Methoxyl-Radical-Induced Decomposition of Methyl Formate: Kinetics of Methoxyl and Methyl Radical Reactions

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The methoxyl-radical-induced decomposition of methyl formate has been studied and a mechanism suggested to account for the decomposition products. The cross-combination of methyl and methoxyl radicals has been studied. Arrhenius parameters (based on values of $10^{13 \cdot 20}$ and $10^{13 \cdot 34}$ cm^3 mole^{-1} sec^{-1} for the rate constants for the combination of methyl and methoxyl radicals, and auto-combination of methyl radicals respectively) have been deduced for the following radical reactions

	log (A/mole^{-1}.cm^3 sec^{-1})	E/kcal mole^{-1}
$CH_3O\cdot + HCOOCH_3 \rightarrow CH_3OH + \cdot COOCH_3$	12·21	8·2
$CH_3O\cdot + \cdot CH_3 \rightarrow CH_2O + CH_4$	13·38	0
$\cdot CH_3 + CH_3OOCH_3 \rightarrow CH_4 + \cdot CH_2OOCH_3$	12·56	10·0

The results indicate that methoxyl radicals are considerably more reactive than are methyl radical in abstracting hydrogen from the formate molecule, and suggest that differences in the A-factors are primarily responsible for the different reactivities. The disproportionation ratio $\Delta(CH_3, CH_3O)$ is found to be 1·51 ±0·2 and not to depend on temperature.

Although the existence of alkoxyl radicals is known and their participation in many reactions has been reported,[1, 2] there are few adequate kinetic data available, and there is uncertainty as to the relative reactivities of such simple radicals as methyl and methoxyl. Wijnen [3, 4] has studied the photolysis of methyl acetate (which is a source of methoxyl), and has deduced that methoxyl radicals are considerably more reactive than methyl radicals in abstracting hydrogen atoms from the parent acetate molecule. His results also indicate that the difference in reactivity is associated with a low activation energy for abstraction by the methoxyl radicals. Shaw and Trotman-Dickenson [5] suggested that Wijnen's data can be interpreted to give to a higher value for the activation energy of hydrogen atom abstraction by these radicals. These authors [5] have investigated the reactions of methoxyl radicals with alkanes and concluded that methoxyl radicals probably have reactivities similar to those of methyl radicals. Further work by Bercés and Trotman-Dickenson [6] on the reaction of methoxyl and cyclopropane and isobutane indicated, however, that methoxyl radicals exhibit a greater reactivity than do methyl radicals.

Methoxyl radicals yield methyl alcohol by abstracting an hydrogen atom (reaction (1)). They also produce alcohol by auto-disproportionation in reaction (2):

$$CH_3O\cdot + RH \rightarrow CH_3OH + R\cdot \qquad (1)$$

$$CH_3O\cdot + CH_3O\cdot \rightarrow CH_3OH + CH_2O. \qquad (2)$$

Although in principle, the contribution of reaction (2) to the total alcohol formed can be deduced by measuring the formaldehyde produced, it is difficult in practice because of the tendency of formaldehyde to polymerize in the reaction system, and it is principally this difficulty that has limited the accuracy of deductions from previous kinetic studies of methoxyl radicals.

A system in which the amount of R• produced in reaction (1) can be measured precisely would offer a solution to this problem. Previous work [7–10] on the radical induced decompositions of formate esters suggests that the abstraction reaction of the formyl hydrogen atom from the ester, leading to the production of an alkoxy carbonyl radical, •COOR, would provide such a system, since these radicals have been shown to decompose exothermically [11] and quantitatively to carbon dioxide and a free alkyl radical:

$$\cdot\text{COOR} \rightarrow \text{CO}_2 + \text{R}\cdot. \qquad (3)$$

Accordingly, the methoxyl radical induced decomposition of methyl formate has been studied from 124 to 185°C. The thermal decomposition of dimethyl peroxide was used as the source of methoxyl radicals. In this way values are derived for the Arrhenius parameters of the hydrogen abstraction reaction from formate by methoxyl radicals and of the disproportionation reaction between methoxyl and methyl radicals. The rate of formation of dimethyl ether is used [6] as the index of the methoxyl radical concentration.

