# MASS SPECTROMETER PYROLYSIS OF AMMONIUM PERCHLORATE AT LOW PRESSURE

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In an effort to further the understanding of the ammonium perchlorate (AP) decomposition and dissociation-sublimation processes, a mass spectrometer technique was employed to examine its pyrolysis behavior under high vacuum conditions where secondary reaction effects are minimized. The results of this study demonstrate that the decomposition product distributions, the rates of decomposition, and the activation energies associated with decomposition are different in a number of respects from those previously reported in studies at higher pressures.

Existing quantitative data on the "low temperature" product distribution (ref. 1) as well as kinetics of AP decomposition and sublimation (refs. 2-5) have been obtained at ambient pressures above 1 mm Hg. Under such conditions, adsorption with chemical reaction, gas phase diffusion and reaction, and sometimes artifacts of the analytical procedures used, can yield product distributions, rates of decomposition, and rates of sublimation that are not necessarily characteristic of the primary processes occurring within the solid.

A recent mass spectrometric study of low temperature AP decomposition by Heath and Majer (ref. 6) suggested that the high vacuum decomposition products may have contained significant quantities of $NO_2$ and HCl in addition to the usual major products given as $Cl_2$, $N_2O$, $O_2$ and $H_2O$ (ref. 1). The reported product distributions were semi-quantitative, however, in that uncorrected ion intensities were given. Since each AP sample was pyrolyzed in a sequence of increasing temperature steps, the respective effects of time and temperature were uncertain. The appearance of somewhat higher decomposition rates under high vacuum, however, was apparent since their sample was entirely consumed by decomposition and sublimation below 200° C. An additional contribution of their study involved determinations of the 70 e.v. $HClO_4$ fragmentation pattern, and the effects of a hot platinum filament on the heterogeneous decomposition of $HClO_4$.

Goshgarian and Walton (ref. 7) studied the low temperature pyrolysis of AP decomposition residues, in high vacuum, using a Knudsen cell mass spectrometer technique. Their relatively large sample size and Knudsen cell geometry prevented a study of the usual "low temperature" decomposition that is characterized by nucleation and growth of reaction interfaces through strained regions of imperfect order (refs. 2, 8), and is evidenced by acceleratory and deceleratory rate regimes wherein about 30 percent of the original AP decomposes (ref. 1). Instead their results apply to a system

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where the decomposition and dissociation-sublimation products of presumably highly ordered AP are in a quasi-equilibrium state within the Knudsen cavity; both heterogeneous and homogeneous gas phase reactions can occur under these conditions. Their sublimation results are discussed later in this paper.

A Bendix direct inlet probe was used in conjunction with a Bendix 12-107 time-of-flight mass spectrometer. A schematic of the sampling configuration is shown in Figure 1. About 5 mg. of Matheson Coleman and Bell reagent grade AP was loosely packed in the upper 9 x 1 mm I. D. section of glass capillary. The open end of the capillary was positioned about one inch from the 70 e.v. ionizing electron beam. Samples were generally degassed at room temperature for one day. A chromel-alumel thermocouple junction was located in the lower adjoining section of the sample capillary. A heating filament was wound uniformly about the sample and thermocouple sections of the capillary. Care was taken to assure that the same sampling configuration was maintained throughout the investigation. After the furnace was switched on, about 90 percent of the desired temperature was usually achieved in four minutes; after five minutes the set temperature was generally maintained within ±2° C throughout a run. Adjustments in heating filament voltage of less than 5 percent were usually adequate to maintain temperature; thus endothermic and exothermic pyrolysis effects did not appear to alter the actual sample temperature history appreciably.

Liquid nitrogen was employed in the conventional cold trap located above the mercury diffusion pump; pressures generally below $10^{-6}$ mm Hg. were maintained in the ion source region. The pumpdown of products following exhaustion of a sample sometimes reduced the ion intensity by nearly an order of magnitude in one minute; thus the concentration of residual gases in the ion source region was assumed to be low in comparison to the evolved gases during the major phases of pyrolysis.

Chlorine, one of the six principal decomposition products found, was used as a basis to characterize the rate of decomposition, as well as the product distribution, in a number of constant temperature pyrolyses. The appropriateness of using chlorine will be supported later by product distribution ratios that are approximately constant with time when chlorine is used as a reference.

Figure 2 illustrates the decomposition rate history obtained at 211° C, which roughly corresponds to the middle of the investigated temperature range. Argon, arising from an inherent air leak into the mass spectrometer (partially from the direct inlet probe seal), was used to normalize all the ion intensities. The resulting Argon normalized ion intensities were assumed to be proportional to the rate of decomposition in the sample capillary, since line of sight sampling and molecular flow conditions prevailed in the ion source region directly above the sample capillary. There was no indication of components other than Argon present in the m/e = 40 peak.

Perchloric acid, arising from the dissociation-sublimation process, was employed as a second means of normalizing the decomposition product ion intensities. Since the $Cl_2/HClO_4$ ratio was found to be less sensitive to minor temperature fluctuations than $Cl_2/Ar$ during the course of a run, it provided an important check on the kinetic analysis.

The acceleratory and deceleratory phases of decomposition are clearly seen in each of the rate curves of Figure 2. Accumulative integrations of the rate curves yielded fractional decompositions $\alpha$, defined as a function of time by

$$\alpha = {}^{t}\!\int_0 I\,dt / {}^{\infty}\!\int_0 I\,dt \qquad (1)$$

where I represented either $Cl_2/Ar$ or $Cl_2/HClO_4$ ion intensity ratios. Plots of $\alpha$ versus time gave the usual sigmoid fractional decomposition curves.

