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THE THERMAL SENSITIVITY OF EXPLOSIVES AND PROPELLANTS (U)

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THE THERMAL SENSITIVITY OF EXPIOSIVES AND PROPELLANTS (U)

Prepared by

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ABSTRACT: The thermal sensitivity test, first developed at the Naval Ordnance Laboratory, has been applied to a number of energetic solids and liquids, including some new and unusual compounds. The correlation between the temperature at which a solid organic explosive reacts in 250 microseconds and the materials impact sensitivity has been extended and supported by new experimental data. The thermal sensitivities of a number of energetic mixtures have been determined and interpreted on the basis of the kinetics and heat output of the initiating decomposition reaction. A scale of thermal sensitivities for liquid explosives and propellants has been established and considered on the basis of current understanding of the sensitivity of liquids. Although the thermal sensitivity results generally do not agree with the results of accepted sensitivity tests, it is recommended that thermal sensitivities be run on newly synthesized, energetic liquids. The meaning of the thermal sensitivity results in terms of Arrhenius parameters governing the initial stage of the explosive decomposition reaction is considered briefly. (U)

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White Oak, Silver Spring, Maryland

NOLTR 61-97 1 September 1961

The Thermal Sensitivity of Explosives and Propellants

The reliable assessment on a small scale of the relative handling hazards of explosives, and particularly of liquids, is an important but difficult problem. This report, an extension of NavWeps Report (NOL) 7328, "The Behavior of Explosives at Very High Temperatures", describes further work on a continuing effort to understand the apparently predominant chemical basis of sensitivity.

This research has been supported by Task RUME 3E 017.

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Captain, USN
Commander

Albert Lightbody
ALBERT LIGHTBODY
By direction

CONTENTS

TABLES

Title

CONTENTS
(Cont'd)

ILLUSTRATIONS

I. INTRODUCTION

A rapid method of heating minute, heavily confined explosive samples has recently been described (1). The explosives are contained in fine, stainless steel, hypodermic needle tubing. The technique is based on the high strength, small heat capacity, high electrical resistivity, and useful temperature coefficient of resistivity of the tubing.

Energetic materials may be introduced into the tubing by suction when they are in the liquid state. The tubing can then be heated to a high temperature in about 20 microseconds by the energy from a discharging capacitor. By suitable circuitry (1), the resistance of the tubes can be monitored to provide a record of the wire temperature and the explosive event. Using this method, time-temperature curves can be obtained over the range 50 microseconds to 100 milliseconds. The results of this procedure may be regarded as a sort of thermal sensitivity for the materials considered.

The thermal sensitivity which is measured in these experiments is primarily a function of the rate of heat evolution in the thermal decomposition of the material. This property generally governs the impact sensitivities of pure, solid, organic explosives as measured at this laboratory by the ERL impact machine (2). The impact sensitivity of a solid explosive gives a good indication of the dangers involved in its shipping, handling and abuse.

The tests which are used to ascertain the sensitivity of liquids are not generally capable of characterizing the hazards involved in their use and abuse.

This report describes some further experiments with meltable solid explosives performed with the hope of extending our understanding of the effects of the heat and rate of thermal decomposition reactions on observed sensitivity. The thermal sensitivities of a variety of energetic liquids have also been determined.

II. EXPERIMENTAL

The experiments described in this report were performed by the methods outlined in reference (1). A more complete description of the experimental details of the thermal sensitivity test is given in reference (3). In order to simplify the test procedure, a new method of delay time measurement is described in reference (3). The new method makes use of an electronic counter stopped by the signal from a microphone to record the explosive event. The new method obviates the necessity for frequent changes in oscilloscope sweep speed. At the same time certain errors in the temperature measurement are introduced which are discussed in reference (3). All the results in this report were obtained using the original procedure and the results are directly comparable with those in reference (1).

The impact sensitivities cited in this report were determined by the ERL method (2) at NOL. The Drop Weight and Card Gap values were obtained from the literature and were determined by the standard JANAF procedures (9).

III. RESULTS AND DISCUSSION

A. GENERAL CONSIDERATIONS

The thermal sensitivities of over 20 different explosive compositions have been studied by the hot tube test technique since the last report (1) was prepared. The results are summarized in Tables 1 and 2. For many materials the delay times vary with temperature over a considerable range according to the expression:

$$\gamma = Ae^{B/RT}$$

where γ is the delay time, T is the absolute temperature, R is the gas constant and A and B are constants for the material under consideration. These A and B values are listed in Tables 1 and 2. The constant B has the units kcal/mole and may be related to, but is not equivalent to, the activation energy for the thermal decomposition reaction.

The slopes of the time-temperature curves obtained in the hot-tube experiments are lower than those expected on the basis of isothermal measurements of decomposition kinetics made at

TABLE 1. THE THERMAL SENSITIVITY OF SOLID EXPLOSIVES

EXPLOSIVE	-log A sec.	$B \times 10^{-3}$ kcal/mole	CRITICAL TEMP. (for explosion in 250 microsec.) °C	IMPACT SENSITIVITY (50% ht 2.5 kg wt type 12 tools) cm
BIS(2,2,2-TRINITROETHYL) FORMAL (TEFO)	11.6	25.9	430	10
BIS(2,2,2-TRINITROETHYL) SUCCINATE (BTNES)	8.3	17.9	550	28
ETHYL 2,2,2-TRINITROETHYL CARBONATE (ETNEC)	7.9	17.4	610	60
BIS(2,2-DINITROPROPYL) FORMAL (DNPFO)	7.7	19.6	760	180
2,2',4,4',6,6'-HEXANITRO-BIPHENYL (HEXA)	9.7	28.7	890	90
PICRIC ACID	6.6	15.9	903	90
BIS(2,2-DINITROPROPYL) CARBONATE (BDNPC)	5.9	12.5	930	65
75% TNETB (2,2,2-TRINITRO-ETHYL 4,4,4-TRINITROBUTYRATE)-25% TNT	...	...	560	24
50% TNETB - 50% TNT	...	...	640	32
25% TNETB - 75% TNT	...	...	770	43
TNT (revised)	7.2	20.5	970	160
AMMONIUM NITRATE	8.0	19.5	690	>320

TABLE 2. THERMAL SENSITIVITY OF LIQUIDS

LIQUID	-log A	$Ex10^{-3}$ kcal/mole	"CRITICAL TEMPERATURE" (250 microsec.) °C	IMPACT SENSITIVITY type 13 tools cm.	DROP WEIGHT SENSITIVITY kg.cm.
HYDRAZINE-DEKAZENE,7.5:1 (mole ratio)	8.4	15.5	430	12	2-4
BIS(2-CHLORO-2,2-DINITRO-ETHYL) FORMAL (CLEFO)	9.5	21.0	500	51	...
1,2-BIS(DIFLUORAMINO)-2-METHYLPROPANE (IBA)	8.5	18.6	550	131	8-10
BIS(2-FLUORO-2,2-DINITRO-ETHYL) FORMAL (FEFO)	8.5	20.2	620	37	...
CAVEA-B 120	8.4	19.8	620	...	90-150
BIS(DIFLUORAMINO) FURAN (3 isomers)	10.9	31.4	660	60-90	4-8
1-FLUORO-1,1-DINITRO-ETHANE (DAPHNE)	7.3	17.6	780	114	120
DITHEKITE	6.6	15.4	860	...	...
ETHYL NITRATE-NITROBENZENE 50-50 (weight percent)	6.5	13.9	780	...	...
DI-β-NITROXYETHYL NITRAMINE (DINA)-NITROBENZENE,50-50 (weight percent)	5.7	9.5	730	...	...
TETRANITROMETHANE (TNM)	5.8	10.6	800	320	...
TNM-NITROBENZENE 2-1 (parts by volume)	6.9	14.2	680	...	...

lower temperatures. Zinn (4) has performed a mathematical analysis of the physical events which lead to an explosion in the configuration used in these experiments. He finds that he is able to relate the hot-tube results with the isothermal measurements by considering the depletion of the explosive by reaction during the time lag before explosion. Previous similar calculations (5,6) on thermal explosions have omitted this complicating factor by assuming that very little of the explosive is used up during the time lag, so that concentration can be considered constant, independent of time. Zinn found that the shape of the time-temperature curve was strongly dependent on the value of the heat of reaction. In fact, for TNT, he obtained curves which agreed well with those observed in the thermal sensitivity test by assuming a constant value for the heat of decomposition which was lower than the heat of explosion. The results were also consistent with results obtained at lower temperatures with larger samples (4).

B. SOLID EXPLOSIVES

The results for solid explosives are shown in Table 1. Also listed are the impact sensitivities, as measured on the ERL impact-machine, with type 12 tools, 2.5 kg wt, and sandpaper, and the "critical temperatures" at which explosion takes place in 250 microseconds. The relationship between this critical temperature and impact sensitivity has been discussed before (1).

Figure 1 shows the critical temperatures determined thus far for solid explosives plotted against their measured impact sensitivities. Previously reported values (1) are included for comparison. The relationship is seen to hold reasonably well although there are significant deviations.

Data obtained on the individual compounds are shown in Figures 2 through 11. Some interesting features are discussed in the subsequent sections.

1. Picric Acid and Hexanitrobiphenyl. Hexanitrobiphenyl, (HEXA), a promising heat resistant explosive, is quite stable at temperatures as high as 260°C giving off gas at a rate of only 0.9 cc/g/hr. Picric acid, a relatively stable high explosive gives off 2.8 cc/g/hr at only 210°C. The two materials have roughly the same impact sensitivity, about 90 cm. In previous studies (7) it has been suggested that where there is a change in the ordering of explosives between the vacuum stability test and the impact test, there should be a significant difference in the activation energies of their thermal decomposition

reactions, since it is felt that both tests are primarily functions of decomposition kinetics. Thus, there should be intersections in their rate-temperature curves between the thermal stability test temperature and the initiation temperature.

The results for the two materials are shown in Figure 2. Although the time-temperature plot for HEXA is curved, it is steeper than the plot for picric acid. Moreover, the two plots cross in the initiation region near 250 microseconds. It is evident that two materials of comparable sensitivity should behave similarly in the initiation region. It is also evident that the more stable material should have the greater slope and thus be less reactive at lower temperatures. The activation energies for the thermal decomposition of these two materials have not been determined, but it seems safe to infer that the activation energy for HEXA is higher than that for picric acid.

2. TNT-TNETB Mixtures. The results for a series of TNT-2,2,2-trinitroethyl 4,4,4-trinitrobutyrate (TNETB) mixtures are shown in Figures 3, 4 and 5. The tubes were filled with a molten solution of the two materials. Solidified samples of the melts were ground and submitted for impact sensitivity determinations. The Figures show that the strange shape of the TNETB time-temperature plot, Figure 4, is manifested in these experiments as a curvature, but the upturn seems to have vanished. In general the points are closer to the TNETB than to the TNT data.

It would appear that the TNT is acting as an inert diluent. The curves for the pure materials show that at a given temperature TNT is reacting 100 fold more slowly than TNETB. If the chemical decomposition which leads to initiation is a first order reaction, one would expect that in a 50% solution the rate of decomposition per unit volume would approximately be halved, and the time delay doubled. Since this would shift the time-temperature relationship by only 0.3 log units, it would effect only a slight shift on a graph such as Figure 3. If the reaction were of higher order, the effect would still be relatively slight. One can easily calculate the curves of TNETB solutions based on the linear portion of the TNETB curve and using the first order rate law for different concentrations.

By such a procedure one would predict new "critical temperatures" which may be used to estimate impact sensitivities from Figure 1. These predicted sensitivities are shown in Table 3. If the sensitivity of mixtures were a linear function of concentration as has been suggested by Kamlet (8), one would expect the sensitivities shown in the third column of Table 3.

The actual results are plotted in Figure 6 and are seen to lie between the two predicted curves. The deviations from the kinetic prediction are probably due to the dependence of the delay times on both the rate and energy of reaction as will be discussed below.

TABLE 3

TNETB-TNT MIXTURES

Concentration of Mixture		Impact Sensitivity		
		Linear Rel.	1st Order	Observed
Wt % TNETB	Wt % TNT	cm	cm	cm
100	0	...	...	18
75	25	31	19	24
50	50	53	22	32
25	75	93	27	43
0	100	...	...	160

C. THE SENSITIVITY OF LIQUIDS

The determination of the sensitivity of energetic liquids has been accomplished by a variety of means. The JANAF Panel on Liquid Propellant Test Methods has recommended a series of test procedures which give relative values for the ignitability, detonability, thermal stability, and sensitivity of liquids(9). Unfortunately, the various sensitivity tests do not give the same indication as to the hazardousness of a given material. For example, a B-N monopropellant system, dekazene dissolved in hydrazine, has been studied extensively. For a mole ratio of 7.5 or 8.0 hydrazine to one dekazene, impact sensitivities varying from 2 to 5 kg cm have been reported(10), indicating a rather hazardous material. At the same time, the card-gap sensitivities for this material have been in the 1-5 card range indicating a quite insensitive material(10). Practical experience during rocket motor firings shows that the monopropellant is indeed hazardous(11).

