

The Kinetics of Hydrogen Abstraction by Difluoroamino-radicals, from Propionaldehyde, and n- and Iso-butyraldehyde, and their Acyl Radical Decompositions

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The kinetics of the aldehydic hydrogen abstraction by difluoroamino-radicals have been studied between 100 and 175 °C for propionaldehyde and between 80 and 150 °C for n- and iso-butyraldehyde. The following Arrhenius parameters were found:

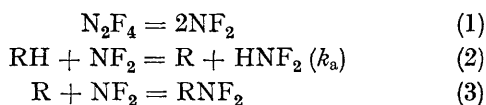
Aldehyde	Temp. (°C)	<i>E</i> (kcal. mole ⁻¹)	log <i>A</i> (c.c. mole ⁻¹ sec. ⁻¹)
Propionaldehyde	100—175	16.91 ± 0.27	10.75 ± 0.04
n-Butyraldehyde	80—150	16.28 ± 0.15	10.57 ± 0.03
Isobutyraldehyde	80—150	15.74 ± 0.15	10.31 ± 0.03

The kinetics and pressure-dependence of the decompositions of the resulting acyl radicals have been studied. The limiting high-pressure rate constants for the acyl radical decompositions have been obtained by extrapolation.

Radical	Temp. (°C)	<i>E</i> (kcal. mole ⁻¹)	log <i>A</i> (sec. ⁻¹)
EtCO	100—175	11.10 ± 0.24	12.47 ± 0.08
Pr ⁿ CO	80—150	9.52 ± 0.18	12.50 ± 0.03
Pr ⁱ CO	80—150	9.75 ± 0.25	13.04 ± 0.04

The Arrhenius parameters for the acyl radical attacks on difluoroamine and for the acyl radical formations have been calculated from thermodynamic data.

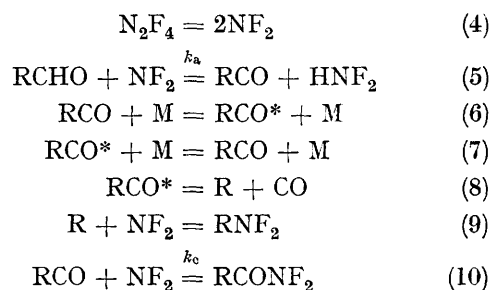
HYDROGEN abstraction from alkanes,¹ alkenes,²⁻⁴ and acetone⁵ by difluoroamino-radicals have been previously studied. The mechanism suggested was as shown in reactions (1)—(3). Aldehydic hydrogen ab-



straction by difluoroamino-radicals to form the corresponding *NN*-difluoroamide and difluoroamine has been reported,⁶ but not studied quantitatively. Hydrogen abstraction by other radicals from propionaldehyde,^{7,8} n-butyraldehyde,^{9,10} and isobutyraldehyde^{9,11} has been reported, but the corresponding acyl radical decompositions were not studied because of the complexity of the systems. Radical decompositions have been reviewed by Kerr and Lloyd.¹² Only a few acyl radical decompositions have been studied.¹²⁻¹⁷

Aldehydic hydrogen abstraction by difluoroamino-radicals affords a simple method of producing the acyl radical, and because the difluoroamino-radical acts as a radical trap, the acyl radical decomposition can be studied quantitatively.

The suggested mechanism, consistent with the results, is reactions (4)—(10).



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), a Springham spiral gauge (magnification 4.2), or a mercury manometer. The pressure in the reaction vessel was varied with added propane or butane because of the low volatility of the aldehydes.

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² 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.

³ D. G. E. Probert, Ph.D. Thesis, 1966, University of Wales.

⁴ C. Dodwell, unpublished work.

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¹⁰ J. A. Kerr and A. F. Trotman-Dickenson, *Trans. Faraday Soc.*, 1959, **55**, 572.

¹¹ J. A. Kerr and A. F. Trotman-Dickenson, *Trans. Faraday Soc.*, 1959, **55**, 921.

¹² J. A. Kerr and A. C. Lloyd, *Quart. Rev.*, 1968, **12**, 549.

¹³ R. J. Cvetanović, *Canad. J. Chem.*, 1955, **33**, 1684.

¹⁴ H. E. O'Neal and S. W. Benson, *J. Chem. Phys.*, 1962, **36**, 2196.

¹⁵ J. C. Amphlett and E. Whittle, *Trans. Faraday Soc.*, 1967, **63**, 80.

¹⁶ J. A. Kerr and A. C. Lloyd, *Trans. Faraday Soc.*, 1967, **63**, 2480.

¹⁷ J. A. Kerr, A. Smith, and A. F. Trotman-Dickenson, *J. Chem. Soc. (A)*, 1969, 1400.

