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EXPLOSIVE SENSITIVITY OF METHYLAMMONIUM PERCHLORATES

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The explosive sensitivity of methylammonium perchlorates has been investigated by differential thermal analysis, thermogravimetric analysis, mass spectrometry and explosion delay experiments. The decomposition temperature of these compounds increases in the order $CH_3NH_3ClO_4 > (CH_3)_2NH_2ClO_4 > (CH_3)_3NHClO_4$. The activation energy shows the reverse order, indicating thereby that the stability increases with increasing substitution. Mass spectrometric investigation, however, suggests an increasing reactivity with increasing substitution. A possible explanation for such behaviour is proposed. It appears that explosion delay is correlated with thermal decomposition and impact sensitivity.

During the past few years there has been increasing interest in the thermal studies of methyl-substituted ammonium perchlorates [1–5]. It is amazing to note that ammonium perchlorate, a comparatively stable compound, becomes almost an explosive on substitution of one or more of its protons by a methyl group [1]. The explosion temperature of monomethylammonium perchlorate has been reported to be 338° [6]. The relative thermal stability of the methyl-substituted ammonium perchlorates, however, seems to be dependent upon the technique employed for investigation. For example, from a thermal decomposition study using a mass spectrometer, Guillory and King [3] have concluded that the substitution of methyl groups into the ammonium cation stabilizes these perchlorates. This is based upon their observation that the dissociation temperatures increase with increasing methyl substitution into the cation, i.e. in the order $NH_4ClO_4 < CH_3NH_3ClO_4 < (CH_3)_2NH_2ClO_4 < (CH_3)_3NHClO_4$. Further, the impact sensitivity results obtained by Stammler et al. [1] indicate monomethylammonium perchlorate to be most sensitive, whereas the decomposition temperatures of these compounds as revealed by differential thermal analysis seem to decrease as the methyl substitution increases, showing thereby that their stabilities probably decrease with increasing substitution.

Though speculations about the similarity or dissimilarity of the mechanisms of explosion by impact and by heat could be misleading [7], recent work by Pai Verneker and Avrami [8] suggests a definite correlation between the explosive sensitivities of barium azide to heat, impact or friction. The present investigation

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is an attempt to study the reactivity of methyl-substituted ammonium perchlorates, using different thermal decomposition techniques, and using these data to elucidate a correlation between the thermal decomposition and the explosive behaviour.

Experimental

a) *Materials*

Monomethyl-, dimethyl- and trimethylammonium perchlorates were prepared by reacting 70% perchloric acid with aqueous solutions of the corresponding amines. The solutions were evaporated to reduce the volume, and crystallised on cooling to room temperature. The crystals were filtered off and washed with ice-cold water and then with alcohol. They were recrystallised from aqueous alcohol and the resulting crystals, after being washed with cold alcohol, were vacuum-dried. Tetramethylammonium perchlorate was prepared by reacting equimolar amounts of the corresponding iodide in aqueous alcohol with silver perchlorate in water. Tetramethylammonium iodide was prepared by treating trimethylamine with methyl iodide. The perchlorate was washed with water and recrystallised from water containing some alcohol. It was washed with alcohol and vacuum-dried.

The purities of the compounds were checked by chemical analysis and NMR spectroscopy. Chemical analysis results and NMR data are listed in Table 1.

Table 1

Analytical data

Compound	% Perchlorate		NMR* parameteres		
	Found	Calc.	τCH_3	τNH	
				observed	reported**
$CH_3NH_3ClO_4$	75.26	75.67	7.46	2.6	2.57
$(CH_3)_2NH_2ClO_4$	68.00	68.36	7.35	1.7	1.88
$(CH_3)_3NHClO_4$	62.02	62.33	7.17	-0.3^+	–
$(CH_3)_4NClO_4$	57.03	57.36	6.85	–	–

* Spectra were recorded with a Varian T 60 spectrometer. DMSO-d_6 was used as the solvent and tetramethylsilane as the internal standard.

$^+$ A very small, but very broad hump was observed at approximately −0.3 for the NH proton but only when the amplification was ten times that used for other signals in the series.

