[Contribution from the Department of Chemical Engineering, Massachusetts Institute of Technology]

OXIDATION OF METHANE WITH NITROGEN PEROXIDE

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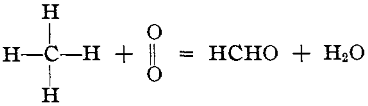
The products ordinarily formed in the direct oxidation of methane are carbon dioxide, carbon monoxide and water. According to Bone's hydroxylation theory, however, the reaction proceeds stepwise with methanol, formaldehyde and formic acid as the intermediate products of oxidation.[1] Although it has been possible to isolate formaldehyde by carefully controlled partial oxidation of methane, nevertheless, no success has been met with in trying to produce methanol by the same procedure. This is supposedly due to the fact that the alcohol is so much more readily oxidized than the hydrocarbon, thus making successive quantities of oxygen attack the initially formed methanol molecules in preference to the remaining methane. Hence methanol is never permitted to build up to concentrations sufficient for its detection. The same reasoning holds for formaldehyde, which, however, represents a further step in the oxidation and therefore is less difficult to isolate when the oxygen concentration is kept low. In normal combustion, however, with a high concentration of oxygen and high temperature, reaction proceeds beyond the formaldehyde stage, with the resulting formation of the ultimate products, carbon monoxide and dioxide.

If this line of reasoning be correct, it should be possible to isolate the intermediately formed alcohol if the process could be carried out under such conditions that the available oxygen, present in only limited concentration, could be consumed by the methane molecules almost instantaneously, avoiding any further reoxidation. It would seem that this could be accomplished by bringing a mixture of nitrogen peroxide with an excess of methane up to reaction temperature, followed by rapid cooling to stabilize the oxidation products against thermal decomposition. Since nitrogen peroxide is capable of liberating 1 atom of oxygen, the tendency for further oxidation of the initially formed methanol would be materially reduced.[2] With elementary oxygen, on the other hand, the conditions seem less favorable in that the consumption of two atoms of oxygen is more probable



$$\begin{array}{c}\mathrm{H}\\ |\\ \mathrm{H{-}C{-}H}\\ |\\ \mathrm{H}\end{array} + \begin{array}{c}\mathrm{O}\\ \|\\ \mathrm{O}\end{array} = \mathrm{HCHO} + \mathrm{H_2O}$$

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[1] Bone, "Coal and its Scientific Uses," p. 176.

[2] There is, of course, a further possibility of direct reaction of nitrogen peroxide with methane, and from such intermediate substances the final oxidation products may result.

Attempts to isolate intermediate products by oxidation of methane with nitrogen peroxide have already been reported on by Bailey,[3] who found that formaldehyde was produced at a minimum reaction temperature of 450° when a mixture of the two gases was passed through a heated porcelain tube. Bibb[4] has claimed the production of valuable oxidation products from methane by a similar procedure, except that he employed the nitrogen peroxide merely as a gas phase catalyst, limiting its concentration to 2%.

In the present investigation a minimum reaction temperature below 450° with production of methanol was sought, using more than 2% of nitrogen peroxide as an oxidizing agent and various surface catalysts.

Experimental Procedure

In the apparatus, which was made entirely of Pyrex glass, nitrogen peroxide was generated from copper and fuming nitric acid, dried and then liquefied in a bulb surrounded by melting ice. Carefully metered and measured natural gas containing 98.3% of methane was slowly bubbled through the peroxide and saturated with it at 0°. Measured methane was then added to adjust the percentage of peroxide in the mixture to that desired and the gases were passed through a reaction chamber 14 cm. long and of 2.8 sq. cm. in free cross section. A central tube extending through the entire length of the reactor held a thermocouple with a movable weld. The chamber was externally heated by a coil of resistance ribbon. Following the chamber, liquid product was removed through a condenser to a cooled bulb, while the gases were scrubbed and discarded. For the recovery of the nitrogen oxides, oxidation and absorption in sulfuric acid worked successfully.