On the other hand, the card-gap test shows nitromethane to be quite sensitive while the impact sensitivity test gives a contrary indication. Nitromethane has been handled in large quantities as an article of commerce, but even this material has been known to detonate catastrophically.

By means of the hot-tube test technique, it is possible to establish a scale of thermal sensitivities for a variety of liquid explosives and propellants. Such a scale, shown in Table 4, may be obtained by considering the relative positions of the temperature time relations for different materials on a graph such as Figure 12. This scale of sensitivities shows only marginal correlation with the results of other tests. In Table 4, the thermal sensitivity scale is compared with the results of the drop-weight test. The qualitative correlation is clearly not as good as that obtained by comparing the thermal sensitivity test with the ERL impact test for solids.

TABLE 4

SCALE OF SENSITIVITIES FOR LIQUIDS

Order of Thermal Sensitivity (drop weight sensitivity in parentheses, by Olin-Mathieson Test)

Nitroglycerine(1.6)·BN Monopropellant(2-4)·IBA(8-10)>FEFO-

CAVEA B-120(90-150)·Bis furan adducts(4-8)·Daphne(120)>Nitromethane (67)

The ERL impact machine in use at the Naval Ordnance Laboratory was developed specifically to reflect the hazardousness of solid explosives. Practical experience in the handling and shipping of explosives provided a scale of reference for the design of the instrument. In the ERL machine, which uses flat steel hammer and anvil, the sample of explosive is held on a small sheet of sandpaper. The introduction of sandpaper serves to provide many sites for initiation so that the test serves as a true test of the ease of initiation of a solid explosive. This procedure cannot be used with liquids because they flow and wet the sandpaper. On the bare tools of the ERL test machine the confinement does not seem sufficient to contain a liquid sample. Thus, it seems easier to initiate viscous liquids than mobile ones by this procedure. For this reason, most impact

sensitivity tests for liquids require that the sample be placed under heavy lateral confinement. Such impact tests, when applied to solids have been found to cause reversals in the more normal order of sensitivity behavior (12).

There is a danger, inherent in interpreting the results of a given explosive sensitivity test, that one physical property (extraneous to determining the material's hazardousness) will exert an overriding influence on the relative sensitivities which are measured. In the case of liquids, for example, such properties as a material's vapor pressure or its susceptibility to air oxidation might strongly influence the results of a drop weight test without materially affecting its inherent handling characteristics.

It is felt that none of the accepted sensitivity tests for liquids yield a generally trustworthy indication of hazardousness. It has not been proven that such an ideal test is even possible. It would seem that bulk liquids are inherently more dangerous than crystalline organic solids of equivalent energy and stability. Evidently liquids provide more facile mechanisms by which initiation may occur.

The author feels that the minimum information required on a new experimental energetic liquid would be the impact sensitivity, the result of the thermal sensitivity test and, perhaps, the result of the JANAF thermal stability test. At the present time it is not possible to specify small scale sensitivity tests which will characterize unequivocally the sensitivity of an energetic liquid.

D. THE THERMAL SENSITIVITY OF LIQUID EXPLOSIVES AND PROPELLANTS

The experimental results for a number of energetic liquids are summarized in Table 2. The results for individual compounds are shown in Figures 13 to 19. Some interesting comparisons and relationships are considered in the next few sections.

1. The TEFO Series. A series of compounds based on bis(2,2,2-trinitroethyl) formal (TEFO), including bis(2-fluoro-2,2-dinitroethyl) formal (FEFO), bis(2-chloro-2,2-dinitroethyl) formal (ClEFO), and bis(2,2-dinitropropyl) formal (DNPFO), give the results shown on Figures 10 and 13. This group is of interest because two of the compounds are solids and two are liquids and it presents a convenient series with which to compare the sensitivities of the two classes of explosives.

Vacuum thermal stabilities at 100°C for these materials have been determined by the standard NOL procedure. The least stable compound was CLEFO which gave off 4.9 cc/gm/48 hours. TEFO gave off 1.0 cc, followed by DNPFO and FEFO each of which gave off less than 0.1 cc. Results of the thermal sensitivity test for these materials are shown in Figures 10 and 13. The thermal stability and thermal sensitivity tests correlate well. The ERL impact sensitivity values for the two liquids shown in Table 2 are not consistent with the thermal sensitivity result. In this instance, the thermal sensitivity test has proven itself capable of comparing an homologous series of both liquids and solids. The great improvement in stability in going from TEFO to FEFO is in line with the predictions made by Kamlet (13) before first synthesizing the fluorodinitro group.

2. The Behavior of Solutions. A study of the behavior of solutions in the thermal sensitivity test would permit an understanding of the effect of chemical interactions on sensitivity. A 50-50% solution of ethyl nitrate in the inert liquid, nitrobenzene, gave the results shown in Figure 14. In this case the dilution gave a parallel relationship with times about threefold longer than for pure ethyl nitrate. A solution of 50% DINA in nitrobenzene gave the result shown in Figure 15. In this case the curve was less steep than that for pure DINA and seemed to merge with the DINA curve at low temperatures. On the other hand, a solution of tetranitromethane (TNM) in nitrobenzene gave the results shown in Figure 16. In this case, the time temperature curve of the solution was steeper than that of the pure compound, but seemed to merge with it at higher temperatures.

This behavior can be partially explained by a consideration of Zinn's theoretical analysis of this experiment. In the cases of ethyl nitrate and of DINA, the nitrobenzene must be regarded as an inert diluent. As such it has relatively little effect on the magnitude of the rate of thermal decomposition. However, its presence does have a significant effect on the heat of reaction. Zinn has shown that given a constant activation energy, the slope of these curves is quite sensitive to the heat of reaction. The presence of an inert diluent should then give a line of lesser slope which almost merges with the relationship for the pure material at low temperatures where reaction rate alone is the determining factor. The DINA-nitrobenzene solution shows just this sort of behavior. The TNT-TNETB solid mixtures show similar behavior if the TNT is regarded as an inert diluent. In the case of ethyl nitrate-nitrobenzene, the solution merely appears less thermally sensitive without showing any change in slope.

The TNM-nitrobenzene solution shows the opposite effect. In this case, the diluent is inert kinetically but once a reaction is initiated by the decomposition of the reactive component, its presence adds greatly to the overall heat of reaction. Thus, resorting again to Zinn's analysis, a process of similar activation energy but enhanced energy release would be expected to show the observed behavior. Clearly, additional work on the thermal sensitivity of solution would be of value.

3. The Behavior of Explosive Materials of Unusual Composition. A variety of energetic materials of new or unusual composition have become available in recent years as a result of the search for superior propellants for the space program. Many of these newly synthesized pure materials are liquid at ordinary temperatures and as previously indicated the sensitivities of liquids are not easy to establish or compare. Some of these materials have proved to be quite hazardous and considerable effort has been devoted to the charaterization of their sensitivity. Although considerable information has been obtained about the sensitivity of organic nitro-containing explosives and the dependence of sensitivity on structure and energy, this understanding is not immediately applicable to the interpretation of the behavior of the newer classes of materials. These materials may be compared by the standard sensitivity tests but the results are not always reliable.

The thermal sensitivities of a number of these new materials have been determined using the hot tube technique. The results for the monopropellant composition dekazene in hydrazine mole ratio 1:7.5 are shown in Figure 17. This is one of the most thermally sensitive materials thus far studied. It is quite sensitive to the drop weight test but the card-gap test failed to indicate that the material was extremely hazardous. Most investigators who have dealt with this material extensively regard it as dangerously sensitive to handling (11).

Since the discovery that tetrafluoro hydrazine would add to double bonds, the adducts of this material with various unsaturates have been of growing interest although relatively little is known about their sensitivity. A few such adducts have been obtained in small quantity and their thermal sensitivities ascertained. The results for the isobutylene adduct obtained through the courtesy of the Rohm and Haas Company are shown in Figure 17. Six different adducts of tetrafluoro hydrazine and furan (three bis and three tetrakis) have been obtained from the ESSO Research and Engineering Company. Since there was only sufficient material for a relatively few shots

on each material, the three bis adducts are treated as a single compound. Results for the bis isomers are shown in Figure 18. The slope of the time-temperature plot is extremely high. By comparison with Figure 12, the position of the plot and the value of the "critical temperature" indicate that the thermal sensitivity of these materials is relatively low. On the other hand, the Olin-Mathieson drop weight test and the ERL impact indicate that the materials are fairly sensitive. This observation has been confirmed by practical experience. It would seem that the steepness of the plot contributes to the sensitivity of these materials by assuring the propagation of any incipient initiation.

The results for the tetrakis isomers are confusing but there are strong indications that their behavior is essentially identical to that of the bis compounds.

Another class of compounds of considerable interest to the propellant field are the series of amine nitrates which make energetic monopropellants when dissolved in nitric acid (14). One of the most promising and extensively studies of these propellant compositions, Cavea B 120, obtained through the courtesy of the Wyandotte Chemical Corporation, has been subjected to the thermal sensitivity test.

Results for this material are shown in Figure 19. This material appears quite insensitive to the JANAF drop weight and card-gap tests, whereas its thermal sensitivity is moderately high. In at least one instance the material has detonated during the course of a rocket motor test (15).

A related compound, the liquid explosive dithekite has also been studied with the result shown in Figure 19. This material was prepared by mixing 425 parts of 88.9% nitric acid with 77.6 parts of benzene.

The inorganic high explosive ammonium nitrate can also be discussed under the present heading because of its chemical and physical differences from the more common class of high explosives. The results for this material are shown in Figure 11. This material shows the rather peculiar behavior previously observed for some of the polynitro aliphatic high explosives. Its thermal sensitivity seems somewhat excessive in view of its behavior in other tests and its known handling qualities. However, the physical properties of this material are sufficiently different from those of the organic explosives to invalidate the expectation of its adherence to the thermal sensitivity-impact sensitivity correlation.

E. CHEMICAL KINETIC CONSIDERATIONS

The determination of the magnitude of the Arrhenius parameters governing the initial, endothermic, and, ostensibly, rate determining step of the pyrolysis reactions of explosives has been the subject of a vast amount of research and speculation. It has even been suggested, by a practitioner, that the subject has been pursued ad nauseum. Various investigators have reported activation energies for explosive decomposition reactions ranging from 10-70 kcal/mole. Cook (16) has expressed the belief that the uncatalyzed decomposition reactions of a number of CHNO explosives of varying sensitivity including nitroglycerine, RDX, TNT, PETN, EDNA, and perhaps others, are governed by essentially similar Arrhenius parameters. According to Cook, all these explosives would have an activation energy in the neighborhood of 32 kcal/mole.

Serbinov (17) has also considered the problem of the thermal decomposition of explosives and has concluded that there are indeed significant differences in activation energy. He believes however, that all decompositions are governed by the theoretical (for unimolecular reactions) pre-exponential factor of $10^{13.6}$ He has collected a variety of data from several authors for three explosives to support his contention. His argument is based, however, on the validity of the assumption of a constant value for the pre-exponential factor.

Cook's belief in the essential similarity of explosives insofar as their decomposition kinetics are concerned would appear to be untenable in view of the results obtained from thermal sensitivity studies. TNT and PETN, two of the explosives he cites as having equivalent uncatalyzed decomposition rates at all temperatures, have been shown by the present method to have explosion delay times which differ by one thousand fold over a considerable range of temperatures. Moreover, these results have been demonstrated in a region of high temperature and rapid decomposition such that catalytic effects are unlikely to have much significance.

According to Serbinov's analysis the idealized, uncatalyzed rate temperature-curves for all explosives should converge on the pre-exponential factor $10^{13.6}$ at a value of 1/T of zero. This would preclude any intersections between explosive decomposition rate curves. The thermal sensitivity procedure has demonstrated many examples of such intersections. The author has interpreted the differences between the ordering of explosives in relatively low temperature thermal stability tests and impact sensitivity tests to be due to such intersections among decomposition curves (20).

Differences in activation energy and intersections have also been inferred by Dacons (7) in a study of the stability and sensitivity of polynitro aromatic explosives. It does not seem reasonable in view of these examples of intersections that Serbinov's analysis of the problem is completely accurate. Moreover, it is not necessary that a decomposition reaction occurring in a solution or in a gas at high pressure exhibit a log A of 13-14. Steele and Laidler have recently considered the high frequency factors which are observed in pyrolysis reactions and concluded that these are allowable and may be the rule rather than the exception (18).

