This is in accord with the proposed mechanism, involving the reversible formation of the adduct radical, and is good evidence in support of the mechanism. At the same time it would seem to indicate the formation of a σ-complex from addition to the butenes since the isomerization would be less likely from a π-complex.

The Arrhenius parameters for the radical decomposition reaction (9) can be calculated from the values of $(E_9 - E_{10})$ and log (A_9/A_{10}) on the assumption that $k_{10} = 13.4$ ml mol^{-1} s^{-1}. The values are given in Table 3, where it can be seen that in general both log A_9 and E_9 decrease by the introduction of substituents into the olefin.

4 Hydrogen-abstraction Reactions

A. Alkanes.—Grzechowiak *et al.*[4] found that when a mixture of tetrafluorohydrazine and an alkane was heated, the rate of disappearance of the alkane is consistent with the abstraction of a hydrogen atom from the alkane followed by the coupling of the alkyl radical thus formed with a difluoroamino-radical to form an alkyl-difluoroamine, as shown in equations (12)—(14):

$$N_2F_4 \rightleftharpoons 2\cdot NF_2 \tag{12}$$

$$RH + \cdot NF_2 \rightarrow R\cdot + HNF_2 \tag{13}$$

$$R\cdot + \cdot NF_2 \rightarrow RNF_2 \tag{14}$$

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[25] K. R. Jennings and R. J. Cvetanovic, *J. Chem. Phys.*, 1961, **35**, 1233.
[26] R. J. Cvetanovic, *Canad. J. Chem.*, 1960, **38**, 1678.
[27] P. I. Abell, *Trans. Faraday Soc.*, 1964, **60**, 2214.

Table 3 *Radical decomposition reactions*

Reaction	*Temperature range*/K	log A_9/ s^{-1}	E_9/ kJ mol^{-1}
$\cdot C_2H_4NF_2 \rightarrow \cdot NF_2 + C_2H_4$	373—428	12.9	57.3
$\cdot C_3H_6NF_2 \rightarrow \cdot NF_2 + C_3H_6$	334—391	13.4	56.4
$\cdot C_4H_8NF_2 \rightarrow \cdot NF_2 + CH_2{=}CHCH_2CH_3$	334—391	12.5	43.1
$\cdot C_4H_8NF_2 \rightarrow \cdot NF_2 + CH_3CH{=}CHCH_3$ (*trans*)	334—391	14.0	56.8
$\cdot C_4H_8NF_2 \rightarrow \cdot NF_2 + CH_3CH{=}CHCH_3$ (*cis*)	334—391	14.0	56.8
$\cdot C_5H_{10}NF_2 \rightarrow \cdot NF_2 + (CH_3)_2C{=}CHCH_3$	314—373	13.3	40.5
$\cdot C_6H_{12}NF_2 \rightarrow \cdot NF_2 + (CH_3)_2C{=}C(CH_3)_2$	314—373	12.1	34.7
cyclo-$C_5H_8NF_2 \rightarrow \cdot NF_2$ + cyclo-C_5H_8	334—391	11.4	38.9
$\cdot C_2H_3BrNF_2 \rightarrow \cdot NF_2 + C_2H_3Br$	351—405	12.3	47.7
$\cdot C_2H_3ClNF_2 \rightarrow \cdot NF_2 + C_2H_3Cl$	351—405	10.9	38.5

Arrhenius parameters for this attack were obtained by following the consumption of the alkane with time. Recently,[28] the rate of hydrogen abstraction from alkanes has been found directly by measurement of the rate of formation of the corresponding alkyl-difluoroamine. The results are given in Table 4.

Table 4 *Rates of hydrogen abstraction from alkanes by difluoroamino-radicals*

	Temperature range/K	log *A*/ ml mol^{-1} s^{-1}	*E*/ kJ mol^{-1}	log *k* (400 K) (per H atom)	*Ref.*
Primary H					
C_3H_8	352—463	11.80	109	−3.18	28
Neopentane	453—555	13.22	112	−2.48	4
Secondary H					
C_3H_8	352—463	10.39	94.4	−2.25	28
n-C_4H_{10}	352—463	12.29	103	−1.78	28
cyclo-C_5H_{10}	352—463	11.36	92.3	−1.64	28
n-C_4H_{10}	453—555	11.83	92.9	−0.88	4
cyclo-C_5H_{10}	453—555	10.93	83.3	−0.97	4
Tertiary H					
Isobutane	352—463	11.04	86.15	−0.24	28
	428—555	10.49	77.29	0.37	4

The results in Table 4 show that the ease of hydrogen abstraction increases in the sequence: primary C—H < secondary C—H < tertiary C—H, as expected. The abstraction of primary hydrogen from neopentane at 400 K is a factor of five faster than from propane when compared on a per hydrogen atom basis.

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[28] P. Cadman, C. Dodwell, A. F. Trotman-Dickenson, and A. J. White, *J. Chem. Soc.* (*A*), 1971, 2967.

Grzechowiak's rates[5] are on the whole faster than the recent[28] ones, although the results for secondary hydrogen abstraction are very similar, especially when allowance is made for the differences in secondary carbon–hydrogen bond energies in propane, n-butane, and cyclopentane. Grzechowiak's method of analysis did not allow for the concurrent attack on the primary hydrogen atoms of n-butane. If this allowance is made by using his primary hydrogen abstraction results, his n-butane results are nearly a factor of ten larger than the more recent results. This factor is also present when the two results for cyclopentane are compared, where no correction is necessary. The difference in the two sets of results may be associated with impurities released by the attack of difluoroamine (HNF_2) and/or difluoroamino-radicals on the Pyrex glass at the higher temperatures used in the alkane-consumption method.

Comparison of the rates (or activation energies) of hydrogen abstraction by difluoroamino-radicals with those of methyl, trifluoromethyl, iodine, and bromine[29–39] shows that difluoroamino-radicals are less reactive than methyl, trifluoromethyl, and bromine but more reactive than iodine; the Figure shows this. The activation energy of hydrogen abstraction from alkanes has been found previously to be related to the strengths of the carbon–hydrogen bond broken by the semi-empirical Evans–Polanyi equation (15):

$$E = \alpha[D(\mathrm{R{-}H}) + \beta] \tag{15}$$

This relationship is also shown in the Figure. A value of $\alpha = 0.90$ is obtained for the difluoroamino-radical compared with $\alpha(\cdot\mathrm{I}) = 0.97$, $\alpha(\cdot\mathrm{Br}) = 0.86$, and $\alpha(\cdot\mathrm{Me}) = \alpha(\cdot\mathrm{CF_3}) = 0.49$. It seems likely that the same factors which govern the activation energies of hydrogen abstractions by the other species shown in the Figure also govern those of the difluoroamino-radical.

