Flash Photolysis of Methyl Acetate in Gas Phase. Products and Rate Constants of Reactions between Methyl, Methoxy and Acetyl Radicals

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Products of the flash photolysis of methyl acetate at 298 K and at initial pressures of methyl acetate from 1.5 to 100 Torr were analyzed by gas chromatography. Relative values of rate constants of seven addition or hydrogen abstraction reactions between methyl, methoxy and acetyl radicals were calculated. About 80 % of methyl acetate is dissociated by $\alpha(C-O)$ bond breaking and 20 % by $\alpha(C-C)$ bond breaking; $\beta(C-O)$ bond breaking is negligible.

The primary photodissociation of esters occurs at the $\alpha(C-C)$, $\alpha(C-O)$ or $\beta(C-O)$ bond.[1] $\beta(C-O)$ bond breaking is not important in the photolysis of aliphatic esters.[1] According to Linnett, Gilbert and Read[2] and Wijnen,[3,4] about 80 to 90 % of the dissociation of methyl acetate takes place at the $\alpha(C-O)$ bond. Methyl, methoxy and acetyl radical intermediates are formed,[2-4] in addition to CO and CO_2, and these radicals react to form the products CH_4, C_2H_6, CH_3OCH_3, CH_3OH, CH_3COCH_3 and $(CH_3CO)_2$. Small amounts of CH_2O and CH_2CO have been found[3] as well, but could not be measured quantitatively. The formation of CH_3OOCH_3 has also been suggested.[2,3]

In this study we have measured the amounts of products of the flash photolysis of methyl acetate in the gas phase and calculated the rate constants of radical reactions. The values of rate constants are expected to be reliable since high concentrations of radicals are produced during the flash and the reactions between radicals are much faster than the reactions between radicals and methyl acetate.

EXPERIMENTAL

Materials. Methyl acetate was dried with phosphorus pentaoxide, distilled and degassed. It was found to be pure by gas chromatography.

Methods. The flash apparatus was similar to that described earlier.[5] A 5 cm^3 loop was used to collect samples of gas mixtures. The samples were analyzed by gas chromatography on a temperature-programmed 6 mm column filled with Chromosorb 102 or Porapak Q. A TC-detector was employed. All main products were identified through reference to the retention times of known substances and some also by mass spectroscopy. The areas of the peaks of the gas chromatograms were measured with a planimeter and the amounts of products in mol relative to the amount of carbon dioxide were calculated from the equation

$$n_x = \frac{F_x A_x \, 44 \, \text{mol g}^{-1}}{F_{CO_2} A_{CO_2} M_x} \tag{1}$$

where A_x is the peak area, F_x the weight factor, M_x the molar mass and n_x the relative amount of substance x. The weight factors were obtained by calibration with known amounts of substances. The weight factors and retention times α relative to the CO_2 peak are given in Table 1.

Ethene and acetaldehyde have not been found previously among the products of photolysis of methyl acetate. Conversely, the dimethyl peroxide and ketene reported by Linnett[2] and Wijnen[3] were not found among the products in our experiments. It is difficult[6] to detect small amounts of ketene by gas chromatography, however. Small amounts of formaldehyde could not be measured quantitatively, but larger amounts were reliably measured as shown by comparison with calibrated values.[7] The peaks of methanol and dimethyl ether

Table 1. Values of relative retention times $\alpha = (t_x - t_{N_2})/(t_{CO_2} - t_{N_2})$ and relative weight factors F of the reaction products of flash photolysis of methyl acetate analyzed on Chromosorb 102 and Porapak Q columns at 413 and 453 K.

