UCRL 6280

UNIVERSITY OF
CALIFORNIA

Ernest O. Lawrence

Radiation Laboratory

LIVERMORE SITE

DISCLAIMER

UCRL-6280

UNIVERSITY OF CALIFORNIA

Lawrence Radiation Laboratory

Livermore, California

Contract No. W-7405-eng-48

A DIFFERENTIAL THERMAL ANALYSIS STUDY OF THE RARE EARTH ETHYL SULFATES

Marcel W. Nathans

January 25, 1961

THIS PAGE

WAS INTENTIONALLY

LEFT BLANK

A DIFFERENTIAL THERMAL ANALYSIS STUDY OF THE RARE EARTH ETHYL SULFATES*

Marcel W. Nathans

Lawrence Radiation Laboratory, University of California

Livermore, California

January 25, 1961

ABSTRACT

Differential thermal analysis (DTA) curves were obtained for all rare earth ethyl sulfates in a stationary air atmosphere at an upheat rate of about 10°C per minute. The effects of particle size, upheat rate and the conditions of the surrounding atmosphere were investigated. A partial interpretation of the peaks was made by a modified thermogravimetric method and other analytical means.

The decomposition of the salts follows more or less the following general pattern:

$$M(C_2H_5SO_4)_3 \cdot 9H_2O \rightarrow M(C_2H_5SO_4)_3 \cdot 5H_2O \rightarrow M(C_2H_5SO_4)_3 \rightarrow M(HSO_4)_3$$
$$\rightarrow \text{intermediates} \rightarrow M_2(SO_4)_3,$$

where M represents any rare earth metal. The first three steps all occur below 200°. The last step is certainly completed at 500°. The intermediates are possible double salts of the sulfates and the bisulfates or have the composition $pM_2(SO_4)_3 \cdot qH_2SO_4$.

---

*Work was performed under the auspices of the U. S, Atomic Energy Commission.

The dehydration and the decomposition of the organic radical have activation energies of the order of 12 and 16 kcal/mole, respectively. The bisulfate decomposition may have an activation energy of something like 8.5 kcal/mole. The reactions are first order, with one exception, which appears to be of fractional order.

A DIFFERENTIAL THERMAL ANALYSIS STUDY OF THE RARE EARTH ETHYL SULFATES

Marcel W. Nathans

Lawrence Radiation Laboratory, University of California

Livermore, California

INTRODUCTION

The thermal decomposition of rare earth salts has been studied in some detail only during the past five years, particularly by Wendlandt.[1] The principal aim of these studies was to determine the minimum temperature range in which a particular composition would be stable. This is of interest for gravimetric analysis. A secondary aim was the comparison of the behavior of the different rare earths. Thus studies have been made, by DTA or with the thermobalance, of the oxalates, 8-hydroxyquinolates and related salts, cupferrates and neocupferrates, chlorides, fluorides, sulfamates and nitrates.[1] The ethyl sulfates, although not of analytical interest, are of some spectroscopic interest, and it appeared worth while to obtain a comparison of rare earth behavior in this salt. They have the composition $M(C_2H_5SO_4)_3 \cdot 9H_2O$ and are crystallographically isostructural.

---

[1] A brief review with literature references can be found in P. C. Stevenson and W. E. Nervik, The Radiochemistry of the Rare Earths, Scandium, Yttrium and Actinium, Lawrence Radiation Laboratory report UCRL-5923 (1960), pp. 48-60, to be published by the Subcommittee on Radiochemistry of the Committee on Nuclear Science, National Academy of Sciences.

EXPERIMENTAL

Cerium ethyl sulfate was prepared from the sulfate as obtained from the G. Frederick Smith Chemical Co., by a double decomposition reaction with the stoichiometric amount of barium ethyl sulfate. All other ethyl sulfates were prepared from the oxides obtained from Lindsay Chemical Corp. (Er_2O_3 from Research Chemicals Corp.). The oxides were first converted to the sulfates by dissolution in the minimum amount of dilute sulfuric acid and subsequent crystallization. The sulfates were then converted to the ethyl sulfates as in the case of the cerium salt. The barium ethyl sulfate was "electronic grade" reagent from City Chemical Corp. Potassium ethyl sulfate was reagent-grade chemical from Eastman. All materials were at least 99% pure.

The purity of the ethyl sulfates was not exactly known. Not enough was made for a satisfactory analysis. Most ethyl sulfates appeared slightly wet. The weights of the pyrolysis residues showed, however, that the purities did not differ significantly from 100%.

The DTA furnace assembly was the Robert L. Stone Co. model CS-2 with the liquid sample holder. The samples are placed in cups which allow weighings. Auxiliary equipment included a Leeds and Northrup model-G potentiometer recorder with a Beckman model-14 breaker amplifier to record differential temperatures, and an L and N model-H cam-type programmer-recorder with a CAT proportional control and a Fidelity saturable reactor.

The thermobalance used for the lanthanum salt was a modified Ugine-Eyraud continuous recording thermobalance with an L and N Speedomax type-G X_1-X_2 recorder having a range of 20 mg ± 1/2% full scale.

Some samples of the lanthanum salt which were heated in a muffle oven at different temperatures were analyzed. The products of pyrolysis below 500°C were soluble in water, the 1100° product was dissolved in hydrochloric acid. Sulfate was determined by precipitation as $BaSO_4$, filtering the next day, dissolution of the precipitate in a known amount of ammonical EDTA and back titration with standard $MgCl_2$ with eriochrome T as the indicator. Hydrogen ion was determined by titration with standard base.

Samples of about 100 mg were used in all experiments. Standard particle size was -100/+200 mesh. Standard upheat rate was about 10°C per minute. These conditions were modified for a few experiments. After a complete DTA curve was obtained a new sample was run, but with interruptions shortly after a peak in order to weigh the sample. The samples were removed from the furnace and weighed as rapidly as possible in order to keep the uptake of water from the air to a minimum. Occasionally some fumes were still coming off when the furnace was removed.

RESULTS

The DTA curves under standard conditions are shown in Fig. 1. Below about 250°C the curves are all similar. There are basically three peaks which are in nearly all cases well resolved, and sometimes some additional structure. Between 250° and 500° there is varying behavior. The lanthanum and cerium salts show one sharp peak between 300° and 400° and one or two weak endotherms at higher temperatures. The salts from praseodymium through holmium have at least two well defined endotherms, which sometimes show structure. The remaining rare earth salts show only one endotherm of medium intensity which peaks just above 300°. For comparison I have included the curves of barium and potassium ethyl sulfate.

