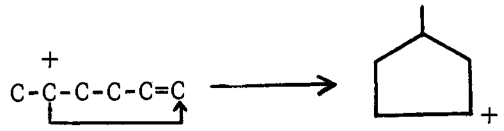

Figure 1. Cyclization of nC_6

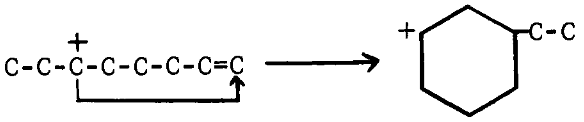

Figure 2. Cyclization of nC_8

but not a six-membered ring; whereas, in the case of *n*-octane, for example, it can also lead to the formation of a six-membered ring (Figure 2). This accounts for the higher rate of dehydrocyclization of *n*-octane as compared to *n*-hexane, and for the fact that the dehydrocyclization reaction results in a much more selective conversion to aromatics in the case of *n*-octane.

The small extent of dehydrocyclization of 2,2,4-trimethylpentane, particularly to aromatics, is presumably due to the difficulty of rearranging to a structure which can satisfactorily undergo ring closure. The difficulty in rearranging the structure is also indicated by the observation that essentially no methylheptanes or dimethylhexanes are formed.

The observation that the rate of dehydrocyclization of 3-methylhexane is only moderately lower than that of *n*-heptane indicates that the former can rearrange to the normal readily. This makes a path available for the direct formation of a six-membered ring via a secondary carbonium ion intermediate.

LITERATURE CITED

(1) Ciapetta, F.G., Dobres, R.M., Baker, R.W., "Catalysis," Vol. 6, p. 586, Reinhold, New York, 1958.
(2) Ciapetta, F.G., Hunter, J.B., *Ind. Eng. Chem.* **45**, 147 (1953).
(3) Ciapetta, F.G., Hunter, J.B., *Ibid.*, **45**, 155 (1953).
(4) Hettinger, W.P., Jr., Keith, C.D., Gring, J.L., Teter, J.W., *Ind. Eng. Chem.* **47**, 719 (1955).
(5) Myers, C.G., Munns, G.W., Jr., *Ibid.*, **50**, 1727 (1958).
(6) Sinfelt, J.H., Hurwitz, H., Rohrer, J.C., *J. Phys. Chem.* **64**, 892 (1960).
(7) Sinfelt, J.H., Rohrer, J.C., *Ibid.*, **65**, 978 (1961).
(8) Voge, H.H., "Catalysis," Vol. 6, 447, Reinhold, New York, 1958.

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Dichromate Catalysis of Deflagrating Ammonium Nitrate

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An experimental technique is described for studying a qualitative catalytic action of heterogeneous solids on the gaseous products from molten, decomposing ammonium nitrate (AN). Freshly prepared chromic oxide ash produced by the thermal decomposition of ammonium dichromate (AD) will (catalytically) decompose a portion of the gaseous products of AN at relatively high temperatures into nitrogen dioxide gas. Further evidence suggests that the NO_2 is produced by the decomposition of nitric acid vapor which is present. The studies show that chromic oxide ash prepared freshly by the thermal decomposition of AD differs in its catalytic behavior from laboratory-grade chromic oxide. This difference in behavior is presumably due to differences in its surface properties (area and/or composition) from those of laboratory-grade chromic oxide, which is usually prepared by a different method.

