Journal of Hazardous Materials, 2 (1977/78) 163–170
© Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

REACTION KINETICS OF TEMPERATURE CYCLED CYCLOTRIMETHYLENETRINITAMINE (RDX)

Thomas G. Floyd
Air Force Armament Laboratory (AFSC)
Explosives Branch
Eglin Air Force Base, Florida

ABSTRACT

The effects on kinetic constants as a function of temperature cycling of cyclotrimethylenetrinitramine (RDX), Grade A, has been investigated using isothermal DSC and Henkin time-to-explosion methods.

Temperature variations were used to simulate storage and aerodynamic heating conditions which could be experienced by the high explosive in a munition. Some variations in the kinetic constants suggest an increase in the sensitivity of the RDX.

1. INTRODUCTION

Scale up of explosives testing in the laboratory to the operational level is a major consideration when attempting to characterize an explosive. An area of concern is in the calculation of kinetic characteristics and associated constants of decomposition.

In the past, kinetic studies of decomposition of an explosive have been done using fresh, purified explosives samples. This condition fails to take into account that the explosive, at the time of detonation in an actual bomb, may have previously undergone several periods of heating and cooling both as a result of storage and under aerodynamic heating conditions.

The purpose of this experiment, then, was to determine whether these periods of thermal variation appreciably affect the kinetic character of the decomposing explosive.

2. THEORY

Kinetic data were obtained using the isothermal differential scanning calorimetric method developed by R. N. Rogers.[1,2]

The differential scanning calorimeter (DSC) presents data in the form of a deflection from a baseline on a time-base recorder. This deflection, b, is directly proportional to the rate that heat is evolved by the sample, dq/dt, and hence, the rate of reaction, dx/dt, where x is the reacted fraction of the sample. For a first-order reaction:

$$\alpha b = \beta \frac{dq}{dt} = \frac{dx}{dt} = k(1-x)$$

where α and β are proportionality constants and k is the rate constant, then:

$$b = \frac{k}{\alpha}(1-x) \text{ and}$$

$$\ln b = \frac{k}{\alpha} + \ln (1-x)$$

Again considering a first-order reaction:

$$\ln (1-x) = -kt + C$$

where C is a constant of integration. Thus:

$$\ln b = -kt + C$$

Therefore, k is obtained as the negative slope of the plot of ln b vs time.

Since the entire kinetic development was based on the assumption of first order kinetics, it is important to verify that the actual reaction order is approximately one. From the previously discussed theory:

$$\alpha b = \frac{dx}{dt} = k\ (1-x)^n \quad \text{therefore:}$$

$$\ln b = \ln\ (1-x)^n + \ln\frac{k}{\alpha} = n \ln\ (1-x) + C.$$

A plot of ln b vs ln (1-x) gives the order as the slope.

To calculate the activiation energy, E_a, and the collision frequency factor, Z, for a series of k vs temperature measurements, the Arrhenius equation is used:

$$k = Z\ e^{-E_a/RT} \text{ or } \ln k = \ln Z - E_a/RT.$$

Therefore, a plot of ln k vs $1/T(10^{-3})$ gives a slope of $-E_a/R$ with E_a in Kcal/mole, and an intercept of ln Z where Z is the collision frequency factor.

3. DSC THEORY

Basically the DSC measures the difference in heat energy required to keep the two pans at a constant temperature. When both pans are empty, the heat energy required is equal for both. Heat energy is required since an inert N_2 atmosphere is constantly circulated to provide cooling and decomposition gas removal. When the sample decomposes in the sample pan, the heat evolved is detected as differential heat required by the DSC to keep the pans equilibrated. This is the deflection, b, and is proportional to dq/dt for the reaction.

4. EXPERIMENTAL

4.1 SAMPLES

The explosive used in this experiment was cyclotrimethylenetrinitamine (RDX), Grade A. Each sample was sealed in an aluminum capsule with aluminum cover cold welded together with a capsule cover perforated with two holes of constant diameter and containing between 1.50 to 1.90 mg of RDX. The reference sample was composed of an empty pan with a perforated cover.

