

Catalysis of Solid Phase Reactions Effect of Doping of Cupric Oxide Catalyst on the Thermal Decomposition and Explosion of Ammonium Perchlorate

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Received April 10, 1962

In the presence of cupric oxide the decomposition of ammonium perchlorate takes place to the extent of 55-60% below 700°C, and explosion occurs at 260°C, i.e. at a temperature 200°C below that of the explosion of pure ammonium perchlorate. Increase in the defect electron concentration of cupric oxide catalyst (building-in of lithium oxide) accelerates the reaction rate and shortens the induction period. An opposite effect was experienced when chromic oxide was built in. The effect of the defect electron concentration of the catalyst was shown in the explosion of ammonium perchlorate, since this occurred at the lowest temperature in the presence of cupric oxide doped with the lithium oxide. The activation energy of the decomposition between 180-200°C is 31 kcal. A similar value (30.5 kcal) was obtained from the dependence of the time necessary to reach explosion as a function of temperature. The results obtained are discussed in accordance with the electron transfer mechanism. The decomposition of ammonium perchlorate was also studied between 200-230°C. Here the activation energy is 41 kcal.

INTRODUCTION

Recently the thermal decomposition of ammonium perchlorate in the presence of ferric oxide has been studied in detail (1). The activation energy of the catalytic decomposition at low temperature (between 245-270°C) was about 31 kcal. This value agrees fairly well with the activation energy of the decomposition of pure ammonium perchlorate by the electron transfer mechanism, 32 kcal (2). The catalytic effect of ferric oxide can probably be interpreted as being similar to that of manganese dioxide (3), that is, as an electron transfer catalyst it promotes the formation of a perchlorate radical, and the transfer of an electron from the perchlorate to the ammonium ion. From this assumption it was expected that changes in the electronic structure of the catalyst would affect the catalyzed decomposition. In our experiments with ferric oxide it was diffi-

cult to alter the electronic structure of the catalyst. This could, however, be done with zinc oxide, the conductivity of which may largely be influenced by the building in of foreign ions.*

The extent and rate of decomposition of ammonium perchlorate also increased considerably in the presence of zinc oxide. The activation energies were also found to support an electron transfer mechanism (5,6) The rate-accelerating effect of zinc oxide can, however, be ascribed primarily to a melting phase due to zinc oxide, and this presumably does not take part directly in the electron mechanism (6). With the object of emphasizing the significance of the electronic structure of the catalyst and

* The conductivity of ferric oxide may also be altered by the building in of titanium dioxide in small amounts (4), but this requires a very high temperature of pretreatment (1100-1200°C), at which temperature ferric oxide loses its activity.

of supporting the mechanism assumed for ferric oxide, the decomposition of ammonium perchlorate was studied in the presence of cupric oxide where, from our own observation, a melting phase cannot be considered. The conductivity of cupric oxide may be greatly increased or decreased by the building in of small amounts of ions of different valency (7).

EXPERIMENTAL

Materials

Merck c.p. ammonium perchlorate was purified by repeated recrystallization from twice distilled water and powdered for 20 min. Mean grain size: about 0.0046 cm.

CuO catalyst was prepared by gradual heating of c.p. $\text{Cu}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$ for 1 hr at 200°C, 300°, and 400°C, and for 3 hr at 450°.

$\text{CuO} + 1$ mole % Li_2O , and $\text{CuO} + 1$ mole % Cr_2O_3 . The mixed oxides were prepared by adding lithium and chromic nitrates to cupric nitrate in the required amount and then heating as for the pure cupric oxide. The cupric oxide obtained at 450°C was treated for 5 hr at 750°C. Since the conductivity of cupric oxide changes with the conditions of its preparation, it appeared necessary to control the conductivity of the cupric oxide samples. To this end pellets of about 6–7 mm diameter and of 7–8 mm height were compressed from cupric oxide powder, and the conductivity was determined in the manner previously described (8).

The mixing of the salts was accomplished by shaking them for 1 hr. The powder mixture was compressed into pellets under a pressure of 2700 kg/cm². The ammonium perchlorate content was about 0.2 g.

Measurements

To avoid the sublimation of ammonium perchlorate, kinetic measurements were done at atmospheric pressure. The course of the reaction was followed by measuring the volume of the gases formed. The experimental apparatus and method have been described elsewhere (1, 9).

EXPERIMENTAL RESULTS

The decomposition of pure ammonium perchlorate varies with temperature. Orthorhombic ammonium perchlorate decomposes between 200° and 240°C, and cubic between 244° and 270°C. At both temperatures the reaction proceeds only to about 30%. A conversion of 100% is obtained only far above 300°C.

The decomposition of ammonium perchlorate is similarly divided into several periods in the presence of cupric oxide. The decomposition takes place between 180° and 200°C, and 200° and 240°C, and at a higher temperature (about 260°C) explosion occurs.

a. Experiments between 180° and 200°C

First the effect of the amount of cupric oxide present was investigated. While pure ammonium perchlorate scarcely decomposes below 200°C, the conversion is more than 50% complete in the presence of cupric oxide.* However, the decomposition is preceded even then by a very long induction period. The induction period becomes shorter for amounts of CuO up to 1:1 ammonium perchlorate-cupric oxide mole ratio, but it then becomes longer again (Table 1). The catalytic effect of cupric oxide is observable even in the presence of 0.5 w % cupric oxide. As may be seen from Fig. 1, the reaction is autocatalytic, although the shape of the curve α vs. t is far less symmetric than in measurements done in the presence of zinc and ferric oxides.

