# THE THERMAL DECOMPOSITION OF NITRYL PERCHLORATE

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The thermal decomposition of solid nitryl perchlorate (NO<sub>2</sub>ClO<sub>4</sub>) has been studied over a temperature range of 69.99 to 112.3°. The products have been analyzed. The fractional rates of decomposition are independent of sample size. The theory of Mampel gives an excellent fit to the data from 0.5 to 95% decomposition. The rate constants are  $k_{\text{initiation}} = 10^{12.6 \pm 0.6} e^{-23.6 \pm 0.8 \text{ kcal/mole/}RT} \text{ sec.}^{-1}$  and  $k_{\text{growth}} = 10^{12.5 \pm 0.6} e^{-27.6 \pm 0.9 \text{ kcal/mole/}RT}$  sec.

## Introduction

Numerous studies have been made on thermal decomposition of ionic solids.<sup>1</sup> Some progress has been made in correlating the observed behavior to chemical reactions in the case of the azides<sup>2</sup>; however, these systems are complicated by the presence of a secondary solid phase as one of the products. The kinetics of the ammonium perchlorate decomposition have been extensively studied<sup>3-6</sup> and all of the products are gaseous. It was thought that the kinetics of the decomposition of another ionic perchlorate giving only gaseous products would be of considerable interest. Nitryl perchlorate was chosen as the compound for investigation as it was available and decomposed in a reasonable temperature region. This investigation is on the bulk powder. It is hoped that a suitable solvent can be found so that ultimately data can be gathered on single crystals. Considerable care was taken in the gathering of the data so that differential rates could be obtained as these furnish more sensitive criteria in analyzing the data.

#### Experimental

Nitryl Perchlorate.—This material was obtained from the Callery Chemical Co., Callery, Pa. The material contained less than one-half cation, mole per cent NO<sup>+</sup> as determined by a KMnO<sub>4</sub> titration. The particle size, as seen under a microscope, was about 10  $\mu$  or less. This material was transferred in a drybox that did not fume TiCl<sub>4</sub>.

Nitrogen Dioxide.—This material was tank material and was purified by distillation and by bubbling oxygen through the liquid at 0°. Absorption coef. at 436 m $\mu = (2.01 \pm 0.03) \times 10^5$  cc./mole/cm.

**Chlorine.**—The chlorine was tank material and was purified by distillation and storage over CaO at  $-78^{\circ}$ . Absorption coef. at 330 m $\mu$  = (6.53 ± 0.04) × 10<sup>4</sup> cc./mole/cm.

**Chlorine Dioxide**.—The chlorine dioxide was prepared by the method listed in ref. 7. Absorption coefficient at 454 m $\mu$  =  $(2.25 \pm 0.37) \times 10^6$  cc./mole/cm.

Apparatus.—The apparatus consisted of a Pyrex vacuum line, the various volumes being calibrated. A pressure transducer was connected to the line. One end of the vacuum line had a standard ball joint to which a Pyrex reaction tube containing the sample could be connected. When the reaction tube was connected to the line, the bottom portion of the tube, with the sample, was immersed in an oil bath. All joints were lubricated with Kel-F stopcock grease. With the exception of the reaction tube and the pressure transducer, all of the system was at room temperature.

Pressures were measured with a Consolidated Engineering Corporation, No. 4-312, 0–25 p.s.i.a. transducer, which was there

(1) W. E. Garner, Ed., "The Chemistry of the Solid State," Butterworth, London, 1955. See particularly chapters 7, 8, and 9.

(2) F. P. Bowden and A. D. Yoffe, "Fast Reactions in Solids," Academic Press, Inc., New York, N. Y., 1958.

(3) A. K. Galway and P. W. M. Jacobs, J. Chem. Soc., 837 (1959).
(4) A. K. Galway and P. W. M. Jacobs, Proc. Roy. Soc. (London), A254, 455 (1960).

(5) L. L. Bicumshaw and B. H. Newman, ibid., A227, 115 (1954).

(6) L. L. Bicumshaw and B. H. Newman, *ibid.*, A227, 228 (1955).

(7) "Handbuch der Praparativen Anorganischen Chemie," Herausgegeben

von Georg Brauer, Band I, Ferdinand Enke Verlag, Stuttgart, 1960, p. 274.

mostated at 29.6  $\pm$  0.1° and calibrated against an absolute manometer. A stabilized d.c. power source was used for the voltage input to the transducer. The transducer output was partially bucked out with a 0.1- $\mu$ v. potentiometer; the remaining signal was amplified with a d.c. microvolt amplifier and sent to a recorder. Readings corresponding to  $\pm$ 0.1  $\mu$ v. transducer output could be made on the recorder. Noise made these readings uncertain to  $\pm$ 0.2  $\mu$ v. The long time stability of the system was  $\pm$ 1  $\mu$ v. The transducer had sensitivity of about 60 mm./ mv. output. The transducer was electrically calibrated before each run. The response of the transducer was linear to  $\pm$ 0.1% over the region of the measurements. The recorder time could be read to  $\pm$ 1 sec.

