

THERMAL DECOMPOSITION OF HYDRAZINIUM MONOPERCHLORATE IN THE MOLTEN STATE

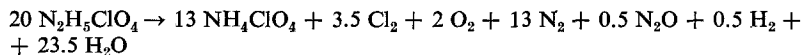
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The thermal decomposition of hydrazinium monoperochlorate (HP-1) in the molten state has been investigated using differential thermal analysis, thermogravimetric analysis, a constant volume manometric technique and mass-spectrometry. The stoichiometry of the reaction can be represented by the equation:



The data seem to indicate that the mechanism, which involves an associated complex, remains unchanged from 140 to 190°. Consequently, impurities capable of forming associated complexes with the hydrazinium or the perchlorate ion desensitize the thermal decomposition of HP-1, the extent of desensitization being determined by the size, the charge and the concentration of the impurity.

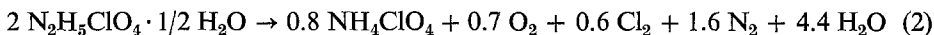
Hydrazinium perchlorate (HP-1) is a white crystalline solid whose melting point has been reported to be 132, [1] 140–142 [2] and 138° [3]. It forms a hemihydrate, $\text{N}_2\text{H}_5\text{ClO}_4 \cdot 1/2 \text{H}_2\text{O}$, which can readily be dehydrated at 65° under vacuum. The thermal decomposition of HP-1 in the solid state in the temperature range 80–120° was reported recently [4]. The thermal decomposition in the molten state has been the subject of many investigations [1, 3, 5, 6, 7]. Jacobs and Russell-Jones [3] and Grelecki and Cruice [7] have studied the decomposition in some detail.

Grecki and Cruice (GC) [7] carried out their investigation on dehydrated HP-1 in the range 140 to 200° in a constant-volume reactor made of glass, and measured the pressure rise with a Sickie gauge. After the completion of the reaction, gas samples were collected through a break-off seal and analyzed on a mass-spectrometer. The condensed-phase residues were analyzed by conventional wet analytical techniques. The first 10% of the reaction was acceleratory, followed by a constant rate over the 10–70% decomposition range. The activation energy (A.E.) calculated from the constant rates was found to be 23.8 kcal.mole⁻¹ between 140 and 200°. The reaction products were found to be in accordance with the following reaction:



They infer that the initial step in the thermal decomposition of HP-1 is the dissociation of the acid-base complex to give free perchloric acid. Because of the similarity of the temperature coefficients of HP-1 and HClO_4 , the decomposition of perchloric acid is argued to control the rate of the overall reaction.

Jacobs and Russel-Jones (JRJ) [3] studied the thermal decomposition of hydrazinium monopерchlorate hemihydrate by two methods: (1) with a conventional constant-volume vacuum system using a liquid nitrogen trap (LNT) covering the temperature range 195 to 280°, and (ii) by thermogravimetry (TG) at atmospheric pressure in the temperature range 180 to 229°. The decomposition followed a decelerating trend. The kinetics did not conform to any of the usual rate equations. Rate constants were therefore determined from the initial slopes at the respective temperatures and an A.E. of 30.3 kcal.mole⁻¹ was obtained. By using different types of coolants for the trap and from analysis of the residue, they inferred the formation of Cl_2 and H_2O and proposed the following reaction for the thermal decomposition of HP-1:



It is interesting to note that while the decomposition products (Equations (1) and (2) and the A.E.'s, 23.8 and 36.3 kcal.mole⁻¹) are considerably different, both studies [3, 7] emphasize the role of heterogeneous decomposition of HClO_4 on the walls of the vessel. The differences in the A.E.'s and the reaction products of the two investigations could arise primarily from three factors:

- (1) GC used dehydrated HP-1, while JRJ used the hemihydrate.
- (2) GC's investigation was in the temperature range 140 to 200°, while JRJ's temperature range was 180 to 280°, where NH_4ClO_4 , one of the solid decomposition products, itself starts decomposing.
- (3) GC allowed the decomposition gases to accumulate over the sample, thereby permitting secondary reactions between two gases or a gas and solid, while JRJ either allowed the gaseous products to escape (TG) or trapped the condensibles in a LNT, thereby preventing any secondary reactions between the gaseous products and the solid. The present investigation is intended to clarify some of the existing discrepancies and help towards an understanding of the mechanism of thermal decomposition of HP-1.