The Arrhenius parameters for the reverse reactions, *i.e.* the attack of alkyl radicals on difluoroamine, can be calculated from the activation energies of the forward reactions together with the enthalpy–entropy changes of the reactions by use of equations (16) and (17):

$$E_{-n} = E_n - \Delta H_n^\circ - \Delta nRT \tag{16}$$

$$\log A_{-n}/A_n = (-\Delta S/2.3R) + \Delta n \log RT + \Delta n/2.3 \tag{17}$$

The results calculated from the Arrhenius parameters quoted in ref. 28 are summarized in Table 5. $\Delta H_f^\circ(\cdot\mathrm{NF_2})$ was taken[13] as 35.6 kJ mol^{-1}, $S^\circ(\cdot\mathrm{NF_2})$ as[40]

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[29] D. M. Golden, R. Walsh, and S. W. Benson, *J. Amer. Chem. Soc.*, 1965, **87**, 4053.
[30] D. B. Hartley and S. W. Benson, *J. Chem. Phys.*, 1963, **39**, 132.
[31] P. S. Nangia and S. W. Benson, *J. Amer. Chem. Soc.*, 1964, **86**, 2773.
[32] E. E. Chekhov, A. C. Isailingols, and I. I. Ioffe, *Neftekhimiya*, 1967, **7**, 717.
[33] H. Teranishi and S. W. Benson, *J. Amer. Chem. Soc.*, 1963, **85**, 2887.
[34] G. C. Fettis, J. H. Knox, and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1960, 4177.
[35] W. M. Jackson, J. R. McNesby, and B. deB. Darwent, *J. Chem. Phys.*, 1962, **37**, 1610.
[36] A. S. Gordon and S. R. Smith, *J. Phys. Chem.*, 1962, **66**, 521.
[37] P. B. Ayscough, J. C. Polanyi, and E. W. R. Steacie, *Canad. J. Chem.*, 1955, **33**, 743.
[38] P. B. Ayscough and E. W. R. Steacie, *Canad. J. Chem.*, 1956, **34**, 103.
[39] G. O. Pritchard, H. O. Pritchard, H. I. Schiff, and A. F. Trotman-Dickenson, *Trans. Faraday Soc.*, 1956, **52**, 849.
[40] S. W. Benson, 'Thermochemical Kinetics', Wiley, New York, 1968.

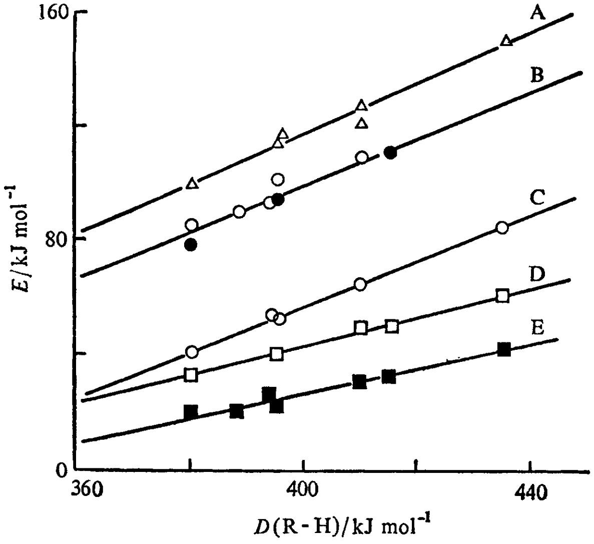

Figure *Polanyi plot for* X + RH *where* X = A, ·I; B, ·NF_2; C, ·Br; D, ·Me; E, ·CF_3. *The values for* ·I *and* ·Br *have been displaced upwards by* 10 kJ mol^{-1}

249.8 J mol^{-1} K^{-1}, $\Delta H_f°(HNF_2)$ as[41] −65.3 kJ mol^{-1}, and $S°(HNF_2)$ as[42] 253.1 J mol^{-1} K^{-1}. The thermochemical values for the alkanes and alkyl radicals were taken from refs. 40 and 43. The only Arrhenius parameters published for a comparable reaction are those for the attack of methyl radicals on ammonia, which has been found[44] to have a considerably higher activation energy of abstraction, probably owing to a stronger N—H bond being broken.

B. Alkenes.—The Arrhenius parameters for the hydrogen-abstraction reaction from alkenes[22,45,46] by difluoroamino-radicals are given in Table 6. But-1-ene produces three products, each with the same molecular weight and each in the same amount. Complete analysis of the three isomers, however, has not been carried out.[47] In general, these results for the hydrogen abstraction from alkenes are not in agreement with those for the hydrogen abstraction from alkanes,[4,28]

[41] A. V. Pankratov, A. N. Zercheninov, V. I. Chesnokov, and N. N. Zhdanova, *Russ. J. Phys. Chem.*, 1969, **43**, 212.
[42] K. Mitteilungen, *Z. phys. Chem.*, 1963, **39**, 262.
[43] S. W. Benson and H. E. O'Neal, 'Kinetic Data on Gas Phase Unimolecular Reactions', NSRDS-NBS 21, Washington D.C., 1970.
[44] D. A. Edwards, J. A. Kerr, A. C. Lloyd, and A. F. Trotman-Dickenson, *J. Chem. Soc.* (*A*), 1966, 621.
[45] C. Dodwell, unpublished work.
[46] D. G. E. Probert, Ph.D. Thesis, University of Wales, 1966.
[47] C. Dodwell, personal communication.

Table 5 *Summary*[a] *of results for attack of alkyl radicals on difluoroamino-radicals* [*Reaction* (−13)]

RH	ΔH_f°(RH)/ kJ mol^{-1}	ΔH_f°(R·)/ kJ mol^{-1}	S°(RH)/ J mol^{-1} K^{-1}	S°(R·)/ J mol^{-1} K^{-1}	E_{-13}/ kJ mol^{-1}	$\log A_{-13}$/ ml mol^{-1} s^{-1}
Propane (p)	−104.0	87.9	269.9	286.3	18.0 ± 8.4	11.8 ± 0.4
(s)	−104.0	73.6	269.9	278.8	17.6 ± 8.4	9.7 ± 0.6
n-Butane (s)	−126.2	52.7	310.1	318.4	25.3 ± 8.4	11.7 ± 0.3
Isobutane (t)	−134.5	28.0	294.5	312.1	14.4 ± 8.4	10.0 ± 0.3
Cyclopentane	−77.4	102.1	292.9	301.2	13.7 ± 8.4	10.8 ± 0.4

[a] The errors are based upon errors in data used. Thermochemical values taken from refs. 40 and 43.

Table 6 *Rates of hydrogen abstraction from alkenes by difluoroamino-radicals*

Alkene	*Temperature range*/K	*E*/ kJ mol^{-1}	log *A*/ ml mol^{-1} s^{-1}	*Ref.*
But-1-ene	334 -424	64.0	9.32	45
3-Methylbut-1-ene	352—424	60.2	9.20	45
Penta-1,4-diene	352—424	46.0	7.7	45
Cyclopentene	334—391	56.1	9.1	22
Cyclohexene	373—405	61.5	10.22	46

the activation energies being some 40 kJ mol^{-1} and the *A* factors about a factor of 10 lower than those for alkanes. These discrepancies are surprising as the results for the alkenes are based upon the rate of formation of the difluoroamine product, the rate of disappearance of both the difluoroamino-radical and the olefin owing to the addition reaction being taken into account.

C. Aldehydes.—Aldehydic hydrogen abstraction by difluoroamino-radicals to form the corresponding *NN*-difluoroamide and difluoroamine (HNF_2) was reported in the early sixties,[48] but the reaction was not studied quantitatively until the late sixties.[49–51] Aldehydic hydrogen-abstraction reactions by alkyl radicals have been investigated,[52–63] but the corresponding acyl radical decom-

Table 7 *Aldehydic hydrogen abstraction by difluoroamino-radicals*

Aldehyde	E_{18}/ kJ mol^{-1}	log A_{18}/ ml mol^{-1} s^{-1}	*Temperature*/ K	*Ref.*
Acetaldehyde	69.6	10.37	353—448	50
Propionaldehyde	70.7	10.75	373—448	49
n-Butyraldehyde	68.1	10.57	353—423	49
Isobutyraldehyde	65.8	10.31	353—423	49
n-Valeraldehyde	66.7	10.78	353—423	50
Isovaleraldehyde	66.7	10.78	353—423	50

[48] R. C. Petry and J. P. Freeman, *J. Amer. Chem. Soc.*, 1961, **83**, 3912.