Samples of liquid product were fractionated and the specific gravity, acidity and formaldehyde content found. With the aid of exit gas analyses, material balances were made and minimum reaction temperatures were investigated. Variations in the minimum reaction temperature and in the quantity and quality of product with variation in rates of gas flow (from 8 to 45 liters per hour) and percentage of nitrogen peroxide in the inlet gas mixture (from 8 to 35%) were studied, as well as the effects of pumice, platinized asbestos, vanadium pentoxide, nickel wire and hopcalite as catalysts.

Results

The results of a series of experiments made with an open chamber and with the chamber filled with pumice granules are given in Table I. Despite great difficulties in the measurement of the corrosive gases and in gas and liquid analyses, the material balances were satisfactory.

The minimum temperature was taken as the point above which the gases issued colorless from the reaction chamber, and below which they came out colored brown by nitrogen peroxide, the absence of color being taken as evidence of reduction of the peroxide as a result of reaction with methane. From the data for the open chamber, it will be noted that the minimum reaction temperature varies both with the rate of gas flow and the ratio of nitrogen peroxide. As shown in Fig. 1, the temperature registered by the thermocouple increases linearly with the rate of flow,

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[3] Bailey, U. S. Pat. 1,319,748, Oct. 28, 1919.

[4] Bibb, U. S. Pat. 1,392,886, Oct. 4, 1921.

Table I

Oxidation of Methane with Nitrogen Peroxide

Basis, 1 hour

CH_4+NO_2 entering, l.	NO_2 in entering gas, %	Minimum reac. temp., °C.	Exit gas analysis, %: NO	CO_2	CO	H_2	CH_4	N_2	Liq. prod. cc.	% Entering carbon going to: HCHO	Waste as $CO+CO_2$	Unchanged	Unaccd. for
						Open chamber							
32.3	35.5	538	..	...	...	..	..	...	7.9	...	..	..	...
32.9	35.5	532	25.2	4.1	8.8	24.4	36.3	1.2	7.5	2.0	25.2	70.9	1.9
9.3	35.5	465	24.4	4.3	9.4	27.4	33.6	0.8	1.6	3.4	27.0	67.5	2.1
43.1	35.5	568	29.5	3.1	3.4	8.2	54.3	1.5	9.8	0.9	10.5	88.1	0.5
24.9	22.5	482	16.3	3.7	9.5	22.9	46.5	1.1	4.8	2.0	21.3	75.2	1.5
21.7	12.6	451	12.0	1.0	5.1	6.3	74.4	1.2	2.7	1.8	7.4	89.6	1.2
14.0	8.6	440	7.6	0.0	4.6	10.3	76.2	1.3	0.8	1.5	5.6	91.8	1.1
						Pumice							
20.0	35.5	605	27.3	7.1	6.5	12.5	44.9	1.7	5.0	1.1	22.9	75.6	0.4
38.8	35.5	680	28.9	5.6	3.4	10.6	49.5	2.1	8.5	0.8	15.3	83.8	.1
9.3	6.0	534	6.1	0.0	3.0	0.4	89.5	1.0	0.6	1.0	3.2	95.0	.8

being higher with greater concentrations of nitrogen peroxide. This shows the combined effect of radiation from the electric heating wire, which obviously is at a higher temperature the higher the rate of gas flow through the chamber, and of the heat liberated by the reaction. By extrapolating to zero rate of flow, however, the minimum reaction temperature for the open tube is determined as about 430°.

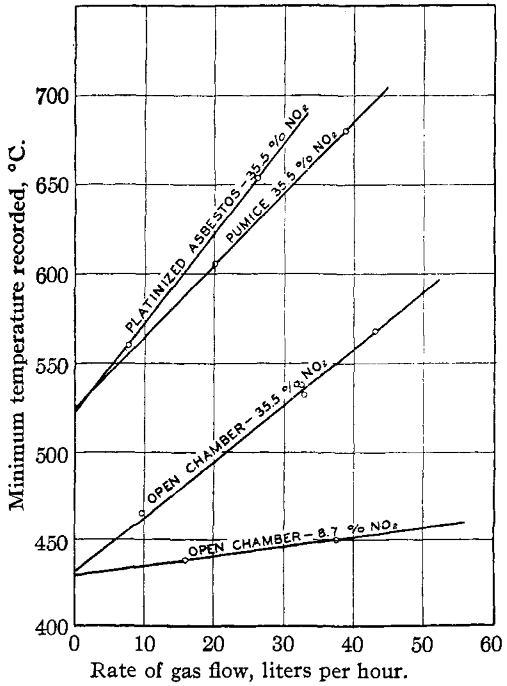

Fig. 1.

