

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

THE DECOMPOSITION OF ETHYL AND ISOPROPYL ALCOHOLS AT SURFACES OF MANGANOUS COMPOUNDS

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In the Fourth Report of the Committee on Contact Catalysis¹ and in a subsequent paper,² a theory was advanced to account for the different modes of decomposition of alcohols effected by catalytic surfaces. The former paper treated the broader problem of heterogeneous reactions, whereas the latter introduced a new concept to account for the variation in the hydrogen-olefin ratio resulting from changes in the active surface. This concept was essentially that dehydrogenation occurred on the positive ions of the surface, and dehydration on the negative ions. In addition to the experimental evidence advanced in the same paper, support has been found for the theory in the results of Hoover and Rideal³ and of Taylor.⁴

The investigation to be described below tested the theory by determining the variation in the hydrogen-olefin ratio when one ion of the catalyst was fixed and the other was different from case to case. The chosen contact agents were the oxide, sulfate, phosphate and pyrophosphate of manganese.

The dual surface theory would predict that the oxide and sulfate would give hydrogen-olefin ratios of the same order of magnitude, due to the equivalence of the negative ions. But, on using the trivalent phosphate and the tetravalent pyrophosphate ions, relatively larger yields of olefin would be expected, since the dehydration is assumed to be effected on these ions which, by their higher ionic charge, might be expected to adsorb the reactant relatively more strongly.

The experimental investigation consisted in passing alcohol vapors over the various catalysts at high temperatures, and analyzing the gaseous products formed.

Materials.—Manganous oxide was prepared by ignition at 400° of manganous oxalate made⁵ by the interaction of concentrated solutions of potassium permanganate and oxalic acid in the presence of acetic acid. The oxalate is a well crystallized salt, readily freed from alkaline impurities by washing in distilled water.

The orthophosphate was precipitated from a hot solution of manganous chloride by the slow addition of secondary sodium phosphate solution. The precipitate was very thoroughly washed until all tests for chloride were negative and then further washed with a large volume of distilled water.

¹ H. S. Taylor, *J. Phys. Chem.*, **30**, 145 (1926).

² H. S. Taylor, "Colloid Symposium Monograph," The Chemical Catalog Co., Inc., New York, 1926, Vol. IV, p. 25.

³ Hoover and Rideal, *THIS JOURNAL*, **49**, 104 (1927).

⁴ H. S. Taylor, *Z. Elektrochem.*, **35**, 542 (1929).

⁵ Kessler, *Z. anal. Chem.*, **11**, 270 (1872).

The sulfate was recrystallized from a solution of the c. p. compound.

The pyrophosphate was prepared by ignition of manganese ammonium phosphate at 650°.

Ethyl alcohol was purified by refluxing 95% grain alcohol with potash to resinify aldehydes, distilling, refluxing over lime and distilling from the lime under anhydrous conditions.

Isopropyl alcohol was dried by treating the 97% Eastman brand with lime in the same manner.

Apparatus.—The decompositions were carried out in a Pyrex tube surrounded by a preheater and an electric furnace. The catalyst was placed in the center of the portion surrounded by the furnace, its temperature being given by a nitrogen-filled thermometer. The alcohol was forced into the preheated region by a generator of the type described by Adkins and Nissen.⁶ Gas analysis was carried out with absorbents for carbon dioxide and olefins. Hydrogen and carbon monoxide were oxidized by copper oxide at 300°, while paraffins were burned on a platinum spiral and the resulting carbon dioxide was absorbed.

Miscellaneous.—The alcohol was always introduced at a constant rate of 45 cc. per hour, and the gas samples were taken after the run had been in progress for an hour and a half.

In the following tables a "fresh" catalyst (F) refers to one which is going through its first run, a "second" (2) to one which is going through its second run, and so on. Between each run the system was cooled to room temperature. The gas rate is the total evolution, measured over water at room temperature. As it is meant to give relative values only, it has not been reduced to standard conditions. The figures given are cubic centimeters per minute. Values for the various gaseous decomposition products are expressed in percentage by volume.

Catalysts employed for the decomposition of ethyl alcohol were introduced as 1.00-g. samples. With isopropyl alcohol, 2.00 g. was always used.

Experimental Results

The following tables give the results of analyses of the effluent gases.

TABLE I
ETHYL ALCOHOL DECOMPOSITION
i. Manganous Oxide

Temperature, °C.	330	350	375	375	350	375	425	375
	(F)	(F)	(F)	(F)	(2)	(2)	(2)	(3)
H ₂	92.0	84.7	67.5	52.3	86.9	74.2	80.6	84.9
C ₂ H ₄	0.7	2.8	4.5	2.7	1.2	5.0	4.9	2.2
CO ₂	2.8	9.6	25.6	40.0	8.8	13.4	11.4	4.8
CO	2.4	1.7	0.9	2.8	3.4	5.5	1.6	6.3
CH ₄	2.1	1.2	1.5	2.2	0.7	1.9	1.5	1.8
Gas rate	0.2	1.4	5.2	5.5	1.7	4.2	17.0	2.6

	ii. Manganous Sulfate				iii. Manganous Orthophosphate			
Temperature, °C.	425	425	425	425	400	425		
	(F)	(2)	(2)	(3)	(F)	(F)		
H ₂	93.3	94.4	92.3	89.8	25.5	22.8		
C ₂ H ₄	4.6	3.2	5.0	3.8	71.3	68.8		
CO ₂	0.5	0.5	0.2	1.6	0.7	3.4		

⁶ Adkins and Nissen, THIS JOURNAL, 46, 130 (1924).