** As reported in reference [9]. τCH_3 values obtained for these perchlorates are almost identical to those reported for the corresponding chlorides [10].

b) *Apparatus*

The differential thermal analysis (DTA) and thermogravimetric analysis (TG) were carried out with apparatus described elsewhere [11]. The DTA of undiluted material was performed using platinum cups held in position by placing them inside the two holes made in a stainless-steel block, which also served to reduce the possible self-heating.

Mass spectrometric investigations were carried out with an Associated Electrical Industries, MS 10 mass spectrometer. After evacuation, the sample was isolated from the system by closing a stopcock between the ion source and the sample, heated for a fixed time, and then opened to the "ion source cage".

The explosion delay set-up was a modified version of that described by Agrawal and Agrawal [12]. The explosion delay measurements were carried out by plunging a test tube containing a definite amount (40 mg) of the compound into a $KHSO_4$ bath which was electrically heated and maintained at a fixed temperature. The temperature was measured by employing a chromel-alumel thermocouple, inserted into another test tube containing $KHSO_4$. This test tube was immersed to the same depth as the sample tube inside the bath. The time between the moment of plunging the sample tube and the moment of an audible explosion was noted by using a stopwatch. Each experiment was repeated at least four times and the average value of the delay was taken.

Results and discussion

The DTA traces of the methyl-substituted ammonium perchlorates are presented in Fig. 1, and the data are tabulated in Table 2. The general features of the DTA results are broadly in agreement with those obtained by Stammler et al. (Table 2). No endotherm could be observed at 340° for tetramethylammonium perchlorate in the present case. Stammler et al. [1] observed this endotherm when the sensitivity was increased ten times. In the case of methylammonium perchlorate a second exotherm was observed at 408°, which has been attributed to the decomposition of ammonium perchlorate [13]. The exact decomposition temperatures for dimethyl- and trimethylammonium perchlorates were not reported by Stammler et al. The decomposition temperatures of the mono-, di- and trimethylammonium perchlorates decrease as the methyl-substitution on the nitrogen atom increases.

Diluting the samples with alumina (Table 2) has a remarkable effect on their decomposition temperatures, although the phase transitions appear to remain unaffected. The peak temperatures of the exotherms are markedly lowered as a result of this dilution. However, the trend in decomposition temperatures remains the same. The lowering of the decomposition temperature may be due to the catalytic effect of alumina. This effect on monomethylammonium perchlorate is shown by the fact that when a mixture of the compound and alumina was kept at 280° it exploded mildly after 5 minutes, whereas the same amount of the compound kept at the same temperature for 5 minutes did not explode and lost only 2% of its weight. Further, when an identical mixture was kept at 260° for 10 minutes, extracted with water and filtered, the filtrate gave a positive test for aluminium with alizarin S, suggesting the intermediate formation of aluminium perchlorate. A similar effect has also been observed in the decomposition of perchloric acid in the presence of alumina [14].

Table 2

DTA and TG data

Compound	TG		DTA peak temperatures, °C*		
			Observed		
	inflection point, °C	% wt. loss	undiluted, in platinum cup	diluted with alumina	Reported**
$CH_3NH_3ClO_4$	319	87	50 (−) 180 (−) 258 (−) 343 (+) 408 (+)	51 (−) 181 (−) 258 (−) 295 (+) 355 (+)	48 (−) 178 (−) 255 (−) 330 (+)
$(CH_3)_2NH_2ClO_4$	312	97.3	182 (−) 328 (+)	179 (−) 283 (+)	38 (−) 180 (−) ~300 (+)
$(CH_3)_3NHClO_4$	305	95.4	114 (−) 209 (−) 278 (−) 320 (+)	112 (−) 203 (−) 268 (−) 276 (+)	116 (−) 207 (−) 275 (−) >275 (+)
$(CH_3)_4NClO_4$	422	98.5	402 (+)	412 (+)	340 (−) 430 (+)

* (+) and (−) given after temperatures in the Table denote exotherm and endotherm, respectively.