CHROMATE AND DICHROMATE salts which are soluble in molten ammonium nitrate (AN) are effective catalysts for both the thermal decomposition of molten AN, and the deflagration of solid AN (*4, 5*). The exact mechanism of the catalytic activity is not known in either case, but it is well established that the catalyzed decomposition of both molten (*4, 5*) and deflagrating (*6*) solid AN produces gases containing nitrogen dioxide; where as, the thermal decomposition of molten pure AN gives nitrous oxide, water vapor, nitric acid, and ammonia. On the basis of the results of the molten catalyzed AN decomposition, it was usually considered that chromates and dichromates influence the deflagration characteristics of solid AN principally through a liquid-phase reaction (*5*). However, it was subsequently postulated that in the case of ammonium dichromate (AD) it is the chromic oxide produced by thermal decomposition of the AD which is the dominant catalyst, and that it is effective in the gas-phase reactions (*1*). The possible importance of heterogeneous catalysis of the gas-phase reactions by other catalysts was also emphasized. This hypothesis was based on the observations that small percentages of AD (and other typical burning catalysts) have no effect on the linear pyrolysis rate of pure solid AN. In addition, for the case of AD, hot freshly-prepared chromic oxide is capable of catalyzing the decomposition or reaction of the gaseous products from vaporizing molten AN, giving NO_2 as one of the products. This latter observation, of which only the final results were briefly reported, has subsequently created some interest. This article describes the experimental technique and results leading to the above conclusion and elaborates on the results.

EXPERIMENTAL TECHNIQUE AND RESULTS

The experiment was designed so that the gaseous products from molten AN would pass through the catalyst. A stainless-steel screen (200 mesh) was placed over a heated platinum crucible about three-fourths full of molten pure AN. Because it was believed that the initial decomposition products of deflagrating AN are predominantly HNO_3 and NH_3 (*1*), the temperature of the molten AN in the crucible was kept high (> 240° C.) to ensure the presence of

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substantial quantities of these gases. Under these conditions a steady stream of white fumes issued from the molten AN up through the screen. These fumes presumably contained N_2O, H_2O, HNO_3, and NH_3. A thin layer of reagent grade powder AD (average particle size 40 microns) was then sprinkled over the screen. Some of the escaping hot white fumes condensed on the AD on the screen to give a melt which dissolved the AD. The subsequent liquid reaction on the screen was clearly exothermic as was evidenced by the boiling and bubbling of the melt; this reaction apparently corresponds to the liquid catalytic reaction of AD observed in references (*4*) and (*5*). The melt then gradually darkened in color and became somewhat hardened. Suddenly a fast reaction occurred, during which the melt turned to a voluminous, grayish-green ash with a very porous texture, and which was presumably chromic oxide. At this point, most of the escaping white vapors changed into the characteristic brown color of NO_2. The brown color of the gases lasted for several seconds and then turned white again, the ash presumably becoming poisoned or inactivated, after which stage NO_2 was no longer produced. Both the removal of the screen from the crucible while the brown fumes were given off and then replacing it, and also the use of a glass crucible so that the crucible contents might be observed during the reaction, substantiated the belief that it was the freshly formed ash which produced the brown gas from the white fumes. The ash was observed to glow at various small spots during the evolution of NO_2.

Freshly prepared chromic oxide ash prepared by heating AD by itself in a crucible was also tested on the screen and found to be effective in producing NO_2 after sufficient melt had accumulated on it for it to become hot. Again the ash lost its effectiveness after a few seconds of use. Standing in air for an hour apparently does not impair the ability of the unused ash to produce NO_2. The freshly formed ash, when digested with molten AN, was found to accelerate only very slowly the decomposition of the AN; however, it was impossible to prepare ash which did not give a positive test for dichromate ion and, therefore, the activity of the ash in this latter case is probably due to the dichromate ion.

Reagent-grade chromic oxide was investigated by using the screen technique and was found not to produce NO_2 from molten AN fumes. Chromic oxide, freshly prepared by the thermal decomposition of AD, differs in certain properties from commercial reagent-grade chromic oxide. It (presumably reagent grade) has been found to not be an effective catalyst for the decomposition of molten AN (*5*).

Vapor from boiling nitric acid was passed through freshly prepared ash from the thermal decomposition of AD. The ash was found to be very effective in producing brown gas (NO_2) from the vapor. On the other and the hot ash was not effective in producing the brown gas from either ammonia or nitrous oxide gases.