Analysis.—The products were frozen in liquid air and carbon monoxide was pumped away. The amount of carbon monoxide produced was periodically checked in a gas burette and was equal to the amount of alkyl difluoroamine produced. The reaction products were analysed by g.l.c. on a 20% dibutyl phthalate-60-80 mesh Celite

and carbon tetrachloride. The alkyl difluoroamines had the same retention times as the products from the reaction of tetrafluorohydrazine with the corresponding alkane. Mass spectrometric analysis of the alkyl difluoroamines gave the spectrum of the corresponding alkyl radicals but not the parent ion peak. Difluoroamine (HNF_2) is assumed

TABLE 1
Propionaldehyde *

Temp. (°C)	Time (sec.)	[Aldehyde]	$[\text{N}_2\text{F}_4]$	$[\text{NF}_2]$	[Amine]	[Amide]	k_a (cc. mole ⁻¹ sec. ⁻¹)	[Propane]	k_a/k_c	P (effective) (cm. Hg)
100	14,400	1.76	1.01	0.192	0.93	39.9	8.39	0	4.47	3.22
101	10,800	2.98	0.633	0.148	1.19	30.2	6.59	0	5.83	5.46
102	53,600	1.70	0.514	0.134	5.08	81.7	7.11	12.93	8.33	26.7
100	46,800	0.615	1.24	0.222	1.60	44.1	7.15	15.58	8.07	29.7
125	7320	0.638	0.813	0.362	0.93	54.1	32.6	0	6.21	1.17
125	8100	0.933	1.36	0.482	2.93	122	34.0	0	7.74	1.71
125	7620	1.81	0.812	0.362	6.38	222	45.7	0	10.9	3.52
125	3060	3.27	0.878	0.379	3.06	82.0	22.5	0	14.1	6.00
125	5400	0.992	1.59	0.525	3.46	93.0	21.8	13.15	19.5	26.0
125	5400	0.570	1.59	0.525	1.60	48.5	31.0	13.91	17.3	26.6
151	1800	0.641	0.527	0.488	1.34	58.4	106	0	11.2	1.16
150	900	0.791	0.617	0.541	1.06	39.9	106	0	14.4	1.45
150	840	1.77	0.786	0.630	3.72	104	115	0	22.6	3.24
152	600	3.25	0.528	0.489	5.08	73.1	82.0	0	34.0	5.95
150	600	2.90	0.532	0.492	6.56	63.1	75.3	6.06	51.1	16.4
151	600	2.26	1.52	0.942	5.53	100	82.6	11.84	52.1	25.9
152	900	1.72	0.737	0.605	7.31	69.0	81.5	12.39	64.1	25.9
175	330	0.628	0.584	0.567	1.33	42.8	376	0	17.8	1.15
175	300	0.786	0.813	0.777	1.60	64.1	359	0	19.4	1.44
175	300	1.58	0.857	0.815	4.52	135	361	0	27.2	2.81
175	240	3.15	0.911	0.852	8.25	144	234	0	48.1	5.77
175	360	0.521	0.960	0.900	7.30	67.5	443	14.21	97.2	27.1
175	360	1.05	0.938	0.880	1.20	10.5	352	14.55	107	28.7

* Concentrations: Reactant, 10^{-6} mole c.c.⁻¹; Products, 10^{-9} mole c.c.⁻¹; k_a/k_c , 10^{-9} mole c.c.⁻¹. $[\text{NF}_2]$ calculated from equilibrium data given by F. A. Johnson and C. B. Colburn, *J. Amer. Chem. Soc.*, 1961, **83**, 3043.