[49] P. Cadman, C. Dodwell, A. F. Trotman-Dickenson, and A. J. White, *J. Chem. Soc. (A)*, 1970, 2371.

[50] P. Cadman, A. F. Trotman-Dickenson, and A. J. White, *J. Chem. Soc. (A)*, 1970, 3189.

[51] A. J. White, Ph.D. Thesis, University of Wales, 1970.

[52] R. K. Brinton and D. H. Volman, *J. Chem. Phys.*, 1952, **20**, 1053.

[53] G. O. Pritchard, H. O. Pritchard, and A. F. Trotman-Dickenson, *J. Chem. Phys.*, 1953, **21**, 748.

[54] P. Ausloos and E. W. R. Steacie, *Canad. J. Chem.*, 1955, **33**, 31.

[55] R. E. Dodd, *Canad. J. Chem.*, 1955, **33**, 699.

[56] R. N. Birrell and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1960, 2059.

[57] R. E. Dodd and J. W. Smith, *J. Chem. Soc.*, 1957, 1465.

[58] D. H. Volman and R. K. Brinton, *J. Chem. Phys.*, 1954, **22**, 929.

[59] J. A. Kerr and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1960, 1611.

[60] J. A. Kerr and A. F. Trotman-Dickenson, *Trans. Faraday Soc.*, 1959, **55**, 572.

[61] J. A. Kerr and A. F. Trotman-Dickenson, *Trans. Faraday Soc.*, 1959, **55**, 921.

[62] J. A. Kerr and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1960, 1602.

[63] E. L. Metcalfe and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1960, 5072.

Table 8 *Summary*[a] *of results for attack of acyl radicals on difluoroamine* [*reaction* (−18)]

R	$\Delta H_f°$ (RCHO)/ kJ mol^{-1}	*Ref.*	$\Delta H_f°$ ($R\dot{C}O$)/ kJ mol^{-1}	*Ref.*	$S°$(RCHO)/ J mol^{-1} K^{-1}	*Ref.*	$S°$($R\dot{C}O$)/ J mol^{-1} K^{-1}	*Ref.*	ΔH_{18}/ kJ mol^{-1}	E_{-18}/ kJ mol^{-1}	log A_{-18}/ ml mol^{-1} s^{-1}
Me	−165.9	64	−24.2	64	263.8	64	265.4	40	41.0±8.4	28.4±8.4	10.1±1.0
Et	−190.6	65	−41.8	estimated	306.8	66	304.7	estimated	48.1±12.5	22.6±12.5	10.7±1.0
Pr^n	−204.4	65	−62.3	estimated	345.3	66	344.0	estimated	41.4±12.5	26.8±12.5	10.4±1.0
Pr^i	−216.1	estimated	−71.1	estimated	349.9	estimated	341.9	estimated	41.0±12.5	24.7±12.5	10.6±1.0
Bu^n	−227.8	estimated	−86.5	estimated	391.2	estimated	383.7	estimated	40.5±12.5	32.6±12.5	11.3±1.0
Bu^i	−236.6	estimated	−94.9	estimated	389.2	estimated	381.6	estimated	41.0±12.5	25.9±12.5	11.0±1.0

[a] The errors are estimates based upon the errors of the data used. Estimated values based upon the additivity rules in reference 40.
$\Delta H_f°(\cdot NF_2)$ taken as 35.5 kJ mol^{-1} (ref. 13) and $\Delta H_f°(HNF_2)$ as −65.2 kJ mol^{-1} (ref. 41).
$S°(\cdot NF_2)$ taken as 249.5 J mol^{-1} K^{-1} (ref. 40) and $S°(HNF_2)$ as 252.9 J mol^{-1} K^{-1} (ref. 42).

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[64] J. A. Devore and H. E. O'Neal, *J. Phys. Chem.*, 1969, **73**, 2644.

[65] E. Buckley and J. D. Cox, *Trans. Faraday Soc.*, 1967, **63**, 895.

[66] I. A. Vasil'ev and A. A. Vvedenskii, *Russ. J. Phys. Chem.*, 1966, **40**, 453.

position reaction was not studied because of the complexity of the systems. Aldehydic hydrogen abstraction by difluoroamino-radicals, however, afforded a simple method of producing the acyl radical and, because the difluoroamino-radical acts as a 'radical-trap', the acyl radical decomposition reactions were studied quantitatively.[49–51] The suggested mechanism is given in equations (18)—(23):

$$\mathrm{RCHO} + \cdot\mathrm{NF_2} \rightarrow \mathrm{R\dot{C}O} + \mathrm{HNF_2} \qquad (18)$$

$$\mathrm{R\dot{C}O} + \mathrm{M} \rightarrow \mathrm{R\dot{C}O^*} + \mathrm{M} \qquad (19)$$

$$\mathrm{R\dot{C}O^*} + \mathrm{M} \rightarrow \mathrm{R\dot{C}O} + \mathrm{M} \qquad (20)$$

$$\mathrm{R\dot{C}O^*} \rightarrow \mathrm{R}\cdot + \mathrm{CO} \qquad (21)$$

$$\mathrm{R}\cdot + \cdot\mathrm{NF_2} \rightarrow \mathrm{RNF_2} \qquad (22)$$

$$\mathrm{R\dot{C}O} + \cdot\mathrm{NF_2} \rightarrow \mathrm{RCONF_2} \qquad (23)$$

The results for the aldehydic hydrogen-abstraction reaction by the difluoroamino-radical are given in Table 7. The A factors for the attack of difluoroamino-radicals on aldehydes are less than those for the corresponding attack by alkyl radicals.[52–63] Low A factors for hydrogen abstraction by difluoroamino-radicals appear to be the norm rather than the exception (for a more detailed discussion of this see Section 5). Table 7 shows that the Arrhenius parameters are very similar for one particular radical attacking a series of aldehydes. This is indicative, though not conclusive, of constant RCO—H bond energies in this series of aldehydes. This is also indicated by the fairly consistent values of ΔH_{18} in Table 8. As $\Delta H_{18} = D(\mathrm{F_2N{-}H}) - D(\mathrm{RCO{-}H})$, and $D(\mathrm{F_2N{-}H})$ is a constant, ΔH_{18} will be constant if $D(\mathrm{RCO{-}H})$ is independent of the R group. The average value of ΔH_{18} is 42.2 kJ mol^{-1}, hence the mean aldehydic bond strength in this series of aldehydes is 361 kJ mol^{-1} [assuming[50] that $D(\mathrm{F_2N{-}H})$ is 319 kJ mol^{-1}].

ΔH_{18} is also related to the activation energies of the forward and back reactions of reaction (18) by $\Delta H_{18} = E_{18} - E_{-18}$ ($\Delta n = 0$). Hence E_{-18} can be estimated (see Table 8). The A factors of the forward and back reactions of reaction (18) are also related by $\log (A_{18}/A_{-18}) = \Delta S_{18}/2.3R$, hence $\log A_{-18}$ can be estimated (see Table 8). Very few abstractions are known with which the values calculated for E_{-18} and $\log A_{-18}$ can be compared. The energy of abstraction of hydrogen from hydrogen iodide[67] by acetyl radicals has been found to be 6.3 kJ mol^{-1}. From thermochemical considerations, the reactions of acyl radicals with difluoroamine might be expected to have slightly higher activation energies as the bond in difluoroamine is about 20 kJ mol^{-1} stronger than in hydrogen iodide. The calculated values of E_{-18} are in the region 20—30 kJ mol^{-1} and therefore seem plausible. The abstraction of hydrogen from hydrogen bromide[68] by acetyl radicals does not fit the calculated results, but as this reaction was only inferred and not measured directly, the results might be considered suspect.