Compound	α Chromosorb 102		α Porapak Q		F This work	F Ref. 21
	413 K	453 K	413 K	453 K		
CO	0	0	0	0	0.58	0.58
CH_4	0.40	0.33	0.43	0.40	0.39	0.39
CO_2	1.00	1.00	1.00	1.00	0.79	0.79
C_2H_4	1.80	1.67	2.00	1.80	0.51	—
C_2H_6	2.00	1.91	2.71	2.40	0.51	0.51
CH_2O	4.00	3.67	3.29	1.80	0.50	—
CH_3OH	7.20	6.33	8.14	5.20	0.50	0.50
CH_3OCH_3	7.60	7.00	8.00	5.05	0.49	—
CH_3CHO	10.40	9.00	11.57	7.40	0.58	0.58
$HCOOCH_3$	14.60	11.67	—	—	0.58	—
CH_3COCH_3	28.00	20.33	37.29	19.80	0.58	0.58
CH_3COOCH_3	33.40	23.67	48.14	24.40	0.68	—
$(CH_3CO)_2$	73.60	44.00	—	40.40	1.00	—
$CH_3OCOOCH_3$	81.00	50.00	—	44.20	—	—
$CH_3COOC_2H_5$	86.00	56.00	—	50.60	0.68	0.68

Table 2. Relative amounts ($CO_2 = 100$ ml) of products of the photolysis of methyl acetate at 298 K (extrapolated values) corresponding to the first flash at different pressures P of methyl acetate. When the relative values are multiplied by the constant C, absolute partial pressures of products are obtained.

Products	P/Torr 0	1.5	3.2	6.5	12.5	25	50	100	∞
CO	250	228	204	162	119	152	159	140	150
CO_2	100	100	100	100	100	100	100	100	100
CH_4	76	74	77	69	61	63	63	63	63
C_2H_4	21	19	17	11	8	8	4	3	1
C_2H_6	112	97	103	82	67	73	63	69	64
H_2CO	(35)				76	94	107	117	130
CH_3OH	15		22	14	23	22	41	48	53
CH_3OCH_3	70		74	66	72	79	76	67	77
CH_3CHO	34	35	37	39	42	55	56	64	71
$HCOOCH_3$	1					1	1	1	1
CH_3COCH_3	40	42	43	48	57	59	64	70	77
$(CH_3CO)_2$	12	10	16	15	20	28	34	38	45
$CH_3OCOOCH_3$	2		3	3	4	6	5	6	7
$CH_3COOC_2H_5$	1				1	1		1	1
10^5 C/Torr		1.5	3.0	5.8	9.4	14	29	37	

were partly overlapping, introducing a small additional experimental error to the values of the amounts of these products.

The relative amounts of products were calculated from analyses of the reaction mixtures obtained after photolyzing methyl acetate with 5 to 100 flashes. The relative amounts of products formed after the first flash were found by extrapolation (Table 2).
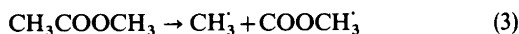
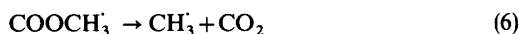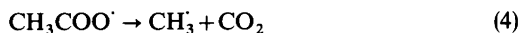The total amount of methyl acetate that reacted during one flash was calculated from the amounts of products:

$$\Delta CH_3COOCH_3 = CO_2 + CO + CH_3CHO + CH_3COCH_3 + 2(CH_3CO)_2 + HCOOCH_3 + CH_3OCOOCH_3$$
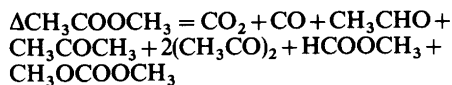
For example, at 100 mmHg pressure of methyl acetate 0.17 % of the ester was photodissociated during one flash. If the amount of methyl acetate formed in reaction 10 is estimated to be approximately equal to the amount of acetaldehyde formed in reaction 11 the photodissociation of methyl acetate must be about 0.19 %.

