Kinetics of Hydrogen Abstraction by Difluoroamino Radicals from n-Propyl Formate and the n-Propoxycarbonyl Radical Decomposition

By P. Cadman* and A. J. White

Edward Davies Chemical Laboratories, Aberystwyth SY23 1NE

and A. F. Trotman-Dickenson

U.W.I.S.T., Cardiff CF1 3NY

The kinetics of the formyl hydrogen abstraction by difluoroamino radicals from n-propyl formate, using tetrafluorohydrazine as a thermal source of these radicals, has been studied between 398 and 463 K. The rate equation for this abstraction was given by

$$\log [k/(\text{ml mol}^{-1} \text{ s}^{-1})] = (8.48 \pm 0.88) - (77800 \pm 7200)/2.3RT$$

where $R = 8.314$ J mol^{-1} K^{-1}. The decomposition reaction of the resulting n-propoxycarbonyl radical was also studied. No pressure dependence on this decomposition of the radical was observed in this temperature range and in the pressure range 11-76 Torr. The rate equation was given by
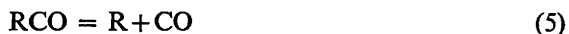
$$\log (k/\text{s}^{-1}) = (14.11 \pm 0.89) - (53000 \pm 7300)/2.3RT$$

where $R = 8.314$ J mol^{-1} K^{-1}.

The kinetics and mechanism of the hydrogen abstraction reactions by difluoro-amino radicals from alkanes,[1, 2] alkenes [3-5] and ketones [6, 7] have been studied previously using tetrafluorohydrazine as a thermal source of these radicals. The results were consistent with a difluoroamino radical abstracting a hydrogen atom and the resulting radical combining with another difluoroamino radical (1)-(3):

$$N_2F_4 = 2 NF_2 \tag{1}$$

$$RH + NF_2 = R + HNF_2 \tag{2}$$

$$R + NF_2 = RNF_2 \tag{3}$$

This type of reaction has also been used to study the aldehydic hydrogen abstraction reaction by difluoroamino radicals and the subsequent decomposition reactions of the corresponding acyl radicals [8, 9] (1), (4)-(7):

$$RCHO + NF_2 = RCO + HNF_2 \tag{4}$$

$$RCO = R + CO \tag{5}$$

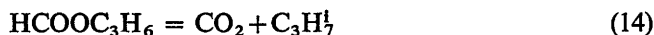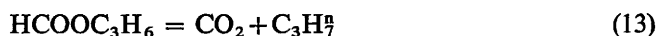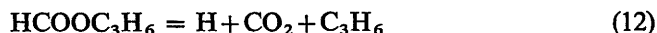$$R + NF_2 = RNF_2 \tag{6}$$

$$RCO + NF_2 = RCONF_2 \tag{7}$$

Difluoroamino radicals have also been used as a radical trap to study the de-composition of the t-butoxy radical formed in the thermal decomposition of di-t-butyl peroxide.[10]

Thynne [11-13] investigated the decomposition of alkyl formates, including n-propyl formate, by methyl radical photosensitization. With methyl formate, the rates of

formation of methane and carbon dioxide were approximately equal. He concluded that the formyl hydrogen atom was attacked exclusively and that the decomposition of the alkoxyl carbonyl radical so produced was a good " thermal " source of alkyl radicals. He did not check the methane-to-carbon dioxide ratio with the other formates studied. His proposed mechanism is given by eqn (8)-(10):
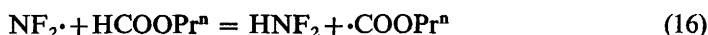
$$CH_3COCH_3 + h\nu = 2CH_3 + CO \tag{8}$$

$$CH_3 + HCOOR = CH_4 + \cdot COOR \tag{9}$$

$$\cdot COOR = R + CO_2 \tag{10}$$

Grotewold and Kerr,[14] however, claimed that abstraction from the alkoxyl group of n-propyl formate occurs to a significant extent. This conclusion was reached because of the formation of isobutane which could only have arisen from eqn (11)-(15)

$$CH_3 + HCOOPr^n = CH_4 + HCOOC_3H_6 \tag{11}$$

$$HCOOC_3H_6 = H + CO_2 + C_3H_6 \tag{12}$$

$$HCOOC_3H_6 = CO_2 + C_3H_7^n \tag{13}$$

$$HCOOC_3H_6 = CO_2 + C_3H_7^i \tag{14}$$

$$C_3H_7^i + CH_3 = (CH_3)_3CH \tag{15}$$

Arthur and Gray[15] have employed the use of isotopic labelling to determine the position and extent of hydrogen abstraction from the formyl and methoxyl 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 methoxyl. Similar conclusions were reached by Donovan et al.[16] using methyl and methyl-d_3 radicals and methyl formate and methyl formate-d.

