Yu. N. RYABININ, A. M. MARKEVICH, and I. I. TAMM

1957

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

Yu. N. RYABININ, A. M. MARKEVICH, and I. I. TAMM

FORMATION OF NITRIC OXIDE DURING ADIABATIC COMPRESSION OF COMBUSTIBLE MIXTURES

(Presented by Academician N. N. Semenov, 24 VII 1956)

We have shown (1) that, in the case of strong adiabatic compression of air, a thermal reaction of formation of nitric oxide takes place in the latter. However, the yield of nitric oxide upon compression of air even to pressures of 9000 kg/cm^2 was comparatively small and did not exceed 1% in experiments with pure air, despite the high degree of cooling of the reaction products provided by the adiabatic apparatus with a moving piston used in the work (2). This occurred as a result of the insufficiently high temperature obtained upon compression of air. Thermodynamic calculation shows that, with increasing temperature, the equilibrium shifts toward the formation of nitric oxide. In order to obtain a higher temperature without resorting to especially high degrees of compression, a certain amount of combustible gases and oxygen was added to the reaction mixture. Such mixtures make it possible to obtain a higher temperature at the expense of the heat of combustion. This heat is released during compression of the mixture at the time of reaction, as additional energy to the energy of adiabatic compression, which substantially raises the temperature of the mixture.

In the present work, the formation of nitric oxide was studied during compression of mixtures of nitrogen and oxygen with combustible gases—methane, hydrogen, and carbon monoxide.

Mixtures were investigated with nitrogen and oxygen contents close to stoichiometric for NO in the reaction products. At the same time, the concentration of the combustible component for each gas was selected so that the calorific value of the initial mixture remained constant and amounted to 470 cal per 1 l of mixture. The experiments were carried out under the same conditions as in the preceding work (1). The apparatus operated in a single-stroke mode, in which the piston in the barrel made a forward motion (compression) and a backward motion (expansion) only once. Such experimental conditions were achieved in each individual case by special selection of the parameters of the check valve (2). Analysis of the gases for NO content was performed in the same way as in the preceding work; the sample for analysis was taken no later than 1-2 sec after the end of the experiment.

Fig. 1. Dependence of the yield of nitrogen oxide on the maximum compression pressure for different mixture variants. Explanation in the text

Figure 1: Fig. 1. Dependence of the yield of nitrogen oxide on the maximum compression pressure for different mixture variants. Explanation in the text

Experiments with methane mixtures. Methane was taken directly from the Saratov—Moscow main pipeline and was not subjected to any additional purification. As impurities it contained higher hydrocarbons (2-4%) and nitrogen (3-4%). The content of this natural gas in the mixture under investigation, which we shall hereafter call "methane," was 5.5% of the total volume of the mixture in all experiments.

The results of analysis of the compression products, i.e., of the gases present in the barrel of the apparatus after compression, for nitric oxide content are presented graphically in Fig. 1. Curve 1 represents the NO yield upon compression of air with 5.5% methane (piston weight 41.2 g). Curve 2 was obtained for a mixture enriched with oxy-

with oxygen. In this case the mixture had the following composition: methane 5.5%, oxygen 52.7%, nitrogen 41.8% (piston weight 40.5 g).

In these experiments it was established that, on compressing air with 5.5% methane, nitrogen oxide is formed when a compression pressure of 250 kg/cm^2 is reached (compression ratio 41). A further increase in pressure increases the yield of nitrogen oxide, and at 1400 kg/cm^2 (compression ratio 102) the yield of NO in the cooled products is about 1.5%. When compressing a mixture of the composition: methane 5.5%, oxygen 52.7%, nitrogen 41.8%, the formation of nitrogen oxide begins at pressures below 100 kg/cm^2 (compression ratio 27). Increasing the compression pressure increases the yield of NO, and at pressures of about 2000 kg/cm^2 (compression ratio 130), the yield of NO in the cooled products exceeds 3%.

Fig. 1. Dependence of the yield of nitrogen oxide on the maximum compression pressure for different mixture variants. Explanation in the text

Experiments with hydrogen mixtures. A mixture of the following composition was investigated: hydrogen 18.3%, oxygen 45.4%, nitrogen 36.3%.

The analytical data for the NO content in the reaction products are presented in Fig. 1 (curve 3). In these experiments it was established that formation of nitrogen oxide begins at compression pressures of about 50 kg/cm^2 (compression ratio 18). The maximum yield of nitrogen oxide in the cooled products at a compression pressure of 770 kg/cm^2 (compression ratio 88) was 2.91%.

