417. *The Reactions of Alkyl Radicals. Part VI.* The Reactions of Methyl Radicals with Aliphatic Aldehydes.*

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The rate constants for the reactions of methyl radicals, produced by the thermal decomposition of di-t-butyl peroxide between 119° and 175°, with eight aliphatic aldehydes have been determined; the Arrhenius parameters for the reactions are given. The rate constant at which methyl radicals abstract hydrogen atoms from the aldehydes at 182° is approximately $10^{8 \cdot 25}$ mole^{-1} cm.^{3} sec.$^{-1}$; it does not depend upon the nature of the alkyl group.

There are two reasons why the rate at which methyl radicals abstract hydrogen atoms from a series of aliphatic aldehydes would be of interest. First, it is probable that the aldehydic hydrogen atoms are by far the most reactive in the molecules, so that the rates would show the influence of the structure of alkyl groups on the reactivity of $-CHO$. Secondly, comparisons may be made between the reactivity of methyl with a series of molecules, $R\cdot CHO$, and the reactivity of a series of alkyl radicals $R\cdot$ with their parent aldehydes: the result would indicate whether variations in rate should be attributed to variations in the reactivity of R or of $R\cdot CHO$. Very little information is yet available on either of these general problems.

Previous workers have determined the rate of abstraction of hydrogen atoms by methyl from acetaldehyde, using the decomposition of di-t-butyl peroxide,[1] the photolysis of azomethane,[2] and the photolysis of the aldehyde [3] as radical sources (see also Pritchard, Pritchard, and Trotman-Dickenson [4]). The rates of reaction of methyl with propionaldehyde [5] and crotonaldehyde [6] (at one temperature) have also been determined, with di-t-butyl peroxide as the source of methyl. Since this work was completed the rate of reaction with formaldehyde has been determined for methyl obtained by photolysis of azomethane [7] and decomposition of di-t-butyl peroxide.[8] No work on the higher aldehydes has been reported.

In the present investigation the decomposition of di-t-butyl peroxide was used as the source of methyl. The amounts of methane and ethane formed when the decomposition of the peroxide took place in the presence of the aldehyde were determined. An allowance of about 2% was made for the amount of methane formed by reaction of methyl with the

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* Part V, *J.*, 1960, 1611.

[1] Brinton and Volman, *J. Chem. Phys.*, 1952, **20**, 1053.

[2] Ausloos and Steacie, *Canad. J. Chem.*, 1955, **33**, 31.

[3] Dodd, *Canad. J. Chem.*, 1955, **33**, 699.

[4] Pritchard, Pritchard, and Trotman-Dickenson, *J. Chem. Phys.*, 1953, **21**, 748.

[5] Brinton and Volman, *J. Chem. Phys.*, 1954, **22**, 929.

[6] Pitts, Thompson, and Woolfolk, *J. Amer. Chem. Soc.*, 1958, **80**, 66.

[7] Toby and Kutschke, *Canad. J. Chem.*, 1959, **37**, 672.

[8] Blake and Kutschke, *Canad. J. Chem.*, 1959, **37**, 1462.

