nificant one should not expect any profound changes due to the replacement of a hydrogen atom (χ_H = 2.13) with a methyl group (χ_{CH_3} = 2.35) since they are of comparable values. However, when changes in the substituent at the α-position are made, appreciable changes occur. The observed carbonyl frequencies in Raman spectra of a number of liquid esters are listed in Table IV.

The average carbonyl frequencies for the various esters listed above, plus the value for $CF_3 \cdot COOC_2H_5$ reported by Fuson[7] (ν(C=O) = 1780 cm.$^{-1}$) are plotted in Fig. 3 as a function of the effective electronegativities of group X, which are listed for the most part in Table II. If one assumes that the effective electronegativity of the group -O-R is constant and has the value $\chi_{\text{-O-R}}$ = 1.81, the standard deviation of the observed ester carbonyl frequencies from those predicted on the basis of equation 2 is only ±6.0 cm.$^{-1}$.

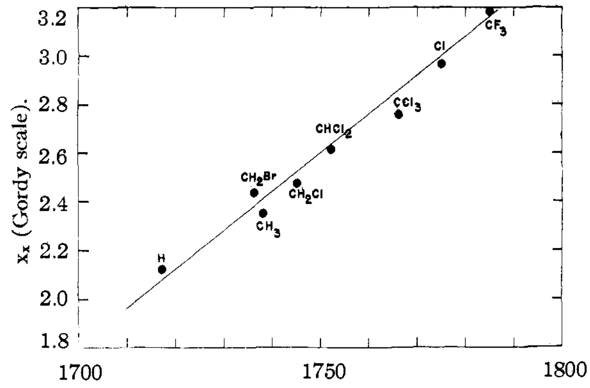

Fig. 3.—Plot of the electronegativity of substituents X *versus* the observed carbonyl frequencies in esters of the type X·CO·OR.

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[7] N. Fuson, M. L. Josien, E. A. Jones and J. R. Lawson, *J. Chem. Phys.*, **20**, 1627 (1952).

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Differential Thermal Analysis of the Thermal Decomposition of Ammonium Nitrate

BY A. G. KEENAN

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The general method of differential thermal analysis (DTA) is well known and has been used extensively in the study of phase changes, dehydrations and general condensation phenomena.[1,2] It does not appear to have been applied, however, to the exothermic decomposition of thermally unstable materials. The results of such an application to the decomposition of ammonium nitrate, reported in the present note, show that the DTA method can give interesting results in this field also.

Experimental.—The DTA apparatus was similar to that described by Vold.[3] A Brown Type 152 preset-program temperature controller, operating a proportioning motor and Variac, was used to cause the wall of the furnace to rise in temperature at a uniform rate of 2° per minute in the range from room temperature to 300°. Absolute and differential temperatures were recorded on a Leeds and Northrup Model S Speedomax Type G two-pen strip-chart X_1–X_2 millivolt recorder. A d.c. microvolt amplifier could be added to the differential temperature circuit, when necessary, by means of appropriate switches. The temperature sensing elements were in all cases single junction, 30 gage, iron–constantan thermocouples, duplex type, insulated with braided nylon and fiber glass. The samples were contained in 10 × 70 mm. Pyrex test-tubes which were suspended from holes in a Transite shelf mounted in the center of a furnace of the type described by Vold.[3] The thermocouples entering the sample test-tubes were inserted into lengths of 3 mm. Pyrex tubing sealed at the bottom.

One-gram samples of reagent grade ammonium nitrate crystals were used and the modifying salt, if any, was added in excess of this. Preliminary experiments showed no change in the DTA curves when the salts were first dried *in vacuo* over P_2O_5. Prior to a run, the apparatus was allowed to equilibrate by maintaining the temperature constant at some value in the range 185–200° for about 30 min. When a steady state had been reached, the differential temperature had in general fallen to some negligible value amounting to about 2% or less of the thermal effects being measured. Duplicate DTA curves agreed to within about 4% or better at all points.