EXPERIMENTAL

MATERIALS

Dimethyl peroxide was prepared according to Hanst and Calvert.[12] However, peroxide prepared in this manner contained about 15 % dimethyl ether. Since low-temperature fractionation did not remove all the ether, the peroxide was further purified by gas chromatography. A 20-ft column of dimethyl sulpholane on firebrick at room temperature was able to separate the ether and peroxide. Helium was used as the carrier gas (flow rate of 60 ml min^{-1}). The peroxide was then stored in a blackened bulb, surrounded by a Cardice trap, and showed no ether impurity on further chromatographic analysis. When it was analyzed on a mass spectrometer (AEI Ltd., MS 2), the following cracking pattern was obtained:

mass number	relative intensity* (this work)	relative intensity* (ref. (13))	relative intensity* (ref. (14))
12	0·3	1·6	0·2
14	1·6	6·2	1·6
15	20·2	34·5	17·3
28	7·4	7·4	3·2
29	56·7	100	60·1
30	21·8	24·4	16·0
31	94·8	96·2	80·6
32	11·1	13·6	8·6
44	0·3	0·5	0·1
45	0·7	1·2	3·3
46	0·1	0·6	1·6
61	9·74	5·2	9·0
62	100	58·4	100
63	2·3	1·2	2·2

* Ionizing Voltage 70 V.

Dimethyl ether was collected from the gas chromatographic preparations of the peroxide described above and stored in a glass bulb. It was shown to be pure by mass spectrometric and further gas chromatographic analysis.

Methyl formate (B.D.H. Ltd.) was distilled, dried and stored after further bulb-to bulb distillation on the vacuum line. Ethane (B.O.G. Ltd.) was obtained from a cylinder. The carbon dioxide, of 99·9 % purity, was a gift from Dr. Willix of these laboratories.

APPARATUS AND PROCEDURE

The essential features of the apparatus and techniques employed [15] have been described previously. Mixtures of the formate and peroxide were made up in a 1 l. bulb before expansion into the reaction system. No attempt was made to analyze either the methyl alcohol, or the formaldehyde produced by reaction (2).

RESULTS AND DISCUSSION

Hanst and Calvert [12] have established the main features of the thermal decomposition of dimethyl peroxide over the temperature range used here, and consequently the kinetics of the thermal decomposition of dimethyl peroxide were not studied extensively. It was, however, observed that some hydrogen was present in the non-condensable reaction products, presumably being formed by a sequence of reactions such as:

$$CH_3OOCH_3 \rightarrow 2CH_3O\cdot$$
$$CH_3O\cdot + CH_3O\cdot \rightarrow CH_3OH + CH_2O$$
$$CH_3O\cdot + CH_2O \rightarrow CH_3OH + \cdot CHO$$
$$\cdot CHO \rightarrow CO + H$$
$$2\cdot CHO \rightarrow H_2 + 2CO.$$

STOICHIOMETRY AND REACTION MECHANISM FOR THE DECOMPOSITION OF METHYL FORMATE INDUCED BY METHOXYL RADICALS

The analytical results are presented in table 1. The nature and distribution of the reactions products can be accounted for by the following reaction mechanism:

$$CH_3OOCH_3 \rightarrow 2CH_3O\cdot \tag{4}$$
$$CH_3O\cdot + HCOOCH_3 \rightarrow CH_3OH + \cdot COOCH_3 \tag{5}$$
$$\cdot COOCH_3 \rightarrow CO_2 + \cdot CH_3 \tag{5a}$$
$$\cdot CH_3 + HCOOCH_3 \rightarrow CH_4 + \cdot COOCH_3 \tag{6}$$
$$\cdot CH_3 + CH_3O\cdot \rightarrow CH_4 + CH_2O \tag{7}$$
$$\cdot CH_3 + CH_3O\cdot \rightarrow CH_3OCH_3 \tag{8}$$
$$2\cdot CH_3 \rightarrow C_2H_6 \tag{9}$$
$$\cdot CH_3 + CH_3OOCH_3 \rightarrow CH_4 + \cdot CH_2OOCH_3 \tag{10}$$
$$CH_3O\cdot + CH_2O \rightarrow CH_3OH + \cdot CHO \tag{11}$$
$$\cdot CHO \rightarrow CO + H \tag{12}$$
$$2\cdot CHO \rightarrow H_2 + 2CO \tag{13}$$

No account is taken of the possible abstraction of a hydrogen atom from the methyl group of the formate, since it could not reasonably lead to the formation of either carbon dioxide or methyl radicals. Dimethyl ether can be formed only by reaction (8), and its estimation thus presents a convenient method of determining the methoxyl concentration if k_8 (the rate constant for combination of methyl and methoxyl radicals) is known. As yet, no direct experimental value for k_8 has been reported and the semi-empirical value of 13·20 for $\log(k_8/\text{cm}^3\ \text{mole}^{-1}\ \text{sec}^{-1})$ proposed by Bercés and Trotman-Dickensen [6] will be adopted in this paper. This value * is derived from the cross-combination expression $k_8 = 2(k_9k_{-4})^{\frac{1}{2}}$.