Mathematical approximation of the curve of α vs. t was attempted by the Prout-Tompkins

$$\log [\alpha/(1 - \alpha)] = k_1 t + C$$

and the Avrami-Erofeyev equations:

$$[-\log (1 - \alpha)]^{1/3} = k_2 t$$

By the Prout-Tompkins theory a curve consisting of two parts was obtained. The point of break was at about $\alpha = 0.36$. The Avrami-Erofeyev equation is valid in the range $\alpha = 0.03$ –0.58.

* The percentage conversion was determined by the weight changes of the pellets.

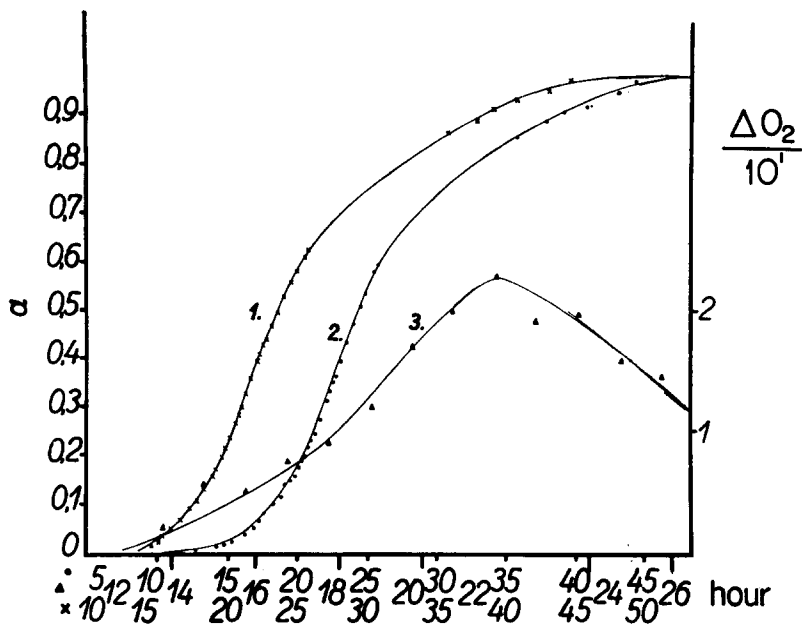


FIG. 1. Thermal decomposition of ammonium perchlorate in the presence of cupric oxide below 200°C. (Reaction temperature; 184.5°C.) 1. Plot of a vs. t at NH_4ClO_4 -CuO mole ratio of 1:1. 2. Plot of a vs. t at NH_4ClO_4 -CuO mole ratio of 5:1. 3. Plot of rate vs. t at NH_4ClO_4 -CuO mole ratio of 1:1.

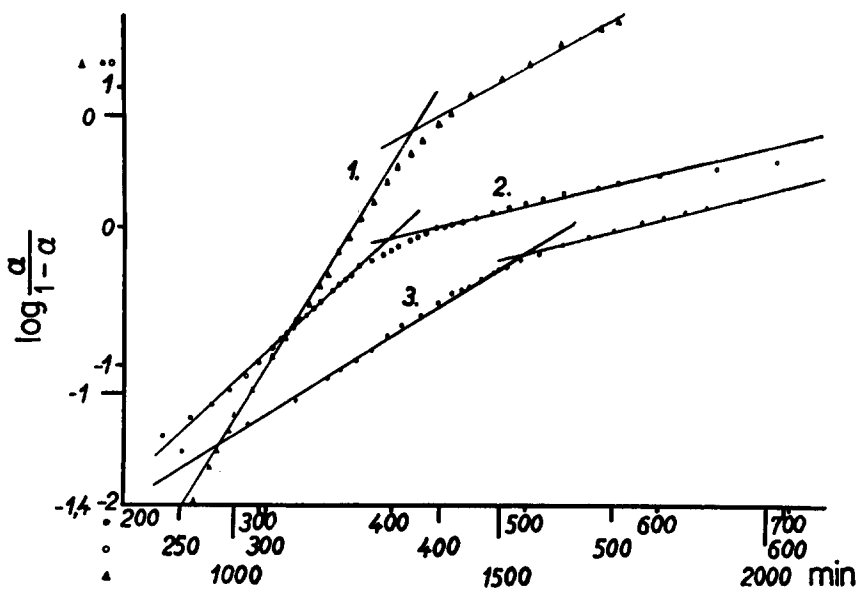


FIG. 2. Kinetic analysis of the decomposition of ammonium perchlorate catalyzed by CuO, by the Prout-Tompkins equation. 1. At 184.5°C, NH_4ClO_4 -CuO mole ratio, 1:1; 2. 199.5°C, NH_4ClO_4 -CuO, 5:1; 3. 194.0°C, NH_4ClO_4 -CuO, 5:1.