DISCUSSION

The three possible primary dissociation reactions of electronically excited methyl acetate are:

$$CH_3COOCH_3 \rightarrow CH_3COO^{\cdot} + CH_3^{\cdot} \qquad (1)$$

$$CH_3COOCH_3 \rightarrow CH_3CO^{\cdot} + CH_3O^{\cdot} \qquad (2)$$

$$CH_3COOCH_3 \rightarrow CH_3^{\cdot} + COOCH_3^{\cdot} \qquad (3)$$

The possible secondary dissociation reactions of the radicals formed in reactions 1 to 3 are:

$$CH_3COO^{\cdot} \rightarrow CH_3^{\cdot} + CO_2 \qquad (4)$$

$$CH_3CO^{\cdot} \rightarrow CH_3^{\cdot} + CO \qquad (5)$$

$$COOCH_3^{\cdot} \rightarrow CH_3^{\cdot} + CO_2 \qquad (6)$$

$$COOCH_3^{\cdot} \rightarrow CH_3O^{\cdot} + CO \qquad (7)$$

Products resulting from reactions of $CH_3COO^{\cdot}$ radicals were not found in the flash photolysis of methyl acetate. The most likely product of reactions of $CH_3COO^{\cdot}$ radicals is CH_3COOCH_3, but it was not found by Wijnen[4] during the photolysis of CH_3COOCD_3 in the gas phase. The thermal decomposition of diacyl peroxide produces two $CH_3COO^{\cdot}$ radicals, but no methyl acetate was found in the gas phase.[8,9] Methyl acetate was formed in the liquid phase, however. The rate constant k_1 for the unimolecular decomposition of the $CH_3COO^{\cdot}$ radical has been estimated[9] at between 10^9 and 10^{10} s^{-1}. The dissociation is thus about 10^4 times faster than the radical combination reactions in our flash experiments, and it cannot be concluded whether reaction 1 occurs or not in the photolysis of methyl acetate.
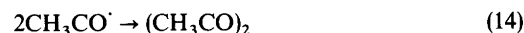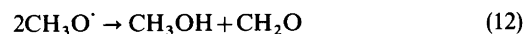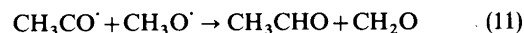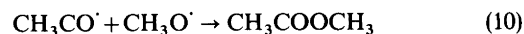
The photolysis[10] of methyl phenylacetate in methanol at 298 K, which is expected to occur by a

similar mechanism as the photolysis of methyl acetate, produces carbon monoxide and carbon dioxide. The value of the ratio $(CO)/(CO_2)$ is 1.4, which is close to the value 1.5 obtained for methyl acetate photolysis at the high pressure limit. The photolysis of methyl acetate and methyl phenylacetate in each case can produce $COOCH_3$ radicals. These could dissociate by reactions 6 and 7 forming carbon dioxide and carbon monoxide, respectively, and the ratio of these products should be the same for the two acetates. Photolysis[11] of benzyl phenylacetate in methanol at 299 K leads to a much lower value of the ratio $(CO)/(CO_2)$, namely, 0.03. Here the dissociation of $COOCH_2C_6H_5$ radicals by a reaction similar to 6 is more important than the dissociation by a reaction similar to 7. Thynne[12] has demonstrated that thermodynamically only reaction 6 is possible for the dissociation of methoxycarbonyl radical $COOCH_3$.

Small amounts of products derived from $COOCH_3^{\cdot}$ radicals, methyl formate and dimethyl carbonate, were obtained in the flash photolysis of methyl acetate (Table 2). In our experiments large radical concentrations are produced by the high energy flash and radical combination reactions producing radical addition products compete with the unimolecular dissociation of $COOCH_3^{\cdot}$.

Large amounts of acetone, biacetyl and acetaldehyde were obtained (Table 2) from combination reactions of acetyl radicals. The dissociation of thermally equilibrated acetyl radicals (Reaction 5) is slow[13] and not important in our flash experiments.[14] Some of the acetyl radicals formed in reaction 2 are expected to contain an excess of energy, however, and could dissociate[15] by reaction 5.