Experimental

Materials

High-purity HP-1 was prepared by neutralizing 60% aqueous perchloric acid with 75% hydrazine at temperatures from 0 to 25°. The salt precipitated from water at 0° and was filtered cold through a sintered glass funnel. The fine white crystals were gently removed with a teflon spatula and placed in a drying tube at 70° for two hours at a constant vacuum of 0.05 mm Hg to dehydrate the hemihydrate. Samples were titrated to a phenolphthalein end-point with 0.1 N NaOH.

The characteristic purity factor ranged from 99.2 to 99.8%. This dehydrated HP-1, which will be termed Preparation *A* in the text, was used for all the experiments, except when a comparison was made with the other preparations of HP-1.

Instead of crystallizing HP-1 at 0° from an aqueous solution, if the crystallization is done at 75°, the resultant product is anhydrous HP-1 (termed Preparation *B*). A third preparation of anhydrous HP-1 (Preparation *C*) was obtained by decomposing hydrazinium diperchlorate (HP-2) below 140°.

Apparatus

The kinetics of thermal decomposition of HP-1 were followed in the temperature range 145 to 195° in a constant-volume vacuum line with an initial pressure of 1×10^{-6} torr. The pressure rise was measured using a McLeod gauge and a LNT was included in the system to trap all reactive gases. The gaseous products of decomposition were analyzed in situ with an AEI-MS-10 mass-spectrometer (no LNT was employed during such measurements). The solid residue was analyzed conventionally for NH_4^+ and ClO_4^- , and also by X-ray analysis.

A TG unit consisting of a quartz spiral spring and a cathetometer was used for weight loss measurements. Differential thermograms (DTA) were obtained on a unit set up in the laboratory and calibrated against standard materials. The TG runs were carried out in air whereas the DTA were run at a pressure of 1 torr.

Results

A typical DTA trace of HP-1 (Preparation *A*), presented in Fig. 1, shows a melting endotherm peaking at 133°, followed by a decomposition exotherm at 147°. The rest of the trace is representative of a DTA of ammonium perchlorate [8]

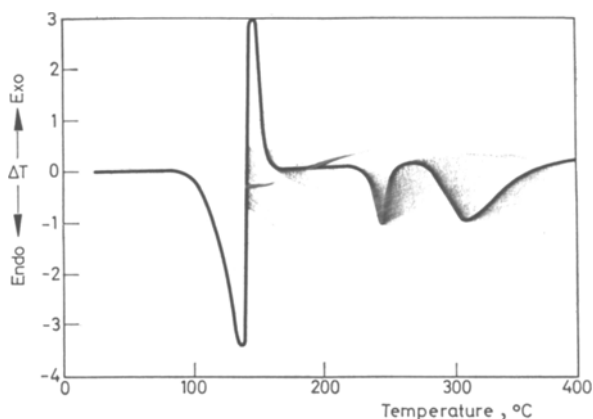


Fig. 1. A DTA trace of HP-1 at a pressure of 1 torr, employing a heating rate of 10°/min and 20 mg sample weight

at pressures below 20 torr, i.e. a phase transition at 246° followed by a broad sublimation endotherm at 300°. No residue was left at the end of the run at 400°.

Study of the fractional decomposition, α , as a function of the time of heating (isothermal runs) of HP-1 was carried out by pressure measurements as well as by the weight loss technique (TG) in the temperature range 145 to 195°. Throughout this temperature range, the α vs. t curves were sigmoid in nature. Some typical runs are shown in Fig. 2. In agreement with the observations of earlier workers

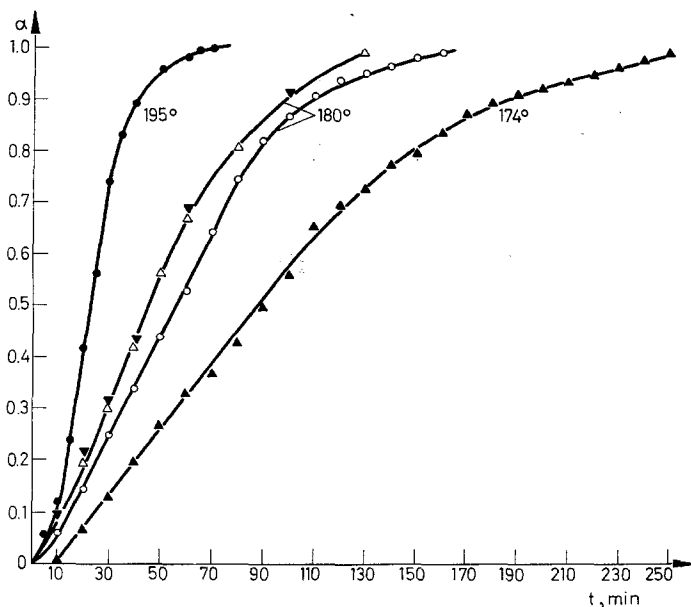


Fig. 2. A plot of the fractional decomposition, α , vs. the heating time, t . \bullet , \blacktriangle : Preparation A; \triangle , \blacktriangledown : Preparations B and C, respectively