4.2 KINETIC RUNS AND CYCLES

Kinetic calculations were done by taking DSC runs of samples at nine different temperatures ranging between 505 and 543°K. At each of these temperatures, two samples were run and from the deflection curves (digital samples of the curve at regular intervals), see Fig 1 for a sample deflection curve, the kinetic rate constant was calculated as previously described. From the resulting rate constant vs temp gradient, the activation energy and collision frequency factor was calculated via Arrhenius plot.

The above determination was done with a baseline of lab stock, uncycled RDX and with cycled RDX explosive. Cycled RDX was prepared by running the RDX through a predetermined temperature profile of heatings and coolings in a preprogrammed oven. Note: to ensure that no decomposition was occurring during these profiles, one representative sample was cycled in the DSC at high sensitivity settings for each temperature profile. The profiles used in this study are shown in Figure 2. They were designed to simulate the aerodynamic heating and/or storage cycling.

4.3 DSC PROCEDURE

The instruments used for this experiment were the Perkin Elmer DSC-IB and DSC-2. The DSC pans were brought to the run temperature with the empty pans intact. The recorder was then started and the sample introduced onto the empty sample pan. The cold sample causes a sharp break in the recording which indicates the time of the introduction (see Figure 1). As the sample decomposes, the resulting heat, dq/dt, will be indicated.

4.4 DSC AND RECORDER SETTINGS

1. Before any runs are attempted, the DSC must be adjusted both in the average and differential calibration settings. This is accomplished in accordance with the DSC operation manual using standard samples or by the method described by Rogers and Ortiz.[3]

2. Both the chart sensitivity and the DSC scale range were adjusted to produce the largest possible deflection without exceeding the scale. (Since the deflection is simply proportional to dq/dt, various settings could be tried without any consideration in the calculations.)

3. Chart speed: 40mm/min-160mm/min

4. N_2 flow: This was kept constant since it affects the heat needed to keep the pans at the run temperature; for this experiment, 30 ml/min.

5. DATA

Data were taken at the time interval indicated (deflection data) as a digital signal converted from the analog chart signal by a digital sampler.

Useful deflection data was only of the first order portion of the curve (from maximum deflection to the end), thus any readings before the maximum may be disregarded. Also, the data were "corrected" before use in the calculations by normalizing it to a minimum of zero baseline. This procedure is done for convenience of reporting and again due to proportionality having no effect on the results.

6. METHOD OF CALCULATION

The treated data (corrected) were then plotted as previously stated by computer to give a computer printout.

6.1 RATE PLOT

From the rate plot, ln b vs time, a relatively straight portion (near the top where nongaseous decomposition is occurring) was selected and via linear least squares approximation of the tangent to the curve at that point, the slope of the curve at that point was calculated and thus k, (k = - slope).

6.2 ORDER PLOT

In order to construct the order plot, ln b vs ln (1-x), the fraction remaining and thus ln (1-x) must be found for times along the reaction's profile. These were calculated via an integration of the area under the deflection curve. Since dq/dt relates directly to dx/dt, the fraction unreacted is directly proportional by the same constant to the change in area between consecutive time intervals over the total area under the curve.

Thus $\frac{dA}{dt}\Big|_{A}^{t=y,\ t=x}$ = fraction decomposed

during the time interval t = x to t = y. The area calculations were performed via a Simpson's [4] rule approximation.

Once the values for ln (1-x) were calculated, the order plot of ln b vs ln (1-x) was computer determined. Once again a relatively straight portion was selected and the slope (and likewise the order) was calculated via linear least squares approximation.

By tabulating the temperature of the run (actually 1/T) and the respective rate constants for that temperature, the data for the previously discussed Arrhenius plot is available to calculate the activation energy (E_a) and the collision frequency factor (Z).

7. ERROR CALCULATIONS

The confidence[5] limits for all values were calculated according to the t-distribution method:

$$T = n-2 \quad \frac{X - \mu}{s_x}$$

Note that two degrees of freedom are assumed and a distribution of 90 percent ($t_{.90}$) was used.

8. ERROR DISCUSSIONS

Obviously the method used in determining the kinetic constants was uncertain due to the digital sampling techniques at long time intervals. This sampling may have totally overlooked fluctuations in the actual decomposition curve. The specific heat of the pans, although constant for the materials of both sample and reference pans, may have caused significant error due to nonuniformity of the pans. Another error consideration was the differential temperature calibration of the DSC. Since this was directly responsible for a correct balance between the two sides of the DSC, a slight imbalance would cause a definite change in the deflection, b. The greatest possible source of error in this study is ascertained to be the minute decomposition which may have occurred in cycling the explosive in the oven. However, previous experiments had shown that a sample of RDX in the DSC II showed no deflection or drift on the most sensitive scale. Additional DTA/TGA studies showed no weight loss from the RDX cycled up to 180°C for the profiles selected.