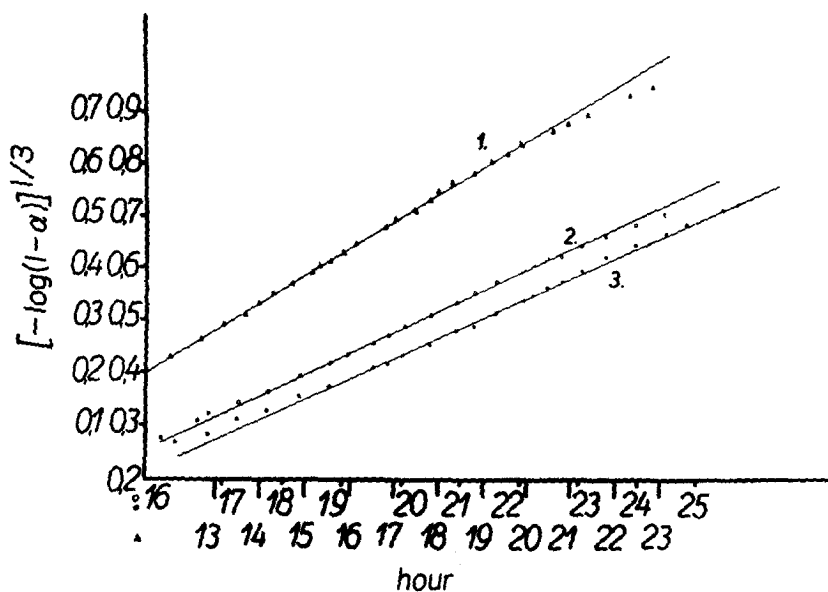


FIG. 3. Kinetic analysis of the decomposition of ammonium perchlorate catalyzed by CuO by the Avrami-Erofeyev equation. 1. At 181.5°C, NH₄ClO₄-CuO mole ratio. 5:1; 2. 184.5°C, NH₄ClO₄-CuO, 1:1; 3. 184.5°C, NH₄ClO₄-CuO, 5:1.

TABLE 1
INDUCTION PERIODS AND RATE CONSTANTS OF THE DECOMPOSITION OF AMMONIUM PERCHLORATE AT 194°C AS FUNCTIONS OF THE AMOUNT OF CuO

NH ₄ ClO ₄ + CuO	$\tau_{1 \text{ ml}}^a$	$\tau_{0.5 \text{ ml}}$	$\tau_{1/2 v_f}^b$	$\tau_{1/10 v_f}$	τ_{max}	$k_1 \times 10^3$	$k_2 \times 10^3$	Conversion (%)
100:1	194	640	960	458	660	1.88	0.52	48.6
50:1	252	468	666	426	540	4.47	1.40	66.9
16:1	248	364	477	340	400	8.57	2.62	61.4
1:1	196	344	568	350	380	9.23	2.39	60.3
1:5	327	590	810	572	640	7.37	1.84	62.6

^a τ_x is the time in minutes to reach the volume x.

^b v_f , gas volume at the end of decomposition.

TABLE 2
INDUCTION PERIODS OF THE DECOMPOSITION OF AMMONIUM PERCHLORATE AS A FUNCTION OF DOPING OF CuO^a

	$\tau_{0.5 \text{ ml}}^b$	$\tau_{1 \text{ ml}}$	$\tau_{0.5 \text{ ml}}$	$\tau_{1/2 v_f}$	$\tau_{1/10 v_f}$	τ_{max}
NH ₄ ClO ₄ + CuO						
5:1	100	260	396	560	375	470
NH ₄ ClO ₄ + (CuO + 1% Cr ₂ O ₃)						
5:1	211	320	438	607	407	530
NH ₄ ClO ₄ + (CuO + 1% Li ₂ O)						
5:1	95	200	295	422	275	350

^a Temperature of reaction: 194.5°C.

^b τ_x is the time in minutes to reach the volume x.

^c v_f is the gas volume at the end of decomposition.

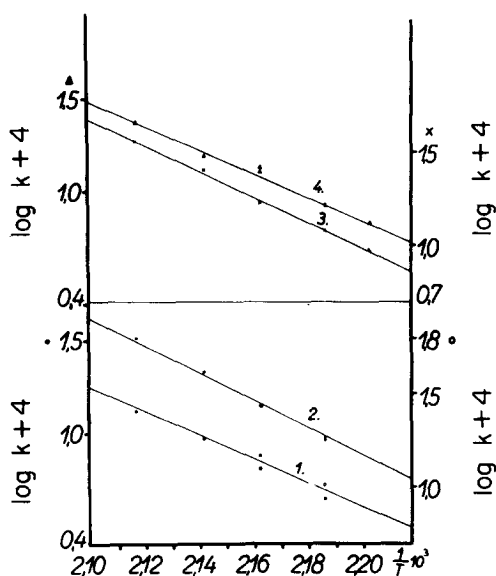


FIG. 4. Logarithms of rate constants calculated by the Avrami-Erofeyev eqn. as functions of $1/T$. 1. $\text{NH}_4\text{ClO}_4\text{-CuO}$ mole ratio 5:1; 2. $\text{NH}_4\text{ClO}_4\text{-CuO}$, 1:1; 3. $\text{NH}_4\text{ClO}_4\text{-CuO} + 1\% \text{Li}_2\text{O}$, 5:1; 4. $\text{NH}_4\text{ClO}_4\text{-CuO} + 1\% \text{Cr}_2\text{O}_3$, 5:1.