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* The value 13·5 for $\log k_8$ in ref. 6 has been corrected for an arithmetical slip.

TABLE 1

T°K	t(sec)	10^{-17} molecules cm^{-3}		10^{-12} molecules cm^{-3} sec^{-1}						$\frac{10^{12}R_{CO_2}^{(5a)}R_{C_2H_6}^{\frac{1}{2}}}{R_{CH_3OCH_3}[M]}$	$\frac{10^{12}R_{CH_4}^{(5a)}R_{C_2H_6}^{\frac{1}{2}}}{R_{CH_3OCH_3}[M]}$
		P	M	CH_4	CO	H_2	C_2H_6	CH_3OCH_3	CO_2		
393·3	240	1·46	4·97	2·22	11·2	0·37	1·24	0·59	7·60	28·7	20·2
393·7	1860	1·16	19·09	1·59	3·44	0·12	2·56	0·34	6·92	15·5	15·9
394·5	360	2·10	2·10	1·82	16·0	0·48	0·54	0·53	4·49	29·2	22·3
397·5	600	1·66	18·65	4·32	15·6	0·69	8·12	1·48	22·9	22·3	21·4
402·8	1800	1·40	23·0	NA	NA	NA	3·61	0·40	12·6	17·5	—
411·3	360	1·26	14·12	6·19	14·8	0·60	7·52	1·97	24·6	22·9	21·5
411·5	600	0·95	10·93	4·07	12·2	0	4·11	1·16	13·5	20·2	20·2
412·3	840	0·79	8·81	3·05	9·0	0	3·48	1·07	11·9	22·0	20·5
413·0	600	0·98	11·33	5·02	11·2	0·27	5·41	1·42	17·8	24·4	23·4
414·3	120	1·65	5·87	12·8	70·7	NA	8·61	6·14	32·5	26·2	29·5
414·6	180	2·08	7·42	14·2	67·7	NA	9·64	5·50	38·2	28·4	29·0
414·8	150	1·97	7·02	10·5	57·6	1·6	6·97	4·45	34·8	28·9	23·9
414·9	120	1·08	3·85	8·9	40·5	1·0	4·04	4·36	20·6	27·2	28·3
418·7	360	1·48	18·5	12·0	24·8	1·36	16·8	3·92	54·7	30·3	27·2
419·2	600	1·28	17·1	6·60	12·9	0·52	9·34	1·62	29·1	29·8	27·4
423·2	960	0·88	14·5	6·36	13·1	0·42	7·93	1·34	24·6	32·9	31·4
423·5	150	3·07	5·88	16·4	61·6	1·78	7·32	3·75	30·5	36·6	37·5
430·0	450	0·81	10·5	7·93	19·9	0·48	10·2	2·45	35·3	41·4	35·6
441·0	60	3·59	6·88	47·6	200	5·08	28·9	11·9	110	70·3	75·1
453·2	60	2·00	8·73	92·2	309	9·3	66·2	34·2	266	69·1	67·5
453·4	30	0·88	5·76	41·9	181	4·7	33·6	14·2	103	73·6	73·5
454·2	120	2·45	5·69	60·9	302	8·2	21·1	12·9	119	72·9	67·8
454·5	120	1·60	5·29	47·1	234	6·2	15·3	8·65	87·5	73·4	72·3
454·7	60	1·39	6·09	NA	NA	NA	40·2	18·1	170	91·9	—
454·7	150	1·99	8·71	61·1	252	3·09	41·5	18·7	173	66·4	62·3

N.A. = not analyzed; P = concentration dimethyl peroxide, 10^{17} molecules cm^{-3}; M = concentration methyl formate, 10^{17} molecules cm^{-3}; rate of change of concentration of reaction products expressed as 10^{12} molecules cm^{-3} sec^{-1}.

ARRHENIUS PARAMETERS FOR REACTIONS OF METHYL RADICALS: HYDROGEN ABSTRACTION FROM CH_3OOCH_3 AND CH_3O

The methane produced during the reaction will be formed by reactions (6), (7) and (10). That produced by reaction (6) can be calculated and corrected for using previously reported data.[8] The remaining methane produced by reactions (7) and (10) is described by the equation:

$$\frac{R_{CH_4}^{\text{total}}-R_{CH_4}(6)}{R_{CH_3OCH_3}}=\frac{k_7}{k_8}+\frac{k_{10}k_9^{\frac{1}{2}}}{k_8}\frac{[CH_3OOCH_3]}{R_{C_2H_6}^{\frac{1}{2}}}.$$

Plotting this equation at a series of temperatures yields a series of values for both $k_{10}k_9^{\frac{1}{2}}/k_8$ and k_7/k_8. These values are plotted in fig. 1, curves 1 and 2, respectively.