TABLE 2
n-Butyraldehyde

Temp. (°C)	Time (sec.)	[Aldehyde]	$[\text{N}_2\text{F}_4]$	$[\text{NF}_2]$	[Amine]	[Amide]	k_a (c.c. mole ⁻¹ sec. ⁻¹)	[Butane]	k_a/k_c	P (effective) (cm. Hg)
80	54,000	0.840	0.644	0.076	2.83	6.34	2.68	0	33.6	1.54
80	36,000	0.997	1.84	0.129	2.63	9.11	2.54	0.971	37.2	3.41
80	43,200	0.573	0.824	0.086	1.68	3.66	2.52	5.53	39.4	11.2
80	20,580	0.540	0.936	0.091	1.16	2.61	3.71	15.05	40.6	28.6
100	7200	0.529	0.857	0.176	1.57	5.07	9.91	0	54.3	0.97
100	7200	0.802	0.578	0.143	3.36	7.76	13.5	0	61.8	1.47
100	10,800	0.600	1.62	0.245	3.57	13.4	10.7	0.868	65.2	2.69
101	5400	0.878	0.660	0.153	2.84	6.05	12.3	3.53	71.9	8.09
100	5400	0.633	1.22	0.211	2.21	6.05	11.4	8.65	77.2	17.0
100	7800	0.584	0.802	0.169	2.73	5.96	11.3	15.1	78.5	28.7
125	900	0.649	0.955	0.396	2.52	8.44	47.4	0	118	1.19
125	900	1.06	1.05	0.419	4.41	13.4	44.5	0	138	1.94
125	1200	0.567	1.13	0.435	3.99	9.48	45.6	2.97	183	6.48
125	1200	0.557	0.655	0.320	3.47	5.81	43.4	10.1	191	19.5
125	780	0.747	0.895	0.382	3.05	5.87	40.0	15.5	197	29.8
150	360	0.600	1.45	0.915	4.51	21.4	131	0	193	1.10
150	240	0.884	0.715	0.594	3.89	10.8	117	0	214	1.62
150	320	1.60	0.944	0.701	11.8	34.8	130	0	238	2.94
150	252	0.808	0.895	0.683	5.25	11.3	119	2.35	317	5.78
150	300	0.633	0.769	0.622	8.61	14.0	191	13.6	384	26.1

* Concentrations as in Table 1

column at 42 °C and detected on a gas density balance detector (Gow Mac) with nitrogen as carrier gas. The only products were the *NN*-difluoroamide and the corresponding alkyl difluoroamine. These products were identified by re-injecting known volumes of each product through the chromatography system and determining the molecular weight of each product. The gas density balance had been calibrated with known amounts of butane, dichloromethane,

to be the other product of the reaction, but this could not be analysed quantitatively owing to its instability or reactivity. The stability of the other $-\text{NF}_2$ products was checked by injecting known amounts into the chromatography system and varying the temperature of the column. Analysis showed that these compounds were stable and did not decompose in the temperature range used.

Materials.—Propionaldehyde (Fluka) and *n*- and iso-

butyraldehyde (B.D.H.) were thoroughly degassed before use. Purities were estimated to be >99% by g.l.c.

RESULTS AND DISCUSSION

Propionaldehyde.—The results are in Table 1. Two products were obtained: *NN*-difluoroethylamine and *NN*-difluoropropionamide.

n-Butyraldehyde.—The results are in Table 2. Two products were obtained: *NN*-difluoro-*n*-propylamine and *NN*-difluorobutyramide.

with the aldehydic hydrogen abstraction from these

$$\log k_a \text{ (c.c. mole}^{-1} \text{ sec.}^{-1}) = 10.75 \pm 0.04 - (16,910 \pm 270)/2.3RT \quad (11)$$

for propionaldehyde

$$\log k_a \text{ (c.c. mole}^{-1} \text{ sec.}^{-1}) = 10.57 \pm 0.03 - (16,280 \pm 150)/2.3RT \quad (12)$$

for *n*-butyraldehyde

$$\log k_a \text{ (c.c. mole}^{-1} \text{ sec.}^{-1}) = 10.31 \pm 0.03 - (15,740 \pm 150)/2.3RT \quad (13)$$

for isobutyraldehyde

TABLE 3
Isobutyraldehyde *

Temp. (°C)	Time (sec.)	[Aldehyde]	[N ₂ F ₄]	[NF ₂]	[Amine]	[Amide]	k_a (c.c. mole ⁻¹ sec. ⁻¹)	[Butane]	k_d/k_c	P (effective) (cm. Hg)
78	10,800	1.62	1.41	0.113	1.68	4.45	3.10	0	42.7	2.97
80	22,400	0.846	1.44	0.114	2.73	4.08	3.15	7.21	76.2	14.8
80	10,860	1.71	2.21	0.142	3.18	5.37	3.24	11.7	84.1	24.6
80	12,800	1.57	0.553	0.070	2.60	2.00	3.29	13.2	90.5	27.1
100	14,400	0.566	0.708	0.159	4.36	15.5	15.3	0	44.8	1.04
100	3600	0.802	0.895	0.180	1.79	5.50	14.0	0	58.6	1.47
100	3600	1.17	0.721	0.161	4.49	5.00	14.0	6.02	145	13.2
102	3600	0.689	3.77	0.326	4.84	9.95	18.3	6.98	159	14.1
100	3600	1.22	0.927	0.183	5.67	5.83	14.3	9.08	178	18.9
100	3600	1.34	1.36	0.224	5.67	7.33	12.0	11.8	166	24.1
100	4200	1.36	0.721	0.172	8.26	7.42	16.0	12.6	191	25.6
128	2400	0.671	0.633	0.314	6.43	19.7	51.7	0	102	1.23
127	1800	0.726	0.595	0.303	5.20	13.9	48.2	0	112	1.33
125	780	1.60	0.819	0.364	6.82	13.1	43.8	0	190	2.93
127	2520	0.709	0.775	0.353	15.5	17.0	51.5	6.06	322	12.4
127	660	2.56	3.47	0.799	22.6	42.4	48.2	4.87	426	13.6
125	900	1.61	1.66	0.540	17.1	23.5	51.9	11.6	411	24.2
125	1200	1.53	0.619	0.307	15.0	9.58	43.6	12.8	481	26.3
150	550	0.617	1.18	0.809	7.66	33.3	149	0	186	1.13
152	600	1.29	0.503	0.479	19.6	33.4	126	0	281	2.36
151	600	1.54	0.464	0.450	33.6	28.9	150	3.27	523	8.82
152	600	0.612	1.90	1.07	25.0	49.5	190	6.49	542	13.0
152	600	0.615	0.739	0.607	20.0	15.6	159	9.33	779	18.2
151	600	2.14	0.487	0.464	55.0	29.4	142	7.97	867	18.5
150	600	1.44	0.540	0.497	52.8	26.9	187	13.2	975	26.7
150	600	1.34	0.536	0.495	46.8	31.4	196	13.3	739	26.9