There is another physical factor in addition to decomposition rate which appears to influence the relative thermal sensitivity behavior of explosives. Zinn (4) has shown the importance of the magnitude of the energy of decomposition in influencing the slope of these delay time-temperature curves. Rideal and Robertson (19) have reported estimates of heats of decomposition based on the analysis of the gaseous products of slow thermal decomposition. These results are summarized in the following table. Also included for the purpose of comparison are the computed heats of explosion.

TABLE 5

Heats of Decomposition
as Estimated by Rideal and Robertson (19)

Explosive	Heat of Decomposition cal/g	Heat of Explosion cal/g
EDNA	573	1194
Tetryl	191	1047
RDX	860	1228
HMX	855	1222
PETN	234	1416

The heats of decomposition are seen to be substantially lower than the heats of explosion and it appears evident that the products and energy release in thermal decomposition reactions would be temperature dependent. It seems likely that variations in the heat of decomposition among explosives could cause some of the differences in slope and intersections which are observed.

It would appear that the problem of determining the relative values of the Arrhenius parameters for the thermal decomposition of explosives can be only partially resolved by the thermal sensitivity method. It appears evident that there are significant differences among explosives and that these differences are reflected in the widely varying sensitivity behavior which is observed. It is also evident that additional studies of heats of decomposition and their temperature dependence are necessary as at least a first step toward a more complete understanding of these problems.

IV. ACKNOWLEDGMENT

The author wishes to acknowledge the advice and assistance of Mr. Clayton W. Klotz and Mr. Peter J. Holsberg in carrying out the thermal sensitivity tests. The impact sensitivities reported herein were determined by Mrs. Sarah F. Duck. The author also wishes to acknowledge helpful discussions with Drs. J. M. Rosen, J. C. Dacons, M. J. Kamlet, and D. V. Sickman.

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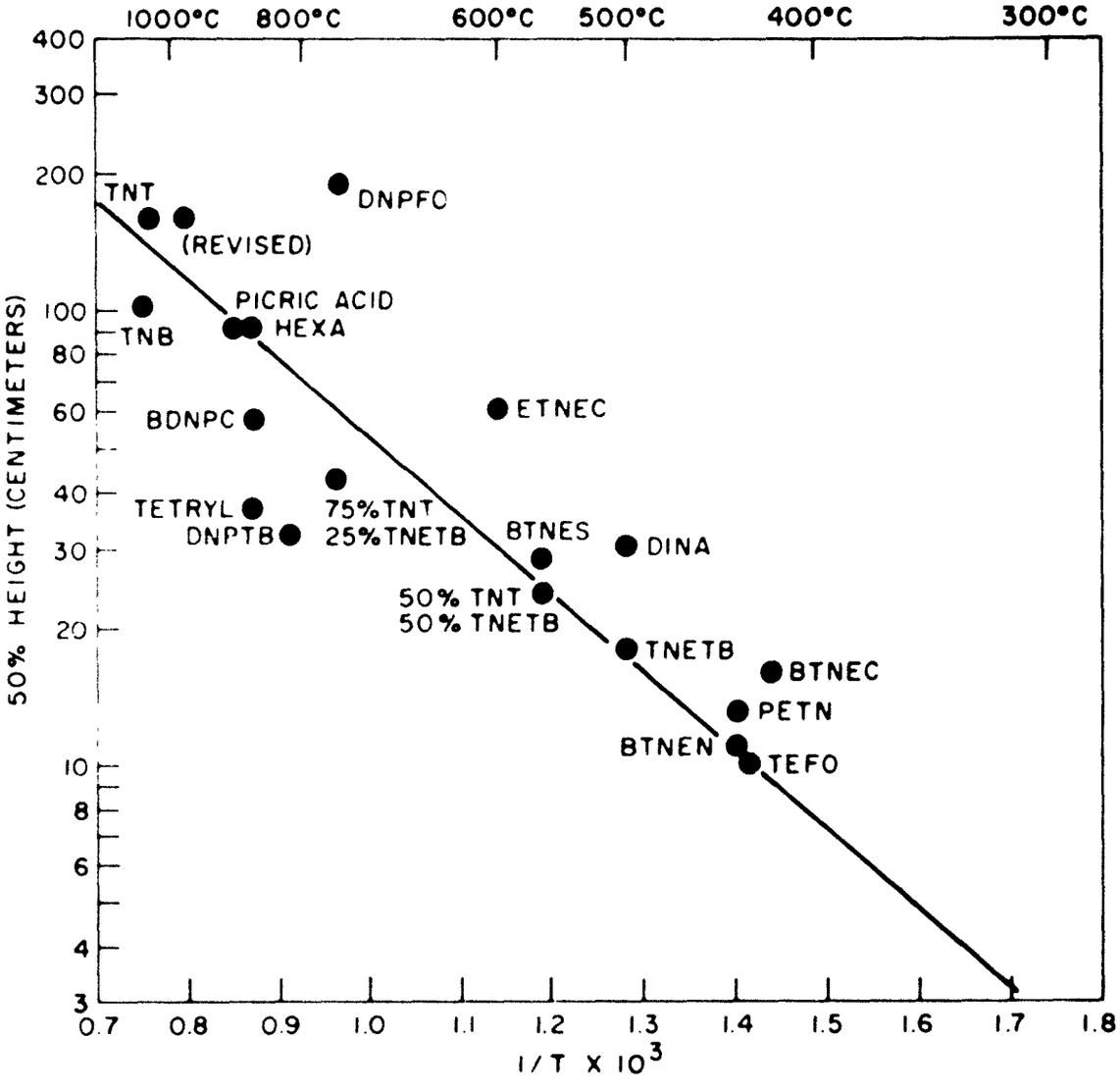