The reaction tube was inserted to a depth of about 5 cm. into an oil bath. The temperature of this bath could be controlled to  $\pm 0.02^{\circ}$ . The copper-constantan thermocouple used to measure the temperature was calibrated against the melting point of N.B.S. Calorimetric benzoic acid (temp. taken as 122.38°) and against the NaBr  $2H_2O = NaBr + 2H_2O$  transition (temp. taken as 50.67°). The correction was linear in mv. output and was  $\pm 0.27^{\circ}$  at 122.38°.

A Beckman DK-2 recording spectrophotometer was used with a 10-cm. cell for all spectral measurements. Corrections for N<sub>2</sub>O<sub>4</sub> absorption were made<sup>8</sup> at 330 m $\mu$ , as well as corrections for Cl<sub>2</sub> absorption at 436 m $\mu$ .<sup>9</sup>

**Products of the Reaction**.—For this series of runs, liquid nitrogen was placed around two traps in the system and the system's volume was recalibrated to correct for the apparent increase in volume. The traps were between the reaction tube and the collection volume.

The decompositions were carried out in the same manner as for the rate runs except that the recorder was used as a null instrument.

At the completion of the decomposition, the pressure of noncondensables in the system was measured and a sample of the gas was analyzed on a mass spectrometer. The condensed material was separated into three fractions. The first fraction was volatile at  $-112^{\circ}$ , the second fraction was volatile at  $-78^{\circ}$ , and the third fraction was nonvolatile at  $-78^{\circ}$ .

Fraction Noncondensable at Liquid Nitrogen Temperature.— This fraction was analyzed on a mass spectrometer and was at least 99% O<sub>2</sub>. It contained no N<sub>2</sub>.

Fraction Volatile at  $-112^{\circ}$ .—The total pressure of this fraction was measured in a calibrated volume. The gas was then sparked with a Tesla coil until there was no further increase in pressure. All condensables were frozen out at liquid N<sub>2</sub> temperature and the residual noncondensable pressure was recorded. The noncondensable material was assumed to be O<sub>2</sub>. The noncondensable material was pumped out. The condensables were allowed to vaporize into the calibrated volume and their pressure measured. Samples, at known pressures, were subjected to spectrophotometric analysis.

**Results.**—The only spectral species observable before sparking were  $ClO_2$  and  $Cl_2$ . Although pure samples of  $ClO_2$  could be analyzed quantitatively on spectrophotometer, mixtures obtained from the decomposition were unstable and did not give consistent results upon expansion. The spectra were only used for qualitative identification. After sparking,  $Cl_2$  and  $NO_2$  were the only spectrally observable species. From the pressure before sparking, the pressure after sparking, the pressure of noncondensables after sparking, and the quantitative amounts of  $Cl_2$  and  $NO_2$  observed in the spectrophotometric cell, the only reasonable original composition derived for this fraction was

(9) N. S. Bayliss and R. C. Aickin, Trans. Faraday Soc., 33, 1333 (1937).

<sup>(8)</sup> T. C. Hall and F. E. Blacet, J. Chem. Phys., 20, 1745 (1952).

Cl<sub>2</sub>, ClO<sub>2</sub>, NO<sub>3</sub>Cl. The chlorine made up about 90% of this fraction although the exact values varied from run to run.

A mass spectrum of a sample before sparking showed no  $N_2O$ . The Fraction Volatile at  $-78^{\circ}$ .—This fraction was treated in the same manner as the  $-112^{\circ}$  volatile fraction. The only reasonable composition was  $ClO_2$  and  $NO_3Cl$  with small amounts of  $Cl_2$  present in one sample.

The Fraction Nonvolatile at  $-78^{\circ}$ .—This fraction was found to contain only one absorbing species—NO<sub>2</sub>. Upon long standing or upon sparking, the pressure and NO<sub>2</sub> content both increased. A mass spectrometer showed no species but oxides of nitrogen. The NO<sub>2</sub> did not account for all of the pressure. The residual pressure after correction for N<sub>2</sub>O<sub>4</sub><sup>10</sup> was assumed to be N<sub>2</sub>O<sub>5</sub>. Quantitative decomposition of the N<sub>2</sub>O<sub>5</sub> was not possible as both long standing and sparking produced some NO, as deduced from a blue deposit at liquid nitrogen temperature.

The results of the analyses are given in Table I. The results are quite variable, as might be expected from a mixture of such species,  $ClO_2$  and  $N_2O_5$  being unstable and  $NO_2$  and  $ClO_2$  reacting to give  $NO_3Cl.^{11}$  With the exception of the N atom balance, the material is all accounted for within experimental error.

## TABLE I

Moles of Product per Mole of Nitryl Perchlorate at 106.97°

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	<del>~-</del>	Run	
Product	A	в	С
$O_2$	1.830	1.739	1.843
NO3Cl	0.148	0.091	0.153
$ClO_2$	.148	.169	.115
$Cl_2$	.354	.351	.372
$\mathrm{NO_2}^a$	.804	.563	.773
$N_2O_5$	.000	.149	.013
$\Sigma$ N atoms	.952	.952	.952
$\Sigma$ O atoms	6.008	5.960	5.941
$\Sigma$ Cl atoms	1.004	0.962	1.000
	NO LOOTO	<b>`</b>	

<sup>a</sup> Total NO<sub>2</sub> from NO<sub>2</sub> +  $2(N_2O_4)$ .