* Concentrations as in Table 1.

TABLE 4
Aldehydic hydrogen abstractions

Aldehyde	Radical and source *	E (kcal. mole ⁻¹)	$\log A$ † (c.c. mole ⁻¹ sec. ⁻¹)	Temp. range (°C)	Ref.
Propionaldehyde	Me DTBP T	6.6	11.8	122—156	7 (b)
	Et DTBP T	6.6	11.9	134—157	7 (b)
	Et EtCHO P	4.9	11.2	91—315	8 (b)
	NF ₂ N ₂ F ₄ T	16.91	10.75	100—175	(e)
<i>n</i> -Butyraldehyde	Me DTBP T	7.3	11.8	119—175	9 (a)
	Pr ⁿ Pr ⁿ CHO P	6.7	11.2	98—361	10 (c)
	NF ₂ N ₂ F ₄ T	16.28	10.57	80—150	(e)
Isobutyraldehyde	Me DTBP T	8.7	12.6	119—175	9 (a)
	Pr ⁱ Pr ⁱ CHO P	6.3	11.3	117—354	11 (d)
	NF ₂ N ₂ F ₄ T	15.74	10.31	80—150	(e)

* T, Thermal; P, photolysis; DTBP, di-*t*-butyl peroxide. † Based on k_c for combination reactions (c.c. mole⁻¹ sec.⁻¹) of (a) methyl radicals, $10^{13.34}$; (b) ethyl radicals, $10^{14.2} \exp(-2000/2.3RT)$; (c) *n*-propyl radicals, $10^{13.8}$; (d) isopropyl radicals, 10^{14} ; (e) This work.

Isobutyraldehyde.—The results are in Table 3. Two products were obtained: *NN*-difluoroisopropylamine and *NN*-difluoro-1-methylpropionamide.

Abstraction Reaction (5).—Linear relations were obtained by plotting $\log k_a$ against $1/T$ corresponding to equation (11)–(13). These results can be compared

three aldehydes by other radicals (Table 4). The A factors for the attack of difluoroamino-radicals on these aldehydes are less than those for the corresponding attack by alkyl radicals. This lower A factor for difluoroamino-radical hydrogen abstractions has been found previously.^{1–5} Table 4 shows that the A factors and

activation energies remain nearly constant for any particular radical attacking a series of aldehydes, and is independent of the aldehyde. This indicates that the bond strength of the C-H_{aldehyde} bond is nearly constant, and is borne out below when it is found that ΔH_5 is approximately the same for each aldehyde studied. As $\Delta H_5 = D(\text{F}_2\text{N}-\text{H}) - D(\text{RCO}-\text{H})$, and $D(\text{F}_2\text{N}-\text{H})$ is a constant, ΔH_5 will be a constant if $D(\text{RCO}-\text{H})$ is independent of the R group. ΔH_5 can be calculated from the heats of formation of the species involved.

ΔH_5 is also related to the activation energies of the forward and back reactions of reaction (5) by $\Delta H_5 = E_5 - E_{-5}$ ($\Delta n = 0$). Hence E_{-5} can be estimated. The A factors of the forward and back reactions of reaction (5) are also related by $\log A_5/A_{-5} = \Delta S_5/2.3RT$, and hence $\log A_{-5}$ can be estimated.