here for mixtures of 5:1 and 1:1 mole ratio. Rate constants and activation energies are given in Table 5. The activation

energies here are much greater than in measurements below 200°C . The effect of foreign ions was also studied. Doping of the cupric oxide with lithium oxide shortened the induction period and markedly increased the reaction rate. An opposite effect was experienced when the cupric oxide was doped with chromic oxide. The activation energy was the smallest in the presence of a catalyst containing lithium. These results are also given in Table 5.

c. Experiments between 250° and 285°C

Above 250°C the decomposition of ammonium perchlorate is extremely rapid and, after a short induction period, a powerful explosion occurs, accompanied by ignition of the pellets. Explosion occurred even when the amount of cupric oxide added was only 0.15%. The time necessary for explosion to occur increased as the amount of cupric oxide was decreased from the initial 16:1 $\text{NH}_4\text{ClO}_4\text{:CuO}$ ratio. A similar increase of the time necessary for explosion to occur may be observed in mixtures of 1:1 mole ratio, while at 1:5 ratio explosion did not occur even at 280°C ; under these

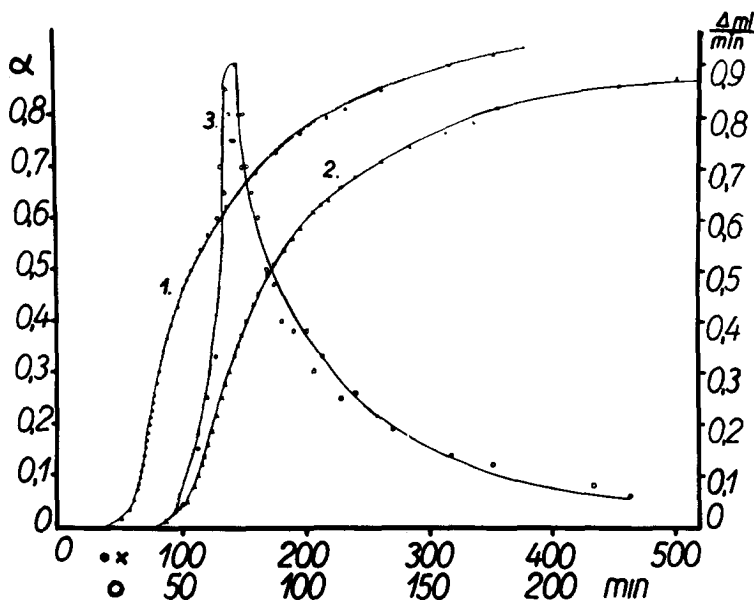


FIG. 5. Thermal decomposition of ammonium perchlorate in the presence of cupric oxide over 200°C . 1. Plot of α vs. t at 219.0°C , $\text{NH}_4\text{ClO}_4\text{-CuO}$ mole ratio 1:1; 2. α vs. t at 211.5°C , $\text{NH}_4\text{ClO}_4\text{-CuO}$, 5:1; 3. Plot of rate vs. t at 219.0°C , $\text{NH}_4\text{ClO}_4\text{-CuO}$, 1:1.

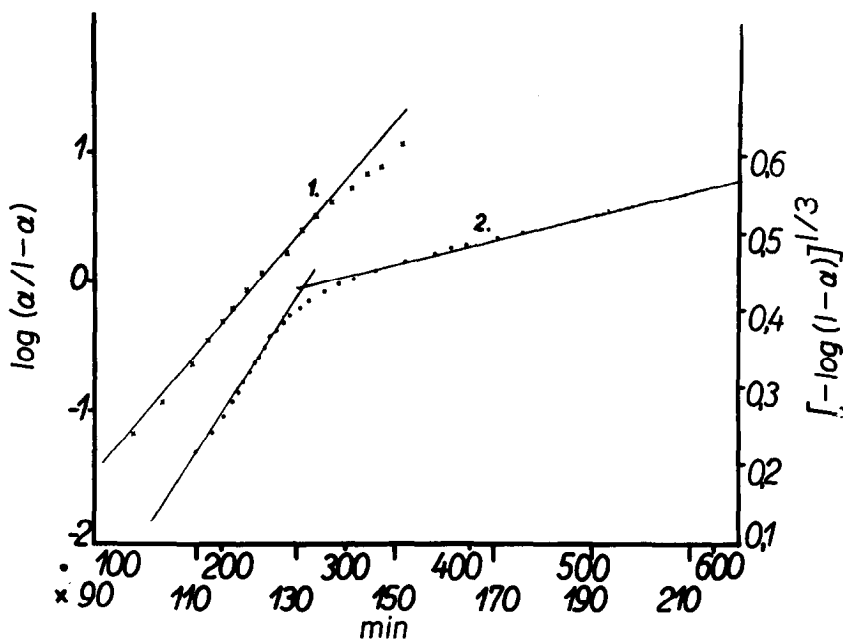


FIG. 6. Kinetic analysis of the decomposition of ammonium perchlorate catalyzed by CuO by the Prout-Tompkins and the Avrami-Erofeyev equations. 1. $[-\log(1-a)]^{1/3} = k_2 t$ at 206.5°C, mole ratio: 1:1; 2. $\log[a/(1-a)] = k_1 t + C$ at 209.2°C, mole ratio: 5:1.

conditions only a very mild deflagration occurred.

