ene–oxygen flames[4] and by Clingman, Brokaw and Pease for methane–oxygen flames.[5]

For the hydrogen–bromine flames, the variations observed experimentally do not follow the patterns which might be expected on the basis of thermal or diffusion effects alone, *i.e.*, on the basis of variations in flame temperatures and heat conductances, or in diffusion coefficients. Such comparisons do not, of course, take into account kinetic effects on the reactions involved. Rabinowitch[6] has, for example, found the order of effectiveness of these molecules in causing recombination of hydrogen and bromine atoms to be $N_2 > H_2 > A > He$, with helium and hydrogen being much less effective than the heavier molecules. Rice[7] found the effective diameters for *dissociation* of molecular bromine to be $N_2 > A > H_2 > He$. The available data do not, however, permit any quantitative comparison between these and other factors.

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[4] P. V. Wheatly and J. W. Linnett, *Trans. Faraday Soc.*, **48**, 338 (1952).

[5] W. H. Clingman, R. S. Brokaw and R. N. Pease, "4th Symposium on Combustion," Williams and Wilkins Co., Baltimore, 1953, p. 310.

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[7] O. K. Rice, *J. Chem. Phys.*, **9**, 258 (1941).

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The Radical Sensitized Decomposition of Mixtures of Acetaldehyde and Formaldehyde[1]

BY JAMES E. LONGFIELD[2] AND W. D. WALTERS

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In connection with an investigation of the thermal decomposition of formaldehyde initiated by radicals from ethylene oxide, it was of interest to compare the rates of the radical sensitized decompositions of acetaldehyde and formaldehyde when they are present together. Previous studies have shown that both acetaldehyde[3] and formaldehyde[4] can undergo induced decompositions in the presence of added substances yielding free radicals. Moreover, these aldehydes occur together as intermediates in certain thermal decompositions.[5] Therefore, experiments were conducted with mixtures of acetaldehyde and formaldehyde with and without a sensitizer, such as ethylene oxide.

Experimental

Formaldehyde was prepared from paraformaldehyde according to the method of Spence and Wild,[6] and vapor pressure measurements over the range −74 to −18° were in agreement with their values (within the limits of experimental error ±0.5°). The ethylene oxide was from the same supply and had the same rate of pyrolysis as reported earlier.[7] The biacetyl from the Eastman Kodak Company was dried with anhydrous calcium sulfate and fractionated twice under vacuum. The acetaldehyde (Eastman) used in the preliminary experiments was fractionated under vacuum through a 70-cm. Vigreux column. The acetaldehyde samples from Eimer and Amend (Expts. 220–225) and Baker and Adamson (Expts. 241–247) were shaken for 30 minutes with sodium bicarbonate, dried over calcium sulfate and fractionated at atmospheric pressure through the above column with a partial condensation head.[8] The material used in experiments 220–225 was a middle fraction with a boiling point of 19.8° at 745 mm. For experiments 244–245 the acetaldehyde was allowed to stand two hours at 0° over a small amount of hydroquinone and then distilled before use. All samples were carefully outgassed before introduction into the reaction vessel.

The reaction vessel was a 550-ml. cylindrical Pyrex bulb surrounded by three concentric aluminum tubes (6 mm. thick) and contained in an electrically heated furnace. The temperature at the center of the reaction bulb was measured with a platinum, platinum–13% rhodium thermocouple connected to a Leeds and Northrup Type K-2 potentiometer.

The initial analyses of the gaseous products removed at −196° were conducted by the mass spectrometric method.[9] Since the mass spectrometric results indicated that only hydrogen, carbon monoxide and methane would be present in the non-condensable fraction, a method of gas analysis involving the oxidation of hydrogen and carbon monoxide over heated copper oxide was used. The unoxidized portion of the gas sample was considered to be methane. Tests with known mixtures showed essentially quantitative separation of the non-condensable gases (±0.5%) and satisfactorily correct percentages of the components (±0.5%).

Results

Table I shows the results of the analyses of the non-condensable gases present after mixtures of acetaldehyde and formaldehyde have been decomposed to the extent of about 30%. Inspection of the data reveals that the amount of pressure increase during a reaction is very nearly equal to the sum of the pressures of hydrogen and methane formed, while ordinarily the carbon monoxide is slightly larger than this sum. As in the case of the thermal decompositions of acetaldehyde[3] and formaldehyde[4b] investigated separately, the data are in agreement with the following reactions as the principal over-all processes

$$CH_3CHO \longrightarrow CH_4 + CO \qquad (1)$$

$$H_2CO \longrightarrow H_2 + CO \qquad (2)$$

along with a lesser amount of the reaction

$$2H_2CO \longrightarrow CH_3OH + CO \qquad (3)$$

Reaction 3 has been found to occur with pure formaldehyde alone and the addition of 2 mm. of ethylene oxide at 415° does not appear to increase its rate more than 50%.[4b] The chain lengths for reactions 1 and 2 are moderately long so that the ratio of methane to hydrogen can be used as a

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[1] The preliminary phases of this work were supported by the Office of Naval Research.