Procedure During a Run.—The reaction tube was evacuated, weighed, and then taken into the drybox where a sample (0.3 to0.7 g.) of nitryl perchlorate was placed in it. Care was taken not to remove any grease from the joints. The tube was reassembled and the stopcock was closed. The tube was taken out of the box and placed on a vacuum line and continuously evacuated at  $\sim 1 \mu$  for 16 hr. The tube was closed, taken off of the line, and weighed to give a rough sample weight. The pressure measuring system was calibrated and the recorder was started. A metal tube with a closed end was inserted in the thermostated bath and the reaction tube was connected to the system with the sample inside the metal tube. This arrangement kept the sample below the bath temperature while the system was being evacuated. When the system had evacuated to  $\sim 0.01$  mm. or less, the system was sealed. The shield was removed from around the sample and simultaneously the reaction tube was opened to the system. This point was marked on the recorder and was taken as zero time. The pressure was continuously recorded as a function of time on the recorder. Periodically the potentiometer was readjusted to buck out the additional voltage from the transducer; in this way the full sensitivity and full range of the transducer system could be used.

At the completion of the run ( $\sim 90\%$  decomposition) the reaction tube was closed and removed from the system. The tube was carefully cleaned and weighed. The tube was opened to the air and the remaining sample was decomposed over a flame. The sample tube was evacuated and weighed to give an empty weight. This second weight was taken as the true empty weight and usually did not differ from the first empty weight by more than a few milligrams.

During the decomposition, some sublimation to the region of the bath-air interface occurred. The total amount of sublimation was very small (visually only a thin film).

It is interesting to note that even at 90% decomposition the visible volume of solid in the reaction tube had changed very little from the original size.

# The Data

From the final pressure of the gases and the weight loss of the sample, the amount of gas per gram of decomposition was computed. This ratio was assumed to be constant over the whole course of the reaction. No attempt was made to correct for any reactions occurring in the gas phase. No correction was made for the  $NO_2 \implies N_2O_4$  equilibrium as a trial test in the worst case gave results for corrected and uncorrected data that differed by less than the experimental error.<sup>12</sup> The fraction decomposed,  $\alpha$ , was computed as a function of time. Suitable intervals of time were chosen and  $\Delta \alpha / \Delta t$  was computed and considered as a derivative.

Plots of  $\alpha$  vs. t or  $d\alpha/dt$  vs. t did not show any variation with a factor of 10 variation in sample size, although there were apparent minor shifts in the time axis from run to run. When the data were plotted as  $d\alpha/dt$  vs.  $\alpha$ , the agreement was excellent (Fig. 1).

The  $\alpha$  vs. t plots were typical sigmoid curves with inflection points at  $\alpha \sim 0.2$ , consequently, the  $d\alpha/dt$ vs.  $\alpha$  curves were skewed bell shaped curves with a maximum in  $d\alpha/dt$  at  $\alpha \sim 0.2$ . The latter portions of the  $d\alpha/dt$  vs.  $\alpha$  plots, past the maximum, showed a linear decrease of  $d\alpha/dt$  with increasing  $\alpha$ .  $d\alpha/dt$ extrapolated to zero at  $\alpha = 1$ . In the early portion of the plots  $\alpha$  was very nearly proportional to  $t^4$  with an induction period. During this induction period, a slow, nearly constant evolution of gas was observed. The total gas evolution corresponded to about 0.5% decomposition. In a sample from a new batch of material, this initial gas evolution corresponded to only  $^{1/_{20}}\%$  decomposition. The rates for a 5-g. sample agreed within experimental error with the data presented here and agreed with the extrapolation of the present data from 1/2 and 1/20% after correction for the initial gas evolution. The over-all form of the curves suggests a first-order initiation of nuclei followed by three-dimensional growth of these nuclei. The gas evolution early in the run may be due to decomposition of absorbed gases.

One run was periodically interrupted by quenching to room temperature. The system was then evacuated and after 15 to 100 min., the sample was reinserted in the bath and more data were taken. The data when plotted as  $d\alpha/dt vs. \alpha$  showed, except for warm-up periods of about 200 sec., complete agreement with uninterrupted runs at the same temperature (Fig. 2). This behavior of the interrupted runs suggests that the nuclei, once formed, are stable, and that the rate is not controlled by a steady state. The total pressure in the system during the interrupted runs was never greater than that corresponding to 5% decomposition. This fact plus the independence of the data on sample size show that the product gases have little or no effect on the decomposition.

# Discussion

Mampel<sup>13</sup> has developed an elegant treatment for the decomposition of uniform spherical particles. The particles are assumed to be randomly initiated on the surface and the nuclei so formed are assumed to grow as

<sup>(10)</sup> F. H. Verhoek and F. Daniels, J. Am. Chem. Soc., 53, 1250 (1931).
(11) H. Martin, Angew. Chem., 70, 97 (1958).

<sup>(12)</sup> The total moles of gas evolved per mole of reactant lost appear within the limits of weighing error—to be constant  $\pm 10\%$ . The nature of the mixture is such that constancy of composition is not to be expected.