Evaluation of the dependence on temperature of the logarithm of the induction period gave activation energy values of 29–31 kcal. Lowering the ammonium perchlorate content of the pellets to 100 and 50 mg decreased the induction period, but the activation energies remained essentially unaltered.

This shows that the increased self-heat-

ing observed in larger pellets exerts only a very slight effect on the activation energies calculated from induction periods. Some results are shown in Table 6.

The effect of doping with foreign ions was observable here also, if only to a lesser extent, since in the presence of cupric oxide doped with lithium oxide, ammonium perchlorate explodes at a lower temperature than with pure cupric oxide, or especially when cupric oxide is doped with chromic

TABLE 4
INDUCTION PERIODS AND RATE CONSTANTS OF THE DECOMPOSITION OF AMMONIUM PERCHLORATE AT 214°C AS FUNCTIONS OF THE AMOUNT OF CuO

	$\tau_{0.5 \text{ ml}^3}$	$\tau_{1 \text{ ml}}$	$\tau_{5 \text{ ml}}$	$\tau_{1/2 v_f^b}$	$\tau_{1/10 v_f}$	τ_{max}	$k_1 \times 10^2$	$k_2 \times 10^3$	Conv. (%)
300:1	82	140	298	508	230	382	0.465	1.29	82.3
200:1	70	123	244	374	230	320	0.725	2.16	83.7
100:1	65	82	106	165	105	124	2.65	6.84	85.0
50:1	50	77	108	154	106	120	3.01	8.36	84.0
16:1	33	76	97	135	94.5	88	6.69	18.7	80.0
1:1	33	71	84	148	96	103	3.76	9.31	86.71
1:5	40	102	140	207	138	156	2.77	7.5	88.2

^a τ_x is the time in minutes to reach volume x .

^b v_f gas volume at the end of decomposition.

TABLE 5
KINETIC DATA ON THE DECOMPOSITION OF AMMONIUM PERCHLORATE CATALYZED BY CuO BETWEEN 200–230°C*

Temperature (°C)	NH ₄ ClO ₄ + CuO 5:1			NH ₄ ClO ₄ + (CuO + 1% CrO ₂) 5:1			NH ₄ ClO ₄ + (CuO + 1% Li ₂ O) 5:1			NH ₄ ClO ₄ + CuO 1:1		
	k ₁ × 10 ²	k ₂ × 10 ³	Conv. (%)	k ₁ × 10 ²	k ₂ × 10 ³	Conv. (%)	k ₁ × 10 ²	k ₂ × 10 ³	Conv. (%)	k ₁ × 10 ²	k ₂ × 10 ³	Conv. (%)
201.5	1.61	4.68	70.0	1.66	4.62	67.6	2.08	5.38	67.7	1.29	3.13	81.0
206.0	1.72	5.27	81.2	2.15	5.84	82.1	2.35	5.9	85.8	1.68	4.64	86.3
209.2	3.13	7.91	—	2.38	8.33	—	3.62	10.75	—	1.49	4.89	—
216.5	6.5	22.3	87.8	7.3	19.64	77.6	6.0	16.6	80.4	2.45	6.33	—
220.0	8.48	24.4	86.0	8.7	30.0	85.2	7.61	21.8	85.3	3.76	9.31	86.7
225.5	12.7	36.77	—	12.5	32.57	—	12.0	37.6	—	4.68	13.5	85.5
Activation energy (kcal)	42.9	40.9	—	41.2	42.6	—	37.1	37.0	—	40.2	42.2	—

* Rate constants of the decay-period of the Prout-Tompkins equation are not published since their dependence on temperature could not be estimated.

TABLE 6
EXPLOSION OF AMMONIUM PERCHLORATE IN THE PRESENCE OF CuO AT VARIOUS TEMPERATURES.†
NH₄ClO₄-CuO MOLE RATIO: 16:1

Temperature (°C)	NH ₄ ClO ₄ content of pellets		
	0.22 g	0.11 g	0.55 g
	Time to explosion (τ) in sec		
286	—	113	123
284	—	—	106
282.5	—	144	134
280	—	157	156
277.5	—	163	178
276	238	—	—
275	234	223	180
272.5	272	227	220
270	—	265	259
269	307	—	—
265	360	No explosion	No explosion
260.5	504	—	—
255	660	—	—
Activation energy (kcal)	29.8	31.2	29.9

oxide (Fig. 8). But at a temperature where explosion of all three mixtures occurs, there are scarcely any differences in the induction periods. Some of the experimental results are plotted in Fig. 8.