Experiments with mixtures containing carbon monoxide. The initial mixture had the following composition: carbon monoxide 15.6%, oxygen 46.1%, nitrogen 38.3%. The results of analysis of the compression product for NO content are presented in Fig. 1 (curve 4). A mixture of this composition lies at the boundary of the lower ignition limit (the ignition limit of the CO + O_2 mixture is 15.5% CO) (^{3}). This explains the difficulty of igniting such a mixture. Therefore, this curve probably has a considerably flatter course than in the case of methane or hydrogen mixtures. Gas analysis of the compression products shows that at compression ratios up to 65 the carbon monoxide has practically no time to burn, and nitrogen oxides are not formed. Formation of nitrogen oxide begins at compression pressures of 250–300 kg/cm^2 (compression ratio about 70), when, apparently, combustion of carbon monoxide begins. The maximum yield of nitrogen oxide for this mixture was 2.41% at a compression pressure of 1780 kg/cm^2 and a compression ratio of 142. The experimental data obtained are given in Table 1 without any correction for gas leakage into the clearance between the piston and the barrel of the apparatus, and represent directly measured quantities. According to cautious estimates, this correction is apparently no less than 10–15% in the direction of increasing the yield of nitrogen oxide. It should be noted that the experimental data are fully reproducible, which makes it possible to obtain clearly expressed dependences.

As follows from the experimental data, the yield of NO differs for mixtures with different fuels: mixtures with hydrogen require the lowest compression pressure, and mixtures with carbon monoxide the highest. At the same time, the total heats of combustion of the mixtures, as indicated above, are equal, and the heat capacities of their combustion products are practically equal. Since the formation of NO is a purely thermal reaction (^{6},^{1}), the dependence obtained on the nature of the fuel must be attributed to the difference in the rates of heat release due to different combustion rates. Naturally, in the case of hydrogen, whose combustion rate is high and whose concentration lies within the ignition region, the burning rate of the mixture is higher than in the case of carbon monoxide, for which not only is the combustion rate relatively low, but the concentration of CO in the mixture lies at the boundary of the lower ignition limit. Therefore, the above-noted difference in the yield of NO is caused by different ki-

Table 1

Compression ratio	Maximum compression pressure (kg/cm^2)	NO yield (%)	Compression ratio	Maximum compression pressure (kg/cm^2)	NO yield (%)	Compression ratio	Maximum compression pressure (kg/cm^2)	NO yield (%)

Methane –5.5%; air –94.5%; piston weight –41.2 g

Compression ratio	Maximum compression pressure (kg/cm^2)	NO yield (%)	Compression ratio	Maximum compression pressure (kg/cm^2)	NO yield (%)	Compression ratio	Maximum compression pressure (kg/cm^2)	NO yield (%)
38	120	0,00	53	650	0,97	77	1080	1,40
41	240	0,00	53	620	1,06	82	1100	1,43
43	360	0,37	62	750	1,17	86	1140	1,44
46	440	0,50	75	810	1,22	73	1150	1,46
49	550	0,77	75	1060	1,37	102	1410	1,52
44	470	0,82	73	1120	1,39	—	—	—

Methane —5.5%; oxygen —52.7%; nitrogen —41.8%; piston weight —40.5 g

Compression ratio	Maximum compression pressure (kg/cm^2)	NO yield (%)	Compression ratio	Maximum compression pressure (kg/cm^2)	NO yield (%)	Compression ratio	Maximum compression pressure (kg/cm^2)	NO yield (%)
28	110	0,17	72	1080	2,52	139	2070	2,91
31	132	0,19	100	1340	2,77	95	1520	2,92
32	240	0,56	86	1430	2,77	112	1790	2,92
33	290	0,80	121	1860	2,81	134	2100	2,99
35	315	0,85	101	1340	2,83	105	1760	3,02
40	480	1,59	121	1860	2,84	114	1810	3,08
54	760	2,12	134	2020	2,86	—	—	—

Hydrogen —18.3%; oxygen —45.4%; nitrogen —36.3%; piston weight —40.7 g

Compression ratio	Maximum compression pressure (kg/cm^2)	NO yield (%)	Compression ratio	Maximum compression pressure (kg/cm^2)	NO yield (%)	Compression ratio	Maximum compression pressure (kg/cm^2)	NO yield (%)
18	65	0,07	38	350	1,01	74	630	2,67
21	110	0,14	41	385	1,24	85	730	2,76