Although these errors presented are definite considerations, the experiment actually depended very little on widely fluctuating variables and thus presented fairly accurate results.

9. HENKIN TEST

The RDX used for the DSC studies was from the same lot as used in the Henkin test.

Samples were sealed in the aluminum tubes and cycled in a modified gas chromatograph oven fitted with thermocouples to monitor the temperature. An electric timer was used to monitor the elapsed time of the cycles.

Continuous problems were encountered with the Henkin test setup. The apparatus was modified with a thermocouple placed directly at the center point of the tube corresponding to the center of the explosive sample. This was connected to a digital thermometer, accurate to ± 0.1°F.

Temperatures were recorded for immersion and for time of explosion. It was observed that the temperature of the woods metal would drop 4-10°F when the tubes were placed in the molten metal bath. Also, problems were encountered with the thermocouple moving and giving erratic readings.

Literature value for RDX is given as 217°C; our baseline was 222°C, and the cycled sample to 176°C gave 224°C.

However, due to the inherent problems and erratic data, these data have been disregarded until further testing can be performed.

10. RESULTS

Below are tabulated average values for E_a and log Z for the baseline and both cycles:

RDX A	E_a (Kcal/mole)	Log Z
Baseline	44.569 ± 6.069	17.069 ± 2.530
Cycle A3	41.649 ± 6.580	15.858 ± 2.743
Cycle D3	39.915 ± 10.373	15.097 ± 2.324

Figures 3 and 4 represent plots of activation energy and log pre-exponential versus temperature profile. Figure 5 represents the order plots for the temperature profiles of the RDX. The plot shows an increase in the order profile for the 350°F (176.6°C) liquid phase decomposition. It was also seen in the order plots that the early part of the reaction below the melting point is not simple; relatively large negative orders were obtained for the cycled RDX. This increase suggests an increase in the rate of decomposition.

This area is being investigated further along with the delay time obtained from the DSC recording.

It was noted that shorter delay times were obtained on the 160°F and 350° F than the baseline RDX. Correlation of this delay time with the time-to-explosion on the Henkin apparatus was the objective; however, no reproducible data could be obtained with the Henkin. Further investigation will continue along these routes.

11. DISCUSSION

The activation energies for the baseline and cycles show a trend which might suggest an increased sensitivity in the explosive samples upon cycling at higher temperature profiles and a possible increase in thermal instability over extended "cycling" conditions. This trend is certainly only the very beginning as in itself it cannot be considered conclusive of an actual decrease in stability. However, work at Los Alamos Scientific Laboratories (LASL) on selected explosives, using the wedge test have shown some increase to shock sensitivity between 25°C and 125°C.

It appears from the data collected that a destabilization of the thermal decomposition of the RDX is detectable. The important points here are: (1) the significance of this indication in terms of experimental uncertainties, (2) its meaning in terms of the mechanism of the decomposition, and (3) its validity for application to scale up to the actual weapon system level.

The frequency factor gives an indication of an increase in reaction rate with cycled explosive. The number of collisions approximately remained the same while the time required was decreased.

Both of these observations tend to uphold the preresearch theory that the explosive would show increase in sensitivity under temperature cycling.

It should be noted that in real systems more complex cases may be observed as results of the complexity of the mechanism by which the chemical reaction of decomposition takes place. It is, however, always necessary to take into consideration the possibility of progressive dissolution of the original explosive in the reaction products, with a corresponding change in the kinetic laws governing the reaction.

REFERENCES

(1) Rogers, R. N., "Differential Scanning Calorimetric Determination of Kinetics Constants of Systems That Melt with Decomposition," Los Alamos Scientific Laboratory, 1976.

(2) Rogers, R. N., "Simplified Determination of Rate Constants by Scanning Calorimetry," Los Alamos Scientific Laboratory, 1973.

(3) Ortiz, L. W. and Rogers, R. N., "Simplification of Differential Temperature Calibration and Emittance Measurements in DSC," unpublished.