[2] E. I. du Pont de Nemours and Company Fellow, 1950–1951.

[3] A. O. Allen and D. V. Sickman, THIS JOURNAL, **56**, 2031 (1934); C. J. M. Fletcher and G. K. Rollefson, *ibid.*, **58**, 2135 (1936); A. Boyer, M. Niclause and M. Letort, *J. chim. phys.*, **49**, 345 (1952).

[4] (a) S. Kodama and Y. Takezaki, *J. Chem. Soc., Japan, Pure Chem. Sect.*, **73**, 13 (1952); (b) unpublished results of James E. Longfield obtained in this Laboratory.

[5] (a) D. M. Newitt and M. A. Vernon, *Proc. Roy. Soc. (London)*, **A135**, 307 (1932); (b) W. Ure and J. T. Young, *J. Phys. Chem.*, **37**, 1169 (1933); (c) W. B. Guenther and W. D. Walters, THIS JOURNAL, **73**, 2127 (1951).

[6] R. Spence and W. Wild, *J. Chem. Soc.*, 338 (1935).

[7] K. H. Mueller and W. D. Walters, THIS JOURNAL, **73**, 1458 (1951).

[8] The rates of pyrolysis upon comparison with values tabulated by J. C. Morris, *ibid.*, **66**, 584 (1944), agreed satisfactorily with the data of J. C. Morris and those of R. E. Smith and were slightly higher than the results of M. Letort.

[9] Analyses by Dr. F. L. Mohler and the staff of the National Bureau of Standards.

TABLE I

NON-CONDENSABLE GASES FROM THE RADICAL SENSITIZED DECOMPOSITION OF MIXTURES OF ACETALDEHYDE AND FORMALDEHYDE

Expt. no.	$p_0^{H_2CO}$, mm.	$p_0^{CH_3CHO}$, mm.	Sensitizer,[d] mm.	Press. increase, mm.	Press. of products, mm.		
					H_2	CH_4	CO
			Temp., 415°				
90	92	95	2.2E	55	33[b]	26[b]	56[b]
222	90	92	2.2E	56	27	29	61
220	92	92	1.2E	50	24	25	52
221	47	138	1.2E	57	14.5	45	57
			Temp., 476.5°				
241	96	86	1.22B	59	27	32	67
242	93	92	0	44	20	24	59
244[a]	92	94	0	43	21	24	56
247	92	93	0	43	21[c]	24[c]	55[c]

[a] Acetaldehyde treated with hydroquinone. [b] Mass spectrometric analysis by the National Bureau of Standards. [c] A portion of this sample analyzed mass spectrometrically by the Consolidated Engineering Corporation gave values of 22, 22 and 56 for H_2, CH_4 and CO, respectively. [d] B, biacetyl; E, ethylene oxide.

measure of the relative amounts of acetaldehyde and formaldehyde decomposed in the radical sensitized reactions. The decomposition of small quantities of sensitizer should not affect the ratio appreciably. The mass spectrometric analysis of the products from experiment 247 (Table I) is in relatively good agreement with the chemical analysis, but the data for the preliminary experiment 90 analyzed by the mass spectrometer are not in complete accord with the other results. However, all of the results show that acetaldehyde and formaldehyde are decomposed to about the same extent at 415°.[10]

The results from Table I, as well as the data from other experiments, have been used in Table II to ascertain the effect of changes in experimental conditions upon the ratio of the amounts of acetaldehyde and formaldehyde decomposed. The ratio of methane to hydrogen seems to vary directly as the relative concentrations of acetaldehyde and formaldehyde, but does not change with an increase in the concentration of sensitizer. Since the percentage of formaldehyde that disappears per unit time seems to be about the same as that for acetaldehyde, the relative concentrations of acetaldehyde and formaldehyde do not change significantly during the first 30% of the decomposition which has been used for these experiments. Increasing the temperature from 384 to 477° even with a change in the sensitizer does not appreciably alter the ratio of methane to hydrogen (for a constant acetaldehyde to formaldehyde ratio).

