ciation, eq. 3 and 4 are the most probable processes for the lower nitromethane mole fractions. As the

$$I(HOAc) + HClO_4 \rightleftharpoons IH^+ClO_4^- + HOAc$$

$$IH^+ + ClO_4^- \quad (3)$$

$$I(CH_3NO_2) + HClO_4 \rightleftharpoons IH^+ClO_4^- + CH_3NO_2$$

$$IH^+ + ClO_4^- \quad (4)$$

activity of the HOAc decreases with increasing CH_3NO_2, the competitive solvate in eq. 4 will become more significant even though acetic acid is a stronger acid than nitromethane. Since proton transfer to each of the solvated forms of the base gives the same acidic species, one would expect an increase in D to shift these equilibria toward the right in the same manner as occurs in acetic acid–acetic anhydride.[12] However, the results in Table I indicate this is not true for the higher mole fraction range in nitromethane.

The effect of the salt upon the indicator color ratio in pure acetic acid has been described by Higuchi, Feldman, and Rehm[18] as an anion exchange between the salt and the solvated base form of the indicator. However, the limiting slope of unity in the presence of nitromethane (Figure 2) instead of the slope of 0.5 found in pure acetic acid[13] results from the appearance of invalid approximations when the same mechanism is applied to the binary solvent of higher dielectric constant. The acetolysis of the salt in the presence of the indicator base (for simplicity written as the unsolvated base) may be represented by eq. 5a, 5b, and 5c. The proportionality between $1/R$ and $\sqrt{C_{NaClO_4}}$

$$I + HOAc + Na^+ClO_4^- \rightleftharpoons IH^+ClO_4^- + NaOAc \quad (5a)$$

$$IH^+ClO_4^- + CH_3NO_2 \rightleftharpoons IH^+ClO_4^- \cdot CH_3NO_2 \rightleftharpoons$$

$$IH^+ + CH_3NO_2 \cdot ClO_4^- \quad (5b)$$

(18) T. Higuchi, J. Feldman, and C. Rehm, *Anal. Chem.*, **28**, 1120 (1956).

$$Na^+ClO_4^- + CH_3NO_2 \rightleftharpoons Na^+ClO_4^- \cdot CH_3NO_2 \rightleftharpoons$$

$$Na^+ + CH_3NO_2 \cdot ClO_4^- \quad (5c)$$

was obtained from the assumptions that the indicator perchlorate ion pair (and multiple ion aggregate) dissociations can be ignored in acetic acid and that the concentration of NaOAc equals that of the dissociated $HClO_4$. For the binary solvent, the only approximate relationship that is suitable for very low concentrations of sodium perchlorate is eq. 6, obtained from eq. 5a, in which the proportionality between $1/R$ and C_{NaClO_4}

$$\frac{[IH^+ClO_4^-]}{[I]} = C_{NaClO_4} K_{eq} \frac{[HOAc]}{[NaOAc]} \quad (6)$$

is a lower limiting condition. As the sodium perchlorate concentration increases, the fraction of the total C_{NaClO_4} available for acetolysis becomes smaller as self-association of the salt takes place in addition to solvation of sodium perchlorate in eq. 5c. The curves in Figure 2 are consistent with these trends and indicate that eq. 5a proceeds more extensively to the right for the more basic indicator.

Even though the quantitative validity of the Kolthoff–Bruckenstein method may be questionable when applied to proton exchange between a weak acid and weak base in a binary solvent of low dielectric constant,[5] the experimental distinction between strong and weak protonic acids can be made in such solvent systems. Semiquantitative evidence for ion pair and multiple ion aggregates can be deduced from the application of graphical parts of the Kolthoff–Bruckenstein method to a protonic–aprotic solvent pair in the dielectric constant range from 6.2 to 24.8 at 25°.

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The Induction Period of the Chloride-Catalyzed Decomposition of Ammonium Nitrate

By C. I. COLVIN, P. W. FEARNOW, AND A. G. KEENAN

A novel procedure of flushing with inert gas at reaction temperature to establish a zero time enables accurate measurements of induction periods to be made in ammonium nitrate melts containing chloride. The resulting data together with pH measurements are interpreted to indicate that the mechanism of the induction period consists of an acid-autocatalyzed adjustment of the melt acidity from one steady-state level to another. The data also support the mechanism previously published for the chloride-catalyzed thermal decomposition of ammonium nitrate.

Introduction

A detailed mechanism[1] proposed for the chloride-catalyzed thermal decomposition of ammonium nitrate

(1) A. G. Keenan and B. Dimitriades, *J. Chem. Phys.*, **37**, 1583 (1962).

has recently received strong support[2] from mass spectral analyses of the product gases from the isotopically-labeled reagent. The published mechanism pertains

(2) C. I. Colvin, A. G. Keenan, and J. B. Hunt, *ibid.*, **38**, 3033 (1963).