<sup>(13)</sup> K. L. Mampel, Z. physik. Chem., A187, 235 (1940).

sections of spheres into the particles. The radii of the nuclei are assumed to grow linearly with time. A sub-surface at depth z beneath the geometrical surface of a particle is considered and the average fractional decomposition is computed for all such surfaces throughout the mass. An integration over all z is performed to obtain the total fractional decomposition for the whole mass. In terms of dimensionless parameters Mampel's solution is

$$\alpha = 3 \int_0^x (1-\xi)^2 \left\{ 1 - e^{-\frac{x}{4} \left[ \frac{x^3}{3} - x\xi^2 + \frac{2}{3} \frac{\xi^3}{1-\xi} \right]} \right\} d\xi} \\ \text{for } 0 \le x \le 1 \quad (1a)$$
$$\alpha = 3 \int_0^{2-x} (1-\xi)^2 \left\{ 1 - e^{-\frac{x}{4} \left[ \frac{x^3}{3} - x\xi^2 + \frac{2}{3} \frac{\xi^3}{1-\xi} \right]} \right\} d\xi + \frac{1}{2} \left\{ 1 - e^{-\frac{x}{4} \left[ \frac{x^3}{3} - x\xi^2 + \frac{2}{3} \frac{\xi^3}{1-\xi} \right]} \right\} d\xi + \frac{1}{2} \left\{ 1 - e^{-\frac{x}{4} \left[ \frac{x^3}{3} - x\xi^2 + \frac{2}{3} \frac{\xi^3}{1-\xi} \right]} \right\} d\xi + \frac{1}{2} \left\{ 1 - e^{-\frac{x}{4} \left[ \frac{x^3}{3} - x\xi^2 + \frac{2}{3} \frac{\xi^3}{1-\xi} \right]} \right\} d\xi + \frac{1}{2} \left\{ 1 - e^{-\frac{x}{4} \left[ \frac{x^3}{3} - x\xi^2 + \frac{2}{3} \frac{\xi^3}{1-\xi} \right]} \right\} d\xi + \frac{1}{2} \left\{ 1 - e^{-\frac{x}{4} \left[ \frac{x^3}{3} - x\xi^2 + \frac{2}{3} \frac{\xi^3}{1-\xi} \right]} \right\} d\xi + \frac{1}{2} \left\{ 1 - e^{-\frac{x}{4} \left[ \frac{x^3}{3} - x\xi^2 + \frac{2}{3} \frac{\xi^3}{1-\xi} \right]} \right\} d\xi + \frac{1}{2} \left\{ 1 - e^{-\frac{x}{4} \left[ \frac{x^3}{3} - x\xi^2 + \frac{2}{3} \frac{\xi^3}{1-\xi} \right]} \right\} d\xi + \frac{1}{2} \left\{ 1 - e^{-\frac{x}{4} \left[ \frac{x^3}{3} - x\xi^2 + \frac{2}{3} \frac{\xi^3}{1-\xi} \right]} \right\} d\xi + \frac{1}{2} \left\{ 1 - e^{-\frac{x}{4} \left[ \frac{x^3}{3} - x\xi^2 + \frac{2}{3} \frac{\xi^3}{1-\xi} \right]} \right\} d\xi + \frac{1}{2} \left\{ 1 - e^{-\frac{x}{4} \left[ \frac{x^3}{3} - x\xi^2 + \frac{2}{3} \frac{\xi^3}{1-\xi} \right]} \right\} d\xi + \frac{1}{2} \left\{ 1 - e^{-\frac{x}{4} \left[ \frac{x^3}{3} - x\xi^2 + \frac{2}{3} \frac{\xi^3}{1-\xi} \right]} \right\} d\xi + \frac{1}{2} \left\{ 1 - e^{-\frac{x}{4} \left[ \frac{x^3}{3} - x\xi^2 + \frac{2}{3} \frac{\xi^3}{1-\xi} \right]} \right\} d\xi + \frac{1}{2} \left\{ 1 - e^{-\frac{x}{4} \left[ \frac{x^3}{3} - x\xi^2 + \frac{2}{3} \frac{\xi^3}{1-\xi} \right]} \right\} d\xi + \frac{1}{2} \left\{ 1 - e^{-\frac{x}{4} \left[ \frac{x^3}{3} - x\xi^2 + \frac{2}{3} \frac{\xi^3}{1-\xi} \right]} \right\} d\xi + \frac{1}{2} \left\{ 1 - e^{-\frac{x}{4} \left[ \frac{x^3}{3} - x\xi^2 + \frac{2}{3} \frac{\xi^3}{1-\xi} \right]} \right\} d\xi + \frac{1}{2} \left\{ 1 - e^{-\frac{x}{4} \left[ \frac{x^3}{3} - x\xi^2 + \frac{2}{3} \frac{\xi^3}{1-\xi} \right]} \right\} d\xi + \frac{1}{2} \left\{ 1 - e^{-\frac{x}{4} \left[ \frac{x^3}{3} - x\xi^2 + \frac{2}{3} \frac{\xi^3}{1-\xi} \right]} \right\} d\xi + \frac{1}{2} \left\{ 1 - e^{-\frac{x}{4} \left[ \frac{x^3}{3} - x\xi^2 + \frac{2}{3} \frac{\xi^3}{1-\xi} \right]} \right\} d\xi + \frac{1}{2} \left\{ 1 - e^{-\frac{x}{4} \left[ \frac{x^3}{3} - x\xi^2 + \frac{2}{3} \frac{\xi^3}{1-\xi} \right]} \right\} d\xi + \frac{1}{2} \left\{ 1 - \frac{x^3}{3} - \frac{x^3}{3}$$