** As reported in reference [1].

TG traces of the substituted ammonium perchlorates show only one distinct weight loss region in the temperature range 40–425°. Decomposition temperatures and the corresponding weight losses as shown by TG experiments are listed in Table 2. Here again the decomposition temperatures decrease with increasing methyl-substitution. Tetramethylammonium perchlorate, however, has the highest decomposition temperature.

The results of the mass spectrometric analysis of the products from the thermal decomposition of the substituted ammonium perchlorates are presented in Table 3. Owing to the relatively high decomposition temperature, tetramethylammonium perchlorate did not decompose when kept under the same conditions as in the other three cases.

Guillory and King [3], using mass spectral data, have shown that mono-, di- and trimethylammonium perchlorates dissociate at 230, 190 and 300°, respectively, into perchloric acid and the corresponding amines. Along with the dissociation products, they also observed decomposition products in minute quantities. In the present study the same amount of the materials (excepting tetramethylammonium perchlorate) were decomposed at 285° for 10 minutes and the decomposition products examined. The relative intensities of the mass numbers corresponding to the respective amines were very low, indicating almost complete decomposition. Some of the products identified from the mass spectra are CO_2, CO, N_2, H_2O, HCl and O_2, along with traces of N_2O and NO_2. Though the formation of CO_2 and CO as decomposition products was not reported by Guillory and King, their presence is almost certain, as revealed by the present data. The presence of m/e 44 can be due to N_2O^+ and/or CO_2^+. The fragmentation pattern of N_2O shows an N_2O to NO ratio of 3 : 1. Assuming that the observed m/e 30 is due to NO^+ only, the relative intensity of m/e 44 is much more than can be accounted for by N_2O^+ and may be mostly due to CO_2^+. The presence of m/e 22, presumably due to CO_2^{++}, further supports the formation of CO_2^+. Similarly m/e 28 may be due to N_2^+ or

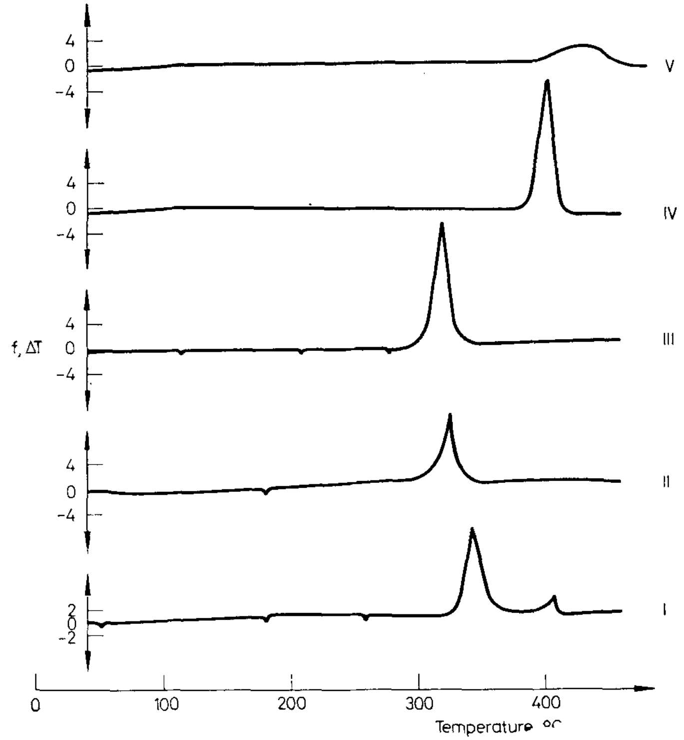


Fig. 1. DTA traces of mono- (I), di- (II), tri- (III), and tetramethylammonium (IV) perchlorates in air at atmospheric pressure and of tetramethyl-ammonium perchlorate at ~ 1mm Hg pressure (V)