[67] H. E. O'Neal and S. W. Benson, *J. Chem. Phys.*, 1962, **37**, 540.

[68] M. J. Ridge and E. W. R. Steacie, *Canad. J. Chem.*, 1955, **33**, 383.

D. Ketones.—Table 9 summarizes the results of the hydrogen abstraction by difluoroamino-radicals from ketones.[5,69,70] The Arrhenius parameters for this attack were obtained by following the consumption of ketone with time. Both the *A* factors and the activation energies are lower than those obtained for the attack of difluoroamino-radicals on alkanes[4] using this same method, and they are considerably lower than those obtained by measuring the rate of formation of the alkyl-difluoroamine.[28] This indicates that the method of measuring the rate of disappearance of the ketone must be suspect, probably owing to impurities released by the attack of difluoroamine and/or the difluoroamino-radical on the Pyrex glass at the higher temperatures employed.

Table 9 *Hydrogen abstraction by difluoroamino-radicals from ketones*

Ketone	*Temperature range*/K	*E*/ kJ mol^{-1}	log *A*/ ml mol^{-1} s^{-1}	*Ref.*
Me_2CO	451—553	81.3	10.7	5
Et_2CO	453—555	72.5	10.2	69
Pr^iCOMe	453—555	79.2	10.8	70

E. Formates.—Thynne[71–73] investigated the decomposition of alkyl formates by methyl radical photosensitization. He concluded that the formyl hydrogen atom was attacked exclusively and that the decomposition of the alkoxy-carbonyl radical so produced was a good 'thermal' source of alkyl radicals. Grotewold and Kerr,[74] however, claimed that abstraction from the alkoxy-group of n-propyl formate occurs to a significant extent. Arthur and Gray[75] have employed the use of isotopic labelling to determine the position and extent of hydrogen abstraction from the formyl and methoxy sites in methyl formate by methyl and trifluoromethyl radicals. They found that attack was principally at the formyl group, but at 455 K a significant proportion of abstraction occurred from the methoxy-group. Similar conclusions were reached by Donovan *et al.*[76] using methyl and [$^2H_3$]methyl radicals and methyl formate and methyl [^2H]formate.

The reaction of n-propyl formate and the difluoroamino-radical has been investigated,[77] the proposed mechanism being given by equations (24)—(27):

$$\cdot NF_2 + HCO_2Pr^n \rightarrow HNF_2 + \cdot CO_2Pr^n \qquad (24)$$

$$\cdot CO_2Pr^n \rightarrow Pr^{n}\cdot + CO_2 \qquad (25)$$

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[69] J. Grzechowiak, *Roczniki Chem.*, 1966, **40**, 895.
[70] J. Grzechowiak, *Chem. Stosowana* (*A*), 1967, **11**, 215.
[71] J. C. J. Thynne, *Trans. Faraday Soc.*, 1962, **58**, 676.
[72] J. C. J. Thynne, *Trans. Faraday Soc.*, 1962, **58**, 1394.
[73] J. C. J. Thynne, *Trans. Faraday Soc.*, 1962, **58**, 1533.
[74] J. Grotewold and J. A. Kerr, *J. Chem. Soc.*, 1963, 4342.
[75] N. L. Arthur and P. Gray, *Trans. Faraday Soc.*, 1969, **65**, 424.
[76] T. R. Donovan, W. Dorko, and A. G. Harrison, *Canad. J. Chem.*, 1971, **48**, 828.
[77] P. Cadman, A. J. White, and A. F. Trotman-Dickenson, *J.C.S. Faraday I*, 1972, **68**, 506.

$$\mathrm{Pr^{n}\cdot + \cdot NF_2 \rightarrow Pr^{n}NF_2} \qquad (26)$$

$$\mathrm{\cdot NF_2 + \cdot CO_2Pr^{n} \rightarrow NF_2CO_2Pr^{n}} \qquad (27)$$

The rate equation was found to be given by log k_{24} (in ml $\mathrm{mol^{-1}\,s^{-1}}$) = 8.48 ± 0.88 − (77 800 ± 7200)/2.3RT where R = 8.314 J $\mathrm{mol^{-1}\,K^{-1}}$.

The A factor for this formyl hydrogen abstraction reaction by difluoroamino-radicals is about 10^2 lower than a 'normal' A factor for hydrogen-abstraction reactions by difluoroamino-radicals. Abstraction of the formyl hydrogen by methyl radicals has also been found to have a lower A factor than found for other methyl radical reactions. No hydrogen abstraction from the n-propoxy-group was observed even at the higher temperatures – the product was looked for but was not found. Because of the unusually low A factor, the results were tested fairly rigorously for consistency with the proposed mechanism.[77]

Although the extent of methyl radical attack on the alkoxy-group has not completely been resolved, it seems certain that the formyl hydrogen is much more reactive than the alkoxy-group. It is expected that difluoroamino-radicals, which are much less reactive than methyl, would be more discriminating and hence would be even less likely to attack the n-propoxy-group. This is confirmed by the absence of any products from this reaction.

Comparison of the activation energies for the attack of methyl,[71–76] iodine,[78] and difluoroamino-radicals on alkyl formates shows that difluoroamino-radicals are slightly more reactive than iodine atoms but much less reactive than methyl. This is the same order of reactivity found for the attack on alkanes[4,28] and aldehydes.[49,50]

5 Combination Reactions

The cross-combination reaction of difluoroamino-radicals with ethyl and isopropyl radicals was investigated[79] by photolysing the corresponding dialkyl ketone in the presence of very small concentrations of tetrafluorohydrazine, and hence the difluoroamino-radical. The results can be discussed in terms of the mechanism in equations (28)—(32):

$$\mathrm{RCOR} + h\nu \rightarrow \mathrm{R\cdot + R\dot{C}O^{+}} \qquad (28)$$

$$\mathrm{R\dot{C}O^{+} \rightarrow R\cdot + CO} \qquad (29)$$

$$\mathrm{R\cdot + R\cdot \rightarrow R{-}R} \qquad (30)$$

$$\mathrm{R\cdot + \cdot NF_2 \rightarrow RNF_2} \qquad (31)$$

$$\mathrm{R\dot{C}O + \cdot NF_2 \rightarrow RCONF_2} \qquad (32)$$

where $\mathrm{R\dot{C}O^{+}}$ is vibrationally excited.

The mechanism involved in the photolysis of both diethyl and di-isopropyl

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[78] R. K. Solly and S. W. Benson, *Internat. J. Chem. Kinetics*, 1969, **1**, 427.

[79] P. Cadman, Y. Inel, A. F. Trotman-Dickenson, and A. J. White, *J. Chem. Soc.* (*A*), 1971, 1353.

ketones is well known[80] and occurs *via* reactions (28)—(30). Reactions (31) and (32) are invoked to explain the products found in the presence of difluoroamino-radicals.