FIG. 1 IMPACT SENSITIVITY VS. RECIPROCAL OF "CRITICAL TEMPERATURE" FOR EXPLOSION IN 250μ SECONDS

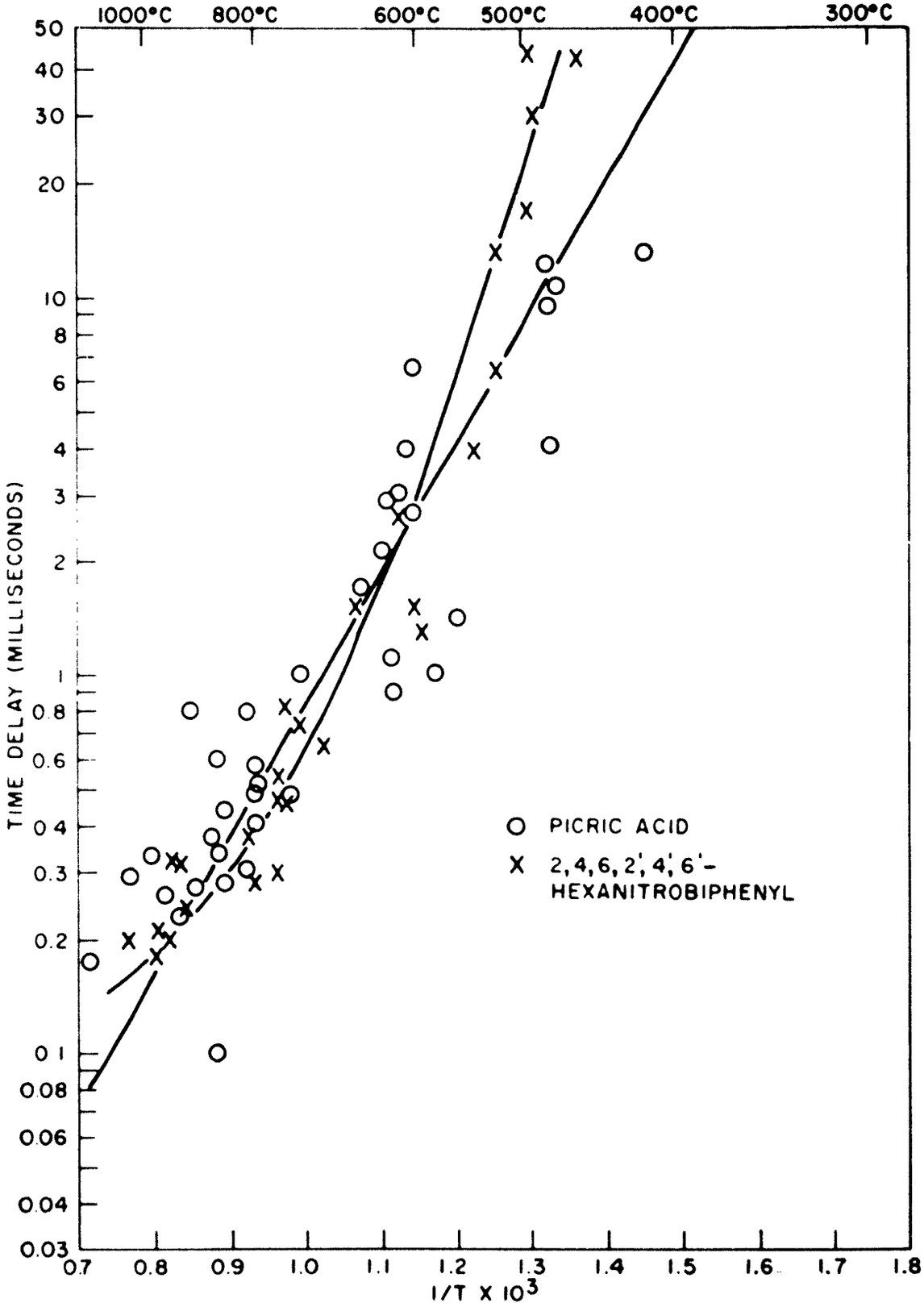

FIG. 2 PICRIC ACID AND HEXANITROBIPHENYL

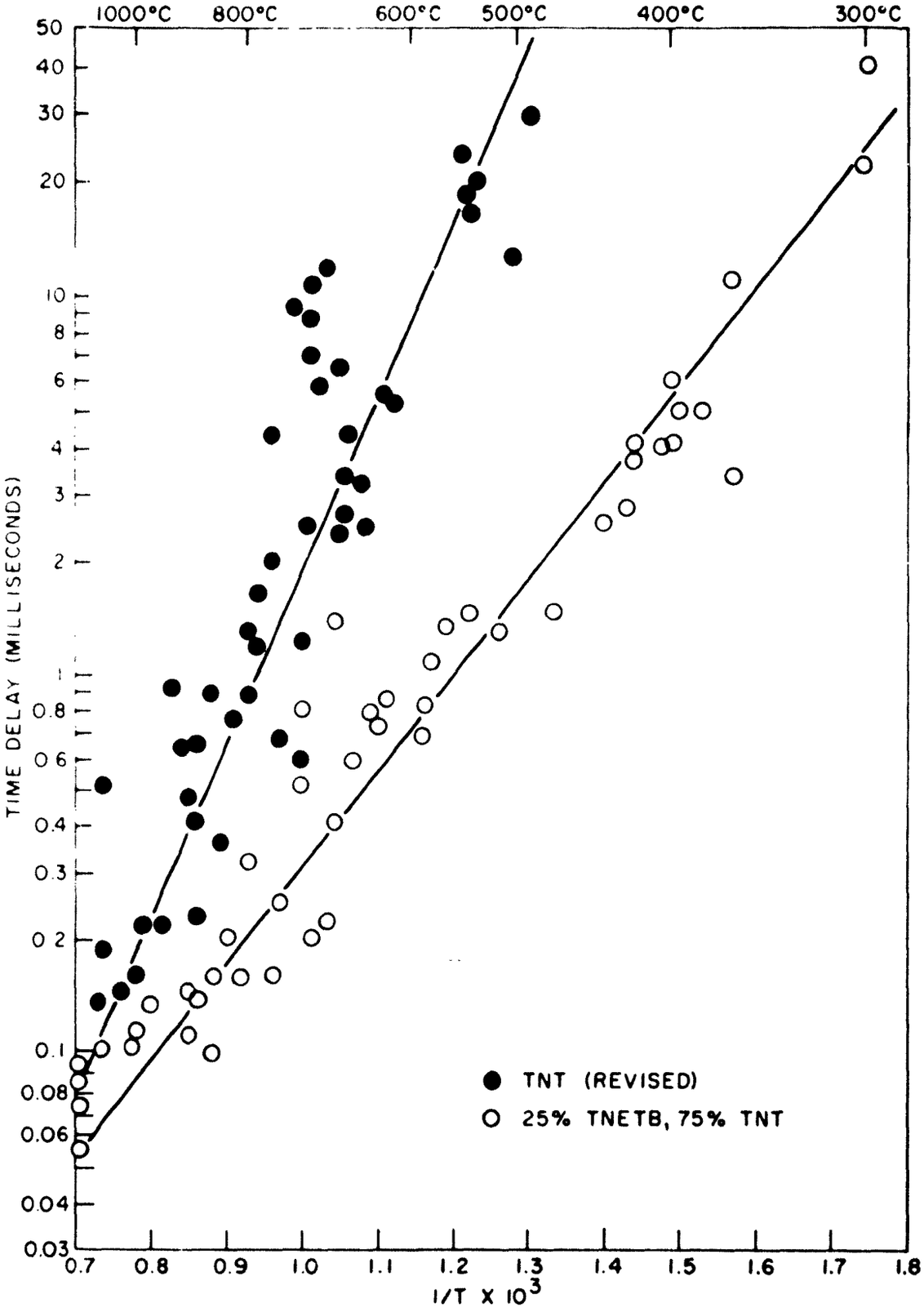

FIG. 3 TNT AND 25% TNETB - 75% TNT

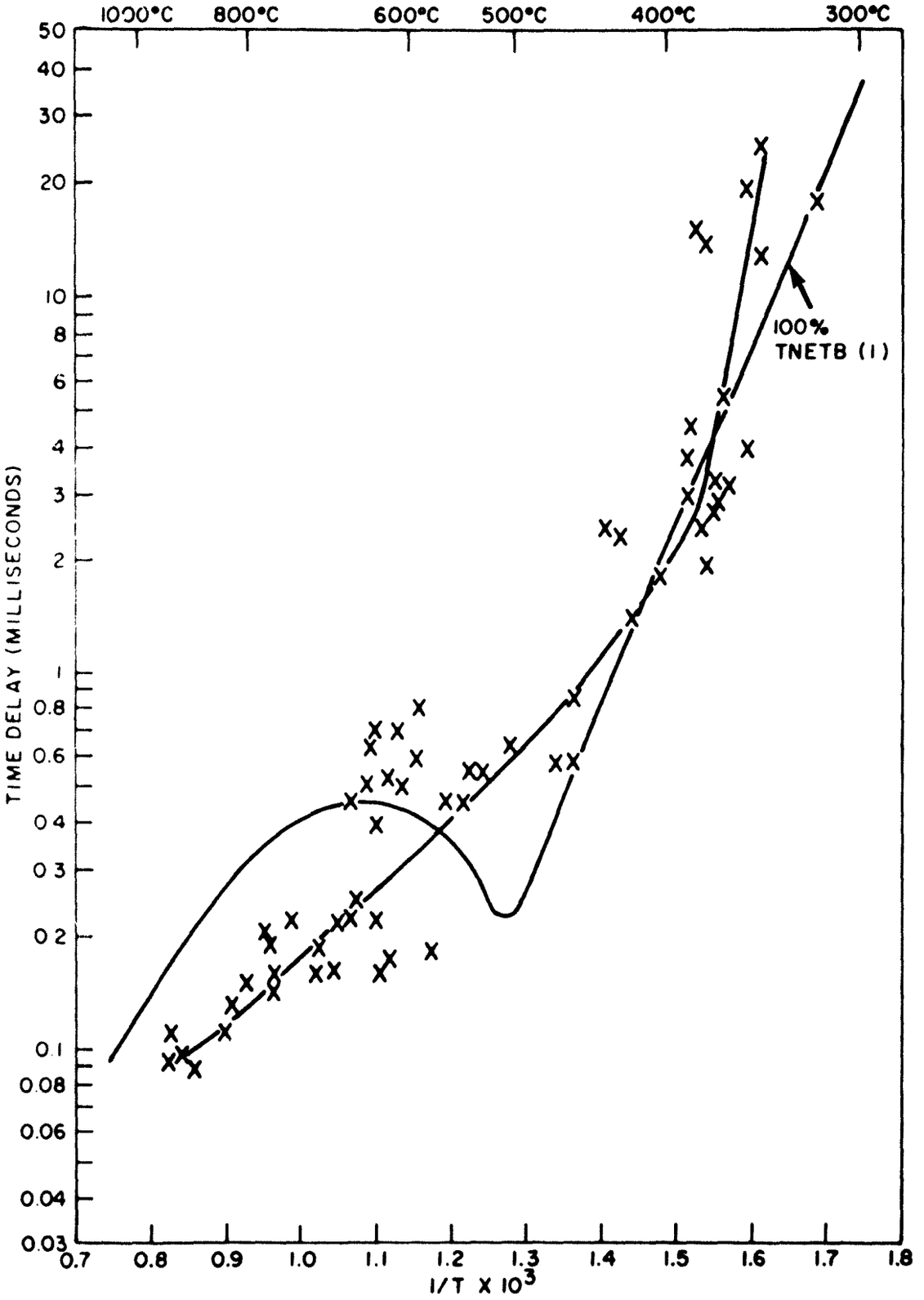