Certain aspects of the curves are sensitive to the nature of the sample and the heating rate. Figure 2 shows the effect of particle size on the DTA of the gadolinium salt. The best resolution is obtained for the -100/+200 mesh fraction. The resolution is almost as good with -200 mesh fraction, but unsatisfactory with the +100 mesh fraction.

The effect of atmospheric conditions was examined on the lanthanum salt. DTA curves were obtained in air and in a dynamic argon atmosphere. The results are shown in Fig. 3.

The effect of upheat rate was investigated with the erbium salt with striking results (Fig. 4). First of all, peaks shift to lower temperatures as was expected when the upheat rate is slowed down. The two lowest temperature peaks, which are dehydration peaks as I shall show later, are almost entirely unresolved at the lowest upheat rates except perhaps for a shoulder. The next peak is resolved into two peaks at 2.5°/min, shows some structure at 5°/min but appears single at 10°/min and 25°/min. The last peak shows similar behavior. It is completely unresolved at 25°/min and at 10°/min, is resolved into two and possibly four peaks at 5°/min, but in no more than two peaks at 2°/min.

The interpretation of the peaks is based on measurements of the weights of samples at points indicated by numbers in Fig. 1. Compositions were calculated from these weighings and compared with theoretical compositions. The results are tabulated in Table 1. The numbers listed are weight % left after heating. Additional weighings were made of the lanthanum and holmium salts after the first and second peaks (Table 2). Chemical analyses were carried out on some of the decomposition products of the lanthanum salt after heating in a muffle oven (Table 3). In order to make the interpretation a little more positive pyrolysis products of the potassium and barium salts were also weighed or analyzed (Table 4).

The data lead to the following interpretation. The decomposition of the rare earth ethyl sulfates starts with dehydration. Besides the enneahydrate which is stable at room temperature at least one other hydrate exists, probably the pentahydrate. The anhydrous ethyl sulfates are rather unstable and decompose a little below 200°C to the bisulfates. The bisulfates decompose either directly or in steps to the anhydrous sulfates. In some cases (La, Ce, Pr, Gd, Dy, Yb) the bisulfate starts to decompose before the decomposition of the ethyl group is complete. The intermediate compositions shown in Table 1 are given with some reserve. The DTA curves indicate the existence of double salts of the bisulfates with the sulfates. The most consistently occurring composition is $M(HSO_4)_3 \cdot M_2(SO_4)_3$. It is likely that such a double salt has independent existence. Other compositions suggested by the table as having independent existence are $4M(HSO_4)_3 \cdot M_2(SO_4)_3$ and perhaps $2M(HSO_4)_3 \cdot M_2(SO_4)_3$. These compositions certainly are in need of confirmation. A few x ray diffraction patterns obtained from pyrolysis products of the lanthanum salt were inconclusive.

Confirmation of the interpretation of the peak just below 200° was found from the potassium and barium salts. The former has only one endotherm corresponding to the reaction

$$K(C_2H_5SO_4) \rightarrow KHSO_4 + C_2H_4 .$$

The latter has two low temperature peaks, which correspond to dehydration. The third sharp endotherm results from the reaction

$$Ba(C_2H_5SO_4)_2 \rightarrow Ba(HSO_4)_2 + 2\ C_2H_4 .$$

The last peak, at about 300° corresponds to the reaction

$$Ba(HSO_4)_2 \rightarrow BaSO_4 + H_2O + SO_3 .$$

This peak occurs at about the same temperature as a similar peak for the erbium, thulium, ytterbium and lutecium peaks, which have been interpreted the same way.

An attempt was made to establish the stability ranges of some of the low temperature pyrolysis products. The weight of lanthanum ethyl sulfate was followed with the thermobalance in a flow of about 100 cm^3 of nitrogen per minute (at room temperature). After an initial run at 10°/min a more detailed experiment was done at about 2°/min. Figure 5 shows both the weight loss curve and the DTA curve at 2.5°/min. There is little positive correlation between the two curves. It is clear, however, that there is no stability range for the intermediate hydrate.

Static experiments were done with the ethyl sulfates of La, Pr, Tb, Dy, Er, Tm, and Yb. The results are shown in Table 5 and Fig. 6. The samples (except the La salt) were held at 50° for three days, at 73° for one day, and at 105° for 42 days. The lanthanum salt was only heated at 106°. At 50° constant weight appears to be reached after only a few hours at about 80%, indicating perhaps the existence of a mono- or dihydrate. The Pr and Tb salts may have reached the anhydrous form already at 50°. After further heating the weight increased a little, however. This suggests that the constant weight composition is very sensitive to the humidity of the atmosphere. Yet there is no indication of a stable pentahydrate. No constant weight was reached at 73°, except perhaps with the Dy salt. It looks as if the Dy, Er, Tm, and Yb salts may have a stability region at about the composition of the anhydrous salt (about 77%). The other two salts lost additional weight at 73°. The behavior at 106° is very interesting. The lanthanum, praseodymium and dysprosium salts appear to have a stable composition at about 60%, in accordance with weight data obtained from the dynamic measurements of the

last two. The erbium and thulium salts have stable products at about 50%, that is, at the composition $Er(HSO_4)_3 \cdot Er_2(SO_4)_3$. This composition was not found in the dynamic experiments. Finally, the terbium and ytterbium salts did not reach a stable composition at all. They both tend to yield the anhydrous sulfate at this temperature. The weight loss rates do not decrease in regular fashion. This may be explained by assuming two consecutive reactions, the second one being the decomposition of the product of the first one.

An estimate was made of the activation energy of some of the reactions of the erbium salt. According to Kissinger[2] the activation energy, E, is given by

$$E = -R \frac{d \ln(\phi / T_m^2)}{d (1/T_m)},$$

where R is the gas constant, ϕ the heating rate, and T_m the peak temperature in degrees K. Values of E were calculated with the data obtained from Fig. 4 for the first dehydration peak, the 200° peak, and the bisulfate decomposition peak. For the last calculation I took the average of the doublet. The results are shown in Fig. 7. The activation energies come out to be about 12,000 cal/mole for the dehydration, about 16,500 cal/mole for the ethyl decomposition, and about 8500 cal/mole for the bisulfate decomposition. These values must be considered tentative, however.

