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SYNTHESIS OF PICRYL CHLORIDE

D. V. Hayes & F. I. Honea

July 1970
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for

Sandia Corporation

Sandia Laboratory Albuquerque

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SYNTHESIS OF PICRYL CHLORIDE

D. V. Hayes & F. I. Honea

July 1970
Purchase Order 93-1840

ABSTRACT

A total of six pilot-scale batches of picryl chloride were made. These included three 5-kg batches and three 10-kg batches.

The three 5-kg batches were made to investigate the problems encountered with actual production and materials handling. The three 10-kg batches were made to study the process parameters and the yield problems originally encountered with the 5-kg batches.

The yields on the 5-kg batches ranged from 40 to 60% of approximately 50% purity. The yields on the 10-kg batches were 80, 86 and 91% in chronological order. The purities were 95, 99+ and 99+ percent respectively.

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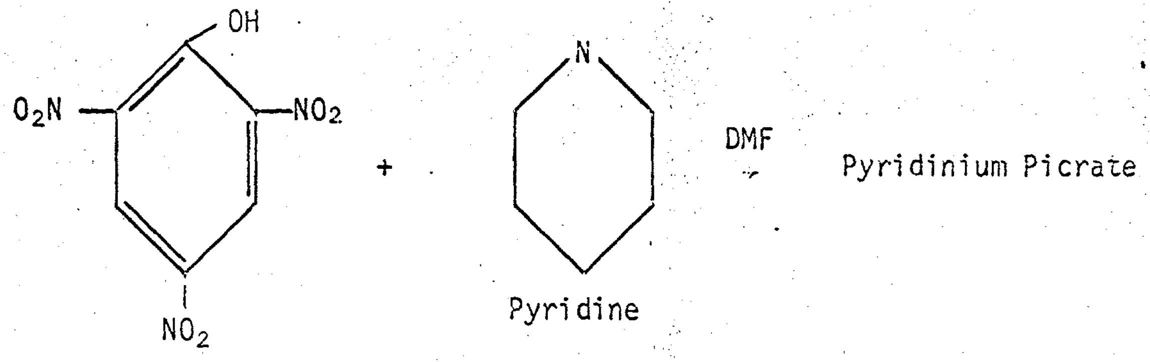
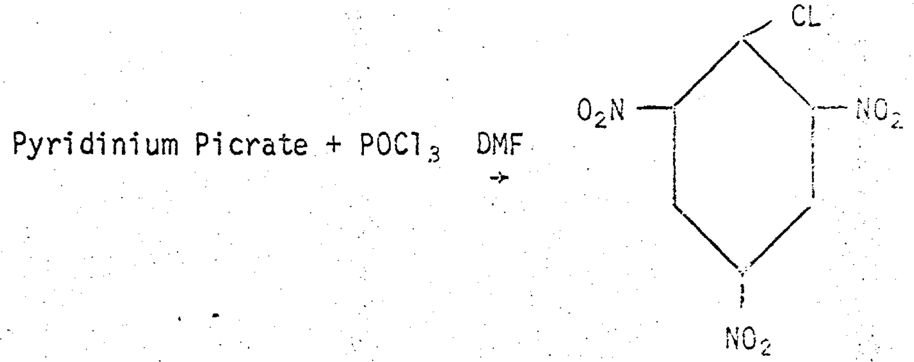
DISCUSSION

The synthesis of picryl chloride is a two step reaction: first picric acid is reacted with pyridine to form pyridinium picrate which is chlorinated with phosphorus oxychloride to form the picryl chloride.



Picric Acid



Picryl Chloride

The basic procedure used was that provided by Sandia[1] for laboratory scale (50 gm) work. Several variations of this basic procedure were tried. The procedure which produced the best quality also had the highest yield.

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[1] *Dr. David M. C'Keefe, Org. 2341*

I. Procedure

The picric acid is dissolved in about one-half the required dimethyl formamide (DMF) and filtered before being placed in the 200-liter Reactor. The rest of the DMF is then added to the reactor.

The pyridine is then mixed with the required DMF and poured rapidly into the picric acid/DMF solution and allowed to mix for about one hour with agitation (150 rpm). The temperature rise on addition of the pyridine was between 5 and 10°C for all batches. Heat of reactions have been calculated from this data and compared to theoretical values (Section IV).

The phosphorus oxychloride is added to the reaction mixture through a polyethylene tube which extends just below the surface of the reaction mixture. Addition times varied between 58 and 26 minutes. Cold water (21-22°C) is circulated through the lower reactor cooling coils (6.5 gpm) during the $POCl_3$ addition. The flow rate reproducibility could be improved by use of a metering pump. The heat of reaction has been calculated and compared to theoretical values (Section IV).

Two procedures were tried at this point. The preferred method was to let the mixture stand overnight with agitation. The reaction mixture is then pulled from the 200-Liter to the 200-Gallon Reactor where a 2 normal hydrochloric acid bath has been prepared. The agitation is as violent as possible (120 rpm). The other method was to heat the mixture for 2 to 3 hours with hot water (5.0 gpm, temperature ~ 48°C), then allow the mixture to cool overnight before dumping it into the HCL bath as described previously.