The liquid products collected in the condenser contained varying amounts of nitric and, probably, nitrous acid, usually corresponding to a normality of the order of one. Careful fractionation[5] of the liquid products failed to reveal any methanol and only indefinite and small fractions indicating formic acid were obtained. No information could be obtained from the literature in regard to the problem of distinguishing formic acid from mixtures of nitric and nitrous acids, and after many futile attempts the effort to positively identify formic acid was finally abandoned. The conversion of entering methane to formaldehyde varied roughly between 1 and 3.5%, as shown in Table I. In general, the lower the minimum reaction temperature the better the yield of formaldehyde. From a comparison of the data for the various experiments it follows that a low rate of flow with a gas mixture containing a low concentration of nitrogen peroxide results in the highest ratio of formaldehyde to carbon monoxide and dioxide. The formation of these latter compounds, representing further stages of oxidation, is quite considerable. Even in the best experiments the ratio of formaldehyde to carbon monoxide and dioxide, figured on a methane basis, is less than 1:3. Although it might have been possible to improve the formaldehyde yield, such attempts were beyond the scope of this work.

As would be expected, a high yield of formaldehyde on the basis of methane reacting coincides with a low carbon dioxide production, both being characteristic of mild oxidation of the methane molecule.

The loss of nitrogen peroxide by complete decomposition to elementary nitrogen is small, being of the order of magnitude of 1% per passage through the reactor.

In addition to the runs recorded in Table I some fifty experiments were made, mostly with pumice and other contact substances.[6] In the case of catalysts, the reaction temperature was invariably higher than with the open chamber, other conditions being the same, due to localization of the reaction and the formation of a hot spot, as detected by the movable thermocouple. Curves for pumice and platinized asbestos are given in Fig. 1. Vanadium pentoxide gave temperatures in the same region, while a nickel wire introduced into the chamber brought the temperature up by another hundred degrees. The only exception was hopcalite, which gave reaction at approximately the same temperature as the open chamber.

An interesting point is the possibility of reaction between the higher hydrocarbons, present in small amounts, and liquid nitrogen peroxide to form acetic acid. After each run the remainder of the nitrogen peroxide was allowed to evaporate and in almost every case there appeared a residue of several cubic centimeters of a clear, yellow-tinged liquid. This material undoubtedly contained nitric acid and dissolved oxides of nitrogen, but upon careful qualitative analysis it gave a pronounced odor of acetic acid, which apparently was present in considerable quantity.

Conclusions

The fact that methanol is not detected among the products of reaction does not necessarily imply that the alcohol is not formed in methane oxidation. Quite the contrary, methanol seems to be a logical intermediate compound when methane is oxidized with nitrogen peroxide, which splits off only one atom of oxygen per molecule. The failure of the alcohol to appear among the final products can hardly be due solely to further oxidation to formaldehyde, for, as is outlined in the introduction, it is

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[5] Cooper and Fasce, *Ind. Eng. Chem.*, **20**, 420 (1928).

[6] A. H. Waitt, M. I. T. "Thesis," 1926; P. J. Harrington, M. I. T. "Thesis," 1927.

improbable that all the initially formed methanol molecules would be brought in contact with a second molecule of nitrogen peroxide. It is far more reasonable to believe that the high temperature of operation is responsible for thermal decomposition of the alcohol. While methanol is perfectly stable with respect to carbon monoxide and hydrogen at room temperature, it has been pointed out by Lewis and Frolich[7] that the equilibrium constant changes rapidly with temperature, leaving less than 2% of methanol in an equilibrium mixture at 300°. At the temperatures in question, 430° and above, it may therefore be expected that the initially formed methanol decomposes quantitatively into carbon monoxide and hydrogen. Furthermore, the heat of reaction undoubtedly raises the temperature of the alcohol molecules formed to a level above that recorded by the thermocouple as the average for the entire gas mixture. The high content of carbon monoxide and hydrogen in the off-gases may well account for such thermal decomposition of intermediately formed methanol.[8] Instead of decreasing the temperature of reaction, catalysts make the conditions less favorable to the stabilization of methanol by causing a temperature increase and hence even the yield of formaldehyde goes down in the presence of catalysts.