Table 3

Mass spectrometric data

m/e		Relative intensities*			
		$CH_3NH_3ClO_4$	$(CH_3)_2NH_2ClO_4$	$(CH_3)_3NHClO_4$	$(CH_3)_4NClO_4$
2	H_2^+	0.3	0.45	0.65	80.0
12	C^+	10.0	13.6	20.2	10.9
14	N^+	0.6	4.0	2.0	12.3
15	CH_3^+	3.6	17.0	16.0	77.88
16	O^+	14.6	21.9	29.0	67.84
17	OH^+, NH_3^+	0.1	0.9	1.5	1.66
18	H_2O^+	0.3	3.0	6.0	4.3
22	CO_2^{++}	2.0	3.8	3.0	1.1
28	CO^+, N_2^+	80.0	147.0	193.0	171.8
30	NO^+	0.1	0.6	2.0	4.15
31		–	–	–	0.71
32	O_2^+	0.7	1.5	0.5	0.63
35	Cl^+	0.7	0.9	1.0	0.56
36	HCl^+	2.0	3.8	1.0	0.84
44	CO_2^+	125.0	159.5	177.0	60.0
45		–	2.4	–	1.5
46	NO_2^+	0.3	0.6	2.0	0.34
51		6.0	10.4	12.0	1.0
53		2.0	3.4	3.9	0.32

* The relative intensities of mono-, di- and trimethylammonium perchlorates could be compared with one another since each experiment was carried out under identical conditions, with 15 mg of the sample being kept at 285° for 10 min. In the case of $(CH_3)_4NClO_4$, which was decomposed at 363–385° for 15 min, the gaseous products were led to the ion source cage as it was heated, which was not the case for the other three compounds.

CO^+, the latter being formed as a decomposition product and/or as a fragment of CO_2. However, a careful analysis of the results indicates that most of it is due to CO^+ formed as a decomposition product.

The presence of *m/e* 51 and 53, in a ratio of roughly 3 : 1 and in fairly significant amounts, indicates the probable formation of chlorine-containing species. Existence of these species still needs an explanation. One is tempted to postulate the presence of NH_2Cl^+ rather than ClO^+ as one of the decomposition products, since ClO^+ can form only as a fragmentation pattern of $HClO_4$. However, no other mass numbers such as 67, 83, 100, etc., which also are the fragments of $HClO_4$, are observed.

Though the amounts of sample, as well as the temperatures at which the mass spectra were run, were the same, the relative intensities of the prominent mass numbers such as 44, 28, 18, 16, 30, 35, 46 and 51 increased with increasing substitution on the nitrogen atom. Assuming that the gases produced due to decomposition of a compound at a particular temperature is a measure of its stability, there appears to be a trend in stability in these compounds similar to that obtained from the decomposition temperatures in DTA and TG experiments. That is to say, the stability of these perchlorates with respect to decomposition decreases as the substitution increases.

However, the relative intensities of *m/e* 36 (HCl^+) and 32 (O_2^+) do not show the same trend as CO_2, CO, N_2, etc. This may be explained if we assume that HCl and O_2 are the products of decomposition of $HClO_4$ which, in turn, is an intermediate product of decomposition of all these three salts. Since it is known that dissociation becomes more and more difficult with increasing substitution, and since the relative intensities of HCl and O_2 depend on the amount of $HClO_4$, the relative intensities of *m/e* 36 and 32 may be expected to be in the order $CH_3NH_3ClO_4 > (CH_3)_2NH_2ClO_4 > (CH_3)_3NHClO_4$. We observe, however, that the actual order is $(CH_3)_2NH_2ClO_4 > CH_3NH_3ClO_4 > (CH_3)_3NHClO_4$. $CH_3NH_3ClO_4$ yields smaller amounts of HCl and O_2 than the other salts, probably because a part of the $HClO_4$ is used up in a competitive reaction, as postulated elsewhere [13]:

$$CH_3NH_3ClO_4 \begin{array}{l} \nearrow CH_3NH_2 + HClO_4 \\ \searrow NH_3 + CH_3ClO_4 \end{array}$$

$$NH_3 + HClO_4 \rightarrow NH_4ClO_4$$

The observation that NH_4ClO_4 is formed as a product of decomposition of $CH_3NH_3ClO_4$ (and not in the case of the other salts) leads us to suggest that ammonia may be formed in the decomposition process and this may use up a part of the perchloric acid, resulting in NH_4ClO_4 formation. Thus, a consequent lowering of the $HClO_4$ concentration accounts for the relatively low *m/e* 36 and 32 values.