The picryl chloride remains in the HCl bath for about 30 minutes before filtration can be completed. The solids are then washed with 50 gallons of deionized water and air dried for about one hour. The picryl chloride is then vacuum dried for 48 hours or until dry.

The increase in both yield and purity that was achieved with the 10-kilogram batches compared to the 5-kilogram batches appears to lie with four major factors. First, the reaction mixture was allowed to stand with agitation for approximately one hour prior to the $POCl_3$ addition. Second, the $POCl_3$ addition was made much slower and it was introduced through a polyethylene tube which extended just below the reaction mixture. Third, after the $POCl_3$ addition was complete, the mixture was allowed to stand overnight before being added to the HCl solution. Fourth, the filtration time was reduced from 24 hours on the first batch to about 30 minutes for the 10-kilogram batches.

The primary test for purity was the melting point. A Hoover melting point apparatus was used for these determinations. DTA's (Figs. 3, 4, and 5) were also run on the solids and compared to Sandia-furnished samples (Fig. 2). Samples of the three 10-kilogram batches were titrated with a sodium hydroxide solution to determine purity. The samples were placed in water and allowed to stand about 1 to 2 minutes to insure all picric acid in the sample was dissolved. It was then titrated with an NaOH solution to determine the amount of picric acid in each solution. Since picryl chloride hydrolizes slowly to picric acid, the amount of picric acid shown by the titration should be more than was actually there as an impurity.

II. Source and Quality of Materials

Material	Source	Quality
Picric Acid	Southern Dyestuff Company	Technical Grade
Pyridine	Aldrich Chemical Company Wilshire Chemical Company	ACS Reagent Grade ACS Reagent Grade
$POCl_3$	Alfa Inorganics, Ventron Corp.	Purity Unknown
DMF	Fisher Scientific	ACS Reagent Grade
HCl	Mallinckrodt Allied Chemical	Analytical Reagent ACS Reagent Grade
Water	Pantex Deionized	Max. Impurities 3ppm

III. Equipment

The equipment layout is shown in Fig. 1.

A. Primary-Reaction Vessel

The primary reaction vessel was a Dow Corning 200-liter glass reaction vessel with condenser and variable speed agitator. The heat can be supplied by either a quartz heating mantel or a special immersion coil inside the reactor. Hot or cold water or steam can be circulated through the coil.

B. Hydrochloric Acid Bath Vessel

The vessel used for the HCl bath is a Pfaudler glass lined steel-jacketed 200-gallon reactor with an air-driven agitator. The unit is equipped with a Corning glass condenser.

C. Filtration

Filtration was done in two U.S. Stoneware ceramic filters. Vacuum was supplied with a water sealed vacuum pump.

D. Drying

All drying operations were done with a Stokes vacuum shelf dryer.

E. Miscellaneous

All valves on vessel drain were Grenell-Saunders glass-lined valves. All transfer hoses were Teflon lined.

IV. Calculated Temperatures of Reactions

The preparation of picryl chloride from picric acid involves several exothermic reactions: (1) pyridinium picrate from picric acid and pyridine and (2) picryl chloride from the pyridinium picrate and $POCl_3$. For these types of chemical reactions, analytical techniques are being developed in order to predict the temperature rise of the reaction. These predictions (or estimates) are necessary in order to assure adequate reaction temperature control for a good yield and to prevent dangerous operating conditions due to excessive temperatures.

A. Pyridinium Picrate Reaction

For analysis, the pyridinium picrate reaction has been assumed as a first-order reaction with time since the pyridine solution is dumped into the picric acid solution in a short time period. For this reaction, the concentration of reactants can be assumed to decay exponentially (first-order type) versus time. The energy balance can be presented as

$$UA\,(T-T_c) + \rho C_p V\frac{\delta T}{\delta t} = VK_0 e^{-\lambda t} \;\ldots \qquad (1)$$

where

U = overall heat transfer coefficient

A = heat transfer area

T = batch temperature

T_c = coolant temperature

ρ = density of batch

C_p = specific heat of batch

V = volume of batch

K_0 = constant, energy of reaction

λ = reaction time constant

Integration of this equation (1) yields

$$T-T_c = \frac{K_0}{\rho C_p(\lambda-P)} (e^{-P\tau}-e^{-\lambda\tau}) \ldots\ldots \qquad (2)$$

$$P = \frac{UA}{\rho C_p V}$$

$$\tau = t-t_0$$

t_0 = initial time

The equation (2) has been rearranged into dimensionless groups and plotted for various ratios of λ/P in Fig. 6.

In order to solve equation (2), the constants, K_0 and λ, must be established from the heat of reaction and the time for the concentration of reactants to decay to a low relatively steady-state level. The heat of formation of pyridinium picrate is unknown so that a direct balance could not be made. Therefore, the total reaction has been considered as a change in bonds similar to those encountered in the solution reactions of the type $NH_3 + HCl \rightarrow H_3N{:}HCl$. Consideration of a number of these typical reactions indicated that the heat of reaction was usually near -12.5 Kcal/g-mole. This value was then used for the calculation of K_0.

