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COMBUSTION OF THE INORGANIC SALTS AMMONIUM IODATE AND HYDROXYLAMIN SULFATE

A. A. Shidlovskiy

The necessary condition for a chemical reaction to proceed in the form of combustion is that it be exothermic. However, it is still unclear whether the condition that it be exothermic is sufficient for the chemical reaction to be capable of proceeding in the form of combustion, when certain conditions are observed. In recent years combustibility has been observed in compounds which had previously been considered incombustible by selecting the appropriate conditions when carrying out the experiments; included among these compounds are ammonium nitrate [1-3] and ammonium perchlorate [4,5]. However, the decomposition of these compounds evolves a considerable amount of heat: ammonium nitrate up to 350 kcal/kg (for this compound the heat of reaction may vary widely with a change in the composition of the products of the combustion reaction), and ammonium perchlorate up to 390 kcal/kg.

We believe that any chemical system in which an exothermic reaction is possible showed prove capable of having a combustion reaction initiated and propagated in it, when the appropriate external conditions have been chosen. A substantial proof in favor of the hypothesis which we are defending would be the prediction of the possibility of combustion of compounds which decompose with the evolution of a small amount of heat, and then the experimental verification of the fact that these compounds, not previously considered combustible, are capable of stable combustion under certain conditions. As the first objects for the experiment we chose the two salts: ammonium iodate and hydroxylamine sulfate.

Ammonium iodate, first prepared by Gay-Lussac [6], is of no practical importance, and therefore has been studed relatively little. Regarding the behavior of the salt during heating, it was known only that at 150° it suddenly decomposes without melting and liberates steam, iodine vapor, and also nitrogen and oxygen [7,8]. By experimental means we found the heat of formation of this salt to be equal to 94 kcal/mole [9]. Our calculation showed [5] that when the salt decompose according to the equation

$$NH_4JO_{3\,crys} = 2H_2O_{gas} + 0.5J_{2\,gas} + 0.5O_2 + 0.5N_2,$$

it evolves heat equal to Q = 14.1 kcal/mole, which corresponds to a total of q = 72 kcal/kg.

Regarding hydroxylamine sulfate, it was known that when it was heated to 125-130° a certain loss in weight is observed, which rapidly increases as the compound is heated to 136° [10]. It is also known that the salt melts and decomposes at 169-170°. The products of the decomposition of the salt according to Ross' account [11] are

$$3(NH_3OH)_2SO_{4\,crys} = (NH_4)_2SO_{4\,crys} + 2SO_2 + 2N_2O + 8H_2O_{gas}$$

The heat of formation of the original salt is known and is equal to 282.5 kcal/mole [12].

After finding in a handbook [12] the values of the heats of formation of the products of the reaction, we computed, using Hess' law, that the heat of decomposition of the salt is equal to

$Q = 281.9 + 71.2$ $Q = 281.9 + 71\cdot2 - 19.5\cdot2 + 57.8\cdot8 - 282.5\cdot3 = -0.2$ kcal. However, according to our assumption, when it decomposes according to the equation

$$(NH_3OH)_2SO_{4\,crys} = 4H_2O_{gas} + N_2 + SO_2,$$

the salt can release a small amount of heat $Q = 57.8.8\cdot4 + 71 - - 282.5 = 19.7$ kcal/kg.

As is known, stable combustion is possible only under conditions of equality between the incoming heat (heat of reaction) and the outgoing heat (losses to the surrounding space).

On the basis of the general assumptions of the theory of combustion [13] it is possible to draw the conclusion that such factors as increased temperature and increased pressure, as well as the presence of a catalyst in the substance being burned, favor combustion. Moreover, the greater the dimensions of the sample being burned (the layer the diameter of the tube), the fewer (with respect to the total incoming heat) the heat losses to the surrounding space, which is also conducive to stability of combustion. All this was taken into account by us in carrying out the experiment.

Experimental Part*

Ammonium iodate was obtained by neutralizing an aqueous solution of analytical grade iodic acid with a slight excess of an aqueous solution of analytical grade ammonia. The ammonium iodate precipitate was separated from the solution in a Buchner funnel, washed with a small amount of water, and dried to constant weight at 60°. A determination of the purity of the compound by the iodometric method

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*K. V. Valkina and A. A. Nosko participated in carrying out the experiment.

gave a result of 100.7%.