Results.—Typical DTA curves obtained in this work and plotted in the conventional form are shown in Figs. 1 and 2. Numerical data are given in Table I where ΔT_{max} gives the height of the maximum in the differential thermal curve and T gives the temperature at which it occurs. The actual numerical values depend, of course, on the appara-

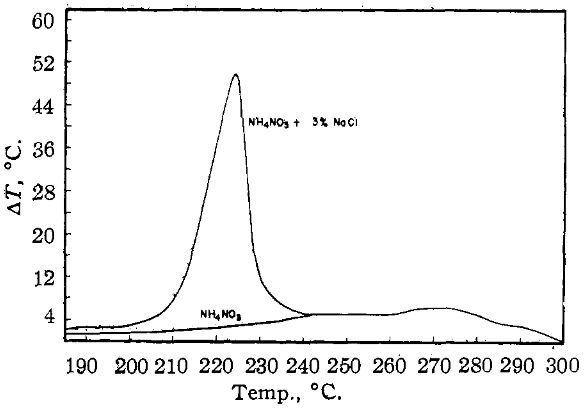

Fig. 1.—Thermal decomposition of ammonium nitrate.

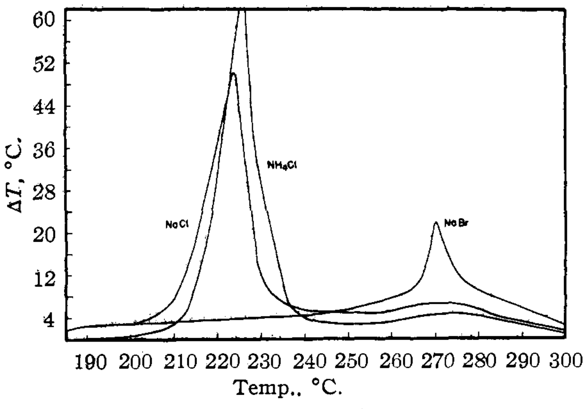

Fig. 2.—Thermal decomposition of ammonium nitrate. Salts shown were added in mole ratio 0.05:1.

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[1] W. J. Smothers, Y. Chiang and A. Wilson, "Bibliography of Differential Thermal Analysis," Research Series Publication No. 21, University of Arkansas, November, 1951.

[2] L. F. Audrieth, J. R. Mills and L. E. Netherton, *J. Phys. Chem.*, **58**, 482 (1954).

[3] M. J. Vold, *Anal. Chem.*, **21**, 683 (1949).

tus used but the comparative results are general. The dependence of ΔT on NaCl concentration in the ammonium nitrate melt was also investigated briefly and the 0.05 to 1 mole ratio was found to give the largest value for $\Delta T_{\max}$. This is probably also close to the solubility of NaCl in the melt.

TABLE I

DIFFERENTIAL THERMAL ANALYSIS OF AMMONIUM NITRATE DECOMPOSITION

Salts listed were added in mole ratio 0.05:1.

Salt added	T, °C.	ΔTmax, °C.
..	270	6
NaF	270	7
NaI	270	7
$(NH_4)_2SO_4$	270	12
NaBr	270	22
NaCl	225	50
NH_4Cl	225	~64
$(NH_4)_2Cr_2O_7$	182	247

The decrease in ΔT after the maximum is passed is due in large part to disappearance of the sample by decomposition. However, examination of the sample tube when the temperature had reached 300° showed in general the presence of a few drops of a clear melt refluxing gently up the sides. In another connection, a similar residue was refluxed at 400° in a vacuum for about 10 min. without noticeable increase in pressure. A quantitative microanalysis of this material showed it to be ammonium nitrate. These observations provide another illustration of the fact, noted by Friedman and Bigeleisen,[4] that pure, dry ammonium nitrate is relatively stable to thermal decomposition. Presumably, in the above instances the water and other impurities had been purged out by the initial partial decomposition.