Since the λ constant for the decay is dependent on the mass diffusion and reaction rates in the batch, the equation (2) has been solved for peak temperature for various values of $P\tau$. (These peaks automatically lead to a specific ratio of λ/P for each value of $P\tau$.) Results for peak temperature versus time are presented in Fig. 7 and indicate a rise of 10 to 22°F in the probable decay time zone.

Comparison of the measured temperatures with the predicted values yields close agreement and a temperature profile is even more remarkable as indicated in Fig. 7.

B. Picryl Chloride Reaction

The reaction of $POCl_3$ with pyridinium picrate to form picryl chloride is very exothermic. As a result, in order to control the temperature rise during the reaction, the $POCl_3$ solution is added very slowly to the pyridinium picrate solution. This slow addition of the strong reactant results in a relatively constant concentration level and rate of reaction. Consequently, the reaction has been represented analytically as a constant zero-order reaction up to the point of completion. The energy balance is similar to (1) except a constant, R, replaces the exponential, $K_0e^{-\lambda t}$. The equation for constant heat of reaction is

$$UA(T-T_0) + \rho C_p V\frac{\delta T}{\delta t} = RV-UA(T_0-T_c) \;\ldots\ldots \qquad (3)$$

where

T_0 = initial temperature of batch

R = constant heat of reaction/volume-time

Again, in this reaction, the heat of reaction is difficult to obtain and a value of -63.9 Kcal/g-mole has been derived. This value is based on bond-energy differences and the known heats of formation for $POCl_3$ and H_3PO_4. The constant, R, in equation (3) is easily obtained by conversion of units from the heat of reaction and mass flow rate of the $POCl_3$ reactant.

The comparison of measured and calculated temperatures of the reaction as presented in Fig. 8 indicate fairly good agreement. The theoretical peak temperature of 96.5°F compares well with the measured value of 98.2°F. However, the theoretical time-to-completion of the reaction of 16.5 minutes is faster than the measured value of 22 minutes. This time difference may be due to a lag in the mass diffusion as is indicated by the temperature lag at the start of the run. (This lag appears to be about 5 minutes at 90°F).

The heats of reaction for this picryl chloride reaction and the pyridinium picrate reaction as inferred from the test results are in good agreement (within 6%) with the assumed values. This comparison indicates another important potential use of the data in conjunction with the analytical procedures to determine the apparent heat of reaction.

FUTURE WORK; COMMENTS; CONCLUSIONS

The procedure for manufacture of picryl chloride has been sufficiently established to produce yields of 80 to 90 percent on the 10-kilogram scale. The product produced is 99 percent picryl chloride without recrystallization.