The acceleratory-deceleratory variation of $Cl_2/HClO_4$ with time over more than two orders of magnitude demonstrates an apparent chemical independence of the decomposition and dissociation-sublimation processes. Since $O_2$ and HCl were found to be proportional to $Cl_2$ over the most of the decomposition history as shown in Figure 4, the direct decomposition reaction (ref 6).

$$HClO_4 \rightarrow HCl + 2O_2$$

can be neglected as a source of these decomposition products under the present conditions.

Pyrolyses having "Staircase" temperature-time histories were performed to examine the temperature dependence of the sublimation process. Generally, five minutes or longer was allowed for the attainment of temperature equilibrium at each step. The rate of $HClO_4$ evolution was shown to be essentially independent of the fractional decomposition, for increasing temperatures, and a function of temperature only. Figure 3 shows the resulting Arrhenius plot for $HClO_4$ from two runs which differed significantly in temperature-time history. The derived activation energy of 21.7 K cal./mole, for the rate of dissociation-sublimation based on these data, compares favorably with 21.5 K cal./mole obtained by Bircumshaw and Phillips (ref. 4) from rate of weight loss measurements in vacuo, between 260-320° C, on AP decomposition residues. The weight loss in this case was attributed entirely to the dissociation-sublimation process

$$NH_4ClO_4\ (s) \rightleftarrows NH_3\ (g) + HClO_4\ (g)$$

The present 21.7 value also compares favorably with 22.2 K cal./mole reported by Goshgarian and Walton (ref. 7) on AP decomposition residues pyrolyzed in their Knudsen cell mass spectrometer combination.

Figure 4 shows the principal decomposition products, as a function of time, for the 211° C constant temperature run depicted in Figure 2. The time interval shown corresponds to the range of 7 - 96 percent fractional decomposition, based on the $Cl_2/HClO_4$ ratio. With the exception of water, cracking patterns (70 e.v.) and relative sensitivities were determined experimentally in order to calculate mole ratios from relative ion intensities. The sensitivity for water was estimated. The principal decomposition product ratios (based on $Cl_2$) shown in Figure 4 are interpreted as being approximately constant with time or fractional decomposition. Similar plots were obtained from several other constant temperature runs, ranging from 157 to 232° C, and the same conclusions were drawn regarding the time independence of the decomposition product ratios. Atom balances comparing total nitrogen to chlorine in the decomposition products were generally satisfied within ± 10 percent over the major portions of the respective decomposition histories. It appeared that most of the observed deviations or fluctuations in product ratios with time were due to (a) line voltage and related instrumental fluctuations, (b) slight instrumental drifts in mass discrimination due to changes in ion focus and vertical and horizontal ion deflection, (c) a small pressure and/or rate dependence of the ion intensities at high decomposition rates, and (d) the increased relative importance of subtracted background values for $H_2O^+$, $O_2^+$, and $N_2O^+$ ($CO_2^+$) at low decomposition rates.

Relatively small quantities of $N_2$ and $ClO_2$ were found as decomposition products (<0.1 $Cl_2$), and the $HNO_3^+$ peak was small in comparison to the $NO_2^+$ peak (<3%). Ions specifically sought but not observed under any of the experimental conditions included the following: $NH_4^+$ (from N-15-AP), $ClO_4^+$, $NH_4ClO_4^+$, $HClO_4 \bullet HClO_4^+$, $NOCl^+$, $N_2O_4^+$, and $Cl_2O_3^+$. Peaks attributed to $HClO_3^+$, $HClO_2^+$, $HClO^+$, and $ClO^+$ were approximately proportional to $HClO_4^+$, and were in agreement with Heath and Majer's 70 e.v. $HClO_4$ cracking pattern (ref. 6); thus these species were not considered decomposition products. On the other hand, the $ClO_3^+/HClO_4^+$ ion intensity ratio often exceeded two early in the decomposition; it then decreased to about 1.54 after completion of decomposition, which was characteristic of the above $HClO_4$ cracking pattern.

Figure 5 represents the temperature dependence of the decomposition product distribution. It should be emphasized here that the product ratios shown are approximate time-averaged values from the constant temperature runs; preferential weight was given to data obtained in the most reliable regions of each run. Nitrogen-15-AP was used to permit a semi-independent determination of $NO_2$ and $N_2O$; this run was especially important since (a) it yielded a value for $N_2O$ (m/e = 46) in the absence of $CO_2$ (m/e = 44) and (b) it provided an important background correction for $CO_2$ formation in the normal N-14-AP runs where $N_2O$ was evaluated at m/e = 44.

As a first approximation it is concluded in Figure 5 that the mole ratios $N_2O/Cl_2$, $HCl/Cl_2$, and $NO_2/Cl_2$ are equal to unity over the investigated temperature range. Figure 6 shows the resulting stoichiometry, since an atom balance forces the $O_2/Cl_2$ mole ratio to be 7/4; this value compares favorably with experimental $O_2/Cl_2$ values of about 2.0 in Figure 5.

It is concluded that the derived stoichiometry in Figure 6 is a more appropriate description of orthorhombic AP decomposition under high vacuum conditions, where secondary reaction effects are minimized; this is in comparison, of course, to the Bircumshaw and Newman stoichiometry (ref. 1) which was derived from data obtained in the millimeter pressure range at temperatures below 300° C. Bircumshaw and Newman detected the presence of $NO_2$ and HCl, using a wet analysis technique, but did not consider either to be present in sufficient quantities to warrant their inclusion in the stoichiometry. On the other hand, quantitative gas chromatographic results, presented by Rosser, Inami, and Wise at this conference, indicated that significant quantities of $HNO_3$ (which probably resulted from the reaction of $NO_2$ and $H_2O$ in their condensible products fraction) and HCl were formed as decomposition products at millimeter pressures and temperatures generally below 300° C.