Discussion.—The thermal decomposition of ammonium nitrate has been studied in some detail previously, the latest results being those of Friedman and Bigeleisen.[4] The major products of decomposition are N_2O and H_2O but some free nitrogen also is formed, the proportion becoming greater at higher temperatures, *e.g.*, about 2% at 260°. Chlorides accelerate the reaction and also increase the proportion of nitrogen in the products to the range 30–50%.[5]

The DTA results obtained in the present research show rather clearly that the thermal decomposition of ammonium nitrate is a complex reaction. As shown in Figs. 1 and 2 and in Table I, there is one reaction, presumably the N_2-producing one, which is strongly catalyzed by chloride ion and, when so catalyzed, has a very high exothermicity with a differential thermal peak at 225° in the present apparatus. A slight indication of this reaction occurring in pure ammonium nitrate is shown by the weak maximum at 245° in Fig. 1. The major reaction occurring in the decomposition of pure ammonium nitrate, presumably the N_2O-producing one, has a relatively low exothermicity and gives a differential thermal peak at 270° in the present apparatus. This reaction is moderately catalyzed by bromide and ammonium ions.

The height of the differential thermal peak ($\Delta T_{\max}$) is a measure of the exothermicity and rate of the reaction while the location of the peak along the temperature axis is related to the activation energy provided due allowance is made for the possible presence of a measurable induction period. While it does not appear that the DTA method can be developed to the point where these various interrelated factors can be measured individually and quantitatively, a great deal of comparative information can nevertheless be obtained.

The DTA curves illustrate in a very graphic manner what may well be the cause of the occasional disastrous explosions which have occurred with ammonium nitrate stored in bulk. NH_4NO_3 is known to decompose explosively around 300°. The relatively moderate amount of heat liberated by the slow decomposition of pure NH_4NO_3, which may be occurring at ambient temperatures, may be dissipated even from the interior of a large mass without the temperature rising to the explosion point (which may differ from 300° due to the pressure in a large mass). However, if an appreciable concentration of chloride impurity were present, even in localized spots, the highly exothermic nature of the chloride-induced reaction, as illustrated by Figs. 1 and 2, could cause the temperature to rise locally until an explosive condition resulted. This would be aggravated by the fact that the surrounding volume would sinter, plugging the pores, and the pressure would rise due to the gaseous products evolved. The location of the DTA maxima along the horizontal temperature scale in Figs. 1 and 2 is of course dependent on the constants of the present apparatus and under other conditions the chloride-catalyzed reaction could become significant at much lower temperatures. This reaction for example has an appreciable rate already at around 160°. The significant point shown up by the DTA curves is that, once this reaction is set off, it raises the temperature extremely rapidly relative to the decomposition of pure NH_4NO_3. Other impurities than chloride might have the same effect but chloride would appear to be one of the most likely to be present.

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Thallous Complexes in Chloride Solutions[1]

BY KUO-HAO HU AND ALLEN B. SCOTT

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Previous work[2–4] suggests that the luminescence of solutions of alkali halides containing thallium may be due to thallium halide complexes. Some evidence of complex formation was given by

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[4] L. Friedman and J. Bigeleisen, *J. Chem. Phys.*, **18**, 1325 (1950).

[5] H. L. Saunders, *J. Chem. Soc.*, **121**, 698 (1922).

[1] Supported by the Office of Ordnance Research. Published with the approval of the Oregon State College Monographs Committee, Research Paper No. 260, Department of Chemistry, School of Science.

[2] B. E. Gordon and A. Schischlowski, *Phys. chim. Acta U.S.S.R.*, **13**, 247 (1940).

[3] R. Hilsch, *Proc. Phys. Soc. London*, **49** extra part, 40 (1937).

[4] P. Pringsheim, *J. Chem. Phys.*, **16**, 241 (1948).