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NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

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SYNTHESIS AND PURIFICATION OF ALKYLDIPHENYLMETHANE HYDROCARBONS

I - 2-METHYLDIPHENYLMETHANE, 3-METHYLDIPHENYLMETHANE 2-ETHYLDIPHENYLMETHANE, 4-ETHYLDIPHENYLMETHANE AND 4-ISOPROPYLDIPHENYLMETHANE

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SUMMARY

The syntheses of five alkyldiphenylmethane hydrocarbons, 2-methyldiphenylmethane, 3-methyldiphenylmethane, 2-ethyldiphenylmethane, 4-ethyldiphenylmethane, and 4-isopropyldiphenylmethane, are described. The preparation of these hydrocarbons was based on the reaction of the appropriate arylmagnesium halides with benzaldehyde to yield the corresponding alkylbenzhydrols, which were subsequently converted to the hydrocarbons by hydrogenolysis. The physical properties tabulated include melting point, boiling point, index of refraction, density, viscosity, heat of fusion, and heat of combustion. Time-temperature melting curves are plotted for all compounds prepared.

INTRODUCTION

The synthesis and the purification of several alkyldiphenylmethane hydrocarbons, 2-methyldiphenylmethane, 3-methyldiphenylmethane, 2-ethyldiphenylmethane, 4-ethyldiphenylmethane, and 4-isopropyldiphenylmethane, were undertaken in conjunction with a program being conducted at the NACA Lewis laboratory to study hydrocarbons as possible fuels for jet-propulsion aircraft engines. A review of the literature disclosed few data on this series of compounds.

The hydrocarbon 2-methyldiphenylmethane has been prepared by the Clemmensen reduction of 2-methylbenzhydrol or 2-methylbenzophenone (reference 1) and by the catalytic reduction of ethyl o-benzoylbenzoate (reference 2).

Methods of synthesis that have been employed for the preparation of 3-methyldiphenylmethane include the reduction of 3-methylbenzophenone by hydriodic acid and phosphorus (reference 3) and the reaction of m-methylbenzylchloride with benzene in the presence of aluminum chloride (reference 4).

No mention of 2-ethyldiphenylmethane has appeared in the literature and the only reference to 4-isopropyldiphenylmethane described a preparation by the reduction of 4-isopropylbenzophenone with sodium in ethyl alcohol (reference 5).

Three methods for the synthesis of 4-ethyldiphenylmethane are given: the reaction of ethyl benzene with benzyl chloride in the presence of zinc dust (reference 6) and in the presence of beryllium chloride (reference 7) and the reduction of 4-ethylbenzophenone with hydriodic acid and phosphorus (reference 8).

Except for those cited in references 1 and 2, the methods of preparation previously mentioned could not be expected to yield pure products. Each of the five alkyldiphenylmethane hydrocarbons discussed herein was prepared by hydrogenolysis of the solid benzhydrol (reference 1), which was synthesized by the condensation of the appropriate arylmagnesium halide with benzaldehyde. The hydrogenolysis was accomplished catalytically instead of by the Clemmensen reaction as in reference 1.

PREPARATION

The aryl halides required for the preparation of the various benzhydrols were purified from commercial products by fractional distillation. The m-iodotoluene was steam-distilled from strong caustic solution prior to the fractionation. Physical constants of o-bromoethylbenzene and p-bromoethylbenzene are reported in reference 9; the data on m-iodotoluene and p-bromoisopropylbenzene are included herein.

Each of the five benzhydrols was prepared by reacting the appropriate arylmagnesium halide with benzaldehyde in absolute ether and subsequently hydrolyzing the Grignard complex by pouring it onto a mixture of cracked ice, water, and hydrochloric acid. This hydrolysis procedure is very important if good yields of the benzhydrols are to be obtained. Hydrolysis by the addition of dilute hydrochloric acid or saturated ammonium chloride to the ether solution of the Grignard complex resulted in extremely poor yields in every case and no desired benzhydrol could be isolated in the attempted preparation of 4-ethylbenzhydrol by this procedure. The yields of 3-methylbenzhydrol, 4-ethylbenzhydrol, and 4-isopropylbenzhydrol were increased 5 to 10 percent by employing less than the theoretical quantity (75 to 80 percent) of benzaldehyde for the condensation of the Grignard reagent. This phenomenon, discussed in reference 10, was not investigated in the preparations of 2-methylbenzhydrol and 2-ethylbenzhydrol.

