Bonner[5] gave consistently lower values for the C–C Hooke's law constant than other calculations presumably more accurate since they took into account interactions.[3,6] Bonner assumed that hydrocarbons and alkyl groups could be regarded as simpler molecules by grouping together certain atoms. Thus he took ethane to be R–R and propane to be R–R′–R (non-linear) in which $R = CH_3$ and $R' = CH_2$. On this basis the force constants average around 3.8×10^5 dynes/cm., whereas calculations which take into account interactions show values averaging about 6.0×10^5 dynes/cm. In spite of this large difference, Bonner's results are quite useful as long as they are used in the same way as they were obtained.

For the frequencies 2123.5 cm.$^{-1}$ and 3305 cm.$^{-1}$ of methylacetylene it appears from the table that the molecule can be regarded as $R-C\equiv C-H$ where $R(= CH_3)$ behaves like a single atom of atomic weight 15. It is probably true that for any molecule which is linear or partially linear, bonds farther away than the bond adjacent to the one of most importance in the vibration have little effect on the frequency.

As to the accuracy of the results in Table I, the following remarks can be made. The values of the percentages for frequencies around 1400 cm.$^{-1}$ are probably the least accurate of those given since those results are quite sensitive to changes in the force constants and to changes in the frequencies. The results are nevertheless correct to the right order of magnitude. The other values are more accurate, particularly the high percentage figures. The percentage error of the low percentages may be large, but such errors would not alter the interpretation nor change the picture of the motion greatly. In conclusion the author wishes to express his appreciation to Professor W. H. Rodebush for his kind interest in the calculations.

Summary

The fractions of the total potential energy contributed by the various bonds of methylacetylene and ethane were calculated for each of the non-degenerate frequencies of the molecules. These fractions are taken as a measure of the extent to which a given mode of vibration can be assigned to a particular bond type. It is found that the so-called "carbon–carbon" single bond frequencies in particular are not pure carbon–carbon vibrations. Some generalizations are indicated which show when molecules can be treated successfully by approximate methods.

URBANA, ILLINOIS RECEIVED NOVEMBER 3, 1937

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(5) L. G. Bonner, *J. Chem. Phys.*, **5**, 293 (1937).

(6) J. B. Howard, *ibid.*, **5**, 442 (1937).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MARYLAND AND THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Two Alkoxyacetaldehydes, their Preparation and Properties[1]

BY NATHAN L. DRAKE, H. M. DUVALL, THOMAS L. JACOBS, H. T. THOMPSON AND H. M. SONNICHSEN

Inasmuch as several β-alkoxyethanols are now readily available and cheap substances, it seemed to us that the dehydrogenation of such substances should offer the most convenient approach to the corresponding aldehydes.

Alkoxyacetaldehydes have been prepared by various methods, and a review of earlier work is to be found in an article by Rotbart,[2] who synthesized a number of these substances by way of their acetals. Sabetay[3] has also described the preparation of alkoxyacetaldehydes by the action of lead tetraacetate on α-monoethers of glycerol. The failure of attempts[4] to dehydrogenate β-ethoxyethanol over copper, silver, and copper chromite in the presence of air at temperatures of 300–400° is understandable in view of the conditions of the experiments, and no attempt seems to have been made to prepare methoxyacetaldehyde by a similar method.

Ethoxyacetaldehyde was first prepared by Klüger,[5] who reported a boiling point of 71–73°. Later workers[4,6] were unable to check this boiling point, and were usually satisfied with a concentrated aqueous solution of the aldehyde, boiling

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(1) An investigation of methoxyacetaldehyde was carried out in the laboratories of the University of Maryland during the summer of 1933. When it was later learned that similar work was being conducted in the Harvard Laboratories, it was decided to present the results in a joint publication. Part I describes the work at the University of Maryland and Part II describes the work at Harvard University, which was carried out during the summers of 1936 and 1937.

(2) Rotbart, *Ann. chim.*, [11] **1**, 439 (1934).

(3) Sabetay, *Bull. soc. chim.*, [5] **2**, 1744 (1935).

(4) Dunn, Redemann and Smith, *J. Biol. Chem.*, **104**, 511 (1934).

(5) Klüger, *Monatsh.*, **26**, 879 (1905).

