Synergistic Catalysis of Ammonium Nitrate Decomposition[1]

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Abstract: Chloride and various transition metal ions, notably chromium and copper, exhibit an unexpectedly large synergistic effect in the catalysis of the thermal decomposition of ammonium nitrate. Mechanisms are proposed for these reactions. In the case of copper and chloride, the proposed mechanism involves the operation of redox cycles in which reactions occur by electron transfer in chloro-bridged activated states. NH_4^+ and NH_3 are oxidized to NH_3^+ and NH_2, and NH_2Cl is produced by reaction of NH_2. The original cupric catalysts are then regenerated through oxidation by NO_2^+ and NO^+. The proposed mechanism for chromium catalysis depends on the participation of dichromate in a fused-salt acid–base reaction with nitrate in which nitronium and chromate ions are formed. Both mechanisms produce intermediates which also occur in the mechanism proposed in previous publications for the simple chloride-catalyzed decomposition of ammonium nitrate. A survey of the effects of 23 metals indicates that synergistic catalysis with chloride generally requires a metal capable of forming chloro complexes of reasonable stability in two oxidation states differing by one electron unit. Chromium is a special case in which oxo complexes are believed to be involved.

The pronounced catalysis of the thermal decomposition of ammonium nitrate by chloride ion[2-5] and by transition metals[6-11] is well known. A mechanism has been proposed[3] for the chloride catalysis which contains two cycles in which chloride ions are oxidized to atoms by NO_2^+ and NO^+ (eq 1 and 4) and reduced back to ions by NH_4^+ and NH_3 (eq 2 and 5). Radical recombinations in the reaction cages produce nitramide (eq 3) and nitrosamine (eq 6), which are the unstable precursors for the products N_2, N_2O, and H_2O. The

$$NO_2^+ + Cl^- \longrightarrow NO_2 + Cl \qquad (1)$$

$$Cl + NH_4^+ \longrightarrow NH_3^+ + HCl \qquad (2)$$

$$NO_2 + NH_3^+ \longrightarrow [O_2NNH_3^+] \xrightarrow{\text{fast}} N_2O + H_3O^+ \qquad (3)$$

$$NO^+ + Cl^- \longrightarrow NO + Cl \qquad (4)$$

$$NH_3 + Cl \longrightarrow NH_2 + HCl \qquad (5)$$

$$NH_2 + NO \longrightarrow [H_2NNO] \xrightarrow{\text{fast}} N_2 + H_2O \qquad (6)$$

NO_2^+ comes from the ionic self-dehydration of HNO_3 produced by dissociation of molten ammonium nitrate. NO^+ is produced by the disproportionation of NO_2. A third cycle in the mechanism involves chlorine atom recombination and production of N_2 from a chloramine precursor (eq 7). This mechanism has received support

$$NH_3 + Cl_2 \longrightarrow [NH_2Cl] \xrightarrow{\text{fast}} N_2 + HCl \qquad (7)$$

from mass spectrometric[4] and other[5] studies.

Among the transition metals, chromium compounds are outstanding in their catalytic power. The reaction appears to be of such complexity, however, that despite the amount of quantitative data which has been obtained,[10] only qualitative statements have been made relating the probable mechanism to redox cycles which depend on the facility of chromium and nitrogen for existing in multiple oxidation states.

In the course of recent electrometric measurements[12,13] using a silver-ion frit electrode in chloride-containing ammonium nitrate melts, it was observed that leakage of silver ion caused a synergistic catalysis which was orders of magnitude greater than the sum of the catalytic effects to be expected from silver and chloride ions individually. Further study has shown this synergistic catalysis to be characteristic of many other metal ions.

Experimental Section

Some of the initial work on silver catalysis was done with the differential rate method using a soap-film flowmeter as described previously.[14] Most of the work was done by direct thermal analysis. The heat release was so large that the differential thermal analysis method previously used[2] was not necessary. A charge consisting of 6 g of ammonium nitrate and the necessary catalysts was placed in a 18 × 150 mm test tube set in a tube furnace regulated at 185°. Sparging with dry nitrogen at 50 cc/min was initiated in order to quench the incipient reaction while a reproducible steady-state set of initial conditions with respect to acidity and water content was attained in the melt. This procedure has been described previously.[5] An iron-constantan thermocouple in a thin glass tube was also introduced and the temperature of the melt followed as a function of time on an electronic potentiometric recorder. Temperatures and times were reproducible to within a few degrees and a few minutes, respectively, on replicate runs.