Propionaldehyde. Taking $\Delta H^\circ_f[\text{HNF}_2]^{18} = -15.6$ kcal. mole⁻¹, $\Delta H^\circ_f[\text{NF}_2]^{19} = 8.5$ kcal. mole⁻¹, $\Delta H^\circ_f[\text{EtCHO}]^{20} = -45.6$ kcal. mole⁻¹, and estimating²¹ $\Delta H^\circ_f[\text{EtCO}] = -10.0$ kcal. mole⁻¹ (based on $\Delta H^\circ_f[\text{MeCO}] = -5 \pm 1$ kcal. mole⁻¹), we obtain $\Delta H_5 = 11.5 \pm 3$ kcal. mole⁻¹, hence $E_{-5} = 5.4 \pm 3$ kcal. mole⁻¹. Taking $S^\circ(\text{HNF}_2) = 60.5$ e.u.,²² $S^\circ(\text{NF}_2) = 59.7$ e.u.,²¹ $S^\circ(\text{EtCHO}) = 73.4$ e.u.,²³ and estimating²¹ $S^\circ(\text{EtCO}) = 72.9$ e.u., we obtain $\Delta S_5 = 0.3$ e.u. at 25 °C for the standard state of 1 atm. As $\Delta n = 0$ for reaction (5), then $\Delta S_5 = 0.3$ e.u. at 25 °C for the standard state of 1 mole c.c.⁻¹. Hence $\log A_{-5} = 10.7 \pm 1.0$. This gives that $\log k_{-5}$ (c.c. mole⁻¹ sec.⁻¹) = $10.7 \pm 1.0 - (5400 \pm 3000)/2.3RT$.

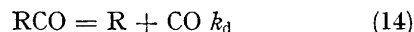
n-Butyraldehyde. Taking the above thermodynamic values for HNF_2 and NF_2 and $\Delta H^\circ_f[\text{Pr}^\text{n}\text{CHO}]^{20} = -48.9$ kcal. mole⁻¹ and estimating²¹ $\Delta H^\circ_f[\text{Pr}^\text{n}\text{CO}] = -14.9$ kcal. mole⁻¹, we find ΔH_5 to be 9.9 ± 3 kcal. mole⁻¹. Hence $E_{-5} = 6.4 \pm 3$ kcal. mole⁻¹. Taking $S^\circ(\text{Pr}^\text{n}\text{CHO}) = 82.6$ e.u.,²⁰ and estimating²¹ $S^\circ(\text{Pr}^\text{n}\text{CO}) = 82.3$ e.u., $\Delta S_5 = 0.5$ e.u. at 25 °C for the standard state of 1 atm. and also for the standard state of 1 mole c.c.⁻¹ we find $\log A_{-5} = 10.4 \pm 1.0$ and $\log k_{-5}$ (c.c. mole⁻¹ sec.⁻¹) = $10.5 \pm 1.0 - (6400 \pm 3000)/2.3RT$.

Isobutyraldehyde. Taking the above thermodynamic values for HNF_2 and NF_2 and estimating²¹ $\Delta H^\circ_f[\text{Pr}^\text{i}\text{CHO}] = -51.7$ kcal. mole⁻¹ and $\Delta H^\circ_f[\text{Pr}^\text{i}\text{CO}] = -17.0$ kcal. mole⁻¹, we find $\Delta H_5 = 9.8 \pm 3$ kcal. mole⁻¹ and hence $E_{-5} = 5.9 \pm 3$ kcal. mole⁻¹. Estimating²¹ $S^\circ(\text{Pr}^\text{i}\text{CHO}) = 83.7$ e.u. and $S^\circ(\text{Pr}^\text{i}\text{CO}) = 81.8$ e.u., we find $\Delta S_5 = -1.1$ e.u. at 25 °C for the standard state of 1 atm. and for the standard state of 1 mole c.c.⁻¹. Hence $\log A_{-5} = 10.6 \pm 1.0$, and hence $\log k_{-5}$ (c.c. mole⁻¹ sec.⁻¹) = $10.6 \pm 1.0 - (5900 \pm 3000)/2.3RT$.

Very few abstraction reactions have been studied with which the values calculated for reaction (-5) can be compared. The abstraction of hydrogen from

hydrogen iodide and bromide by acetyl radicals^{24,25} have activation energies in the region of 0–3 kcal. mole⁻¹. From thermochemical considerations, reactions of EtCO , $\text{Pr}^\text{n}\text{CO}$, and $\text{Pr}^\text{i}\text{CO}$ with difluoroamine might be expected to have activation energies slightly higher; i.e., in the region of the calculated values, 5–7 kcal. mole⁻¹.