$$3 \int_{2-x}^{1} (1-\xi)^{2} \left\{ 1 - e^{-3} \right\}^{1-x} + \xi < 1 = 0$$
 for  $1 \le x \le 2$  (1b)

$$\alpha = 1 - \frac{3}{2} \left(\frac{3}{\varkappa}\right)^{7/2} e^{-\varkappa(x-1)} \times \left[\frac{\sqrt{\varkappa}}{3} e^{\frac{3}{3}} - \int_{0}^{\sqrt{\frac{1}{3}}} e^{n^{2}} dn\right] \text{for } x \ge 2 \quad (1c)$$

where

 $\begin{array}{l} \alpha &= \text{fractional decomposition} \\ x &= \frac{k_{\mathrm{g}}t}{R}; \ n^2 = \frac{\pi}{3} \ (1 - 2\xi + \xi^2); \ \xi = Z/R \\ k_{\mathrm{g}} &= \text{growth rate constant} \\ R &= \text{radius of a particle} \\ t &= \text{the time} \\ \varkappa &= \frac{4\pi k_1 N_0 R^2}{k_{\mathrm{g}}/R}; \ k_1 = \text{initiation rate constant} \\ \hline \end{array}$ 

Equation 1a applies for short time and reduces for very short time to  $\alpha$  proportional to  $t^4$ . Equation 1b gives the intermediate portion and spans the inflection point in the  $\alpha vs. t$  curve. Equation 1c is the first-order decay portion at long time. As can be seen, both  $\alpha$  and its first derivative are continuous at the boundaries of the three equations. For the purpose of analysis of the data, it is more convenient to consider the first derivative. This choice also eliminates a cumulative error introduced in  $\alpha$  by the gas evolution during the induction period. Let

$$\frac{1}{4\pi k_i N_0 R^2} \frac{\mathrm{d}\alpha}{\mathrm{d}t} = F(x, \varkappa)$$

Then differentiation and rearrangement of eq. 1a, 1b, and 1c give

$$F(x,x) = \frac{3}{4} \int_0^x (1-\xi)(x^2-\xi^2) e^{-\frac{x}{4} \left[\frac{x^3}{3}-x\xi^2+\frac{2}{3}\xi^3\right]} d\xi$$
  

$$0 \le x \le 1 \quad (2a)$$
  

$$F(x,x) = \frac{3}{4} \int_0^{2-x} (1-\xi)(x^2-\xi^2) e^{-\frac{x}{4} \left[\frac{x^3}{3}-x\xi^2+\frac{2}{3}\xi^3\right]} d\xi$$
  

$$+ 3\sqrt{\left(\frac{3}{x}\right)^3} e^{-x(x-1)} \int_0^{(x-1)\sqrt{\frac{x}{3}}} n^2 e^{n^2} dn$$
  

$$1 \le x \le 2 \quad (2b)$$



Fig. 1.— $d\alpha/dt vs. \alpha$  at 112.38° showing the agreement between two separate runs (open and closed circles). The points have been selected.



Fig. 2.— $d\alpha/dt vs. \alpha$  at 101.97° showing the effect of interruption upon the data. The open circles are from an uninterrupted run. The closed circles are from an interrupted run. The interruptions occurred after the first point and between every other point thereafter. The points have been selected.

$$F(x,x) = 1 - \alpha; \quad x \ge 2 \tag{2c}$$

Equations 2a and 2b can be expanded in series and evaluated for various x and x.

These equations were fitted to the nitryl perchlorate decomposition data in the following fashion. The data past the maximum in the rate were plotted as  $d\alpha/dt vs. \alpha$ . The straight line obtained (Fig. 3) has a slope from eq. 2c of  $-4\pi k_i N_0 R^2$ . This line was forced through the point  $d\alpha/dt = 0$ ,  $\alpha = 1.0$ . Derivations between the high rate portions and this point varied positive or negative from run to run and appear to be due to room temperature fluctuations (causing pressure fluctuations). The parameter  $(1/4\pi k_i N_0 R^2)(d\alpha/dt)$  could then be calculated for the data earlier in time than the maximum rate. The parameter was compared with the computed  $F(x, \varkappa)$ .  $F(x, \varkappa)$  was computed at 0.1 unit intervals in x from x = 0 to x = 2.0 for a range of  $\varkappa$ .

Except near the maximum in  $F(x,\kappa)$  this function is not a strong function of  $\kappa$ . The maximum in  $F(x,\kappa)$  does, however, serve to define  $\kappa$ , and  $(1/4\pi k_i N_0 R^2)(d\alpha/dt)$ and  $F(x,\kappa)$  were compared at their maxima to obtain an approximate value of  $\kappa$ . Using this value of  $\kappa$ ,  $F(x,\kappa)$  was interpolated from the calculated curves at 0.1 unit intervals in x. These values of  $F(x,\kappa)$  were marked off on the smoothed curve of  $(1/4\pi k_i N_0 R^2)$ .

