242. *The Reactions of Methyl Radicals with Formamide,* N-*Methyl- and* NN-*Dimethyl-formamide.*

By L. F. R. Cafferata, J. A. Kerr, and A. F. Trotman-Dickenson.

The following rate constants have been obtained for the abstraction of hydrogen atoms from formamides by methyl radicals: formamide (170—247°) $\log k$ (mole^{-1} c.c. sec.$^{-1}$) $= 10{\cdot}5 - (6{,}600/2{\cdot}3\,\boldsymbol{R}T)$; *N*-methylformamide (161—287°) $\log k$ (mole^{-1} c.c. sec.$^{-1}$) $= 10{\cdot}9 - (7{,}600/2{\cdot}3\,\boldsymbol{R}T)$; *NN*-dimethylformamide (120—298°) $\log k$ (mole^{-1} c.c. sec.$^{-1}$) $= 11{\cdot}4 - (8{,}300/2{\cdot}3\,\boldsymbol{R}T)$. These results are compared with methyl-radical reactions with aldehydes and formates.

It was shown by Birrell and Trotman-Dickenson[1] that the rate of attack of methyl radicals on aliphatic aldehydes, *i.e.*,

$$CH_3 + R{\cdot}CHO = CH_4 + R{\cdot}CO$$

is essentially independent of the alkyl group, R. Thynne[2,3] deduced a similar effect with formates, postulating that the reaction

$$CH_3 + H{\cdot}CO_2R = CH_4 + RO{\cdot}CO{\cdot}$$

predominates over methyl-radical attack on the alkyl side-chain. It therefore seemed of interest to study the influence of structure on the reactivity of methyl radical towards methyl formamides.

The photolysis of acetone was chosen as the source of methyl radicals, and the reactions were carried out with light from a full mercury arc filtered by a Pyrex plate to avoid absorption of light by the formamides. Under these conditions the mechanisms can be written as:

$$COMe_2 + h\nu = 2CH_3 + CO \qquad (I)$$

$$2Me = C_2H_6 \qquad (1)$$

$$Me + COMe_2 = CH_4 + {\cdot}CH_2{\cdot}COMe \qquad (2)$$

$$Me + XH = CH_4 + X{\cdot} \qquad (3)$$

where XH represents an amide. Further reactions of the radicals ${\cdot}CH_2{\cdot}COMe$ and X· may be neglected if they do not directly yield methane or ethane. It follows from this reaction scheme that

$$k_3/k_1^{1/2} = [R_{CH_4\,(total)} - (k_2[COMe_2]R_{C_2H_6}^{1/2}/k_1^{1/2})]/R_{C_2H_6}^{1/2}[XH]$$

where $R_{CH_4\,(total)}$ = rate of formation of CH_4 from reactions (2) and (3). From the results of Trotman-Dickenson and Steacie,[4]

$$\log k_2 \text{ (mole}^{-1}\text{ c.c. sec.}^{-1}) = 11{\cdot}6 - (9{,}700/2{\cdot}3\,\boldsymbol{R}T),$$

and $\log k_1$ (mole^{-1} c.c. sec.$^{-1}$) was taken as 13·35 (ref. 5).

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[1] Birrell and Trotman-Dickenson, *J.*, 1960, 2059.
[2] Thynne, *Trans. Faraday Soc.*, 1962, **58**, 676.
[3] Thynne, *Trans. Faraday Soc.*, 1962, **58**, 1533.
[4] Trotman-Dickenson and Steacie, *J. Chem. Phys.*, 1950, **18**, 1097.
[5] Shepp, *J. Chem. Phys.*, 1956, **24**, 939.

TABLE 1.

Hydrogen abstraction by methyl radicals from formamides.