[3, 7], the α vs. t plots (Fig. 2) could not be fitted to any of the usual kinetic equations. Activation energies were therefore calculated employing the Jacobs–Kureishy technique [9], wherein the logarithms of the times taken for the decomposition to proceed from $\alpha = 0.20$ to $\alpha = 0.60$ are plotted against the reciprocals of the absolute temperatures of the respective runs. This is shown in Fig. 3. The A.E. for the thermal decomposition of HP-1 in the molten state turns out to be 35.9 kcal.mole⁻¹.

The gaseous products of the thermal decomposition of HP-1 in a constant volume system at 175° were analyzed directly by an AEI-MS-10 mass-spectrometer connected to the system via a molecular leak; the results are listed in Table 1.

Table 1

Decomposition species for HP-1 at 175° in a constant-volume system connected via a molecular leak to the mass-spectrometer

m/e	Probable assignments	Ion current $\times 10^8$
2	H ₂ ⁺	0.3
14	N ⁺	2.25
16	O ⁺	0.25
17	OH ⁺ , NH ₃ ⁺	1.20
18	H ₂ O ⁺	4.50
28	N ₂ ⁺	12.40
30	NO ⁺	0.30
32	O ₂ ⁺ , N ₂ H ₄ ⁺	2.20
35	Cl ⁺	2.80
37	Cl ⁺	0.90
44	N ₂ O ⁺ , N ₃ H ₂ ⁺	0.95
70	Cl ₂ ⁺	5.10
72	Cl ₂ ⁺	3.40
74	Cl ₂ ⁺	0.70

Analysis of the cracking patterns leads us to eliminate masses 14, 16, 17, 30, 35 and 37, leaving the peaks at masses 2, 18, 28, 32, 44, 70, 72 and 74. From the probable assignments indicated in Table 1, the final decomposition species seem

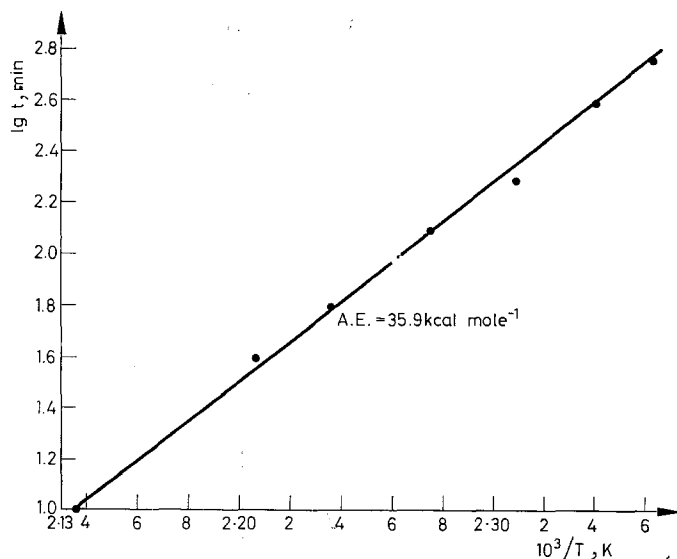


Fig. 3. An activation energy plot for the thermal decomposition of HP-1 in a constant volume system. 't' is the time (minutes) for the sample to decompose between the fractional decomposition limits $\alpha = 0.20$ and 0.60

to be hydrogen, water, nitrogen, oxygen, nitrous oxide and chlorine. The peak heights (Table 1) are given in terms of the ion current which is good for identification purposes.

Relative partial pressures, however, can be obtained from the relationship:

$$\text{relative pressure } (p) = \frac{\text{ion current } (i)}{\text{relative cross section } (\sigma)} \quad (3)$$

The relative cross sections for the species involved in the present work are available from the works of Otvos and Stevenson [10] and Pottie [11]. The relative pressures calculated from equation (3) are given in Table 2.