The metal ions were added as reagent grade nitrate, carbonate, or sulfate, dried at 110° where appropriate, and weighed out according to the label assay. The carbonates were converted to nitrates by the acidity of the melt.[5] Blank experiments showed that sulfate had no detectable effect. Chromium was generally added as potassium dichromate, but the same catalytic effect per unit weight of chromium was observed on addition of potassium chromate or chromic nitrate. Visual observation of color changes indicated that chromium was oxidized to dichromate before the reaction began. The composition of the copper salt was checked electroanalytically. Chloride was added as sodium chloride.

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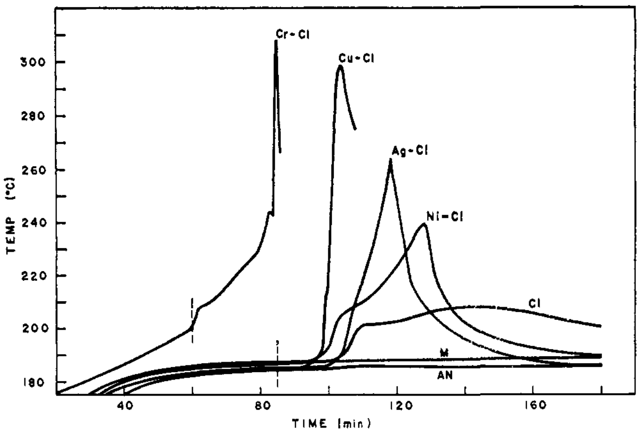

Figure 1. Thermographs showing synergistic catalysis of ammonium nitrate decomposition by chloride with chromium, copper, silver, and nickel ions: AN, ammonium nitrate alone; M, with about 0.1 wt % metal only; Cl, with 3.5% NaCl.

Results

A survey of 23 metal ions with excess chloride at a standard concentration was carried out. Preliminary experimentation established the following as a suitable charge for this survey: ammonium nitrate, 75 mmoles (6 g); sodium chloride, 3.75 mmoles; and metal ion, 0.10 mmole. For most metals this gives a concentration of about 0.1 wt %. The chloride to ammonium nitrate mole ratio is 0.05 as used in previous work,[5] and the chloride to metal atom ratio is 36. Figure 1 shows the thermographs for the four most active metals. The startling degree of synergistic catalysis is brought out clearly. The metal concentrations are so low that even in the case of chromium, which is a very powerful catalyst, the thermograph (curve M) is barely above pure ammonium nitrate. The other metals, used alone, were either undistinguishable from curve M or lay between it and curve AN. The vertical dashed lines represent cessation of sparging. The chromium- and chloride-catalyzed reaction was so violent that sparging did not succeed in keeping the reaction quenched and had to be terminated earlier than the standard time. The first arrest after cessation of sparging, which shows up in all the curves, is an artifact caused by reflux from the cooler parts of the reactor temporarily slowing down the reaction rate. However, in the case of chromium and chloride, a very reproducible though minor peak appears at 82 min and 243° in Figure 1. Visual inspection showed that at this point a violent acceleration of the reaction leading to copious evolution of brown NO_2 fumes occurred. This did not happen with any other metal. The chromium and copper, with chloride, reactions consumed all the ammonium nitrate. In the other cases from 30 to 75% of the melt was left at 180 min.

Of the other metals studied, iron, palladium, gold, cerium, and cobalt showed pronounced synergistic catalysis with chloride. Iron gave a maximum temperature of 250° at 85 min and cerium 225° at 80 min. The others were closely grouped at 220–235° at 130–150 min. Zirconium, manganese, bismuth, lead, zinc, and cadmium salts dissolved to give homogeneous melts but showed no synergistic effect with chloride. Titanium, vanadium, molybdenum, tungsten, aluminum, platinum, and tin salts showed no synergistic effect, but the results are not comparable because of incomplete solubility. Mercury sublimed out as the chloride and could not be tested properly.