On photolysing diethyl ketone in the presence of small concentrations of the difluoroamino-radical above 373 K, the only products found were n-butane and *NN*-difluoroethylamine. No *NN*-difluoropropionamide was formed. From the proposed mechanism,

$$\frac{-\mathrm{d}[\cdot\mathrm{NF_2}]}{\mathrm{d}t} = \frac{\mathrm{d}[\mathrm{C_2H_5NF_2}]}{\mathrm{d}t} = k_{31}[\mathrm{C_2H_5}\cdot]\,[\cdot\mathrm{NF_2}] \qquad (33)$$

and

$$[\mathrm{C_2H_5}\cdot] = (R_{\mathrm{C_4H_{10}}})^{\frac{1}{2}}/k_{30}^{\frac{1}{2}} \qquad (34)$$

Substituting for ethyl in (33) and integrating between the limits $[\cdot\mathrm{NF_2}]_\mathrm{i}$ at time = 0 and $[\cdot\mathrm{NF_2}]_\mathrm{f}$ at time = t gives

$$k_{31} = \frac{2.303k_{30}^{\frac{1}{2}}}{(R_{\mathrm{C_4H_{10}}})^{\frac{1}{2}}t}\log\frac{[\cdot\mathrm{NF_2}]_\mathrm{i}}{[\cdot\mathrm{NF_2}]_\mathrm{f}} \qquad (35)$$

As

$$[\mathrm{N_2F_4}]_\mathrm{i} = [\mathrm{N_2F_4}]_\mathrm{f} + \tfrac{1}{2}[\mathrm{C_2H_5NF_2}] \qquad (36)$$

and the initial and final concentrations of $[\cdot\mathrm{NF_2}]$ are related to the concentrations of $[\mathrm{N_2F_4}]$, k_{31} can be calculated from equation (35).

Below 360 K appreciable amounts of *NN*-difluoropropionamide were formed by reaction (32) occurring as well as reaction (29). The above method could not then be used to calculate k_{31}. In these runs the conversion of tetrafluorohydrazine was kept to less than 10% and equation (37) was used to calculate k_{31}, where $[\cdot\mathrm{NF_2}]_\mathrm{av}$ is the average concentration of difluoroamino-radicals:

$$k_{31} = (R_{\mathrm{C_2H_5NF_2}})\,k_{30}^{\frac{1}{2}}/(R_{\mathrm{C_4H_{10}}})^{\frac{1}{2}}\,[\cdot\mathrm{NF_2}]_\mathrm{av} \qquad (37)$$

$$[\mathrm{N_2F_4}]_\mathrm{i} = [\mathrm{N_2F_4}]_\mathrm{f} + \tfrac{1}{2}[\mathrm{C_2H_5NF_2}] + \tfrac{1}{2}[\mathrm{C_2H_5CONF_2}] \qquad (38)$$

In all cases good agreement existed between $[\mathrm{N_2F_4}]_\mathrm{i}$ calculated by equations (36) or (38) and that measured on the gas burette, although the calculated values were used as they were thought to be more accurate.

The interference of the disproportionation reaction (39) in regard to the use of (36) or (38) is small.[81] Photolysis of diethyl ketone in the presence of varying ratios of difluoroamino-radicals and tetrafluorohydrazine indicates that reaction (40) was not important.

$$\mathrm{C_2H_5}\cdot + \cdot\mathrm{NF_2} \rightarrow \mathrm{C_2H_4} + \mathrm{HNF_2} \qquad (39)$$

$$\mathrm{C_2H_5}\cdot + \mathrm{N_2F_4} \rightarrow \mathrm{C_2H_5NF_2} + \cdot\mathrm{NF_2} \qquad (40)$$

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[80] J. C. Calvert and J. N. Pitts, jun., 'Photochemistry', Wiley, New York, 1966, pp. 396, 402.

[81] P. Cadman, Y. Inel, and A. F. Trotman-Dickenson, *J. Chem. Soc.* (*A*), 1971, 2859.

The rate of attack of difluoroamino-radicals on diethyl ketone [equation (41)] is small[69] in this temperature range and so can be neglected.

$$\cdot NF_2 + C_2H_5COC_2H_5 \rightarrow HNF_2 + \dot{C}_2H_4COC_2H_5 \qquad (41)$$

Using Hiatt and Benson's value[82] of $10^{11.6}$ ml mol^{-1} s^{-1} for k_{30}, log k_{31} (in ml mol^{-1} s^{-1}) = $(8.2 \pm 0.5) - (1100 \pm 3400)/2.3RT$ where $R = 8.314$ J mol^{-1} K^{-1}.

The results obtained for the di-isopropyl ketone photolysis in the presence of small concentrations of difluoroamino-radicals showed that no *NN*-difluorobutyramide was detected even at room temperature, so presumably any isobutyryl radicals formed as in equation (28) decompose by equation (29). This is supported by the mass balance of difluoroamino-radicals obtained using equation (36) above. k_{31} was calculated using equations (35) and (36) together with Hiatt and Benson's value[83] of $10^{11.6}$ ml mol^{-1} s^{-1} for k_{30}. The disproportionation of isopropyl and difluoroamino-radicals [equation (42)] has been found[81] to be much smaller than the combination [equation (31)] and can be disregarded by comparison with equation (34).

$$\text{i-}C_3H_7\cdot + \cdot NF_2 \rightarrow HNF_2 + C_3H_6 \qquad (42)$$

Least-mean-square analysis of the results gave log k_{31} (in ml mol^{-1} s^{-1}) = $(9.2 \pm 0.3) - (5300 - 1700)/2.3RT$ where $R = 8.314$ J mol^{-1} K^{-1}.

The results show that the rate of combination of both ethyl and isopropyl radicals with difluoroamino-radicals is much smaller than that for ethyl–ethyl and isopropyl–isopropyl recombinations. They are, however, in the same region as that for t-butyl–t-butyl radical recombination.[84] The small activation energies are probably not significant considering the experimental error.

From the collision diameters of ethyl,[85] isopropyl,[86] and difluoroamino-radicals[87] the collisional efficiency for combination of these alkyl radicals with difluoroamino-radicals can be calculated to be 10^{-4}—10^{-5}, compared with the value of about 10^{-2} obtained for small alkyl–radical combinations.[82–84] This slower rate of combination involving difluoroamino-radicals was predicted by Simons[20] from MO calculations. He concluded that the unpaired electron, being in a $2b_1\,\pi$-orbital perpendicular to the molecular plane and held near the nitrogen by the inductive effect of the fluorine atoms, hampers the reactions of difluoroamino-radical. Suitable orientation and close contact must both occur before any orbital overlap is possible. This factor also explains the low pre-exponential factor obtained in abstraction reactions of difluoroamino-radical.

Table 10 shows the results for difluoroamino-radical combination reactions. The acyl radical–difluoroamino-radical combination must have a value close to the collision frequency in order to give reasonable *A* factors for the acyl radical

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[82] R. Hiatt and S. W. Benson, *J. Amer. Chem. Soc.*, 1972, **94**, 6886.

[83] R. Hiatt and S. W. Benson, *Internat. J. Chem. Kinetics*, 1972, **4**, 151.

[84] R. Hiatt and S. W. Benson, *Internat. J. Chem. Kinetics*, 1973, **5**, 385.

[85] H. S. Johnston, 'Gas Phase Reaction Rate Theory', Ronald Press, New York, 1966, p. 153.

[86] J. S. Rowlinson, *Quart. Rev.*, 1954, **8**, 168.

[87] L. M. Brown and B. deB. Darwent, *J. Chem. Phys.*, 1965, **42**, 2158.