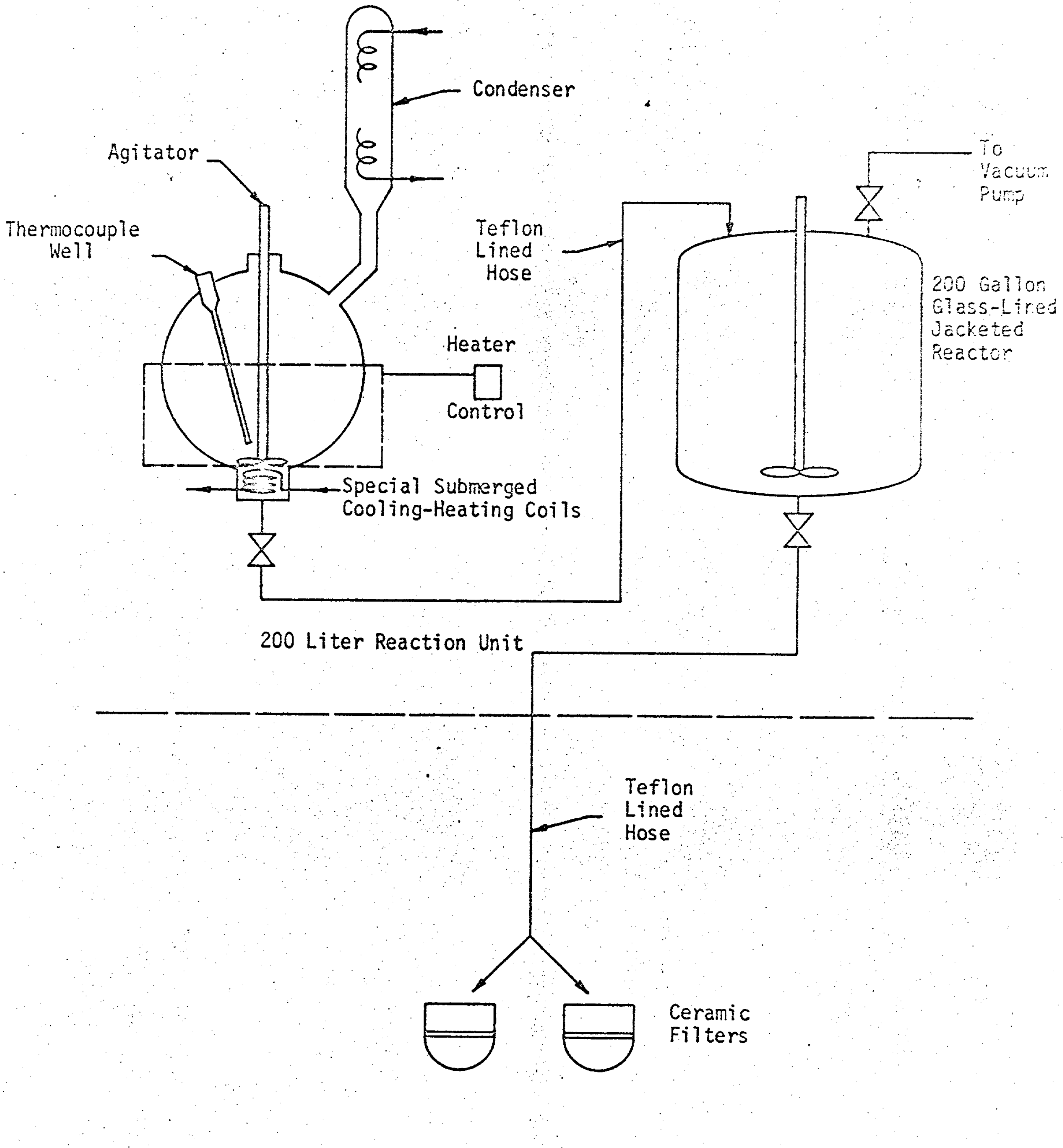


Fig. 1

Equipment Layout for Picryl Chloride Synthesis

Fig. 2

<u>Sandia Picryl Chloride, Batch No. 7-50-1</u>