A kinetic analysis of the deceleratory rate periods yielded some interesting results that pertain to the competition between decomposition and dissociation-sublimation. Figures 7 and 8 illustrate the application of the Prout-Tompkins equation (9)

$$\ln [\alpha/(1 - \alpha)] = kt + c \qquad (2)$$

The fractional decomposition $\alpha$ was determined by accumulative graphical integration of smoothed rate curves (such as Figure 2) according to Equation 1. The Prout-Tompkins equation was found to fit the $\alpha$ versus t plots quite well in the region $0.50 < \alpha < 0.98$, for $\alpha$ 's defined by either $Cl_2/Ar$ or $Cl_2/HClO_4$.

A simplified version of the Avrami-Erofeyev equation for three dimensional growth following nucleation (ref. 3)

$$- \ln(1 - \alpha) = (kt)^3 + c \qquad (3)$$

was also applied, but the region of fit was no better than with the Prout-Tompkins equation.

Figure 9 shows the resulting Arrhenius plot for the deceleratory period rate constants. These are more than an order of magnitude higher than corresponding Prout-Tompkins values obtained by Bircumshaw and Newman from accumulatory runs, where final pressures of noncondensibles reached about 2 mm Hg. Careful checking of the rate analyses, and two further observations, have provided strong evidence that the transition in activation energy (from 10.4 to 55. K cal./mole with increasing temperature) was a valid experimental fact. It should be pointed out, however, that the respective values may be in error by as much as 20 percent due to the limited data.

First, the three lower temperature decompositions at 211° C and below were complete before the decomposition residue was consumed by sublimation. The three higher temperature runs, to the left of the transition, were characterized by a simultaneous termination of decomposition and sublimation.

Secondly, time-averaged mole ratios of $Cl_2$ to $HClO_4$ shown in Table I, were computed as

$$\overline{Cl_2/HClO_4} = \frac{1}{t_{0.98} - t_o} \int_{\alpha = 0}^{\alpha = 0.98} (Cl_2/HClO_4) \, dt$$

An appropriate relative sensitivity for $HClO_4$, required for mole ratio calculations, was obtained by finding a value which satisfied the assumption $NH_3/HClO_4 = 1$ in the final phases of the constant temperature and staircase temperature-time runs; here the $OH^+$ intensity was sufficiently small that the $NH_3^+$ contribution could be reliably calculated. The required sensitivity for $NH_3$ was determined experimentally when $Cl_2$ and the other gases were run. Prout-Tompkins deceleratory period rate constants, based on the $Cl_2/HClO_4$ ratio, are also given in Table I.

## TABLE I

Some Chemical and Kinetic Properties of the Constant Temperature Pyrolyses of Ammonium Perchlorate

| Temperature, °C | $\overline{Cl_2/HClO_4}$ | k, min.$^{-1}$ |
|---|---|---|
| 157 | 15.8 | 0.0140 |
| 183 | 9.66 | 0.0331 |
| 211 | 7.19 | 0.0540 |
| 221 | 3.24 | 0.130 |
| 232 | 3.78 | 0.572 |
| 232 | 3.92 | 0.511 |
| 204(N-15-AP) | 4.02 | 0.438 |

It can be seen that the time-averaged mole ratio, $\overline{Cl_2/HClO_4}$, decreased with increasing temperature for the three low temperature runs; the three higher temperature runs, however, exhibited nearly constant ratios. The N-15-AP run at 204° C exhibited the same characteristics as the higher temperature normal AP runs; the higher rate constant may have been due partially to the smaller crystal size of this sample.

In general, the activation energy transition at low pressures appears to define a transition temperature, for a given sample geometry, at which competition between decomposition and sublimation alters the apparent kinetics of the decomposition process. At ambient pressures of a few millimeters and higher, this transition would be shifted to higher temperatures. The results obtained below the transition suggest that the decomposition of strained intergranular material is characterized by a substantially lower activation energy, under high vacuum conditions, than the usual 25-30 K cal./mole observed at higher pressures. The difference in this case may be due to enhanced desorption and/or diffusion of decomposition products from these regions. The results obtained above the transition suggest that highly ordered unstrained material participated significantly in the decomposition at these higher temperatures; the competition between sublimation and decomposition for strained intergranular material would appear to be an important factor here.