A careful examination of the results of Guillory and King [3] concerning the decomposition products of mono- and dimethylammonium perchlorates also reveals higher relative intensities of the product mass numbers 44, 36, 32, 28, 18

Table 4

Kinetic data

Compound	Activation energy, kcal/mole	Range of α
$CH_3NH_3ClO_4$*	14.4	0.1 –0.5
	18.4	0.55–0.75
$(CH_3)_2NH_2ClO_4$	57.2	0.25–0.75
$(CH_3)_3NHClO_4$	79.6	0.25–0.75
$(CH_3)_4NClO_4$	50.4	0.25–0.75

* An activation energy of 40 kcal/mole has recently been reported [5] for decomposition of this compound. However, details are not available.

and 46 for dimethylammonium perchlorate than for monomethylammonium perchlorate and this too at a temperature lower by 40°. Thus, their decomposition results appear to be in line with our observation. This trend, however, does not appear to be the same as that exhibited by their dissociation results.

To help understand this phenomenon, isothermal decompositions of these compounds were studied employing the TG technique. The α vs. t plots are presented in Figs 2, 3 and 4, the α vs t plot for $CH_3NH_3ClO_4$ being given elsewhere [13]. The activation energies were calculated by the Jacobs–Kureishy method [15]. There may be some uncertainty involved in the values of the activation energy (Table 4) because of sublimation, which may occur along with decomposition at atmospheric pressure, as shown by a very thin layer of the sublimate on the cooler parts of the TG set-up. The formation of the sublimate, however, definitely indicates that dissociation of these compounds occurs at atmospheric pressure. The

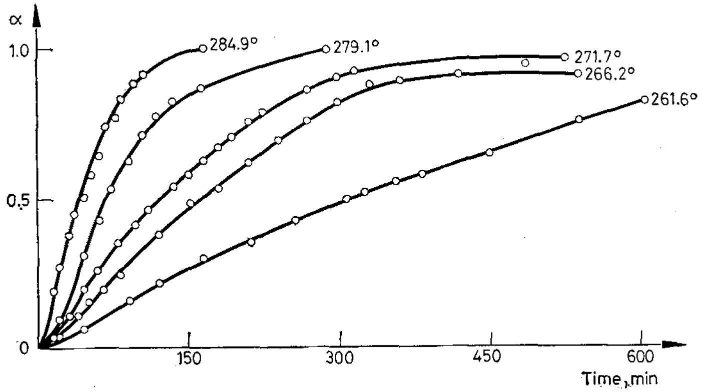


Fig. 2. α vs. t plots for dimethylammonium perchlorate

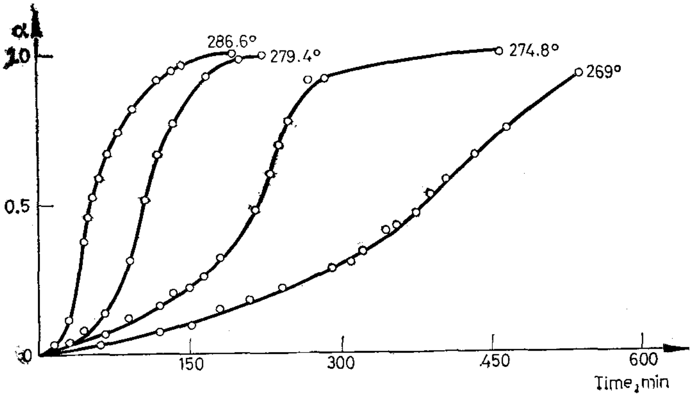


Fig. 3. α vs. t plots for trimethylammonium perchlorate

activation energy increases considerably from mono- to di- and to trimethylammonium perchlorates. Assuming dissociation [4] involving a proton transfer to be the rate-determining step in the decomposition of mono-, di- and trimethylammonium perchlorates, these activation energy values suggest that the barrier for proton transfer becomes higher as the substitution increases. This may be because of the fact that proton transfer from the substituted ammonium ion to the perchlorate anion becomes more and more difficult with increasing methyl-substitution, as a consequence of the inductive effect (electron-donating) of the $-CH_3$ groups [16] and the resulting increased efficiency of the $-\underset{/\,|\,\backslash}{N^+}$ ion to retain the proton. The mass spectral data of Guillory and King also point to this effect.

