DETONATION OF LIQUID HYDRAZOIC ACID
AND ITS AQUEOUS SOLUTIONS

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Results of an experimental determination of the characteristics of a detonation wave are presented: velocity D_0, pressure P, and temperature T of the detonation of hydrazoic acid HN_3 and the detonation velocity D of its aqueous solutions. Owing to the extreme explosiveness of HN_3 its practical use is almost impossible, but it attracts the attention of investigators as one of the model systems for checking theoretical calculations in the high-pressure and temperature region. The great danger of handling liquid HN_3 and its solutions has held up a study of their detonation. Some data on measuring the detonation velocity of aqueous solutions of HN_3 are given in [1]. Despite the uncertainty of the absolute values of the detonation velocities in [1], we can conclude from their examination that aqueous solutions of HN_3 are capable of detonation with discrete velocities: with high (normal) and with the most diverse low velocities. This phenomenon was confirmed in the experiments described below. The detonation velocity of liquid HN_3 was reported earlier in [2]. In the present study we checked the purity of the HN_3 used, refined the value of the detonation velocity of liquid HN_3, and determined the detonation velocities of a number of aqueous solutions in the HN_3 concentration range from 100 to 54%. It was established that the normal detonation velocity of aqueous HN_3 solutions is related with the detonation velocity D_0 of pure HN_3 and its concentration α in solution by the expression $D \approx D_0 \sqrt{\alpha}$ only in a rough approximation. The true values of D are always greater than $D_0 \sqrt{\alpha}$, and this divergence increases as α decreases.

The detonation pressure of HN_3 at the Chapman-Jouguet point, measured by the split-off method, is equal to 166 kbar; the isentropic exponent is 2.89.

The detonation temperature of liquid HN_3 was measured by the brightness and color methods. Here it was established that the values of the brightness and color temperatures for HN_3 coincide, and consequently the radiation of the detonation of HN_3 is Planckian; the detonation temperature of HN_3 is 4700°K.

This article also presents the results of calculating the parameters of the detonation wave and composition of the explosion products for mixtures of HN_3 and water of various concentrations for a density of 0.01 g/cm³ with the use of the equation of state of an ideal gas.

As before [2], the HN_3 for the experiments was obtained by the action of 75% orthophosphoric acid (H_3PO_4) on dry sodium azide (NaN_3) with subsequent distillation on a water bath at 50-60°C and condensation in a Liebig condenser. The condensate receiver, which is simultaneously the charge envelope, was attached beforehand on a special stand in the field of view of the recording instrument. In determining the detonation velocity the recording instrument was a "streak" camera, and in determining the temperature, the optical part of a photomultiplier and spectrograph located in the forechamber room. Owing to the high explosion hazard of HN_3 and its concentrated aqueous solutions, their production and testing were accomplished by remote control. The device for producing HN_3 was rolled away at the appropriate time on a movable reaction table. When investigating the solutions, the required amount of water was added to the receiver beforehand. The degree of purity of HN_3 used in [2] was not determined, although it could be assumed that the content of impurities in it was small. In connection with this, one of the problems of this

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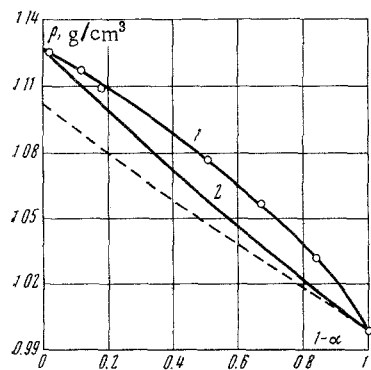
Fig. 1
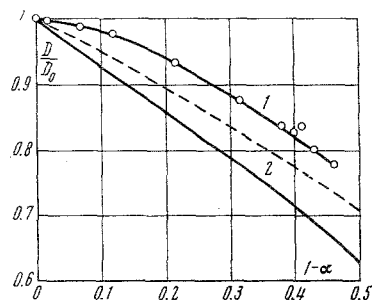
Fig. 2