The benzhydrols were purified by distillation at reduced pressure, followed by several crystallizations from petroleum solvents prior to hydrogenolysis in the presence of copper chromite catalyst. The yields on hydrogenolysis were nearly quantitative.

PURIFICATION AND DETERMINATION OF PHYSICAL PROPERTIES

Final purification of the alkyldiphenylmethane hydrocarbons consisted of fractional distillation of 3 to 4 liters of material through 6-foot (30-mm diam.) glass columns, packed with 3/16-inch glass helices, at reduced pressures (3 to 18 mm Hg). After approximately 200 milliliters, consisting of three or four fractions, were removed, the subsequent individual fractions from each distillation were of constant refractive index and did not vary in melting point more than 0.2° C. The purest fractions in each distillation were combined to obtain the desired 500-milliliter quantity of each hydrocarbon with an estimated purity of more than 99.9 mole percent.

The physical constants of the five hydrocarbons are shown in table I. The melting points of the benzhydrols are included in the text under the individual compounds. The time-temperature melting curves were determined with a platinum resistance thermometer and a G-2 Mueller bridge with accessory equipment and by methods described in reference 11; the melting points were determined from the curves according to the graphical method described in reference 12. Densities were determined by use of a gravimetric balance according to the method of reference 13, and the indices were measured with a Bausch and Lomb precision oil-model five-place instrument. The boiling points were determined by the use of a platinum resistance thermometer in an apparatus modified from that described in reference 14. The system was pressurized with dry air from a surge tank and held at constant pressure by adjusting a continuous bleed. The kinematic viscosities were determined in viscosimeters that had been calibrated with National Bureau of Standards standard viscosity samples H-5, H-7, D-7, or L-17. The A.S.T.M. procedure of reference 15 was followed. The net heats of combustion were determined according to reference 16 in an oxygen bomb calorimeter that had been calibrated on Bureau of Standards benzoic acid. The heats of fusion were obtained by use of a method and apparatus similar to that described in reference 17. The estimated mole percent purities, determined according to methods described in reference 18, are also included.

The magnitude of the uncertainties is estimated as follows:

Melting point, °C	0.02
Density, gram/ml	0.00005
Refractive index	0.0002
Boiling point, °C	0.1
Kinematic viscosity relative to 1.007 centistokes for water at 20° C, percent	0.5
Net heat of combustion, kcal/mole	10
Heat of fusion, percent of determined value	5

The precision of measurements is as follows:

Melting point, °C	±0.003
Density, gram/ml	±0.00002 to 0.00003
Refractive index	±0.0001
Boiling point, °C	±0.04
Kinematic viscosity, percent of determined value	±0.2
Net heat of combustion, kcal/mole	±5
Heat of fusion, percent of determined value	±2.5

EXPERIMENTAL DETAILS

Alkylbenzhydrols

In a 10-gallon glass-lined reactor, 40 moles of arylhalide was reacted with 973 grams (40 moles) of magnesium turnings in 16 liters of absolute ether. To the cooled solution of the arylmagnesium halide was gradually added 9 liters of an ether solution of 30 to 40 moles of freshly distilled technical-grade benzaldehyde. The reaction mixture was hydrolyzed by withdrawing it from the 10-gallon reactor and adding it rapidly to a mixture of 100 pounds of cracked ice, 3.25 liters of concentrated hydrochloric acid (40 moles HCl), and 3 to 5 gallons of cold water in a 30-gallon reactor. After hydrolysis was complete, the acid-water layer was drained off and the ether solution washed successively with cold water, with dilute sodium bicarbonate solution, and again with cold water. The main bulk of the ether was stripped by heating with steam, after which the reddish-amber benzhydrol solution was drained out of the reactor.

2-Methylbenzhydrol. - In the synthesis of 2-methylbenzhydrol, the arylhalide employed was o-bromotoluene (n_D^{20} 1.5564; freezing point, -26.8° C) and 40 moles of benzaldehyde was used to condense with the Grignard complex.

