TABLE I

LATTICE CONSTANTS AND COEFFICIENTS OF EXPANSION OF THE ALUMS BETWEEN 20–50°

$KAl(SO_4)_2 \cdot 12H_2O$		$NH_4Al(SO_4)_2 \cdot 12H_2O$		$TlAl(SO_4)_2 \cdot 12H_2O$		$NH_4Cr(SO_4)_2 \cdot 12H_2O$	
Temp., °C.	a, Å.	Temp., °C.	a, Å.	Temp., °C.	a, Å.	Temp., °C.	a, Å.
19.3	12.1333	19.2	12.2141	18.8	12.2047	22.1	12.2501
19.9	12.1335	19.4	12.2142	19.0	12.2045	25.0	12.2510
25.0	12.1336	19.5	12.2148	19.1	12.2040	50.5	12.2539
50.5	12.1372	50.4	12.2180	25.0	12.2050	51.1	12.2543
51.1	12.1378	50.8	12.2181	50.6	12.2095		
52.2	12.1373	51.4	12.2179	51.1	12.2093		
$\alpha \cdot 10^6 = 11.0 \pm 0.3$		$\alpha \cdot 10^6 = 9.5 \pm 0.2$		$\alpha \cdot 10^6 = 13.1 \pm 0.3$		$\alpha \cdot 10^6 = 10.6 \pm 0.4$	

ing values of $\alpha \cdot 10^6$ for the first three alums listed above: 3.3, 6.8 and 18.3, respectively. These values are of the right order of magnitude but, otherwise, are in poor agreement with the X-ray values. No data are available for comparison with the result for ammonium chrome alum.

Potassium chrome alum was also studied at this same time but the inability, after numerous attempts, to get photographs in the vicinity of 50° without dehydration led to its abandonment.

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Summary

The linear thermal expansion coefficients α for several alums have been measured for the approximate range, 20–50°, by means of X-ray diffraction. The values of $\alpha \cdot 10^6$ observed are as follows: potassium alum, 11.0 ± 0.3; ammonium alum, 9.5 ± 0.2; thallium alum, 13.1 ± 0.3; and ammonium chrome alum, 10.6 ± 0.4.

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[CONTRIBUTION FROM THE DIVISION OF CHEMISTRY, COLLEGE OF AGRICULTURE, UNIVERSITY OF CALIFORNIA]

The Vapor Phase Photo Decomposition of Methyl Formate

BY DAVID H. VOLMAN[1]

Recently, experiments on the photolysis of methyl formate have been reported by Royal and Rollefson.[2] Experiments on this same problem had been in progress in this Laboratory. The results for the photolysis products in this investigation are in substantial agreement with those given by Royal and Rollefson. In addition, data on the determination of methanol in the reaction products, and an approximate evaluation of the quantum yield for the reaction were obtained.

In a subsequent paper on the photolysis of methyl acetate, Roth and Rollefson[3] have given data on the determination of methanol as a photolysis product by oxidizing the alcohol to formaldehyde and treating with Schiff reagent. However, they were unable to analyze for the small amounts of methanol usually obtained in the decomposition runs, and were forced to obtain comparatively large amounts of decomposition products by carrying out the reaction in a three-liter bulb. The method given below using a Grignard reagent suffices for the small amounts usually obtained and enables analyses to be made for all of the decomposition experiments conducted.

Experimental Method

The apparatus employed was essentially the same as already reported.[4] The source of radiation was an Hanovia Alpine mercury lamp. Quantum yields were determined approximately by using monochloroacetic acid as an actinometer in a manner previously described[4,5] using the reliable value for the hydrolysis quantum yield given by Smith, Leighton and Leighton.[6]

Methyl formate was synthesized by allowing formic acid and methanol to react in the presence

(1) On leave of absence. Present address: The Technological Institute, Northwestern University, Evanston, Illinois.

(2) Royal and Rollefson, THIS JOURNAL, **63**, 1521 (1941).

(3) Roth and Rollefson, *ibid.*, **64**, 490 (1942).

(4) Volman, *ibid.*, **63**, 2000 (1941).

(5) Weizmann, Bergmann and Hirshberg, *ibid.*, **58**, 1675 (1936).

(6) Smith, Leighton and Leighton, *ibid.*, **61**, 2299 (1939).

of hydrochloric acid. The methyl formate was removed by distillation and washed with concentrated potassium hydroxide. After a second distillation, the ester was dried over phosphorus pentoxide and fractionated. The fraction used distilled at 31.8–32.0°.

After irradiation for definite periods, the gases non-condensable in a liquid-air trap were collected by means of a Toepler pump and analyzed by the use of a Blacet–Leighton apparatus for micro gas analysis.

The following method was used in analyzing for methanol. A methyl Grignard reagent in ethyl ether solution was placed in a trap connected to the photolysis apparatus by means of a stopcock. Prior to an experiment the Grignard reagent was thoroughly outgassed and frozen by use of liquid air. When it was desired to analyze for methanol, the condensable reaction products plus undecomposed ester were distilled into the trap containing the Grignard reagent. Then the mixture was allowed to warm to room temperature and successively frozen and warmed several times. Finally, the non-condensable gas, methane, was collected and determined, both by volumetric measurement and by combustion.

An attempt was made to produce hydrogen from methanol by passing the photo-decomposition products over a sodium mirror. However, the results were not reproducible and were consistently lower than expected or found by the Grignard reagent method.

Complete analytical results and values of decomposition quantum yield, Φ_d, are given in the accompanying table. The pressure of methyl formate was 75.0 mm. in each experiment. Irradiation was for twenty minutes at 25°, and approximately 600 cu. mm. of gas was collected each time. Φ_d is based on the sum of carbon dioxide and carbon monoxide.

TABLE I

METHYL FORMATE PHOTOLYSIS PRODUCTS AND QUANTUM YIELDS

CO, %	H_2, %	CH_4, %	CO_2, %	C_2H_6, %	CH_3OH, %	Φ_d
41.3	10.3	5.1	15.0	1.3	27.2	0.7
40.5	9.3	5.6	14.9	0.7	29.1	.7
39.1	9.0	6.0	14.9	1.6	29.5	.8
38.2	9.3	7.3	14.4	0.9	29.9	.8

Discussion

The demonstration that methanol is produced in the photolysis of methyl formate is evidence that

$$HCOOCH_3 \longrightarrow CO + CH_3OH$$

one of the net reactions postulated by Royal and Rollefson,[2] does occur.

The reaction products were found to be the same as previously reported.[2] The small variation in the mole percentages of the non-condensable products from the values given by Royal and Rollefson may be attributed to the difference in experimental details, especially pressure of methyl formate and time of illumination.

The variety of products indicates that the overall photolysis is complex. However, since Φ_d is less than unity, no appreciable chains are involved.

Summary

1. The presence of methanol in the photolysis products of methyl formate has been shown.

2. The decomposition quantum yield for the photolysis was found to be approximately 0.75 for an ester pressure of 75.0 mm. at 25°.

3. The reaction products were found to have the following average values: H_2, 9.5%; CO, 40.0%; CH_4, 6.0%; CO_2, 14.8%; C_2H_6, 1.1%; CH_3OH, 29.0%.

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