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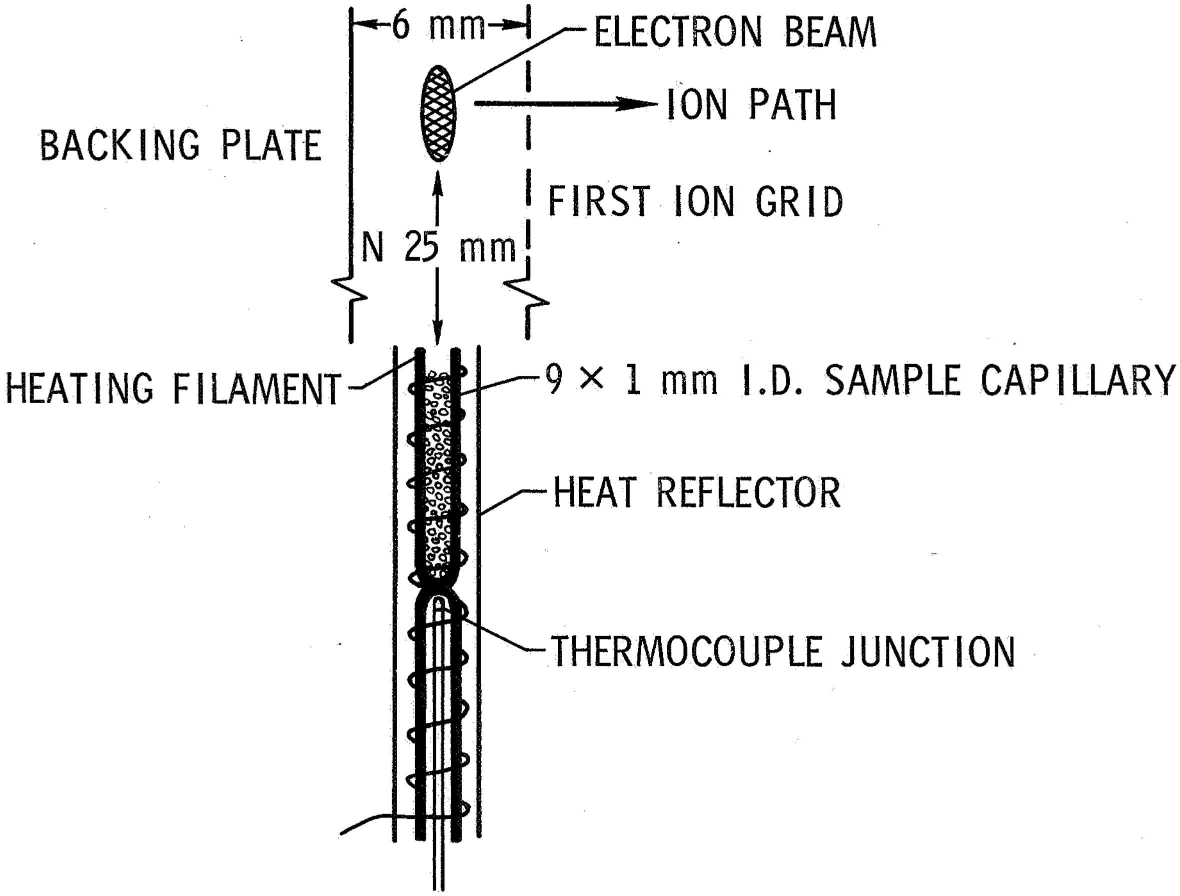

Figure 1.- Sampling configuration.

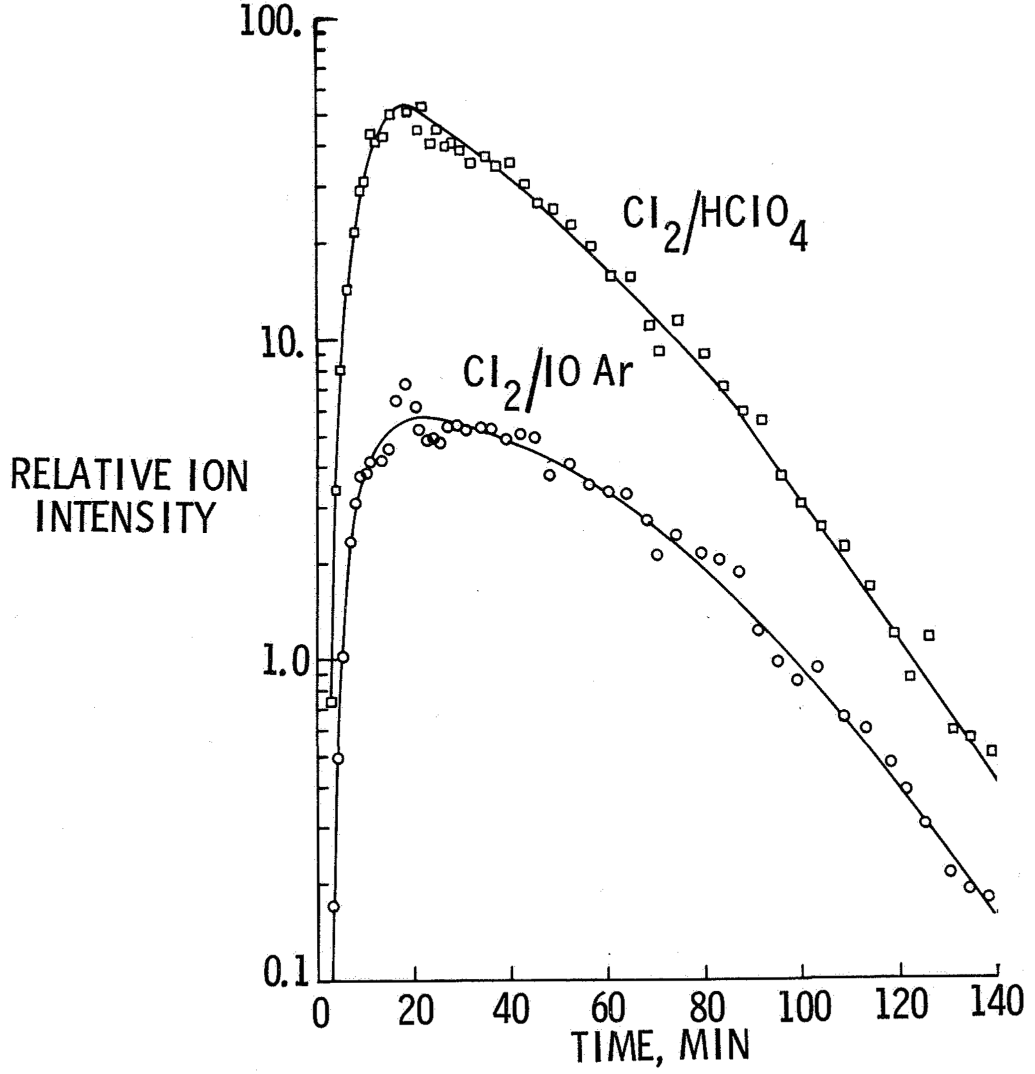

Figure 2.- Time dependence of chlorine formation during decomposition at 211° C.

