Mechanism of Oxidation of Methanol Vapour by the Use of Heavy Oxygen.

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(Received May 18, 1946.)

Vapour of methanol was burned in heavy oxygen, and the heavy oxygen contents of the products, water and carbon dioxide, were determined. Thus it was examined with which atom, hydrogen or carbon, the oxygen atom, previously existing in methanol composition, will remain combined preferencially. The results show that the difference in heavy oxygen contents is small, and it is concluded that during the oxidation the oxygen in methanol goes through some condition where it equalizes with supplied oxygen, such as intermediate production of peroxide-like substance. The effects of the addition of tetraethyl lead and of the presence of catalyser were also examined, and it was observed that they somewhat promote the separation of carbon-oxygen bond rather than hydrogen-oxygen bond in methanol.

Introduction. When the combustion reaction of methanol vapour goes on stepwisely in the following way:

$$CH_3OH+\frac{1}{2}O_2^* = HCHO+H_2O^*,$$

$$HCHO+\frac{1}{2}O_2^* = HCOO^*H,$$

$$HCOO^*H+\frac{1}{2}O_2^* = COO^*+H_2O^*,$$

(O^* indicates supplied oxygen marked with heavy oxygen),

then after the reaction, the methanol oxygen, previously contained in its composition, will come to exist combined with carbon. And therefore if we assume that the excess density of supplied heavy oxygen be a (determined as water), the excess density of oxygen of produced water and of carbon dioxide must be a and $\frac{1}{2}a$, respectively. In moderate reactions some evidences as to the firmness of carbon-oxygen bond have been disclosed. For example, when alcohol esterifies with organic acid, dissociation of alcohol occurs at O-H bond, not at C-O bond.(1) However, when we consider the steric constitution of methanol molecule, we find, on one hand, that the bond energy of C-O is only 70.0 kcal/mol compared with 110.2 kcal/mol of O-H bond and, on the other, that the atomic distance of C-O, 1.43A, is much larger than that of C-H, 1.09A, and accordingly

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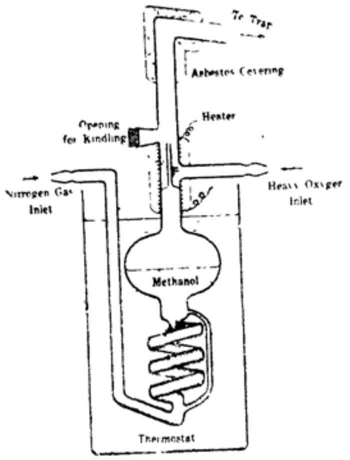
(1) B. Holmberg, *Ber.*, **45** (1912), 2997; E. H. Ingold and C. K. Ingold, *J. Chem. Soc.*, **112** (1932), 756; M. Polanyi, A. L. Szabo, *Trans. Faraday Soc.*, **30** (1934), 508.

the -OH group of methanol molecule must stand out of -CH_3 group. From this point of view, it is probable that the methanol molecule be separated at C-O bond and yield free methyl radical as the foremost stage of reaction, especially in such severe one as combustion. In this case the relation of excess densities between produced water and carbon dioxide (measured as converted water) is the reverse of the first case, and must be larger in carbon dioxide. Moreover, as the third case, we can consider some stage of reaction during the whole oxidation, where both oxygens, i.e. one in methanol composition and the other supplied for combustion, are equalized, such as intermediate production of peroxide CH_3OO^*H. When this is the case the resultant compositions of oxygens, combined with carbon and hydrogen atoms, will be nearly equal with each other. The main aim of the following experiments is to determine which is the case, and in addition to confirm the existence or the nonexistence of the effects due to the added impurities or catalysers.

Experimental procedures.



The apparatus used for combustion of methanol vapour in heavy oxygen is shown in the accompanying figure, all of which is made of Pyrex glass. Liquid methanol is to be placed in vapour saturation vessel(2) heated to desired temperature by thermostat. Through this, introducing nitrogen gas with controlled velocity, saturated vapour of methanol with known velocity is obtained and let it gush out from a narrow jet 1 mm. in diameter, into a concentric tube about 10 mm. in diameter through which heavy oxygen with known velocity is passed. This part of the apparatus is heated up to about 100°C. to avoid the condensation of methanol vapour. After kindling flame, the gas and vapour mixture of combustion is introduced into an ice-cooled trap and then into a liquid-air-cooled trap (both not shown in the figure). The carbon dioxide, solidified in the second trap, is reduced to water by hydrogen with known isotopic composition, by the use of Ti-ThO_2 catalyser. Lastly, both of the waters, i.e. one condensed in the first trap and the other obtained by the reduction of carbon dioxide, are purified and their excess densities are measured. If we wish to carry on the oxidation in the existence of catalyser, the methanol vapour saturated in nitrogen gas should be mixed beforehand with heavy oxygen and then introduced over the catalyser heated to the desired temperature.

