

cadmium alloyed with gold and copper show intermediate values.

TABLE IV

BOGUSKI'S CONSTANT K_1 CALC'D. AT 25 AND 40° AND THE TEMPERATURE COEFFICIENT

Alloy, Cd with Cd, chem. pure ¹⁰	Acid, N	Soln. rate const. K_1		Temp. coeff. $K_2 - 10/K_1$
		25°	40°	
Cd, chem. pure ¹⁰	6 HCl	1.74	^a	1.74
	8 HCl	7.27	^a	1.86
	10 HCl	19.2	^a	1.4
	14 H ₂ SO ₄	0.2	0.5	1.7
0.48 at. % Pt	5 HCl	70.6	115.3	1.4
	6 HCl	103.5	148.1	1.3
	7 HCl	177.2	230.0	1.2
	8 H ₂ SO ₄	13.5	33.1	1.8
	10 H ₂ SO ₄	9.2	22.7	1.8
	12 H ₂ SO ₄	4.8	(10.5)	(1.7)
.98 at. % Pt	14 H ₂ SO ₄	0.9	4.3	2.8
	5 HCl	78	250	2.2
	6 HCl	165	302	1.5
	7 HCl	266	354	1.2
	8 H ₂ SO ₄	16.3	46.4	2.0
	10 H ₂ SO ₄	15.8	32.0	1.6
	12 H ₂ SO ₄	3.7	9.0	1.8
	14 H ₂ SO ₄	1.4	3.5	1.8
.97 at. % Au	5 HCl	24.2	53.0	1.7
	6 HCl	51.8	107.1	1.6
	7 HCl	78.9	153.0	1.6
	10 H ₂ SO ₄	2.2	12.6	3.2
	12 H ₂ SO ₄	2.7	7.8	1.3
	14 H ₂ SO ₄	1.7	3.1	1.5

0.79 at. % Cu	6 HCl	3.3	7.1	1.7
	8 HCl	5.8	13.5	1.8
	10 HCl	21.4	40.3	1.5
	12 HCl	54.6	86.0	1.4
	14 H ₂ SO ₄	0.3	1.12	1.8

^a Results obtained by M. Centnerszwer¹⁰ for 50°. K_1 at 50° was: 6 N HCl, 6.9; 8 N HCl, 34.5; 10 N HCl, 42.5.

In sulfuric acid the solution rate is much slower and the chemical reaction rate seems to be the governing mechanism, and diffusion plays a minor role in the reaction.

In conclusion, one of us (F. G.) would like to thank the Kościuszko Foundation of New York for a scholarship, which made the above work possible.

Summary

The rate of solution of cadmium and cadmium alloyed with platinum, gold and copper has been measured in sulfuric and hydrochloric acids, with and without stirring. The effects of varying temperature, rotation, concentration of the acids, and amount and kind of admixture on the reaction velocity, solution rate constant, and duration of the period of induction have been studied.

WARSAW, POLAND

RECEIVED OCTOBER 25, 1937

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Heats of Organic Reactions. VI. Heats of Hydrogenation of Some Oxygen-containing Compounds

BY M. A. DOLLIVER, T. L. GRESHAM, G. B. KISTIAKOWSKY, ELGENE A. SMITH AND W. E. VAUGHAN

In the previous papers of this series¹ we have reported the heats of hydrogenation of a considerable number of unsaturated hydrocarbons and have determined some regularities correlating the thermo quantity and molecular structure. This publication concerns itself with the heats of hydrogenation of some oxygen-containing compounds; in it we shall show some further effects of various substituents on the ethylenic linkage and also give some derived values for other reactions.

Preparation of Compounds

Vinyl Acetate.—A pure grade of vinyl acetate containing an inhibitor was obtained from Shawinigan Chemicals Limited. This was systematically fractionated in column

(1) See, for a summary, Paper V, Dolliver, Gresham, Kistiakowsky and Vaughan, *THIS JOURNAL*, **59**, 831 (1937).

A. Sixty-six per cent. of the distillate boiled at 72.32 = 0.01° at 765 mm.; n^{20}_D 1.3953, f. p. -100.2°.²

Methyl Methacrylate.—Inhibitor-free methyl methacrylate of 99.9+ % purity was kindly sent us by D. E. Strain of the du Pont Company. While in our possession it was stored in ice in the dark. The refractive index as measured by us was $n^{20.1}_D$ 1.4149³ and the f. p. -48.0°.

Crotonaldehyde.—Crotonaldehyde from Carbide and Carbon Chemicals Corporation was distilled through column B giving a fraction boiling at 102.26-102.42° at 765 mm.; this was refractionated through column A. The portion, representing 50% of the material, distilling at 102.29-102.30° at 765 mm. was collected for use in the calorimeter; f. p. -76.6°, n^{20}_D 1.4366.⁴

(2) Morrison and Shaw, *Trans. Electrochem. Soc.*, **63**, 443 (1933), give f. p. below -84°, b. p. 73°, n^{20}_D 1.3958.

(3) Contributions from E. I. du Pont de Nemours and Co., *Ind. Eng. Chem.*, **28**, 1160 (1936), give $n^{16.5}_D$ 1.4168, m. p. -48°.

(4) "I. C. T.," Vol. I, p. 186, gives m. p. -75°, b. p. 104°; p. 276, n^{20}_D 1.4373.

Allyl Alcohol.—Allyl alcohol was prepared as described in "Organic Syntheses."⁶ The alcohol having a specific gravity of 0.900 was dried with anhydrous potassium carbonate and systematically fractionated through column C. The material distilling flatly at 97.3° at 771 mm. was then fractionated in column A; 80% of the distillate boiled at 97.16 ± 0.01° at 765 mm., n_{D}^{20} 1.4135.⁸ No freezing point was obtainable, as a glass was formed on cooling.

Ethyl Vinyl Ether.—Eastman acetal was passed at the rate of 20 drops per minute, using nitrogen as a carrier, over a 5% platinum-on-asbestos catalyst in a glass tube 70 × 2 cm. maintained at 280–290° in an electrically heated furnace.⁷ The product was collected by condensation in a water-cooled condenser and fractionated through a short indented column to obtain the portion boiling from 35–78°. Distillation was continued to recover undecomposed acetal, the fraction boiling at 96–104° being repassed through the furnace. The material boiling at 35–78° was distilled through a small Podbielniak-type column to give a fraction boiling at 35–50°. Three hundred and ninety-two grams of this crude ether was obtained from 1400 g. of acetal, corresponding to a yield of 42%. The best yield from any one run was 48%. The crude ether was allowed to stand over calcium chloride for two days and was then fractionated in column A; 367 g. gave 219 g. with b. p. 35.72 ± 0.01° at 760 mm., n_{D}^{20} 1.3768,⁸ f. p. –115.8°.