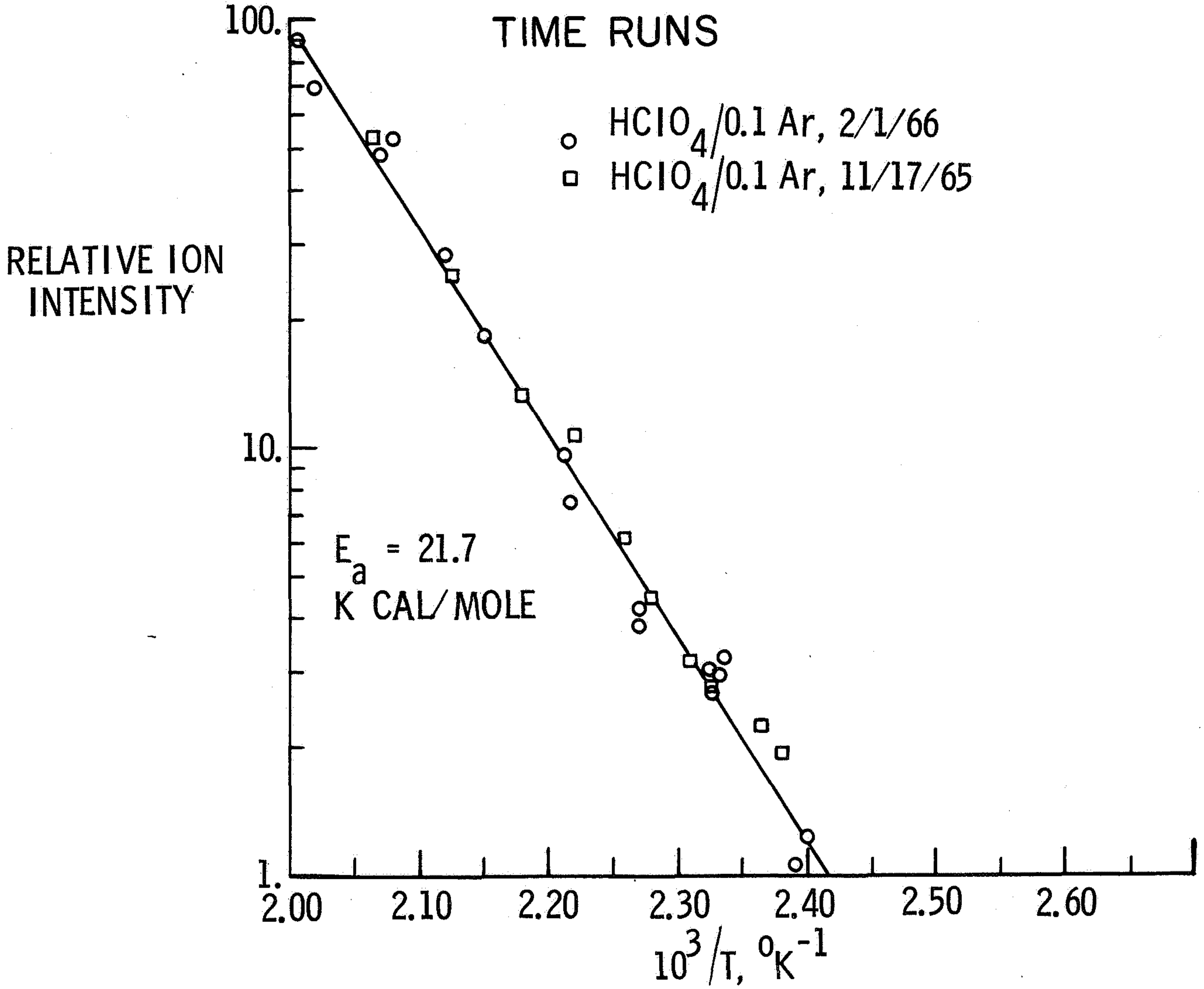

Figure 3.- Arrhenius plot for perchloric acid formation in "staircase" temperature-time pyrolyses.

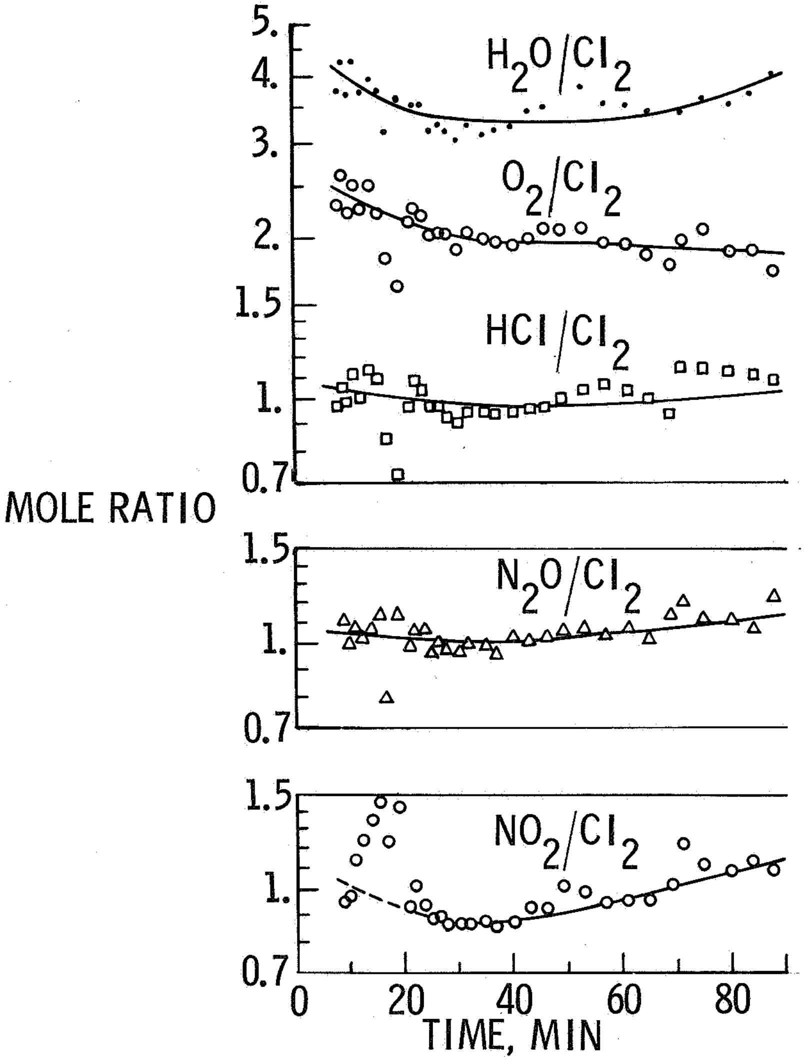

Figure 4.- Decomposition product history at 211° C.