Table 2

Relative partial pressures of the decomposition species in HP-1 at 175°

Species	Relative cross sections, σ	Relative partial pressures, p
H ₂	1.40	1.2
N ₂	2.82	26.4
O ₂	3.00	4.3
Cl ₂	8.30	6.7
N ₂ O	4.32	1.3

The calculations have not been extended to water because of the uncertainty in the experimental determination of its ion intensity.

The residue at the end of the run was analyzed quantitatively and found to be pure ammonium perchlorate. This was confirmed by infrared and X-ray analyses.

Table 3

Effects of impurities on the thermal decomposition of HP-1 at 195°

Intentional impurity	Concentration, in mole %	Time for completion of the reaction, in minutes
Nil	0	70
NH ₄ ⁺	0.1	75
NH ₄ ⁺	0.5	80
Ca ²⁺	0.5	90
Ca ²⁺	0.5	100
Al ³⁺	0.1	90
Al ³⁺	0.5	120
Al ³⁺	1.0	140
SO ₄ ²⁻	0.1	80
SO ₄ ²⁻	0.5	85

All tests for chloride ion were negative. The weight of the residue left over in a TG run (isothermal) at 160° amounts to 13 moles of NH_4ClO_4 from a starting weight of 20 moles of $\text{N}_2\text{H}_5\text{ClO}_4$. This is shown in Fig. 4.

The method of preparation of HP-1 has a significant effect on the rate of thermal decomposition, as shown in Fig. 2. It can be seen that the reactivity of preparation *A* is much less than that of preparation *B*, which is comparable to that of preparation *C*. However the A.E.'s for all the preparations are identical. The effects of impurities on the thermal decomposition of HP-1 are presented in Table 3.

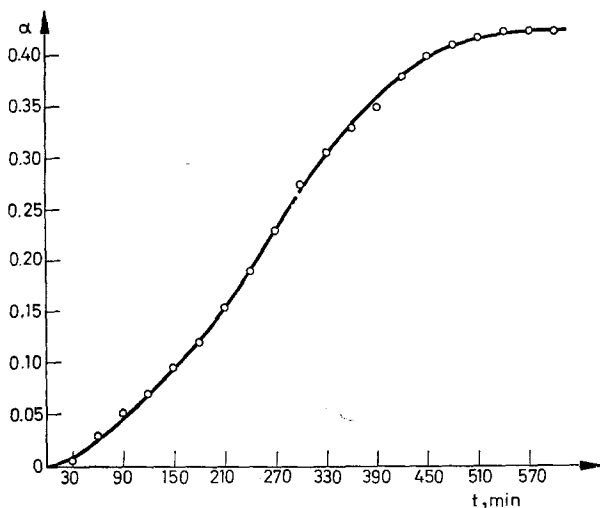
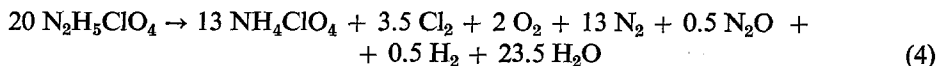


Fig. 4. Weight loss measurements (TG) of HP-1 at 160° (isothermal). The fractional decomposition, α , plotted against the heating time, t , in minutes

It can be seen that the dopants SO_4^{2-} , NH_4^+ , Ca^{2+} and Al^{3+} all tend to desensitize the decomposition, and further the desensitization for any given dopant is a function of the dopant concentration. As might be expected, in the study of the decomposition of the melt physically admixed impurities show the same behaviour as the doped impurities.

Discussion

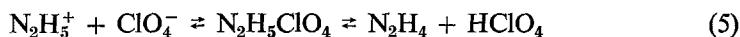
The TG data (Fig. 4), together with the mass-spectrometric analysis of the gaseous products (Tables 1 and 2) of decomposition of HP-1, lead us to the following chemical equation:



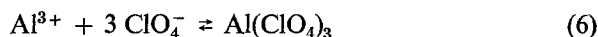
A comparison between this equation and equation (2) presented by JRJ [3] suggests that when the reaction is carried out above 195° about 38% of the ammonium perchlorate residue from the HP-1 decomposition also decomposes, giving higher yields of the gaseous products. The A.E. value of 35.9 kcal·mole⁻¹ (Fig. 3) obtained in the temperature range 145 to 195° is in good agreement with the values of 36.4 and 36.9 kcal·mole⁻¹ obtained by JRJ [3] in the temperature range 180 to 280°. The products of the decomposition are also substantially the same as found by JRJ (the present work has identified N₂O and H₂ as additional products). This investigation, however, was carried out in the same temperature range and on the same type of material (polycrystalline dehydrated HP-1) as that of GC [7] (their chemical equation: $8 \text{N}_2\text{H}_5\text{ClO}_4 = 7 \text{NH}_4\text{ClO}_4 + \text{NH}_4\text{Cl} + 4 \text{N}_2 + 4 \text{H}_2\text{O}$; their A.E. = 23.8 kcal·mole⁻¹). Although the isothermal runs leading to the determination of A.E.'s were carried out in a constant-volume apparatus employing a LNT, thereby preventing a secondary reaction between the condensibles and HP-1 or ammonium perchlorate formed, the apparatus employed for mass-spectrometric analysis of the products did not include any trap and as such was equivalent to the system used by GC [7]. The DTA (Fig. 1) also shows only one exothermic process for the decomposition of HP-1 in the molten state. It would appear, therefore, that the thermal decomposition of HP-1 proceeds via the same path throughout the temperature range 145 to 280°, the rate-determining step remaining unaltered.

In agreement with the earlier work [3, 7], the present study also points to the heterogeneous nature of the reaction, as evidenced by the higher rates in the TG runs where a silica reaction vessel was employed. Further, the method of preparation of the anhydrous HP-1 seems to play a significant role in its reactivity. Preparation C was obtained from the thermal decomposition of HP-2 below 140°. As HClO₄ is the main product (analyzed by mass-spectrometer), Preparation C might be expected to contain traces of HClO₄, which would catalyze the reaction [7]. However, Preparation B, which shows the same reactivity as Preparation C (higher than that of Preparation A), was prepared from the same batch as Preparation A, except that Preparation A was crystallized at 0° while Preparation B was crystallized at 75°. The higher reactivities of Preparation B and C, therefore, cannot be attributed solely to the presence of traces of HClO₄. In general, however, foreign impurities cocrystallize more favourably at lower temperatures, and hence one may speculate that the presence of impurities in Preparation A may be responsible for its low reactivity. In fact, when HP-1 (Preparation A) is doped with intentional impurities (SO₄²⁻, NH₄⁺, Ca²⁺ and Al³⁺), a systematic decrease in the HP-1 reactivity is observed (Table 3). For a mole % Al³⁺ dopant concentration, the time for completion of the thermal decomposition is double that for the undoped sample (140 min for doped, and 70 min for undoped HP-1). This decrease is a function of the dopant concentration. Further, it is observed that for a given concentration the desensitization follows a trend in the order NH₄⁺, SO₄²⁻, Ca²⁺, Al³⁺. The understanding of this effect can be facilitated if one assumes that in undoped molten HP-1, prior to proton transfer, the

hydrazinium ion, $N_2H_5^+$, forms an associated complex with the perchlorate ion, ClO_4^- :



At any given time the rate of decomposition will then depend on the concentration of the complex, $N_2H_5ClO_4$. When an impurity such as Al^{3+} is present, competition arises for the complex formation:



A negative ion impurity such as SO_4^{2-} will likewise compete with ClO_4^- to form a complex with the hydrazinium ion. The probabilities for the complex formation can be calculated qualitatively by estimating the attractive potentials between the opposite ions from the relationship:

$$\text{Attractive potential } F = \alpha \frac{Z_1 Z_2}{(r_1 + r_2)^2} \quad (7)$$

where Z_1 , Z_2 , r_1 and r_2 are the charges and the ionic radii of the respective ions. These data are presented in Table 4.

Table 4

Attractive potentials between the impurities and $N_2H_5^+$ and ClO_4^-

Host ion		Impurity ion		Relative attractive potential, F
Z	r	Z	r	
1	ClO_4^- 2.2 Å	1	NH_4^+ 1.46 Å	0.0746
1	ClO_4^- 2.2 Å	2	Ca^{2+} 0.099 Å	0.197
1	ClO_4^- 2.2 Å	3	Al^{3+} 0.51 Å	0.408
1	$N_2H_5^+$ 2.15 Å	2	SO_4^{2-} 1.78 Å	0.152

A plot of the attractive potentials *vs.* the rates (expressed as time for complete decomposition) shows a remarkably good fit (Fig. 5), considering the fact that the effective attractive potential calculation has ignored the change in the dielectric constant of the medium in the presence of impurities.