Table 10 *Difluoroamino-radical–radical combination reactions*

Radical	*Temperature*/K	*Rate constant*/ ml mol^{-1} s^{-1}	*Ref.*
$\cdot NF_2$	400	3×10^{10}	87
$\cdot$Et	297—448	1.6×10^{8}	79[b]
$\cdot$Pr^i	297—448	$\log k = 9.2 - 5300/2.3RT$	79[b]
R$\dot{C}$O [a]	353—448	10^{14}	49, 50
Pr^{n}O$\dot{C}$O	398—463	$10^{13} - 10^{14}$	77
Bu^{t}O$\cdot$	373—423	3.16×10^{10}	88

[a] R group in R$\dot{C}$O = Et, Pr^n, Pr^i, Bu^n, or Bu^i.
[b] Recalculated using refs. 82 and 83.

decomposition and formation reactions[43,50] and to correlate with previous results.[89,90] It would therefore be surprising if this rate was much less than 10^{14} ml mol^{-1} s^{-1}. These arguments also apply to the combination of n-propoxycarbonyl radicals with difluoroamino-radicals.[77] If this rate was much lower than 10^{14}, then the A factor for the n-propoxycarbonyl radical decomposition would be low, whereas evidence[78] favours a normal value for this type of radical decomposition. The rate of combination of t-butoxyl and difluoroamino-radicals has been assumed[88] to be $10^{10.5}$ ml mol^{-1} s^{-1}.

In order to rationalize these different values and the results of Simons' calculations,[20] it is possible that combination rates are slow except where there is a carbonyl multiple bond adjacent to the odd electron. The carbonyl π-orbital may be able to overlap much more easily with the $2b_1$ π-orbital of the difluoroamino-radical than can the σ-orbital of the free electron.

The rates of combination reactions of nitric oxide, nitrogen dioxide, and amino-radicals[40,43,91–96] with themselves and with alkyl and alkoxyl radicals have also been found to be in the range 10^{9}—10^{12} ml mol^{-1} s^{-1}, *i.e.* similar to the difluoroamino-radical. Benson[43] has discussed these low rates. The results presented in this review support his suggestion that the combination rates of species containing the unpaired electron on a nitrogen atom are often anomalous. It is unfortunate that no acyl radical–nitric oxide or –nitrogen dioxide cross-combination reactions have been reported with which to compare the acyl radical–difluoroamino-radical combination and its suggested high value.

The entropies of *NN*-difluoroethylamine and *NN*-difluoroisopropylamine can

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[88] P. Cadman, A. F. Trotman-Dickenson, and A. J. White, *J. Chem. Soc. (A)*, 1971, 2296.
[89] J. A. Kerr and A. C. Lloyd, *Trans. Faraday Soc.*, 1967, **63**, 2480.
[90] H. E. O'Neal and S. W. Benson, *J. Chem. Phys.*, 1964, **40**, 302.
[91] L. Phillips and R. Shaw, '10th International Symposium on Combustion', Pittsburg, Pennsylvania, The Combustion Institute, 1964, p. 453.
[92] I. M. Napier and R. G. W. Norrish, *Proc. Roy. Soc.*, 1967, **A299**, 313.
[93] W. C. Sleppy and J. G. Calvert, *J. Amer. Chem. Soc.*, 1959, **81**, 769.
[94] M. I. Christie and J. S. Frost, *Trans. Faraday Soc.*, 1965, **61**, 468.
[95] D. L. Cox, R. A. Livermore, and L. Phillips, *J. Chem. Soc. (B)*, 1966, 245.
[96] T. Carrington and N. Davidson, *J. Phys. Chem.*, 1953, **57**, 418.

be calculated from that of *NN*-difluoromethylamine[97] by bond additivity principles to be 321.3 and 358.6 J mol^{-1} K^{-1}. Using the known entropies[40] of ethyl, isopropyl, and difluoroamino-radicals, $\Delta S_{31}{}^{\circ}$ can be calculated to be -178.7 and -170.3 J mol^{-1} K^{-1} at 298 K, respectively (standard state 1 mol ml^{-1}). From the pre-exponential factors given above for equation (31), log A_{-31} can then be calculated as 13.9 (R = Et) and 14.4 (R = Pr^{i}). These values are slightly lower than usually found for the decomposition reactions of compounds into radicals.

6 Disproportionation Reactions

The disproportionation reactions of alkyl radicals to give alkenes and alkanes are well known,[98–100] although the question whether this reaction takes place *via* the same transition state as occurs in combination or *via* a different one has not yet been settled. It has been suggested that loose bending frequencies occurring in the combination transition state are responsible for the occurrence of disproportionation reactions.[98,101] Benson[102] has suggested an ionic transition state for disproportionation, different from that for combination.

Disproportionation reactions between radicals other than two alkyls have not been as well studied, although they have been reported to occur between alkyl radicals and nitric oxide,[103] alkyl and amino-radicals,[104,105] alkoxyl radicals and nitric oxide,[106–111] and also alkyl and difluoroamino-radicals.[81] This latter reaction was studied by photolysing di-isopropyl ketone and methyl t-butyl ketone in the presence of tetrafluorohydrazine.

The photolysis of di-isopropyl ketone is well known,[80] and the products formed in the presence of tetrafluorohydrazine can be explained in terms of reactions (43)—(46):

$$(\text{i-C}_3\text{H}_7)_2\text{CO} + h\nu \rightarrow 2\ \text{i-C}_3\text{H}_7\cdot + \text{CO} \qquad (43)$$

$$\text{N}_2\text{F}_4 \rightleftharpoons 2\,\cdot\text{NF}_2 \qquad (44)$$

$$\text{i-C}_3\text{H}_7\cdot + \cdot\text{NF}_2 \rightarrow \text{i-C}_3\text{H}_7\text{NF}_2 \qquad (45)$$

$$\rightarrow \text{C}_3\text{H}_6 + \text{HNF}_2 \qquad (46)$$

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[97] L. P. Pierce, R. G. Hayes, and J. F. Beecher, *J. Chem. Phys.*, 1967, **46**, 4352.
[98] J. A. Kerr and A. F. Trotman-Dickenson, *Progr. Reaction Kinetics*, 1961, **1**, 107.
[99] A. F. Trotman-Dickenson and G. S. Milne, 'Tables of Bimolecular Reactions', NSRDS-NBS9, Washington D.C., 1967.
[100] E. Ratajczak and A. F. Trotman-Dickenson, 'Supplementary Tables of Bimolecular Gas Reactions', UWIST, Cardiff, 1970.
[101] J. N. Bradley, *J. Chem. Phys.*, 1961, **35**, 748.
[102] S. W. Benson, *Adv. Photochem.*, 1964, **2**, 1.
[103] J. Heicklen and N. Cohen, *Adv. Photochem.*, 1968, **5**, 284.
[104] W. E. Groth, U. Schurath, and R. N. Schlindler, *J. Phys. Chem.*, 1968, **72**, 3914.
[105] U. Schurath, P. Tiedemann, and R. N. Schlindler, *J. Phys. Chem.*, 1969, **73**, 456.
[106] E. A. Arden, L. Phillips, and R. Shaw, *J. Chem. Soc.*, 1964, 5126.
[107] R. A. Livermore and L. Phillips, *J. Chem. Soc.* (*B*), 1966, 640.
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Now difluoroamino-radicals add to propene to give 1,2-bis(difluoroamino)propane[21] [reaction (47)] and this reaction consumes between 0 and 15% of the propene formed in reaction (46), depending on the temperature. The rate of addition has been shown to be limited by the addition of one difluoroamino-radical to the double bond of the alkene and this rate is given by equation (48), where k_{47} is a composite rate coefficient calculated from the rate coefficients of the individual steps of the mechanism and depending on the total pressure of the system.

