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KINETICS OF THE THERMAL DECOMPOSITION OF SOLID PETN

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by

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ABSTRACT

The thermal decomposition of PETN below its melting point has been investigated. Separate monitoring of six product gases allowed individual initial rates of reaction and activation energies to be calculated. The activation energies for the production of both N_2O and H_2O are between 50 and 56 kcal·mol^{-1}, pointing to a single process operant over the entire temperature range 363 - 408 K. The other four observed products have activation energies that are significantly higher. The activation energies for CO_2 and N_2 formation are 65 - 66 kcal·mol^{-1} while those for the production of CO and [NO + NO_2] are 71 - 75 kcal·mol^{-1}. Whether these values represent two or only one additional mechanism is not clear; however, for the 2σ width uncertainty limits overlap. The processes or process involved in the formation of CO_2, N_2, CO, and [NO + NO_2] appear(s) to change at 373 K, as a dramatic drop in activation energies is observed at lower temperatures.

INTRODUCTION

The sublimation, vaporization, and chemical decomposition of PETN (pentaerythritoltetranitrate, $C_5H_8N_4O_{12}$) have been investigated, under a variety of conditions, in past years.[1-5] By and large all the rate studies assumed a single overall reaction and the data were analyzed in terms of Arrhenius-type processes. For changes of state, the activation energies and preexponential factors calculated should be meaningful. For decomposition studies, there is serious question as to whether the assumed single reaction is permissible. Clearly its validity has never been demonstrated. The process is almost certainly much more complex. For example, it is known that the oxides of carbon, nitrogen, and hydrogen are all present in various amounts as the gaseous products of the decomposition. Thus, it is very difficult to see how a single reaction coordinate could be sufficient to adequately describe the system. Rather, it appears that the thermal decomposition is best represented by a set of N possible reaction paths such as:

$$\begin{array}{ll} \mathrm{PETN(s)} & \xrightarrow{k_a} \{A\} \\ & \xrightarrow{k_b} \{B\} \\ & \xrightarrow{k_n} \{N\} \end{array} \qquad (1)$$

The value of N will depend upon the number of products considered to be formed in the decomposition. Each of these paths, of course, will have its own activation energy and preexponential factor.

Another abnormal aspect of the decomposition behavior of PETN must also be considered. This is that the apparently most favorable thermodynamic paths (largest negative standard free energy changes) do not always occur. It is a well documented fact that products other than those calculated to be the most stable are produced. Berlow, Barth, and Snow give[6] the PETN detonation stoichiometry as

$$\mathrm{PETN(s)} \rightarrow 2\ \mathrm{CO(g)} + 3\ \mathrm{CO_2(g)} + 4\ \mathrm{H_2O(g)} + 2\ \mathrm{N_2(g)} \qquad (2)$$

and report a heat of detonation in the range of -463 to -488 kcal·mol^{-1}. A thermochemical calculation of the Helmholtz standard free energy change, ΔA^0_{298}, for the stoichiometry of Eg. (2), using the Ornellas heat of formation of PETN,[4] entropy calculation techniques described by Benson,[7] and handbood thermochemical data[8] for the product gases, yields a value of $\Delta A^0_{298} = -635.8$ kcal·mol^{-1}. Ornellas and coworkers[4] have determined the detonation stoichiometry of PETN initiated in a bomb calorimeter to be

$$\text{PETN(s)} \rightarrow 3.50\ CO_2(g) + 1.50\ CO(g) + 2.00\ N_2(g) + 0.5\ H_2(g) + 3.50\ H_2O(g) + <0.0002\ NH_3(g) + <0.0002\ CH_4(g) \quad . \qquad (3)$$

(The stoichiometric coefficients in Eq. (3) are rounded off to nearest half integers such that exact atomic balance is achieved.) The standard free energy change for this reaction is calculated to be −640.20 kcal·mol^{-1}. In a closed system held at 483 K, Rideal and Robertson,[5,9] give the reaction stoichiometry as

$$\text{PETN(s)} \rightarrow 0.52\ NO_2(g) + 2.11\ NO(g) + 0.42\ N_2O(g) + 0.07\ N_2(g) + +0.28\ CO_2(g) + 0.93\ CO(g) + 0.09\ H_2(g) \qquad (4)$$

with unquantified amounts of water, formaldehyde and "residue". Because Reaction (4) is not mass balanced, it is difficult to calculate a free energy change. Calculated free energy changes for three reaction channels that produce oxides of nitrogen however, indicate in general less favorable thermodynamics than for reactions that which do not form those products. That is,

$$\text{PETN(s)} \rightarrow 3\ NO_2(g) + 2\ C_2H_2(g) + 2\ H_2O(g) + CO(g) + NO(g) + O_2 \qquad (5)$$

$$\text{PETN(s)} \rightarrow 4\ NO(g) + 4\ CO_2(g) + CH_4(g) + 2\ H_2(g) \qquad (6)$$

$$\text{PETN(s)} \rightarrow 2\ N_2O(g) + 4\ CO_2(g) + CH_4(g) + 2\ H_2O(g) \qquad (7)$$