In conclusion, the thermal decomposition of HP-1 in the molten state seems to occur via an associated complex, the mechanism remaining unchanged throughout the temperature range 145 to 280°. Impurities which form associated complexes

with the hydrazinium or the perchlorate ion can desensitize HP-1, the extent of desensitization being determined by the size, the charge and the concentration of the impurity. Further, as the A.E. of the thermal decomposition of HP-1 remains unaltered on doping, it seems likely that the rate-determining step is the formation or the dissociation of the associated complex $N_2H_5ClO_4$.

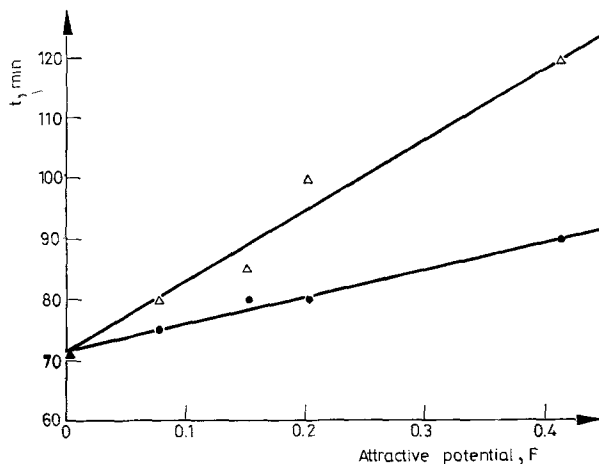
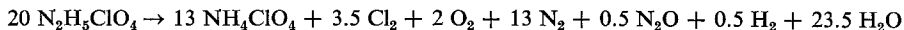


Fig. 5. Plot of the attractive potentials, F , against the time, t , for the completion of the reaction of HP-1 at 195° . Impurity concentration: (●) 0.1 mole % and Δ 0.5 mole %, \blacktriangle represents undoped HP-1

References

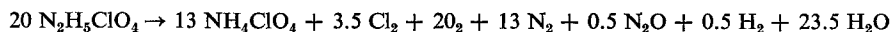
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RÉSUMÉ — La décomposition thermique en milieu fondu du monoperochlorate d'hydrazinium (HP-1) a été étudiée par analyse thermique différentielle, thermogravimétrie, manométrie à volume constant et spectrométrie de masse. La réaction peut être représentée par l'équation suivante:



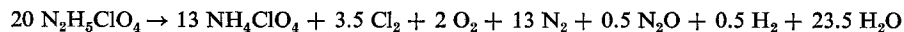
Les données semblent indiquer que le mécanisme mettant en jeu un complexe associé reste inaltéré dans l'intervalle de températures allant de 140 à 190°. Par conséquent, les impuretés qui pourraient former des complexes associés avec les ions hydrazinium ou perchlorate désensibilisent la décomposition thermique de HP-1, le taux de désensibilisation étant déterminé par la taille, la charge et la concentration de l'impureté.

ZUSAMMENFASSUNG — Die thermische Zersetzung von Hydrazin-monoperchlorat (HP-1) im geschmolzenen Zustand wurde unter Einsatz der Differentialthermoanalyse, der thermogravimetrischen Analyse, der manometrischen Methode mit konstantem Volumen und der Maßenspektrometrie untersucht. Die Stöchiometrie der Reaktion kann durch folgender Gleichung dargestellt werden:



Die Angaben zeigen, dass der Mechanismus, in welchen ein assoziierter Komplex mit inbegriffen ist, im Temperaturbereich von 140° bis 190° C unverändert bleibt. Folglich setzen Verunreinigungen, die mit dem Hydrazin- oder dem Perchlorat-Ion assoziierte Komplexe zu bilden imstande sind, die Empfindlichkeit der thermischen Zersetzung von HP-1 herab, wobei das Ausmaß der Herabsetzung von der Größe, der Ladung und der Konzentration der Verunreinigung abhängt.

Резюме — Исследовано термическое разложение расплава гидразиний моноперхлората (HP-1), используя дифференциальный термический анализ, термогравиметрический анализ, постоянно-объемную манометрическую технику и масс-спектрометрию. Стехиометрия реакции может быть представлена уравнением:



Данные указывают на то, что механизм, который включает какой-либо связанный комплекс, остается неизменным на всем протяжении температуры от 140° до 190°. Следовательно, примеси, способные образовывать связанные комплексы с гидразиний- или перхлорат ионом, десенсибилизируют термическое разложение HP-1, причем степень десенсибилизации определяется размером, зарядом и концентрацией примеси.