TABLE II

EFFECT OF TEMPERATURE AND REACTANT RATIOS UPON THE RELATIVE RATES OF FORMATION OF METHANE AND HYDROGEN

Expt. no.	Temp., °C.	Sensitizer,[d] mm.	N_1 CH_3CHO/H_2CO	N_2, CH_4/H_2	N_2/N_1
223[a]	384	1.2E	0.98	1.01	1.03
220	415	1.2E	0.99	1.03	1.04
221	415	1.2E	2.96	3.08	1.04
222	415	2.2E	1.03	1.07	1.04
224[a]	424	1.2E	0.99	1.00	1.01
241	477	1.2B	0.90	0.96	1.06
242	477	0.0	0.99	1.19	1.20
244[b]	476	0.0	1.03	1.13	1.10
247	476	0.0	1.01	1.07[c]	1.06
245[a,b]	487	0.0	1.01	1.04[c]	1.03

[a] The total pressure of acetaldehyde plus formaldehyde in these experiments was about 183.5 mm. The pressures in the other experiments are given in Table I. [b] Acetaldehyde treated with hydroquinone. [c] Average of chemical and mass spectrometric analyses (CEC). [d] B, biacetyl; E, ethylene oxide.

In a consideration of these data it is to be noted that if the methane and hydrogen-producing processes had similar characteristics with the exception of a 2 kcal./mole difference in activation energy, the rates at 415° would differ by a factor of 4.3. With an activation energy difference of 2 kcal./mole, if frequency factors were chosen to make the rates equal at 384°, the ratio of rates would change to 1.21 at 476°.

Discussion

For the interpretation of the data several possibilities may be considered. Case I. (i) The rates and activation energies for the hydrogen abstraction by a given radical or atom may be approximately equal for CH_3CHO and H_2CO, or (ii) any difference in the rate of (a) $CH_3 + CH_3CHO$ and (b) $CH_3 + H_2CO$ might be counterbalanced by a difference in the rate of (c) $H + CH_3CHO$ and (d) $H + H_2CO$. For case I the reactions may be written as

$$R + CH_3CHO \longrightarrow RH + CH_3CO \longrightarrow RH + CH_3 + CO \quad (4)$$

$$R + H_2CO \longrightarrow RH + HCO \longrightarrow RH + H + CO \quad (5)$$

where the formyl and acetyl radicals ordinarily decompose before they can abstract a hydrogen atom from an aldehyde molecule. The methyl radicals and hydrogen atoms react with aldehyde molecules to continue the chain. The data available at present are not sufficiently extensive to permit an exact comparison of the rates of reactions (a) and (b) or (c) and (d). Various values have been proposed for the activation energy and frequency factor of reaction (a); the recent work of Volman and Brinton[11] indicates a value of 7.5 kcal./mole for the activation energy and 3.7×10^{-3} for the steric factor. For reaction (b) an activation energy of 5.63 kcal./mole has been reported[12]; for reaction (d) activation energies of $\leqslant 5$ kcal./mole[13] and 3.63 kcal./mole[12] have been observed recently. A difference of 1.9 kcal./mole between the activation energies of (a) and (b) would not be expected from the present results unless there is some compensating factor.

Case II. One of the aldehydes, *e.g.*, formaldehyde, might be attacked more readily by radicals

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(10) On the other hand the rate of the induced decomposition of a mixture containing only acetaldehyde and ethylene oxide at 415° is about two and one-half times the rate of a mixture containing formaldehyde and ethylene oxide under similar conditions.

(11) D. H. Volman and R. K. Brinton, *J. Chem. Phys.*, **20**, 1764 (1952).

(12) S. Kodama, Y. Takezaki and R. Fujie, *J. Chem. Soc. Japan, Pure Chem. Sect.*, **72**, 892 (1951).

(13) J. G. Calvert and E. W. R. Steacie, *J. Chem. Phys.*, **19**, 176 (1951).

or atoms than the other one; however, in a subsequent step some of the radicals (or atoms) might react with the other aldehyde (acetaldehyde) and regenerate the first aldehyde. One process which might be used as an illustration is the reaction of some of the formyl radicals with acetaldehyde:

$$HCO + CH_3CHO \longrightarrow H_2CO + CH_3CO \quad (6)$$

This would be of importance only when reaction (6) can compete with the decomposition of the formyl radical; such a process might compensate for the greater loss of formaldehyde in the initial attack. There is evidence that the pre-exponential term in the rate expression for the formyl decomposition may be low.[14]

In view of the lack of precise information concerning some of the radical reactions which might be involved no attempt will be made to interpret the results in detail, but one other aspect of the experiments warrants comment. The rate at which pure acetaldehyde decomposes into methane and carbon monoxide at 476° is much greater than the rate at which formaldehyde decomposes into hydrogen and carbon monoxide (at least five times greater for $P_0 = 125$ mm.). If acetaldehyde and formaldehyde decompose by independent molecular processes, then the decomposition of an equimolar mixture of acetaldehyde and formaldehyde (without sensitizer) should produce a large amount of methane and only a small amount of hydrogen. The fact that the ratio of methane to hydrogen in the experiments without added sensitizer is not more than slightly higher than in those with sensitizer shows that free radical chain processes are probably involved. The results can be explained on the basis that the decomposition of acetaldehyde proceeds by way of an initial split to form radicals which induce the chain decompositions of acetaldehyde and formaldehyde to approximately the same extent. This indication of the free radical character of the acetaldehyde decomposition is in agreement with the results of isotopic tracer experiments involving acetaldehyde.[15]

[14] F. B. Marcotte and W. A. Noyes, Jr., THIS JOURNAL, **74**, 783 (1952).