Summary

1. The minimum reaction temperature for the oxidation of methane with nitrogen peroxide is about 430° in an open Pyrex tube. The presence of catalysts results in higher temperatures due to the formation of a hot spot.

2. Methanol cannot be detected among the products of reaction. It is surmised that the alcohol is formed intermediately but decomposes into carbon monoxide and hydrogen, rather than being quantitatively reoxidized.

3. Formaldehyde is formed in good quantities, the maximum yield observed corresponding to somewhat less than one-quarter of the methane reacting. Formaldehyde production is favored by conditions which tend to lower the reaction temperature. These conditions are: low nitrogen peroxide concentration, slow rate of flow and absence of contact surfaces. The accompanying losses of nitrogen peroxide by decomposition to elementary nitrogen are small.

4. The presence of formic acid, as indicated by fractionation of the liquid condensate, could not be verified by direct analysis, due to the disturbing influence of the relatively high concentrations of nitric and nitrous acids.

[7] Lewis and Frolich, *Ind. Eng. Chem.*, **20**, 285 (1928).

[8] It is assumed that the low hydrogen concentration in the last experiment in Table I is due to an analytical error.

5. Attention is called to the possible formation of acetic acid by reaction in the cold of liquid nitrogen peroxide with small amounts of higher hydrocarbons present in the methane.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

SYMMETRICAL AND ANTISYMMETRICAL HYDROGEN AND THE THIRD LAW OF THERMODYNAMICS. THERMAL EQUILIBRIUM AND THE TRIPLE POINT PRESSURE

BY W. F. GIAUQUE AND H. L. JOHNSTON

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The suggestion of Heisenberg[1] that hydrogen and other homopolar molecules exist in two forms, symmetrical and antisymmetrical, offers the most satisfactory explanation for the alternating intensity observed in the band spectra of these substances. This suggestion has been used by Dennison[2] to explain the heat capacity of hydrogen gas over the low temperature range in which it is taking up its rotational degrees of freedom. Dennison's theoretical curve is the first one of a large number offered by various authors which has agreed with the experimental heat capacity data within the limit of error.

A physical conception of symmetry and antisymmetry in the hydrogen molecule arises from the assumption of nuclei which may spin on their own axes. When the two spinning protons oppose each other, the molecule is symmetrical; when their angular momentum is additive, it is antisymmetrical. The statistical weight of the latter variety is increased by the factor three, since a total spin of $j = 1$, one-half unit for each proton, is assumed, and the *a priori* probability p is as usual taken equal to $(2j + 1)$. The symmetrical form takes up only the even rotation states $j = 0, 2, 4, 6, \ldots\ldots,$ while the antisymmetrical assumes the rotation states $j = 1, 3, 5 \ldots\ldots$

In order to explain the heat capacity of hydrogen, Dennison found it necessary to assume that the transitions between symmetrical and antisymmetrical states are so rare that they do not occur appreciably during the experimental determination of heat capacity. Dennison's assumptions are supported by the band spectra data and interpretation of Hori.[3] Birge[4] has shown that Hori's data lead to a value of 0.480×10^{-40} g. cm.^{2} for the moment of inertia of the hydrogen molecule in its normal state. Hori gave 0.467×10^{-40} as the value which the molecule would have if it lost its last half unit of vibration. This latter value should not be used

[1] Heisenberg, *Z. Physik*, **41**, 239 (1927).

[2] Dennison, *Proc. Roy. Soc.*, **115A**, 483 (1927).

[3] Hori, *Z. Physik*, **44**, 834 (1927).

[4] Birge, *Proc. Nat. Acad. Sci.*, **14**, 12 (1928); *Nature*, Jan. 28, 1928.