(4) Thomas, George B., Jr., Calculus, 2nd Ed, Reading, Mass., Addison-Wesley Publishing Company, Inc., 1966.

(5) Lindgren, B. W., and McElrath, G. W., Introduction to Probability and Statistics, 3rd Ed, New York, MacMillan Company, 1969.

BIOGRAPHY

Mr. Thomas G. Floyd attended Vanderbilt University and Eastern Kentucky University, receiving his B.S. in chemistry in 1961. Mr. Floyd has done additional studies at the University of Minnesota, Indiana State University and has taken short courses in gas chromatography, IR and thermal analysis.

Mr. Floyd worked in medical research at the University of Cincinnati from 1961-63. From 1963-64 he was instructor in chemistry and physics and began work with the Navy in 1964 until 1970 at the Naval Weapons Support Center, Crane, Indiana.

Mr. Floyd has been at Eglin AFB since 1970, where he has worked in the fields of flame fuels, incendiary and FAE. His assignment to the High Explosives Research and Development Laboratory was in 1975 where he has been involved in various aspects of the explosives field.

He has publications in the fields of rheology, formulation of new flame fuels, accelerated aging and reaction kinetics.

Mr. Floyd is currently involved in the area of thermally stable explosives and kinetics of conventional explosives at Eglin AFB, Florida.

He is a member of the American Chemical Society and the Association for the Advancement of Science.

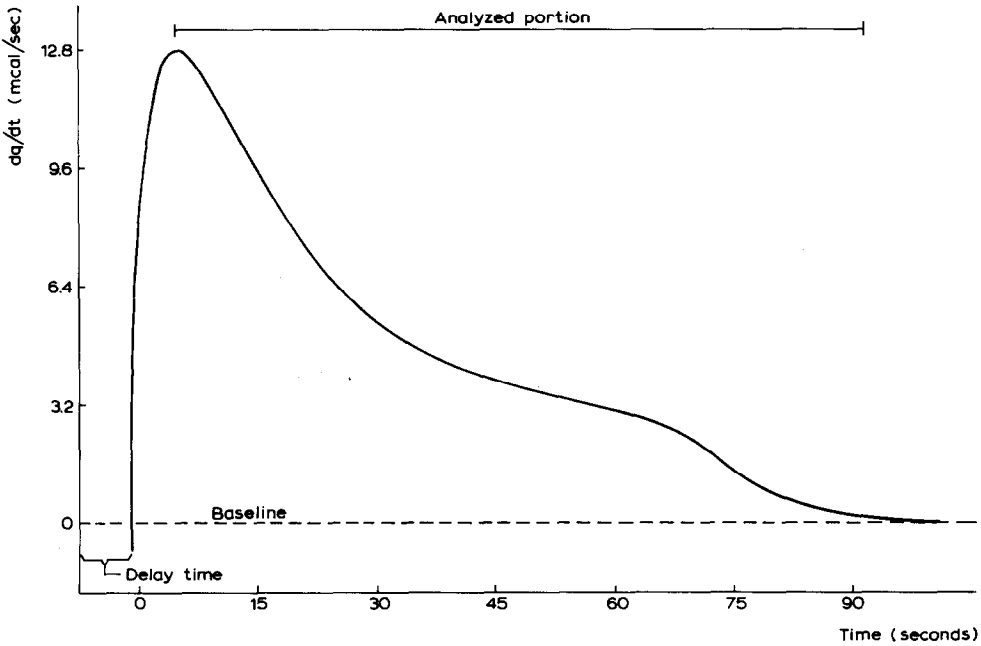
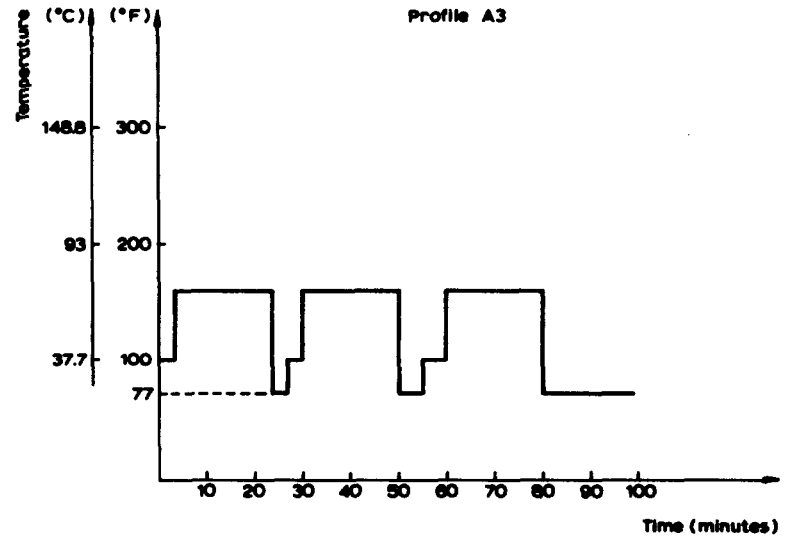