Decomposition Reaction (14).—From the suggested



mechanism under steady-state conditions we can write equations (15) and (16), and from equations (17) and (18) we obtain (19).

$$d[\text{RCO}^*]/dt = k_6[\text{RCO}][\text{M}] - k_7[\text{RCO}^*][\text{M}] - k_8[\text{RCO}^*] = 0 \quad (15)$$

$$[\text{RCO}^*] = k_6[\text{RCO}]/(k_7 + k_8/[\text{M}]) \quad (16)$$

$$\text{Now } R(\text{RNF}_2) = R(\text{CO}) = k_d[\text{RCO}] = k_8[\text{RCO}^*] \quad (17)$$

$$R(\text{RCONF}_2) = k_c[\text{NF}_2][\text{RCO}] \quad (18)$$

$$\frac{R(\text{RCONF}_2)}{R(\text{RNF}_2)} \frac{1}{[\text{NF}_2]} = \frac{k_c}{k_d} = \frac{k_c k_7}{k_6 k_8} + \frac{k_c}{k_6 [\text{M}]} \quad (19)$$

At high pressures (k_d)_∞ tends to $k_6 k_8 / k_7$ and hence plots of k_c/k_d against $1/[\text{M}]$ at a particular temperature should be linear with intercepts equal to $k_c/(k_d)_\infty$, where (k_d)_∞ is the limiting high-pressure rate constant.

Plots of k_c/k_d against $1/[\text{M}]$ at various temperatures were linear. $[\text{M}]$ was taken as the sum of the concentrations of aldehyde and propane (or butane). The concentrations of N_2F_4 and NF_2 were not included as these have been reported² to be poor third bodies. Values of $k_c/(k_d)_\infty$ at various temperatures were found from the intercepts of the plots. An Arrhenius treatment of these rate constants yielded (E_d)_∞, the limiting high-pressure activation energy, and (A_d)_∞, the limiting high-pressure Arrhenius A factor.

This treatment has limitations. O'Neal and Benson¹⁴ and Kerr and Lloyd¹⁶ concluded that the error in the (k_d)_∞ values determined by this extrapolation for the acetyl and propionyl radical decompositions, respectively, was less than a factor of 5. This conclusion also applies to our work as this was studied at similar pressures. Although our plots are linear, this is only because the pressure range is limited. (The pressure could only be varied by a factor of 30). When the pressure is varied by a factor of about 10⁴ or more, deviations arise owing to neglect in the theory of the effects on the rate constant of differing energy contents of the energized molecules.

It should be noted that the limiting high-pressure rate constants obtained by this treatment are minimum values.¹⁴

Propionaldehyde. Table 5 shows the values of the intercepts at the various temperatures from Figure 1.

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TABLE 5

Values of the intercepts obtained from the pressure-dependent plots

Propionaldehyde		n-Butyraldehyde		Isobutyraldehyde	
Temp. (°C)	$10^6(k_c/k_d)_\infty$ (c.c. mole ⁻¹)	Temp. (°C)	$10^6(k_c/k_d)_\infty$ (c.c. mole ⁻¹)	Temp. (°C)	$10^6(k_c/k_d)_\infty$ (c.c. mole ⁻¹)
100	109	80	24.5	80	10.1
125	50.1	100	12.9	100	5.00
150	14.6	125	4.94	125	1.90
175	10.2	150	2.75	150	1.15

A good Arrhenius plot was obtained from $\log(k_d)_\infty/k_c$ against $1/T$ corresponding to equation (20).

$$\log(k_d)_\infty/k_c \text{ (mole c.c.}^{-1}\text{)} = -1.53 \pm 0.08 - (11,100 \pm 240)/2.3RT \quad (20)$$

If we assume that $k_c = 10^{14}$ c.c. mole⁻¹ sec.⁻¹, then equation (21) follows.

$$\log(k_d)_\infty \text{ (sec.}^{-1}\text{)} = 12.47 \pm 0.08 - (11,100 \pm 240)/2.3RT \quad (21)$$

n-Butyraldehyde. Table 5 shows the values of the intercepts at the various temperatures from Figure 2. An Arrhenius plot corresponded to equation (22).

$$\log(k_d)_\infty/k_c \text{ (mole c.c.}^{-1}\text{)} = -1.50 \pm 0.03 - (9520 \pm 180)/2.3RT \quad (22)$$