Temp.	Time (sec.)	$[COMe_2]$ (10^{-6} mole c.c.$^{-1}$)	[Amide] (10^{-6} mole c.c.$^{-1}$)	CO	CH_4 (total)	$CH_4(2)$ *	$CH_4(3)$ *	C_2H_6	$k_3/k_1^{1/2}$
				Formamide					
170°	5100	0·45	0·43	5·97	3·81	0·90	2·91	3·40	3·64
196	6600	0·39	0·37	6·01	4·41	1·33	3·08	2·74	5·06
204	4140	0·43	0·39	6·42	5·28	1·76	3·52	2·77	5·74
212	2700	0·35	0·35	6·40	4·85	1·49	3·36	2·24	6·42
217	2700	0·41	0·34	6·89	6·08	2·24	3·84	2·92	6·62
227	2160	0·38	0·35	7·71	6·43	2·29	4·14	2·44	7·43
243	1500	0·37	0·33	9·10	7·44	2·78	4·66	2·05	9·88
247	1500	0·31	0·31	8·63	5·95	2·05	3·90	1·34	10·7
				N-Methylformamide					
161	1620	0·87	0·58	15·9	6·59	2·28	4·31	8·67	2·52
162	1560	0·80	0·64	14·1	6·49	2·01	4·48	7·56	2·54
162	960	0·78	0·70	16·1	7·53	2·13	5·40	8·85	2·57
180	1140	0·83	0·60	18·3	9·25	3·46	5·79	8·42	3·33
180	1500	0·80	0·61	20·1	10·0	3·42	6·62	8·84	3·67
185	1080	0·79	0·57	19·3	10·5	3·78	6·73	9·10	3·91
197	900	0·78	0·57	20·0	11·4	4·93	6·44	9·07	3·76
198	900	0·72	0·57	21·0	11·1	4·66	6·41	9·02	3·76
199	900	0·78	0 57	25·1	13·1	5·36	7·79	9·52	4·39
200	900	0·76	0·34	21·8	12·0	5·27	6·74	9·63	3·96
220	720	0·76	0·55	29·3	16·8	6·64	10·1	6·57	7·18
228	900	0·64	0·60	34·4	18·9	7·52	11·4	8·46	6·53
230	900	0·66	0·60	33·5	19·0	7·87	11·2	8·03	6·60
251	900	0·71	0·52	41·4	21·6	8·60	13·0	4·02	12·5
264	600	0·65	0·51	48·6	23·7	10·15	13·5	3·78	13·6
264	600	0·68	0·51	46·3	24·4	10·51	13·9	3·85	14·0
287	600	0·58	0·57	58·1	28·9	11·63	17·3	3·17	16·9
287	600	0·59	0·56	53·9	29·1	11·38	17·7	3·14	17·2
				NN-Dimethylformamide					
120	1965	0·82	0·78	15·5	4·19	0·75	3·44	11·7	1·29
122	1815	0·81	0·78	16·5	4·44	0·80	3·64	12·2	1·33
125	2160	0·82	0·64	17·7	4·27	0·95	3·32	13·4	1·41
132	1800	0·80	0·77	19·4	6·10	1·13	4·97	13·2	1·77
132	1800	0·80	0·75	14·8	5·39	9·92	4·47	8·89	2·00
134	1200	0·79	0·75	18·8	6·06	1·13	4·93	12·1	1·89
140	910	0·75	0·96	14·2	6·40	0·91	5·49	6·11	2·30
153	990	1·70	0·57	45·5	15·9	6·78	9·14	30·9	2·88
153	1260	1·71	0·57	43·7	15·0	6·56	8·49	28·5	2·80
155	955	1·87	0·36	49·8	14·2	8·28	5·91	35·0	2·72
160	900	0·75	0·72	23·7	11·3	2·25	9·08	12·4	3·57
164	1080	0·72	0·75	29·7	14·3	2·81	11·5	16·1	3·82
175	960	0·75	0·71	31·2	14·8	3·41	11·4	13·1	4·44
176	982	0·73	0·70	29·2	13·8	3·18	10·7	11·9	4·41
186	915	0·72	0·65	31·3	17·4	4·01	13·4	11·6	6·02
187	900	0·76	0·66	35·6	18·4	4·55	13·8	13·5	5·32
195	840	0·70	0·68	30·0	16·3	3·95	12·4	8·09	6·35
200	900	0·65	0·68	30·2	18·2	3·81	14·4	6·76	8·12
203	1020	0·68	0·64	43·1	20·4	4·73	15·7	8·33	8·34
204	900	0·68	0·64	30·3	18·3	4·37	13·9	7·11	8·12
207	1080	0·68	0·64	32·8	19·2	3·77	14·5	7·00	8·47
211	720	0·67	0·63	34·0	20·5	5·15	15·3	7·42	8·98
214	900	0·67	0·64	32·4	21·1	5·45	15·7	6·84	9·45
229	1080	0·65	0·62	31·7	23·6	5·65	17·9	4·39	13·8
241	1080	0·65	0·58	34·8	25·9	7·01	18·9	4·31	15·6
259	750	0·63	0·58	42·5	33·0	9·31	23·7	3·76	21·1
261	615	0·60	0·58	40·0	31·3	8·05	23·2	3·39	21·8
269	540	1·89	0·32	74·5	71·1	48·9	22·2	9·56	21·7
273	840	0·64	0·64	47·8	34·8	9·14	25·6	2·49	25·2
295	960	0·67	0·65	45·2	38·7	10·6	28·1	1·40	36·9
298	1140	0·63	0·72	47·8	36·8	9·96	26·8	4·35	32·0