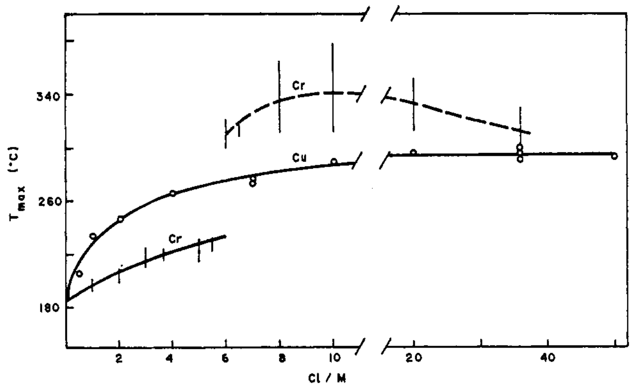

Figure 2. Variation of maximum temperature with Cl/M ratio for chromium and copper with chloride.

Figure 2 shows graphs of maximum temperature against ratio of chloride to metal atoms for the two most active metals, chromium and copper. Smooth curves similar to copper were obtained for several of the other active metals. However, chromium is again anomalous in that the data are less reproducible, and, at a mole ratio of about six chlorides to one chromium, a region of instability sets in followed by a discontinuity of about 80° in the maximum temperature. Below the discontinuity, no secondary peaks appears in the thermographs of Figure 1 and no evolution of NO_2 is observed. When the amount of chromium is reduced, the instability region becomes less well defined and moves to higher chloride to chromium ratios. Interestingly, the time of occurrence of the maximum temperature increases slightly but consistently with increasing chloride.

Discussion

Visually observable color changes as well as the special phenomena described earlier indicate that the mechanism for catalysis by chromium and chloride is different from that for copper and the other metals with chloride. All chromium species added to the decomposing acidic ammonium nitrate melts immediately assumed the characteristic orange color of dichromate. This color persisted throughout the course of the reaction. In fused alkali metal eutectics, dichromate can be converted to chromate by the addition of carbonate, and the accompanying change of color to a lemon yellow is readily visible. This has also been reported by others[15] who further showed that in acidified chloride eutectics at higher temperatures dichromate oxidizes the chloride to Cl_2. Reduction of the chromium, however, is accompanied by the appearance of the purple color of chromium(III). No such color was observed in the melt in the present work.

Since the predominant chromium species in the decomposing melts is dichromate, a simple mechanism may be postulated for the synergistic catalysis which utilizes known reactions and leads directly to the radical intermediates which occur in the already published[3] mechanism for catalysis by chloride alone. Duke and Iverson[16,17] have shown by kinetic studies that dichromate

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produces NO_2^+ in alkali nitrate melts through a Lux-type acid–base displacement.

$$Cr_2O_7^{2-} + NO_3^- \rightleftharpoons 2CrO_4^{2-} + NO_2^+ \quad (8)$$

The rate-determining step which followed was then identical with the one which occurs in the ammonium nitrate mechanism, namely eq 1. In the present instance of synergistic catalysis by chromium and chloride, the original catalytic species would be regenerated by the known acidity of the decomposing melt according to the equilibria

$$H^+ + CrO_4^{2-} \rightleftharpoons HCrO_4^- \quad (9)$$

$$2HCrO_4^- \rightleftharpoons Cr_2O_7^{2-} + H_2O \quad (10)$$

The high temperature and the low solubility of water in the melt ensure that these equilibria are displaced in favor of dichromate.

The final extreme temperature peak in the chromium plus chloride thermograph of Figure 1 and the concomitant evolution of NO_2 vapor are due to oxidation of vapors from ammonium nitrate by chromium residues on the walls of the reactor. Andersen[18] has shown that this reaction occurs with freshly decomposed ammonium dichromate as a catalyst. For systems with low chloride, lying below the discontinuity in Figure 2, the above phenomena were not observed. About one-half of the original clear orange melt remained after the temperature peak. For higher chlorides, however, once the temperature reached approximately 240°, visual observation showed that the melt was depleted to the point where patches of brown residue were being thrown onto the sides of the reactor. This was followed by a violent deflagration originating at the heterogeneous catalytic nuclei, giving rise to NO_2 fumes and the sharp temperature maximum. The lower reproducibility of temperature maxima in this region is due to the depletion of material immersing the thermocouple and the essentially heterogeneous nature of the reaction. The foregoing interpretation of the present results is strongly supported by the data and conclusions of Smith.[7]