Activation energies in these cases were also found to be 29–31 kcal. Decreasing the amount of ammonium perchlorate also causes the induction periods here to decrease, but the values of the activation energies also remain unaffected.

Study of Effect of Compression of Mixtures

In the measurements described so far the substances were compressed, in every case, under a pressure of 2700 kg/cm², which generally is sufficient to obtain reproducible results. Since the effect of solid catalysts on solid phase reactions likely depends on the extent and quality of the contacting surfaces, it could be expected that in developing the catalytic effect the compression of the powder mixture would play an important role.

The effect of compression was examined in the ammonium perchlorate-cupric oxide mixtures of 1:1 and 100:1 mole ratio, at 187°, 220°, 260° and/or 272°C. At 187°C the order in which the reaction started was, in both compositions, 4000, 0 (powder mix-

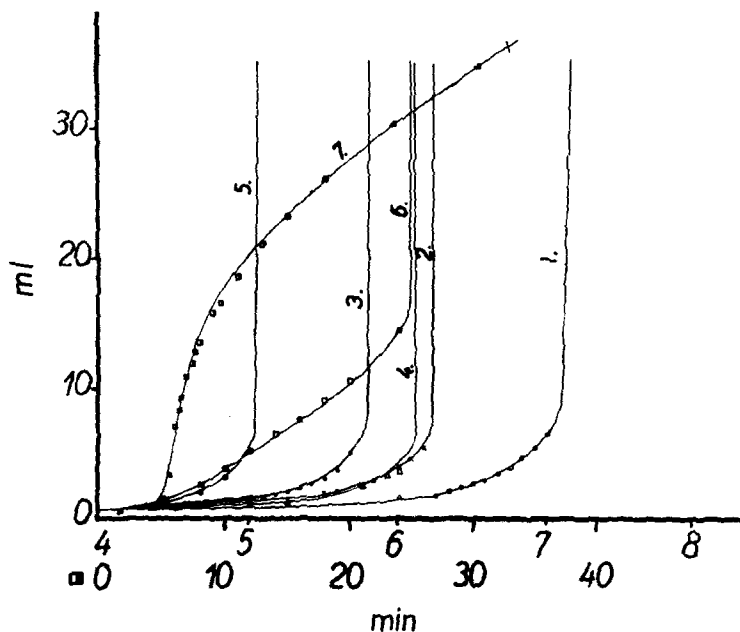


Fig. 7. Explosion of ammonium perchlorate in the presence of CuO. NH_4ClO_4 :CuO mole ratios: 1. 500:1; 2. 300:1; 3. 200:1; 4. 50:1; 5. 16:1; 6. 1:1; 7. 1:5.

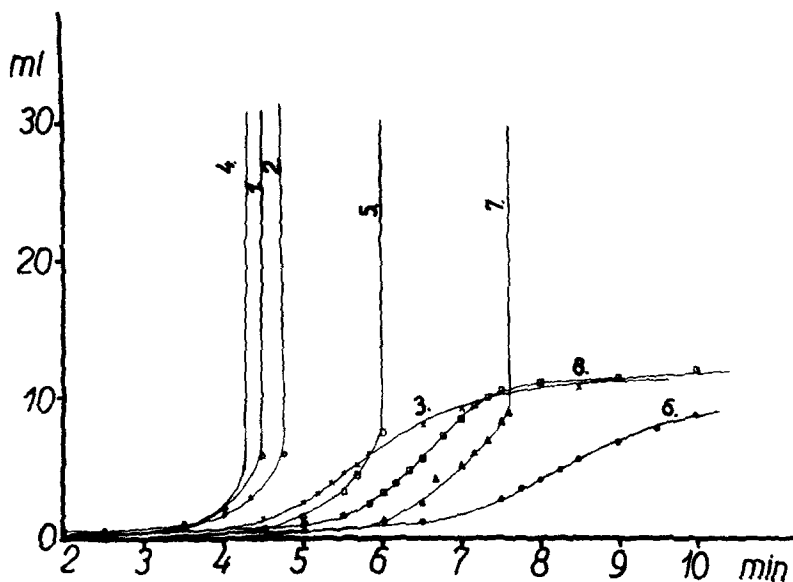


Fig. 8. Explosion of ammonium perchlorate in the presence of CuO doped with lithium and chromic oxides, NH_4ClO_4 :CuO mole ratio 5:1. NH_4ClO_4 content of pellets, about 0.1 g. CuO + 1% Cr_2O_3 at 1., 269.6°C; 2., 266.5°C; 3., 264.0°C; CuO + 1% Li_2O at 4., 269.7°C; 5., 262.2°C; 6., 257.2°C; 7., 260.0°C; 8., pure CuO at 264.0°C.

ture), 400, 2700 kg/cm². The conversion is obviously not dependent on pressure under these conditions.