Rates of formation of products; 10^{-12} mole c.c.$^{-1}$ sec.$^{-1}$.

* CH_4 from reactions (2) and (3) (see reaction scheme above).

EXPERIMENTAL

Apparatus.—Reactant mixtures were photolysed in a cylindrical quartz vessel (206 c.c.) housed in a coaxial electric furnace maintained at ±1°. Light from a medium-pressure mercury arc was filtered by a 3-mm. Pyrex plate and roughly collimated by a quartz lens to fill the cell completely. Metal valves or greaseless stopcocks were used throughout the reaction and analytical systems. All connecting tubing was wound with heating tape and reactant pressures were measured on a dibutyl phthalate–mercury manometer with a magnification of 5·0. The products were separated by low-temperature distillation into three fractions: (1) carbon monoxide and methane; (2) ethane; and (3) other products and unreacted starting materials. The first two fractions were analysed as previously described,[1] except that carbon monoxide was oxidised by iodine pentoxide. The third fraction was analysed by gas chromatography on a 10-ft. column packed with 30—40-mesh magnesium oxide impregnated with 10% by weight of potassium hydroxide and 20% by weight of polyethylene glycol 400.

Materials.—B.D.H. formamides were shaken with solid potassium hydroxide, filtered, and distilled under reduced pressure. Constant-boiling fractions were collected and further distilled bulb-to-bulb under vacuum. B.D.H. AnalaR acetone was used without further purification.

RESULTS AND DISCUSSION

From the results, shown in Table 1, the Arrhenius parameters listed in Table 2 were calculated by the method of least-mean-squares. Results for hydrogen-abstraction reactions by methyl radicals from aldehydes and formates are also given in Table 2 for comparison. It is interesting to compare the rate constants for the different classes of compound calculated at 182°, about the middle of the temperature range, and shown in Table 2. The very high value for aldehydes, which is almost constant throughout the series, was taken as a strong indication that methyl attack occurs predominantly at the acyl hydrogen atom. This is further substantiated for acetaldehyde by the results of Ausloos and Steacie's[7] studies on the reactions of methyl radicals with CH_3·CDO, more than 95% of the abstraction being D atoms. Thynne[2] showed that in the decomposition of methyl formate sensitised by methyl radical, the rate of formation of carbon dioxide is equal to the rate of formation of methane. This is good evidence of methyl-radical attack occurring only at the formyl hydrogen atom in methyl formate. This argument was extended to the

TABLE 2.

Arrhenius parameters for the reaction Me + XH = CH_4 + X.