have values of ΔA^0_{298} of −180.1, −375.1, and −516.6 kcal·mol^{-1}, respectively. Finally, there are at least two other stoichiometrically possible PETN decomposition reactions with quite favorable thermodynamics that do not preferentially occur. These are:

$$\mathrm{PETN(s)} \rightarrow \mathrm{CO(g)} + 4\ \mathrm{CO_2(g)} + 3\ \mathrm{H_2O(g)} + 2\ \mathrm{N_2(g)} + \mathrm{H_2(g)} \qquad (8)$$

and

$$\mathrm{PETN(s)} \rightarrow 5\ \mathrm{CO_2(g)} + 2\ \mathrm{H_2O(g)} + 2\ \mathrm{N_2(g)} + 2\ \mathrm{H_2(g)} \qquad (9)$$

which have ΔA^0_{298} of -642.6 and -649.4 $\mathrm{kcal \cdot mol^{-1}}$, respectively.

In this paper we present the results of a chemical kinetic study of the thermal decomposition of PETN at temperatures below the melting point, 141°C.[10] The amounts of six individual reaction products evolved were measured as a function of time. This allowed the decomposition reaction to be analyzed in terms of the multiple reactions that exist in reality and the kinetic parameters of the various reaction channels to be calculated.

EXPERIMENTAL PROCEDURE AND RESULTS

Commercial PETN manufactured by the Trojan Powder Company, which met military specifications (Mil-P-387A), was recrystallized twice from acetone by the addition of distilled water. The second precipitation was a particle-size adjustment process that gave the material a permeametric specific surface value of 3500 $\mathrm{cm^2/g}$.

For each decomposition run approximately 1 g of PETN was used. The explosive powder was put into a container shaped like a pipette that had a cylindrical bulb 50-mm long and

20-mm in diameter (volume approximately 15 cm^3). After loading, the vessel was evacuated to 1-mm air pressure through one of the attached Pyrex tubes and sealed.

The system was brought to within ±0.5 K of the desired temperature in an electric heating oven. After a given time, the heating was terminated and the container was allowed to cool to room temperature. At that time the bulb was joined to a Consolidated Electrodynamics Corporation (CEC) Model 21-103 mass spectrometer through a second attached Pyrex tube. The gaseous decomposition products were introduced through a heated (383 K) inlet system containing a 3-liter expansion volume equipped with a capacitor-manometer pressure indicator. No analysis of the solid residue was made.

Two examples of the evolution curves are shown in Figs. 1 and 2. They give the mass of product produced per gram of PETN as a function of time for a single run. Approximately 0.5% of the sample is accounted for by the decomposition gases at the lowest temperature and 5% at the highest.

The positive concavity of the curves is an indication that auto-catalysis is occurring even in the very early stages of the reaction. Initial reaction rates were determined by drawing tangents to the curves over the earliest part of the reaction up to the point at which deviation from linearity becomes significant. These initial reaction rates, R_x, are collected in Table I. R_x has reciprocal time units because the data are normalized for one mole of PETN. The initial-rate analysis was performed by considering the rate of evolution of product x as

$$\frac{d(x)}{dt} = \frac{-nd(\mathrm{PETN})}{dt} = nk_x(\mathrm{PETN})^m \tag{10}$$

where (x) = amount of x

(PETN) = amount of PETN(s)

n = stoichiometric coefficient giving the number of moles of x produced per mole of PETN

k_x = the rate constant of x production

m = the order of the reaction .

Over the initial part of the reaction $(\mathrm{PETN})^m$ is a constant equal to $(\mathrm{PETN})_0^m$. In addition, for R_x normalized to one mole of PETN, $R_x = 1/(\mathrm{PETN})_0\ d(x)/dt$. Equation (10) then becomes

$$R_x = nk_x(\mathrm{PETN})_0^{m-1} \quad . \tag{11}$$

Using the Arrhenius expression, $k_x = A_x\exp(-E_x/RT)$, where A_x is the pre-exponential factor, E_x the activation energy, R the gas constant, and T the Kelvin temperature, Eq. (11) may be recast in the logarithmic form

$$\ln R_x = \left[\ln nA_x(\mathrm{PETN})_0^{(m-1)}\right] - E_x/RT \quad . \tag{12}$$

Equation (12) shows that a plot of $\ln R_x$ vs $1/T$ will yield a line of slope $-E_x/R$ and an intercept of $\ln \left[nA_x(\mathrm{PETN})_0^{(m-1)}\right]$. Because m and n are not known there is, unfortunately, no information on A_x to be obtained from the intercept.

Arrhenius plots of ln R_x vs 1/T are quite linear over the full temperature range for the products H_2O and N_2O. For the other products, the point at 363 K is off the best line. This behavior occurs consistently for CO_2, CO, and N_2 suggesting that there may be a change of mechanism at 363 to 373 K. For $[NO + NO_2]$ the rate is actually higher at 363 K than at 373 K. This observation is viewed circumspectly for if this effect is real a negative activation energy would be calculated below 373 K. We do not think this observation is truly indicative of the reaction energetics; rather it is probably due to a non-NO_x producing channel becoming relatively more important at lower temperatures. Figure 3 shows the representative Arrhenius plots for H_2O and $[NO + NO_2]$ production.