SUMMARY OF RATE CONSTANTS						
<i>T</i> , °C.	$4\pi k_1 N_0 R^2$	$k_{f g}/R$	to, sec.	ж		
112.34	$233 \times 10^{-6}$ sec. <sup>-1</sup>	$612 \times 10^{-6}$ sec. <sup>-1</sup>	200	0.381		
106.97	$155  imes 10^{-6}$ sec. $^{-1}$	$491 \times 10^{-6}$ sec. <sup>-1</sup>	600	.316		
101.97	$104  imes 10^{-6}$ sec. <sup>-1</sup>	$293 imes10^{-6}$ sec. <sup>-1</sup>	850	.355		
96.97	$66.9 \times 10^{-6} \text{ sec.}^{-1}$	$191 \times 10^{-6} \text{ sec.}^{-1}$	960	.350		
79.97	$7.57 imes 10^{-6}~{ m sec.}^{-1}$	$31.7 imes 10^{-6}$ sec. $^{-1}$	104	$.239^{a}$		
69.99	$2.81 \times 10^{-6} \text{ sec.}^{-1}$	$7.77 imes10^{-6}~{ m sec.}^{-1}$	$3.5 imes10^4$	.362		
$\Delta E$ act.	$28.47 \pm 0.81$ kcal.	$27.49 \pm 0.93$ kcal.	$-30.73 \pm 1.48$			
$\log A$	$12.57 \pm 0.49$	$12.46 \pm 0.56$	$-15.03 \pm 0.88$			
Av.				$0.353 \pm 0.024$		

TABLE II

<sup>a</sup> Omitted from average. Errors shown are one standard deviation.



Fig. 3.—The first-order decay portion at 106.97° showing the best guess straight line through the points.



Fig. 4.— $d\alpha/dt vs. t$  for x < 2.0 at 106.97°. The solid line is the fit of Mampel's equation to the data.

 $(d\alpha/dt)$  vs. t. The time corresponding to various x was read from this graph and plotted against x. The result was a straight line. The slope of this line gave  $R/k_{\rm g}$  and the intercept gave  $t_0$ , the induction time. From  $R/k_{\rm g}$  and  $4\pi k_1 N_0 R^2$ ,  $\varkappa$  could be calculated and compared with the chosen value at the maximum. The agreement was within  $\pm 10\%$ . Since the scatter in the data is high near the maximum, this agreement is within experimental error. A plot of  $d\alpha/dt$  vs. t and its computed curve are shown in Fig. 4. The agreement is quite good.

Values for  $k_g/R$  and  $4\pi k_i N_0 R^2$  were obtained in this fashion at all temperatures. Both constants obey the Arrhenius equation as does  $t_0$ . The data, together with their least square Arrhenius parameters, are listed in Table II.  $\varkappa$  is also listed and as can be seen is, within experimental error, independent of temperature.

Although the data can be mathematically interpreted in terms of Mampel's theory, there are so a physical difficulties which must be considered.

One such difficulty is that the two rate constants appear to be independent of particle size. Several decompositions were made on a slightly impure (NO<sup>+</sup> titer  $\sim 1.5\%$ ) sample of nitryl perchlorate prepared by the reaction of anhydrous perchloric acid with nitryl chloride. This sample of material had visible particle sizes of 10 to 20 times the sizes of the commercial sample. The observed rates (plotted as  $d\alpha/dt vs. \alpha$ ) were within experimental error of being the same for the two samples. The theory would have predicted the large size sample to have a growth constant smaller by a factor of 0.1 to 0.05 and an initiation rate larger by a factor of 100 to 400. This insensitivity of the rates to visible particle size variation can be explained by assuming that the decomposing unit is a subcrystalline particle smaller than the visible particles and the same for both samples. Nucleation would then have to occur on the interfaces of the subcrystals and desorbing gases and product gases would have to diffuse out by way of the interfaces. A more serious difficulty arises from a consideration of  $4\pi R^2 N_0$ , the number of potential sites per particle. The definition of  $\varkappa$  gives

$$4\pi R^2 N_0 = \frac{\kappa k_g/R}{k_i}$$

The growth constant  $k_{g}$  can be related to a "molecular" rate constant,  $k_{u}$ , by

$$k_{g} = k_{u}\delta$$

Here  $\delta$  is of the order of magnitude of an interionic distance.

$$4\pi R^2 N_0 = \frac{\kappa k_{\rm u}}{R_{\rm i}} \frac{\delta}{R}$$

Now,  $4\pi R^2 N_0$  must be larger than unity if the sites are to be permanent fixtures on a particle. This means that

$$\frac{k_{\rm u}}{k_{\rm i}} \gg 1 \quad \left( \text{since } \frac{\delta}{R} \ll 1 \right)$$

It seems unlikely that this can be true since  $k_u$  and  $k_i$ would have the same activation energies. If the sites are not permanent but are in mobile equilibrium with normal sites then  $4\pi R^2 N_0$  can be less than unity at any given time.  $N_0$  then should have a temperature dependence and the equality of the activation energies for  $4\pi R^2 N_0 k_i$  and  $k_g/R$  would appear to be accidental.

A reasonable interpretation for the data is then the model proposed by Mampel, but with a mobile equilibrium for the active sites. The nuclei grow slowly during an induction period. During this induction period gases are evolved, but are not directly connected with the decomposition. The particle size in Mampel's theory is to be interpreted as a subcrystalline unit.