THE REACTION BETWEEN CH_3 AND CH_3OOCH_3

If a value of $10^{13 \cdot 20}$ mole^{-1} cm^3 sec^{-1} is assumed for k_8 and the reported value [16] of $10^{13 \cdot 34}$ used for k_9 (mole^{-1} cm^3 sec^{-1}), then the rate constant for the abstraction of hydrogen by methyl radicals from dimethyl peroxide can be expressed by

$$\log (k_{10}/\text{mole}^{-1}\text{ cm}^3\text{ sec}^{-1}) = 12{\cdot}56-9960/2{\cdot}303\,RT.$$

No previous value has been reported. Pritchard, Pritchard and Trotman-Dickenson [17] investigated the related abstraction of hydrogen atoms by methyl radicals from di-t-butyl peroxide and obtained values of 12·4 and 11·7 kcal mole^{-1} for log A and E. For the abstraction of hydrogen atoms from dimethyl ether by methyl radicals values for log A and E of 11·5 and 9·5 kcal mole^{-1} respectively have been reported.[19]

DISPROPORTIONATION OF METHOXYL AND METHYL RADICALS

The quotient k_7/k_8 is the disproportionation ratio for methyl and methoxyl radicals, $\Delta(CH_3, CH_3O)$. The rate relation obtained above yields values for k_7/k_8 of $1{\cdot}51 \pm 0{\cdot}2$ which, within a fairly large scatter, are independent of temperature. The results are shown in fig. 1, curve 2; the value of log (k_7/mole^{-1} cm^3 sec^{-1}) is $13{\cdot}38 \pm 0{\cdot}06$.

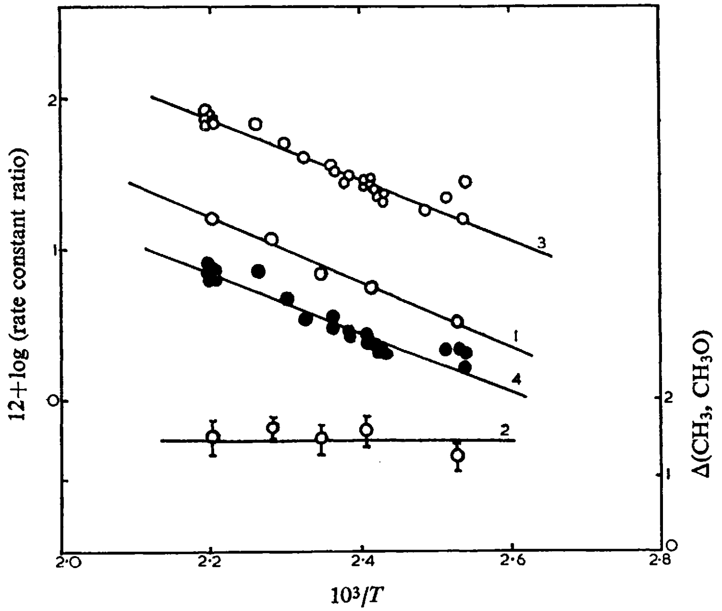

FIG. 1.—Arrhenius plots for methyl and methoxyl radicals:

(1) hydrogen-atom abstraction by methyl radicals from dimethyl peroxide, $k_{10}k_9^{\frac{1}{2}}/k_8$ (molecules$^{-\frac{1}{2}}$ cm$^{3/2}$ sec^{-1});

(2) disproportionation ratio for methyl and methoxyl radicals, k_7/k_8, $\Delta(CH_3, CH_3O)$; Scale on right hand side of figure refers to curve 2;

(3) hydrogen-atom abstraction by methoxyl radicals from methyl formate, $k_5k_9^{\frac{1}{2}}/k_8$ (molecules$^{-\frac{1}{2}}$ cm$^{3/2}$ sec$^{-\frac{1}{2}}$), results based on carbon dioxide produced;

(4) hydrogen-atom abstraction by methoxyl radicals from methyl formate, $k_5k_9^{\frac{1}{2}}/k_8$ (molecules$^{-\frac{1}{2}}$ cm$^{3/2}$ sec$^{-\frac{1}{2}}$), results based on summation of methyl radicals produced.

Curve 4 has been displaced downwards by 1·0 units.