Figure 1. Typical DSC curve for decomposition of RDX (523.0° K)


Profile A3
Temperature
(°C)
(°F)
148.8
300
93
200
37.7
100
77
10
20
30
40
50
60
70
80
90
100
Time (minutes)

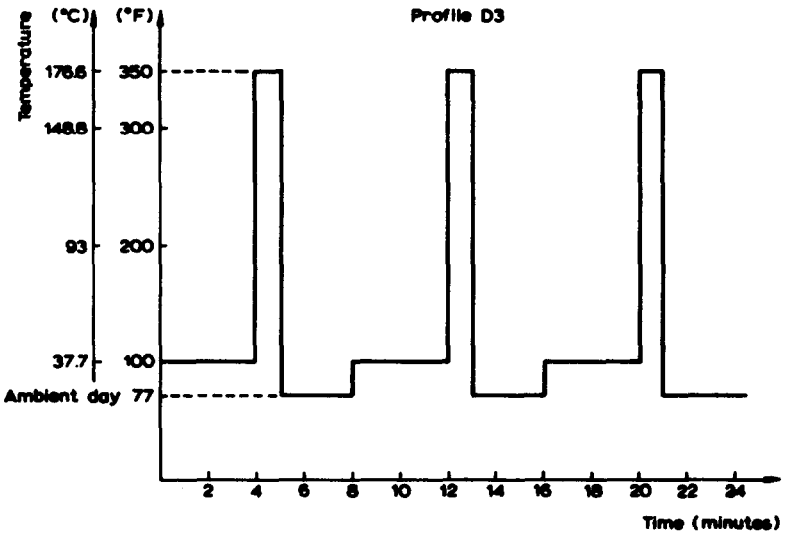

Profile D3
Temperature
(°C)
(°F)
176.6
350
148.8
300
93
200
37.7
100
Ambient day
77
2
4
6
8
10
12
14
16
18
20
22
24
Time (minutes)

Figure 2.

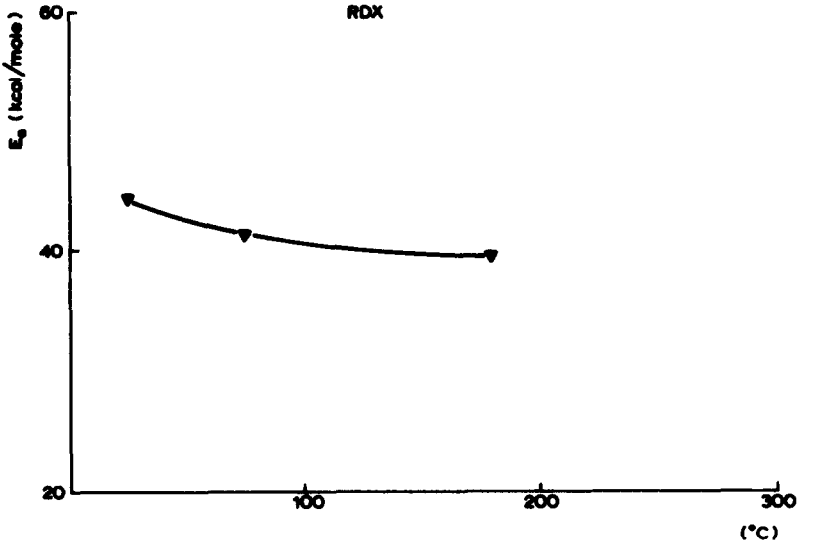


Figure 3. Activation energy vs. temperature profile.