But at 220°C this order changed and

the induction period increased with the decrease of pressure. Greater deviation in the percentage decomposition of ammonium perchlorate was observable at a ratio of

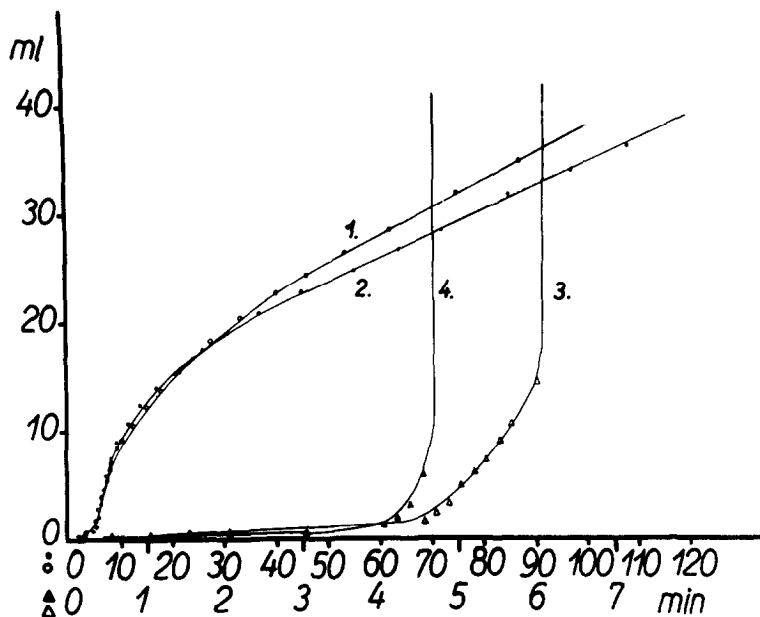


FIG. 9. Decomposition of ammonium perchlorate as a function of the compression of the ammonium perchlorate-CuO mixture (1:1 mole ratio). Reaction temperature: 272°C. 1. Powder mixture; 2. 400 kg/cm²; 3. 2700 kg/cm²; 4. 4000 kg/cm².

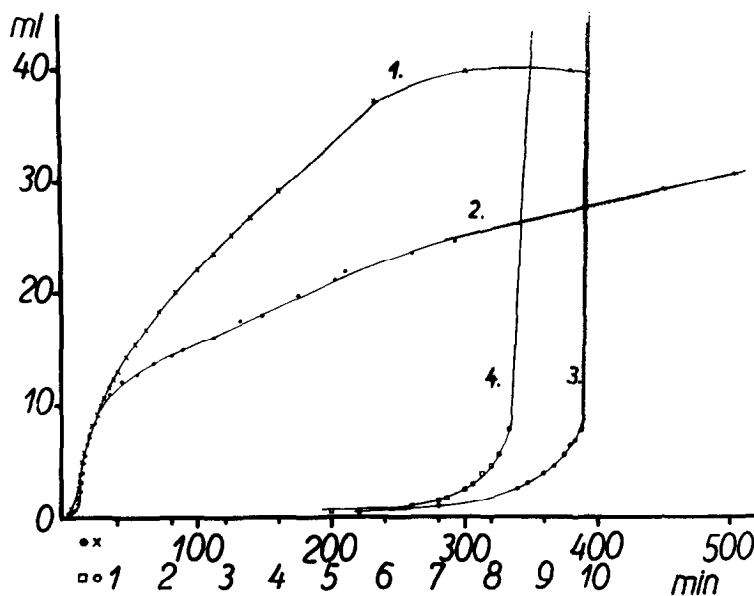


FIG. 10. Decomposition of ammonium perchlorate as a function of the compression of the ammonium perchlorate-CuO mixture (100:1 mole ratio). Reaction temperature: 260°C. 1. Powder mixture; 2. 400 kg/cm²; 3. 2700 kg/cm²; 4. 4000 kg/cm².

100:1. A decomposition of 45% was found in compressed pellets, and only 25% in powder mixtures. Considerable differences also occurred above 260°C where ammo-

nium perchlorate was found to explode only in mixtures compressed at 4000 and 2700 kg/cm². In other cases only a deflagration occurred (Figs. 9 and 10).

DISCUSSION

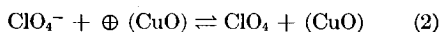
Cupric oxide proved to be a very effective catalyst for the decomposition of ammonium perchlorate, and in its presence the reaction started below 200°C. Values for activation energies found between 180–200°C indicate that here the decomposition of ammonium perchlorate takes place by the electron transfer mechanism (2).

By this mechanism the rate-determining step is the transfer of the electron of perchlorate ion to ammonium ion,



ammonium and perchlorate radicals being formed.

According to our supposition cupric oxide promotes this electron transfer, i.e., the formation of radicals, so that on the one hand it embraces the electron of perchlorate by its defect electrons,

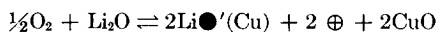


perchlorate radical (positive hole) being formed, and on the other, it gives one electron to the ammonium ion, forming ammonium radical and a defect electron.

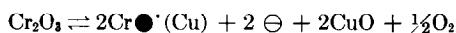


This interpretation is supported by the fact that doping cupric oxide with small amounts of lithium and chromic ions markedly alters the induction periods and rate constants from those of pure cupric oxide.