Compression ratio	Maximum compression pressure (kg/cm^2)	NO yield (%)	Compression ratio	Maximum compression pressure (kg/cm^2)	NO yield (%)	Compression ratio	Maximum compression pressure (kg/cm^2)	NO yield (%)
25	150	0,19	48	470	1,75	88	770	2,91
27	200	0,51	55	500	2,01	–	–	–
31	240	0,53	62	550	2,37	–	–	–

Carbon monoxide –15.6%; oxygen –46.1; nitrogen –38.3%; piston weight –40.7 g

Compression ratio	Maximum compression pressure (kg/cm^2)	NO yield (%)	Compression ratio	Maximum compression pressure (kg/cm^2)	NO yield (%)	Compression ratio	Maximum compression pressure (kg/cm^2)	NO yield (%)
40	130	0,00	75	530	0,37	132	1590	1,89
53	200	0,00	96	720	0,63	154	1880	2,33
77	330	0,05	104	980	1,11	142	1780	2,41
89	440	0,17	120	1280	1,70	–	–	–

kinetics of the combustion process itself. It is possible that, in the case of carbon monoxide, combustion is not completed by the moment the maximum compression is reached, but continues during the expansion process. Methane, as the experimental data show, apparently occupies an intermediate position between H_2 and CO.

The different NO yield for the two methane mixtures is explained by the different ratio of oxygen and nitrogen in the reaction products. Using the law of mass action, it is easy to show that in the case of the oxygen-enriched mixture (Fig. 1,a, curve 2), the yield should be 1.6 times higher. In reality this ratio is somewhat larger.

The fact that nitric oxide is formed during combustion or explosions has long been known, and this method of obtaining fixed nitrogen has been studied many times. However, only the theoretical works of Ya. B. Zeldovich ([6]) clarified the nature of the process and made it possible to explain the reason for the differences in NO yields under different experimental conditions. A variety of research methods were used. In the combustion of combustible mixtures in closed vessels with natural cooling, NO yields of up to 1.4—1.8% were obtained ([4]-[6]). In experiments on burning combustible mixtures in various kinds of continuously operating burners, the yield did not exceed 2% ([6],[7]). Installations with forced cooling were used, which was achieved by throttling the burnt mixture ([8]). In these experiments vessels of large capacity (300 l) were used; the actual cooling rate remained low and, accordingly, the NO yield did not exceed 0.7%.

At present the determining role of quenching ([6]), i.e., of the cooling rate, on the yield of nitric oxide has been strictly demonstrated.

Experiments carried out in an adiabatic apparatus, which made it possible to obtain high cooling rates, allowed the yield of NO to be brought up to 3%, which considerably exceeds the results obtained by the other methods indicated above. A higher yield of NO was achieved only by Townend and Outridge [9], and only because these authors applied an even higher cooling rate of the mixture, using the bursting-membrane method.

It should also be pointed out that the quenching method implemented in the adiabatic apparatus is applicable to the study not only of such processes in which the product under investigation is the final, thermodynamically stable substance, as is the case for the reaction of nitrogen oxide formation studied here. This method can also be successfully applied to the study of quasistable intermediate compounds, which is especially important in the investigation of rapid processes.

Institute of Chemical Physics
Academy of Sciences of the USSR

Received
23 VII 1956

CITED LITERATURE

[1] Yu. N. Ryabinin, A. M. Markevich, I. I. Tamm, DAN, **95**, 111 (1953).
[2] Yu. N. Ryabinin, ZhETF, **23**, 461 (1952).
[3] B. Lewis, G. Elbe, *Combustion, Flames and Explosions in Gases*, IL, 1948.
[4] A. G. Gaydon, R. I. Tanaka, M. V. Polyakov, ZhFKh, **13**, 464 (1939).
[5] M. V. Polyakov, R. I. Genkina, *Acta Physicochim.*, **11**, 443 (1939).
[6] Ya. B. Zel' dovich, P. Ya. Sadovnikov, D. A. Frank-Kamenetskii, *Oxidation of Nitrogen during Combustion*, Publishing House of the Academy of Sciences of the USSR, 1947.
[7] D. M. Newitt, F. G. Lamont, *Proc. Roy. Soc.*, **139**, 83 (1933).
[8] T. Häusser, *J. Soc. Chem. Ind.*, **41**, 253 (1922).
[9] D. A. Townend, L. E. Outridge, *Proc. Roy. Soc.*, **139**, 75 (1933).

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the *original.*