In contrast to chromium, the copper and chloride system exhibited pronounced color changes. During the initial stages of heating when the melt was not very acidic, its pronounced blue color indicated the presence of copper ammine complexes. As sparging continued, increasing the acidity, the color changed to blue-green and then yellowish indicating conversion to chloro complexes. As the reaction speeded up and the acidity increased, the color intensified continuously to a pure yellow. At the rate maximum, vigorous evolution of chlorine occurred and the reaction subsided leaving a yellowish melt. The color changes described could be reproduced in separate experiments using a fused alkali metal nitrate mixture as solvent and changing acidity by addition of sodium carbonate or nitric acid. They have also been reported in varying degrees in the literature.[19,20]

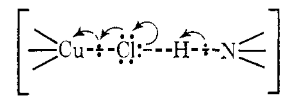
Evidence has already been presented in the literature[21–23] that cupric chloro complexes chlorinate organic species through a mechanism in which the transition state involves a bridged chloro ligand rather than by production of atomic and molecular chlorine. The same change from the blue of predominantly ammine complexes to the green of mixed ligand complexes occurs during the induction period. Chlorine-bridged activated states for inorganic redox reactions have also been found.[24]

A mechanism for synergistic catalysis of ammonium nitrate decomposition may therefore be suggested in which cupric chloro complexes react directly with NH_4^+ and NH_3 to form NH_3^+ and NH_2 *via* bridged activated complexes in which concerted atom abstraction and electron transfer occur, as follows.

$$CuCl_x^{2-x} + NH_4^+ \longrightarrow CuCl_{x-1}^{2-x} + HCl + NH_3^+ \quad (11)$$

$$CuCl_x^{2-x} + NH_3 \longrightarrow CuCl_{x-1}^{2-x} + HCl + NH_2 \quad (12)$$

The activated complex in these would have the structure



The NH_2 radical from reaction 12 then reacts with another complex to form chloramine by a bridging process identical with that of Kochi.[23]

$$H_2N + CuCl_n^{2-n} \longrightarrow [H_2N\text{--}Cl\text{—}Cu^{II}Cl_{n-1} \longrightarrow$$
$$H_2N\text{—}Cl\text{--}Cu^{I}Cl_{n-1}]^{2-n} \longrightarrow NH_2Cl + CuCl_{n-1}^{2-n} \quad (13)$$

Reactions 11, 12, and 13 produce the same intermediates as are employed in the simple chloride-catalyzed reaction (eq 2, 5, and 7, respectively), and with lower activation energy since the concerted processes reduce the number of separate bond splittings.

Regeneration and oxidation of the catalyst back to cupric form can occur easily in the acidic oxidizing ammonium nitrate melt. The most likely oxidizing species are NO_2^+ and NO^+ as in the previous mechanism, yielding NO_2 and NO to continue reactions 3 and 6 as already discussed.

The presence of ammine complexes initially changing to chloro as the reaction progressed was indicated for other metals also. Thus the nickel and chloride melts were initially blue and reaction became rapid only after increasing acidity had converted these predominantly to the amber chloro complexes. Similarly cobalt and chloride melts went from purple to blue. Cessation of reaction at the maximum temperature occurred in each case, as with copper, when the temperature rose so high that the chloro complexes decomposed with the evolution of chlorine and the melt reverted to its initial color.

An attempt was made to correlate synergistic catalysis with chloride ion with various properties of the metal ions such as stability constants of complexes, ionization and oxidation potentials, and ionic and atomic radii. Not all the required data are available for the fused-salt systems in question. The generalization appears tenable, however, that synergistic catalysis of ammonium nitrate decomposition with chloride requires a metal capable of existing in at least two oxidation states separated by a one-electron jump and at the same time capable of forming chloro complexes of moderate sta-

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bility in these states. Other specific factors may prevent a metal from exerting catalysis even though it fulfills these requirements. Thus, chromium, for example, forms such a stable oxo complex of the necessary acid strength that the reaction occurs through a different mechanism. Finally, it was shown that the effects of the recognized ammonium nitrate decomposition catalysts, copper chromite and Prussian Blue, were small compared to the catalysis observed with the best synergistic combinations described herein.