FIG. 4 50% TNETB-50% TNT AND 100% TNETB

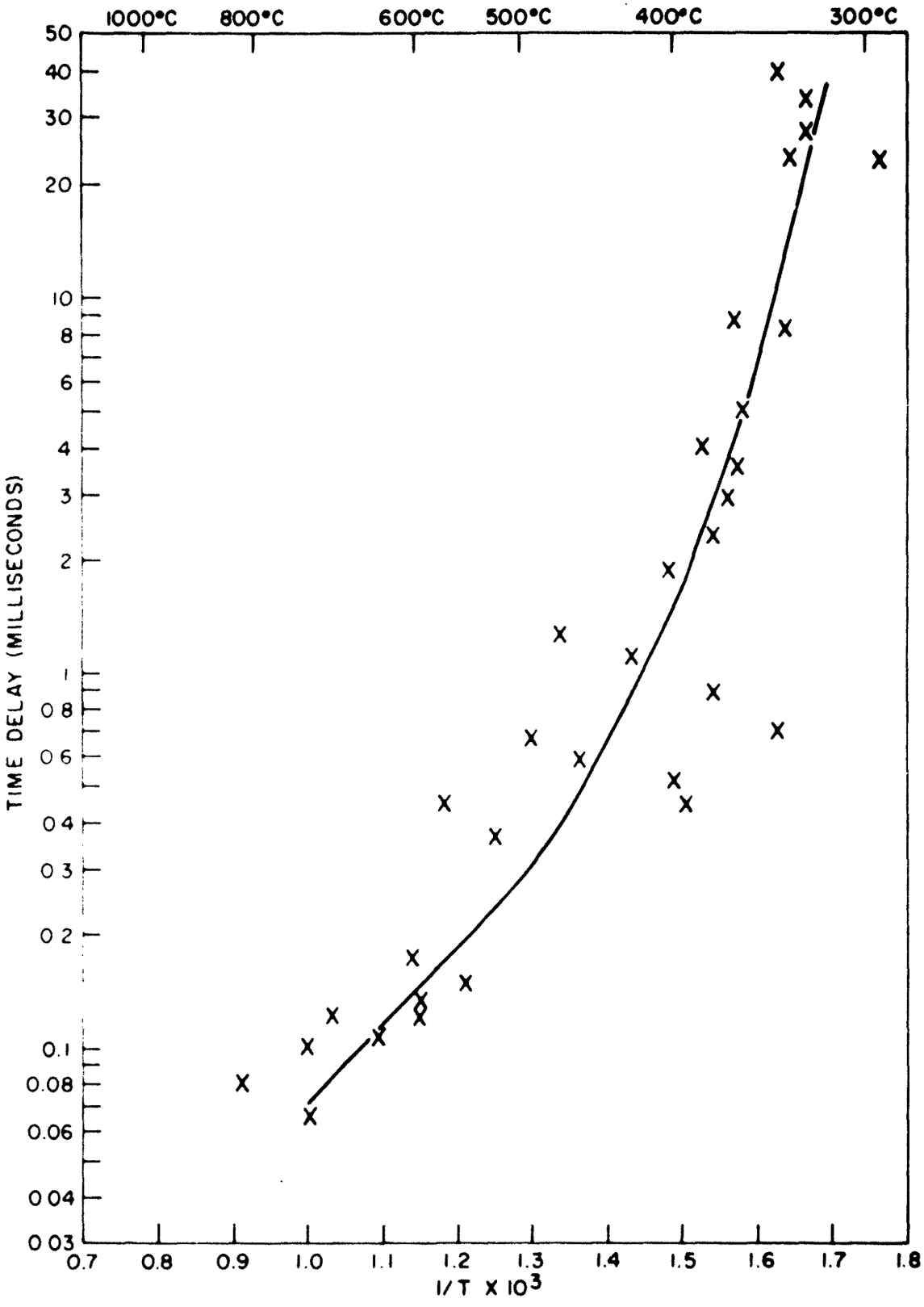

FIG. 5 75% TNETB - 25% TNT

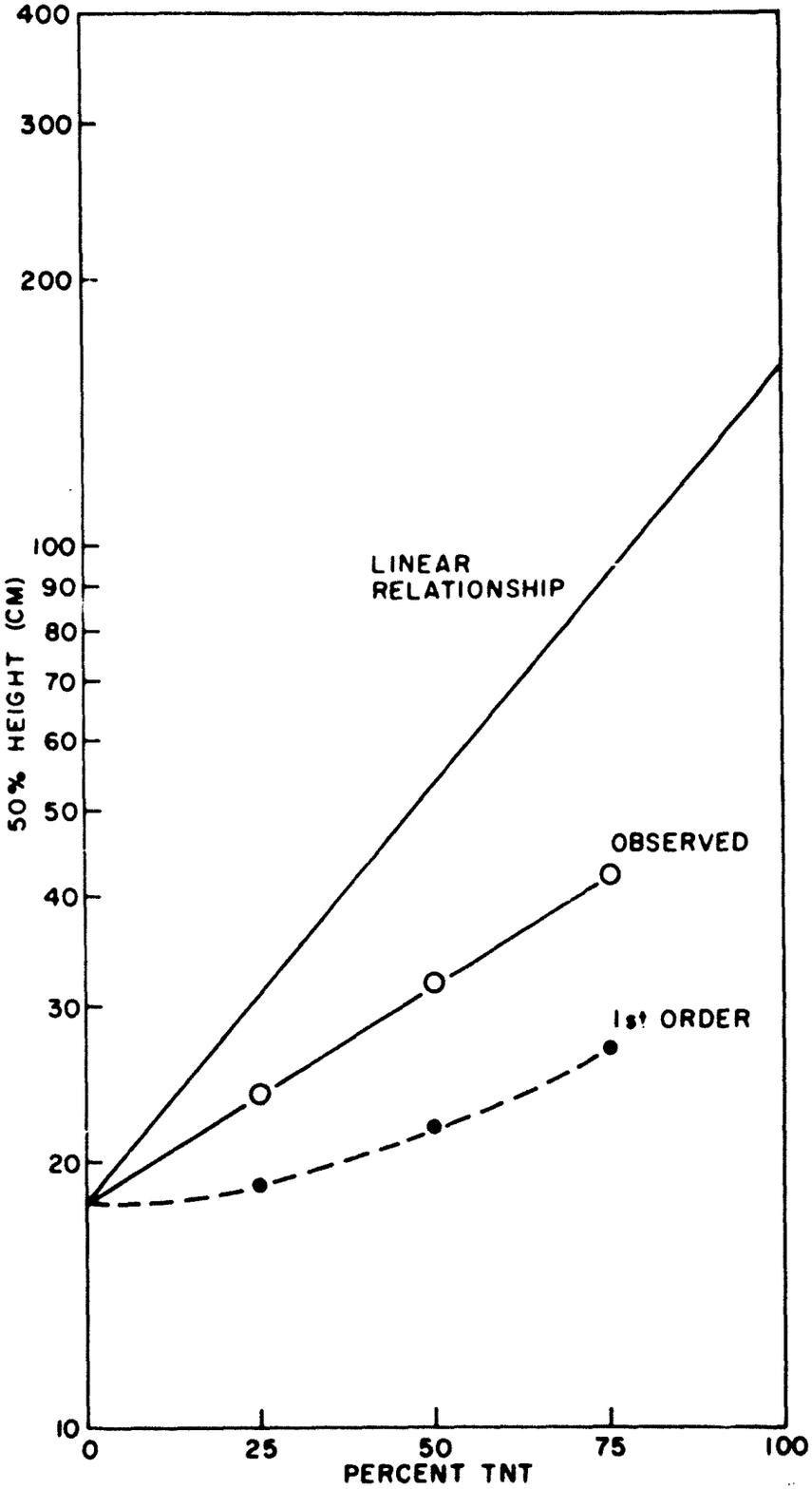

FIG. 6 SENSITIVITY OF TNT-TNETB MIXTURES

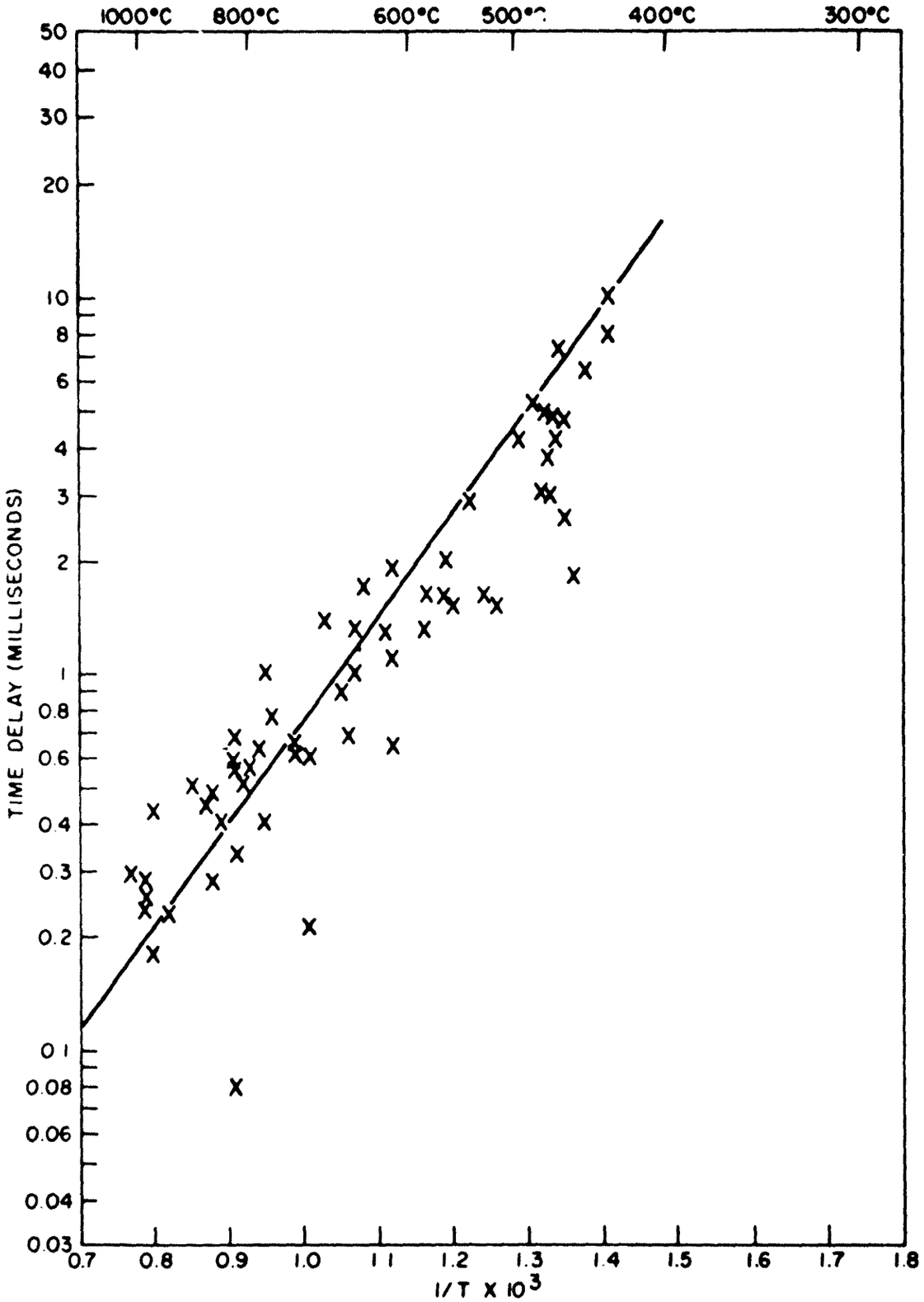

FIG. 7 BIS(DINITROPROPYL) CARBONATE

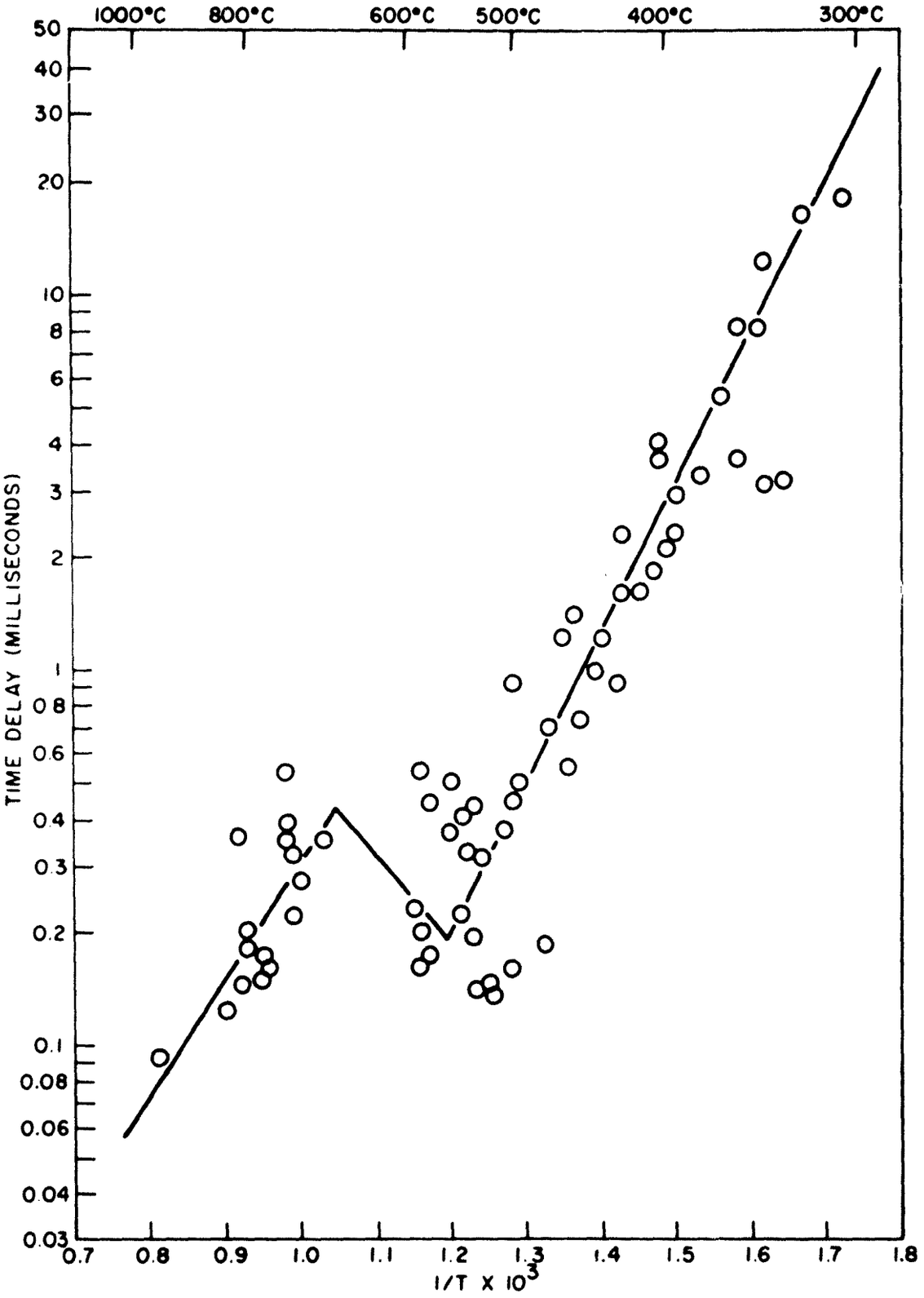