Ref.	XH	log *A* *	*E* (kcal. mole^{-1})	log *k* * (182°)
	Formamide	10·5	6·6	7·3
	N-Methylformamide	10·9	7·6	7·2
	NN-Dimethylformamide	11·4	8·3	7·4
3	Methyl formate	10·7	8·6	6·6
3	Ethyl formate	10·5	8·2	6·6
3	n-Propyl formate	10·1	7·3	6·6
3	Isopropyl formate	10·9	8·9	6·6
3	n-Butyl formate	10·6	8·2	6·7
1	Acetaldehyde	11·9	7·6	8·2
6	Propionaldehyde	12·0	7·5	8·4
1	n-Butyraldehyde	11·8	7·3	8·2
1	Isobutyraldehyde	12·6	8·7	8·4
1	n-Valeraldehyde	12·1	8·0	8·2
1	Isovaleraldehyde	12·3	8·4	8·2
1	2-Methylbutyraldehyde	13·1	10·4	8·2
1	Pivaldehyde	13·0	10·2	8·2

* *A* and *k* are in mole^{-1} c.c. sec.$^{-1}$.

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

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

higher formates,[3] mainly on the basis of the constancy of the rate constant for methyl attack on the formates (see Table 2), although the carbon dioxide–methane equality was not experimentally verified in these cases. Further work, however, on n-propyl formate by Grotewold and Kerr [8] has cast considerable doubt on Thynne's deductions, and more work must be done with isotopically labelled formates before the relative proportions of methyl attack on the formyl hydrogen atom and on the alkyl side-chain will be known. It should be noted that the overall rate-constant at 182° for methyl attack on n-butyl formate is slightly less than that on n-butane, which seems to indicate [8] that methyl can attack the alkyl side-chains in higher formates.

The present results give no direct indication of where methyl radicals attack formamides. It does, however, seem reasonable to assume that aldehydes are attacked almost exclusively at the aldehydic hydrogen and formates at both the formyl and alkyl hydrogen atoms. Since the rate constants obtained here at 182° are intermediate between those for aldehydes and formates, methyl radicals may well attack formamides at both types of hydrogen atom but more on the formyl group than with formates. That attack occurs partially on the amino-group in formamides seems likely from the results of Gray and Thynne [9] with methylamine, for they showed that hydrogen atoms are abstracted from the amino group at a greater rate than from the alkyl group.

It should be noted that, in each case, k_3 is a composite quantity, *i.e.*, $k_3 = k_a + k_b$, where k_a and k_b are the rate constants for attack by methyl radicals on the difference points in the molecule. If the activation energies for reactions (*a*) and (*b*) were considerably different then curved Arrhenius plots of k_3 would be expected. That there is no significant curvature in the present plots may be taken as an indication that the activation energies are fairly similar.

An attempt was made to measure the amine products in the analysis of the third fractions of the three systems studied. None were detected by gas chromatography in the experiments with formamide or *N*-methylformamide. Trimethylamine was, however, observed from the *NN*-dimethylformamide system, amounting to 1—20% of the ethane produced, the proportion increasing with temperature. Presumably the trimethylamine results from the combination of a methyl with a dimethylamino radical, the latter arising from the reactions:

$$\mathrm{Me + H{\cdot}CO{\cdot}NMe_2 = CH_4 + {\cdot}CO{\cdot}NMe_2} \qquad (4)$$

$$\mathrm{{\cdot}CO{\cdot}NMe_2 = CO + {\cdot}NMe_2} \qquad (5)$$

Thus, if it is assumed that most of the dimethylamino radicals combine with methyl radicals, approximate Arrhenius parameters for reaction (4) should be obtained from an Arrhenius plot of the function $R_{\mathrm{NMe_3}}/R_{\mathrm{C_2H_6}}{}^{1/2}\,[\mathrm{H{\cdot}CO{\cdot}NMe_2}]$. Unfortunately our analytical data for trimethylamine are not sufficiently accurate, owing to the very small amounts produced at low temperature, to warrant even an approximate calculation of k_4.

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Edward Davies Chemical Laboratory,
Aberystwyth.

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[8] Grotewold and Kerr, *J.*, 1963, 4342.

[9] Gray and Thynne, *Trans. Faraday Soc.*, 1963, **59**, 2275.