TABLE 1

x	ρ	d	m	D	n	D/D_0
1.0	1.127	10	—	7570 ± 20	6	1.0
0.983	1.125	5—10	—	7540 ± 15	10	0.9960
0.931	1.121	5—10	—	7470 ± 65	5	0.9868
0.882	1.116	10	—	7390 ± 30	7	0.9762
0.784	1.107	10	1.0	7070 ± 70	7	0.9340
0.686	1.098	10	8.0	6630 ± 20	5	0.8758
0.620	1.091	24	8.0	6350 ± 60	3	0.8388
0.600	1.089	25	15.0	6270 ± 10	3	0.8283
0.588	1.088	15—25	8.0	6340 ± 120	12	0.8375
0.570	1.086	27	15.0	6070 ± 25	4	0.8018
0.539	1.082	25—27	15.0	5900 ± 55	5	0.7794

investigation was to determine the degree of purity of liquid HN_3 and to measure its detonation velocity more accurately. For the analysis a portion of the HN_3 condensate was collected in an excess of a 0.5 N solution of NaOH. After neutralization of the excess of the alkali by acetic acid, the quantity of N_3^- ions was determined by argentometric titration [3]. It was established that the content of HN_3 in the condensate was $98.5\pm$ 1.5%. Impurities in an amount of 1.5-3.0% consisted of water and traces of compounds which apparently were the products of the action of HN_3 on the walls of the apparatus. The composition of the impurity was not analyzed.

Pure HN_3 was produced by double distillation through a dephlegmator with intermediate drying of the condensate with magnesium sulfate or calcium chloride. The bath temperature during the second distillation was 50°C. The content of impurities in HN_3 in this case did not exceed 0.2%. Such condensate was used for refining the detonation velocity in glass tubes with a diameter of 10 mm and wall thickness of 0.8-1.2 mm. The height of the column of HN_3 in the tube was at least 150 mm. The temperature of the room in which the HN_3 was produced and tested was 17 ± 1°C. The average value of the detonation velocity of HN_3 obtained from six experiments was 7570 ± 20 m/sec. This value exceeds that obtained earlier [2] by 30 m/ sec, which does exceed the limits of the average error of measuring velocity.

In further investigations we determined the density and detonation velocity of aqueous HN_3 solutions. The density was determined by the pycnometric method. In Fig. 1, where ρ is the density g/cm³ and $(1-\alpha)$ is the weight fraction of water in the HN_3 solution, curve 1 is plotted from the experimental points, straight line 2 is plotted for the case of fulfillment of the rule of additivity of volumes on mixing HN_3 with water, and the dashed line is plotted on the same assumption of additivity of volumes, but the value of the density of HN_3 is taken from [4]. We see from the shape of curve 1 that the dissolution of HN_3 in water is accompanied by a decrease of volume. Extrapolation of curve 1 to the intersection with the y axis shows that the density of pure HN_3 is slightly greater than that established in [4].

In the literature there is only one work [1] in which an attempt was made to measure the detonation velocity of aqueous HN_3 solutions.

From an examination of the values of the detonation velocities given in [1] we can make two conclusions:

1) the value of the high detonation velocity was determined inaccurately;

2) aqueous HN_3 solutions are capable of detonation with normal (high), low, and superlow velocities.

TABLE 2

α	1.00	0.95	0.90	0.85	0.80	0.65	0.55	0.45
D	2852	2730	2628	2535	2445	2150	1911	1634
U	1278	1235	1191	1158	1110	967	854	725
T	4890	4500	4180	3910	3640	2780	2160	1560
k	1.233	1.211	1.202	1.205	1.203	1.223	1.235	1.257
$\langle M \rangle$	20.2	20.2	20.3	20.3	20.3	20.1	19.8	19.5
Q	1160	1100	1060	1010	970	760	560	350
H_2	8.54	9.63	9.92	9.74	9.27	7.54	6.38	5.22
H	6.13	4.10	2.69	1.71	1.03	0.10	0.01	—
H_2O	—	1.82	4·33	7.21	10.32	19.34	24.98	30.53
OH	—	0.60	0.83	0.80	0.57	0.07	—	—
O_2	—	0.01	0.02	0.02	0.02	—	—	—
O	—	0.13	0.11	0.07	0.04	—	—	—
N_2	34.83	32.98	31.24	29.52	27.81	22.65	19.17	15.68
N	0.06	0.02	—	—	—	—	—	—
NH	0.06	0.03	0.02	0.01	—	—	—	—
NO	—	0.22	0.25	0.21	0.20	0.01	—	—