FIG. 8 BIS(TRINITROETHYL) SUCCINATE

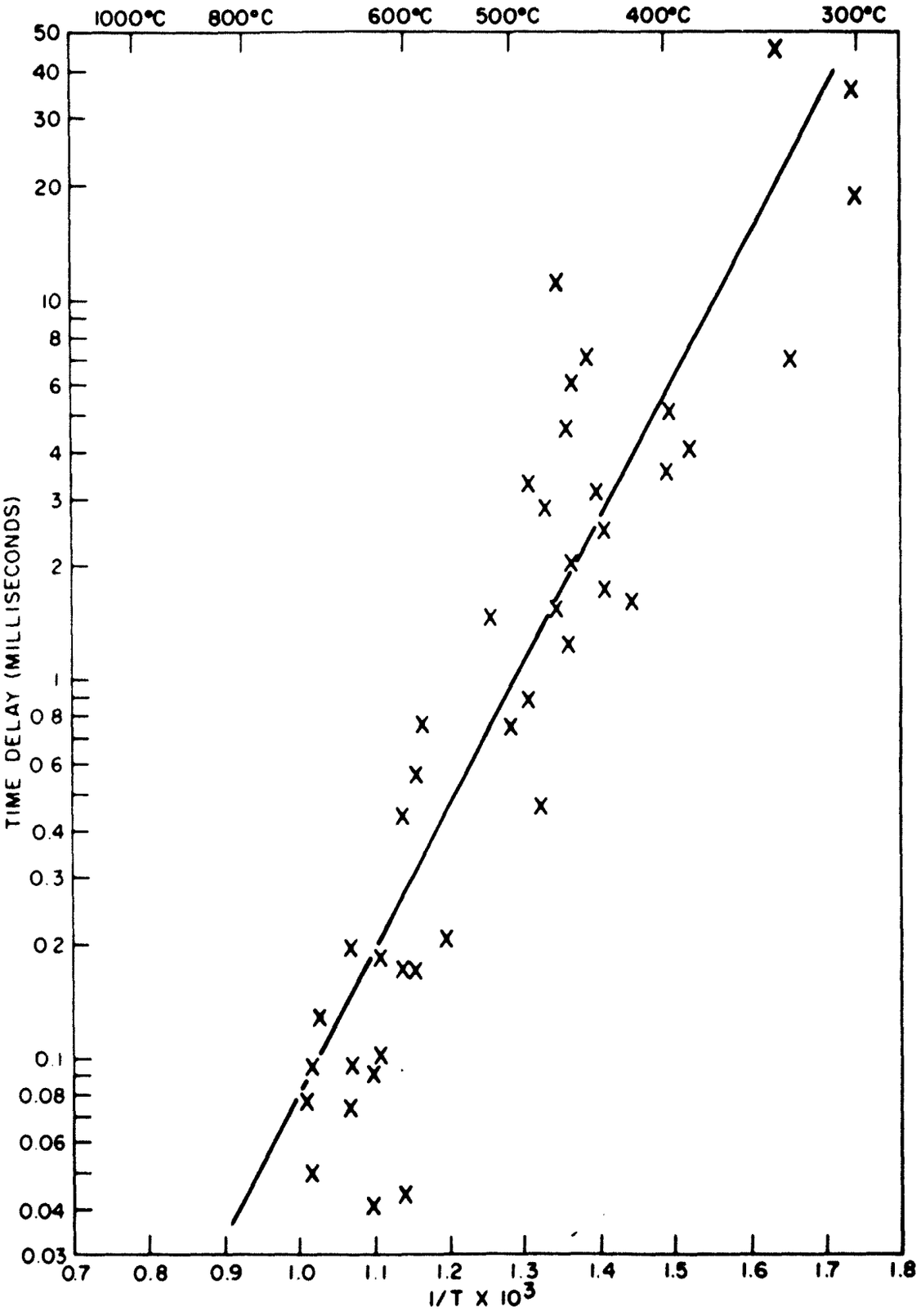

FIG. 9 ETHYL TRINITROETHYL CARBONATE

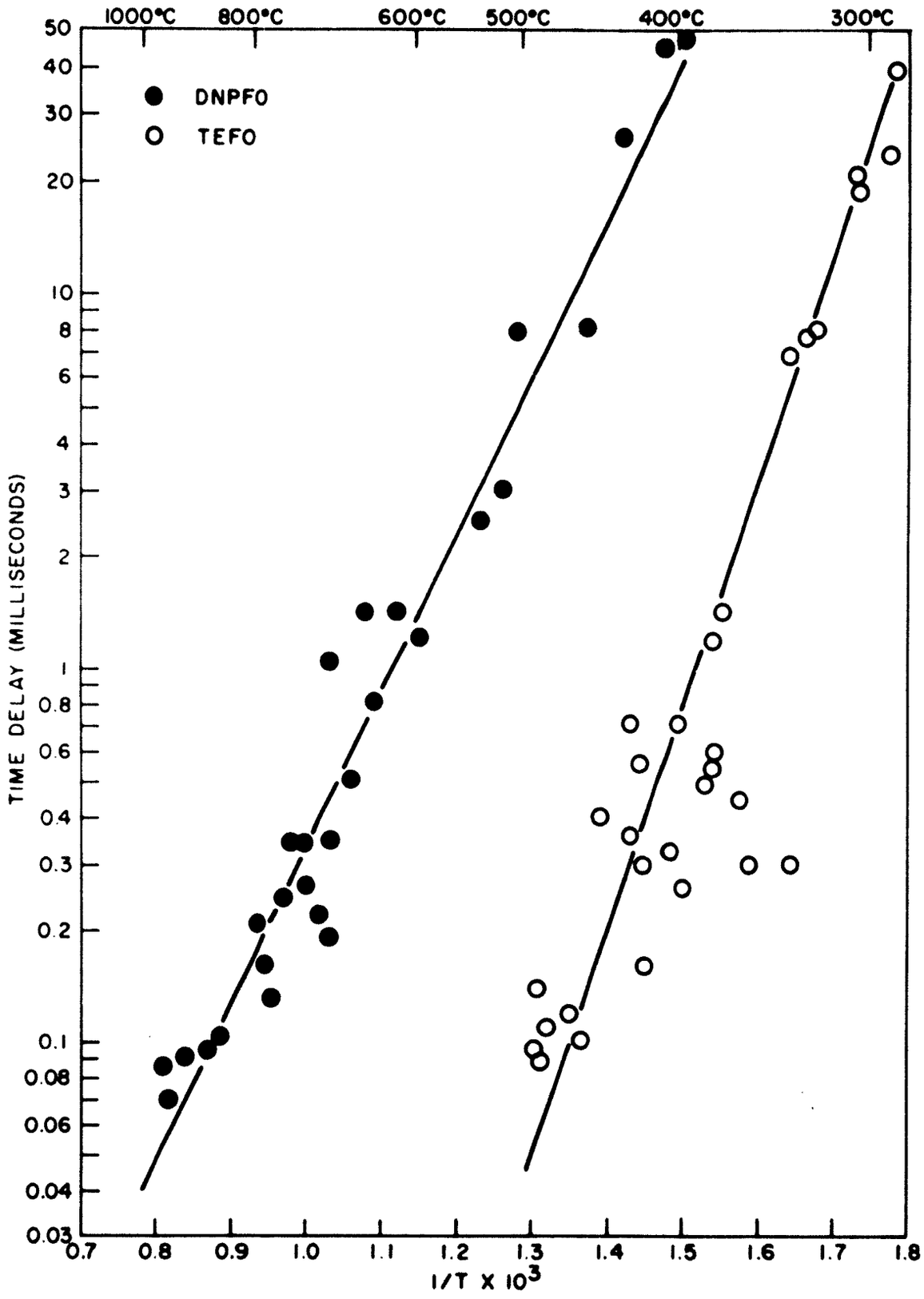

FIG. 10 BIS (DINITROPROPYL) FORMAL AND BIS (TRINITROETHYL) FORMAL

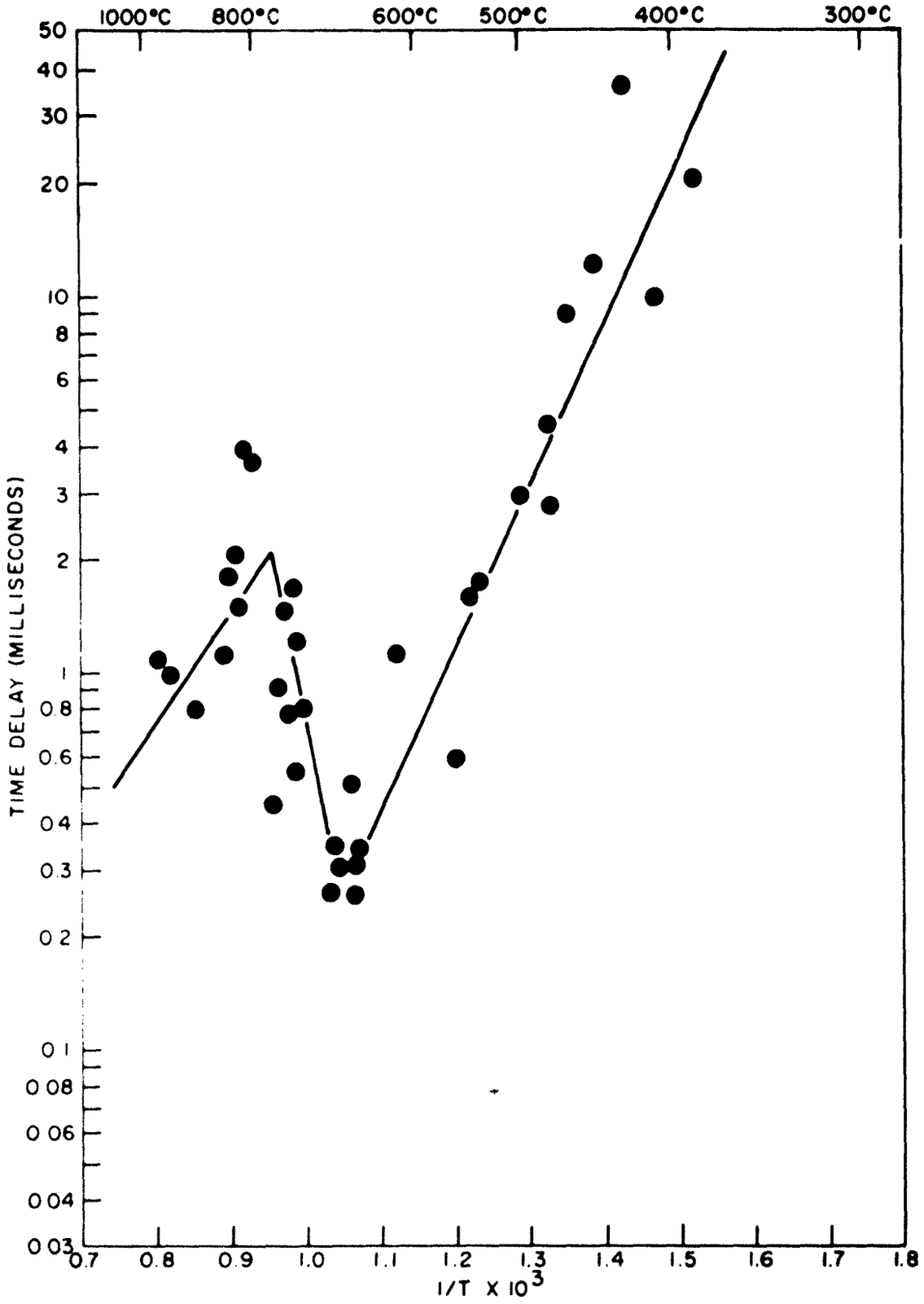

FIG 11 AMMONIUM NITRATE

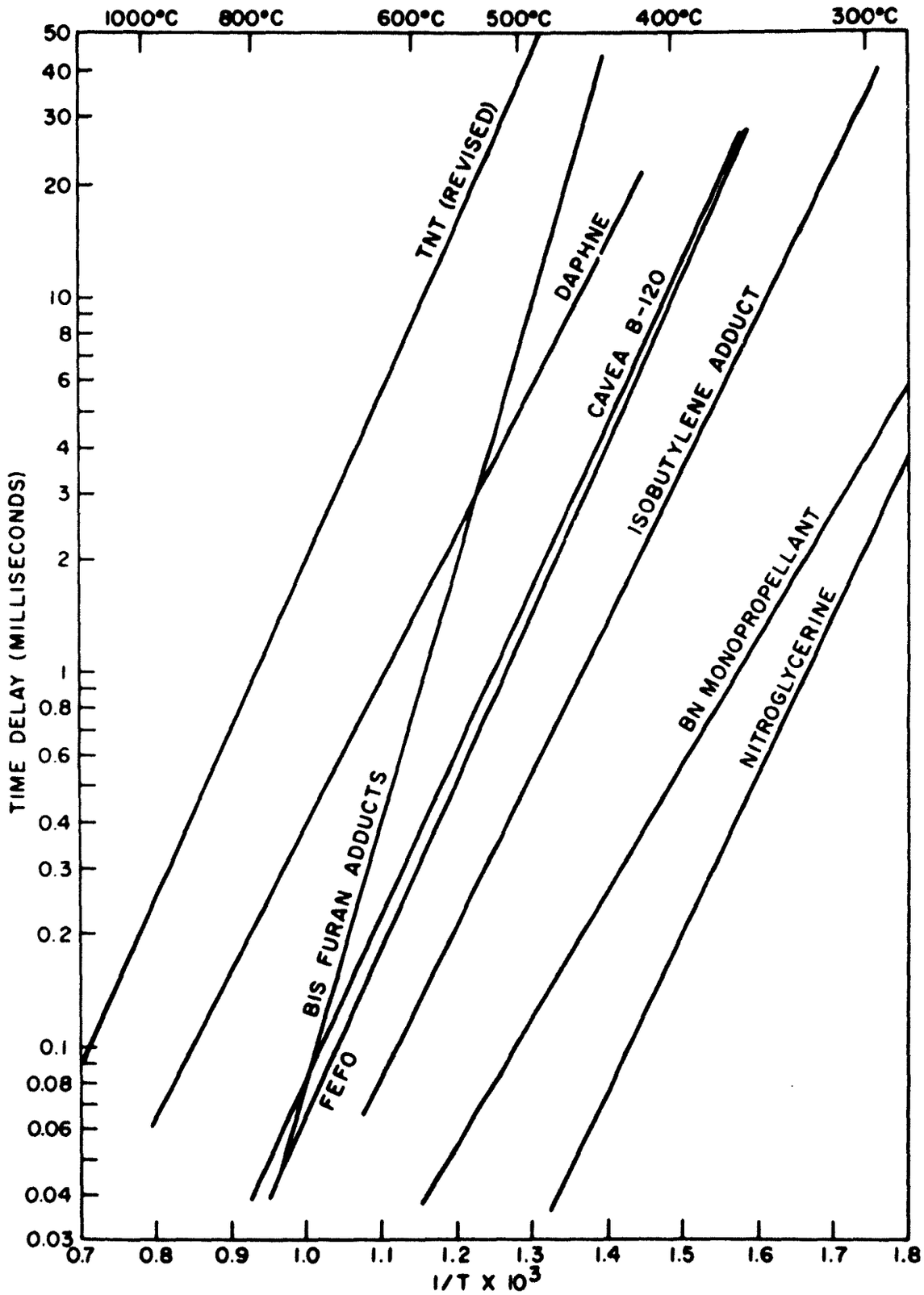