The empirical reaction order can be estimated from the peak shape.[3] All peaks are sufficiently symmetric to allow the conclusion of a first-order reaction for all decomposition steps, except a peak at about 300° for the

---

[2] H. E. Kissinger, J. Research Natl. Bur. Standards 57, 217 (1956).

[3] H. E. Kissinger, Anal. Chem. 29, 1702 (1957).

majority of the ethyl sulfates. The order is given by $n = 1.26\ S^{1/2}$, where S is as defined in Fig. 8. I calculated n to be between 0.7 and 0.4. One possible explanation of the deviation from first order may be the following formulation:

$$2/3\ La(HSO_4)_3 \rightarrow 1/3\ La_2(SO_4)_3 + H_2SO_4,$$

the rate determining step being the formation of a molecule of sulfuric acid. The reaction order would be 2/3 with respect to the bisulfate.

CONCLUSIONS

The path of the thermal decomposition of the rare earth ethyl sulfates below 600°C goes through an intermediate hydrate, the anhydrous salt, the bisulfate, compositions intermediate between the bisulfate and the sulfate, and finally to the anhydrous sulfate. There is no clear division of the salts into types according to their behavior, except that for the four heaviest ethyl sulfates the existence of intermediate compositions is not clear. The intermediate compositions may have the structure $pM(HSO_4)_3 \cdot qM_2(SO_4)_3$ or $pM_2(SO_4)_3 \cdot qH_2SO_4$. Static measurements have shown that the pyrolysis products may be stable in only very limited temperature intervals. It is obviously of interest to continue the static weight loss measurements. It is likely that conditions can be found at which the bisulfates can be prepared. In addition, the exact composition of the products intermediate between the sulfates and the bisulfates should be determined.

The activation energies are of the order of 12,000 cal/mole for the dehydration, 16,500 cal/mole for the decomposition of the organic radical, and about 8500 cal/mole for the bisulfate decomposition. The reactions are first order, except some occurring at about 300°, which are of fractional order.

ACKNOWLEDGMENTS

I wish to thank Mr. C. L. Little, summer trainee and teacher at Manteca High School, for his great help in getting the equipment set up and in making the initial experiments. I also want to acknowledge the help of Mr. F. McMurphy during the later stages of this research, Mrs. G. Stephas for her help with the analyses, Mr. V. Silveira for obtaining the x-ray diffraction patterns, and Mr. G. F. Rynders for making the run in his thermobalance and for several suggestions.

/mr

Table 1.

Table 1.— Weight data for rare earth ethyl sulfates heated to different temperates.*

	1 Bisulfate		2 2/1†		3 1/1†		4 1/2†		5 Sulfate	
	theor.	found	theor.	found	theor.	found	theor.	found	theor.	found
La	63.6	---	56.4	56.4	52.8	---	49.1	42.6 49.0	41.9	42.6
Ce	63.7	61.8	56.4	---	52.8	---	49.2	---	41.9	42.9 40.6
Pr	63.7	64.6 60.0	56.5	---	52.8	---	49.2	50.2 49.1	42.0	40.6 45.1
Nd	64.0	62.6	56.8	---	53.1	---	49.5	50.0	42.3	45.4 45.3
Sm	64.2	60.7 61.2	57.1	---	53.5	---	49.9	51.9	42.8	44.2
Eu	64.3	64.0	57.2	---	53.6	54.9 53.7	50.1	---	43.0	47.3 44.2
Gd	64.6	‡	57.5	55.8	54.0	---	50.5	50.3	43.4	43.3
Tb	64.7	64.6	57.6	(56.9)	54.1	---	50.6	50.9	43.5	42.9
Dy	64.9	60.0	57.9	---	54.4	---	50.9	50.6	43.9	43.0
Ho	64.9	63.1	57.9	---	54.4	53.5	51.0	---	44.0	46.7
Er	65.1	66.2	58.1	---	54.6	---	51.1	---	44.1	47.6 43.5
Tm	65.2	65.5	58.2	---	54.6	---	51.1	---	44.1	48.6
Yb	65.4	---	58.4	58.1	54.9	---	51.4	---	44.4	48.5
Lu	65.4	64.4	58.5	---	54.9	---	51.4	50.9	44.5	---

*Temperatures where samples were taken varied with the peak positions. The first column was obtained at about 230°, the second, third and fourth columns between 230° and 350°, and the fifth column at 450°. Values are reported as percent weight remaining.

†(Equivalents of rare earth in bisulfate)/(equivalents of rare earth in sulfate).

‡No data taken.

Table 2.—Evidence for the existence of rare earth ethyl sulfate pentahydrates.

Compound	Weight (g)	Heating Temp.(°C)	Wt % left	Theor. for pentahydrate (%)
$La(C_2H_5SO_4)_3 \cdot 9H_2O$	1.000	145	88.8	89.4
	0.0655	135	90.5	
$H_0(C_2H_5SO_4)_3 \cdot 9H_2O$	0.0780	135	88.1	88.7

Table 3.—Analyses of lanthanum ethyl sulfate samples heated to different temperatures.

Sample	Temp (°C)	Heating time (min)	Millimoles in original sample				
			La^{+++}(calc)	H^+	$SO_4^=$	SO_4/La	H/SO_4
1	225	15	0.77	1.58	1.80	2.34	0.88
2	375	15	0.77	0.218	1.18	1.53	0.18
3	410	15	0.76	0.128	1.17	1.54	0.11
4	510	15	0.88	(0.02)	1.27	1.44	(~0)
5	510	30	0.80	(0.04)	1.18	1.48	(~0)
6	1050	15	0.76	---	0.40	0.52	---

Theoretical SO_4/La for 4 $La(HSO_4)_3$ + $La_2(SO_4)_3$ is 15/6 or 2.50; for $La_2(SO_4)_3$: 3/2 or 1.50; for $La_2O_2(SO_4)$: 1/2 or 0.50.

Theoretical H/SO_4 for 4 $La(HSO_4)_3$ + $La_2(SO_4)_3$ is 12/15 or 0.80; at 350° and 410° small amounts of bisulfate are still left.

Table 4.—Analyses of barium and potassium ethyl sulfates heated to different temperatures.