TABLE 3

α	d	m	D
0.774	5	—	2750
0.686	10	0.6	2330
0.676	10	0.7	2200
0.637	10	—	2150
0.588	19	1.2	1940

The next stage in this study was to determine the detonation velocity as a function of the concentration of the aqueous HN_3 solution for the normal regime and to establish the limiting concentration below which the aqueous HN_3 solution does not detonate in a normal (high-velocity) regime. The tests of aqueous HN_3 solutions to determine the detonation velocity were carried out in glass tubes with an inside diameter of 10-27 mm and whose length was at least 10 diameters. Initiation was done from the bottom. With such initiation through the glass from a detonating cap, high-velocity detonation was excited only in pure HN_3 and in its highly concentrated solutions. To excite high-velocity detonation in solutions whose concentration was below 80%, we used an additional RDX detonator pressed to a density of 1.65 g/cm³. The weight and diameter of the additional initiator were varied depending on the concentration of the test solution. The measured values of the detonation velocities are presented in Table 1, where D is the detonation velocity in m/sec, α is the concentration of HN_3 in the aqueous solution in weight fractions, ρ is the density of the solution in g/cm³, d is the diameter of the charge in mm, m is the weight of the additional initiator in g, n is the number of experiments, and D/D_0 is the ratio of the detonation velocity of the solution to that of pure HN_3. In Fig. 2, curve 1 shows the dependence of D/D_0 on the weight fraction (1-α) of water in the solution. As is known, the detonation velocity and the quantity Q of heat liberated in the detonation wave are associated by the relation

$$D = \sqrt{2Q(k^2 - 1)} \tag{1}$$

where k is the isentropic exponent of the explosion products. For mixtures of the explosive with inert additives the dependence of the detonation velocity on the concentration of the mixture α can be described approximately (assuming k and Q are constants) by the expression

$$D \approx D_0 \sqrt{\alpha} \tag{2}$$

This dependence is shown in Fig. 2 by a dashed line. As we see, the experimental curve 1 lies above the dashed, i.e., theoretical, line. The maximum divergence in the given case reaches 5%. This difference exceeds the experimental error considerably. Its cause may be a change of the composition of the explosion products and of the magnitude of heat evolution when HN_3 is diluted with water. The liberation of heat per unit weight of acid in solution can increase due to a decrease of the degree of dissociation, ionization, or excitation of the explosion products of HN_3 owing to a decrease of temperature with dilution. The liberation of heat per unit weight of acid in solution differs slightly also due to the thermal effect of dissolution. The divergence between D and $D_0 \sqrt{\alpha}$ is not very great, and therefore when performing exact calculations it is necessary to take into account all possible (even insignificant) factors leading to a change of the heat of explosion, in addition to consideration of the change of the initial density of the solutions and of the molecular weight of the explosion products. A more pronounced divergence between D and $D_0 \sqrt{\alpha}$ as α decreases was found earlier while studying the detonation capacity of the explosive system nitroester−solvent.*

By means of a computer we calculated the detonation velocity of aqueous HN_3 solutions with the use of the equation of state of an ideal gas. The initial density was taken to be equal to 0.01 g/cm³. The enthalpy

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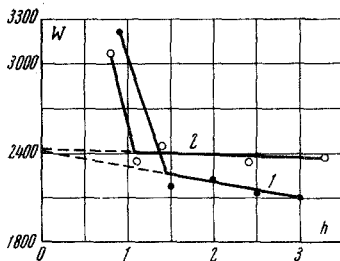*See R. Kh. Kurbangalina, Candidate's Dissertation, Institute of Chemical Physics, 1947.

Fig. 3

of HN_3 and water was taken for the liquid state. The results of these calculations are given in Table 2, where D is the detonation velocity in m/sec, U is the mass velocity in m/sec, T is the temperature of the detonation products at the Chapman–Jouguet point in °K, k is the isentropic exponent, <M> is the average molecular weight, Q is heat evolution in kcal/kg. Table 2 also shows the composition of the detonation products moles/kg (those components whose quantity is greater than 0.01 moles/kg are indicated).