FIG. 12 THERMAL SENSITIVITY OF LIQUIDS

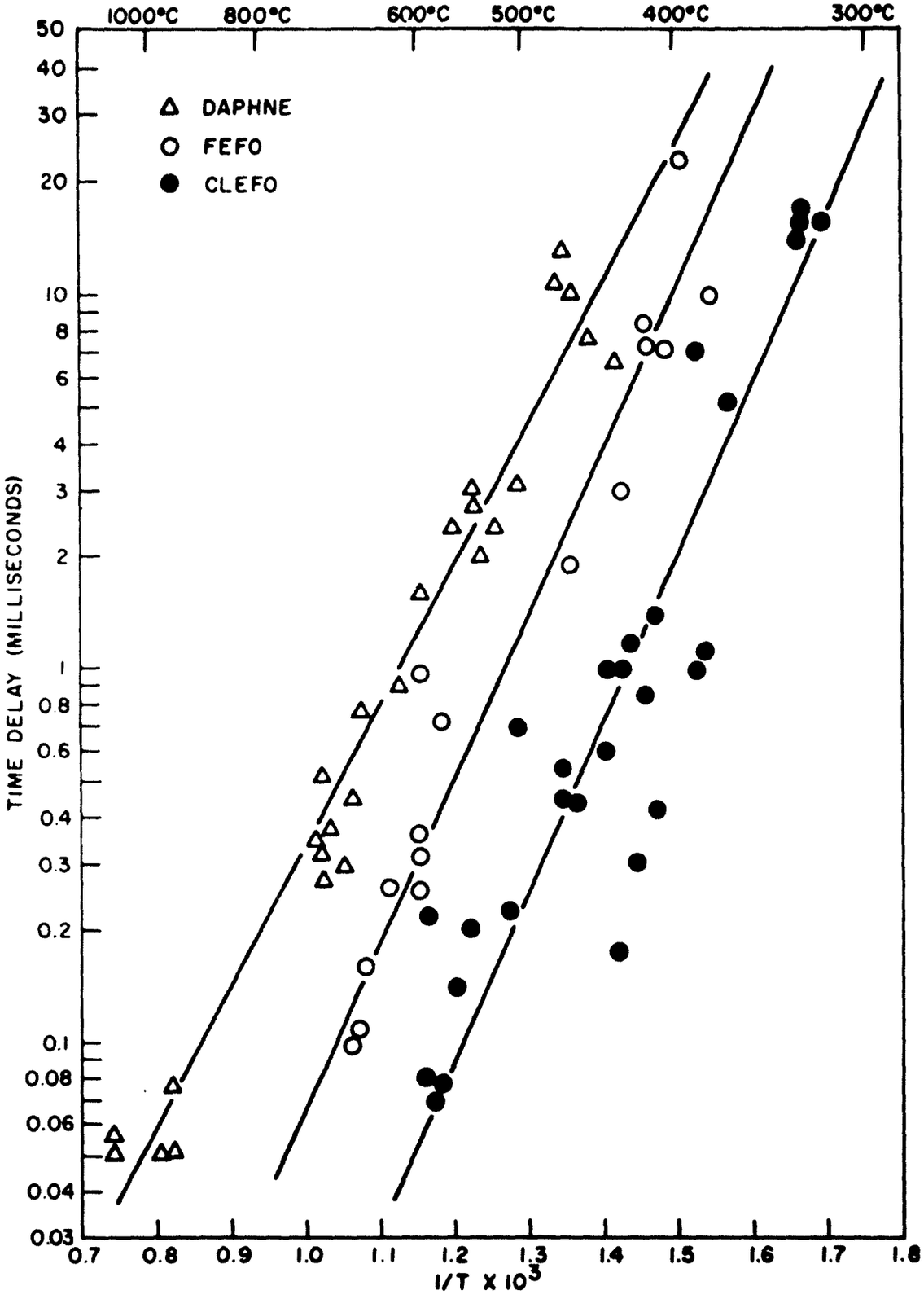

FIG. 13 DAPHNE, FEFO AND CLEFO

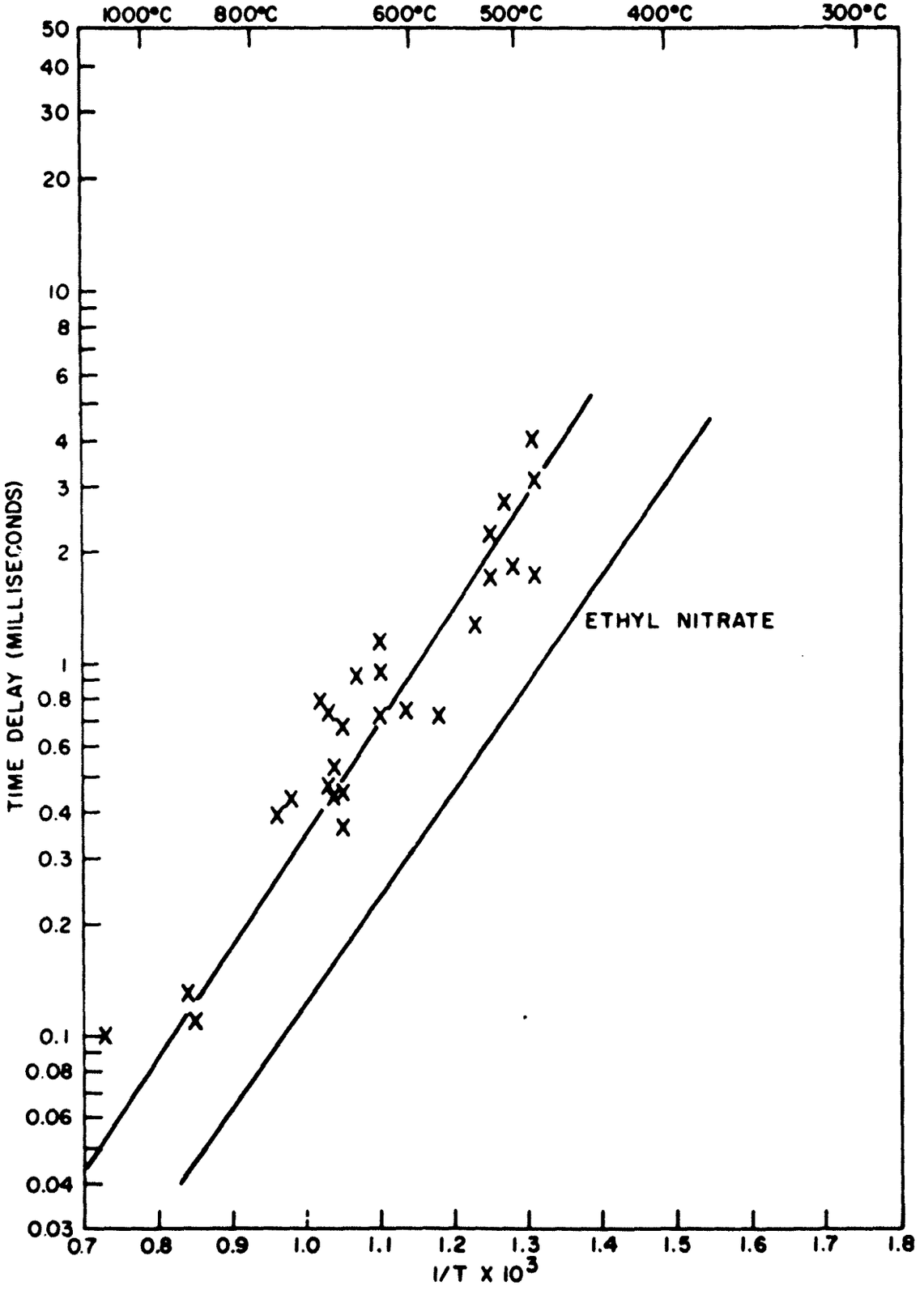

FIG. 14 ETHYL NITRATE-NITROBENZENE

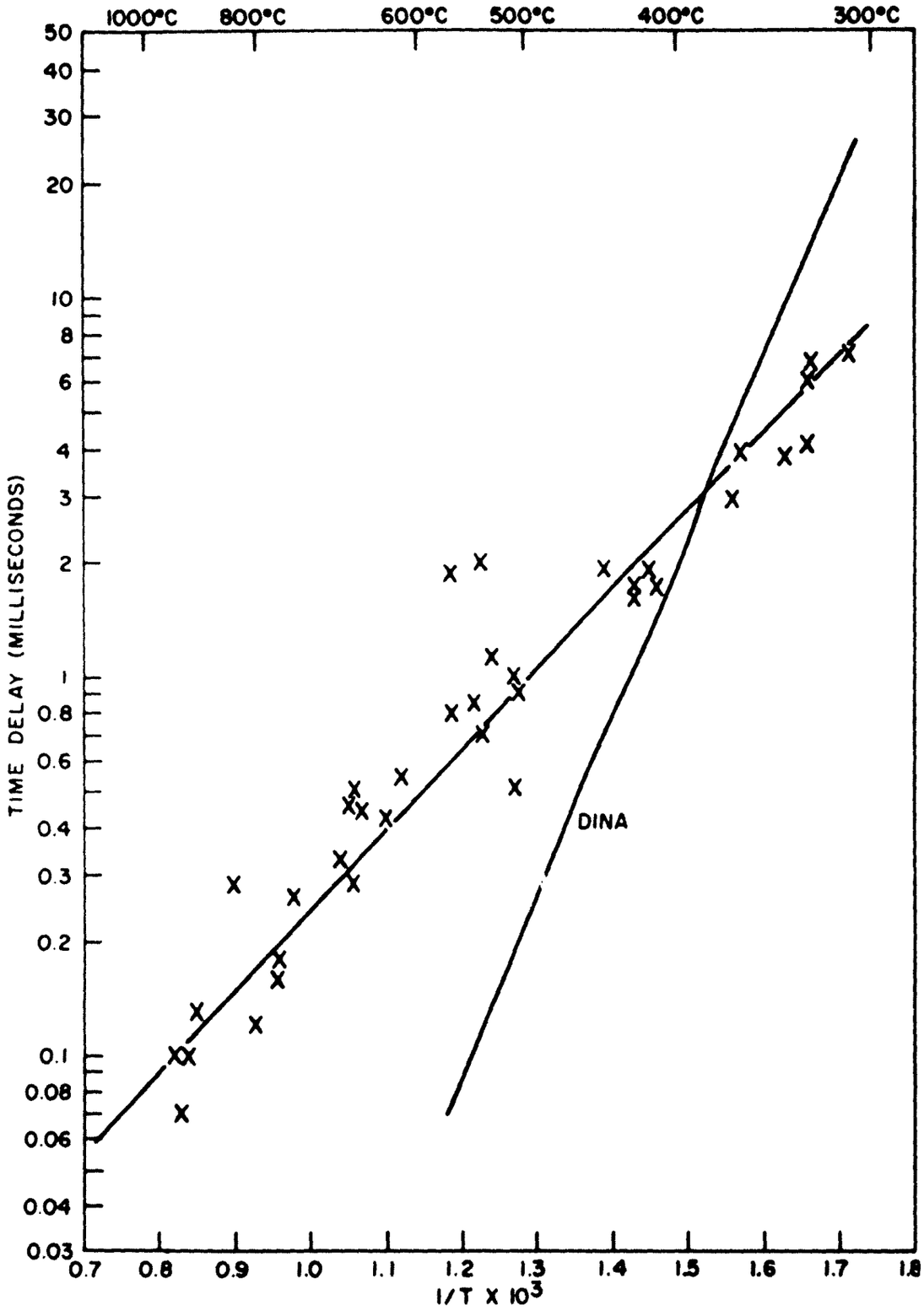

FIG. 15 DINA-NITROBENZENE

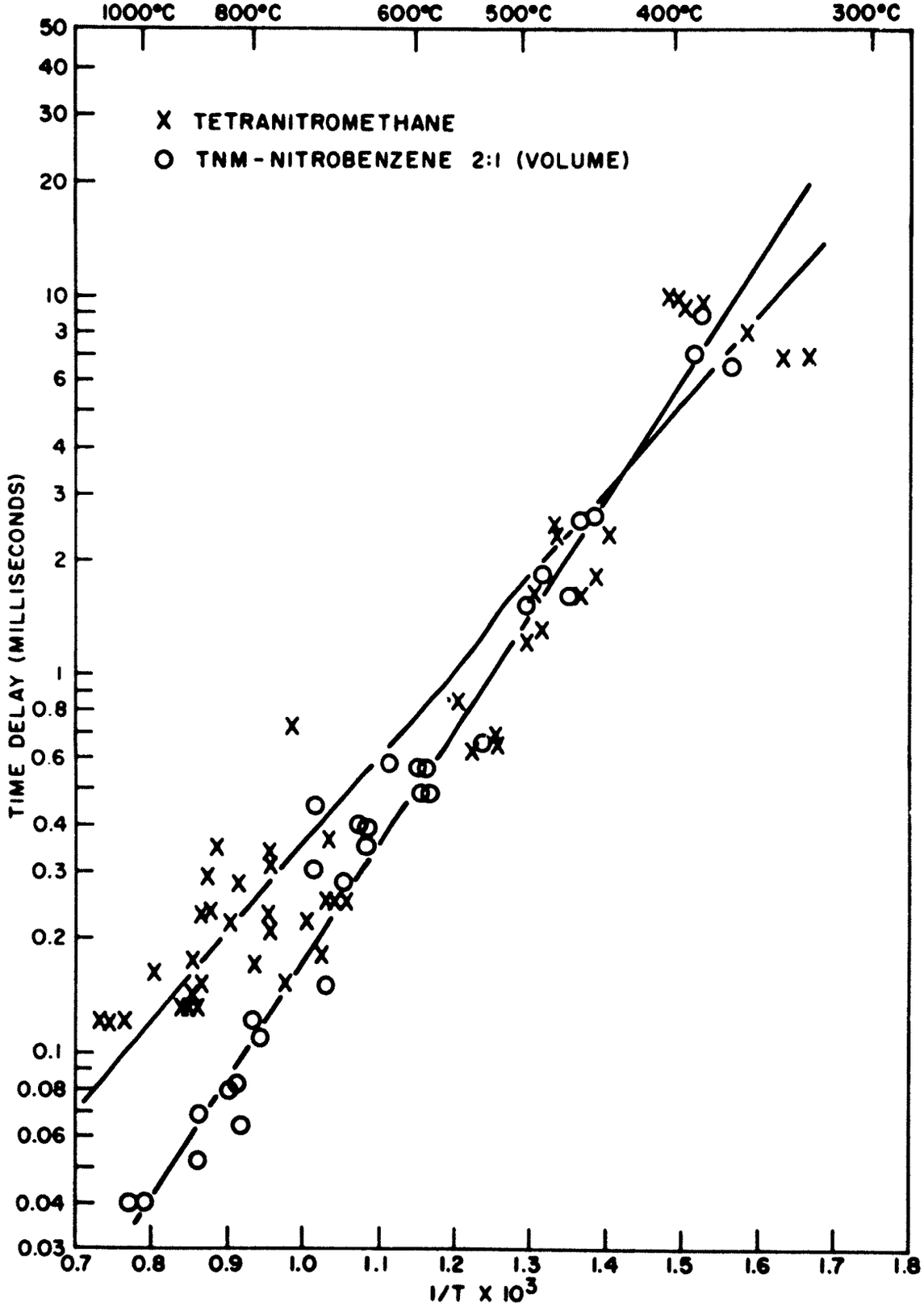