TABLE 1. *Hydrogen abstraction by methyl radicals from aldehydes.*

Temp. (°K)	Time (sec.)	[R·CHO] (10^{-6} mole cm.$^{-3}$)	$\frac{[\text{R·CHO}]}{[\text{Perox.}]}$	R_{CH_4} (10^{-12} mole cm.$^{-3}$ sec.$^{-1}$)	$R_{\text{C}_2\text{H}_6}$ (10^{-12} mole cm.$^{-3}$ sec.$^{-1}$)	k (mole^{-1} cm.^{3} sec.$^{-1}$)
			Acetaldehyde			
394·6°	4800	1·22	1·5	28·1	5·2	47·5
394·6	2400	1·36	1·1	45·5	10·7	47·9
405·9	1200	1·23	1·3	69·8	22·3	56·2
406·9	1800	1·18	1·5	73	21·7	62·1
412·8	1200	1·71	3·1	89·4	12·7	68·9
419·0	480	2·54	6·6	292	41·7	83·5
427·7	180	1·99	4·5	636	245	95·6
436·4	90	2·01	3·7	1400	883	109·7
440·6	90	1·95	8·0	1160	437	133·1
447·3	90	1·70	4·0	2870	2500	162·2
			n-Butyraldehyde			
394·6	4500	1·27	0·8	22·2	2·10	56·5
394·8	4200	1·37	1·7	11·7	0·90	51·2
400·6	5400	1·60	2·8	11·6	0·34	58·1
407·3	1200	1·27	1·4	19·0	1·12	66·3
407·3	3120	1·53	2·0	18·5	0·67	69·0
407·3	1500	1·04	1·1	20·8	1·66	72·9
412·8	1200	1·60	2·1	59·0	5·21	75·9
413·7	1620	1·61	3·5	42·5	1·85	91·2
418·3	720	1·73	4·5	68·2	5·56	78·3
418·3	900	1·80	4·7	92·9	8·25	84·3
419·0	900	2·28	10·0	42·5	1·61	74·9
423·0	240	2·23	4·9	199	20·2	93·3
423·0	360	2·20	8·2	203	22·0	93·5
430·9	360	2·23	6·0	242	28·2	100
436·6	120	1·97	4·5	663	130	138·4
437·8	90	2·21	4·6	744	141	132·6
437·8	75	2·22	3·0	1820	980	123·5
447·3	90	1·90	5·4	1540	643	147·6
			Isobutyraldehyde			
395·8	7200	1·30	0·8	12·6	0·70	55·4
395·8	7200	1·26	1·0	12·3	0·71	54·2
395·8	7800	1·15	1·0	13·5	1·08	53·0
406·6	1920	1·35	1·1	50·6	6·69	67·9
412·7	1200	1·56	3·4	38·9	1·90	84·4
412·9	1200	1·70	1·8	73·5	5·0	90·8
413·4	1200	1·74	2·3	63·2	3·52	90·6
418·8	360	1·93	2·3	133	9·92	103
418·8	300	1·36	2·2	82·9	11·0	86·1
421·5	600	1·68	2·0	178	27·9	94·2
422·7	600	1·28	2·0	132	16·2	119
427·5	300	1·71	3·2	168	15·7	116
427·5	300	1·54	2·0	328	85·5	108
430·9	240	1·81	4·0	265	25·6	138
436·1	180	1·70	8·2	202	15·1	143·4
448·3	120	1·46	3·3	979	267	192
			n-Valeraldehyde			
394·6	5700	1·28	0·9	14·8	1·15	50·1
398·8	2400	1·00	1·0	14·4	5·02	47·2
405·9	1800	1·83	3·0	24·5	1·43	52·7
412·8	1200	1·80	2·0	78·3	8·20	71·3
419·0	600	2·03	6·0	95·9	7·14	82·7
424·0	180	0·90	1·0	214	131	98·0
425·6	180	1·76	2·3	419	143	93·4
436·2	180	1·18	4·0	264	74·2	122
437·8	120	2·00	4·0	874	414	101
447·3	90	1·89	10·5	872	168	167

TABLE 1. (*Continued.*)