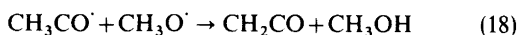The following reactions are proposed to explain the observed products:

$$CH_3^{\cdot} + CH_3O^{\cdot} \rightarrow CH_3OCH_3 \qquad (8)$$

$$CH_3^{\cdot} + CH_3O^{\cdot} \rightarrow CH_4 + CH_2O \qquad (9)$$

$$CH_3CO^{\cdot} + CH_3O^{\cdot} \rightarrow CH_3COOCH_3 \qquad (10)$$

$$CH_3CO^{\cdot} + CH_3O^{\cdot} \rightarrow CH_3CHO + CH_2O \qquad (11)$$

$$2CH_3O^{\cdot} \rightarrow CH_3OH + CH_2O \qquad (12)$$

$$2CH_3^{\cdot} \rightarrow CH_3CH_3 \qquad (13)$$

$$2CH_3CO^{\cdot} \rightarrow (CH_3CO)_2 \qquad (14)$$

$$CH_3CO^{\cdot} + CH_3^{\cdot} \rightarrow CH_3COCH_3 \qquad (15)$$

This scheme is similar to but simpler than that proposed by Wijnen.[3] The reaction

$$2CH_3O^{\cdot} \rightarrow CH_3OOCH_3 \qquad (16)$$
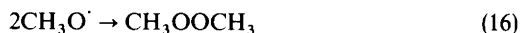
is not important because dimethyl peroxide was not found among the products. Dever and Calvert[16] report a lower limit of $k_{12}/k_{16} \geq 60$, Yee Quee and Thynne[17] a value of about 10 and another value[18] of 67, whereas for the ratio of corresponding reactions of ethoxy radicals Heickelen and Johnston[19] report a value of 9.3 at 25 °C. Our results point to a lower limit of about $k_{12}/k_{16} \geq 50$.

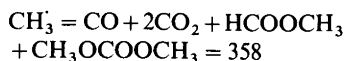The hydrogen transfer reactions of acetyl radicals are slow.[3]

$$CH_3CO^{\cdot} + CH_3^{\cdot} \rightarrow CH_2CO + CH_4 \qquad (17)$$

$$CH_3CO^{\cdot} + CH_3O^{\cdot} \rightarrow CH_2CO + CH_3OH \qquad (18)$$

$$2CH_3CO^{\cdot} \rightarrow CH_2CO + CH_3CHO \qquad (19)$$

No ketene was found among the reaction products. Ketene is difficult to detect[6] by gas chromatography, however. Wijnen[3] reported finding ketene in the photolysis of methyl acetate and calculated a value of $k_{17}/k_{15} = 0.05$. Our results suggest an even smaller value. Small amounts of acetaldehyde were found in the flash photolysis of acetone and biacetyl.[12] In the flash photolysis of methyl acetate, acetaldehyde is formed mainly by reaction 11, but some 10 % of the acetaldehyde obtained could result from reaction 19 involving hot acetyl radicals.

The small amounts of ethene were found among the products of methyl acetate photolysis (Table 2). Small amounts of ethene were also found[14] among the products of flash photolysis of acetone. Since the formation of ethene is completely quenched by methyl acetate at high pressures, the ethene is presumably produced by the reaction of hot methyl or acetyl radicals.[14]

Material balance. The amount of methyl radicals formed in the flash photolysis of methyl acetate can be calculated from the amounts of the products. For example, at infinite methyl acetate pressure the relative amount of methyl radicals is:
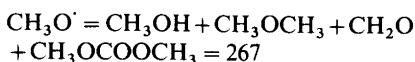
$$CH_3^{\cdot} = 2C_2H_6 + CH_3OCH_3 + CH_3COCH_3 + CH_4 = 345$$
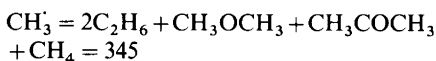
The amount of methyl radicals can also be calculated in the following way:
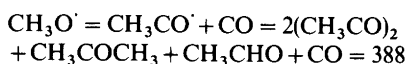
$$CH_3^{\cdot} = CO + 2CO_2 + HCOOCH_3 + CH_3OCOOCH_3 = 358$$

These two values are identical within experimental error.