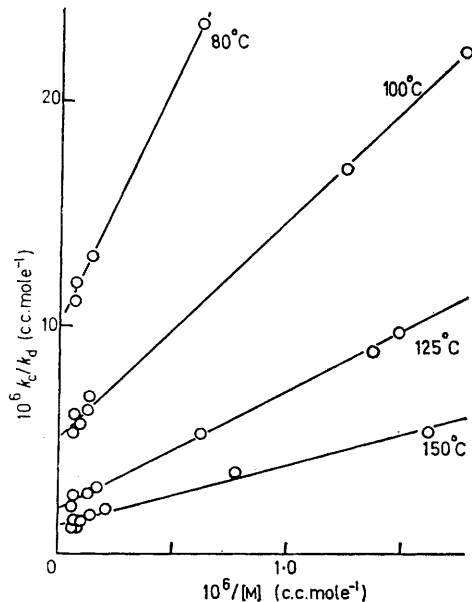


FIGURE 1 Pressure-dependent plot for decomposition of propionyl radicals

If we assume that $k_c = 10^{14}$ c.c. mole⁻¹ sec.⁻¹, then equation (23) follows.

$$\log(k_d)_\infty \text{ (sec.}^{-1}\text{)} = 12.50 \pm 0.03 - (9520 \pm 180)/2.3RT \quad (23)$$

4 N

Isobutyraldehyde: Table 5 shows the values of the intercepts. An Arrhenius treatment gave equation (24).

$$\log(k_d)_\infty/k_c \text{ (mole c.c.}^{-1}\text{)} = -0.98 \pm 0.04 - (9750 \pm 250)/2.3RT \quad (24)$$

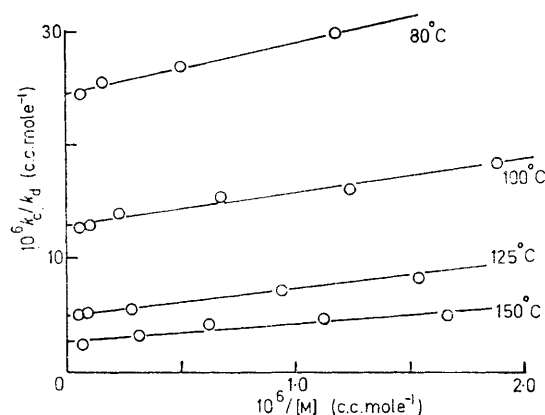


FIGURE 2 Pressure-dependent plot for decomposition of n-butyryl radicals

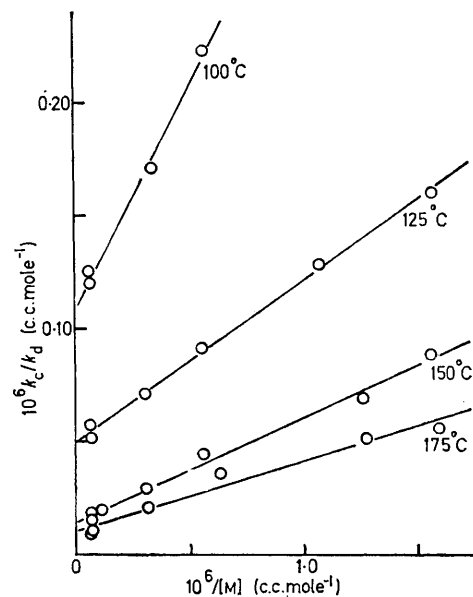


FIGURE 3 Pressure-dependent plot for decomposition of isobutyryl radicals

If we assume that $k_c = 10^{14}$ c.c. mole⁻¹ sec.⁻¹ then equation (25) follows.

$$\log(k_d)_\infty \text{ (sec.}^{-1}\text{)} = 13.02 \pm 0.04 - (9750 \pm 250)/2.3RT \quad (25)$$

These results for the acyl radical decompositions can be compared with the other acyl radical decompositions studied previously (Table 6). They show that, with the exception of cyclo-C₃H₅CO, the acetyl radical is more stable than the other acyl radicals. O'Neal and Benson¹⁴ have rationalised the low *A* factor

for the acetyl radical decomposition; also from the similarity in the fall-off curves of the iodine-catalysed decomposition of acetaldehyde and propionaldehyde, they predicted²⁶ a higher A factor for the propionyl radical decomposition than for the acetyl radical decomposition. Our results and those of Kerr and Lloyd¹⁶ confirm this prediction although differing from

TABLE 6

Arrhenius parameters for acyl radical decompositions

Radical	E (kcal. mole ⁻¹)	$\log A$ (sec. ⁻¹)	Temp. range (°C)	Ref.
HCO	14.4	13.0	25	13
MeCO	15.0 _(∞)	10.3 _(∞)	200–295	14
CF ₃ CO	10	10.4	25–248	15
EtCO	14.7 _(∞)	13.3 _(∞)	30–80	16
	11.10 _(∞)	12.47 _(∞)	100–175	<i>a</i>
Pr ⁿ CO	9.52 _(∞)	12.50 _(∞)	80–150	<i>a</i>
Pr ⁱ CO	9.75 _(∞)	13.04 _(∞)	80–150	<i>a</i>
cyclo-C ₃ H ₅ CO	17.90	11.7	138–186	17

^a This work

one another. This difference in A factors may be within the errors of the extrapolation of the reciprocal pressure plots. The calculation of the rate constant for the propionyl radical decomposition from Kerr and Lloyd's¹⁶ data is more complicated than ours, which could lead to differences.