Acetaldehyde.—To 1077 g. of paraldehyde which had been fractionated in column B, b. p. 123.9–124.0° at 763 mm., was added a mixture of 5 cc. water and 5 cc. concentrated sulfuric acid, the whole charged in column B, and the acetaldehyde formed was distilled off. The yield was 735 g., b. p. 23.4–24°; this in turn was refractionated in column A to give, from 432 g. distilled, 341 g. with b. p. 20.03 ± 0.01° at 760 mm., f. p. –122.6°, $n_{D}^{12.5}$ 1.3353.⁹

Acetone.—A good grade of acetone that had been standing over calcium chloride for six months was purified by treatment with silver nitrate and then through the sodium iodide complex.¹⁰ To 700 cc. of acetone was added 3 g. of silver nitrate in 20 cc. of water and 20 cc. of 1 *N* sodium hydroxide solution. The mixture was shaken for ten minutes, filtered, allowed to stand overnight, and again filtered. The filtrate was distilled, dried over anhydrous potassium carbonate, and treated with sodium iodide. The solid product was filtered dry and the acetone regenerated by distillation on the steam-bath; yield 286 g. Acetone so purified was fractionated in column A, 484 g. giving 25 g. lows and 312 g., Samples 2 and 3, b. p. 56.27 ± 0.01° at 765 mm., n_{D}^{20} 1.3591, f. p. –95.0°.¹¹

2-Ethoxypropene.—Carefully fractionated acetoacetic ester was condensed with pure ethyl orthoformic ester¹²

(obtained from Drs. Fraenkel and Landau), using a small amount of ferric chloride. Equal molal quantities of the two esters were mixed and 1 g. of ferric chloride per mole of the esters was added; the mixture was shaken and left overnight. The low-boiling reaction products were pumped off at room temperature and the β -ethoxycrotonic ester fractionated at 30 mm. pressure; the fraction boiling at 103.3–103.6° was collected. The yield of the pure product was 89%. The ester was then saponified with 20% excess of 50% sodium hydroxide. After the saponification was complete, sufficient water was added to dissolve all the sodium salt and the solution boiled for one hour. This was then cooled to 0° and carefully neutralized by adding the calculated amount of 1-to-1 hydrochloric acid with good stirring while keeping the temperature below 20°. The solid acid was filtered off and well pressed out in a Büchner funnel. The practically dry acid was then stirred with water containing about 0.5% ammonium hydroxide for one hour. It was then filtered off and thoroughly dried. The yield of the pure acid was 85%.

The pure β -ethoxycrotonic acid decomposes smoothly and with little sublimation when heated in a wide-column distilling flask surrounded by an oil-bath at 160–165°, giving a 91% yield of 2-ethoxypropene. This was washed with dilute sodium carbonate solution and dried over anhydrous potassium carbonate. The dried product was fractionated in column A. The physical constants of the pure compound used in calorimetric work are: b. p. at 765 mm., 61.90 ± 0.01° (for 58% of the still charge); f. p., glass formed on cooling; n_{D}^{20} 1.3927.¹³

Anal. Calcd. for C₆H₁₀O: C, 69.7; H, 11.7. Found: C, 69.7; H, 11.7.

Methyl Ethyl Ketone.—Eastman practical grade of methyl ethyl ketone, 1 kg., was purified, after distillation through a 60-cm. fractionating column, by Lochte's¹⁴ sodium iodide method, with a yield of 375 g. of ketone after drying over anhydrous potassium carbonate. Fractionation of the product through column A gave 173 g. with b. p. 79.53 ± 0.01° at 760 mm.; n_{D}^{20} 1.3788, f. p. –86.9°.¹⁵

2-Methoxybutene-2.—2-Methoxy-3-iodobutane was prepared according to Petrov.¹⁶ The procedure was somewhat modified, and carried out on a much larger scale. Two liters of absolute methyl alcohol and three mols of freshly precipitated mercuric oxide free from water were mixed with stirring and cooled to –20° in a five-liter three-necked flask equipped with a condenser cooled with Dry Ice. To this was added three mols of purified butene-2; then 9 mols of powdered iodine at such a rate as not to permit the temperature to rise above –6°. When all the iodine had been introduced, 16 g. additional butene-2 was added to allow for loss during the course of the addition of iodine. The mercuric iodide was then filtered off and the alcohol solution diluted with sufficient water to cause the

(5) "Organic Syntheses," Coll. Vol. I, p. 34.

(6) Timmermans and Henneaut-Roland, *J. chim. phys.*, **29**, 529 (1932), give b. p. 97.0° at 760 mm., n_{D}^{15} 1.41452.

(7) Sigmund and Uchann, *Monatsh.*, **51**, 234 (1929); German Patent 525,836, *Chem. Zentr.*, **102**, II, 1191 (1931).

(8) Chalmers, *Can. J. Res.*, **7**, 464 (1932), gives b. p. 35.5° (corr.), n_{D}^{20} 1.3856.

(9) "I. C. T.," Vol. I, p. 179, gives m. p. –123.5°, b. p. 20.2°; p. 276, n_{D}^{20} 1.3316.

(10) Felsing and Durban, *THIS JOURNAL*, **48**, 2889 (1926).

(11) Parks and Kelley, *J. Phys. Chem.*, **32**, 740 (1928), give m. p. 177.6° K. "I. C. T.," Vol. III, p. 218, gives b. p. 56.10 (760 mm.); p. 45 gives m. p. –99°; *ibid.*, Vol. I, p. 276, gives n_{D}^{20} 1.3591.

(12) Michael and Carlson, *THIS JOURNAL*, **57**, 163 (1935); Claisen, *Ber.*, **26**, 2731 (1893).