$$\mathrm{Ol} + 2\cdot\mathrm{NF_2} \rightarrow \mathrm{Ol(NF_2)_2} \tag{47}$$

$$\frac{\mathrm{d}[\mathrm{C_3H_6(NF_2)_2}]}{\mathrm{d}t} = k_{47}[\cdot\mathrm{NF_2}][\mathrm{C_3H_6}] = -\frac{\mathrm{d}[\mathrm{C_3H_6}]}{\mathrm{d}t} \tag{48}$$

As propene is formed in reaction (46) and consumed in reaction (47), $\Delta(\cdot\mathrm{NF_2}, \cdot\mathrm{Pr^i})$ is corrected for the loss of propene *via* reaction (47) in equation (49):

$$\Delta(\cdot\mathrm{NF_2}, \cdot\mathrm{Pr^i}) = \frac{k_{47}[\cdot\mathrm{NF_2}][\mathrm{C_3H_6}]_t}{R(\mathrm{C_3H_7NF_2})\ \{1 - \exp(-k_{47}[\cdot\mathrm{NF_2}]t)\}} \tag{49}$$

Values of k_{47} were calculated from the rate coefficients of the individual steps in the addition of difluoroamino-radicals to propene which have been published previously.[21] The consumption of propene in terms of percentage loss calculated from relation (49) was found to be significant only at the higher temperatures and never > 15%.

Variation of the concentrations of di-isopropyl ketone and difluoroamino-radicals was found to have no effect on the values of $\Delta(\cdot\mathrm{NF_2}, \cdot\mathrm{Pr^i})$.

The reaction of isopropyl radicals with tetrafluorohydrazine itself can be neglected.[79] The reaction of ethyl radicals with tetrafluorohydrazine [equation (50)] was shown to be unimportant.

$$\mathrm{C_2H_5\cdot} + \mathrm{N_2F_4} \rightarrow \mathrm{C_2H_5NF_2} + \cdot\mathrm{NF_2} \tag{50}$$

$\Delta(\cdot\mathrm{NF_2}, \cdot\mathrm{Pr^i})$ was found to be given by equation (51):

$$\Delta(\cdot\mathrm{NF_2}, \cdot\mathrm{Pr^i}) = (0.0535 \pm 0.005)\exp[+(595 \pm 300)/RT] \tag{51}$$

Methyl t-butyl ketone–tetrafluorohydrazine mixtures were photolysed between 291 and 485 K. The products from the reactions of methyl radicals or R—C=O (where R = Me or $\mathrm{Bu^t}$) with difluoroamino-radicals do not interfere with the analysis or reaction scheme and were not separated in the chromatography. The concentration of difluoroamino-radicals was kept much larger than the concentration of the alkyl radicals to eliminate the reactions between alkyl radicals. No trace of products arising from the reactions between methyl and t-butyl radicals was found.

The products, isobutene and t-butyldifluoroamine, can be explained in terms of the same scheme as before – equations (52)—(54):

$$t\text{-}C_4H_9COCH_3 + h\nu \rightarrow t\text{-}C_4H_9\cdot + CH_3CO\cdot \qquad (52)$$

$$t\text{-}C_4H_9\cdot + \cdot NF_2 \rightarrow t\text{-}C_4H_9NF_2 \qquad (53)$$

$$\rightarrow C_4H_8 + HNF_2 \qquad (54)$$

The rate of addition of difluoroamino-radicals to the product isobutene is faster than the rate of addition to propene. The correction for the loss of isobutene *via* reaction (47) was therefore larger than in the case of propene but was made using the same method.

No Arrhenius parameters were reported for the addition of difluoroamino-radicals to isobutene[22] but the reaction was studied up to 373 K. The large values obtained for k_{47} necessitated larger olefin to difluoroamino-radical ratios to be able to measure k_{47} and this resulted in telomerization. The olefin to difluoroamino-radical ratio is much lower and so telomerization is less likely. The results obtained for the addition of difluoroamino-radicals to isobutene were extrapolated.

$\Delta(\cdot NF_2, \cdot Bu^t)$ was found to be given by equation (55):

$$\Delta(\cdot NF_2, \cdot Bu^t) = (1.98 \pm 0.20) \exp[-(9140 \pm 330)/RT] \qquad (55)$$

The disproportionation–combination ratio between ethyl and difluoroamino-radicals could not be measured with the experimental arrangement used for isopropyl and t-butyl radicals because the disproportionation product, ethylene, has the same molecular weight as the carrier gas, nitrogen. From the results it is likely that this ratio is probably also small.

The disproportionation–combination ratio of isopropyl radicals with difluoroamino-radicals is less than that of the corresponding ratio of t-butyl radicals, which is as expected if the relationship which has been found for alkyl radicals[98] is also true for these pairs of radicals. This relationship[108] showed that Δ per hydrogen atom available for transfer increased from isopropyl to t-butyl and is also consistent with a lower value of $\Delta(\cdot NF_2, \cdot Et)$.

The experimental results showed that $\Delta(\cdot NF_2, \cdot Pr^i)$ is nearly independent of temperature, *i.e.* the difference in activation energies ($E_{46} - E_{45}$) is nearly zero within the experimental error. This independence of temperature of Δ is the same as has generally been found previously for the disproportionation–combination of alkyl–alkyl radicals. E_{45} has been measured[79] and found to be 5.28 kJ mol^{-1}, so E_{46} is probably in the region 4—6 kJ mol^{-1}.

The activation energy difference $E_{54} - E_{53}$ for t-butyl radicals is 9.1 kJ mol^{-1}. This value is obviously very dependent upon the correction for isobutene consumption by difluoroamino-radicals, which is much larger than for propene. Examination of a graph of log $\Delta(\cdot NF_2, \cdot Bu^t)$ *vs.* $1/T$ showed that the higher-temperature points lie near the line drawn through those obtained at lower temperatures, where the correction for olefin loss is small. This indicates the general validity of the correction used. The absolute rate of disproportionation of t-butyl radicals and the activation energy for this reaction could be found because the corresponding rate of combination has not been measured. As the activation energy difference between disproportionation and combination is not the same in the case of the t-butyl as in the isopropyl radical, it would be interesting to find whether it is disproportionation or combination which causes this dissimilarity and has a different activation energy.

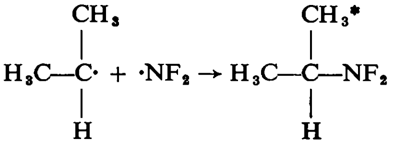
From the rate of combination of isopropyl and difluoroamino-radicals [equation (56)] the absolute rate coefficient for disproportionation of isopropyl and difluoroamino-radicals can be calculated [equation (57)]:

$$\log k_{45} \text{ (in ml mol}^{-1}\text{ s}^{-1}) = 9.2 - 5300/2.3\,RT \qquad (56)$$

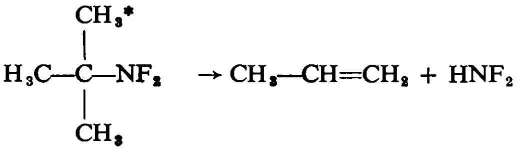
$$\log k_{46} \text{ (in ml mol}^{-1}\text{ s}^{-1}) = 9.15 - 5900/2.3\,RT \qquad (57)$$

The combination rate of both ethyl and isopropyl with difluoroamino-radicals has been found to be much slower than the rate of combination of alkyl–alkyl radicals.[79] These results show that the disproportionation rate is slightly slower than combination.