An additional piece of information can be obtained from the data. This is the average number of nuclei which form per particle during the decomposition. The uncorrected number of nuclei formed per second is

$$\frac{\mathrm{d}M}{\mathrm{d}t} = Np\varkappa \frac{\mathrm{d}x}{\mathrm{d}t}$$

Here  $N_p$  is the total number of particles. From Mampel's eq. 5a and 5b (ref. 13) the fraction of surface, of the whole mass, which has not decomposed is

$$e^{-\kappa x^{3}/12} \quad 0 \le x \le 2$$
$$e^{+4\kappa/3 - \kappa x} \quad x \ge 2$$

The corrected total number of nuclei formed during the decomposition is

$$M = N_{p} \varkappa \left\{ \int_{0}^{2} e^{-\varkappa x^{2}/12} \, \mathrm{d}x + \int_{2}^{\infty} e^{4\varkappa/3 - \varkappa x} \, \mathrm{d}x \right\}$$

The average number of nuclei is then, for  $\kappa = 0.35$ , found by numerical evaluation to be  $M/N_{\rm p} = 1.45$ .

For a nucleus initiated at t = 0, the average maximum number of nuclei that could be formed is  $1 + \int_0^2 x \, dx = 1.7$ .

This shows that after the initial nucleation of a particle about one-third of the subsequent nuclei are phantom.

Mampel's solution is for the special case of surface initiation of uniform spherical particles, followed by isotropic growth of the nuclei. This rate law is so successful in fitting the present data that these assumptions must be examined further. In the real case, the shapes of the particles are probably nonuniform and nonspherical. Since there is only one maximum and no shoulders in the rate as a function of  $\alpha$  there are no large discrete differences in the particle sizes. A narrow and nearly continuous distribution of sizes will lead to a slight broadening of the maximum in the rate, as compared to the result for a single size. The fit of the theory will depend upon how well the true situation can be represented by an average. It will now be shown that the actual geometry of the particles and nuclei is relatively unimportant. Consider a group of uniform particles with initiation constant  $k_i$ . The actual rate law for a single particle will depend upon the number of, position of, and the relative times of the nucleations. Replace these rate laws by an average rate law that is the same for all particles after their first initiation. Let  $\alpha_p$  be the fraction of a particle decomposed at time  $t - t_i$ , where  $t_i$  is the time of first initiation of the particle. The fraction,  $\alpha$ , of the whole mass decomposed at time t will be for first-order initiation

$$\alpha = k_i \int_0^t \alpha_p (t - t_i) e^{-k_i t_i} dt_i$$

This equation can be converted to a differential equation.

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} + k_{\mathrm{i}}\alpha = k_{\mathrm{i}}\alpha_{\mathrm{p}}(t)$$

If each individual particle is consumed in a finite time (or if  $\alpha_p$  is nearly constant after such time), then the differential equation reduces to the first-order decay law as do Mampel's equations. This first-order decay law is independent of the geometry of the system and the site (surface or interior) of initiation. The rate constant  $k_i$  obtained from the first-order portion of the rate law can be used to obtain  $\alpha_p$  as a function of time in the earlier portions of the plot. When this is done it is found that, below  $\alpha_p = 0.4$  (or x = 1.3 in Mampel's equations)  $\alpha_p = K(t - t_0)^3$ . An induction time is needed here as in the fit to Mampel's equations. This rate law corresponds to threedimensional growth of the nuclei (not necessarily isotropic growth). The geometry of the particles is unspecified except that long thin rods are excluded. Between  $\alpha_p = 0.4$  and  $\alpha_p = 1$  this simple  $t^3$  law deviates badly from the data. It is in this range that the effects of geometry and multiple nucleation show up. Models involving either single surface nucleation of spheres or single corner initiation of cubes fit the data much better than the  $t^3$  law and nearly as well as Mampel's equations. Mampel's equations are better because of the consideration of multiple nucleation. As would be expected from the computed average number of initiations, this improvement over single initiation is small.

In short, the geometry used in Mampel's theory should not be taken too seriously for this case. Even the assumption of surface initiation is not important. Mampel's theory is valuable in that it considers both geometrical limiting of nuclear growth and multiple nucleation in tractable mathematical form. The preexponential factors for the derived rate constants will depend upon the exact geometrical model which is chosen. For the growth rate constant this variation will be (in terms of some critical size parameter) only about one order of magnitude. The interpretation of the pre-exponential factor for nucleation will also depend upon whether surface or bulk initiation is chosen. The activation energies for the rate constants should be independent of the assumed geometry of the particles and should be reasonable estimates of the activation energies of the real processes. The induction time still remains an empirical entity, although it may be due to slow growth of small nuclei.

The chemistry of the decomposition is mostly speculation. The following rough scheme may be close to the truth.

- 1. Reactions in the solid
- $ClO_4^- \longrightarrow ClO_4 + e^- \text{ (conduction band)}$  $e^- + NO_2^+ \longrightarrow NO_2$
- 2. Desorption  $ClO_4(surface) \longrightarrow ClO_4(gas)$  $NO_2(surface) \longrightarrow NO_2(gas)$

3. Gas reactions  $ClO_4 \longrightarrow ClO_2 + O_2$   $NO_2 + ClO_2 \longrightarrow NO_3 + OCl$   $OCl + NO_2 \longrightarrow NO_3Cl$   $2OCl \longrightarrow Cl_2 + O_2$  $NO_2 + NO_3 \overleftrightarrow{} N_2O_5 \longrightarrow N_2O_4 + \frac{1}{2}O_2$  The gas phase reactions have all been postulated in other reactions. The important questions concern the reactions in the solid and the nature of the gases coming off of the surface. Since the energies for the solid phase reactions are not known they cannot be compared with the observed activation energies.