(13) Schmitt and Boord, *THIS JOURNAL*, **54**, 758 (1932), give n_{D}^{20} 1.3915, b. p. 61–63° (748 mm.); Sherrill and Walter, *ibid.*, **58**, 742 (1936), report n_{D}^{20} 1.3913, b. p. 61.2–61.8° (760 mm.).

(14) Lochte, *Ind. Eng. Chem.*, **16**, 956 (1924).

(15) Felsing, Shofner and Garlock, *THIS JOURNAL*, **56**, 2252 (1934), give b. p. 79.45–0.65° (760 mm.); n_{D}^{20} 1.37799. Timmermans and Martin, *J. chim. phys.*, **25**, 411 (1928), give b. p. 79.60 (760 mm.), n_{D}^{15} 1.3814, m. p. –86.6°.

(16) Petrov, *J. Gen. Chem. U. S. S. R.*, **4**, 1217 (1934).

2-ethoxy-3-iodobutane to separate out as a dark oil. The compound obtained was washed with sodium thiosulfate solution, and dried over anhydrous potassium carbonate. The yield of product to this stage was about 95% of the theoretical, $n^{17.5}_D$ 1.5012.¹⁷ 1200 cc. of methyl alcohol and 515 g. of potassium hydroxide were used to split out hydrogen iodide from 6.9 moles of the iodide to give the methoxybutene. The reaction ran smoothly and the product was recovered from the reaction mixture by diluting with cold water. The ether layer was washed with two portions of cold water, dried over anhydrous potassium carbonate and fractionated in column B; b. p. 66.5–70°. Distillation of 423 g. in column A gave 134 g. with b. p. 64.61 \pm 0.02° at 770 mm., f. p. –117.8°, n^{15}_D 1.4000.¹⁸

In view of the fact that the compound prepared as above distilled at a temperature about 10° lower than the boiling point reported by Petrov, its structure was determined as follows.

Anal. Calcd. for $C_6H_{10}O$: C, 69.7; H, 11.7. Found: C, 69.3; H, 11.9.

The products of ozonolysis of the compound were found to be acetaldehyde, identified by preparing the *p*-nitrophenylhydrazone; methyl acetate, b. p. 55–60°, identified by saponification with sodium hydroxide, formation of the ethyl ester from the dry sodium salt with ethyl alcohol and sulfuric acid. This ester had the odor of ethyl acetate. These are the ozonolysis products that would be expected from 2-methoxybutene-2.

Further evidence of structure was obtained by treating the ether with semicarbazide hydrochloride in a solution buffered with sodium acetate. Under these conditions the ether would be expected to be hydrolyzed to methyl ethyl ketone which would then be converted into the semicarbazone. This was the product obtained.

Thus it would seem that the difference in boiling point of the compound prepared here and that prepared by Petrov is a real difference.

Divinyl Ether.—Divinyl ether was very kindly supplied by Dr. Randolph T. Major of Merck and Co. The compound as obtained was stored over ammonia. It was washed with several portions of water and dried successively over calcium chloride and sodium wire and fractionated through column A in an atmosphere of nitrogen gas. The middle fraction boiled flatly at 28.49° at 765 mm., f. p. –101.1°, n^{20}_D 1.3989.¹⁹

Furan.—Furan was prepared by decarboxylation of Quaker Oats' best grade of furoic acid by the method of Wilson.²⁰ The only modification was the use of fine white sand in the reaction flask.²¹ 1232 g. of furoic acid gave 669 g. of furan, an 87% yield based on the furoic acid used. The furan was dried over calcium chloride and fractionated in column A. Three fractions, comprising 82% of the charge, distilled at 31.27 \pm 0.01°²² at 760 mm., f. p. –85.6°.

(17) Petrov, *J. Gen. Chem. U. S. S. R.*, gives n^{14}_D 1.5025.

(18) Petrov, *ibid.*, gives b. p. 72–74°, n^{15}_D 1.407.

(19) Ruigh and Major, *THIS JOURNAL*, **53**, 2662 (1931), report n^{20}_D 1.3989, b. p. 28.3 \pm 0.2°.

(20) "Organic Syntheses," Coll. Vol. I, p. 269.

(21) Gilman and Lousinian, *Rec. trav. chim.*, **53**, 156 (1933).

(22) Landolt and Börnstein, *Eq. IIIa*, p. 334, gives b. p. 31.3° at 760 mm.

Data and Results

All compounds for which polymerization was suspected were stored either in ice or Dry Ice and fresh samples used in a freshly cleaned saturating device for each run. Our general procedure was unaltered. In lieu of better data, we have corrected all figures for ΔH to 82° (355°K.) by use of ΔC_p values of –4 cal./deg. for addition of one H_2 and –8 cal./deg. for two H_2 , as in Paper V.

A. Hydrogenation of the Carbon-Carbon Double Bond

Crotonaldehyde + H_2 .—A fresh sample, from Dry Ice storage, was used for each run for this hy-

Run	Moles C_4H_6O	Moles H_2 per min.	Moles C_4H_8O per min.	$-\Delta H_{82}$ cal./mole
1	0.043234	0.00769	12.23 (10^{-4})	25,195
2	.043601	.00802	15.93 (10^{-4})	25,061
3	.043438	.00540	11.81 (10^{-4})	25,166
4	.043107	.01106	9.46 (10^{-4})	25,208
Average				25,158 \pm 48

drogenation over 5% platinum-on-asbestos. The n^{20}_D of the hydrogenation product was 1.3795 and this differed so markedly from other values for butyraldehyde^{23,24} that the product was especially carefully investigated. A test for degradation to methane or ethane was negative, and the sample collected in this test was carefully distilled in a small Podbielniak-type still; the boiling point of the entire amount was 74.7–74.9° (random drift). The freezing point of material directly from the calorimeter was very sharply defined at –96.6° and the "flat" excellent. The density was determined and found to be 0.805 g./cc. (20°). These constants indicate that the product is pure butyraldehyde.²⁵ From Hückel's values²⁶ one may calculate a molar refractivity, P_E , of 20.68 for butyraldehyde; from this and the determined density we find $n = 1.3789$ to be compared with our value of 1.3795. There is, therefore, no doubt but that this hydrogenation is clean cut. No irreversible adsorption on the catalyst was detected.