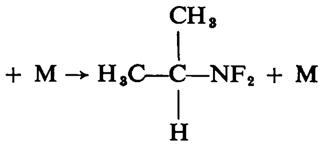
Similar slow rates of both disproportionation and combination have also been found for alkyl and alkoxyl radicals with nitric oxide. This seems to indicate a connection somehow between the transition state for disproportionation and combination, as slow combination rates have even slower disproportionation rates. This may, of course, just be coincidence or it is possible that these reactions occur *via* an energized molecule undergoing molecular elimination [equations (58)—(60)]:



$$H_3C\text{—}\overset{CH_3}{\underset{H}{C}}\cdot + \cdot NF_2 \rightarrow H_3C\text{—}\overset{CH_3{}^*}{\underset{H}{C}}\text{—}NF_2 \qquad (58)$$



$$H_3C\text{—}\overset{CH_3{}^*}{\underset{CH_3}{C}}\text{—}NF_2 \rightarrow CH_3\text{—}CH{=}CH_2 + HNF_2 \qquad (59)$$



$$+ M \rightarrow H_3C\text{—}\overset{CH_3}{\underset{H}{C}}\text{—}NF_2 + M \qquad (60)$$

There was no indication of any pressure dependence of Δ occurring although this was not specifically looked for.

A comparison of the combination–disproportionation results obtained for nitrogen-containing radicals is shown in Table 11. The values obtained for the difluoroamino-radicals are generally less than those obtained for nitric oxide and amino-radicals.

The difference in entropies of the disproportionation and combination products ($\Sigma S°_{dis} - \Sigma S°_{comb}$) has been found to be related to Δ(alkyl, alkyl) radicals.[101] The results for Δ($\cdot NF_2$, R) obtained here fall near the same line as that for Δ(alkyl, alkyl) (within the scatter obtained for alkyl radical disproportionations).

Table 11 *Δ Values for nitrogen-containing radicals*

Radicals		*Δ*	*Ref.*
$\cdot NF_2$	$\cdot Pr^i$	0.064	81
$\cdot NF_2$	$\cdot Bu^t$	0.123	81
$\cdot NH_2$	$\cdot Et$	0.31	105
$\cdot NH_2$	$\cdot Pr^i$	0.21	104
NO	MeO$\cdot$	0.5	106
NO	EtO$\cdot$	0.3	106
		0.45	107
NO	Pr^{n}O$\cdot$	0.4—0.5	110
NO	Pr^{i}O$\cdot$	0.15	108
		0.19	108
NO	Bu^{s}O$\cdot$	0.26	109
NO	Bu^{t}O$\cdot$	0	111

7 Di-t-butyl Peroxide Pyrolysis

The kinetics and pressure dependence of the decomposition of t-butoxyl radicals have been studied in the gas phase between 373 and 423 K by pyrolysing di-t-butyl peroxide (DTBP) in the presence of difluoroamino-radicals.[88] The results for the pyrolysis of DTBP were consistent with those recommended by Shaw and Pritchard,[112] and the rate of decomposition of the butoxyl radical was similar to the value suggested by O'Neal and Benson,[43] showing that the difluoroamino-radical may be used as an effective radical trap.

8 Miscellaneous Thermochemistry

Inel[16] calculated that

$$S° \text{ (total) } (CH_3NF_2) = 280.2 \text{ J mol}^{-1} \text{ K}^{-1}$$

and

$$S° \text{ (P.A.C.)* } (CH_3NF_2) = 280.7 \text{ J mol}^{-1} \text{ K}^{-1}$$

Hence

$$S° (CH_3NF_2) = 280.5 \text{ J mol}^{-1} \text{ K}^{-1}$$

Now using Benson's additivity rules,[40]

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* P.A.C. = partial atomic contributions.

[112] D. H. Shaw and H. O. Pritchard, *Canad. J. Chem.*, 1968, **46**, 2721.

$$S^\circ(CH_3NF_2) = S^\circ\{C - (N)(H)_3\} + S^\circ\{N - (C)(F)_2\}$$
$$S^\circ\{N - (C)(F)_2\} = S^\circ(CH_3NF_2) - S^\circ\{C - (N)(H)_3\}$$
$$= 280.5 - 127.2 = 153.3 \text{ J mol}^{-1} \text{ K}^{-1}$$

Using this value of $S^\circ\{N - (C)(F)_2\}$, Table 12 can be drawn up; Table 13 may also be constructed.

Table 12 *Estimated entropy values for* NF_2 *compounds*

Compound	S°/ J mol^{-1} K^{-1}	S°/ J mol^{-1} K^{-1} *(P.A.C.)*[b]	*(P.B.C.)*[b]
CH_3NF_2	280.5[a]	280.7	275.3
$C_2H_5NF_2$	321.3[a]	320.1	310.0
n-$C_3H_7NF_2$	360.7[a]	—	—
iso-$C_3H_7NF_2$	358.6[a]	350.2	336.0
n-$C_4H_9NF_2$	400.0[a]	—	—
iso-$C_4H_9NF_2$	397.9[a]	—	—
t-$C_4H_9NF_2$	392.0[a]	380.7	370.7

[a] Values estimated using Benson's additivity rules.[40] Errors are probably not more than ± 6.3 J mol^{-1} K^{-1}.

[b] These values based on partial atomic contributions (P.A.C.) and partial bond contributions (P.B.C.) are taken from Inel.[16]

Table 13 ΔH_f° *Values and* D(C—N) *values*[a]

Compound[c]	ΔH_f°/ kJ mol^{-1}	D(C—N)/ kJ mol^{-1}
CH_3NF_2	− 74.9	253
$C_2H_5NF_2$	−102.5	247
n-$C_3H_7NF_2$	−123.0	247
iso-$C_3H_7NF_2$	−138.9	249
n-$C_4H_9NF_2$	−143.9	247
iso-$C_4H_9NF_2$[b]	−149.4	243
t-$C_4H_9NF_2$	−172.4	239

[a] Errors probably not more than ± 11.8 kJ mol^{-1}. D(C—N) values based on N − (C)(F)$_2$ = 32.6 kJ mol^{-1}.

[b] Applied a *gauche* correction of 3.3 kJ mol^{-1} owing to $(CH_3)_2$ and NF_2 on adjacent carbon atoms.

[c] For $(CH_3)_2CHCH_2(NF_2)CH_2NF_2$, ΔH_f° (calc) = − 227.6 ± 15.5 kJ mol^{-1} (*gauche* correction omitted) and ΔH_f° (measured) = −207.4 kJ mol^{-1}.[113]

9 Conclusion

The difluoroamino-radical is probably one of the easiest nitrogen-containing radicals to study. Through the gas-phase kinetic study with organic compounds, much knowledge has been acquired about not only the reactions of this radical but, because of its acting as a convenient radical trap, also those of organic radical decompositions. Furthermore, the study of the difluoroamino-radical–organic radicals cross-combination reactions has led to a better overall understanding of the nature of such cross-combination reactions.

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[113] W. D. Good, D. R. Douslin, and J. P. McCullough, *J. Phys. Chem.*, 1963, **67**, 1312.