A linear least squares fit was performed on all the data plots. The activation energies calculated from the resulting slopes are given in Table II. For CO_2, CO, and N_2 a separate activation energy was calculated below 373 K. The uncertainty limits reported with the activation energies were calculated by drawing maximum and minimum possible slopes based on the error, estimated as two standard deviations (σ), for the points. The uncertainties at temperatures below 373 K may actually be larger than stated in Table II, as it is not clear that the 100°C point can be used with the 363 K point.

DISCUSSION

The activation energy for PETN decomposition also has been determined by Rideal and Robertson as E = 47.0 $\text{kcal}\cdot\text{mol}^{-1}$ over the temperature range 434 to 506 K. Rogers and Morris report E = 47.3 ± 4.0 $\text{kcal}\cdot\text{mol}^{-1}$ from differential scanning calorimeter measurements done in the neighborhood of 473 K. We do not expect these results to compare with those reported here because of the lower temperature range of this study. Furthermore, as the melting point of PETN is 141°C, the literature results cited above are for PETN(ℓ) while the results of this study are for PETN(s). As has been stressed, the fact that this study addresses itself to activation energies for individual reaction channels rather than the overall decomposition process is a further reason to expect different results.

The mechanism for PETN decomposition is unknown but is, no doubt, quite complex. It is conceivable that the mechanism is such that the experimental activation energy for PETN(ℓ) decomposition, E_ℓ, can be expressed as the sum of two terms

$$E_\ell = E_a + \Delta H_v \tag{13}$$

where ΔH_v is the heat of vaporization for PETN and E_a is the activation energy for decomposition of gas phase PETN. For example, Eq. (13) would hold if PETN can only decompose from the gas phase, for then we could write a mechanism such as

$$\mathrm{PETN}(\ell) \underset{}{\overset{K}{\rightleftarrows}} \mathrm{PETN}(g)$$

$$\mathrm{PETN}(g) \xrightarrow{k_2} \text{products}$$

where $K = P_g/a_s = e^{-\Delta G^0/RT}$ is the equilibrium constant for PETN vaporization and $k_2 = \nu e^{-E_a/RT}$ is the rate constant for PETN(g) dissociation. ΔG^0 is the standard Gibbs free energy change for vaporization, P_g is the PETN vapor pressure, a_s is the activity of PETN(s) (taken as unity by convention for solids) and ν is the frequency factor associated with k_2. The rate of the reaction is then given by[11]

$$\frac{d(\text{products})}{dt} = \nu \exp \Delta S_v^0/R-(E_a + \Delta H_v^0)/RT \qquad (14)$$

where ΔS_v^0 is the standard entropy change for vaporization.

Under the same assumption the experimental energy of activation for PETN(s), E_s, can be expressed as

$$E_s = E_a + \Delta H_s \qquad (15)$$

where ΔH_s is the heat of sublimation for PETN.

Using literature[1-3,5] values for E_ℓ, ΔH_v and ΔH_s, E_a in Eq. (13) is found to be 28 ± 6 kcal·mol^{-1} and E_s in Eq. (15) is calculated as 63 ± 9 kcal·mol^{-1}. The experimentally determined equivalent activation energy for PETN(s) decomposition is the product-averaged value of the data in Table II. A reasonable estimate appears to be 65 kcal·mol^{-1}, with a minimum value of 53 and a maximum of 75. This is quite good agreement. Since $E_s - E_\ell = \Delta H_f$ these kinetic parameters yield a value of 16 ± 13 kcal·mol^{-1} for the heat of fusion of PETN. Considering the large uncertainty, this number is not significantly different than the value of 23 kcal·mol^{-1} derived from equilibrium solubility data.[12] This good agreement is expected and required if the assumptions of the aforementioned mechanisms are correct.

CONCLUSIONS

N_2O and H_2O are probably produced through one process that is operant over the entire temperature range of 363 - 408 K. The other observed products cannot be produced by the same process because their activation energies are significantly higher. The similarity of activation energies for CO_2 and N_2 suggest that they may be formed in the same process. This process, however, appears to change at about 373 K, as a dramatic drop in the activation energy is observed at low temperatures. Based again upon similarity of the activation energies, it appears that CO and NO_x are formed in the same process, which may be the same as the one in which CO_2 and N_2 are formed, as the 2σ width uncertainty limits for CO_2, N_2, CO, and NO_x all overlap. Whether there are two or three separate processes that are simultaneously operant is not totally clear from the results, but it is certain that there is more than one and this result is already in contradistinction to any previous information on the PETN thermal decomposition reaction.

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11. The expression given is for constant temperature and pressure conditions. For conditions of constant temperature and volume substitute ΔA^o for ΔG^o and ΔE_v^o for ΔH_v^o.

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FIGURE CAPTIONS

Fig. 1. Mass of gas evolved per gram of PETN as a function of time. Temperature 363 K.

Fig. 2. Mass of gas evolved per gram of PETN as a function of time. Temperature 393 K.