The relative amount of methoxide radicals can be calculated either

$$CH_3O^{\cdot} = CH_3OH + CH_3OCH_3 + CH_2O + CH_3OCOOCH_3 = 267$$

or

$$CH_3O^{\cdot} = CH_3CO^{\cdot} + CO = 2(CH_3CO)_2 + CH_3COCH_3 + CH_3CHO + CO = 388$$

The difference in these two values is most likely due to experimental errors resulting from the difficulty of analyzing small amounts of formaldehyde by gas chromatography.[7]

The relative amounts of products formed from radicals that have accepted a hydrogen atom should be equal to the amounts of products formed from radicals that have donated a hydrogen atom.

$$CH_4 + CH_3OH + CH_3CHO + HCOOCH_3 = 188$$
$$CH_2O + 2C_2H_4 + CH_3COOC_2H_5 = 133$$
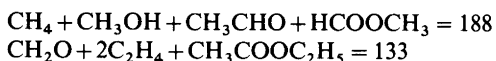
These two values are in fair agreement within experimental error.

Effect of pressure on the product formation. When the pressure of methyl acetate is increased the amounts of products resulting from combination reactions of acetyl radicals are increased and the amounts of products resulting from the dissociation of acetyl radicals are decreased (Table 2). These results indicate that hot acetyl radicals are quenched by methyl acetate

$$CH_3CO^x + CH_3COOCH_3 \rightarrow$$
$$CH_3CO^{\cdot} + CH_3COOCH_3 \qquad (20)$$
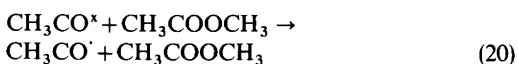
The dissociation of thermally equilibrated acetyl radical is negligible in our experiments.[13] A Stern-Volmer type equation can be applied to the two competing reactions 5 and 20 to extrapolate the amounts of products to infinite pressure and to zero pressure of methyl acetate (Table 2).

The difference in the amounts of the products formed from acetyl radicals at zero and infinite pressure of methyl acetate

$$\Delta CH_3CO^{\cdot} = 2\Delta(CH_3CO)_2 + \Delta CH_3COCH_3 + \Delta CH_3CHO = 140$$

should be equal in absolute value to the difference in the amount of dissociation products of acetyl radicals at the same two pressures: carbon monoxide

$$\Delta CO = -100$$

and methyl radicals

$$\Delta CH_3^{\cdot} = 2\Delta C_2H_6 + \Delta CH_3OCH_3 + \Delta CH_3COCH_3 + \Delta CH_3COOC_2H_5 + 2\Delta C_2H_4 = -92$$

These values are equal within experimental error. The formation of methoxy radicals are not connected with acetyl radicals and should not vary with the pressure of the methyl acetate.

$$\Delta CH_3O^{\cdot} = \Delta CH_3CO + \Delta CO = 40$$

The difference (40) is small, indicating that the variation in methyl acetate pressure has only a small effect on the relative rates of reactions 2 and 7.

Photodissociation of methyl acetate. Thynne[12] has reported that $COOCH_3$ radicals dissociate only by reaction 6 forming carbon dioxide. The carbon monoxide is then formed from hot acetyl radicals, in reaction 5, and not from the dissociation of $COOCH_3$ radicals by reaction 7. Thermally equilibrated acetyl radicals dissociate slowly and can be neglected in our experiments. At high methyl acetate pressures hot acetyl radicals become thermally equilibrated (Reaction 20) and carbon monoxide could also be formed in a competing combination reaction:

$$CH_3CO^x + CH_3COOCH_3 \rightarrow$$
$$CO + CH_3^{\cdot} + CH_3COOCH_3 \qquad (21)$$
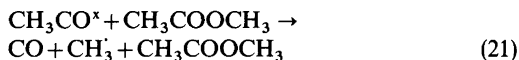
From the amounts of carbon dioxide, carbon monoxide and stable products formed from acetyl radicals, it can be calculated that about 80 % of excited methyl acetate molecules dissociate by reaction 2 and about 20 % by reactions 3 and 1. Reaction 1 is expected to be negligible, however. At low methyl acetate pressures about 70 % of acetyl radicals dissociate by reaction 5 and about 30 % form stable products in reactions 10, 11, 14 and 15. Practically all $COOCH_3^{\cdot}$ radicals formed by reaction 3 dissociate by reaction 6 and only small amounts react to give dimethyl carbonate and methyl formate.