# THE INTERACTION AND NONINTERACTION OF IONS WITH A NATURAL POLYSACCHARIDE<sup>1</sup>

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The interaction of a neutral polysaccharide with various ions in aqueous solution has been investigated. No observable binding took place between the polymer and H<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Ag<sup>+</sup>, Ba<sup>+2</sup>, C<sub>2</sub>H<sub>3</sub>O<sub>2</sub><sup>-</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>-2</sup>, or HSO<sub>4</sub><sup>-2</sup>. The polysaccharide displayed an affinity only for OH<sup>-</sup>, and this affinity has been treated as an adsorption phenomenon. Adsorption isotherms, isosteric heats of adsorption, and integral heats of adsorption were determined for the binding of OH<sup>-</sup> to locust bean gum and are discussed herein.

# Introduction

The aqueous extract of the locust bean (ceratonea siliqua) is a neutral polysaccharide consisting of a main chain of mannose units with short branches of single galactose units attached through 1,6-glycosidic linkages to the polymannose chain.<sup>8</sup>



This gum forms very viscous aqueous solutions and dissolves completely only on prolonged heating and agitation. Preliminary studies in this Laboratory of the turbidity of these solutions indicate that the polymer exists as an aggregate in aqueous solution at room temperature with an aggregate molecular weight of 500  $\times$  10<sup>6</sup>. The present work was undertaken to determine the ability of this polysaccharide to bind small ions in aqueous solution.

#### Experimental

1. Polymer Solutions.—The polysaccharide was extracted from dried locust beans (Cyprus origin)<sup>4</sup> by agitation of mechanically cracked beans with  $80-90^{\circ}$  distilled water for approximately 90 min. The resulting hot solution was filtered through several layers of muslin cloth and cooled to room temperature. The polymer was precipitated by addition of 95% ethanol in a 2:1 volume ratio and redissolved in hot distilled water. This solution was diluted to approximately 0.5% by weight and passed through anion and cation exchange columns. The eluent was concentrated by evaporation and the polymer reprecipitated with 95% ethanol. The gum was washed several times with ethanol and dried at  $70^{\circ}$  overnight. All solutions were prepared from this purified extract by dissolving the gum in hot ion-exchanged water.

2. Viscosity measurements were made with a Cannon-Fenske viscometer No. 100 which was immersed in a water bath thermostated to  $\pm 0.005^{\circ}$ . The viscometer was calibrated with a 40% sucrose solution using the values of  $\eta$  and  $\rho$  from the International Critical Tables. A second determination of several relative viscosities was made with a calibrated Cannon-Fenske viscometer no. 50 with a flow time for distilled water approximately one-fourth as fast at 20° as the flow time of viscometer no. 100. The polymer solution displayed no viscosity dependence on rate of shear in the viscosity range studied.

3. Conductivity data were obtained from resistance measurements of solutions in a standard conductivity cell with 1.3-cm.<sup>2</sup> platinum electrodes using a Leeds and Northrup "Jones" conductivity bridge equipped with a wide frequency range oscillator. The cell was immersed in an oil bath thermostated to  $\pm 0.005^{\circ}$ . The temperatures were measured by means of a calibrated platinum resistance thermometer. Reagent grade KCl and NaCl were purified by double precipitation from concentrated HCl solution and subsequent fusion in a platinum crucible. Baker's reagent grade HCl, H<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>SO<sub>4</sub>, BaCl<sub>2</sub>, AgNO<sub>3</sub>, and NaAc were used without further treatment. NaOH and KOH were prepared from saturated stock solution of the base in ion-exchanged water. The conductivity cell was calibrated with KCl using the data of Jones and Bradshaw.<sup>5</sup>

#### Results

The conductivities of all electrolytes were measured in aqueous solution and in locust bean gum solution and corrected for solvent in the usual manner. Table I gives the specific conductivities of some pure locust bean gum solutions compared with ion-exchanged water at the same temperature. It can be seen that the conductivity of the polymer solutions is extremely low, indicating an almost complete removal of electrolytes by the ion-exchange purification process.

Stock solutions of each electrolyte were prepared and diluted with water or with polymer solution to ensure an accurate comparison. The conductivities of  $H_2SO_4$ , HCl, NaCl, KCl, Na<sub>2</sub>SO<sub>4</sub>, BaCl<sub>2</sub>, NaAc, and AgNO<sub>3</sub> were found to be the same in both solutions within experimental error. This is illustrated in Table II where representative values are given for the specific

(5) G. Jones and B. C. Bradshaw, J. Am. Chem. Soc., 55, 1780 (1933).

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<sup>(2)</sup> Standard Oil Company of California Fellow, 1962-1963.

<sup>(3)</sup> F. Smith, J. Am. Chem. Soc., 70, 3249 (1948).

<sup>(4)</sup> Samples obtained through the courtesy of Tragasol Products, Ltd., Hootan, Wirral, Cheshire, England.