Sample	Temp (°C)	Wt % of initial sample	Theor. wt % of initial sample	Product
$Ba(C_2H_5SO_4)_2 \cdot 2H_2O$	100	98.7	---	---
	170	90.6	91.5	$Ba(C_2H_5SO_4)_2$
	250	75.3	78.0	$Da(HSO_4)_2$
	1050	(x-ray analysis)		$BaSO_4$
$KC_2H_5SO_4$	250	85.9	82.9	$KHSO_4$
	SO_4 found 4.04 mmoles in 0.6775 g			
	theor: 4.14	"	"	"
	H found 4.12	"	"	"
	theor: 4.13	"	"	"

Table 5.

Table 5.—Static weight loss of some rare earth ethyl sulfates at 106°C.

Salt of	Weight % after 0*	24	34	144	195	217	318	481	648	1008 (hr)
Pr	72.06†	62.00	61.23	60.37	60.42	60.23	60.58	59.83	59.58	58.97
Tb	71.35†	59.72	59.15	56.50	56.43	55.56	54.66	50.17	47.82	46.06
Dy	75.64†	64.81	64.95	63.74	63.82	63.36	63.56	61.82	61.17	59.94
Er	76.02†	66.43	65.68	59.23	57.15	55.83	52.44	50.48	50.26	50.74
Tm	76.86†	68.34	67.42	63.00	61.88	61.16	59.51	52.82	50.81	51.77
Yb	74.90†	65.13	64.37	57.34	(58.22)	54.18	53.25	44.47	---	44.41
		---	---	---	---	---	---	---	---	---
	0	12	17	21	36	60	161	324	492	(hr)
La	100‡	64.7	62.8	62.2	60.5	60.0	60.0	58.6	(62.6)	

*Time started after 3 days at 50°, 1 day at 73°.

†Weight percent left after previous heating at 50° and 73°.

‡Heating started at 106°.

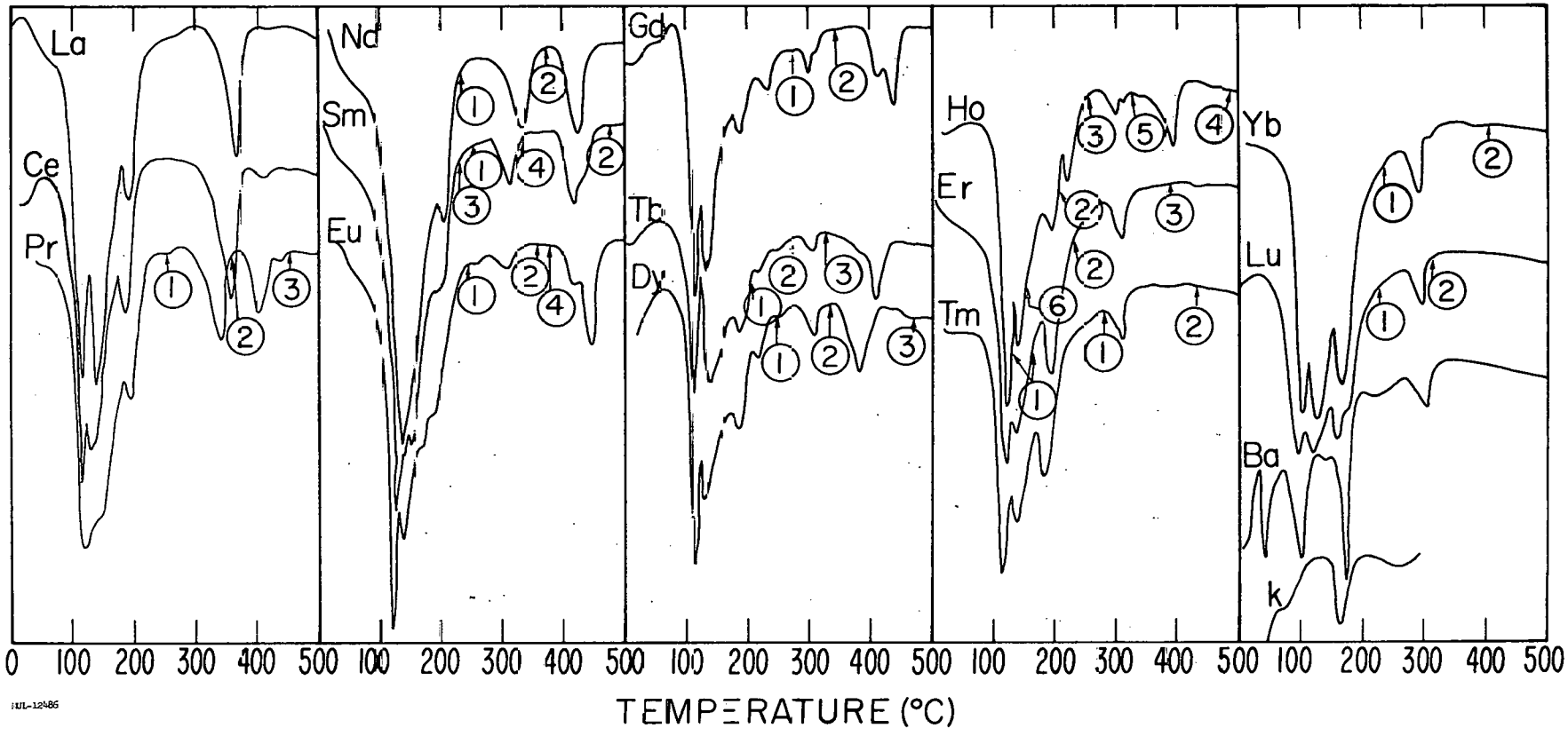

Fig. 1. — DTA curves for the ethyl sulfates of the rare earths, barium and potassium. Upheat rate 10°C/min nominal. 100 mg samples, -100/+200 mesh.