Figure 1.—Effect of rate and duration of flushing with nitrogen on induction period for ammonium nitrate containing sodium chloride at a mole ratio of 0.05 at 185°.

to decomposition under steady-state conditions only. The postulated intermediates, however, are produced during the preceding induction period which is the subject of the present study.

Qualitative observations on the induction period by previous workers have established that ammonium nitrate–chloride melts develop acidity and evolve traces of HNO_3, HCl, and Cl_2 along with the major products of the decomposition, N_2, N_2O, and H_2O, during this period. It has also been demonstrated that addition to the melt of acidic species or of Cl_2 decreases the induction period, whereas basic species increase it. Guiochon[3] has attempted a more quantitative study of the induction period but his values include the time required for melting and thermal equilibration. In the present work, a technique of flushing with inert gas at reaction temperature has been used to reduce the reaction rate to a negligible value. This provides an unambiguous zero time for the measurements. The induction period is defined as the time from cessation of flushing to the rate maximum, R_m (see Figure 1 of ref. 1). The results are highly reproducible and can be interpreted on the basis of acid autocatalysis.

Experimental

Apparatus.—The reactor was similar to those previously described[1,2,4] except that the top was furnished with a ground joint through which either a thermometer or a flushing tube

could be inserted. The latter consisted of 4-mm. tubing with a 2-mm. orifice at the end. The reactor was immersed in a $LiNO_3$–KNO_3 eutectic fused-salt bath regulated at $185.0 \pm 0.1°$. Temperatures were read with a mercury thermometer calibrated against an ASTM precision grade standard. Reaction rates were measured with a soap-film flow meter following a KOH trap.[1,4] The chemicals were reagent grade and the flushing gas was dry N_2.

Procedure.—The heated reactor was charged with 6 g. of NH_4NO_3 and the necessary NaCl to bring the mole ratio either to 0.05 or to 0.10. The preheated flushing tube was inserted after 5 min. and flushing was begun after another 5 min. At the termination of flushing (t_0), an electric timer was started for measurement of the induction period, the flushing tube was replaced with a preheated thermometer, and rate measurements were taken at intervals for a suitable period of time. Some runs were also made in which the chloride was added at the termination of flushing. Values of the induction period were obtained from a plot of rate against time. They were reproducible to $\pm 1\%$. All values given are averages of three or more replicates.

At the requisite time, the reactor was chilled by immersing in cold water. Volhard chloride analyses and pH measurements using a Beckman Model G pH meter, standardized at pH 2.00, were carried out on aliquots of a 100-ml. aqueous solution of the reactor contents. The pH measurements were reproducible to within a few hundredths of a unit.

Results

Data for the 0.05 mole ratio melts in which chloride was added before flushing are shown in Figure 1. The results for the 0.10 mole ratio melts were similar. The induction period for unflushed melts $(t_f = 0)$ was of the order of 75–100 min., depending on the chloride concentration, but was not investigated in detail because experience showed that the reproducibility of the measurements became poorer for shorter flushing times. Furthermore, the label values of the pH of different lots of reagent ammonium nitrate varied from 4.9 to 5.4 and the actual pH values changed on standing.

The induction period at first decreases rapidly with increasing t_f at constant R_f and then, except for $R_f = 10$ cc./min., attains a constant value (± 0.1 min.) for t_f values ranging from about 20 to as long as 60 min. These constant induction period values which are characteristic of each combination of melt composition and flushing rate, and are independent of flushing time over the above range, are assigned the symbol t_i. Numerical values are given in Table I. The induction period values for the cases where chloride was added after flushing were also independent of t_f in the range 20–60 min. and are included in Table I.

TABLE I
INDUCTION PERIODS AT 185°

| R_f, cc./ min. | t_i, min. | | | |
| | NaCl/NH₄NO₃ = 0.05 | | NaCl/NH₄NO₃ = 0.10 | |
	A^a	B^b	A^a	B^b
75	34.9	35.1	33.0	30.6
50	32.9	34.7	32.4	30.1
25	29.8	34.6	28.0	30.0

^{a} A = NaCl added before flushing. ^{b} B = NaCl added after flushing.

Results of pH measurements are given in Table II. The values for pure ammonium nitrate melts containing no chloride at t_0, *i.e.*, at the termination of flushing,

(3) G. Guiochon, *Ann. Chim.* (Paris), **5**, 295 (1960).

(4) A. G. Keenan and B. Dimitriades, *Trans. Faraday Soc.*, **57**, 1019 (1961).