The limiting high-pressure activation energies of the decomposition and formation reactions of the acyl radical are related to the enthalpy change (ΔH_d) by the equation $\Delta H_d = E_d - E_{-d} + mRT$. The mRT term allows for the change in the number of molecules occurring on decomposition, and amounts to about 0.6 kcal. mole⁻¹. The limiting high-pressure Arrhenius A factors of the decomposition and formation reactions of the acyl radical are related to the entropy change (ΔS°_d) by the equation $\log A_d/A_{-d} = \Delta S_d/2.3R$. Hence from the enthalpy and entropy changes, the Arrhenius parameters for the acyl radical formation (—14) can be determined.

Propionyl Radical Formation. Taking $\Delta H^\circ_f[\text{Et}]$ ²¹ =

26.0 kcal. mole⁻¹, and estimating²¹ $\Delta H^\circ_f[\text{EtCO}] = -10.0$ kcal. mole⁻¹, we obtain $\Delta H_d = 9.6 \pm 3$ kcal. mole⁻¹ and hence $E_{-d} = 2.1 \pm 3$ kcal. mole⁻¹. Taking $S^\circ(\text{Et}) = 59.8$ e.u.²¹ and estimating²¹ $S^\circ(\text{EtCO}) = 72.9$ e.u., we find $\Delta S^\circ_d = 34.1$ e.u. at 25 °C for the standard state of 1 atm., which is 14.0 e.u. at 25 °C for the standard state of 1 mole c.c.⁻¹. Hence $\log A_{-d} = 9.4 \pm 1.0$ and for reaction (—14) $\log k_{-d}$ (c.c. mole⁻¹ sec.⁻¹) = $9.4 \pm 1.0 - (2100 \pm 3000)/2.3RT$.

n-Butyryl Radical Formation.—Taking $\Delta H^\circ_f[\text{Pr}^n]$ ²¹ = 21.0 kcal. mole⁻¹, and estimating²¹ $\Delta H^\circ_f[\text{Pr}^n\text{CO}] = -14.9$ kcal. mole⁻¹, we find $\Delta H_d = 9.5 \pm 3$ kcal. mole⁻¹ and hence $E_{-d} = 0.6 \pm 3$ kcal. mole⁻¹. Taking $S^\circ(\text{Pr}^n) = 68.5$ e.u.²¹ and estimating²¹ $S^\circ(\text{Pr}^n\text{CO}) = 82.3$ e.u., we find $\Delta S^\circ_d = 33.4$ e.u. at 25 °C for the standard state of 1 atm., which is 13.3 e.u. at 25 °C for the standard state of 1 mole c.c.⁻¹. Hence $\log A_{-d} = 9.6 \pm 1.0$ and reaction (—14), $\log k_{-d}$ (c.c. mole⁻¹ sec.⁻¹) = $9.6 \pm 1.0 - (600 \pm 3000)/2.3RT$.

Isobutyryl Radical Formation.—Taking $\Delta H^\circ_f[\text{Pr}^i]$ ²¹ = 17.6 kcal. mole⁻¹, and estimating²¹ $\Delta H^\circ_f[\text{Pr}^i\text{CO}] = -17.0$ kcal. mole⁻¹, we find $\Delta H_d = 8.2 \pm 3$ kcal. mole⁻¹ and hence $E_{-d} = 2.2 \pm 3$ kcal. mole⁻¹. Taking $S^\circ(\text{Pr}^i) = 66.7$ e.u.²¹ and estimating²¹ $S^\circ(\text{Pr}^i\text{CO}) = 81.8$ e.u., we find $\Delta S^\circ_d = 32.1$ e.u. at 25 °C for the standard state of 1 atm., which is 12.0 e.u. at 25 °C for the standard state of 1 mole c.c.⁻¹. Hence $\log A_{-d} = 10.3 \pm 1.0$ and for reaction (—14), $\log k_{-d}$ (c.c. mole⁻¹ sec.⁻¹) = $10.3 \pm 1.0 - (2200 \pm 3000)/2.3RT$.

The only experimental result for the addition of alkyl radicals to carbon monoxide is that of Kerr and Calvert²⁷ for methyl radical plus carbon monoxide. They obtained an activation energy of ca. 5 kcal. mole⁻¹. The calculated values above for ethyl, n-propyl, and isopropyl radical addition to carbon monoxide are lower than for methyl radicals plus carbon monoxide.

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