TABLE I (Concluded)

CO	0.5	0.6	1.3	4.0	0.9	3.8
CH ₄	1.1	1.3	1.2	0.8	0.6	1.2
Gas rate	3.5	3.0	1.8	2.0	0.8	2.6

iv. Manganous Pyrophosphate

Temperature, °C.	425 (F)	425 (F)	425 (2)	425 (2)	425 (3)
H ₂	10.6	12.1	9.5	15.3	14.5
C ₂ H ₄	88.2	86.4	88.7	82.1	83.3
CO ₂	0.4	0.4	0.6	0.2	0.5
CO	0.4	0.4	0.4	1.0	0.5
CH ₄	0.4	0.7	0.8	1.4	1.2
Gas rate	4.3	4.3	3.3	1.6	2.0

TABLE II

ISOPROPYL ALCOHOL DECOMPOSITION

i. Manganous Oxide				ii. Manganous Sulfate		
425 (F)	425 (2)	425 (3)	← Temperature, °C. →	425 (F)	425 (2)	425 (3)
91.2	94.0	92.6	H ₂	38.6	52.7	
6.5	4.8	4.4	C ₃ H ₆	61.1	47.2	
0.8	0.5	0.5	CO ₂	0.2	0.0	
0.5	0.7	0.6	CO	0.1	0.1	
1.0	Trace	1.9	CH ₄	0.0	0.0	
72	72	..	Gas rate	32	24	
iii. Manganous Orthophosphate				iv. Manganous Pyrophosphate		
425 (F)	425 (2)	385 (3)	← Temperature, °C. →	425 (F)	425 (2)	385 (3)
0.5	0.6	0.5	H ₂	1.0	0.6	0.3
99.4	99.4	99.5	C ₃ H ₆	99.0	99.4	99.7
0.1	0.0	0.0	CO ₂	0.0	0.0	0.0
0.0	0.0	0.0	CO	0.0	0.0	0.0
0.0	0.0	0.0	CH ₄	0.0	0.0	0.0
135	115	50	Gas rate	180	..	68

The two predominating reactions—dehydration and dehydrogenation—may be compared by collecting values of the quantity $[H_2]/([H_2] + [C_nH_{2n}]) \times 100$.

TABLE III

PERCENTAGE DEHYDROGENATION OF ETHYL ALCOHOL

Temp., °C.	MnO	MnSO ₄	Mn ₂ (PO ₄) ₂	Mn ₂ P ₂ O ₇
330	99.2 (F)			
350	96.8 (F)			
	98.6 (2)			
375	93.8 (F)			
	95.1 (F)			
	93.8 (2)			
	97.5 (3)			
400			26.3 (F)	

TABLE III (Concluded)

Temp., °C.	MnO	MnSO ₄	Mn ₂ (PO ₄) ₂	Mn ₂ P ₂ O ₇
425	94.3 (2)	95.4 (F)	24.9 (F)	12.3 (F)
		94.8 (2)		10.8 (F)
		96.7 (2)		9.8 (2)
		95.9 (3)		15.7 (2)
				14.8 (3)

TABLE IV

PERCENTAGE DEHYDROGENATION OF ISOPROPYL ALCOHOL

Temp., °C.	MnO	MnSO ₄	Mn ₂ (PO ₄) ₂	Mn ₂ P ₂ O ₇
385			0.5 (3)	0.3 (3)
425	93.5 (F)	38.7 (F)	0.5 (F)	1.0 (F)
	95.2 (2)	52.7 (2)	0.6 (2)	0.6 (2)
	95.5 (3)			

Inspection of these results shows that the presence of products from secondary reactions must be taken into account. Carbon dioxide, which is obtainable in large quantities when ethyl alcohol is passed over manganous oxide, is possibly formed by a mechanism which has already been discussed by Lazier and Adkins.⁷ Carbon monoxide and paraffins are produced by the decomposition of aldehydes.

Values for the "gas rate" show that the total decomposition is decreased by aging of the catalyst to a greater degree than is the ratio of dehydrogenation to dehydration. Reference to the "Percentage Dehydrogenation" tables shows that dehydrogenation over manganous oxide becomes relatively predominant with aging of the catalyst.

Comparison of the ethyl alcohol-manganous oxide values for all the given temperatures show that dehydrogenation becomes relatively smaller in magnitude with increase in temperature.

The mean values for dehydrogenation percentages at 425° with fresh catalysts are given in Table V.