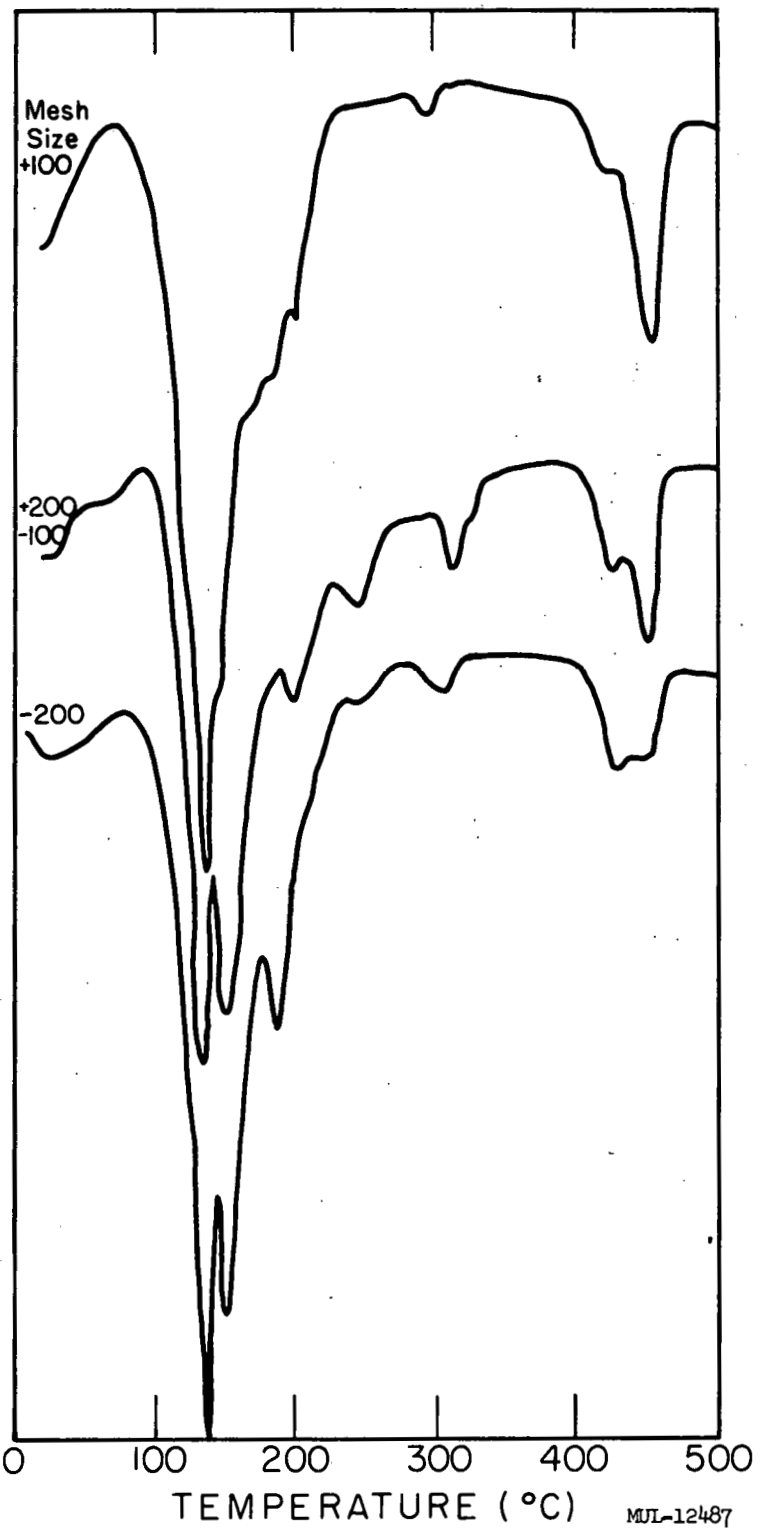

Fig. 2.— Effect of particle size on the DTA of $Gd(C_2H_5SO_4)_3 \cdot 9H_2O$.