The crotonaldehyde had an initial freezing point of –76.7°; this fell off 0.3° to 80% frozen material. However, addition of 0.5% hydrogenation product lowered the initial freezing point 0.1°

(23) Adkins and Broderick, *THIS JOURNAL*, **50**, 499 (1928), give n^{20}_D 1.37875.

(24) "I. C. T.," Vol. I, p. 187, 1.3843; Landolt-Börnstein, Vol. II, p. 975, 1.3843.

(25) Timmermans, *Bull. soc. chim. Belg.*, **36**, 502 (1927), gives –97.1° for m. p. and 74.7° for b. p. "I. C. T.," Vol. I, p. 187, gives 0.817 for d .

(26) Hückel, "Theor. Grundlagen d. Org. Chem.," Akad. Verlag. Leipzig, 1931, Vol. II, p. 94.

and the time-temperature curve fell off much more rapidly.

We estimate the over-all accuracy as 100 cal. per mole.

Allyl Alcohol + H₂.—Attempts were made to perform this hydrogenation over 5 and 10% platinum-on-asbestos at temperatures from 40 to 100°; these trials showed that while the bulk of the alcohol was converted to *n*-propyl alcohol, side reactions of reduction to propane and formation of aldehyde also took place, while a considerable amount of the starting material remained unreacted. However, over the Co-Ni catalyst the reaction was much more satisfactory. The table gives the essential data for the two calorimetric runs performed;²⁷ the average ΔH is that for the reaction uncorrected for the formation of *n*-propyl ether. The product from these runs gave negative aldehyde tests (Schiff's reagent) and no propane was formed.

Run	Moles C ₃ H ₆ O	Moles H ₂ per min.	Moles C ₃ H ₈ O per min.	$-\Delta H_{135}$ cal./mole uncorr.
1	0.033007	0.0114	6.46×10^{-4}	31,539
2	.032928	.0118	6.36×10^{-4}	31,607
Average				31,573 = 34

To determine the amount of ether present, there was collected a large sample of hydrogenation product, prepared under exactly the conditions of the two runs and in the interval between them. The aldehyde test was negative. The n^{20}_D of this material was 1.3853, the same as that from the two runs; the portable Zeiss interferometer proved that the indices of the three samples of product differed by not more than 0.00012 unit. 24.1 g. of the product was placed in the pot of a small Podbielniak-type column (vacuum jacketed) and carefully fractionated at a 5:1 reflux rate; the results were:

Cut no.	Wt. of cut, g.	Boiling range (760 mm.), °C.	n^{20}_D
1	2.2	73.2-93.5 (no flat)	1.3830
2	5.7	93.5-96.9	1.3852-3
3	14.1	96.9-97.0	1.3852-3
Residues	2.1	1.3853

If one adopts the value n^{20}_D 1.3854²⁸ for propyl alcohol and n^{20}_D 1.3807 for *n*-propyl ether,²⁹ it may be computed that the mole fraction of ether

(27) It was considered useless to perform more runs, as the determining feature of this experiment is the estimation of the amount of *n*-propyl ether in the hydrogenation product, not the calorimetric steps.

(28) "I. C. T.," Vol. I, p. 184, b. p. 97.8°. Landolt-Börnstein, Hw. II, 974, gives n^{20}_D 1.3854.

(29) "I. C. T.," Vol. I, p. 276, gives n^{20}_D 1.3807; p. 204, b. p. 89°.

in Cut No. 1 is 0.5. Assuming that the other cuts are pure propyl alcohol, then it is found that the sample consists of 1.3 g. of ether and 22.8 g. of alcohol, or 0.032 mole fraction of ether. Unfortunately the heat of the formation of *n*-propyl ether from the alcohol cannot be computed, as there exist no combustion data for the former. However, we probably may make the computation by analogy with ethyl alcohol and diethyl ether. Using Thomsen's value of 659.6³⁰ for ether vapor and Rossini's of 336.78³¹ for alcohol vapor, we find, on correction for the vaporization of H₂O, $\Delta H = -3.56$ for $2C_2H_5OH$ (g.) \rightarrow H₂O (g.) + (C₂H₅)₂O (g.). Thus the correction to the determined ΔH value is + 115 cal., giving a final figure of 31,458 cal./mole as the heat of hydrogenation of allyl alcohol to *n*-propyl alcohol. The correction is so small that the final figure loses no significance by the use of the ethyl compound combustion data.

Inasmuch as it was impossible to freeze either the starting material or the product (both formed glasses), we have only distillation data and the analytical method to support our claims to accuracy. We may crudely estimate the over-all error as 300 cal./mole.

2-Ethoxypropene + H₂.—This hydrogenation proceeded cleanly on Co-Ni catalyst. The com-

Run	Moles C ₄ H ₁₀ O	Moles H ₂ per min.	Moles C ₄ H ₁₀ O per min.	$-\Delta H_{135}$ cal./mole
1	0.041602	0.0124	9.50×10^{-4}	25,119
2	.037057	.0127	5.80×10^{-4}	25,123
3	.041818	.0079	11.77×10^{-4}	25,062
Average				25,101 = 26

pleteness of each run was shown by the bromine titration method, which had previously been tested and found to be capable of detecting 0.1% of the unsaturated ether in 1 cc. of hydrogenation product; all such tests on runs were negative. The test for irreversible adsorption was also negative. The n^{20}_D of the product was 1.3658.³² The products of the three runs were compared on the interferometer and found to differ by not more than 0.0001 units in *n*. Unfortunately, both the 2-ethoxypropene and its hydrogenation product formed glasses when chilled and freezing curves could not be obtained.

Analysis of hydrogenation product. Calcd. for C₆H₁₂O: C, 68.11; H, 13.73. Found: C, 67.96; H, 13.77

It is difficult to estimate with certainty but it is

(30) Thomsen, *Z. physik. Chem.*, **52**, 347 (1905).

(31) Rossini, *Bur. Standards J. Research*, **13**, 189 (1934).

(32) No data available.

thought that the over-all accuracy is within 100 cal./mole.

2-Methoxybutene-2 + H₂.—The precision of the calorimetric data is not as good as usual, but no trend is to be observed; we can offer no explanation for the variance of the results.