The hydrogen abstraction reaction between methyl acetate and methoxy radicals is slow and the activation energy[3] is about 19 kJ mol^{-1}. The activation energy of the hydrogen abstraction reaction of methyl radicals with methyl acetate is expected to be similar to that of the corresponding reaction between methyl radicals and acetone,[20] about 40 kJ mol^{-1}, and that between methyl radicals and dimethyl carbonate,[17] about 31 kJ mol^{-1}. Photolysis of methyl acetate also produces hot methyl and methoxy radicals which abstract protons from methyl acetate. These reactions occur only to a small extent, however, since only small amounts of ethyl acetate were produced by the

Table 3. Values of rate constants of reactions 8 to 15 between methyl, methoxy and acetyl radicals at 298 K.

Reaction	$10^{-10} k/dm^3 mol^{-1} s^{-1}$ This work[c]	Previous	Ref.
8	3.31	1.26[b]	17
9	2.71	2.40[b]	17
11	3.42		
12	2.32	1.82[b]	17
13		2.70	5
14	2.37	4.5[a]	22
15	3.30	7.5[a]	22

[a] Values are based on $k_{13} = 3.2 \times 10^{10}$ dm^3 mol^{-1} s^{-1}. [b] Values are based on $k_{13} = 2.19 \times 10^{10}$ dm^3 mol^{-1} s^{-1}. [c] Values are based on $k_{13} = 2.70 \times 10^{10}$ dm^3 mol^{-1} s^{-1}.

radical combination reaction of $CH_3COCH_2^-$ and CH_3^- radicals.

Rate constants. The relative amounts of methyl, methoxy and acetyl radicals formed during one flash can be calculated from the amounts of products (Table 2). It is assumed that reactions 10 and 11 are equally fast and the amount of methyl acetate formed is equal to the amount of acetaldehyde. The relative initial amounts of radicals are approximately equal: 315, 338 and 339, respectively. Since, moreover, the rate constants of the reactions 8 to 15 between these radicals are all approximately equal (Table 3), the relative concentrations of these radicals remain approximately constant. The ratios of rates of any two reactions are then equal to the ratio of the respective rate constants times the ratio of the products of the initial concentrations of the respective radicals, and equal to the ratio of the final amounts of the products of the reactions. The rate constants obtained by the method are shown in Table 3, the absolute values being calculated from the known value[5] of the rate constant of reaction 13: namely, $k_{13} = 2.70 \times 10^{10}$ dm^3 mol^{-1} s^{-1}. The values of the rate constants are in good agreement with values reported earlier (Table 3). The calculated values of rate constants would increase by a factor of 1.2 to 1.6 if, contrary to our assumption, reactions 10 and 11 were not equally fast but reaction 10 much slower than reaction 11.

The following values can be calculated from the amounts of products:

$$k_8/(k_{12}k_{13})^{1/2} = (CH_3OCH_3)/(C_2H_6)^{1/2}(CH_3OH)^{1/2} = 1.32$$

$$k_{15}/(k_{13}/k_{14})^{1/2} = (CH_3COCH_3)/(C_2H_6)^{1/2}(CH_3CO)_2^{1/2} = 1.30$$

$$k_{11}/(k_{12}k_{14})^{1/2} = (CH_3CHO)/(CH_3OH)^{1/2}(CH_3CO)_2^{1/2} = 1.46$$

These calculations do not involve approximations. Use of the rate constants shown in Table 3 gave the values 1.32, 1.27 and 1.46, respectively, which are in excellent agreement with the values above, calculated from the amounts of products.

The lower limit of the rate constant of reaction 6, $k_6 \leqq 3 \times 10^6$ s^{-1}, can be calculated from the estimated value of the rate constant, $k_{22} \leqq 3 \times 10^{10}$ dm^3 mol^{-1} s^{-1}, for the reaction

$$COOCH_3^- + CH_3O^- \rightarrow CH_3OCOOCH_3 \qquad (22)$$

and the amounts of dimethyl carbonate and carbon dioxide obtained in photolysis of methyl acetate at high methyl acetate pressures.

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