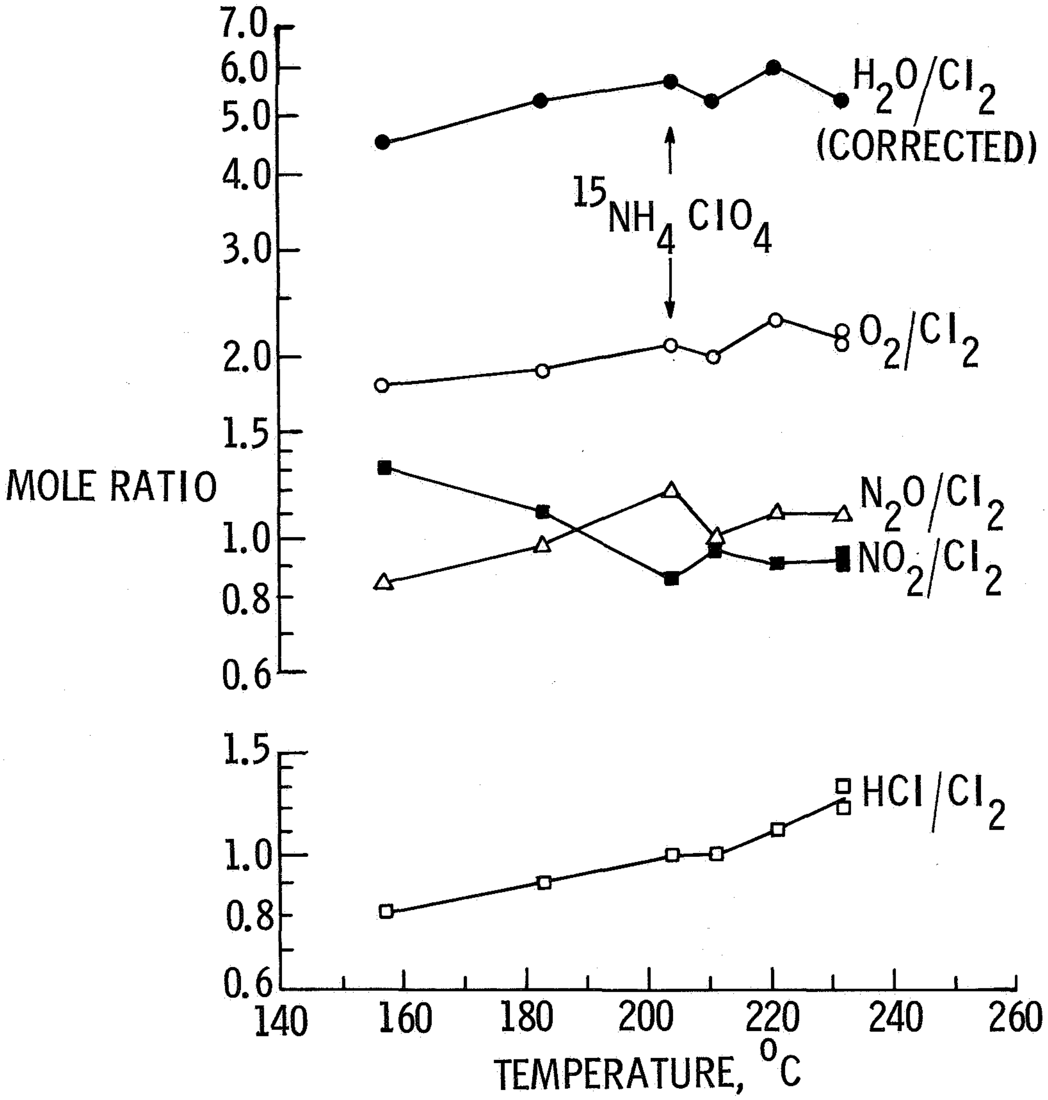

Figure 5.- Time-averaged decomposition product histories from constant temperature pyrolyses.

| PRESENT WORK | BIRCUMSHAW AND NEWMAN |
|---|---|
| $12\ NH_4ClO_4 =$ | $12\ NH_4ClO_4 =$ |
| $4\ Cl_2$ | $6\ Cl_2$ |
| $4\ N_2O$ | $6\ N_2O$ |
| $4\ HCl$ | — |
| $4\ NO_2$ | — |
| $7\ O_2$ | $9\ O_2$ |
| $22\ H_2O$ | $24\ H_2O$ |

DIFFERENCE EXPRESSION:

$$2HCl + 2NO_2 \equiv Cl_2 + O_2 + N_2O + H_2O$$

Figure 6.- Stoichiometry comparison.