TABLE V

MEAN PERCENTAGE DEHYDROGENATIONS AT 425°

	MnO	MnSO ₄	Mn ₂ (PO ₄) ₂	Mn ₂ P ₂ O ₇
C ₂ H ₅ OH	94	94	25	12
(CH ₃) ₂ CHOH	94	39	1	1

With ethyl alcohol the oxide and sulfate, both being bi-bivalent salts, give practically identical values. The shift to the trivalent phosphate and the tetravalent pyrophosphate cause corresponding relative increases in the dehydration.

With isopropyl alcohol the figures given show the same general tendency, with, however, some striking modifications. Most marked is the difference in the effect of oxide from that of the sulfate, in contrast to the close cor-

⁷ Lazier and Adkins, *J. Phys. Chem.*, 30, 895 (1926).

respondence found in the case of ethyl alcohol. Furthermore, the decomposition velocities for isopropyl are far greater than those obtained with ethyl alcohol under similar conditions.

The newer developments of the general subject of activated adsorption resulting from experiments conducted in this Laboratory during the present year^{8,9} suggest a more comprehensive reason for the varying efficiencies of these surfaces in promoting the dehydrogenation-dehydration reactions. It is apparent that in all these cases the relative efficiencies of the surfaces in adsorbing either hydrogen or water in the activated condition must be an important factor in determining the ratio of products. On this view the surfaces producing mainly dehydrogenation must activate hydrogen at lower temperatures than they activate water. Surfaces of predominantly dehydrating activity must activate hydrogen at higher temperatures. It is in accord with this view that we found⁸ that manganous oxide adsorbed activated hydrogen at temperatures in the neighborhood of 200° whereas with manganous pyrophosphate there was negligibly small activated adsorption of hydrogen even at 444°. The decomposition experiments recorded herein show that at this latter temperature dehydration is rapid, pointing to rapid desorption of activated water vapor molecules. Actual experimental test of such activated adsorption of water vapor is to be undertaken.

The more pronounced dehydration of the secondary alcohol on a given surface indicates that the structure of the alcohol is also of importance in determining the ratio of decomposition products. The experimental results are in accord with general ideas concerning the behavior of the OH group in primary and secondary alcohols.

Summary

1. The decomposition of ethyl and isopropyl alcohols has been investigated at atmospheric pressure in the temperature range of 330–425°, with manganous salts as contact agents.
2. Gas analysis has indicated that the important reactions are dehydration and dehydrogenation.
3. The ratio of dehydrogenation to dehydration has been found to decrease as the valency of the anion in the salt increases.
4. Under similar conditions, the rate of decomposition of isopropyl alcohol is much greater than that of ethyl alcohol.
5. Aging of the catalyst, with the accompanying poisoning by reaction products, decreases dehydration more than it does dehydrogenation.
6. Elevation of temperature increases the proportion of olefin in the evolved gas when manganous oxide is the activating surface.

⁸ Taylor and Williamson, *THIS JOURNAL*, **53**, 2168 (1931).

⁹ Taylor, *Chem. Reviews*, August, 1931.

7. The last two observations indicate that the apparent energy of activation is higher for dehydration than for dehydrogenation.

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QUANTITATIVE DETERMINATIONS WITH THE CENTRIFUGE AND FACTORS AFFECTING THEM¹

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Introduction

The first recorded use of the centrifuge in quantitative analysis was by George W. Goetz, who used it for a rapid method of determining phosphorus in iron and steel. The method consisted in oxidizing the phosphorus to phosphate, precipitating as the phosphomolybdate, packing the resulting precipitate into a graduated capillary tube by centrifugal force, and reading the volume of the packed precipitate. By comparing this volume with the volume produced under similar conditions with the use of a standard sample, the phosphorus content of the unknown sample could be estimated. Goetz communicated his findings to Dr. Wedding of Berlin, Germany, who published the first results obtained by this method.²

The method was extended to various steels,³ to rapid filtration,⁴ to separation of colloids and of crystalloids,⁵ and to barium sulfate, calcium oxalate, magnesium ammonium phosphate and nitron nitrate.⁶

Heretofore all the work that has been done on the centrifuge method for quantitative determinations has not taken into account the quantitative relations between the conditions of precipitating and centrifuging and the volume of the packed precipitate. The investigations presented in this paper were therefore undertaken for the following reasons: (1) to determine the degree of accuracy one can expect from centrifuge determinations; (2) to determine what factors enter into these determinations, *i. e.*, to determine how and to what extent the conditions of centrifuging and of preparation of sample affect the volume of the centrifuged precipi-

¹ An abstract of a thesis submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy, University of Cincinnati, 1930.

² Wedding, *Stahl und Eisen*, **7**, 118 (1887).

³ M. Ukena, *ibid.*, **7**, 407 (1887); Bormann, *Z. angew. Chem.*, **2**, 638 (1887); M. A. von Reis, *Stahl und Eisen*, **9**, 1025 (1889); *ibid.*, **10**, 1059 (1890); Reinhart, *Chem.-Ztg.*, **15**, 410 (1891).

⁴ Parker, *THIS JOURNAL*, **31**, 549 (1909).

⁵ Friedenthal, *Ber.*, **44**, 904 (1911).

⁶ Arrhenius, *THIS JOURNAL*, **44**, 132 (1922).