In the measurements of Hauffe and Grunewald (7) the conductivity of cupric oxide was found to increase when either lithium or chromic oxide was built in. Assuming the intrinsic conductivity of cupric oxide, this may be interpreted as showing that it is the defect electron concentration which increases when lithium oxide is built in,



but on building in chromic oxide the electron concentration increases according to the following equation



Our recent experiments on the conductivity of cupric oxide have not proven the

intrinsic conductor character of this compound (10) since, instead of an increase, the conductivity of CuO slightly decreased when chromic oxide was built in (Fig. 11).

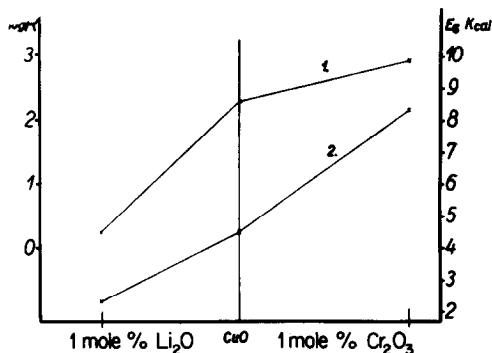


FIG. 11. Changes in resistance of CuO as a function of doping with chromic and lithium oxides. 1. Electric resistance; 2. activation energy of electric conductivity.

This observation supports the *p*-type character of cupric oxide and, in the case of chromic oxide the equation fits the following:



Considering all of this, the effect of doping with lithium oxide, which results in the decrease of the induction period and the increase of the reaction rate, can likely be interpreted as being due to the great defect electron density (Cu^{3+}), i.e. the formation of positive holes. Thus the transfer of an electron from the perchlorate anion to the catalyst takes place more easily. On the other hand, when adding chromic oxide, which decreases the defect electron concentration, the former process cannot take place so easily. From the favorable effect of the defect electron density of the catalyst it could be concluded that for the catalyzed decomposition the decisive factor is the promotion of reaction (2).

Assuming this, it is reasonable to say that *p*-type oxides such as Cu_2O (11) and NiO (12), have great catalytic effect and that cadmium oxide, with great electron density, hardly catalyzes the decomposition of ammonium perchlorate (12). These results lead to the assumption that *n*-type zinc oxide increases the rate of reaction,

not by involving steps (2) and (3), but primarily by promoting the melting of ammonium perchlorate (6).

Cupric oxide exerted a great effect on the explosion of ammonium perchlorate and as little as 0.15% of it decreased the explosion temperature to about 200°C. Zinc oxide (5,6) and Cu_2O (13) have a similar effect. Most likely CuO , formed during the oxidation of cuprous oxide, plays a role in the effect of the latter (13).

The activation energies calculated from the dependence of induction periods on temperature approach those values which fit the electron transfer mechanism. In our opinion the effect of the catalyst can be interpreted as described above, considering that above 240°C some self-heating must be taken into consideration in the decomposition of pure ammonium perchlorate. Because of the effect of CuO in increasing the reaction rate, this self-heating increases so much that it leads to the explosion of the ammonium perchlorate.

The fact that ammonium perchlorate exploded at the lowest temperature in the presence of CuO doped with lithium oxide, is in accordance with the theory since the greatest acceleration of reaction may be expected with catalysts having the greatest defect-electron density.

Values for activation energies between 200° and 240°C considerably exceed 32 kcal. Thus it is likely that this catalyzed reaction is very similar to the noncatalyzed, high temperature process taking place above 350°C. According to Galwey and Jacobs the rate-determining step here is the proton transfer from ammonium to perchlorate ions (with 39 kcal activation energy) (14), while Bircumshaw and Newman favor the rupture of the Cl-O bond with 73 kcal activation energy (15). The basis of this assumption is that, in the measurements of these authors, the activation energy of the decomposition of ammonium perchlorate at high temperature nearly agrees with that of potassium perchlorate. In spite of this agreement, activation energies obtained in the presence of CuO are considerably lower between 200–240°C than those measured by Bircum-

shaw and Newman and, in our opinion, it is likely that in the presence of cupric oxide the decomposition of ammonium perchlorate also takes place by this mechanism. We have pointed out that in our earlier experiments the decomposition of potassium perchlorate is also catalyzed by cupric oxide, which considerably increases the reaction rate and decreases the activation energy. This can only be interpreted as due to promotion of the breakdown of Cl-O bond (9). The previously found (9) values of the activation energy agree well with the present ones.

The observation that alterations in the electrical conductivity of cupric oxide affect the decomposition in this temperature range, too, does not contradict the above picture. Earlier in the examination of the decomposition of potassium chlorate and potassium perchlorate in the presence of semiconductor oxides, it was pointed out that the electronic structure of catalysts plays a definite role and that the increase of the reaction rate and the decrease of the activation energy found in nickel oxide catalysts can be enhanced by increasing the defect electron density of the catalyst (9).

ACKNOWLEDGMENT

The authors wish to express their thanks to Professor Dr. Z. G. Szabó, corresponding member of the Hungarian Academy of Sciences for his valuable advice, and to Mrs. E. Takács for her helpful assistance in the experiments.

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