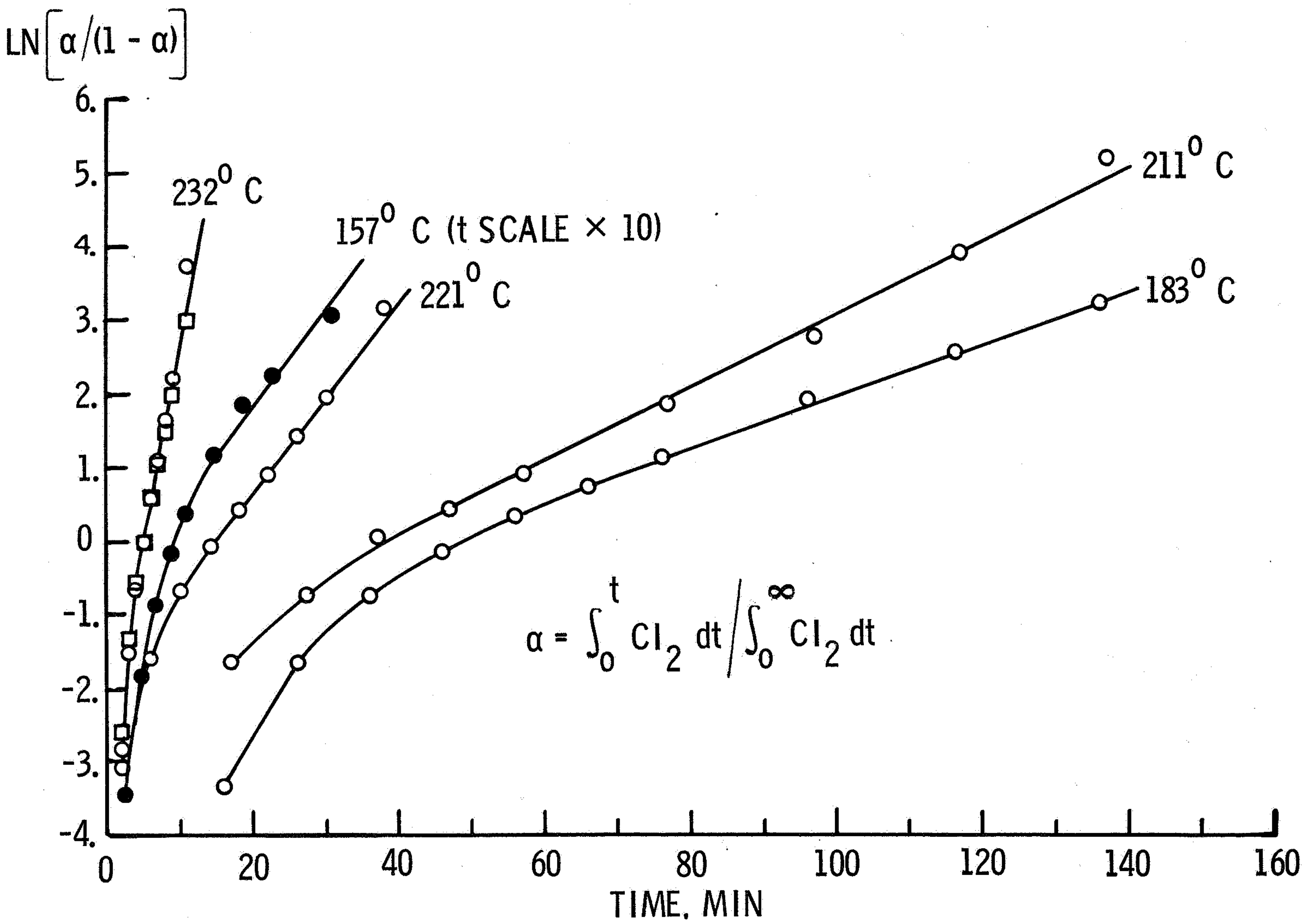

Figure 7.- Kinetic analysis according to the Prout-Tompkins relationship.