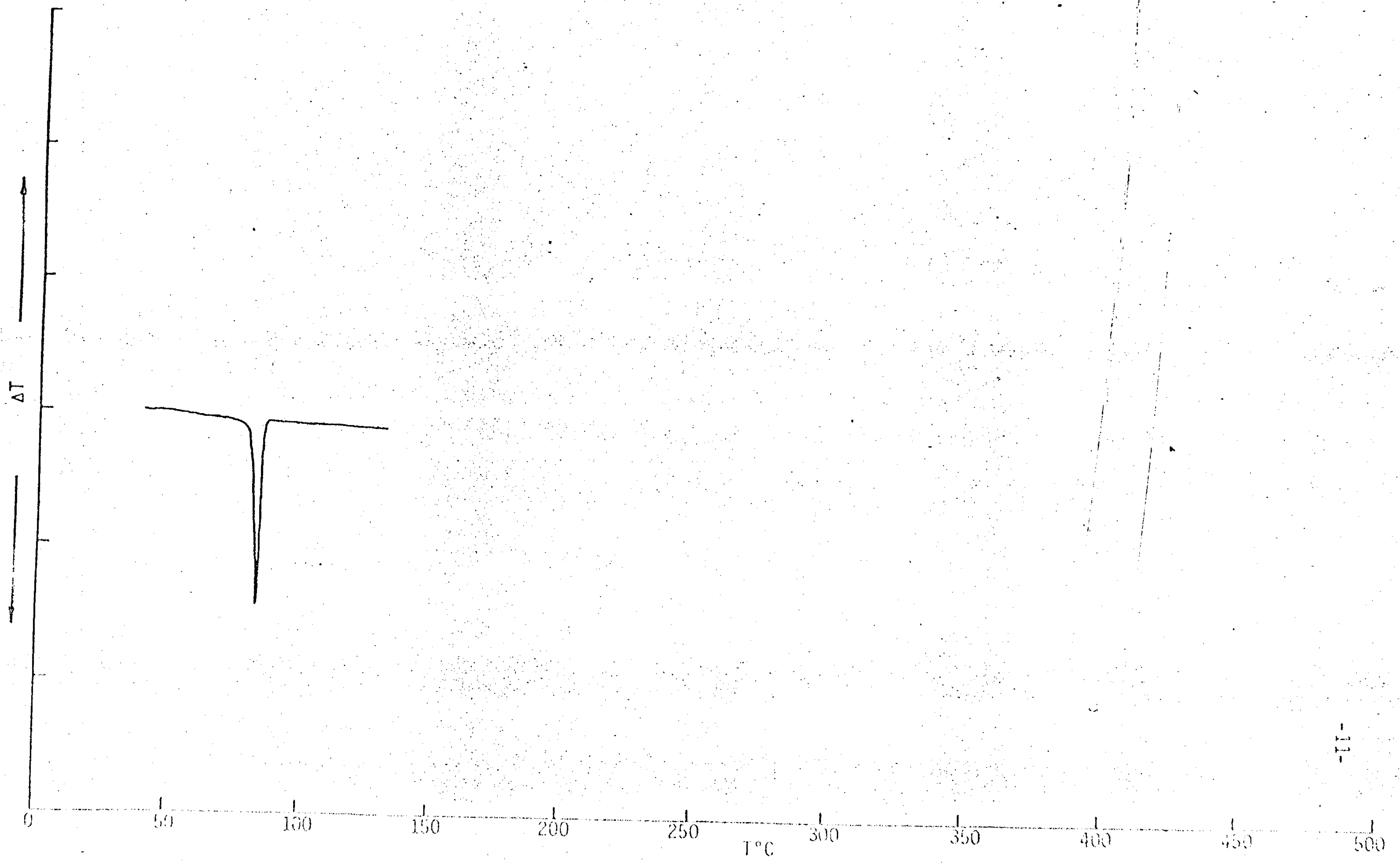


Fig. 3

Picryl Chloride from 0118-05-01 Recrystallized from Ethanol

