D. S. TSIKLIS, M. D. BORODINA

1962

SovietRxiv

Abstract

Full Text

CHEMISTRY

D. S. TSIKLIS, M. D. BORODINA

FORMATION OF HYDROGEN CYANIDE DURING ADIABATIC COMPRESSION OF MIXTURES OF METHANE AND AMMONIA

(Presented by Academician S. I. Vol̆ fkovich, 11 VII 1962)

Hydrogen cyanide can be obtained, unlike by the Andrussow method (^{1}), directly from methane and ammonia without the addition of oxygen, according to the reaction

$$CH_4 + NH_3 = HCN + 3H_2. \tag{1}$$

The equilibrium of this reaction at high temperatures is shifted toward the formation of HCN. It was of interest to investigate the conditions for the formation of HCN during adiabatic compression of mixtures of methane and ammonia, when the initial products can be subjected to rapid heating and quenching. The present work was undertaken with this aim. On the basis of the results of previous investigations (^{2}), it could be assumed that the temperature of adiabatic compression of mixtures of methane and ammonia would be insufficiently high for the formation of HCN under pressure. Therefore the first experiments were performed with ternary mixtures of methane, ammonia, and nitrogen. It turned out, however, that under these conditions, even at the highest degrees of compression, hydrogen cyanide is not formed. Assuming that the compression temperature of these mixtures was also insufficiently high for the formation of hydrogen cyanide, we replaced nitrogen with argon. In this case it proved possible to obtain hydrogen cyanide.

Table 1

Compositions of the mixtures studied (vol. %)

Mixture	Methane	Ammonia	Argon
I	28,4	9,0	62,6
II	18,0	12,0	70,0
III	8,8	2,5	88,7
IV	6,6	12,1	81,3

Table 2

Yield of hydrogen cyanide upon compression of mixtures of methane, ammonia, and argon as a function of pressure

Compression pressure, kg/cm^2	Mixture I a	Mixture I η	Mixture II a	Mixture II η	Mixture III a	Mixture III η	Mixture IV a	Mixture IV η
750	0,02	0,5	0,03	0,7	0,09	3,7	0,18	3,9
1000	0,05	0,9	0,04	0,8	0,20	8,0	0,44	7,4
1500	0,11	1,4	0,07	1,1	0,43	17,2	0,70	10,9
2000	0,19	2,1	0,12	1,3	0,50	20,0	0,76	11,5
2500	0,26	2,9	0,18	1,6	0,51	20,4	0,77	11,7
3000	0,34	3,8	0,26	2,2	0,50	20,0	0,77	11,7
4000	0,46	5,1	0,48	4,0	0,48	19,2	0,75	11,4
5000	0,57	6,3	0,63	5,2	0,46	18,4	0,73	11,1
6000	0,76	7,3	0,75	6,2	0,43	17,2	0,71	10,8
7000	0,74	8,2	0,85	7,1	0,41	16,4	0,69	10,4
8000	0,81	9,0	0,93	7,7	0,38	15,2	0,68	10,3
9000	0,87	9,7	0,99	8,2	0,36	14,4	0,66	10,0
10000	0,92	10,2	1,03	8,6	0,34	13,6	0,64	9,7
11000	0,95	10,5	1,06	8,8	0,34	12,8	0,62	9,4

Note. a –volume percent of HCN in the gas mixture; η –HCN yield as percent of equilibrium.

hydrogen, and therefore all further work was carried out with ternary mixtures of ammonia, methane, and argon.

Mixtures whose composition is given in Table 1 were investigated.

For the study, methane of 97.8% purity, argon of 99.9% purity, and dried ammonia were used. The experiments were carried out on an apparatus described in detail in the literature (^{3}, ^{4}). The experimental procedure, with a few exceptions, remained the same as before (^{2}). Hydrogen cyanide in the mixtures subjected to adiabatic compression was determined by an argentometric method (^{5}). The results of the study are presented in Table 2, where graphically smoothed data are given: the volume percent of hydrogen cyanide in the gas and the yield of hydrogen cyanide (η).