Alkyl Exchange Reactions Involving Organometallic Derivatives of Groups II and III[1]

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Abstract: Kinetic and activation energy studies were made on the methyl group exchange reactions between dimethylcadmium and trimethylgallium, trimethylindium, and dimethylzinc. The results indicate that all reactions are bimolecular in nature with the relative rates of reaction toward dimethylcadmium being $Ga(CH_3)_3 > In(CH_3)_3 \gg Zn(CH_3)_2$. The activation energies for these systems are 7.8 ± 0.8, 8.4 ± 0.2, and 17.0 ± 1.0 kcal/mole, respectively. All kinetic parameters have been obtained by complete line-shape analysis of the nmr spectra by use of modifications of the McConnell equations to simulate theoretical spectra. An attempt is made to correlate the rates of exchange to the Lewis acidity of the organometallic species.

Nuclear magnetic resonance techniques have made possible the study of exchange of alkyl groups in organometallic systems. In the past, however, little quantitative work has been done involving organometallic derivatives of groups II and III.

Much of the effort of group III alkyl exchange has been placed on the study of reactions involving aluminum compounds. It has been reported by Brown and Williams[3] that the rate of methyl group exchange between $Al_2(CH_3)_6$ and $Ga(CH_3)_3$ is determined by dissociation of the trimethylaluminum dimer, with an activation energy of 16.5 kcal/mole. The activated monomer of $Al(CH_3)_3$ then reacts with a molecule of $Ga(CH_3)_3$, thereby effecting exchange. Similar findings were reported for the $Al_2(CH_3)_6$–$In(CH_3)_3$ system.

This dissociation process is found only in the alkylaluminum series since these compounds are unique among the saturated derivatives of group III in that they exist as dimers in solution.[4] It appears, however, that other compounds of groups II and III can assume four-centered structures as intermediates for alkyl exchange and that the rate of formation of such an intermediate would determine the rate of alkyl exchange. It has been found that when two group III compounds are involved in the exchange studies, the rate of exchange is very fast. For example, self-exchange of methyl groups between molecules of $Tl(CH_3)_3$ proceeds in a bimolecular fashion with an activation energy of 6.3 kcal/mole.[5] The rate of exchange of methyl groups between $Ga(CH_3)_3$ and $In(CH_3)_3$ is so fast on the nmr time scale that only one resonance is observed at −70°.[3,6]

Exchange reactions of group II alkyls seem to be much slower. Self-exchange does not occur between $Cd(CH_3)_2$ molecules in the absence of catalytic impurities,[7,8] and neither $Cd(CH_3)_2$ nor $Zn(CH_3)_2$ exchanges with $Hg(CH_3)_2$ on the nmr time scale.[9] Exchange has been observed between $Zn(CH_3)_2$ and $Cd(CH_3)_2$.[10] The results, obtained using simplifying assumptions for the cadmium spectra, indicated a bimolecular reaction very much slower than the group III reactions.

These studies, along with the earlier investigations of McCoy and Allred,[10] show that alkyl exchange between compounds of group III and those of group II to be intermediate between the extremes mentioned above. In this work, we have studied the reactions of three organometallic compounds, $Ga(CH_3)_3$, $In(CH_3)_3$, and $Zn(CH_3)_2$, with one reference compound, $Cd(CH_3)_2$. This has been done in order to study the effect of the various compounds on the formation of the bridged activated species which is reflected in the rates of exchange.

Experimental Section

$Ga(CH_3)_3$,[11] $In(CH_3)_3$,[12] $Cd(CH_3)_2$,[13] and $Zn(CH_3)_2$[14] were all prepared by previously reported methods.

All nmr samples in this study were made by standard high vacuum techniques in 5-mm o.d. sample tubes with either dichloromethane

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[1] Presented in part by K. L. Henold, J. Soulati, and J. P. Oliver at the 156th National Meeting of the American Chemical Society, Atlantic City N. J., Sept 1968.

[2] Recipient of a NASA Traineeship, 1966–1969.

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