Fig. 3. Arrhenius plot: natural logarithm of the initial reaction rate versus the reciprocal of the Kelvin temperature.

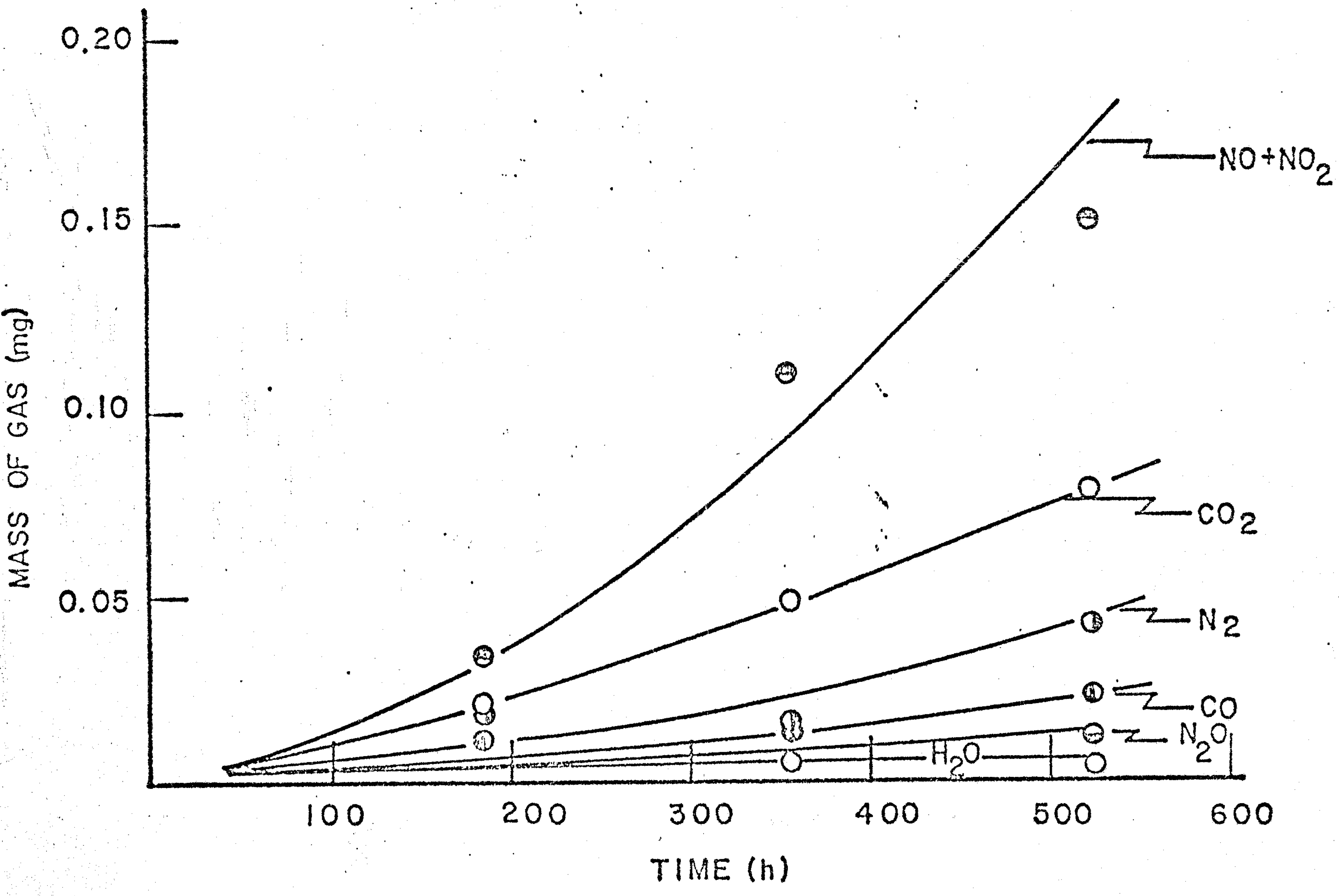
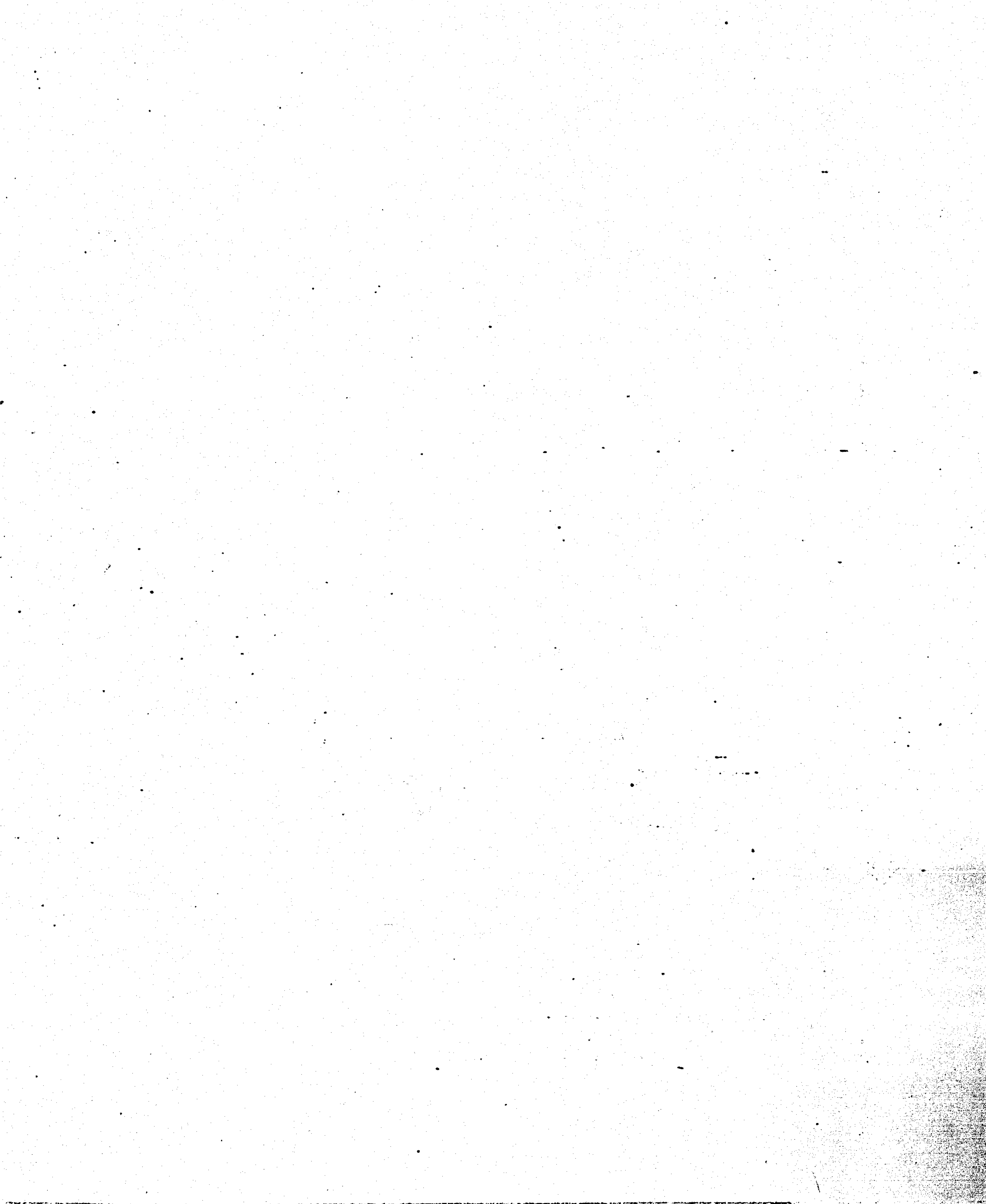
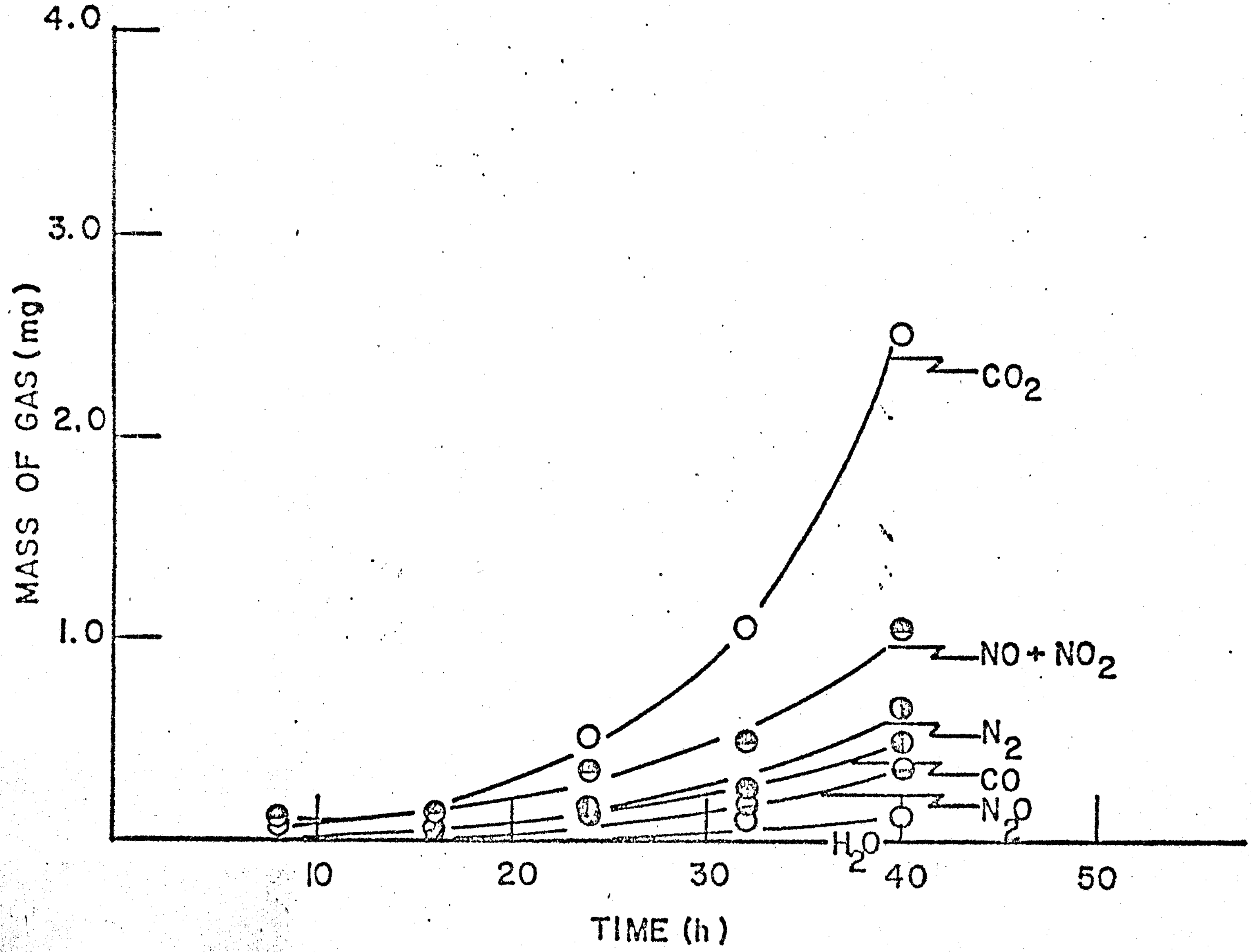