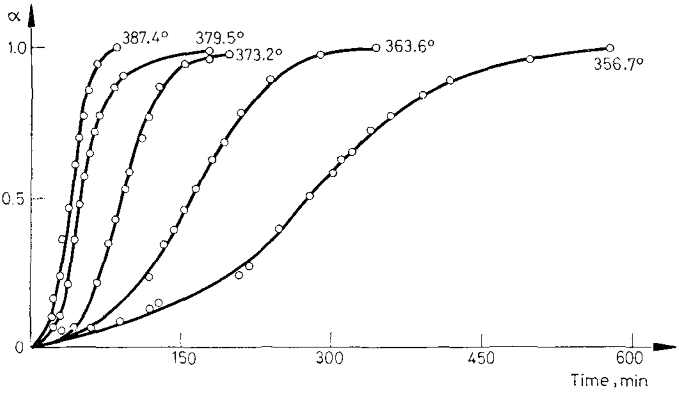
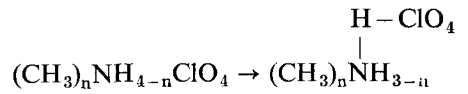


Fig. 4. α vs. t plots for tetramethylammonium perchlorate

Thus, the stability of the methyl-substituted ammonium perchlorates excepting tetramethylammonium perchlorate is seen to increase with increasing substitution. This is true, however, only when one considers the reaction with respect to the dissociation energy E, which may be the energy for the rate-determining step. The dissociation products may still be held to each other by weak forces, as is known in the case of ammonium perchlorate [17]:

$$(CH_3)_nNH_{4-n}ClO_4 \xrightarrow{E} (CH_3)_nNH_{3-n} + HClO_4 \xrightarrow{E'} \text{products}$$



$$(CH_3)_nNH_{4-n}ClO_4 \rightarrow (CH_3)_n\overset{\overset{H-ClO_4}{|}}{N}H_{3-n}$$

where n is the number of methyl groups. The overall decomposition temperatures of these compounds may be dependent on the reaction between perchloric acid and/or its decomposition products and the amine and/or its decomposition products involving net decomposition energy E'. The reactivity of the amines towards an oxidising species is in the order $(CH_3)_3N > (CH_3)_2NH > CH_3NH_2$, and therefore the temperature at which the amine is oxidised is expected to be in the reverse order. This accounts for the trend in decomposition temperatures as observed by DTA and TG, and also for the mass spectrometric results.

The activation energy for tetramethylammonium perchlorate cannot be compared with the values for the other three compounds. It may be noted that as against the proton transfer that may take place as the rate-determining step in the decomposition of the other three cases, one may postulate a methyl group transfer as the rate-determining step in the decomposition of tetramethylammonium perchlorate. A dissociation step taking place along with decomposition seems to be indicated by the fact that the exotherm in the DTA trace at atmospheric pressure is very much diminished in intensity at lower pressure, e.g. at around 1 mm Hg pressure (Fig. 1). A similar observation [18, 19] has been made for ammonium perchlorate, which is known to decompose via dissociation [20, 21]. Further, in the case of tetramethyalmmonium perchlorate at 1 mm Hg, a sublimate is formed on the cooler sides of the DTA apparatus and this observation seems to contribute to the argument in favour of a dissociation step prior to decomposition.