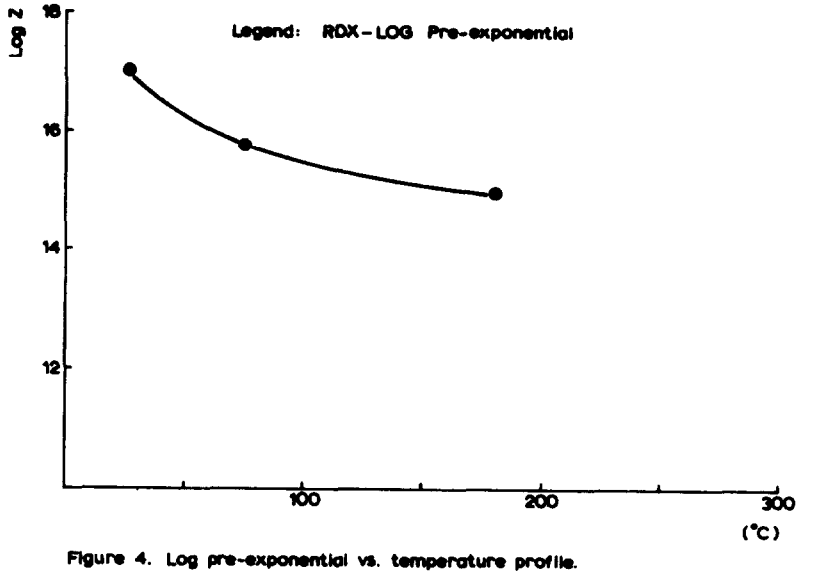


Figure 4. Log pre-exponential vs. temperature profile.

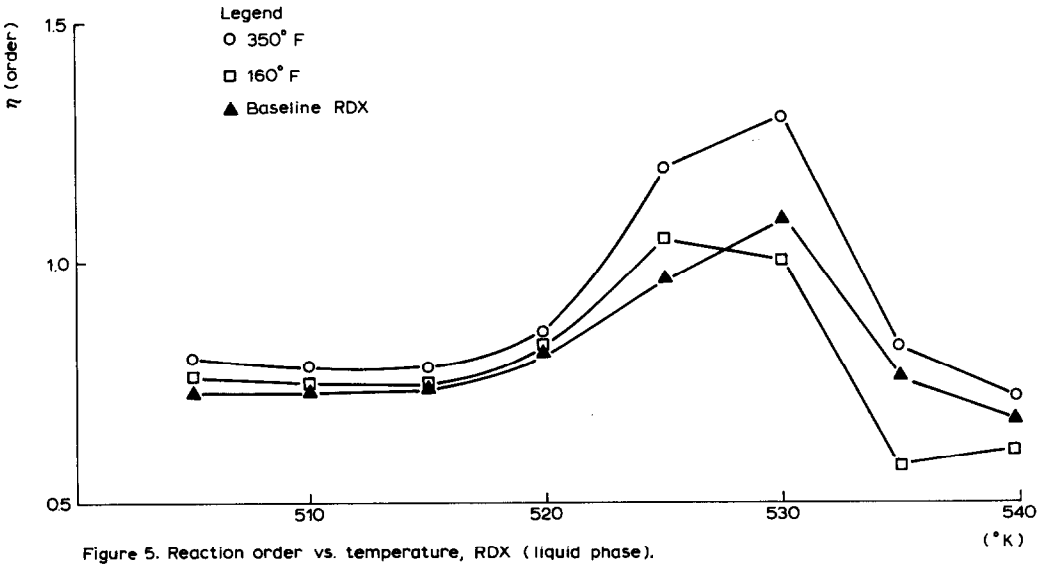


Figure 5. Reaction order vs. temperature, RDX (liquid phase).

REFERENCES

1. A. S. Tompa, D. M. French and B. R. White, NSWC/WOL Tech Report #77-72. Naval Surface Weapons Center, Silver Spring, Maryland, April 1977.

2. I. M. Kolthoff and R. Belcher, Volumetric Analysis, Volume III, 1957, Interscience Publishers, Inc., New York

3. J. C. Schumacher, Perchlorates, 1960, Reinhold Publishing Corp., New York

4. Kirk-Othmer Encyclopedia of Chemical Technology, Volume I, Second Edition, 1963, Interscience Publishers, New York