[15] P. D. Zemany and M. Burton, *J. Phys. Colloid Chem.*, **55**, 949 (1951); L. A. Wall and W. J. Moore, *ibid.*, **55**, 965 (1951); F. O. Rice and R. E. Varnerin, THIS JOURNAL, **76**, 2629 (1954).

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The Preparation of Samarium Metal with Calcium[1]

BY E. I. ONSTOTT

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Two methods of preparing massive samarium metal in substantial quantity with good yield have been reported.[2,3] The technique of the method presented here is not essentially different from the method of Daane, Dennison and Spedding,[2] except that calcium is used as the reductant instead of lanthanum.

Data compiled by Glassner[4] were used as a basis for choosing calcium as the material for reducing samarium oxide. Thorium metal should work equally well, but it is not as cheap or as readily available as is calcium.

Experimental.—The Sm_2O_3 used was essentially the same as that described previously,[3] except that the Eu_2O_3 content was reduced to <0.002% by electrolysis at a mercury cathode.

High purity Ca metal was supplied by R. D. Baker of this Laboratory.

Equipment used has been described also.[3] The reaction crucible was 1 in. in diameter and 3 in. high and was machined from solid tantalum. The distillation plate section was a Ta sleeve 4 in. high which fit snugly over the reaction crucible. Around the inside wall of this sleeve was placed a sheet of 0.002 in. thick Ta, and 4 to 6 connected Ta discs, which served as plates, were placed in the sleeve.

Freshly ignited Sm_2O_3 in amounts of 10 to 20 g. was mixed with the Ca with a spatula. This charge was heated 30–40 min. at 1000° either in a vacuum or in purified argon. Then the Sm and excess Ca were co-distilled in a vacuum of $<1\ \mu$ at 1050–1100° for 30–40 min. Only the bottom half of the crucible assembly was heated by the induction coil. It was sometimes necessary to cut the top section of the crucible assembly to remove the product.

Conditions for the redistillation of Sm-rich fractions were about the same as those for the initial distillation. The pressure was generally 0.1–0.3 μ.

It was observed that the fractions high in Ca had a distinct yellow luster and adhered tightly to the Ta, while relatively pure Sm fractions had the luster of freshly cut iron and were easily stripped from the Ta. Three to four distillations of the most concentrated Sm fractions (bottom plate) were necessary to obtain Sm metal containing <0.1% Ca.

The chemical yield of Sm was determined by recovery of Sm_2O_3 which did not react and distill from the reaction crucible.

Spectrographic analyses of the purified Sm were performed by O. R. Simi. Impurities found were: Ca, 0.01–0.1%; Y, 0.001–0.1%; Mg, Si, Mn, Co, Ag, Pb, each 0.001–0.01%; Na, Sb, each <0.001%. The Ta content was estimated to be <0.1% by weighing the residue left after dissolving a sample in dilute HCl.

Discussion.—In Table I are data which show the effect of three parameters on the chemical yield and concentration of samarium in the vapor distilled from the reaction mixture.

TABLE I

Excess Ca,[a] %	Ca, size-mesh	Reaction atmos.	Chem. yield Sm, %	Sm in distillate, %
17	60–100	Argon	26	42
83	20	Argon	48	47
128	20	Argon	58	46
203	20	Argon	54	35
108	40–60	Argon	50	44
136	40–60	Argon	59	45
193	40–60	Argon	70	46
201	40–60	Argon	66	41
104	40–60	Vacuum	40	38
208	40–60	Vacuum	54	35

[a] Excess over that needed for 100% Sm yield.

Only about 40% of the chemical yield of samarium was recovered as the high purity metal. Redistillation losses were relatively great, since some

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[1] Work done under the auspices of the Atomic Energy Commission.

[2] A. H. Daane, D. H. Dennison and F. H. Spedding, THIS JOURNAL, **75**, 2272 (1953).

[3] E. I. Onstott, *ibid.*, **75**, 5728 (1953); Los Alamos Scientific Laboratory Document LA-1622 (Dec. 1953).

[4] A. Glassner, "A Survey of the Free Energy of Formation of the Fluorides, Chlorides, and Oxides of the Elements to 2500°K.," Argonne National Laboratory Document ANL-5107 (Aug. 1953).