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(2) N. Morita, T. Titani, this Bulletin, **12** (1937), 358, N. Morita, *J. Chem. Soc. Japan*, **62** (1941), 65.

The purifications of the resultant waters for density measurements are done by the ordinary method described in other places.(3) When the oxygen content of reacting mixture is not sufficient to complete the oxidation, a large quantity of impurities will be included in the produced water. Then it is mixed with potassium carbonate, dried at about 200°C. in vacuum beforehand, in the proportion of 5 gr. of it to about 10 gr. of water, and heated gently in water bath to boil out these impurities (mainly methanol and aldehyde). After the smell of methanol vapour has nearly completely vanished, the water is distilled in vacuum, and then purified with the ordinary process. During this process the loss of water is so little that we can neglect changes in isotopic composition of the water, and moreover the exchange reaction of oxygen atoms between water and carbonate is also negligible under these conditions.(4)

Results. For the purpose of confirming the excess densities of hydrogen in methanol composition, of hydrogen gas in bomb to be used for the reduction of carbon dioxide and of heavy oxygen gas, methanol vapour and hydrogen gas in bomb are burned in the air and the latter in heavy oxygen. Table 1 shows the excess densities of the resultant water compared with ordinary water.

Table 1. Excess densities of resultant waters in γ.

Reaction	Exp. 1	Exp. 2	Exp. 3	Exp. 4	Mean
Methanol + Air	5.9	7.0	8.5	5.8	+6.8
Hydrogen in bomb + Air	3.0	3.0	1.4	—	+2.5
Hydrogen in bomb + Air	58.7	60.1	—	—	+59.4

Considering the excess desnsity of 7.0 γ of oxygen in the air compared with that of ordinary water,(5) we can get the results shown in Table 2.

Table 2. Excess densities in γ, determined as water.

Hydrogen of methanol = + 6.8 −7.0 = − 0.2 γ
Hydrogen gas in bomb = + 2.5 −7.0 = − 4.5 γ
Heavy oxygen gas = +59.4 +4.5 = +63.9 γ

By the use of those reagents the combustion experiments of methanol vapour are made and we obtained the results shown in Table 3.

The results obtained by the addition of about 5% tetraethyl lead to liquid methanol in the vapour saturation vessel and by the use of copper catalyser heated to 300°C. are shown in Table 4.

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(3) For example: N. Morita, *J. Chem. Soc, Japan,* **58** (1937), 1151; T. Titani, N. Morita, this Bulletin, **13** (1938), 409.

(4) T. Titani, N. Morita, K. Goto, this Bulletin, **13** (1938), 329; T. Titani, K. Goto, ibid., **14** (1939), 77.

(5) N. Morita, *J. Chem. Soc. Japan,* **57** (1936), 176; N. Morita, T. Titani, this Bulletin, **11** (1936), 414.

Table 3. Combustion of methanol vapour in heavy oxygen.

	Subject	Exp. 1	Exp. 2	Exp. 3	Exp. 4	Exp. 5
	Temperature of Thermostat in °C	50.0	50.0	50.0	50.0	56.0
	Flow velocity of Nitrogen Gas in cc/sec	0.55	0.55	0.73	0.70	0.30
	Flow velocity of Methanol Vapour in cc/sec	0.63	0.63	0.84	0.80	0.70
	Flow velocity of Heavy Oxygen Gas in cc/sec	1.45	2.02	1.80	1.66	1.40
Excess Densities of, in γ	Water, obtained by Combustion	45.7	45.0	45.1	44.9	46.5
	Water, reduced from Carbon Dioxide	—	–	48.7	43.3	44.7
	Oxygen, combined with Hydrogen Atom	45.9	45.2	45.3	45.1	46.7
	Oxygen, combined with Carbon Atom	—	—	53.2	47.8	49.0

Table 4. The effect of the addition of tetraethyl lead and of the existence of copper catalyser.