Sodium and potassium dichromate salts were also investigated briefly using the screen technique, and were found to behave somewhat differently than AD. In these cases the salts dissolved in the condensed vapors of the molten AN to give initially a thick syrupy melt. The reactions in the melt were clearly exothermic, as was evidenced by a frothing and boiling of the melt. The melt then gradually hardened to form a dark-colored thick pasty material and simultaneously gave off a small amount of NO_2 during this process. The NO_2 evolution ceased upon formation of the pasty residue.

DISCUSSION

Chromic oxide ash, which is freshly prepared by the thermal decomposition of AD, will effectively decompose the gaseous products from molten AN to give NO_2; whereas, it has very little effect on the decomposition of molten AN. The ash prepared in this manner has also been reported to be a good deflagration catalyst for AN (*6*), and gives a burning rate which, although slightly lower than the rate of an equivalent concentration of AD, does not differ appreciably in its pressure dependence. Reagent grade chromic oxide does not decompose the vapors from molten AN; it is not an effective catalyst for the decomposition of molten AN (*5*) nor for catalyzing the deflagration of solid AN. These facts suggest that the principal catalytic activity of AD in the deflagration of AN is through heterogeneous catalysis of gas phase reactions by the chromic oxide ash. They are supported by the observation that small quantities of AD do not affect substantially the linear pyrolysis rate of solid AN (*1*). It was not (or is not) claimed that the gas phase catalysis is the only effect of the AD, but rather that it is the dominant effect. Both the above observations and the previous observations (*4, 5*) support the view that minor liquid reactions may possibly occur. Moreover, the work of Whittaker and Barham gives indirect evidence that the exothermic decomposition the AD near the propellant surface may possibly play a role.

The exact manner in which the chromic oxide ash catalyzes the redox gas reactions is not known. Chaiken (*2*) assumed that the heterogenous catalysis influenced the oxidation of ammonia by nitrogen dioxide, which he considered to be the rate controlling gas reaction. This appears plausible in view that chromic oxide has been reported to be a superior catalyst for the vapor-phase oxidation of ammonia. However, it ignores the differences between reagent grade chromic oxide and chromic oxide prepared by heating AD. Both the above observations and the literature suggest that the predominant role of the chromic oxide ash is to catalyze NO_2 formation from the decomposition products of AN. The above experiments suggest that this ash produces NO_2 by facilitating the decomposition of HNO_3. The exact manner in which this is accomplished is unclear, particularly since reagent grade chromic oxide does not possess these properties. Harbard and King reported (*3*) that the oxide resulting from the thermal decomposition of AD contains more oxygen than does ordinary chromic oxide, and that the excess oxygen is probably present as a surface oxide. This oxygen may play a role in inducing NO_2 formation from the vapors of decomposing AN and may account for the observation that the chromic oxide ash is only effective for a short period of time. Whittaker has also suggested (*6*) that the difference in activity was probably due to a difference in the surface properties of the chromic oxide.

LITERATURE CITED

(1) Andersen, W.H., Bills, K.W., Mishuck, E., Moe, G., Schultz, R.D., *Combustion and Flame* **3**, 301 (1959).

(2) Chaiken, R.F., *Ibid*, 285 (1959).

(3) Harbard, E.H., King, A., *J. Chem. Soc.* **1938**, p.955.

(4) Robertson, A.J.B., *J. Soc. Chem. Ind. (London)* **67**, 221 (1948).

(5) Taylor, J., Sillito, G.P., "The use of Ammonium Nitrate as a Solid Fuel to Provide Gas for Propulsive Purposes," *Third Symposium on Combustion, Flame and Explosion Phenomena*, Williams and Wilkins Co., pp.572–79, Baltimore 1949.

(6) Whittaker, A.G., Aerospace Corp., Los Angeles, Calif., private communication, 1962.

(7) Whittaker, A.G., Barham, D. C., "Effect of Catalysts on the Burning Rate of Ammonium Nitrate," unpublished data, 1962.

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