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Abstract

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FORMATION OF HYDROCYANIC ACID UNDER STRONG ADIABATIC COMPRESSION OF GAS MIXTURES

(Presented by Academician V. N. Kondrat' ev, 23 XI 1956)

In previous works ([1–4]), the reaction of formation of nitrogen oxides was studied by the method of adiabatic compression of gas mixtures at high degrees of compression. Carrying out the entire process in ten-thousandths of a second, it was possible, even in the case of pure air ([1]), reaching a compression ratio of the order of 700 and pressures of 8000-9000 kg/cm^2, to obtain a yield of nitrogen oxides of up to 1%. By diluting the mixture under study with argon, which, as a monatomic gas, makes it possible to obtain higher temperatures upon compression, or by adding to the mixture under study a fuel—methane, hydrogen, carbon monoxide—and thereby additionally increasing the temperature of the mixture upon compression at the expense of the heat of combustion, it was possible to raise the yield of nitrogen oxides to more than 3% ([2]). Such a relatively high yield of nitrogen oxides in synthesizing them from the elements was obtained because the adiabatic apparatus with a moving piston ([3]) used in the experiments made it possible to obtain not only high values of pressure and temperature, but also correspondingly high values of cooling rates.

The present communication is devoted to the study of the reaction of synthesis of hydrocyanic acid under adiabatic compression. Thermodynamic considerations indicate that equilibrium in this reaction, with increasing temperature, shifts in favor of the formation of hydrocyanic acid. In this sense the reaction of HCN formation is similar to the reaction of synthesis of nitrogen oxide, where an increase in temperature likewise shifts the equilibrium toward the formation of NO.

It was shown earlier ([4]) that, upon adiabatic compression of mixtures containing hydrogen, nitrogen, argon, and carbon dust (activated carbon, soot) in various ratios, traces of hydrocyanic acid are detected in the compression products.

In the present work, the formation of hydrocyanic acid was studied in mixtures of nitrogen with hydrocarbons—methane and acetylene. Experiments with methane mixtures showed that in a mixture with nitrogen in a 1 : 1 ratio the reaction does not occur up to pressures of 10,000 kg/cm^2. The reaction can be induced only by adding considerable quantities of argon, i.e., by increasing the temperature during compression. The results of experiments with a mixture of CH_4 10%, N_2 13%, and Ar 77% are presented in Fig. 1, 1. The maximum yield of hydrocyanic acid amounted to about 1% of the initial volume of the mixture.

Considerably larger amounts of hydrocyanic acid were obtained with acetylene mixtures. When working with an equimolecular mixture of acetylene and nitrogen, the formation of hydrocyanic acid begins already upon reaching a pressure of about 1000 kg/cm^2. The maximum yield attained at a pressure of 5000–9000 kg/cm^2 was about 3%. The results of these experiments are represented by curve 2 in Fig. 1. The addition of argon to the mixture, as in the previous experiments, makes it possible to raise the temperature upon compression, which leads to a further increase in the yield of hydrocyanic acid. Curve 3 in Fig. 1 presents the results of experiments with a mixture of C_2H_2 25%, N_2 32%, Ar 43%.

In these experiments an HCN yield of 4% was achieved.

In all the experiments described, analysis for the content of hydrocyanic acid was carried out as follows. The gases subjected to adiabatic compression, 1–2 sec after compression, were drawn from the barrel of the adiabatic apparatus into an evacuated glass flask containing 10 ml of 0.1 N alkali solution. After absorption of the hydrocyanic acid, the contents of the flask were titrated with 0.01 N silver nitrate solution in the presence of potassium iodide ([5]). The presence of hydrocyanic acid was also established by qualitative reactions. The experimental data are presented in Table 1.