Run	Moles C ₅ H ₁₀ O	Moles H ₂ per min.	Moles C ₅ H ₁₀ O per min.	-ΔH ₃₃₅ cal./mole
1	0.042346	0.01406	9.02 (10 ⁻⁴)	24,726
2	.033639	.01457	11.67 (10 ⁻⁴)	24,882
3	.033383	.01357	6.12 (10 ⁻⁴)	24,788
Average				24,797 = 55

The product of each run was collected both before and after the calorimetric interval and tested individually for completeness of reaction by the bromine titration method; all results were negative; the reliability of this procedure was demonstrated with blanks. No irreversible adsorption on the Co-Ni catalyst occurred. The product when chilled in liquid air formed a glass which did not crystallize even on prolonged cooling; we have, thus, no good criterion of the purity of the product; *n*²⁰_D 1.3720–1.3723.

Analysis of hydrogenation product. Calcd. for C₅H₁₂O: C, 68.11; H, 13.73. Found: C, 68.34; H, 13.92.

The literature gives no constants for methyl *s*-butyl ether.

The freezing point of the 2-methoxybutene-2 was not sharply defined; a slow rate of heating after the super-cooling interval masked the initial point which was approximately -117.8°. Addition of 0.5% ethyl alcohol altered entirely this behavior. The cooling curve showed no break with the temperature, dropping steadily to complete freezing.

In view of these facts we shall assign an over-all accuracy of 200 cal./mole to this determination.

Ethyl Vinyl Ether.—This material hydrogenated cleanly and the index of the product *n*²⁰_D was 1.3528³³; the interferometer comparisons of pre- and post-run samples showed agreement to within 0.0002 unit in *n*. The freezing point of the

Run	Moles C ₄ H ₈ O	Moles H ₂ per min.	Moles C ₄ H ₈ O per min.	-ΔH ₃₃₅
1	0.039096	0.0147	10.02 (10 ⁻⁴)	26,720
2	.030733	.0074	5.03 (10 ⁻⁴)	26,749
3	.039087	.0114	10.05 (10 ⁻⁴)	26,750
Average				26,740 = 13

hydrogenation product was -123.4° and fell off only 0.4° to 80% frozen material; this corresponds

(33) Compare with product from divinyl ether, *n*²⁰_D 1.3526 and Ref. 34 for diethyl ether.

closely with the β freezing point of diethyl ether.³⁴ There was no irreversible adsorption on the Co-Ni catalyst.

The starting material had an excellent freezing point at -115.8° and addition of 0.5% hydrogenation product caused a marked dropping off in the freezing curve.

We estimate the over-all accuracy at 60 cal./mole.

Divinyl Ether + 2H₂.—A fresh sample of the ether from storage in Dry Ice was used for each run. Tests for degradation to methane or ethane were negative, as was the test for irreversible adsorption on the 5% Pt-on-asbestos catalyst used. As a means of detecting incomplete hydrogenation in the runs, a procedure was devised and standardized, utilizing the formation of a brown color in a few drops of dilute aqueous permanganate solution; this test was sufficiently sensitive to detect 0.1% divinyl ether in 1 cc. of hydrogenation product. All such tests on runs were negative. The controlled freezing-point determination of the divinyl ether was very satisfactory; f. p. -101.1°. Upon addition of 0.5% ethyl ether the time-temperature curve dropped off immediately after the initial point. The hydrogenation product had a sharp freezing point at -116.4°;³⁴ *n*²⁰_D 1.3526.³⁴

Run	Moles C ₄ H ₆ O	Moles H ₂ per min.	Moles C ₄ H ₆ O per min.	-ΔH ₃₃₅ cal./mole
1	0.019028	0.01173	4.90 (10 ⁻⁴)	57,258
2	.019017	.01251	4.73 (10 ⁻⁴)	57,178
3	.019099	.01088	5.78 (10 ⁻⁴)	57,237
4	.019099	.00784	6.90 (10 ⁻⁴)	57,269
Average				57,236 = 29

The over-all accuracy is estimated at 100 cal./mole.

Furan + 2H₂.—Furan would not hydrogenate completely over 5 or 10% platinum-on-asbestos

Run	Moles C ₄ H ₄ O	Moles H ₂ per min.	Moles C ₄ H ₄ O per min.	-ΔH ₃₃₅ cal./mole
1	0.028665	0.0129	6.69 × 10 ⁻⁴	36,568
2	.028644	.0122	6.93 × 10 ⁻⁴	36,651
3	.028657	.0128	7.99 × 10 ⁻⁴	36,641
4	.028674	.0075	8.61 × 10 ⁻⁴	36,658
Average				36,630 = 31

at 82° but the cobalt-nickel catalyst was found to be satisfactory. The bromine titration method (see III) was used to test for incompleteness in each calorimetric run and all such experiments were negative. No degradation to methane or

(34) Timmermans and Martin, *J. chim. phys.*, **25**, 411 (1928), give -116.3° for ethyl ether. "I. C. T.," Vol. I, p. 189, gives: α f. p. -116.3°, β f. p. -123.3°; p. 276, *n*²⁰_D 1.3526.

ethane occurred and there was no irreversible adsorption on the catalyst. The hydrogenation product had a sharp freezing point at -109.1° , drifting only 0.2° to 80% frozen material; n^{20}_D 1.4071. 10.9 g. of the product was distilled in a small Podbielniak-type column and all the distillate, 9.9 g., boiled at 66.5° ; n^{20}_D 1.4071; the pot residues, 1.0 g., had a lower index, 1.4051, but were colored (probably by contamination from cork). It was suspected that the lowered index might be due to *n*-butyl alcohol formed by splitting the ring. This residue was dried with anhydrous cupric sulfate and 0.0603 g. of it treated with methylmagnesium iodide; no gas (methane) was evolved in amounts significant in the micro method used,³⁶ showing the absence of alcoholic OH groups in the product.³⁷

The furan had a freezing point at -85.6° ; addition of 0.5% diethyl ether lowered the f. p. 0.4° and the freezing curve dropped off rapidly. We estimate the over-all accuracy as 120 cal./mole.

Vinyl Acetate + H₂.—Hydrogenation of vinyl acetate on 10% Pt-on-asbestos at 82° gave a product which contained acetic acid (and ethylidene diacetate). However the reaction proceeded cleanly to ethyl acetate on 5% Pt-on-asbestos at 43° . The hydrogenation product had a sharp freezing point at -83.8° ; n^{20}_D 1.3719.³⁹ The products of all runs gave negative tests for free acid. No irreversible adsorption occurred and no splitting-off of methane or ethane took place. The purity of the vinyl acetate was shown by a sharp freezing point at -100.2° , and addition of 0.5% of the hydrogenation product caused the time-temperature curve to drop off rapidly. We estimate the over-all accuracy as 60 cal./mole.