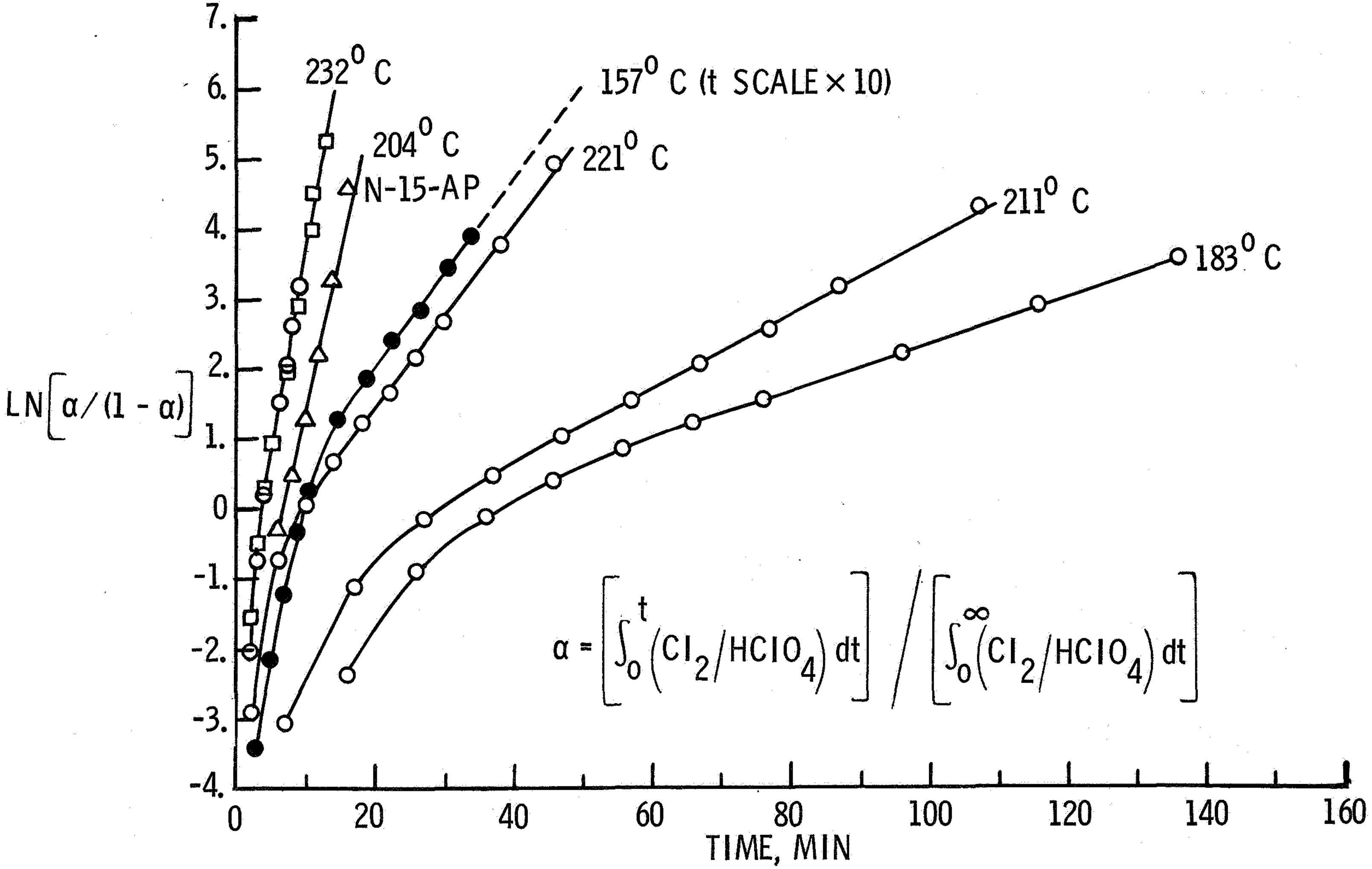

Figure 8.- Kinetic analysis according to the Prout-Tompkins relationship.

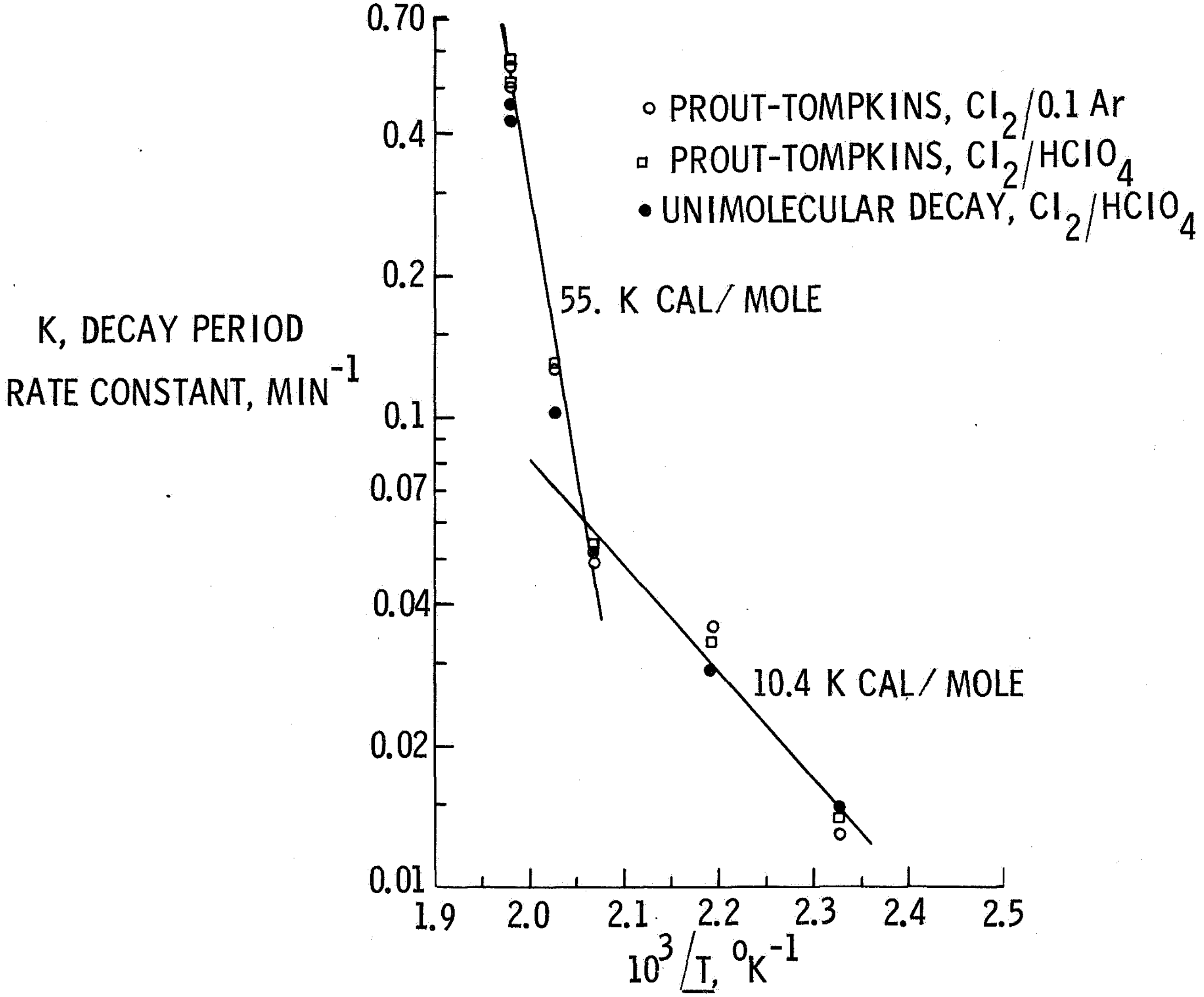

Figure 9.- Arrhenius plot for deceleratory rate constants.

NASA-Langley, 1966