The equilibrium constant of reaction (1) can be calculated from equation (2)

$$\lg K = -\frac{11896}{T} + 10{,}141 \lg T - 2{,}530 \cdot 10^{-3} T +$$

$$+0{,}231 \cdot 10^{-6}T^2 - 0{,}122 \cdot 10^5 T^{-2} - 17{,}14. \tag{2}$$

Having calculated the equilibrium constant at different temperatures (Fig. 1), one can calculate the content of hydrogen cyanide in the equilibrium mixture at given pressures and temperatures, assuming that at high temperatures (thousands of degrees), even at high pressures, the fugacities of the components will differ little from their partial pressures.

Fig. 1. Dependence of the equilibrium constant of reaction (1) on temperature

Denoting the mole fraction of hydrogen cyanide in the final equilibrium mixture by x, that of methane in the initial mixture by B, and that of ammonia by A, we obtain (taking into account the argon content in the mixtures) an expression for calculating the equilibrium content of hydrogen cyanide in the mixture after the reaction

$$K = \frac{27x^4P^2}{(A-x)(B-x)(1+2x)^2}. \tag{3}$$

Having calculated, for each mixture studied, the dependence of the quantity K/P^2 on x, we obtained graphs (one of them, for mixture III, is shown in Fig. 2), with the aid of which the hydrogen cyanide content in the equilibrium mixture was determined.

Fig. 2. Graphical solution of equation (3)

Fig. 3. Dependence of the HCN yield on pressure

For this purpose, the values of K/P^2 were found for the experimental conditions, and from the graph the corresponding value of the mole fraction of hydrogen cyanide was determined.

hydrogen in this mixture at equilibrium. Knowing x and the amount of hydrogen cyanide formed in the experiment (allowing for leakage and discharge (^{2})), the yield (η) was calculated.

The dependence of the yield of hydrogen cyanide on pressure is presented in Table 2 and in Fig. 3. As can be seen from the figure, the highest yield (about 20%) is obtained when mixture III is compressed to a pressure of 3000 atm. This mixture contains the most argon, and the ratio of methane to ammonia content reaches 3.5. When mixture I is compressed, with almost the same ratio of methane to ammonia but with a smaller amount of argon, the maximum yield reaches only 11% of equilibrium at a pressure of 11,000 atm. A. M. Markevich, I. I. Tamm, and Yu. N. Ryabinin (^{6}), having investigated the conditions for HCN formation during adiabatic compression of mixtures of methane with nitrogen and acetylene, obtained curves whose shape is analogous to that of the curve in Fig. 4.

Fig. 4. HCN content in the gas after compression of mixture II

Fig. 4. HCN content in the gas after compression of mixture II

Figure 1: Fig. 4. HCN content in the gas after compression of mixture II

The authors of that work established that the HCN content (%) in the gas at pressures greater than 4000 atm does not depend on pressure, and they explain this fact by the circumstance that the amount of HCN formed in the experiment depends not only on the rate of the forward reaction, but also on the cooling conditions of the reaction products, during which the hydrocyanic acid that has formed may decompose. Estimating the cooling rate during expansion of the mixture, the authors (^{6}) conclude that at pressures greater than 4000 atm the quenching rate is almost independent of the degree of compression, which explains the constancy of the percentage of HCN in the gas.

When mixture II is compressed (mixture I behaves similarly), the HCN content in the gas at pressures greater than 9000 atm does not depend on pressure, which can also be explained by the constancy of the quenching rate. When mixtures III and IV are compressed, however, the HCN content in the gas reaches a maximum at a pressure of about 3000 atm and then begins to decrease slightly. Apparently, under such compressions the role of pressure increases, shifting the equilibrium toward formation of the initial products; i.e., in this case the limiting factor is not kinetics but the thermodynamics of the process.

The authors thank I. R. Krichevsky for his attention to the work and valuable advice.

State Scientific-Research
and Design Institute of the Nitrogen Industry
and Products of Organic Synthesis

Received
9 VII 1962

CITED LITERATURE

1. S. I. Vol' fkovich, *General Chemical Technology*, Moscow–Leningrad, 1959.
2. D. S. Tsiklis, M. D. Borodina, DAN, **140**, No. 6 (1961).
3. Yu. N. Ryabinin, ZhETF, **23**, 461 (1953).
4. D. S. Tsiklis, *Technique of Physicochemical Investigations at High Pressures*, 1958.
5. L. Z. Soborovsky, G. Yu. Epshtein, *Chemistry and Technology of Military Chemical Substances*, 1938.

6. A. M. Markevich, I. I. Tamm, Yu. N. Ryabinin, DAN, **113**, 856 (1957).

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