Run	Moles C ₄ H ₆ O ₂	Moles H ₂ per min.	Moles C ₄ H ₈ O per min.	$-\Delta H_{365}$
1	0.036180	0.01252	13.69 (10 ⁻⁴)	30,932
2	.039191	.00638	15.95 (10 ⁻⁴)	30,951
3	.035814	.00834	14.38 (10 ⁻⁴)	31,001
4	.035607	.01112	9.14 (10 ⁻⁴)	30,930
Average				30,952 \pm 23
				$-\Delta H_{365}$ 31,120

(35) Compared with constants for tetrahydrofuran: Cloke and Ayers, *THIS JOURNAL*, **56**, 2144 (1934), give b. p. $63-67^\circ$; Bourguignon, *Bull. soc. chim. Belg.*, **22**, 87 (1908), reports n^{20}_D 1.40762, f. p. -65° ; Starr and Hixon, *THIS JOURNAL*, **56**, 1595 (1934), give b. p. $64-66^\circ$, n^{20}_D 1.4040.

(36) We are indebted to Dr. Max Tishler for performing this test for us.

(37) The presence of an ether (from alcohol) is not eliminated by this test but it probably would be present in only very small amounts (see data on allyl alcohol) and would not change greatly the ΔH given.

(38) "I. C. T.," Vol. I, p. 188, gives -83.6° for ethyl acetate.

(39) *Ibid.*, p. 276, gives n^{20}_D 1.3727.

Methyl Methacrylate + H₂.—A fresh sample was used for each determination. A test of irreversible adsorption on the Co-Ni catalyst used was negative. The bromine titration test for incompleteness of reaction was also negative; its efficiency was proved in blank experiments. No free acid or aldehyde resulted in the hydrogenation. The product had an index of n^{20}_D of 1.3837⁴⁰ and comparison of the six pre- and post-run samples showed agreement to 0.0001 unit in *n*. The controlled freezing point determination of the product was poor; too great an amount of supercooling (*ca.* 13°) and a very slow heating to the f. p. masked its correct value. A melting point determination of the crystals, however, gave *ca.* -86° .⁴¹

The starting material had a sharp freezing point at -48.0° and addition of 0.5% hydrogenation product lowered the initial value to -48.4° .

We estimate the over-all accuracy as 60 cal./mole.

Run	Moles C ₅ H ₈ O	Moles H ₂ per min.	Moles C ₅ H ₈ O per min.	$-\Delta H_{365}$ cal./mole
1	0.036389	0.0175	8.21 (10 ⁻⁴)	28,632
2	.036508	.0176	10.97 (10 ⁻⁴)	28,632
3	.035996	.0096	5.23 (10 ⁻⁴)	28,644
Average				28,636 \pm 5

B. Hydrogenation of the Carbon-Oxygen Double Bond

Acetaldehyde.—The hydrogenation to ethyl alcohol on Co-Ni proceeded cleanly, no aldehyde being detectable in the hydrogenation product (test by Schiff's reagent). A fresh sample was used for each run. The product, however, formed a glass even on prolonged chilling in liquid air and on repeated meltings and freezings; we thus have no good criterion of purity. n^{20}_D of product was 1.3621;⁴² comparison of the six pre- and post-run samples of product on the interferometer showed that they were the same within 0.0001 unit in *n*.

Run	Moles C ₂ H ₄ O	Moles H ₂ per min.	Moles C ₂ H ₄ O per min.	$-\Delta H_{365}$ cal./mole
1	0.061886	0.01085	12.5 (10 ⁻⁴)	16,726
2	.062359	.01327	16.8 (10 ⁻⁴)	16,719
3	.061457	.01335	9.1 (10 ⁻⁴)	16,811
Average				16,752 \pm 39

There was no irreversible adsorption on the catalyst. The acetaldehyde had an initial freezing point of -122.6° ⁴³ and this dropped off 0.2° to complete freezing. Addition of 0.5% paraldehyde

(40) "I. C. T.," Vol. I, p. 276, gives 1.3840 for methyl isobutyrate.

(41) *Ibid.*, Vol. I, p. 192, gives -84.7° for methyl isobutyrate.

(42) Landolt-Börnstein, II, 969, gives $n^{20}_D = 1.36175$.

(43) "I. C. T.," Vol. I, p. 179, give m. p. -123.5° .

lowered the initial point to -122.9° and the curve dropped off more rapidly.

Parks and Huffman⁴⁴ have summarized some data on the equilibrium between acetaldehyde, hydrogen and ethyl alcohol. Use of their equation (156) for the free energy leads to values of 0.003–0.004% incompleteness in the hydrogenation of acetaldehyde under our experimental conditions. Our failure to detect acetaldehyde in the products is therefore understandable.

We estimate the over-all accuracy of this determination as 100 cal./mole.

Acetone + H₂.—To determine the amount of incompleteness of reaction in each of the calorimetric runs, the vanillin test described by Alyea and Bäckstrom⁴⁵ was adopted: to 1 cc. of the solution to be tested were added 2 cc. of potassium hydroxide solution (100 g. KOH in 60 cc. H₂O) and 1 cc. of 10% vanillin in methyl alcohol and the resulting mixture heated for twenty minutes at 50° ; the appearance of a red color denoted acetone. The product of each run was tested in this manner and the intensity of the resulting color compared with those caused by known amounts of acetone in control experiments; this procedure showed readily detectable differences between 0.1, 0.2, 0.3, 0.4 and 0.5% acetone in methanol.