The detonation temperature at $\rho = 0.01$ g/cm³ decreases linearly with dilution of HN_3 with water. The degree of dissociation of hydrogen and water decreases simultaneously. The heat evolution changes relatively weakly at a water content to 20%, and thereafter this dependence intensifies. In addition to the amount of heat evolved, a change of the isentropic exponent substantially affects the character of the dependence of the detonation velocity on the concentration of the mixture. The calculated values of the detonation velocity of such an idealized solution (curve 2 in Fig. 2) differ considerably from those expected according to (2). This fact once again emphasizes the rough-approximate character of Eq. (2).

The values of the normal detonation velocity of aqueous solutions of HN_3 in the concentration range from 100 to 54 wt.% have presently been determined (Table 1). Solutions whose concentration is less than 54% are also capable of high-velocity detonation (this follows from brisance tests), but their luminescence upon detonating is so weak that it cannot be recorded on photographic film. The limiting concentration below which aqueous solutions cannot detonate in a high-velocity regime has not presently been established. Apparently it will be appreciably less than 54%. For example, detonation was observed (see preceding footnote) in a high-velocity regime of the system nitroglycol-chloroform containing only 30% nitroglycol. The values of the detonation velocities of a number of concentrated aqueous HN_3 solutions upon detonation in the low-velocity regime are given in Table 3, where α is the concentration of HN_3 in weight fractions, d is the diameter of the charge in mm, m is the weight of the intermediate initiator in g, and D is the detonation velocity in m/sec. It follows from the data of Table 3 that a low detonation velocity of solutions decreases almost linearly with concentration. It should be noted that the data in Table 3 were obtained not specially for the purpose of studying the concentration dependence of low velocity but incidentally while selecting the initiators and diameters of the charges for exciting a high-velocity detonation. Therefore, to obtain more reliable information on the character of the dependence of low velocity on solution concentration, additional investigations are needed which eliminate the effect of the charge diameter, thickness of the envelope wall, and initiator, since it is known from observations (see preceding footnote) that these factors noticeably affect the value of low velocity. Thus, in this work, unlike in [1], detonation of an aqueous HN_3 solution of the same composition both in high- and low-velocity regimes (Tables 1 and 3) was accomplished. The values of velocities less than 1000 m/sec found in [1] for solutions with a rather high concentration should be attributed to a "superlow-regime" process (apparently they should not be called detonation). In this work we did not investigate processes of decomposition of aqueous solutions with velocities below 1000 m/sec, but undoubtedly they are feasible and relatively stationary. This was shown earlier (see preceding footnote) for nitroesters.

The substantial difference between the composition of the detonation products of HN_3 and secondary explosives determines the interest in the isentropic exponent. To determine it we measured the detonation pressure of liquid HN_3 with the use of the split-off method. In these experiments the charges had a diameter of 27 mm and length of 45-47 mm; we used aluminum split-off plates (diameter 40 mm), both solid and built-up [5]. The thickness of the plate varied from 0.9 to 3.0 mm. In the case of built-up plates the thickness of the attached plate was 0.4 mm. In the experiments we measured directly the speed of motion W of the free surface of the split-off plate. The measurement results are shown in Fig. 3, where W is plotted in m/sec on the y axis and the plate thickness in mm on the x axis. In Fig. 3 curve 1 is drawn through points obtained with solid plates, and curve 2 with built-up plates. Both curves have a jog which is accounted for by the different plate thicknesses. Continuation of the gently sloping branches of curves 1 and 2 to the intersection with the y axis leads to values W = 2430 and 2420 m/sec.