FIG. 16 TNM-NITROBENZENE

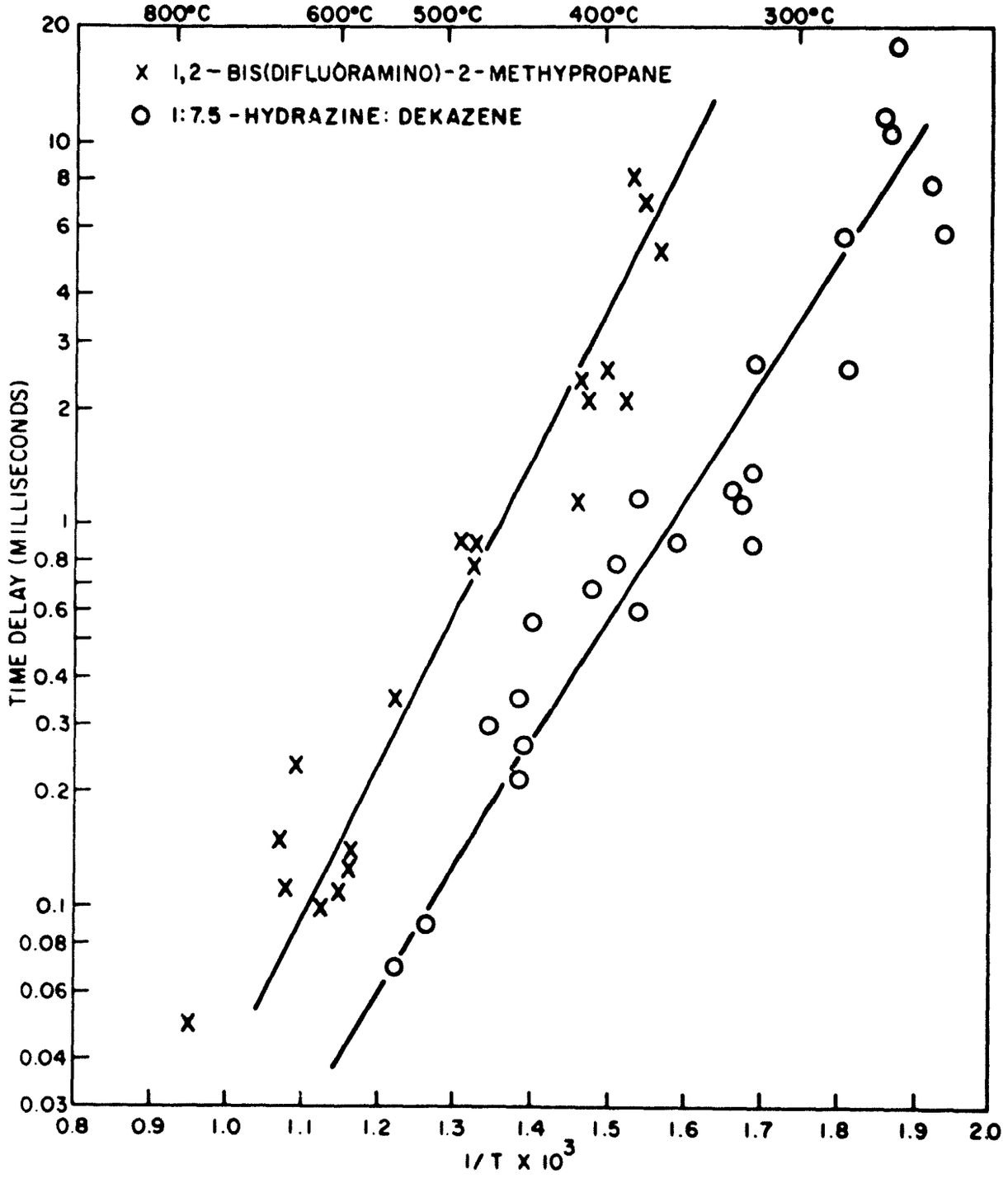

FIG. 17 B-N MONOPROPELLANT AND ISOBUTYLENE ADDUCT

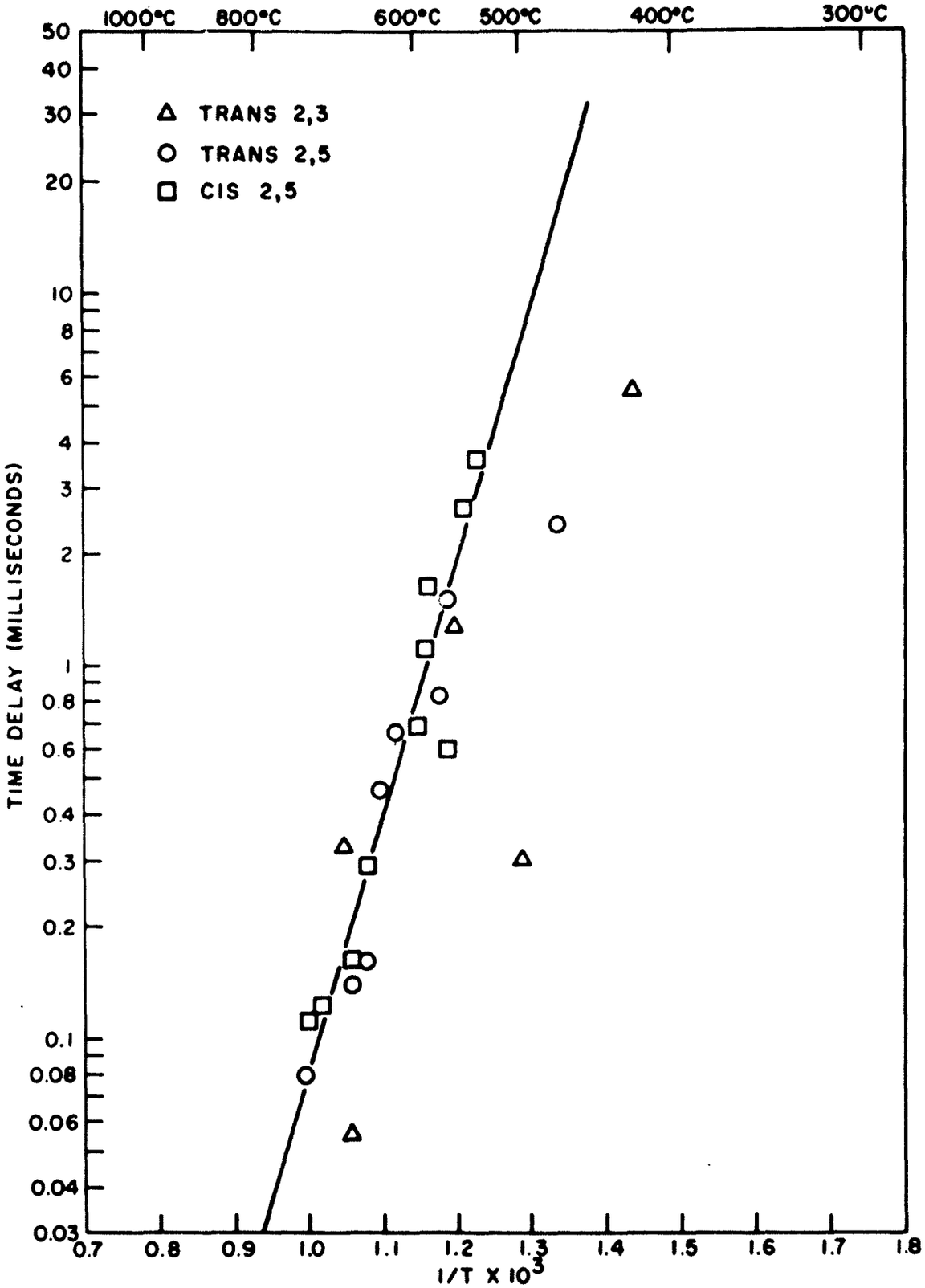

FIG.18 BIS(DIFLUORAMINO) FURANS

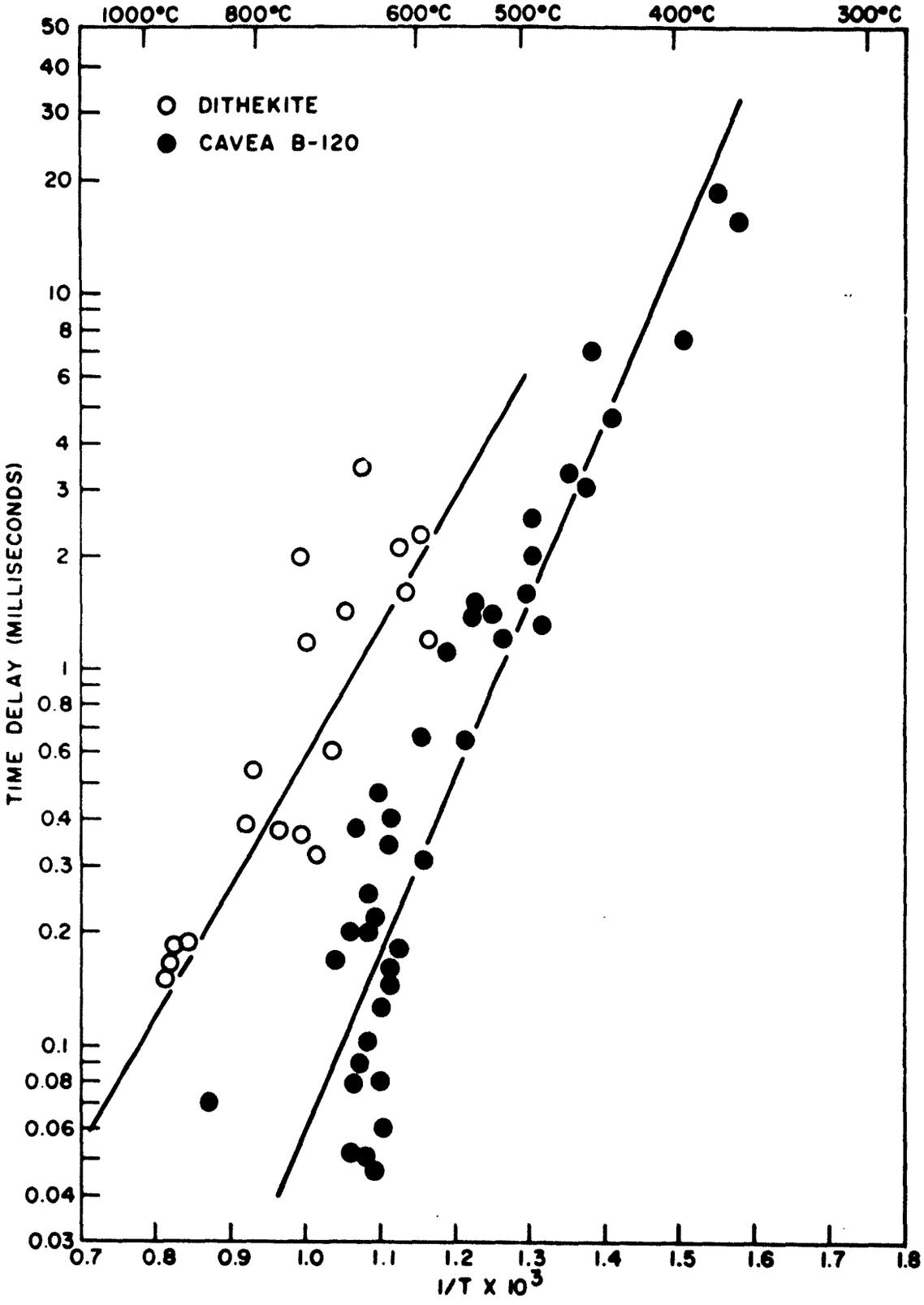

FIG. 19 CAVEA B-120 AND DITHEKITE

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