Run	Moles C ₃ H ₆ O	Moles H ₂ per min.	Moles C ₃ H ₆ O per min.	$-\Delta H_{355}$ cal./mole uncorr.	% C ₃ H ₆ O in prod. by chem. test	Corr. in cal.	$-\Delta H_{355}$ cal./mole corr. for incompleteness
1	0.077811	0.01510	13.22 (10^{-4})	13,359	0.5	67	13,426
2	.077584	.01461	11.05 (10^{-4})	13,356	.6	80	13,436
3	.078658	.01685	21.57 (10^{-4})	13,323	.2	27	13,350
4	.078701	.00947	22.92 (10^{-4})	13,322	.7	93	13,415
Over-all average							13,407 \pm 28
Average, neglecting Run 3							13,426 \pm 7

It is seen from the table that the correction for incompleteness is small and that the results lose none of their significance by the application of it. The elimination of Run 3 from the average is justified on the basis of the trend of the refrac-

Run	$n_{D, 20}$ refractometer	Relative index compared with No. 1 by interferometer
(Isopropyl alcohol)	1.37757 ⁴⁶
1	1.3778
2	1.3778	-0.00006
3	1.3776	-0.00012
4	1.3774	-0.00032
(Acetone)	1.3591 ⁴⁷	

(44) Parks and Huffman, "Free Energies of Organic Compounds," Chem. Cat. Co., N. Y., 1932, pp. 159–162.

(45) Alyea and Bäckstrom, *THIS JOURNAL*, **51**, 90 (1929).

(46) "I. C. T.," Vol. VII, p. 12.

(47) *Ibid.*, Vol. I, p. 276.

tive indices of the products of several runs, as contrasted with the results of the chemical analyses. It would seem that in the case of Run 3 the chemical test was in error. In any event the point is a relatively trivial one.

The pure acetone gave a fairly sharp freezing point at -95.0° ⁴⁸ and while no dropping-off of the freezing curve was observed with a sample containing 0.5% isopropyl alcohol, the initial freezing point was 0.1° lower. A test for irreversible adsorption on the Co–Ni catalyst was negative.

We estimate the over-all accuracy at 100 cal./mole.

Parks and Huffman⁴⁹ have summarized the data on the equilibrium $(\text{CH}_3)_2\text{CHOH}(\text{g}) \rightarrow (\text{CH}_3)_2\text{CO}(\text{g}) + \text{H}_2$ in the temperature range 378.1 to 548.1° K.; their equation (5b) gives $\Delta F_{355} = 4,110$ cal./mole, and $K = 0.00305$. Under the conditions of our runs (excess H₂) this corresponds to 0.3 to 0.5% incompleteness in the hydrogenation of acetone. An extrapolation of the equilibrium data by Parks and Huffman to the temperature of our calorimetric experiments with the use of the now determined heat of hydrogenation leads to a slightly higher equilibrium constant and to an incompleteness in the hydrogenation which is in even better agreement with the data of the preceding table.

Methyl Ethyl Ketone + H₂.—To determine the amount of ketone remaining in the hydrogenation product, the salicylaldehyde test of Alyea and Bäckstrom⁵⁰ was used. To 0.25 cc. of product were added 2 cc. of potassium hydroxide solution (100 g. KOH in 60 cc. water) and 1 cc. of salicylaldehyde solution (10% in ethyl alcohol); the mixture was warmed for twenty minutes at 40° , and diluted with 15 cc. of 20% ethyl alcohol in water. Comparison of the intensity of the resultant yellow color with standards made with methyl ethyl ketone in ethyl alcohol enabled one to estimate the degree of incomplete reaction to 0.1%.

(48) "I. C. T.," Vol. III, p. 45, gives -99° as the f. p. of acetone, and Parks and Kelly, *J. Phys. Chem.*, **32**, 750 (1928), give 177.6°K. (-95.5°C.).

(49) Parks and Huffman, "Free Energies of Some Organic Compounds," Chem. Cat. Co., N. Y., 1932, pp. 22–28, 162.

(50) Alyea and Bäckstrom, *THIS JOURNAL*, **51**, 97 (1929).

Run	Moles C ₄ H ₈ O	Moles H ₂ per min.	Moles C ₄ H ₈ O per min.	-ΔH ₃₃₅ cal./mole uncorr.	% C ₄ H ₈ O in prod. by chem. test	Corr. in cal.	-ΔH ₃₃₅ cal./mole corr. for incompleteness
1	0.063269	0.01548	15.37 (10 ⁻⁴)	13,165	0.2	26	13,191
2	.063750	.01127	22.68 (10 ⁻⁴)	13,144	.2	26	13,170
3	.062783	.01433	11.45 (10 ⁻⁴)	13,193	.2	26	13,219
Average							13,193 ± 17

The indices of the products from the three runs were compared on the interferometer and found to be identical: n_D^{20} 1.3970.⁵¹ The test for irreversible adsorption on the Co-Ni catalyst was negative.

The freezing curve for the methyl ethyl ketone was satisfactory; the initial f. p. was -86.9° ⁵² and dropped off 0.1° to 70% frozen material; addition of 0.5% hydrogenation product lowered the initial f. p. 0.1° and the curve dropped off more rapidly.

The over-all accuracy is *ca.* 100 cal./mole.

Ketene.—Pure ketene was prepared by cracking acetone and subjecting the products to a careful fractionation in a 3-ft. (91-cm.) Podbielniak-type column. The material was freshly distilled into the regular saturating device and hydrogen was saturated with the vapor at Dry Ice temperature, for passage through the calorimeter. Care was taken to exclude all air and water. After the experiments it distilled cleanly back into the storage bulbs in the distilling train.

An attempt was made to hydrogenate ketene over the Co-Ni catalyst at 82° ; the principal product was ethyl acetate, but in addition at least one other product, acetic acid, was formed. The activity of the catalyst decreased and irreversible adsorption occurred. A 5% platinum-on-asbestos was also used; in this case acetaldehyde was the principal product, but reaction was not complete; this was shown by a f. p. on the product, -146° , while acetaldehyde freezes at -122.6° . Because of these difficulties the experiments were discontinued.

Discussion

An examination of the data presented here on the heats of hydrogenation of the carbon-carbon double bond in oxygen-containing compounds reveals that generalizations formulated in previous papers of this series can still be applied. The substituents are again found to decrease the numerical value of the heat of hydrogenation, but in this series of compounds effects of conjugation reveal more interesting facts.

(51) Compare with Webb and Lindsley, *THIS JOURNAL*, **56**, 874 (1934), n_D^{20} 1.3970 for *s*-butyl alcohol; and Houston, *ibid.*, **55**, 4131 (1933), n_D^{20} 1.3983.

(52) Timmermans and Martin, *J. chim. phys.*, **26**, 411 (1928), give -86.6° .