To calculate the pressure we took a value of W equal to 2425 m/sec. The magnitude of pressure at the Chapman–Jouguet point was determined by the approximate formula

$$P = \frac{1}{4} \rho_0 D_0 W (1 + \rho_2 U_2/\rho_0 D_0)$$ (3)

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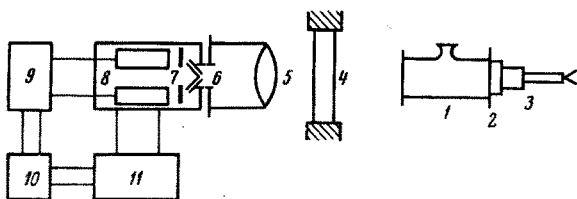Fig. 4

where U_2 is the velocity of a shock wave in aluminum, ρ_2 is the density of aluminum, ρ_0 and D_0 are the density and detonation velocity of HN_3. The velocity of the shock wave in aluminum was calculated on the basis of its shock adiabat

$$U_2 = 5.25 + 0.695 \; W \qquad (4)$$

The magnitude of the detonation pressure of HN_3 at the Chapman–Jouguet point was found to be equal to 166 kbars. The value of the isentropic exponent k of the detonation products of HN_3, calculated from the relationship

$$P = \rho_0 D_0{}^2 / (k + 1) \qquad (5)$$

with the use of the experimentally determined values of P and D_0, was equal to 2.89. Despite the substantial difference in composition of detonation products from secondary explosives (TNT, RDX, PETN), the value of the isentropic exponent for detonation products of HN_3 is approximately the same as for these substances [5-7].

The temperature at the front of the detonation wave of HN_3 was measured by the color and brightness methods. The device used for the measurements is shown schematically in Fig. 4, where 1 is a glass vessel with HN_3, 2 is a stopcock, 3 is a lens-shaped detonating charge, 4 is a window (porthole) of organic glass in the wall of the explosion chamber, 5 is the objective lens, 6 is an adjustable slit, 7 is a system of mirrors separating the light signal into two rays, 8 is photomultipliers, 9 is the oscillograph, and 10 and 11 are the high-voltage regulator and source. In the experiments we measured directly the magnitude of the electric signals coming from the photomultipliers and proportional to the intensity of the luminous fluxes in two portions of the spectrum. Two bands were cut out from the spectrum by a set of glass filters. One transmission band with a peak at $\lambda = 400$ mμ was created with a set of SS-8, NS-3, NS-7, NS-9, and NS-2 filters, and the other with a transmission peak at $\lambda = 630$ mμ by a set of KS-13, ZhZS-18, NS-7, and NS-8 filters.

The width of each band did not exceed 10 mμ. Preliminary experiments with the ISP-51 spectrograph showed that the luminescence of the front of the detonation wave of HN_3 has a continuous spectrum. The ratio of intensities of the luminous fluxes can be expressed by the formula

$$E_1 / E_2 = A + B / T \qquad (6)$$

In deriving this expression we used Wien's law for a gray body. Here $B = B (\lambda_1, \lambda_2, C_2)$, C_2 is a constant, λ_1 and λ_2 are the wavelengths corresponding to the maximum transmission coefficient of the set of filters. The value of the transmission coefficient depends on the spectral sensitivity of the photomultiplier, the general transmission coefficient of the optical system, band width, and emissivity.

We assumed that the emissivity does not depend on wavelength. This assumption was not checked directly for HN_3, but the coincidence of the brightness temperatures for different wavelengths and the coincidence of the brightness and color temperatures apparently confirm the validity of this assumption.

Since the value of coefficients A and B in Eq. (6) cannot be calculated with sufficient accuracy, it was determined by calibration. For this purpose we used an IFK-120 flashlamp and dc carbon arc.

The brightness temperature was determined by comparing the brightnesses of the luminescence of the detonation front of HN_3 and nitromethane, whose detonation temperature is known [8].

The values obtained for the color and brightness temperatures of the detonation of HN_3 were respectively 4720 ± 120°K and 4700 ± 150°K. The agreement of these temperature values means that the detonation front of HN_3 emits as a blackbody and the measured temperature is true. We need call attention to the fact that the measured detonation temperature of liquid HN_3 is close to the calculated value for a density of 0.01 g/cm³. However, this does not mean that the detonation temperature of HN_3 does not depend on density.

Few experiments have presently been carried out to determine the detonation temperature of aqueous solutions: it follows from the preliminary data that the values of the brightness and color temperatures for them diverge. This circumstance requires a more detailed investigation of the luminescence upon detonation of solutions.

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