TABLE II

pH OF STANDARD AQUEOUS SOLUTIONS

R_f, cc./ min.	t_f, min.	NH₄NO₃ t_0	NaCl/NH₄NO₃ = 0.05			NaCl/NH₄NO₃ = 0.10		
			t_0	t_i	$t_i + 15$	t_0	t_i	$t_i + 15$
	20	3.51	3.60			3.71		
75	40	3.53	3.62	2.27	2.31	3.72	2.26	2.29
	60	3.52	3.59			3.70		
	20	3.53	3.50			3.65		
50	40	3.52	3.46	2.32	2.31	3.63	2.32	2.30
	60	3.54	3.49			3.63		
	30	3.52	3.45			3.53		
25	40	3.52	3.39	2.28	2.29	3.47	2.29	2.30
	60	3.52	3.29			3.37		

are constant at 3.52 ± 0.01 for all R_f and t_f values. In the case of the chloride-containing melts, however, the pH shows significant variations greater than the reproducibility of the measurements. The chloride analyses indicated that the loss of chloride during flushing was negligible.

Discussion

The precision of the t_i measurements and the constancy of the values after 15–20 min. flushing for R_f greater than 10 cc./min. indicates the establishment of a reproducible melt composition in each case. The flushing procedure, therefore, appears satisfactory for initiating accurate induction period measurements in systems of this type. Furthermore, since the flushing is carried out at reaction temperature, the t_i values do not include the time required for melting and for thermal equilibration as in previous work.

In Figure 1, the initial rapid decrease of induction period with increasing t_f indicates that flushing removes a volatile inhibitor. The relative positions of the initial portions of the curves show that the more rapid the flushing, the more rapid the removal of inhibitor and the sooner steady-state conditions are reached. When the induction period becomes constant, however, the curves have all crossed and a higher R_f now corresponds to a longer t_i. Turning to the pH values of the chloride-containing melts in the t_0 columns of Table II, it is seen that flushing has increased the acidity of the melts relative to values in the range 4.9–5.4 which, as mentioned earlier, are characteristic of unflushed melts. No change in acidity on further flushing occurs in the region in which t_i is constant, *i.e.*, a true steady-state condition exists. The higher this steady-state acidity, the shorter is t_i, and the lower was the flushing rate which produced it.

The above observations together with the known chemistry of these systems indicate that the following mechanisms are operating during the induction period. Initially NH₃ is preferentially volatilized by flushing. The resulting increase in melt acidity has two effects. First, the dissociation of NH₄NO₃ is repressed and the rate of NH₃ removal decreased. Secondly, the increased acidity catalytically initiates the decomposition reaction which increases the acidity further. Volatilization of acid therefore increases according to the usual

Henry's law concept. A steady state is reached when NH₃ and acid are removed in such a ratio that the melt acidity remains constant. The rate of volatile acid removal by flushing equals the sum of the rates of acid generation by slow decomposition and of acid release from the NH₄NO₃ due to the residual rate of NH₃ volatilization. When flushing is terminated, the acid autocatalytic reaction gradually builds up the acidity and the reaction rate increases until a new steady state is reached. The evolution of product gases N₂, N₂O, and H₂O now performs the flushing function and maintains the acidity constant at a higher level, as shown by the entries in the t_i and $t_i +$ 15 columns of Table II. The time required for this readjustment of acidity levels is the explanation of the induction period.

Further study of correlations among the data, some of which appear anomalous at first, serves to corroborate the picture developed so far. The increase in t_i with increase in R_f for a given initial chloride concentration is explained on the basis that increase of R_f lowers the steady-state concentration of volatile acids and a longer period of time will be required to generate the acidity necessary for termination of the induction period (columns A in Table I). This view is substantiated by the fact that a constant induction period is not attained at an R_f as low as 10 cc./min. (Figure 1). The rate of removal of volatile acid at this low R_f does not balance the rate of generation through decomposition. At the next higher rate, $R_f = 25$ cc./min., a constant t_i is attained, but it will be noted that in the t_0 columns of Table II there is a small but consistent increase in acidity in contrast to the very constant values for $R_f = 50$ and 75. Apparently this is a borderline case where the R_f is not quite sufficient to maintain the acidity constant but the effect is not large enough to show up in the t_i measurements.

The pH data for pure ammonium nitrate in Table II show that these melts also develop a constant acidity on flushing. In the absence of the chloride catalyst, however, this acidity is not high enough to initiate decomposition at this temperature and these melts show no induction period. In contrast to the chloride-containing melts, the acidity is rigorously independent of R_f as well as of t_f since the acid autocatalytic reaction

is not operating in the absence of chloride. The volatile acid in pure ammonium nitrate melts is HNO_3. In the chloride-containing melts, volatilization of HCl and of Cl_2 also occurs, the rate depending on the respective Henry's law coefficients and on the melt concentrations. Although the loss of chloride was not detectable analytically, it may be sufficient to account for the fact that in Table II the pH of the 0.10 mole ratio melts at the termination of flushing (t_0) is uniformly about 0.1 unit higher at each t_f than for the 0.05 melts.