Thermal decomposition is a much slower process than explosion and the two need not necessarily bear any correlation to each other. To verify this, explosion delay experiments were carried out, and the data are listed in Table 5. The times for explosion at a fixed temperature do not seem to show any regular trend. However, the activation energy for explosion does seem to show a trend, viz. the value increases as the substitution increases. Although the activation energy for explosion is different from that for thermal decomposition, the trend in the activation energy values for the two processes seems to be the same, indicating thereby a correlation between the explosion delays and the thermal dissociation of the mono-, di- and trimethylammonium perchlorates. Further, the impact sensitivity results [1] also show the same trend in their sensitivities as the activation energy for explosion, and there appears to be a better correlation between impact sensitivity and the activation energy for explosion than that for the thermal dissociation process. This is probably to be expected, as these two processes resulting in

Table 5

Explosion delay data

Compound	Time (in sec) for explosion at °C							Activation energy, kcal/mole	Impact sensitivity data from Ref 1 (cm)
	330	345	360	380	400	410	420		
$CH_3NH_3ClO_4$	48.2	39.8	30.0	21.9	—	—	—	12.5	20
$(CH_3)_2NH_2ClO_4$	58.8	44.8	29.3	23.4	—	—	—	14.8	22
$(CH_3)_3NHClO_4$	57.0	43.0	26.2	20.4	—	—	—	16.6	25
$(CH_3)_4NClO_4$	—	—	—	—	81	59	47.1	25.3	35

explosion are similar in nature and much faster than the thermal decomposition. In a slow process like thermal decomposition the steps involved in the process of decomposition can at times be distinctly observed and the step controlling the process can be pinpointed.

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Résumé — On a étudié la sensibilité explosive des perchlorates de méthylammonium par ATD TG, spectrométrie de masse et expériences de retard à l'explosion. La température de décomposition de ces composés augmente dans l'ordre suivant: $CH_3NH_3ClO_4 > (CH_3)_2NH_2ClO_4 >$ $> (CH_3)_3NHClO_4$. L'énergie d'activation suit un ordre inverse indiquant une augmentation de la stabilité des composés avec le degré de substitution. L'étude par spectrométrie de masse permet en plus de conclure que l'augmentation de la substitution entraîne une réactivité plus grande. On propose une explication de ce comportement. Il semble que le retard à l'explosion soit en corrélation avec la décomposition thermique et la sensibilité d'impact.

Zusammenfassung — Die Explosionsempfindlichkeit von Methylammoniumperchlorat wurde durch DTA, TG und Massenspektrometrie, sowie durch Explosionsverzögerungsversuche untersucht. Die Zersetzungstemperatur der Verbindungen nimmt in der Reihenfolge $CH_3NH_3ClO_4 > (CH_3)_2NH_2ClO_4 > (CH_3)_3NHClO_4$ zu. Die Aktivierungsenergiezunahme verläuft entgegengesetzt, was dafür spricht, daß die Stabilität mit steigender Substitution wächst. Die massenspektrometrische Prüfung hingegen zeigt zunehmende Reaktivität mit steigender Substitution. Eine mögliche Erklärung der experimentellen Ergebnisse wurde gegeben. Es scheint, daß die Explosionsverzögerung mit der thermischen Zersetzung und Stoßempfindlichkeit in Zusammenhang ist.

Резюме — Было проведено исследование чувствительности взрываемости различных метилзамещенных перклората аммония с помощью дифференциального термического анализа, термогравиметрического анализа, масс-спектрометрии и экспериментов с замедленным взрывом. Температура разложения этих соединений увеличивается в ряду $CH_3NH_3ClO_4 > (CH_3)_2NH_2ClO_4 > (CH_3)_3NHClO_4$. Однако, энергии активации имеют обратный порядок в этом ряду, показывая тем самым, что стабильность изученных соединений увеличивается с увеличением числа метильных групп. Вместе с тем, масс-спектрометрические исследования указывают на увеличение реакционной способности при переходе от моно- к ди- и триметилзамещенным перклората аммония. Предложено наиболее вероятное объяснение такого поведения. Кажется, что защищенный взрыв имеет тенденцию к корреляции с термическим разложением и ударной чувствительностью.