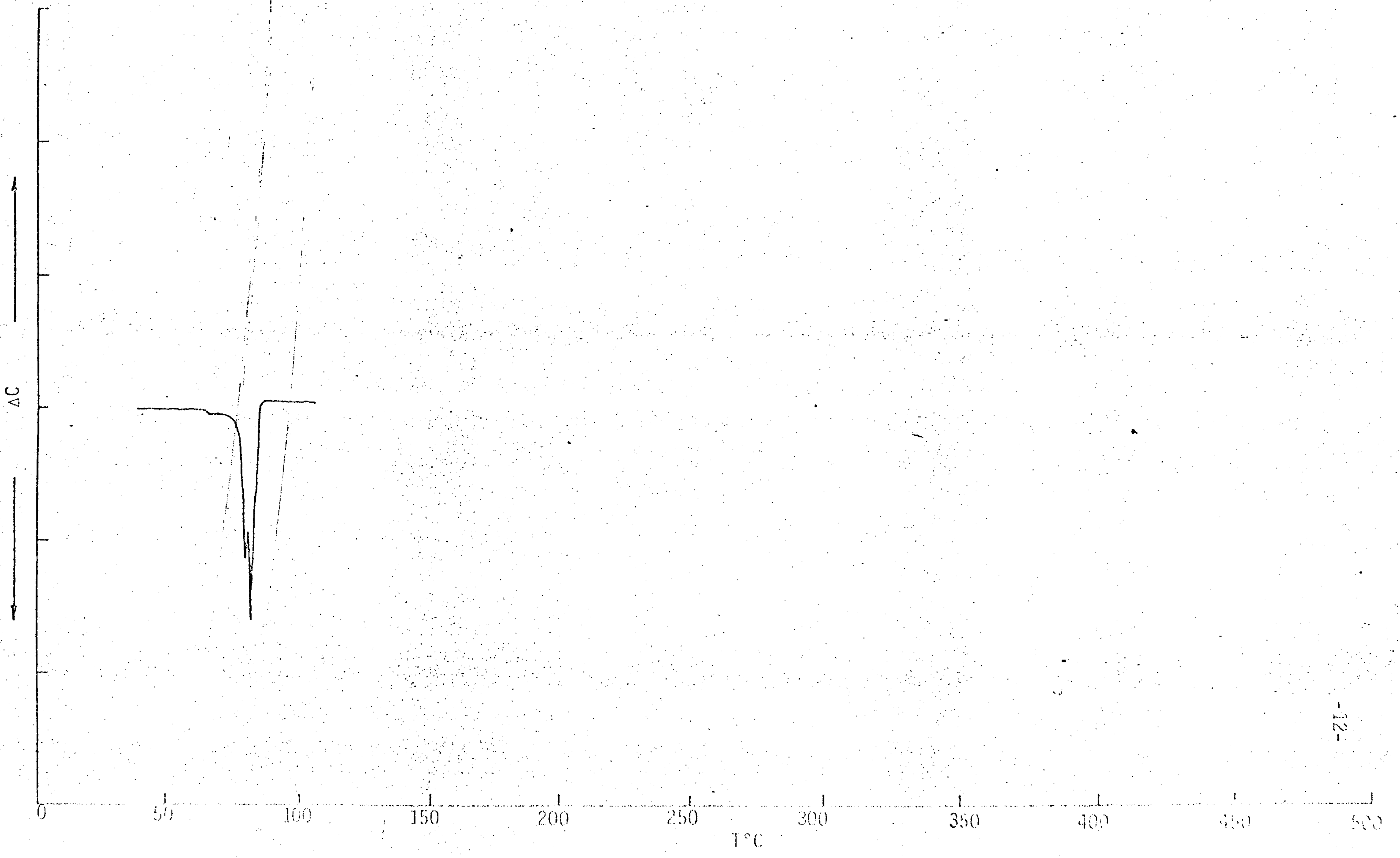


Fig. 4

<u>Picryl Chloride from 0127-05-01 Not Recrystallized</u>

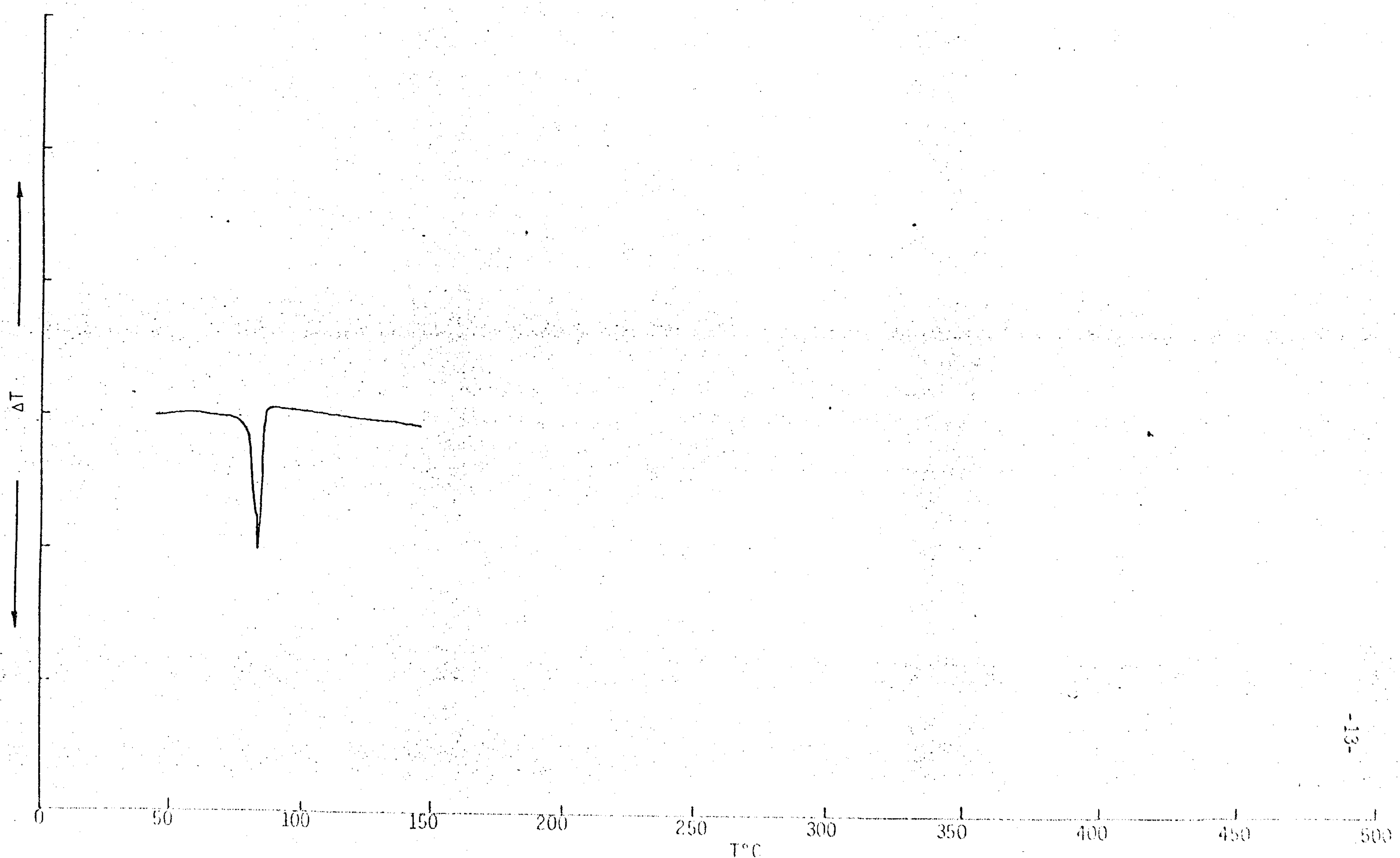