0.20
0.15
0.10
0.05
MASS OF GAS (mg)
100
200
300
400
500
600
TIME (h)
NO+NO$_2$
CO$_2$
N$_2$
CO
N$_2$O
H$_2$O

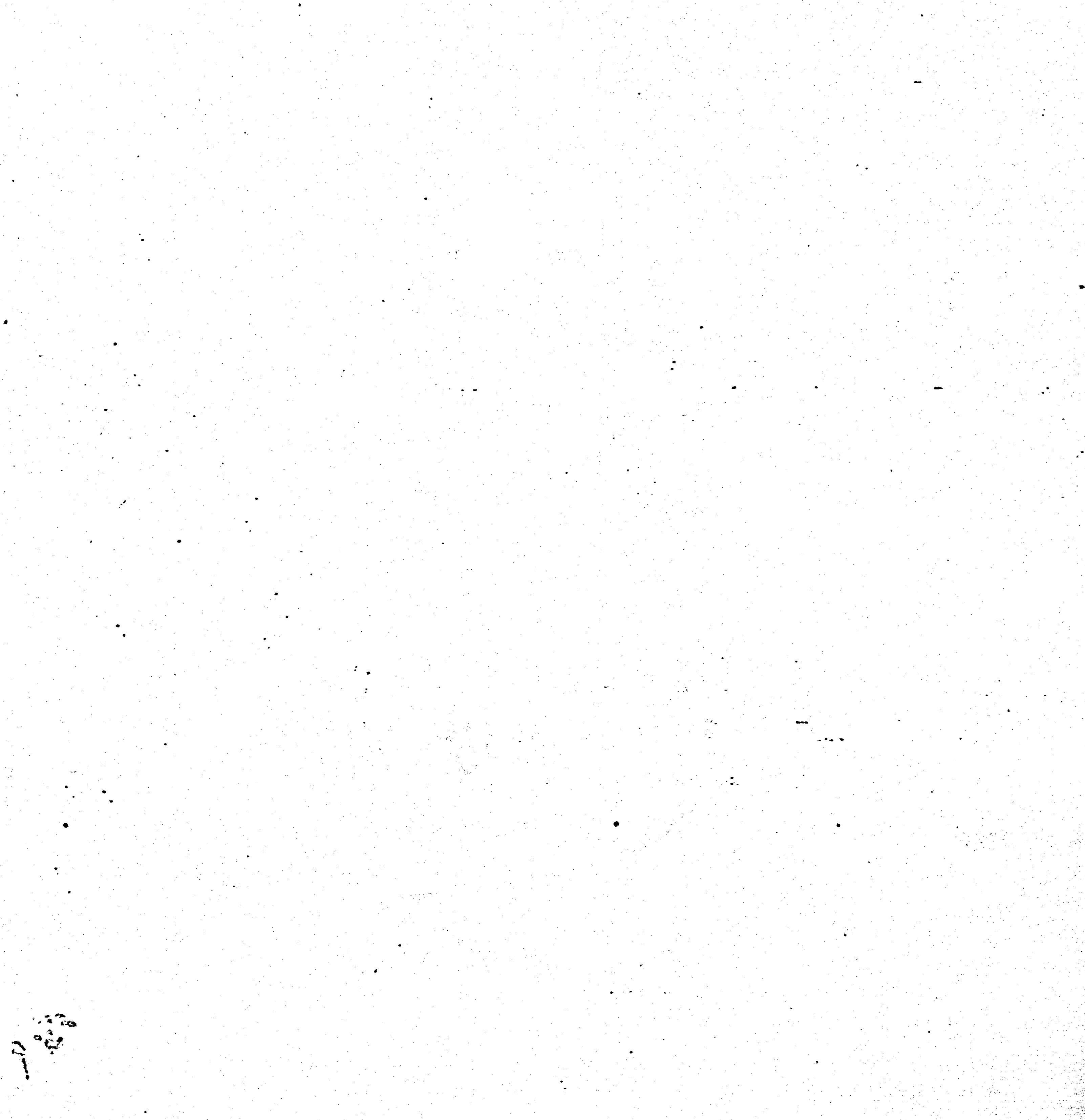
Fig. 1. Mass of gas evolved per gram of PETN as a function of time. Temperature 363 K.