In this paper we have applied our previously established method for studying radical decompositions to the n-propoxyl carbonyl radical. This radical was formed by formyl hydrogen abstraction by difluoroamino radicals from n-propyl formate. From our previous studies a mechanism can be proposed for this reaction:

$$N_2F_4 = 2NF_2 \cdot \tag{1}$$

$$NF_2 \cdot + HCOOPr^n = HNF_2 + \cdot COOPr^n \tag{16}$$

$$\cdot COOPr^n = Pr^n \cdot + CO_2 \tag{17}$$

$$Pr^n \cdot + NF_2 = Pr^n NF_2 \tag{18}$$

$$NF_2 \cdot + \cdot COOPr^n = NF_2COOPr^n \tag{19}$$

EXPERIMENTAL

APPARATUS AND PROCEDURE

The experiments were carried out in a conventional static system with a 50.3 cm^3 cylindrical Pyrex reaction vessel in an electrically-heated oil-bath. Reactant pressures were measured on a dibutyl phthalate-mercury manometer (magnification 8.2).

ANALYSIS

The products were frozen in liquid air and analyzed by g.l.c. on a 20 % dibutyl phthalate-60-80 mesh Celite column at 42°C and detected on a gas density balance detector (Gow Mac) with nitrogen as carrier gas. The only products analyzed were the N,N-difluoro-n-propyl-amine and the n-propyl-N,N-difluoroaminoformate. These products were identified by re-injecting known volumes of each product through the chromatography system and de-termining the molecular weight of each product. The gas-density balance had been

calibrated with known amounts of butane, dichloromethane and carbon tetrachloride. The N,N-difluoro-n-propylamine also had the same retention time as the N,N-difluoro-n-propylamine prepared from the reaction of tetrafluorohydrazine and propane, and tetra-fluorohydrazine and n-butyraldehyde. Difluoroimide (HNF_2) could not be analyzed due to its instability. The carbon dioxide was not analyzed because it had the same retention time as that of the tetrafluorohydrazine.

MATERIALS

n-Propyl formate (Eastman) was thoroughly degassed before use. Purity was estimated to be greater than 99 % by g.l.c.

RESULTS AND DISCUSSION

The results are given in table 1. The concentration of difluoroamino radicals was calculated from the initial pressure of tetrafluorohydrazine added and the equilibrium data for (1) given in ref. (17). The results were tested for consistency with the mechanism proposed above (1), (16)-(19) in the following manner:

(1) $[HCOOPr^n][NF_2]/R(NF_2COOPr^n)$ should vary with the reciprocal difluoroamino concentration. Here R( ) is the rate of formation of that product. Analysis of the results for 448 K showed that this was true.

(2) If the N,N-difluoropropylamine comes from the n-propoxycarbonyl radical then $R(Pr^nNF_2)[NF_2]/R(NF_2COOPr^n)$ should be constant at constant temperature. The results obtained at 448 K confirm this prediction.

(3) $[R(Pr^nNF_2)+R(NF_2COOPr^n)]/[HCOOPr^n][NF_2]$ was also constant at constant temperature.

(4) $[HCOOPr^n]/R(Pr^nNF_2)$ should be inversely proportional to the concentration of difluoroamino radicals at constant temperature. This relationship was found to hold using the results at 448 K.

ABSTRACTION REACTION (16)

This rate was calculated from the overall reaction. A linear relationship was obtained by plotting $\log k_{16}$ against $1/T$ corresponding to $\log k_{16}$ (ml mol^{-1} s^{-1}) = $8.48\pm0.88-(77800\pm7200)/2.3\,RT$ where $R = 8.314$ J mol^{-1} K^{-1} and the errors are 95 % confidence limits.

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.[1-9] 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-propoxyl group was observed even at the higher temperatures—the product was looked for but could not be found.