Table 1

Compression ratio	Max. compression pressure, kg/cm^2	HCN yield, vol. %	Compression ratio	Max. compression pressure, kg/cm^2	HCN yield, vol. %	Compression ratio	Max. compression pressure, kg/cm^2	HCN yield, vol. %
Initial mixture: CH_4 10%, N_2 13%, Ar 77%. Piston weight 375 g	Initial mixture: CH_4 10%, N_2 13%, Ar 77%. Piston weight 375 g	Initial mixture: CH_4 10%, N_2 13%, Ar 77%. Piston weight 375 g	Initial mixture: C_2H_2 50%, N_2 50%. Piston weight 187 g	Initial mixture: C_2H_2 50%, N_2 50%. Piston weight 187 g	Initial mixture: C_2H_2 50%, N_2 50%. Piston weight 187 g	Initial mixture: C_2H_2 25%, N_2 32%, Ar 43%. Piston weight 187 g	Initial mixture: C_2H_2 25%, N_2 32%, Ar 43%. Piston weight 187 g	Initial mixture: C_2H_2 25%, N_2 32%, Ar 43%. Piston weight 187 g
420	3300	0.09	100	300	0.00	70	800	0.00
520	3600	0.17	146	900	0.03	85	1200	0.19
600	3800	0.25	173	1650	0.50	135	1600	1.02
610	4300	0.30	230	2400	1.18	152	1900	1.33
790	4800	0.53	230	2900	1.39	174	2250	2.03
910	4800	0.65	230	3550	1.87	215	2650	2.59
810	5200	0.58	330	4800	2.46	280	3250	3.14
1170	6000	0.87	330	4800	2.70	300	4200	3.60
1440	7480	0.96	385	4950	2.85	410	5300	4.00
1480	8300	0.98	330	5000	2.78	485	6500	4.00
1480	8500	1.01	365	5300	2.82	550	7400	4.08
			460	5300	3.09			
			430	6100	2.72			
			445	6700	2.67			
			475	7350	3.12			
			620	9200	3.04			

The results obtained are of interest, in our opinion, not only as the realization of the synthesis of hydrocyanic acid by adiabatic compression of mixtures of nitrogen with hydrocarbons. The form of the experimental curves deserves special attention (Fig. 1): they are characterized—this being especially noticeable for acetylene mixtures—by a transition to saturation. Increasing the compression pressure above 4000-5000 kg/cm^2 does not lead to an increase of HCN in the reaction products. Such a course of the curves cannot be explained, for exam-

Fig. 1. Formation of hydrocyanic acid during adiabatic compression of mixtures: 1–CH_4 10%, N_2 13%, Ar 77%; 2–C_2H_2 50%, N_2 50%; 3–C_2H_2 25%, N_2 32%, Ar 43%

Figure 1: Fig. 1. Formation of hydrocyanic acid during adiabatic compression of mixtures: 1–CH_4 10%, N_2 13%, Ar 77%; 2–C_2H_2 50%, N_2 50%; 3–C_2H_2 25%, N_2 32%, Ar 43%

ple, by saying that in the region of high compression ratios the temperature increases comparatively weakly with pressure and, consequently, the reaction rate changes little. It must also be taken into account that in the pressure interval 4000-8000 kg/cm^2 the concentration of the reactants doubles. All this indicates that the reaction rate in the indicated pressure interval must change.

Fig. 1. Formation of hydrocyanic acid during adiabatic compression of mixtures: 1–CH_4 10%, N_2 13%, Ar 77%; 2–C_2H_2 50%, N_2 50%; 3–C_2H_2 25%, N_2 32%, Ar 43%.

On the other hand, the thermodynamic calculations carried out by Kreze and Mackey ([6]) do not make it possible to explain the saturation simply by attainment of the equilibrium thermodynamic concentrations of hydrocyanic acid, since in that case the yield should have been not 4% (Fig. 1, 3), but a considerably larger value. The explanation of the constancy of the yield of hydrocyanic acid

at pressures greater than 4000-4500 kg/cm^2 should apparently be sought in the cooling regime, which in the present case is set by the very conditions of the experiment on the adiabatic apparatus. It is known that under certain conditions the experimental regime, or, more precisely, the cooling regime, can have a very substantial influence on the results of the experiment. Indeed, it is precisely with the process of cooling of reacting systems that the so-called concept of "quenching" is associated. In our opinion, it is quenching that must explain the observed constancy of the HCN yield.