4.0
3.0
2.0
1.0
MASS OF GAS (mg)
10
20
30
40
50
TIME (h)
CO_2
$NO + NO_2$
N_2
CO
N_2O
H_2O

Fig. 2. Mass of gas evolved per gram of PETN as a function of time.
Temperature 393 K.



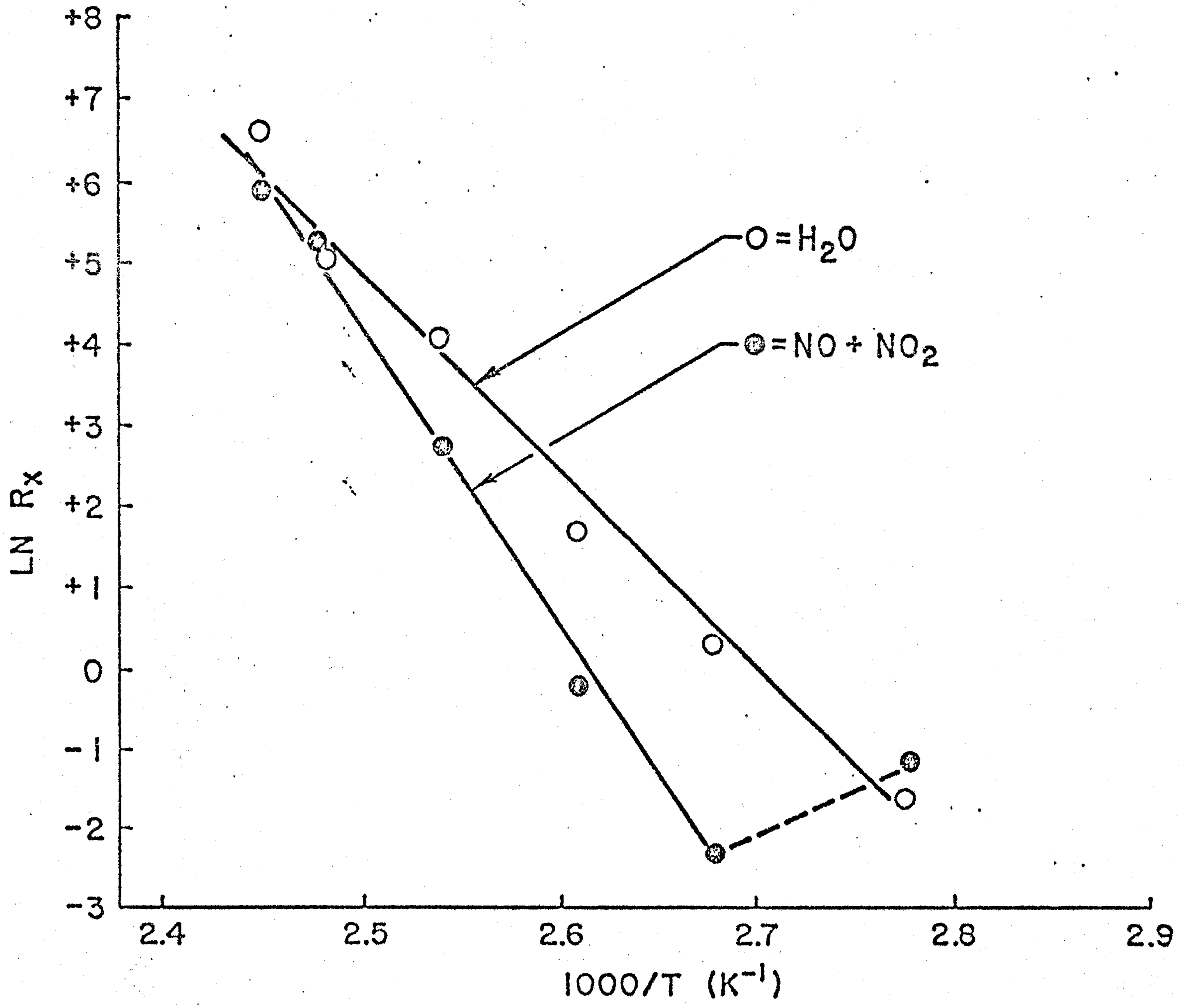

○ = H_2O
● = $NO + NO_2$
LN R_x
+8
+7
+6
+5
+4
+3
+2
+1
0
-1
-2
-3
2.4
2.5
2.6
2.7
2.8
2.9
1000/T (K^{-1})

Fig. 3. Arrhenius plot: natural logarithm of the initial reaction rate versus the reciprocal of the Kelvin temperature.