In crotonaldehyde the conjugation between the C=C and the C=O bonds is seen to be nearly the same as that between two C=C bonds in the butadiene derivatives; thus the hydrogenation of pentadiene-1,3 to pentene-1 releases 24,000 cal. and that of crotonaldehyde to butyraldehyde 25,100, which values are to be compared with the 28,000 cal. (weighted mean of *cis* and *trans* compounds) from the hydrogenation of butene-2. More interesting, however, is the fact that the oxygen atom itself can act as a conjugating agent in certain circumstances. Comparing the heats of hydrogenation of ethyl vinyl ether, 2-ethoxypropene, and 2-methoxybutene-2 with the heats released by hydrocarbons with the same number of substituents next to the double bond, it is found that the first compound gives a value lower by 3600, the second lower by 3300, and the third lower by 2100 cal. In interpreting this observation use must be made of quantum mechanical resonance between the unshared pair of electrons on the oxygen and the carbon-carbon double bond, which has been discussed by Pauling and Sherman.⁵³ Evidently, then, oxygen is capable of conjugating with double bonds in two ways; firstly, when a double bond binds it to carbon, in configurations such as C=C-C=O, and secondly, when a single bond binds it to carbon but when the configuration is C=C-O-. The second action is not transmitted over any distances in the molecule, as is evidenced by allyl alcohol, with the configuration C=C-C-O, in which no conjugation is observed but rather a slight exaltation of the heat of hydrogenation, analogous to that observed with the configuration C=C-C-C=C (*cf.* IV). Without implying that the following observations stand in a simple causal relation to each other, we want to call attention to the parallelism between the heats of hydrogenation and the chemical reactivity of the same grouping of atoms. Thus in the series ethylene to tetramethylethylene both the heat of hydrogenation and the ease of addition to the double bond decrease very markedly, while the allenic configuration C=C=C has an exceptional reactivity and

(53) Pauling and Sherman, *J. Chem. Physics*, **1**, 606 (1933).

a very high heat of hydrogenation. The conjugated system $C=C-C=C$, showing a low heat of hydrogenation, is also very sluggish toward 1,2-addition,⁵⁴ but the configurations $C=C-C-C=C$ or $C=C-C-O-$, in which an exaltation of the heat of hydrogenation is observed, are also found to be reactive; one needs only to recall in this connection the exceptional reactivity of allyl ethers. Such examples easily could be multiplied but a quantitative correlation of the phenomena is undoubtedly not simple.

In some respects the effect of the unpaired oxygen electrons differs importantly from that of a double bond in the matter of conjugation. We have no data on the open chain trienes, but from the unpublished figure recently obtained for cycloheptatriene and also from the older information available on the aliphatic trienes it is probable that in a system $C=C-C=C-C=C$ the conjugation energy is enhanced in comparison with the 1,3-butadienes. In divinyl ether, on the other hand, the total conjugation is the same as in ethyl vinyl ether; upon deducting the value of the latter it is found that the hydrogenation of the second double bond in the former releases 30,500 cal., a value common to monosubstituted ethylenes. Apparently, then, the two double bonds of divinyl ether do not conjugate with each other through the intervention of the centrally placed oxygen atom, as the two outer double bonds in a 1,3,5-hexatriene seem to do. Since the total effect of oxygen conjugation in divinyl ether is the same as in ethyl vinyl ether, the conjugation with each double bond may be said to be halved.

A very striking effect is obtained upon the closure of the divinyl ether chain to a five-membered ring, the furan. This closure allows the two double bonds to conjugate with each other as well as with the oxygen and a large stabilization occurs. A comparison with cyclopentene shows that the conjugation in furan amounts to some 17,200 cal. and is, thus, second only to benzene and its derivatives. As Pauling and Sherman⁵⁵ have pointed out, in the case of furan several energetically comparable structures are possible and resonance among them—entirely analogous to that postulated for benzene—must produce this great stabilization, which makes furan an almost wholly aromatic compound.

(54) 1,4-Addition evidently cannot be directly compared with the other reactions.

If the relative heats of hydrogenation are a measure of the conjugation energy, then the carboxyl group is a configuration in which oxygen atoms do not conjugate with the carbon-carbon double bond, either through their own double bonds or through their unshared electrons. From the two examples presented here it is seen that neither the configuration $-C \begin{array}{l} \diagup O \\ \diagdown \end{array} -C=C$ nor $C=C-C \begin{array}{l} \diagup O \\ \diagdown \end{array} -$ has a heat of hydrogenation which is lower than that of the suitably substituted olefin. The heat given off by the former, 31,120, is to be compared with 30,200 for monosubstituted ethylenes; that given off by the latter, 28,640, with the 28,390 cal. for isobutene. Evidently the carbon-carbon double bond does not conjugate at all in these compounds and Wheland's⁵⁶ suggestion of a resonance of $C=C-C=O$ in the configuration $C=C-C \begin{array}{l} \diagup O \\ \diagdown \end{array} OEt$ cannot be valid in this case. A somewhat formal description may be advanced, which combines the conclusions of Pauling that a strong resonance exists in the carboxyl group between the two oxygen atoms, with the earlier discussed comparison of ethyl vinyl ether with divinyl ether. The conclusion is that the unshared electrons of an oxygen atom can conjugate with only one other electron pair in the molecule.

Of interest in this connection are some recent data of Schjånberg,⁵⁶ who has determined the heats of combustion of esters of some unsaturated and corresponding saturated acids, as well as their heats of vaporization, and thus is able to calculate the heats of hydrogenation of the esters in the vapor phase. The following table indicates the configuration of the acids studied, gives the average heats of hydrogenation, as well as the mean deviations from these values, and the number of esters of each acid studied. Since the author gives no details of his measurements, it is somewhat difficult to estimate the probable errors but perhaps the following reasoning may be tentatively accepted. In allylacetic acid (IV) the double bond is removed so far from the carboxyl group that according to all information available (*cf.* for instance Paper IV of this series) no mutual interference is to be expected. Schjånberg's mean value is 31.1 kcal. whereas the value given in earlier papers of this series for singly substituted ethylene derivatives is 29.9 kcal. at room tem-

(55) Wheland, *J. Chem. Phys.*, **1**, 732 (1933).

(56) Schjånberg, *Z. physik. Chem.*, **179A**, 39 (1937).