Let us suppose that at high degrees of compression and the corresponding temperatures the reaction rate is such that thermodynamic equilibrium has time to be established during compression. Under these conditions the rate of formation of hydrocyanic acid W_1 is equal to the rate of the reverse decomposition reaction W_2. The concentration of hydrocyanic acid will correspond to the equilibrium value $[HCN]^0$. When the temperature is lowered, $[HCN]^0$ decreases in accordance with the equilibrium constant. The true concentration of hydrocyanic acid in the mixture [HCN] when the temperature is lowered from T_1 to T_2 will be determined not only by the equilibrium value $[HCN]^0_{T_2}$, but also by the magnitude of the decomposition rate W_2.

If during the cooling process the rate W_2 is always considerably greater than $d[HCN]^0/dt$ (where t is time), i.e.

$$W_2 \gg \frac{d[\mathrm{HCN}]^0}{dt}, \tag{1}$$

then the true concentration of the acid [HCN] will at all times remain close to the equilibrium concentration, and $[\mathrm{HCN}]_T - [\mathrm{HCN}]_T^0 \approx 0$.

If, however, during cooling the opposite inequality is satisfied,

$$W_2 \ll \frac{d[\mathrm{HCN}]^0}{dt}, \tag{2}$$

then the true concentration [HCN] will always exceed the equilibrium concentration, and $[\mathrm{HCN}]_T - [\mathrm{HCN}]_T^0 > 0$.

Introducing a new variable $\varphi = dT/dt$, we rewrite inequality (1) in the form:

$$W_2 \gg \varphi \frac{d[\mathrm{HCN}]^0}{dT}, \tag{3}$$

where the cooling rate φ is in practice always set by the experimental regime, while W_2 and $d[\mathrm{HCN}]^0/dt$ are determined by kinetic and thermodynamic factors. As the temperature is lowered, W_2 decreases according to an exponential law, while the change $d[\mathrm{HCN}]^0/dT$ is specified by the expression for the equilibrium constant.

If, as the temperature is lowered, the left-hand side of inequality (3) decreases faster than the right-hand side, then, starting from some temperature T_k, inequality (3) changes sign and relation (2) begins to be satisfied. Consequently, beginning with some critical temperature T_k, the difference $[\mathrm{HCN}]_{T_\mathrm{k}} - [\mathrm{HCN}]_{T_\mathrm{k}}^0$ becomes different from zero.

Other conditions being equal, the value T_k is determined only by the cooling rate φ. The greater φ, the greater T_k. At $T > T_\mathrm{k}$, the reaction, according to the definition of Ya. B. Zel' dovich ([7]), is characterized by high mobility, and $[\mathrm{HCN}]_T - [\mathrm{HCN}]_T^0 \approx 0$.

At $T < T_\mathrm{k}$, under conditions of low mobility of the reaction, the true concentration [HCN] remains close to $[\mathrm{HCN}]_{T_\mathrm{k}}^0$, i.e.

$$[\mathrm{HCN}]_T^0 < [\mathrm{HCN}]_T \approx [\mathrm{HCN}]_{T_\mathrm{k}}^0. \tag{4}$$

This, strictly speaking, is what constitutes the concept of quenching. Consequently, the amount of hydrocyanic acid actually determined in the reaction products may not at all correspond to the amount of HCN that was reached at the maximum temperature of the experiment, but may be considerably smaller.

Returning to the experiments described above, we note that cooling of the reaction products is an integral part of the adiabatic cycle. Calculations show that

in our experiments on the adiabatic apparatus the cooling rate in the region of compression ratios ~ 350 was of the order of 10^7 degrees/sec and changed little with a further increase in the compression ratio. This makes it possible to explain the presence of a horizontal segment on the curves of Fig. 1 precisely in the pressure region beginning at 4000–4500 kg/cm^2.

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