Temp. (°K)	Time (sec.)	[R·CHO] (10^{-6} mole cm.$^{-3}$)	[R·CHO]/[Perox.]	R_{CH_4} (10^{-12} mole cm.$^{-3}$ sec.$^{-1}$)	$R_{C_2H_6}$ (10^{-12} mole cm.$^{-3}$ sec.$^{-1}$)	k (mole^{-1} cm.^{3} sec.$^{-1}$)
			Isovaleraldehyde			
399·2	1530	0·98	0·8	21·0	5·87	52·1
404·8	720	1·08	0·8	41·8	20·9	50·1
412·4	900	1·10	1·4	76·6	23·3	67·6
421·8	180	0·98	0·8	204	122	98·0
432·6	120	0·93	0·8	526	580	110
435·0	120	1·35	1·5	724	557	106·4
444·3	60	1·06	1·7	1220	1110	163
			2-Methylbutyraldehyde			
385·5	9000	0·87	0·9	2·37	3·20	22·7
392·3	3600	0·83	0·7	6·14	2·39	22·4
397·7	5100	0·87	0·8	8·98	2·17	32·8
405·0	600	1·02	0·7	58·8	33·1	37·3
412·4	720	1·19	1·0	76·1	52·2	42·5
412·4	720	1·14	1·2	75·6	54·4	42·1
413·1	780	0·97	1·0	647	35·8	52·0
420·5	420	1·22	1·8	131	43·1	75·1
426·8	120	0·94	0·8	275	270	83·9
436·4	120	1·53	2·1	775	430	114·4
			Pivalaldehyde			
392·3	14,400	0·80	0·8	6·57	1·36	33·7
398·6	1500	0·81	0·7	17·6	13·3	36·6
404·8	600	1·02	0·6	52·8	29·3	41·8
412·4	1200	1·61	3·0	44·2	9·78	41·1
418·2	180	0·97	0·7	139	102	66·5
423·4	360	1·24	1·6	190	68·4	87·2
426·8	120	0·95	0·8	303	282	88·7
435·1	120	1·64	1·7	774	529	96·3
436·2	180	1·67	5·0	540	149	124·8
			Crotonaldehyde			
394·8	14,820	0·76	1·0	3·61	5·56	9·5
400·6	690	0·88	0·6	14·4	9·80	24·8
407·1	1800	0·95	1·5	13·3	3·73	33·9
407·1	7200	0·89	0·7	17·0	9·68	29·0
413·7	1800	1·11	1·6	34·4	9·58	46·9
427·9	240	1·13	2·5	127	70·4	62·9
427·9	180	1·14	1·2	206	290	50·0
430·9	480	1·13	2·0	122	57·9	66·4
436·6	180	1·05	1·8	285	224	85·3
440·6	180	1·08	1·4	449	444	92·1
448·3	100	0·78	0·8	743	1670	109·8
448·3	120	0·82	1·4	481	645	108·4

parent peroxide, being based on the known rate of this reaction.[9] The rate constants for the reactions (1)

$$CH_3 + R{\cdot}CHO = CH_4 + R{\cdot}CO \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

were then obtained from the expression

$$k_1 = k_2^{\frac{1}{2}}\, R_{CH_4}/R_{C_2H_6}{}^{\frac{1}{2}}[R{\cdot}CHO]$$

where k_2 is the rate constant of reaction (2) and R_{CH_4} is the rate of formation of methane.

$$2CH_3 = C_2H_6 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

We have taken log k_2 = 13·34 mole^{-1} cm.^{3} sec.$^{-1}$ (ref. 10). This expression is only correct if the methyl radicals are released at a uniform rate by the source. Specimen calculations

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[9] Pritchard, Pritchard, and Trotman-Dickenson, *J.*, 1954, 1425.

[10] Shepp, *J. Chem. Phys.*, 1956, **24**, 939.

show that the discrepancy is insignificant if less than 40% of the peroxide is decomposed; less than 15% was decomposed in most runs. Less than 3% of the aldehyde was normally consumed, so that its initial concentration was regarded as invariable.

EXPERIMENTAL

Apparatus.—A spherical Pyrex reaction vessel (700 c.c.) was housed in an electric furnace; the temperature varied less than ±0·25° along the vessel. The peroxide was stored in a 400 c.c. bulb with a cold finger. Pressures were measured on a dibutyl phthalate–mercury manometer with a magnification of 8·07. All the connecting tube was wound with heating tape. A conventional low-temperature distillation train was used to separate the methane + carbon monoxide and ethane. The carbon monoxide was oxidised by copper oxide and the gases were measured in a gas-burette. The ethane was contaminated with small amounts of propane and propene in the runs done with butyraldehyde. The proportion of ethane in the " C_2 " fraction was then determined by gas-chromatography. Ethylene was formed in the runs with crotonaldehyde; it was removed with a " mercuric acetate absorbent." [11]

Materials.—Di-t-butyl peroxide (L. Light and Co.) was used after bulb-to-bulb distillation. The aldehydes were tested for purity by gas-chromatography. The n-butyraldehyde, isobutyraldehyde, and crotonaldehyde (all from B.D.H.) were about 98% pure and were only degassed. Isovaleraldehyde (L. Light) was dried, after which no impurity was detected. n-Valeraldehyde (L. Light) was purified by preparation of the bisulphite complex. 2-Methylbutyraldehyde and pivalaldehyde were prepared by a modification of the Bouveault method.[12] The most probable impurities in each case were isomeric aldehydes; as will be seen, these would have little effect on the results.