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 absence of any products from this reaction.

Comparison of the activation energies for the attack of methyl [11-16] iodine [18] 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.[2]

TABLE 1

temp. /K	10^6[HCOOC$_3$H$_7$] /mol ml^{-1}	10^6[N$_2$F$_4$] /mol ml^{-1}	10^6[NF$_2$] /mol ml^{-1}	10^{15}R[n-C$_3$H$_7$NF$_2$] /mol ml^{-1} s^{-1}	10^{15}R[NF$_2$COOC$_3$H$_7$] /mol ml^{-1} s^{-1}	k_{16} /ml mol^{-1} s^{-1}	$10^6 k_{17}/k_{19}$ /mol ml^{-1}
398	2.75	1.63	0.532	4.59	21.6	0.0229	0.113
398	2.18	2.08	0.607	3.33	18.8	0.0166	0.107
398	2.08	1.01	0.359	3.12	11.8	0.0145	0.095
398	1.13	2.34	0.647	3.69	13.4	0.0233	0.179
423	2.22	1.76	1.03	34.6	67.6	0.0447	0.528
423	1.13	1.44	0.911	15.0	21.8	0.0567	0.647
423	1.80	1.16	0.800	28.5	61.7	0.0627	0.370
423	1.46	1.96	1.10	33.0	79.7	0.0671	0.456
423	2.26	0.829	0.652	30.0	52.7	0.0561	0.371
448	2.12	0.993	0.925	259	310	0.290	0.773
448	1.10	1.59	1.35	144	267	0.277	0.733
448	0.589	0.720	0.695	46.5	41.0	0.214	0.789
448	2.12	1.47	1.27	271	454	0.269	0.759
448	0.775	1.22	1.09	86.6	24.7	0.250	0.759
448	0.644	0.720	0.695	63.1	57.1	0.269	0.768
448 *	0.862	0.960	0.900	84.0	91.6	0.226	0.825
463	1.12	1.77	2.11	468	607	0.455	1.61
463	2.40	0.251	0.445	356	149	0.502	1.16
463	1.82	0.551	0.870	613	461	0.679	1.15

* [N$_2$] = 16.3×10^{-6} mol ml^{-1} in this run.

The concentrations of NF$_2$ were calculated from the initial pressure of N$_2$F$_4$ and the equilibrium data given by F. A. Johnson and C. B. Colburn, *J. Amer. Chem. Soc.*, 1961, **83**, 3043.

DECOMPOSITION REACTION (17)

The decomposition reaction of the n-propoxycarbonyl radical at 448 K was studied over the pressure range 11-76 Torr. A least-mean-square analysis of the plot of k_{17}/k_{19} against $1/[M]$ (where $[M] = [HCOOC_3H_7] + \frac{1}{5}[N_2]$) gave the following equation:

$$k_{17}/k_{19} = 0.02\,(1/[M]) + 1.28 \times 10^6,$$

(nitrogen is assumed to be 20 % efficiency compared to the formate) showing that the pressure dependence of this decomposition reaction at this temperature is negligible. A plot of $\log(k_{17}/k_{19})$ against $1/T$ was linear and gave

$$\log(k_{17}/k_{19})/(\text{mol ml}^{-1}) = 0.11 \pm 0.89 - (53000 \pm 7300)/2.3\,RT$$

Assuming that $\log k_{19}/(\text{ml mol}^{-1}\,\text{s}^{-1}) = 14.0$,

$$\log(k_{17}/\text{s}^{-1}) = 14.11 \pm 0.89 - (53000 \pm 7300)/2.3\,RT,$$

For the decomposition reaction

$$\cdot COOCH_3 = CH_3\cdot + CO_2 \tag{20}$$

Solly and Benson[18] suggested the following Arrhenius equation,

$$\log(k_{20}/\text{s}^{-1}) = 13.5 - 42000/2.3\,RT.$$

These Arrhenius parameters were not determined but assigned from the limits of their experimental results. Comparison of the rate of decomposition of the methoxy-carbonyl radical with that for the n-propoxycarbonyl radical at 423 K shows that the rates are the same to within a factor of less than 10, ($10^{8\cdot3}$ compared with $10^{7\cdot5\pm0\cdot9}$ respectively). The rate of decomposition of the n-propoxycarbonyl radical is also similar to that found for the decomposition of the corresponding acyl radical–n-butyryl,[8] if the assumption is made that the rate of combination for both radicals with difluoroamino radicals is 10^{14}.