(6) Eissler and Pollak, *ibid.*, **27**, 1129 (1906); Fried, *ibid.*, **27**, 1251 (1906); Leuchs and Geiger, *Ber.*, **39**, 2644 (1906).

about 85 to 95°. Yields were always low, and ethoxyacetaldehyde has probably never been obtained pure until now.

Part I[7]

The dehydrogenation of β-methoxyethanol ("methyl cellosolve") proceeds readily over copper at temperatures in the neighborhood of 425°; the dehydrogenation is by no means complete at reasonable space velocities, but no difficulty is experienced in recovering unreacted alcohol by fractional distillation. Copper chromite or zinc chromite catalysts are not satisfactory for this dehydrogenation, and only small quantities of aldehyde were produced by their use.

Methoxyacetaldehyde is best characterized by its *p*-nitrophenylhydrazone or its 2,4-dinitrophenylhydrazone; it has not proved possible to prepare its semicarbazone. The pure dry aldehyde boils at 92° (770 mm.), and forms with water an azeotropic mixture whose boiling point is 88.5° (770 mm.). The azeotrope contains approximately 12.8% of water.

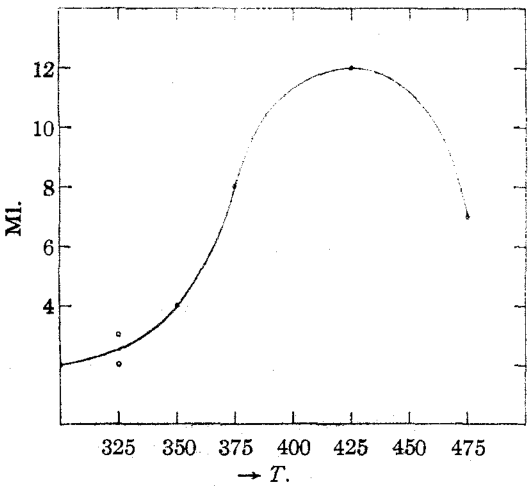

Fig. 1.—Yield of methoxyacetaldehyde (ml. distilled to 95°) as a function of temperature. Cu catalyst.

Experimental

Apparatus.—After a number of preliminary experiments in which various types of apparatus were used, it was decided to employ a type consisting of a vertical tube containing copper on copper gauze heated externally to the desired temperature (measured by a thermocouple in the tube at the top of the catalyst layer), and provided with a suitable connection to a total condenser. Introduction of methyl cellosolve at a regular rate was accomplished by a method similar to one earlier described.[8]

Methyl cellosolve was separated from aldehyde by fractional distillation through a 3 ft. (91 cm.) Podbielniak-type column. A relatively clean separation of aldehyde from methyl cellosolve is possible by collecting material boiling up to 95° as the aldehyde-containing fraction.

Preparation of Catalyst.—The copper catalyst was prepared by precipitating cupric hydroxide by ammonia, and washing the precipitate by decantation at 50° until it began to darken slightly; an additional washing at 30° was then given. The hydroxide was stirred mechanically with the wash water for a period of about one-half hour during each washing, and the washed hydroxide finally collected on a large Büchner funnel and washed carefully on the funnel. The wet hydroxide was spread on rolls of copper gauze 15 cm. long and 10 mm. in diameter, hydrogen was run through the apparatus and the reduction of the catalyst carried on between 290 and 310°. After preliminary experiments with catalyst supported by copper gauze, a different form of catalyst was employed. Moist cupric hydroxide, prepared as above, was partially dried until it could be formed into spaghetti-like worms by means of a sodium press. Material so formed was dried overnight at 110°, cut into pieces of the proper length and reduced by hydrogen in the tube as above.

Determination of Optimum Temperature for Dehydrogenation.—A series of experiments was conducted to determine the optimum temperature for dehydrogenation, a summary of which is given in Fig. 1 where ml. of distillate boiling up to 95° are plotted against temperature. Fifty ml. of methyl cellosolve, carefully distilled and collected over a one degree range, was employed in each experiment. and between four and five hours were necessary for the substance to pass over the catalyst. No attempt was made to refractionate the product of individual experiments, so that the curve of the figure can only be significant in indicating a general trend. It is apparent, however, that the optimum temperature for the dehydrogenation of methyl cellosolve over copper lies in the neighborhood of 425°. Experience with other copper catalysts has confirmed this conclusion.