When the remaining ether in the benzhydrol was evaporated at reduced pressure in a water bath at 60° to 70° C, the brown residue (7535 grams) solidified. This solid was ground and then washed with cool petroleum ether (boiling range, 30° to 60° C). The light yellow solid (6740 grams) was distilled and the clear, colorless fraction, boiling at 143° to 144° C at a pressure of 1.5 millimeters of mercury, was collected. Crystallization was accomplished by saturating hot petroleum ether (boiling range, 60° to 90° C) with the 2-methylbenzhydrol and allowing the hot solution to cool slowly to 20° to 25° C. The benzhydrol precipitated out of the solution as thick colorless prisms (5320 grams), which were recrystallized as before to yield 4900 grams (61.8 percent, based on benzaldehyde) of pure 2-methylbenzhydrol with a melting point of 90.0° C. The theoretical analysis (calculated for $C_{14}H_{14}O$) was as follows: C, 84.81 percent; H, 7.12 percent. The experimental analysis was: C, 84.68 percent; H, 7.07 percent.

3-Methylbenzhydrol. - The arylhalide m-iodotoluene (n_D^{20} 1.6052; melting point, -27.4° C) was employed for the preparation of 3-methylbenzhydrol. Physical properties of a sample of m-iodotoluene purified further are:

Melting point, °C	-27.20
Boiling point (at 760 mm of Hg), °C	213.03
Refractive index, n_D^{20}	1.6053
Density at 20° C, gram/ml	1.7050

The amount of benzaldehyde used was 30 moles (75 percent of the theoretical quantity).

The solution of the benzhydrol from the reactor was heated with hot water at reduced pressure to evaporate the rest of the ether. The ether-free material was distilled and the fraction boiling at a temperature of 150° to 160° C at a pressure of 2 millimeters of mercury was collected. This fraction from a 40-mole run amounted to 4360 grams of clear yellow liquid that solidified on cooling. Quantities of 250 grams each were dissolved in 1.6 liters of hot petroleum ether (boiling range, 30° to 60° C) and allowed to cool slowly to 20° to 25° C. The yellow liquid was decanted and the white solid collected on a filter. The total recovery from the first crystallization was 3710 grams. A second crystallization yielded 3440 grams and a third, 3310 grams (55.7 percent, based on benzaldehyde) of pure white cottony needles of 3-methylbenzhydrol with a melting point of 52.8° C. The theoretical analysis (calculated for $C_{14}H_{14}O$) was as follows: C, 84.81 percent; H, 7.12 percent. The experimental analysis was: C, 84.93 percent; H, 7.18 percent.

2-Ethylbenzhydrol. - The halide o-bromoethylbenzene (n_D^{20} 1.5489; melting point, -67.3° C) was used for the preparation of 2-ethylbenzhydrol. The theoretical quantity of benzaldehyde (40 moles) was used to condense with the prepared Grignard reagent.

The solution of the benzhydrol from the reactor was heated on the steam bath to evaporate the remaining ether. When the solution was cooled, nearly all the benzhydrol solidified and was washed with petroleum ether (boiling range, 30° to 60° C) to yield 5950 grams of nearly white product. This material was distilled and the colorless fraction amounting to 5650 grams and boiling at 170° to 175° C at 2.5 millimeters of mercury was collected. The distilled material was washed again with petroleum ether (boiling range, 30° to 60° C) and 5220 grams were recovered. This product was recrystallized from petroleum ether (boiling range, 60° to 90° C) by dissolving 200-gram portions in 1.2 liters of hot solvent and allowing the mixture to cool to 20° to 25° C. The 2-ethylbenzhydrol precipitated out in fine white needles melting at 60.8° C. The yield was 4490 grams (52.8 percent, based on benzaldehyde). The theoretical analysis (calculated for $C_{15}H_{16}O$) was as follows: C, 84.86 percent; H, 7.60 percent. The experimental analysis was: C, 84.84 percent; H, 7.60 percent.

4-Ethylbenzhydrol. - The Grignard reagent was prepared from 40 moles of p-bromoethylbenzene (n_D^{20} 1.5446; melting point, -45.5° C) and condensed with 30 moles (75 percent of the theoretical quantity) of benzaldehyde to yield 4-ethylbenzhydrol.

The remaining ether in the benzhydrol solution from the reactor was evaporated at reduced pressure. The ether-free material was distilled and the fraction amounting to 4350 grams and boiling at 165° to 175° C at 3 millimeters of mercury was collected. This fraction, which solidified on cooling, was dissolved in hot petroleum ether (boiling range, 30° to 60° C) at the rate of 350 grams in 3 liters of solvent and cooled to 5° C. The yield of crystallized product was 3830 grams. A second crystallization from petroleum ether was carried out in the same manner as the first and 3600 grams (56.5 percent, based on benzaldehyde) of white cottony needles (melting point, 42.6° C) was obtained. The theoretical analysis (calculated for $C_{15}H_{16}O$) was as follows: C, 84.86 percent; H, 7.60 percent. The experimental analysis was: C, 84.91 percent; H, 7.61 percent.