The test for the combustibility of the salt was carried out in the following way. The salt was packed uniformly by stages with a wooden plunger into glass tubes with an inner diameter (d_{in}) of 1.75 cm. Ignition was effected with the aid of a nichrome wire, which was heated white hot by an electric current. The combustion time was measured with a split-second timer. It was established in these experiments that as a result of the heating the salt in the surface layer decomposed, liberating violet iodine vapor, but the process did not extend to the depth of the sample. Thus it was established that at room temperature and atmospheric pressure the salt was incapable of having stable combustion initiated in it. Having established this, we added a catalyst (potassium dichromate) to the NH_4IO_3, since we knew that this compound makes ammonium nitrate capable of combustion at room temperature and atmospheric pressure, and we ignited a mixture of 90% NH_4IO_3 + 10% $K_2Cr_2O_7$. The results of tests of this mixture, and of experiments to test various other compounds of chromium, manganese, and copper*, are given in Table 1

Table 1

Results of an Investigation of the Combustibility of Ammonium Iodate Containing a 10% Additive of Chromium, Manganese, and Copper Compounds P = 1 atm, room temperature, d_{in} = 1.75 cm

Additive	Characteristics of combustion charge		Results of experiment	
	height of salt column (CM)	packing density (g/cm^3)	combustion time (sec)	linear burning velocity (CM/sec)
$K_2Cr_2O_7$	1.9	1.64	35	0.054
			37	0.051
			35	0.054
$CrCl_3 \cdot 4H_2O$	1.5	1.43	Does not burn	
MnO_2	2.5	1.60		
$CuCl_2 \cdot 2H_2O$	1.9	1.56		
Cu_2Cl_2	2.1	1.52	18	0.118

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*MnO_2, Cu_2Cl_2, and $CuCl_2 \cdot 2H_2O$ make possible the combustion of ammonium perchlorate at p = 1 atm and t = 20° [5].

As is apparent from the data in Table 1, the addition of 10% $K_2Cr_2O_7$ or 10% Cu_2Cl_2 to ammonium iodate makes it combustible at room temperature and P = 1 atm. Subsequent experiments showed that ammonium iodate was also capable of combustion under the same conditions with a 5% content of K_2CrO_7 it it, but a decrease in the $K_2Cr_2O_7$ content to 3% deprives the mixture of its combustibility.

A test of the heat stability of ammonium iodate showed that it completely decomposed within 6 minutes at 160°, while at 150° it loses only 2% of its weight in the same time. The mixture of 90% NH_4IO_3 + 10% $K_2Cr_2O_7$ is the least stable thermally and completely decomposes within 6 min. at 135°.

The burning ammonium-iodate samples without any additives at elevated temperature (when P = 1 atm) was carried out in a glass tube sealed at the lower end and having an outlet to allow the gases formed during combustion to escape. The tube was placed in a glass vessel filled with water. The water was heated and mixed with a stirrer. The temperature was measured with a mercury thermometer immersed in the water. The sample being burned was secured in the tube on the stopper. The electric current was supplied with the aid of metal rods. The sample was kept at a set temperature for 40 minutes before ignition. The burning was carried out, beginning at a temperature of 100° and gradually lowering the temperature from experiment to experiment until the ammonium iodate lost its combustibility. The results of the experiment are given in Table 2.

The combustion of the salt was flameless and proceeded with an intense evolution of violet iodine vapor. Stable combustion was achieved, as is apparent from Table 2, only when the initial temperature was no lower than 60°. The burning velocity decreased sharply between 80 and 60°.

Finally, we burned ammonium iodate tablets weighing a total of 5.7 g under elevated pressure in a manometric bomb (32 cm^3 in volume), thereby creating an initial pressure of 120 atm by the burning of 1.5 g of ignition charge (smoking powder). Under these circumstances the ammonium iodate burned completely within 0.27 sec, during which time it developed a pressure of 523 atm in the bomb.