RESULTS AND DISCUSSION

The results obtained are given in Table 1. The Arrhenius parameters for the *k*'s obtained by the method of least squares are given in Table 2, together with the rate constants for the abstractions at 182°. This temperature has been chosen for ease of comparison with other results.

TABLE 2. *Arrhenius parameters for the reactions:* $CH_3 + R{\cdot}CHO = CH_4 + R{\cdot}CO$.

Ref.	R	log *A* *	*E* (kcal. mole⁻¹)	log *k* * (182°)	log *k* * (182°) for RH[13]	R	log *A* *	*E* (kcal. mole⁻¹)	log *k* * (182°)	log *k* * (182°) for RH[13]
7	H	11·1	6·2	8·0	6·7	$\mathrm{Pr^n}$	11·8 ± 0·2	7·3 ± 0·3	8·2	6·8
8	H	11·3	6·6	8·1	6·7	$\mathrm{Pr^i}$	12·6 ± 0·2	8·7 ± 0·3	8·4	6·8
	Me	11·9 ± 0·1	7·6 ± 0·2	8·2	5·0	$\mathrm{Bu^n}$	12·1 ± 0·2	8·0 ± 0·3	8·2	7·1
1	Me	11·9	7·5	8·2	5·0	$\mathrm{Bu^i}$	12·3 ± 0·2	8·4 ± 0·3	8·2	7·3
2	Me	11·2	6·8	8·0	5·0	$\mathrm{Bu^s}$	13·1 ± 0·3	10·4 ± 0·3	8·2	7·1
3	Me	12·3	8·0	8·4	5·0	$\mathrm{Bu^t}$	13·0 ± 0·3	10·2 ± 0·3	8·2	7·3
5	Et	12·0	7·5	8·2	6·2					
6	Allyl	—	—	8·1 (170°)	7·1	Allyl	13·3	10·9	8·1	7·1

* *A* and *k* are in mole⁻¹ cm.³ sec.⁻¹.

The figures indicate that methane is formed predominantly by attack on the aldehyde group. This is suggested by the similarity of the rate constants at 182° for all the aldehydes. Further, the rate constants for the attack of methyl on RH shown in the last column amount only to 10% of the observed rate. Errors in the estimates of rate constants at temperatures close to the experimental range are likely to be small. The evidence is, therefore, compelling that the structure of an alkyl group slightly removed from a centre of reaction has little effect on reactivity of the aldehydic hydrogen. The finding provides direct support for conclusions based on less amenable systems such as alkanes.[13]

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[11] Kerr and Trotman-Dickenson, *Nature*, 1958, **182**, 466.

[12] Campbell, *J. Amer. Chem. Soc.*, 1937, **59**, 1982.

[13] Trotman-Dickenson, " Gas Kinetics," Butterworths, London, 1955.

The fact that the rate constants at 182° for all the reactions are similar makes it surprising that the Arrhenius parameters vary so widely beyond the limits of experimental error. The A factors for isobutyraldehyde, 2-methylbutyraldehyde, and pivalaldehyde are higher than those usually found for the metathetical reactions of methyl. The results with crotonaldehyde may not be reliable because the compound is of a rather different chemical type.

The standard errors obtained by the method of least squares may mislead if systematic errors occur. There is no evidence of this. The results with acetaldehyde agree very well with those of previous workers. Further, n-butyraldehyde and n-valeraldehyde have " normal " parameters, so that it is unlikely that systematic errors are connected with molecular size or low volatility. It appears that the deviations are marked when an alkyl group is attached as branch to the carbon atom next to the CHO group, but further examples are needed to establish this as a generalisation.

The relation between the rates of attack by methyl and by R on R·CHO will be discussed after the photolysis of pivalaldehyde has been described.

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