Estimating[10] $S^0(\cdot COOPr^n) = 396.8\,\text{J mol}^{-1}\,\text{K}^{-1}$ and with the usual thermochemical values[19] for $S^0(CO_2)$ and $S^0(Pr^n)$, $\Delta S_{17} = 103.6\,\text{J mol}^{-1}\,\text{K}^{-1}$ for the standard state of 1 atmosphere, i.e., $11.4\,\text{J mol}^{-1}\,\text{K}^{-1}$ for the standard state of 1 mol ml^{-1}. Now $\log(A_{17}/A_{-17}) = \Delta S_{17}/2.3R$, hence $\log A_{-17} = 13.5\,(\pm0.5)\,\text{ml mol}^{-1}$ s^{-1}. Similarly, by estimating[19] $\Delta H_f^\circ(\cdot COOPr^n)$ as $-210.5\,\text{kJ mol}^{-1}$, and taking the usual thermochemical values[19] for $\Delta H_f^\circ(CO_2)$ and $\Delta H_f^\circ(Pr^n)$, $\Delta H_{17} = -95.1\,\text{kJ mol}^{-1}$. As $\Delta H_{17} = E_{17} - E_{-17} + \Delta nRT$ then $E_{-17} = 150.6\,(\pm11.1)\,\text{kJ mol}^{-1}$. The rate of addition of n-propyl to carbon dioxide at 423 K using the above calculated Arrhenius parameters is about $10^{-5}\,\text{ml mol}^{-1}\,\text{s}^{-1}$. This is a factor of 10^{14} slower than that calculated for the rate of addition of n-propyl to carbon monoxide at 423 K using the Arrhenius parameters calculated from the decomposition reaction.[8]

[1] J. Grzechowiak, J. A. Kerr and A. F. Trotman-Dickenson, *Chem. Comm.*, 1965, 109.
[2] P. Cadman, C. Dodwell, A. F. Trotman-Dickenson and A. J. White, *J. Chem. Soc. A*, 1971, 2967.
[3] A. J. Dijkstra, Ph.D. Thesis, 1965, Leiden; A. J. Dijkstra, J. A. Kerr and A. F. Trotman-Dickenson, *J. Chem. Soc. A*, 1967, 105.
[4] D. G. E. Probert, *Ph.D. Thesis* (University of Wales, 1966).
[5] C. Dodwell, unpublished work.
[6] J. Grzechowiak, J. A. Kerr and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1965, 5080.
[7] J. Grzechowiak, (a) *Roczniki Chem.*, 1966, **40**, 895; (b) *Chem. Stosow Ser. A*, 1967, **11**, 215.

[8] P. Cadman, C. Dodwell, A. F. Trotman-Dickenson and A. J. White, *J. Chem. Soc. A*, 1970, 2371.
[9] P. Cadman, A. F. Trotman-Dickenson and A. J. White, *J. Chem. Soc. A*, 1970, 3189.
[10] P. Cadman, A. F. Trotman-Dickenson and A. J. White, *J. Chem. Soc. A*, 1971, 2296.
[11] J. C. J. Thynne, *Trans. Faraday Soc.*, 1962, **58**, 676.
[12] J. C. J. Thynne, *Trans. Faraday Soc.*, 1962, **58**, 1394.
[13] J. C. J. Thynne, *Trans. Faraday Soc.*, 1962, **58**, 1533.
[14] J. Grotewold and J. A. Kerr, *J. Chem. Soc.*, 1963, 4342.
[15] N. L. Arthur and P. Gray, *Trans. Faraday Soc.*, 1969, **65**, 424.
[16] T. R. Donovan, W. Dorko and A. G. Harrison, *Can. J. Chem.*, 1971, **48**, 828.
[17] F. A. Johnson and C. B. Colburn, *J. Amer. Chem. Soc.*, 1961, **83**, 3043.
[18] R. K. Solly and S. W. Benson, *Int. J. Chem. Kinetics*, 1969, **1**, 427.
[19] S. W. Benson, *Thermochemical Kinetics* (John Wiley, 1968).