Hydroxylamine sulfate. A preparation of pure grade (GOST 7298-54), ground and sifted through a 22 mesh sieve, was used for the experiments. First we verified that $(NH_3OH)_2SO_4$ was incombustible at room temperature and atmospheric pressure in tubes 2 cm in diameter. In the surface layer which was being heated by the nichrome wire the salt melted and began to decompose, but this decomposition did not extend through the entire mass. When the electric current was turned off, the liquid surface layer of the compound began to solidify, and the decomposition phenomena stopped. Having established this, we added chromium, manganese, and copper compounds (the same as in the case of NH_4IO_3) to the hydroxylamine sulfate as catalysts. The results of the burning of the samples are shown in Table 3.

It is apparent from the data in Table 3 that in this case the copper and manganese compounds give rise to combustion, while potassium dichromate, which so easily brings about the combustion of ammonium iodate (and also of ammonium nitrate) does not produce the desired effect in the case of hydroxylamine sulfate. By subsequent experiments we verified that the catalytic action of the copper salts we were testing is very strong, since they gave rise to stable combustion even when we decreased the amount of the additive to 5%, 3% and even 1%. In all of the experiments with catalytic additives combustion of the compound was preceded by fusion, while the combustion

Table 2

Results of an Investigation of the Influence of the Initial Temperature on the Combustibility and Burning Velocity of NH_4IO_3 P = 1 atm; d_{in} = 1.75 cm

Initial temperature (°C)	Characteristics of combustion charge		Results of experiment	
	Combustion time (sec)	Linear burning velocity (cm/sec)	Combustion time (sec)	Linear burning velocity (cm/sec)
100	1.9	1.68	23	0.082
80	1.9	1.66	24	0.079
60	2.0	1.60	36	0.056
50	1.8	1.72	Does not burn	

itself was flameless and accompanied by a spattering of droplets of the fustion out of the tube to a distance of up to 10-15 cm from the tube. By experiments which were carried out in order to ascertain the mechanism of the action of the catalytic additives we verified that the addition of copper salts to $(NH_3OH)_2SO_4$ greatly decreases its thermal stability. Thus the weight loss of pure hydroxylamine sulfate, after being kept at 130° for 6 minutes, was 15% of the initial weight, while mixtures containing 10% $CuCl_2 \cdot 2H_2O$ or 10% Cu_2Cl_2 showed a weight loss of 50% - 70% under the same conditions. The burning of hydroxylamine sulfate without any additives at an elevated temperature showed that this compound at 100° C and atmospheric pressure and with an inner tube diameter of 2.0 cm was capable of stable combustion. The nature of the combustion remained the same as in the previously described experiments; the burning velocity was 0.07 cm/sec.

Table 3

Results of an Investigation of the Combustibility of Hydroxylamine Sulfate Containing a 10% Additive of Chromium, Manganese, and Copper Compounds, P = 1 atm, room temperature, d_{in} = 2.0 cm.

Additive	Characteristics of Charge		Results of Experiment	
	Weight of salt column (cm)	Packing density (g/cm^3)	Combustion time (sec)	Linear Burning Velocity (cm/sec)
$K_2Cr_2O_7$	2.9 2.8	1.04 1.06	Does not burn	
$CrCl_3 \cdot 4H_2O$	2.7 2.6	1.12 1.12	Does not burn	
MnO_2	3.1 3.3	0.94 0.94	42 46	0.074 0.072
$CuCl_2 \cdot 2H_2O$	2.6 2.5	1.18 1.20	36 37	0.073 0.068
Cu_2Cl_2	2.7 2.6	1.12 1.12	8 7	0.34 0.37

Conclusions

1. It has been experimentally demonstrated that the compounds: ammonium iodate and hydroxylamine sulfate, which decompose with the evolution of a small quantity of heat (72 and 120 kcal/kg, respectively) and are not capable of stable combustion with a tube diameter of 2.0 cm at room temperature and atmospheric pressure, acquire this ability when: a) catalysts (chromium, manganese, or copper compounds), which increase their rate of thermal decomposition, are added to them; b) when the experiments are conducted at an elevated temperature (60-100°); c) (when in the case of ammonium iodate) the experiments are carried out under elevated pressure (120 atm).

2. These experiments speak in favor of the assumption, which is entirely valid thermodynamically, that any chemical system, in which an exothermic reaction can occur should prove capable of having a combustion reaction initiated and propagated in it, when the appropriate external conditions are selected. However, this question should be debated not only from a thermodynamic point of view, but also from the standpoint of chemical kinetics, and for its final solution theoretical treatments and, in particular, the accumulation of much factual material are required.

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