Fig. 5

Picryl Chloride from 0146-05-01 Not Recrystallized

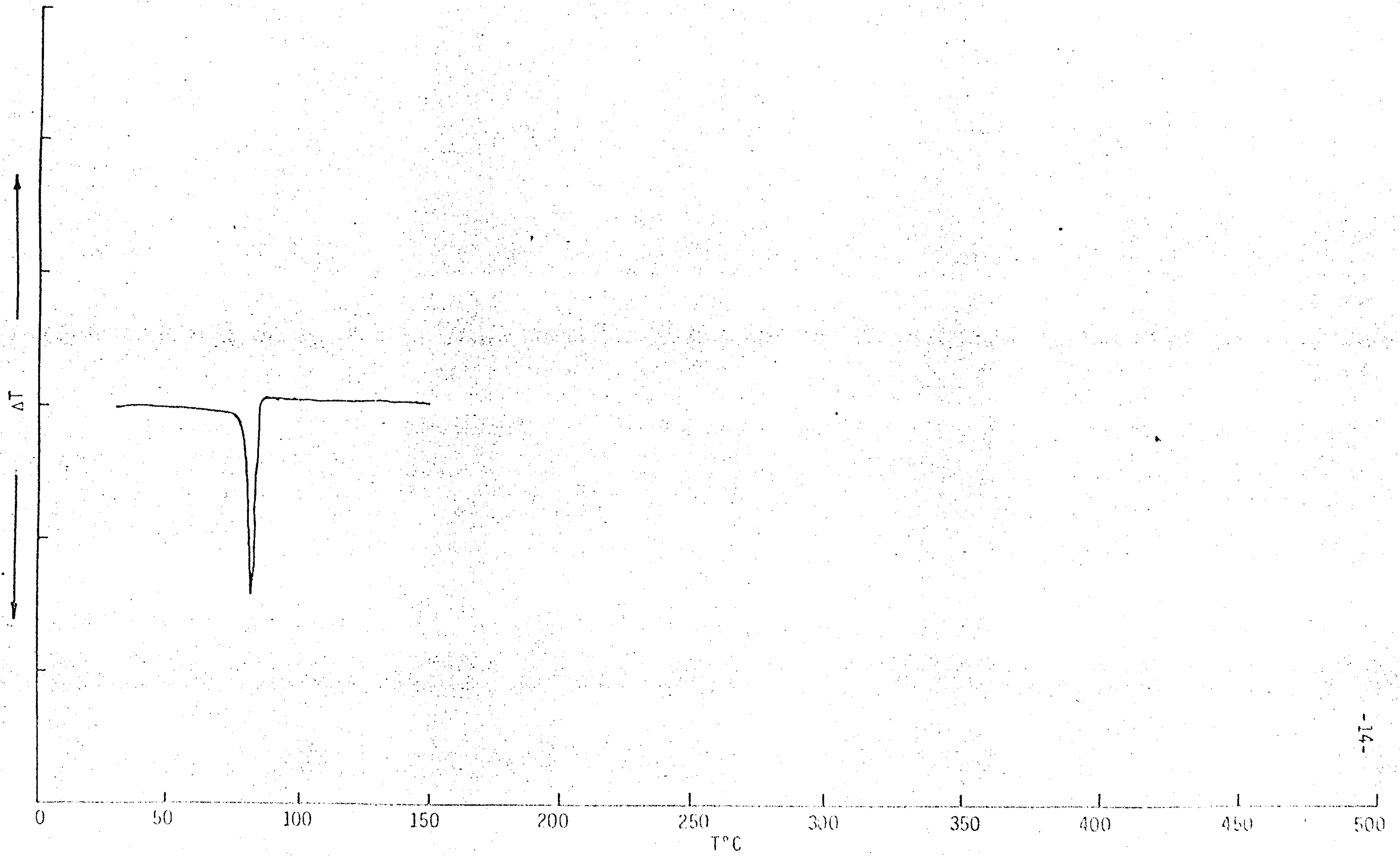
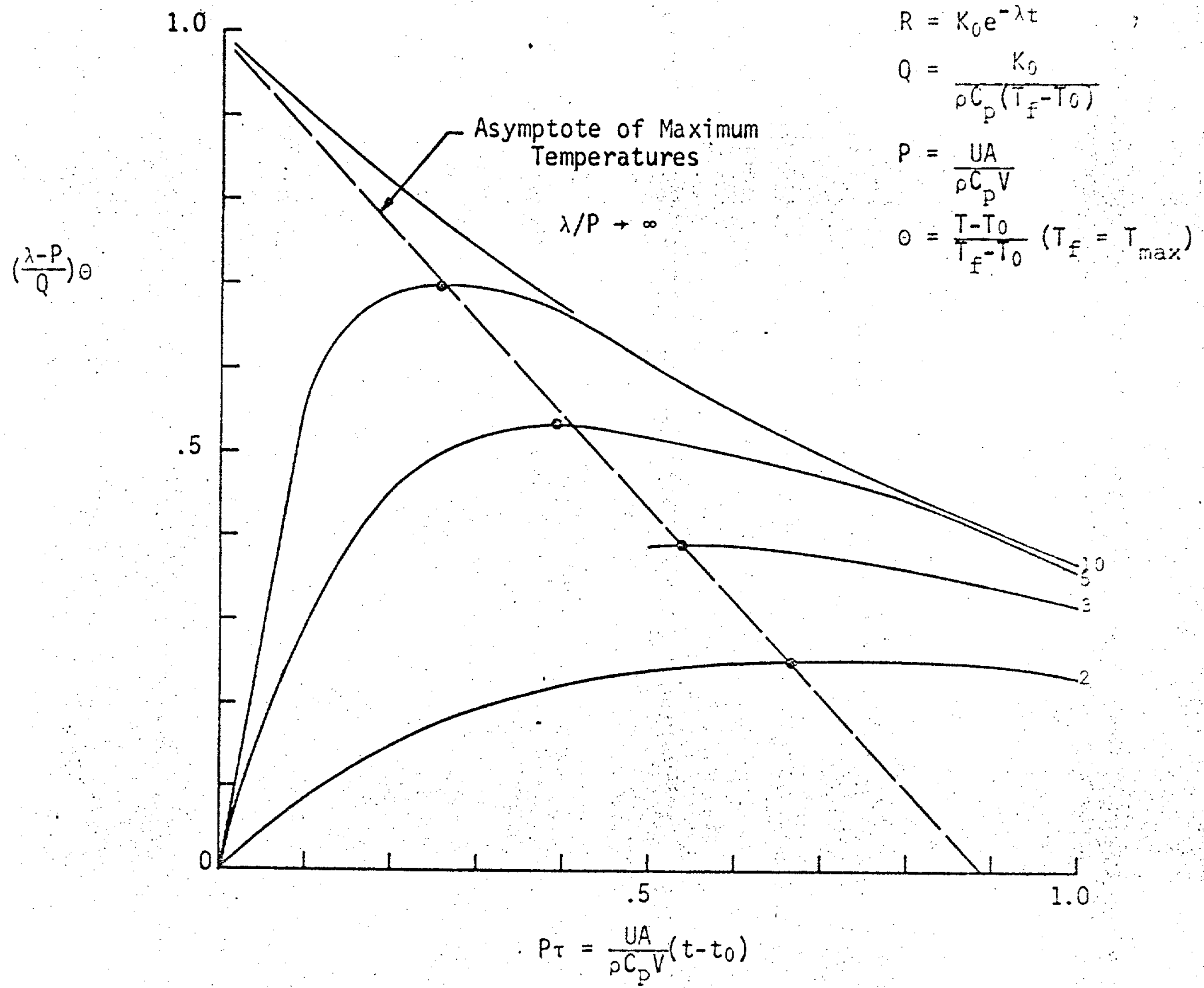