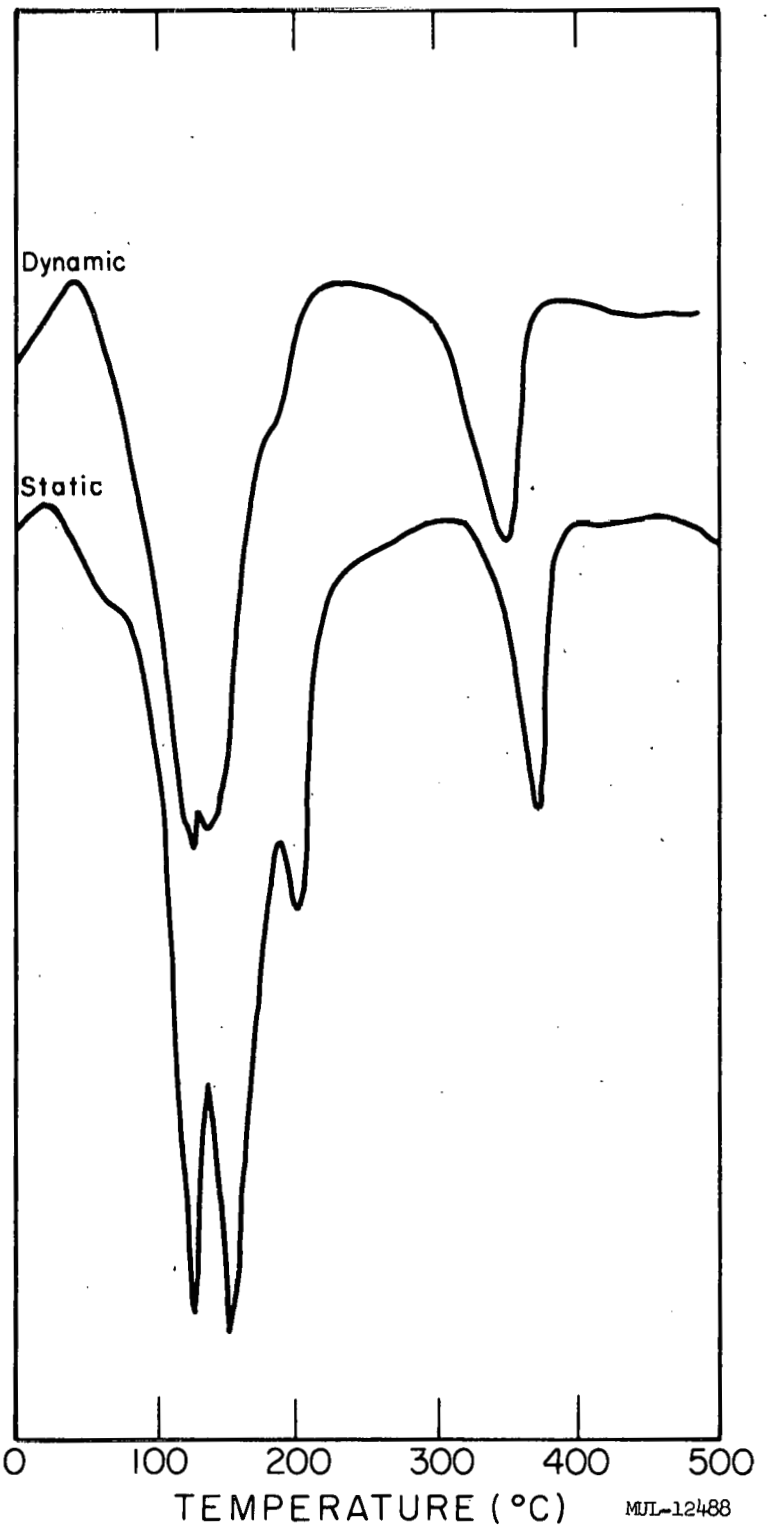

Fig. 3. — Comparison of DTA of $La(C_2H_5SO_4)_3 \cdot 9H_2O$ in static air and dynamic argon atmospheres.

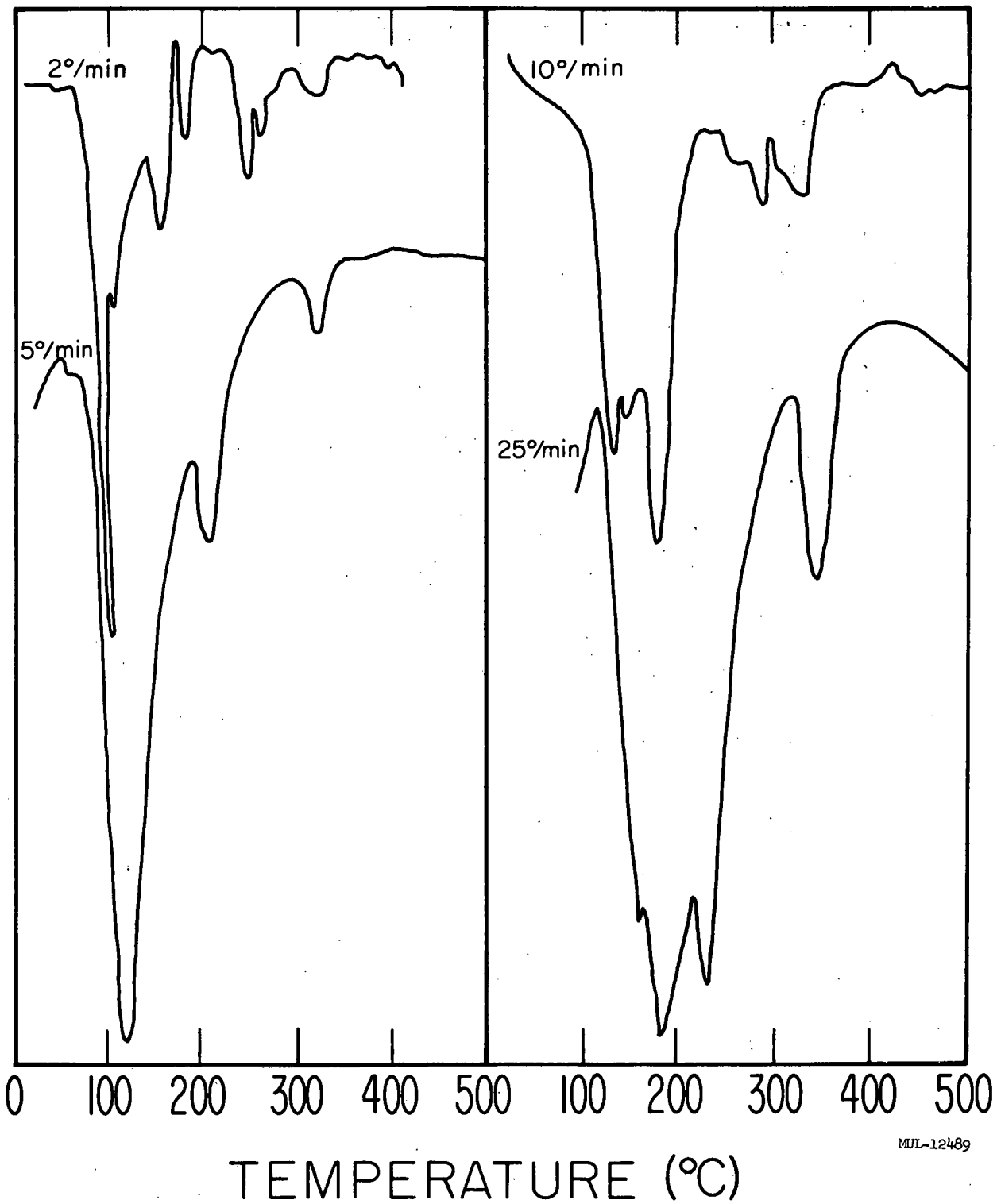

Fig. 4. — Effect of upheat rate on the DTA of $Er(C_2H_5SO_4)_2 \cdot 9H_2O$.