This value of 1·5 may be somewhat greater than the actual value of k_7/k_8 since some of the methane formed will probably have arisen by the interaction of methyl radicals with the formaldehyde or methanol produced during the decomposition, i.e., by reactions (14) and (15):

$$\cdot CH_3 + CH_2O \rightarrow CH_4 + \cdot CHO \tag{14}$$

$$\cdot CH_3 + CH_3OH \rightarrow CH_4 + \cdot CH_2OH \tag{15}$$

The contributions of (14) and (15) are not likely to be considerable, however, since no temperature dependence is observed for k_8/k_9, and mass balances for the reaction products show no consistent methyl radical deficiency. Moreover, other values reported [3, 4] for the disproportionation ratio of methyl and methoxyl radicals are 1·9 and 1·4 for the radicals CH_3 and CD_3O. All these ratios are surprisingly high since they indicate that disproportionation is favoured over recombination, whereas the reverse behaviour is observed when two simple unbranched alkyl radicals react. In view of the isoelectronic character of methoxyl and ethyl radicals it is interesting to note that whereas Δ(Me, MeO) is 1·5, the value reported[8, 18] for Δ(Me, Et) is only about 0·06. From thermodynamic data, $D(H—C_2H_4)$ and $D(H—CH_2O)$ are 40·1 and 24·9 kcal mole^{-1} respectively, and clearly a hydrogen atom may be more easily removed from a methoxyl radical than from an ethyl radical in a disproportonating reaction with a methyl radical. Thus thermochemical considerations aire a more reliable guide to the behaviour of isoelectronic radicals than are applications of the isoelectronic principle. This supports previous conclusions.[11]

ARRHENIUS PARAMETERS FOR THE REACTION OF METHOXYL RADICALS WITH METHYL FORMATE

The mechanism suggested above indicates that

$$R_{CH_3OH}(5) = R_{CO_2}(5a) = R_{CH_3}(5a)$$

The contribution of reaction (6) towards the methyl radical concentration can be ignored, since one methyl radical is generated for each methyl radical consumed.

The following rate-relation can be obtained:

$$R_{CO_2}(5a)R^{\frac{1}{2}}_{C_2H_6}/R_{CH_3OCH_3}[HCOOCH_3] = k_5k^{\frac{1}{2}}_9/k_8.$$

A similar expression can be derived for $R_{CH_3}(5a)$, and gives a check on the value for k_5 calculated on the basis of carbon dioxide measurements. The results obtained are plotted in fig. 1 (curves 3 and 4) and are expressed by the equations:

$$\log (k_5/\text{mole}^{-1}\ \text{cm}^3\ \text{sec}^{-1}) = (12{\cdot}21 \pm 0{\cdot}24) - (8180 \pm 480)/2{\cdot}303\ RT \text{ (based on } CO_2\text{)},$$

and

$$\log (k_5/\text{mole}^{-1}\ \text{cm}^3\ \text{sec}^{-1}) = (12{\cdot}33 \pm 0{\cdot}20) - (8460 \pm 490)/2{\cdot}303\ RT \text{ (based on } CH_3\text{)}.$$

The good agreement between Arrhenius parameters calculated by those two approaches supports the mechanism suggested to account for the decomposition.

No previous values have been reported for comparison. Reaction (6) has values[8] for log *A* and *E* of 10·69 and 8·6 and a value[8] for log k_6 at 182°C of 6·59. Since log k_5 at this temperature is 8·27, methoxyl radicals are considerably more reactive in hydrogen abstraction from methyl formate than are methyl radicals. Wijnen's results for hydrogen abstraction by methoxyl and methyl from methyl acetate (reactions (16) and (17)),

$$CH_3O\cdot + CH_3COOCH_3 \rightarrow CH_3OH + \cdot CH_2COOCH_3 \qquad (16)$$

$$\cdot CH_3 + CH_3COOCH_3 \rightarrow CH_4 + \cdot CH_2COOCH_3, \qquad (17)$$

which lead to values for log k_{16} and log k_{17} of 8·04 and 6·49, respectively, imply that the relative reactivity of methyl and methoxyl radicals is approximately the same (k_5/k_6 is *ca.* 50 and k_{16}/k_{17} is *ca.* 35) as found in this investigation. However, whereas Wijnen reports values for E_{16} and E_{17} of 4·5 and 10 kcal mole^{-1}, respectively, so that in attack on methyl acetate differences in reactivity may be ascribed to differences in activation energies, in our work, since the values of E_5 and E_6 differ by less than 1 kcal mole^{-1}, the difference in reactivity of the radicals towards methyl formate arises from the *A*-factors.

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