Methoxyacetaldehyde.—This substance has an odor resembling that of acetaldehyde; it reduces Fehling's solution and Tollens' reagent, and polymerizes rather readily. In one experiment 135 ml. of material collected from various experiments was dried overnight on anhydrous magnesium sulfate, filtered, and distilled. Only 55 ml. of distillate was collected in the proper range; the bulk of the material was apparently a mixture of high boiling polymers which were not further investigated. Table I shows the physical and analytical data obtained for methoxyacetaldehyde (I) and its azeotropic mixture with water (II).

TABLE I

		(I)	(II)	
B. p., °C.		92.3	88.8	
d^{25}_4		1.005	1.116	
n^{20}_D		1.3950	1.4270	
*M*R (exptl.)		17.78	20.64	
*M*R (calcd.)		17.66		
Calcd. for $C_3H_6O_2$	C, 48.62	Found 48.80	42.53	42.37
	H, 8.17	8.29	8.85	8.59

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(7) From a thesis by H. M. Duvall, University of Maryland, 1936.

(8) Drake and Smith, THIS JOURNAL, 52, 4558 (1930).

According to the above analytical data, the azeotrope contains 12.8% water.

Other Catalysts.—Dehydrogenation of methyl cellosolve over a copper–chromium oxide catalyst[9] and a zinc chromite catalyst[10] was studied. The former was decidedly inferior to the copper catalyst under the conditions studied, and the latter caused the production of considerable quantities of low boiling material which gave a strong test for formaldehyde, and yielded little material boiling in the desired range.

The *p*-Nitrophenylhydrazone of Methoxyacetaldehyde.—Five-tenths gram of the hydrazine was added to 0.5 ml. of concd. hydrochloric acid and 25 ml. of water. After filtration from a very small quantity of undissolved hydrazine, 0.5 g. of methoxyacetaldehyde was added, and the yellow precipitate of hydrazone was recrystallized to constant melting point, 115–115.5°.

Anal. Calcd. for $C_9H_{11}O_3N_3$: C, 51.63; H, 5.30. Found: C, 51.72, 51.84, 51.71; H, 5.33, 5.34, 5.50.

The 2,4-Dinitrophenylhydrazone of Methoxyacetaldehyde.—Twenty-five hundredths gram of the hydrazine was dissolved in 25 ml. of hot ethanol. To this solution was added 0.10 ml. of methoxyacetaldehyde; the mixture was heated to boiling, one drop of concd. hydrochloric acid was added, and the mixture was heated for two minutes. After purification by recrystallization from alcohol the hydrazone melted at 124–125°.

Anal. Calcd. for $C_9H_{10}O_5N_4$: C, 42.50; H, 3.97. Found: C, 42.56; H, 3.88.

Part II[11]

The dehydrogenation of β-ethoxyethanol ("cellosolve") over a copper catalyst gave a 43% yield of theoxyacetaldehyde (based on β-methoxyethanol not recovered) when 1500 g. of the starting material was passed through the dehydrogenator during a day. Part of the aldehyde was obtained pure (b. p. 105–106°), and the rest in the form of an azeotropic mixture (b. p. 91–91.5°; containing 21.8% water).

Both methoxy- and ethoxyacetaldehyde polymerize on standing to yield liquid trimers. Monomeric aldehydes were recovered from these polymers by distillation from a trace of *p*-toluenesulfonic acid, but the yield of methoxyacetaldehyde was very low. A solid tetramer of methoxyacetaldehyde has been obtained.

Preliminary experiments indicated that butoxyacetaldehyde can be prepared by dehydrogenation of butyl cellosolve, but fractionation of the crude product seemed somewhat more difficult than for the other aldehydes. Butoxyacetaldehyde boils between 130 and 135°.

Experimental

Methoxyacetaldehyde.—The apparatus used for the dehydrogenation of methyl cellosolve consisted of a 17-mm. (i. d.) Pyrex tube packed with copper oxide for 70 cm. of its length, and centered in an insulated, electrically-heated tube inclined downward at an angle of about 20° from the horizontal. Methyl cellosolve vapors were distilled directly into this tube and provision was made for sweeping the entire apparatus with hydrogen before and after each run. The methyl cellosolve used was dried and fractionated before use (b. p. 124–125°). The catalyst was prepared by reducing copper oxide (Kahlbaum, granular, for analysis) from which fine material had been removed, in a stream of hydrogen at 150–200°. Water was carefully swept from the tube after the reduction. The catalyst was then heated to about 300° and methyl cellosolve was distilled through at about 40 g./hour. An electrical heater using the vapors of trichlorobenzene for heat transfer gave a uniform distillation rate. The product was condensed with a bath of ice and hydrochloric acid and a very little low-boiling material was caught in an acetone–solid carbon dioxide trap. After each run the tube was swept with hydrogen while cooling, but despite this precaution the catalyst was poisoned fairly rapidly, and could be used for relatively few trials. Operation at temperatures above 300° produced a larger percentage of by-products, and resulted in more rapid deactivation of the catalyst. The product was fractionated through a 3-foot (91 cm.) electrically-heated column packed with glass spirals.[12] Several distillations were required; the results of a run on 400 g. of methyl cellosolve were as follows:

	Yield, %	
	Based on starting material	Based on cellosolve used
Methyl cellosolve recovered, 300 g. (after purification)		
Material boiling below 122°, 70 g. (after first distillation) Not over 5 g. below 83°; 28 g. from 100 to 122°.		
Methoxyacetaldehyde after 3 fractionations, 15 g. 6 g., b. p. 90–91°; 6 g., b. p. 91°; 3 g., b. p. 91–91.5°.	3.7	15
Azeotrope of methoxyacetaldehyde and water, 19 g. b. p. 83–86° (one fractionation).	4.0	16

Analysis of Gas Evolved During Dehydrogenation.—The usual methods of analysis were followed. Hydrogen and saturated hydrocarbons were determined by explosion and calculated as entirely hydrogen.

Carbon dioxide	0.8%
Oxygen, less than	.1%
Unsaturated hydrocarbons	.8%
Carbon monoxide	3.0%
Hydrogen (av. of 2 detns.)	91.1%
	95.8%

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[9] Prepared according to Connor, Folkers and Adkins, This Journal, **54**, 1144 (1932).

[10] Prepared according to W. A. Lazier, U. S. Patent 1,746,783.

[11] By Thomas L. Jacobs, H. T. Thompson, and H. M. Sonnichsen. The experiments on methoxyacetaldehyde were completed before we learned of similar work at the University of Maryland. The alkoxyacetaldehydes serve as starting materials for the preparation of unsaturated ethers by the reactions: $ROCH_2CHO + R'MgX \longrightarrow ROCH_2CHOHR' \longrightarrow ROCH{=}CHR'$. An investigation of these compounds is now under way.

[12] Wilson, Parker and Laughlin, This Journal, **55**, 2795 (1933).

The same constants and derivatives were obtained for methoxyacetaldehyde as are reported in Part I. The compound autoxidizes rapidly in the air, is somewhat hygroscopic, and resinifies with concd. sulfuric acid and with dilute sodium hydroxide.

Molecular weight. Calcd. for $C_3H_6O_2$: 74.08. Found: (cryoscopically in benzene) 113, 117; (cryoscopically in water) 118.

Grignard machine analysis.[13] Gas at 28°, none; gas at 100°, negligible; reagent used, 1.4 moles per mole of compound. This indicates that at 100° under the conditions used, the carbonyl and part of the methoxyl react.

Polymers of Methoxyacetaldehyde.—A sample of pure methoxyacetaldehyde which had remained in a refrigerator for nine months was found to have a molecular weight of 231 (cryoscopically in benzene). The theoretical value for $(C_3H_6O_2)_3$ is 222.2. The material on hand was not purified further, and must be an equilibrium mixture. This polymer is water soluble, but very viscous. Simple distillation or distillation under reduced pressure caused partial depolymerization; the vapors remained around 80–90° with bath temperatures of 150–230°. The distillate appears to repolymerize rapidly. It was possible to recover a 25% yield of monomeric material by slow distillation in the presence of a little *p*-toluenesulfonic acid through a small Podbielniak-type column. The flask residue was a brown tar; molecular weight of distillate (cryoscopically in benzene), 108.

One 20-g. sample of methoxyacetaldehyde yielded 1 g. of a white solid after two days at zero degrees. Long standing did not increase the amount of solid. The material is almost insoluble in ether, sparingly soluble in alcohol and benzene, and fairly soluble in water. It recrystallized from alcohol in needles, m. p. 142–142.5°.

Anal. Calcd. for $(C_3H_6O_2)_n$: C, 48.62; H, 8.17. Found: C, 48.59; H, 8.03. *Molecular weight.* Calcd. for $(C_3H_6O_2)_4$: 296.3. Found: (cryoscopically in benzene) 291; (ebullioscopically in acetone), 278.