	Subject	Addition of tetraethyl lead	Existence of copper catalyser	
			Exp. 1	Exp. 2
	Temperature of Thermostat in °C	55.0	50.0	50.0
	Flow velocity of Nitrogen Gas in cc/sec	0.32	0.47	—
	Flow velocity of Methanol Vapour in cc/sec	0.64	0.54	—
	Flow velocity of Heavy Oxgen Gas in cc/sec	1.60	0.56	
Excess Densities of, in γ	Water, obtained by Combustion	44.4	40.7	39.1
	Water, reduced from Carbon Dioxide	48.4	--	41.9
	Oxygen, combined with Hydrogen Atom	44.6	40.9	39.3
	Oxygen, combined with Carbon Atom	52.9	—	46.4

Discussion.

As shown in Table 2 the excess density of the heavy oxygen used for combustion is 63.9 γ, so that if we consider the case where both of the oxygens, i.e. one originally contained in methanol composition and the other in the supplied gas for combustion, are completely mixed by some intermediate reaction, and assuming the former is the same in its isotopic composition as the oxygen of ordinary water, then it is clear from the reaction equation:

$$CH_3OH+\frac{3}{2}O_2=CO_2+2H_2O,$$

the excess densities of either of the oxygens, combined with hydrogen or carbon atom, must be $63.9\times\frac{3}{4}=48.9\ \gamma$, both determined as water. On the contrary, when the oxygen in methanol composition remains fixed with either carbon atom or hydrogen atom throughout the combustion reaction, then after the reaction the excess density of that oxygen must become $63.9\times\frac{1}{2}=32.0\ \gamma$ and that of the other remains unaffected, that is 63.9 γ. It is shown by Table 3 that in variant proportions and velocities of mixed gases the resultant water and carbon dioxide have nearly the same composition of isotope. This result coincides with the first case, where the oxygen in methanol composition goes through some stage throughout the combustion reaction to equalize its state with that of supplied oxygen, and seems to exclude the second case, where the possibilities of dissociation of methanol molecule may be considerable at the first stage of the combustion, such as to form aldehyde and hydrogen or methyl and hydroxyl radicals. Surely it is possible that the exchange reaction between water and carbon dioxide would occur after the production. But judging from the experimental procedures it is clear that the exchange reaction in the liquid phase must be negligible, and that in the homogeneous phase it is possible only in the very high temperature such as in the flame part of the reaction system, where the extreme dissociations of methanol and oxygen molecule to atoms or ions may occur. The possibility of this case, however, is itself included in the statement that the oxygen in methanol goes through some stage to equalize its state with that of the supplied oxygen. Nevertheless, from the point of activation energy for reaction, it is more pertinent to consider the production of peroxide such as CH_3OOH or $CH_2(OH)_2$ in the early stage of combustion, as it advanced as the intermediate stage of hydrocarbon oxidation, than to postulate the dissociation to atoms or ions.

By the more detailed examination of Table 2, it is shown that the oxygen combined with hydrogen is always somewhat lighter than that combined with carbon. From this, it seems as if the oxygen atom of methanol were more tightly bound with hydrogen atom than with carbon, or in other words, at the combustion reaction the C-O bond of methanol is a little more easily dissociated than O-H bond. The differences shown in the experimental results are small, and then, considering the difficulty of the experimental procedures, it may be possible to attribute this difference to some systematic error such as caused from the difference in the purification processes of both kinds of water. However, it may also be possible to consider the dissociation of some members of methanol molecules to produce free methyl radicals or such others at the early stage of the combustion reaction. The acceptance of this postulate is more convenient to elucidate the results shown in Table 4. There is no conspicuous difference in the results shown in this Table compared with Table 3. But the addition of tetraethyl lead or the existence of copper catalyser seems somewhat to increase the difference in the isotopic compositions between the oxygen combined with hydrogen and that with carbon. In other words, the addition of tetraethyl lead or catalyser may promote the production of free radical in the oxidation reaction of methanol vapour, which is very probable from the catalytic power of these addition substances. But for concluding this hypothesis the experimental repetition is not sufficient and some more elaborate experiments are necessary.

In conclusion, the writer wishes to express his hearty thanks to Prof. K. Onda, of this University, for the loan of the methanol and tetraethyl lead, and to Yahagi Kogyo & Co. for kindly giving him liquid air used in this investigation. The writer is also indebted to Nippon Gakujutsu

Shinkokai (Society for Promotion of Scientific Investigations, Japan) for the financial assistance.

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