Fig. 6

Temperature Increase for Exothermic First-Order Reaction—Well-Stirred, Batch Process



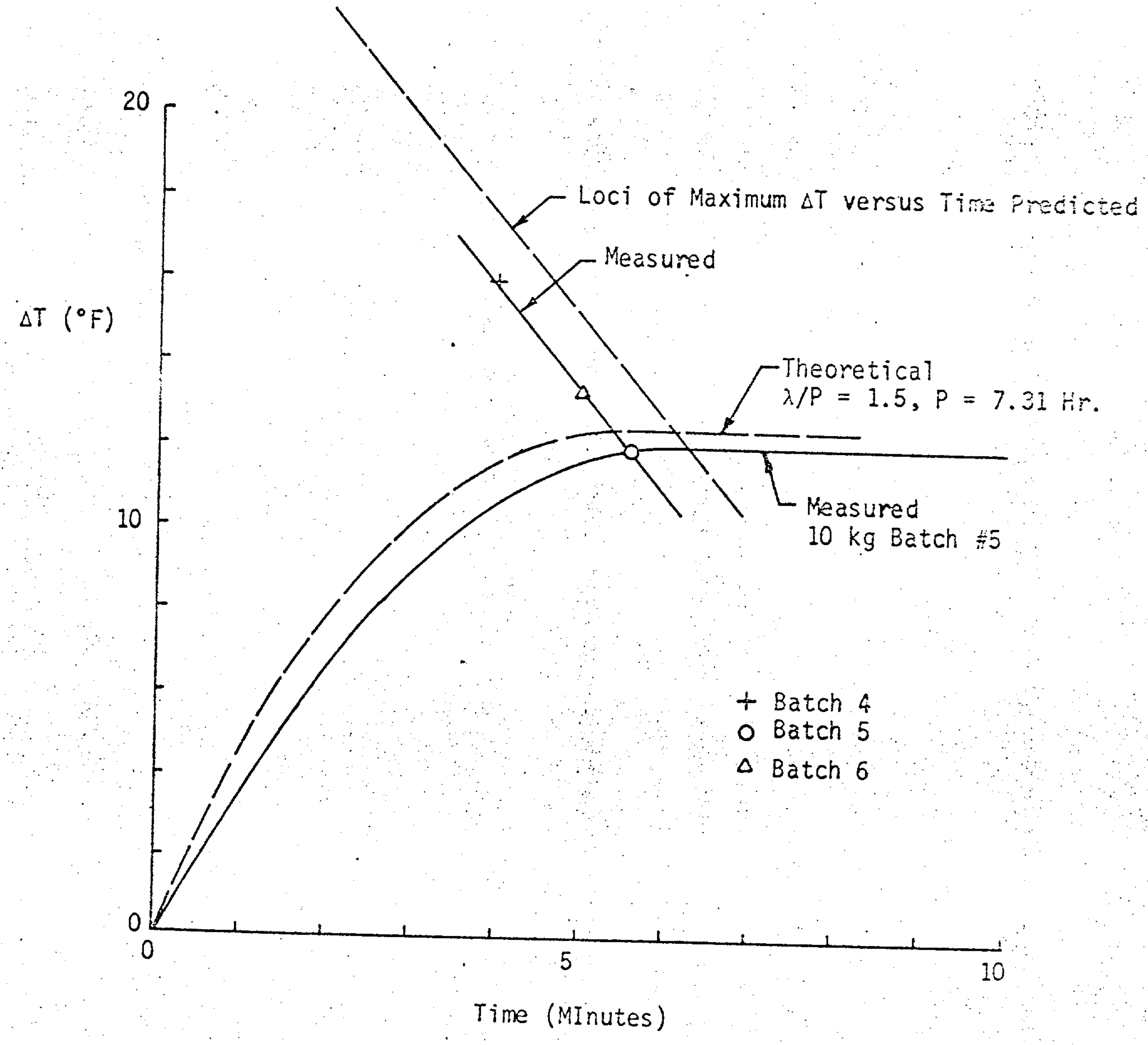


Fig. 7

Temperature Rise for Picric Acid - Pyridinium Picrate Exothermic Reaction—(10 kg Batches)

Fig. 8

Temperature Rise for Picric Acid - Picryl Chloride Exothermic Reaction