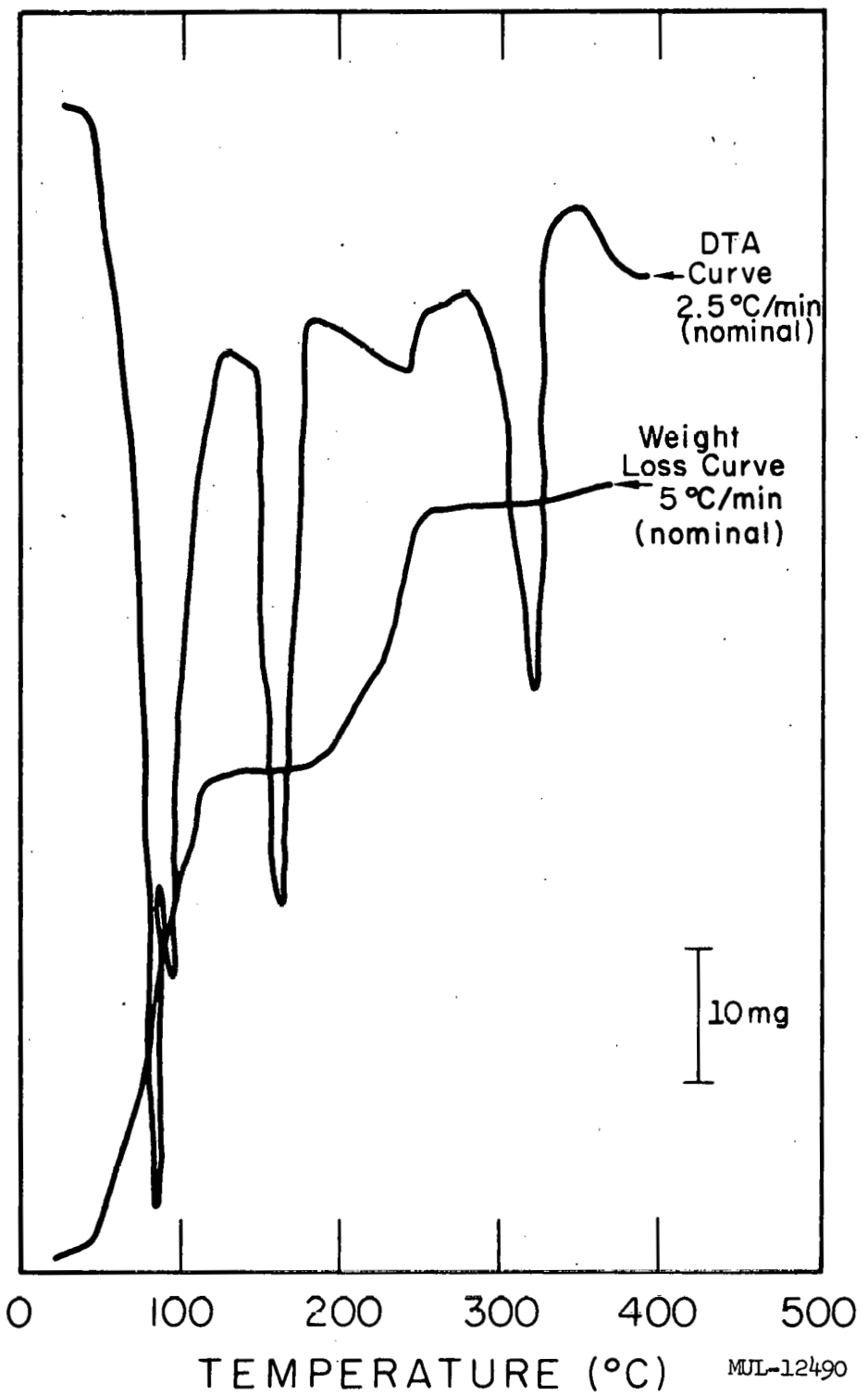

Fig. 5. — Comparison of weight loss curve (2°/min) with DTA (2.5°/min) of $La(C_2H_5SO_4)_3 \cdot 9H_2O$.

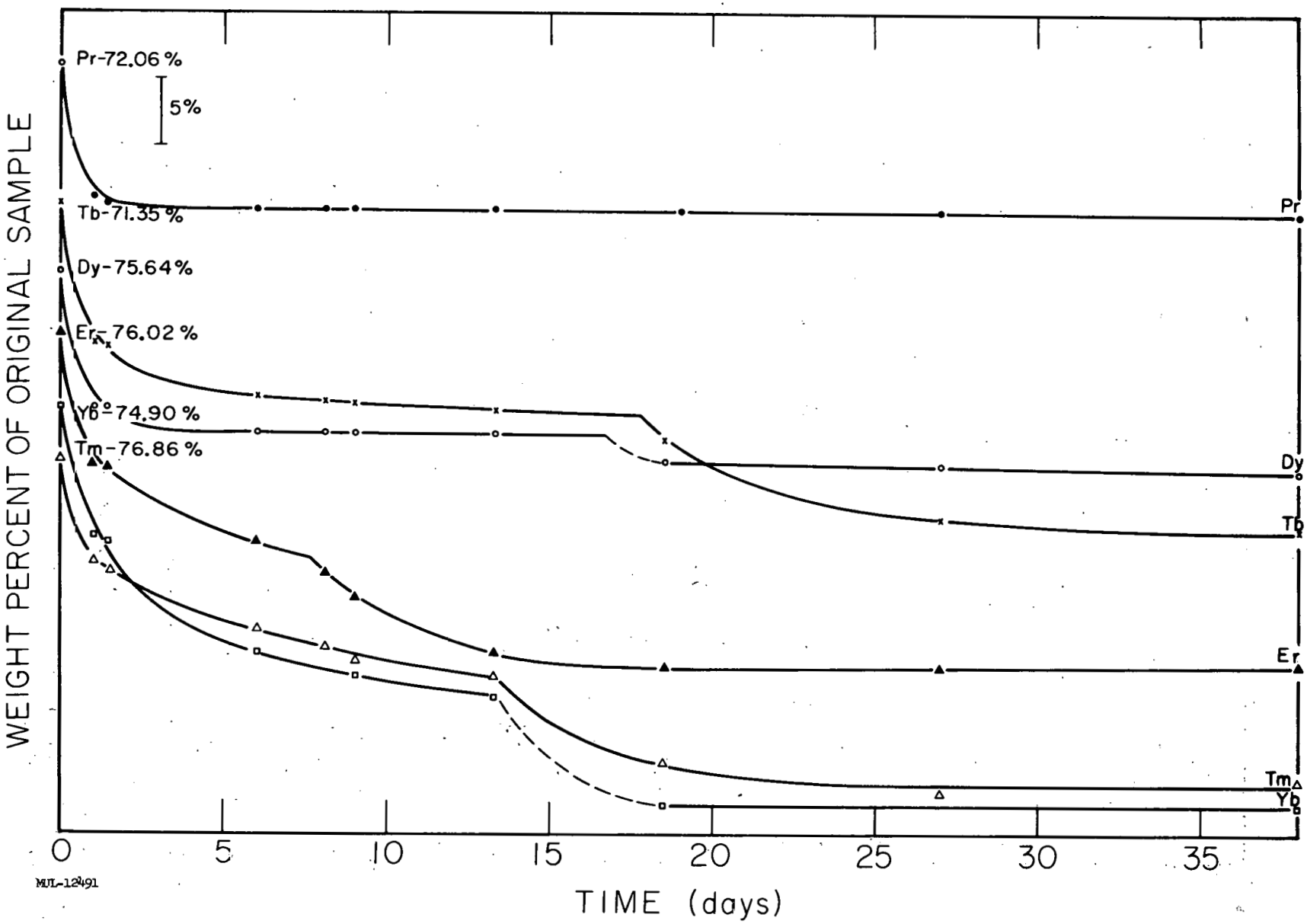

Fig. 6. — Weight loss-time curves for various ethyl sulfates at 106°C after previous heating at 50° and 73°C.