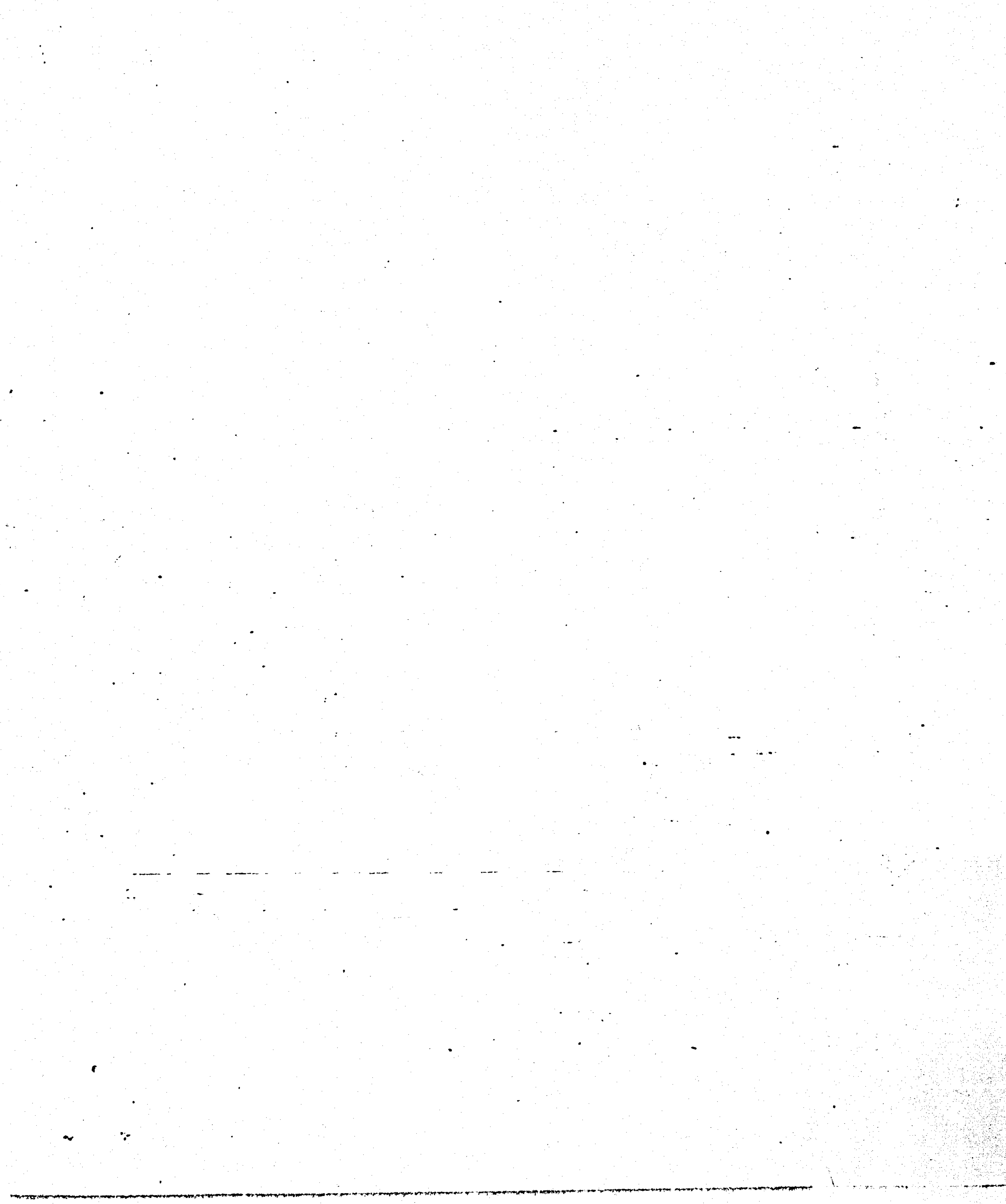


TABLE I

INITIAL RATES OF PRODUCT FORMATION

R_x (h^{-1})

T (K)	H_2O	N_2	N_2O	NO + NO_2	CO	CO_2
363	0.18	0.86	0.14	0.29	0.43	1.01
373	1.33	1.07	0.68	0.095	0.86	1.36
383	5.09	8.58	5.46	0.76	6.43	24.4
393	55.0	106.	45.	15.6	106.	244.
403	176.	1195.	223.	187.	1061.	1572.
408	738.	1411.	452	375	2539.	2247.

TABLE II

ACTIVATION ENERGIES FOR FORMATION OF PRODUCT GASES

	E (kcal$\cdot$mol^{-1})			
Product	363 - 373 K	2σ Range	373- 408 K	2σ Range
N_2O	54.7	51.1-55.6	54.7	51.1-55.6
H_2O	53.0	50.7-54.7	53.0	50.7-54.7
CO_2	7.1	3.0-15.9	64.9	61.9-72-5
N_2	7.6	0-13.9	65.7	60.6-90.4
CO	19.9	11.9-25.8	71.1	64.5-72.5
NO + NO_2	--	--	74.6	67.6-77.5