The t_i values in the B columns of Table I are independent of R_f within experimental error, in marked contrast to the data in the A columns. When chloride is added to the melt after flushing, it is added to a melt of constant acidity, irrespective of R_f, since the data in Table II show that the acidity produced by flushing pure ammonium nitrate is independent of R_f and t_f. The dependence of the induction period on both acidity and chloride concentration undoubtedly accounts for the inability of Guiochon[3] to find any consistent variation of his induction periods with chloride concentration alone.

The complete mechanism for decomposition under steady-state conditions[1] is rather complex, but the important features for the present discussion may be summarized very briefly as follows. The key step is the reaction

$$NO_2{}^+ + Cl^- \longrightarrow NO_2 + Cl$$
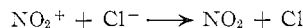
where the $NO_2{}^+$ is generated by the autoprotolysis of the HNO_3 resulting from the dissociation of the ammonium nitrate. The radicals NO_2 and Cl then initiate a set of cage reactions which lead to N_2O through nitramide as a precursor, and to N_2 by two paths with nitrosamine and chloramine as precursors. The mechanism therefore requires an initial excess of acidity to allow formation of $NO_2{}^+$.

It has been shown subsequently[5] that the mass balance is such that the N_2-producing reactions generate more acidity than they consume. The reaction is therefore potentially acid autocatalytic, except that volatilization of acid may produce a steady state at various levels of acidity depending on the conditions. In fact, the observed unsymmetrical bell-shaped rate curve has further been shown[5] to be characteristic of a second-order autocatalytic reaction in which the concentration of the reactants attains a constant value after the rate maximum. In Table II, the pH values at t_i, which represents the rate maximum R_m, and at $t_i + 15$ min., which is well into the region of spontaneous steady-state decomposition, are all constant at 2.30 ± 0.02 pH units irrespective of prior R_f or t_f. The present data, therefore, in addition to providing a mechanistic explanation for the induction period, also confirm the arguments used earlier[1] to justify an important assumption in the mechanism, namely, that the freely decomposing melts spontaneously develop a constant steady-state acidity.

(5) C. I. Colvin, Ph.D. Thesis, University of Miami, 1963.

The Niobium Iodides. Characterization of Niobium(IV) Iodide, Niobium(III) Iodide, and Triniobium Octaiodide[1]

By PYRTLE W. SEABAUGH and JOHN D. CORBETT

The condensed niobium–niobium(V) iodide system contains three intermediate phases, NbI_4, NbI_3, and Nb_3I_8, all qualitatively diamagnetic at room temperature. Niobium tetraiodide is evidently trimorphic. The weakly endothermic $\alpha \rightarrow \beta$ transition observed at *ca.* 348° only on heating is without effect in the powder pattern data. A more substantial $\beta \rightarrow \gamma$ transition occurs at 417°, and γ-NbI_4 melts incongruently at 503° to form an iodide-rich liquid and solid Nb_3I_8. Niobium(III) iodide may be obtained by thermal decomposition of NbI_4, as a sublimate from mixtures with Nb_3I_8, or as the initial product of oxidation of excess metal. The phase is apparently not an equilibrium compound in the system since it decomposes slowly and irreversibly at about 513° into iodide-rich liquid and Nb_3I_8. The phase in equilibrium with the metal is Nb_3I_8 ($NbI_{2.67 = 0.02}$), which may also be obtained by thermal decomposition of higher iodides or as the phase transported from mixtures with metal. The two lower niobium iodides show only a limited correspondence with those reported in the niobium chloride and bromide and tantalum iodide systems.

Introduction

Although several investigators[2-7] have reported synthesis of niobium(V) iodide samples of varying purity,

(1) Work was performed in the Ames Laboratory of the U. S. Atomic Commission.

(2) F. Körösy, *J. Am. Chem. Soc.*, **61**, 838 (1939).

(3) K. M. Alexander and F. Fairbrother, *J. Chem. Soc.*, 2472 (1949).

(4) R. F. Rolsten, *J. Am. Chem. Soc.*, **79**, 5409 (1957).

(5) J. D. Corbett and P. Seabaugh, *J. Inorg. Nucl. Chem.*, **6**, 207 (1958).

(6) L. A. Nisel'son and I. V. Petrusevich, *Zh. Neorgan. Khim.*, **5**, 249 (1960).

(7) D. M. Chizhikov and A. M. Grin'ko, *ibid.*, **4**, 979 (1959).