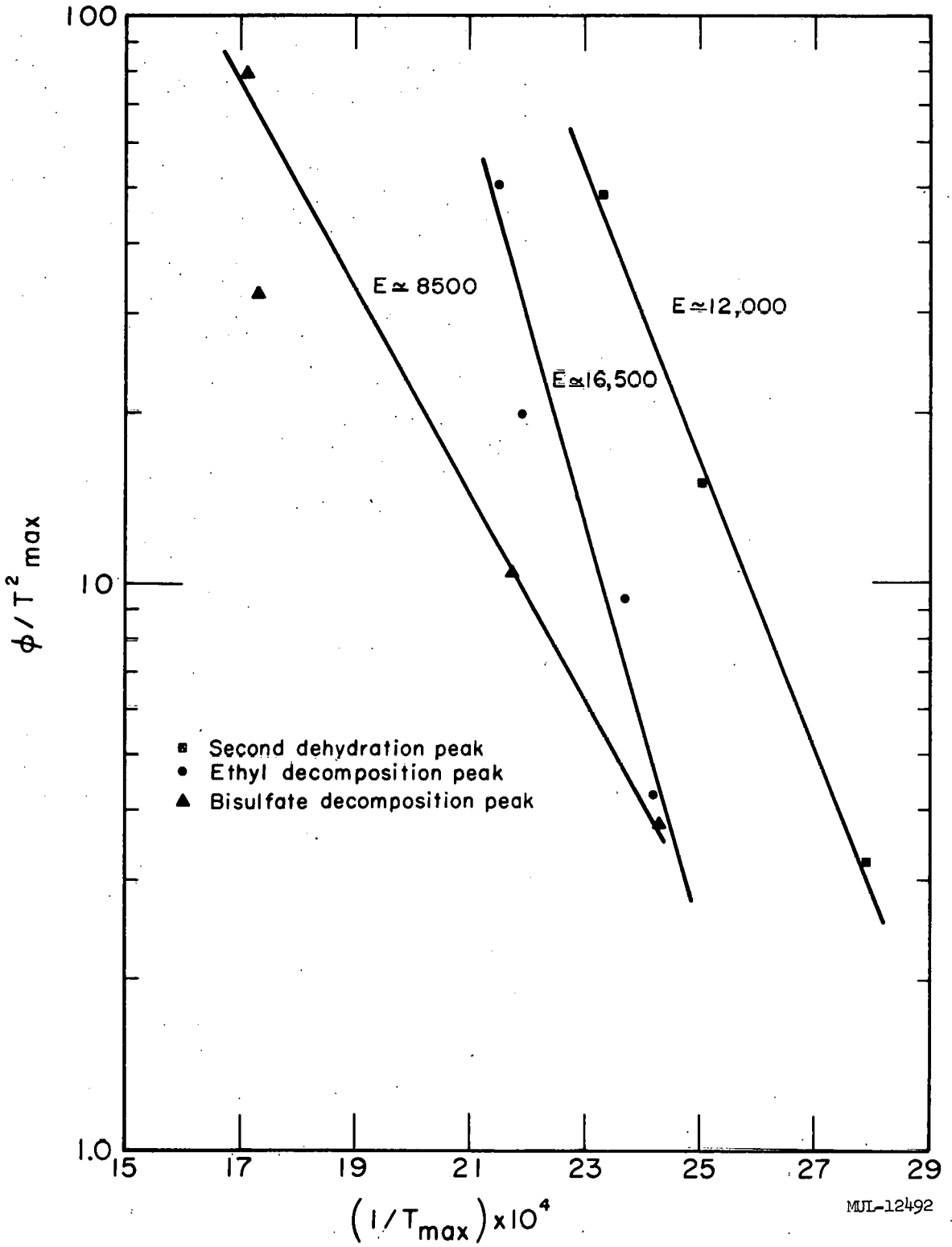

Fig. 7. — Calculation of activation energies of decomposition reactions of $Er(C_2H_5SO_4)_3 \cdot 9H_2O$.

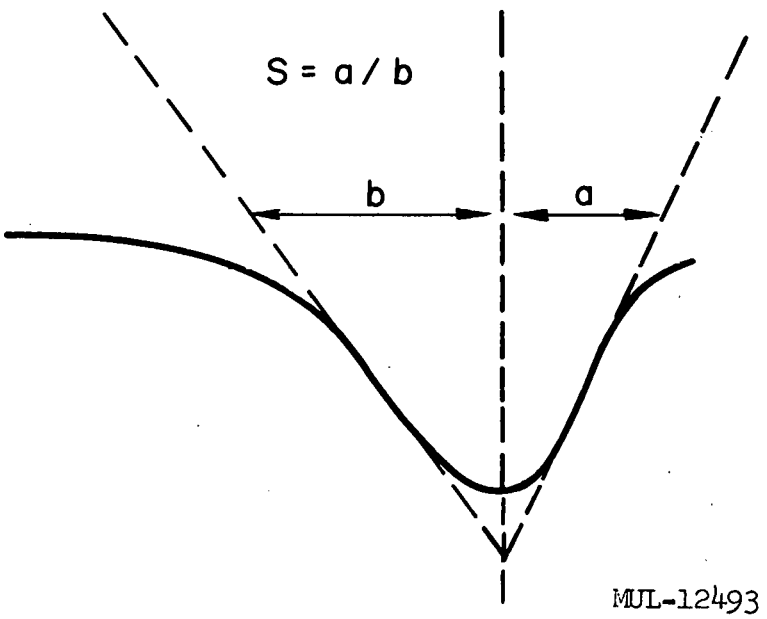

Fig. 8. — Definition of the shape factor S.