The solid does not give a Schiff test.

Seeding of trimeric material with the solid seemed to give a very slow conversion to this form; seeding of a freshly distilled sample of methoxyacetaldehyde did not produce the tetramer after short standing in a refrigerator.

Ethoxyacetaldehyde.—Ethoxyacetaldehyde was prepared in a modified Bouveault apparatus.[14] A 1-liter 3-necked round bottomed flask was connected by a TS joint to an electrically heated Pyrex tube 110 cm. long, 2 cm. i. d. and packed with copper oxide for 90 cm. of its length. A thermocouple extended about half way into the catalyst. A separatory funnel was used to add fresh cellosolve to the flask, and the vapors were distilled into the catalyst tube as for methoxyacetaldehyde. In preliminary experiments the vapors from the catalyst tube passed into a short distilling column and the higher boiling material was returned to the flask through the third neck. This resulted in greatly increased amounts of high boiling material; better yields were obtained when the vapors were condensed with no return, and fractionated in the absence of hydrogen. A 9-foot (2.7-m.) column packed with glass spirals[12] was used for larger runs, and gave good separation in a single distillation. The results on a typical experiment were

Catalyst temperature, °C.	250–275
Cellosolve taken at start	1500 g.
Duration of run	12 hours
Rate of passage of vapors	125 g./hour
Cellosolve recovered	1150 g.
Cellosolve used	350 g.
Material boiling 30–105°	110 g.

		Yield on cellosolve	
	G.	Not recovered, %	Taken, %
Pure azeotrope from low boiling material	80		
Ethoxyacetaldehyde in azeotrope	62.5	18.3	4.2
Pure ethoxyacetaldehyde	87	25	5.8
Total yield	149.5	43.3	10

Ethoxyacetaldehyde is a clear, mobile liquid which resembles methoxyacetaldehyde in odor and general behavior. It is soluble in water and in organic solvents: b. p. 105–106° (760 mm.); $d^{20}{}_4$ 0.942; $n^{20}{}_D$ 1.3956 (Abbé); *M*RD obsd. 22.43; *M*RD calcd. 22.33.

Anal. Calcd. for $C_4H_8O_2$: C, 54.52; H, 9.15; mol. wt., 88.1. Found: C, 54.40, 54.46; H, 9.48, 9.53; mol. wt. (cryoscopically in benzene), 99.5.

Azeotrope of Ethoxyacetaldehyde and Water.—B. p. 90–91° (760 mm.). *Anal.* Found: C, 42.70, 42.58; H, 9.13, 9.50. According to these analytical data, the azeotrope contains 21.8% water. It contains only these two components, for distillation of a mixture of pure ethoxyacetaldehyde and water gave the azeotrope.

***p*-Nitrophenylhydrazone of Ethoxyacetaldehyde.**—Recrystallized from ethyl alcohol, or from methyl alcohol and water; m. p. 113–114°. *Anal.* Calcd. for $C_{10}H_{13}O_3N_3$: C, 53.80; H, 5.87. Found: C, 53.65; H, 5.80.

2,4-Dinitrophenylhydrazone of Ethoxyacetaldehyde.—Recrystallized from methyl alcohol; m. p. 116–117°.

Anal. Calcd. for $C_{10}H_{12}O_5N_4$: C, 44.78; H, 4.51. Found: C, 44.71; H, 4.40.

Polymers are formed gradually when ethoxyacetaldehyde is allowed to stand in the refrigerator: molecular weight of sample after standing one month, 115; molecular weight of sample after standing for twelve months, 283; calcd. for $(C_4H_8O_2)_3$, 264.3.

The polymeric material is very viscous and is insoluble in water. It can be reconverted into monomeric ethoxyacetaldehyde by slow distillation through a small column in the presence of a little *p*-toluenesulfonic acid. The yield of recovered material is 40–50%.

Summary

Methoxy- and ethoxyacetaldehydes have been prepared from the corresponding β-alkoxyethanols by dehydrogenation over a copper catalyst.

COLLEGE PARK, MARYLAND
CAMBRIDGE, MASS.

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[13] Kohler, Stone and Fuson, THIS JOURNAL, **49**, 3181 (1927).

[14] Bouveault, *Bull. soc. chim.*, [4] **3**, 119 (1908).