4-Isopropylbenzhydrol. - The Grignard reagent of 40 moles of p-bromoisopropylbenzene (n_D^{20} 1.5360; melting point, -22.7° C) was employed in the synthesis of 4-isopropylbenzhydrol. Physical properties of a further purified sample of p-bromoisopropylbenzene are:

Melting point, °C	-22.54
Boiling point (at 760 mm of Hg), °C	218.8
Refractive index, n_D^{20}	1.5360
Density at 20° C, gram/ml	1.2855

The amount of benzaldehyde used for the condensation was 32 moles (80 percent of the theoretical amount).

The benzhydrol solution from the reactor was distilled and the fraction boiling from 155° to 165° C at 1.5 millimeters of mercury was collected. This fraction, which solidified on cooling, was slightly yellow and amounted to 6239 grams. The distilled material was crystallized twice from hot isooctane by dissolving 250 grams in 1.7 liters of solvent and allowing the solution to cool slowly to 20° to 25° C. The yield of white cottony needles from the first crystallization was 5100 grams and from the second crystallization was 4500 grams (62.2 percent, based on benzaldehyde). The melting point was 60.5° C. The theoretical analysis (calculated for $C_{16}H_{18}O$) was as follows: C, 84.91 percent; H, 8.02 percent. The experimental analysis was: C, 84.93 percent; H, 8.07 percent.

Alkyldiphenylmethanes

A solution of 2500 grams of alkylbenzhydrol in 1.5 liters of absolute alcohol was mixed with 250 grams of copper chromite catalyst in a 20-liter rocking autoclave and hydrogenated for 20 hours at 225° C and an initial pressure of 1500 pounds per square inch of hydrogen. After the catalyst was filtered and the solvent stripped, the hydrocarbon was distilled to give a 92 to 95 percent yield of product. This material was further purified by fractional distillation at reduced pressure. The melting curves of the individual hydrocarbons are shown in figures 1 to 5.

The 3-methyldiphenylmethane could be crystallized in either of two modifications. The melting curve (fig. 2(a)) was obtained for the lower-melting modification. This sample was immediately cooled and seeded with a crystal of the higher-melting modification; the melting curve shown in figure 2(b) was then determined.

SUMMARY OF RESULTS

The five alkyldiphenylmethane hydrocarbons, 2-methyldiphenylmethane, 3-methyldiphenylmethane, 2-ethyldiphenylmethane, 4-ethyldiphenylmethane, and 4-isopropyldiphenylmethane, were synthesized and purified to an estimated purity of over 99.9 mole percent. The physical properties of these hydrocarbons were determined.

Lewis Flight Propulsion Laboratory,
National Advisory Committee for Aeronautics,
Cleveland, Ohio, August 4, 1950.

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TABLE I - PHYSICAL CONSTANTS

Hydrocarbon	Melting point (°C)	Boiling point at 760 mm (°C)	Index of refraction n_D^{20}	Density at 20° C (g/ml)	Heat of fusion (kcal/mole)	Estimated purity (mole percent)	Net heat of combustion (kcal/mole)	Analysis (percent)				Kinematic viscosity (centistokes)			
								Carbon		Hydrogen		98.89° C (210° F)	60.00° C (140° F)	37.78° C (100° F)	0.00° C (32° F)
								Calculated	Found	Calculated	Found				
2-Methyl-diphenylmethane	6.61	280.50	1.5763	1.00198	5.0	99.9	1735	92.26	92.24	7.74	7.67	1.18	2.08	3.26	10.81
3-Methyl-diphenylmethane	-27.83 -34.46	279.24	1.5712	.99136	4.7	99.9	1750	92.26	92.35	7.74	7.76	1.07	1.76	2.58	6.84
2-Ethyl-diphenylmethane	-11.15	290.88	1.5701	.99213	5.2	99.9	1880	91.78	91.76	8.22	8.17	1.23	2.21	3.45	11.20
4-Ethyl-diphenylmethane	-23.52	297.03	1.5630	.97773	5.2	99.9	1875	91.78	91.65	8.22	8.30	1.08	1.75	2.49	6.01
4-Isopropyl-diphenylmethane	-13.36	305.60	1.5554	.96634	5.2	99.9	2045	91.37	91.48	8.63	8.59	1.25	2.08	3.11	8.46

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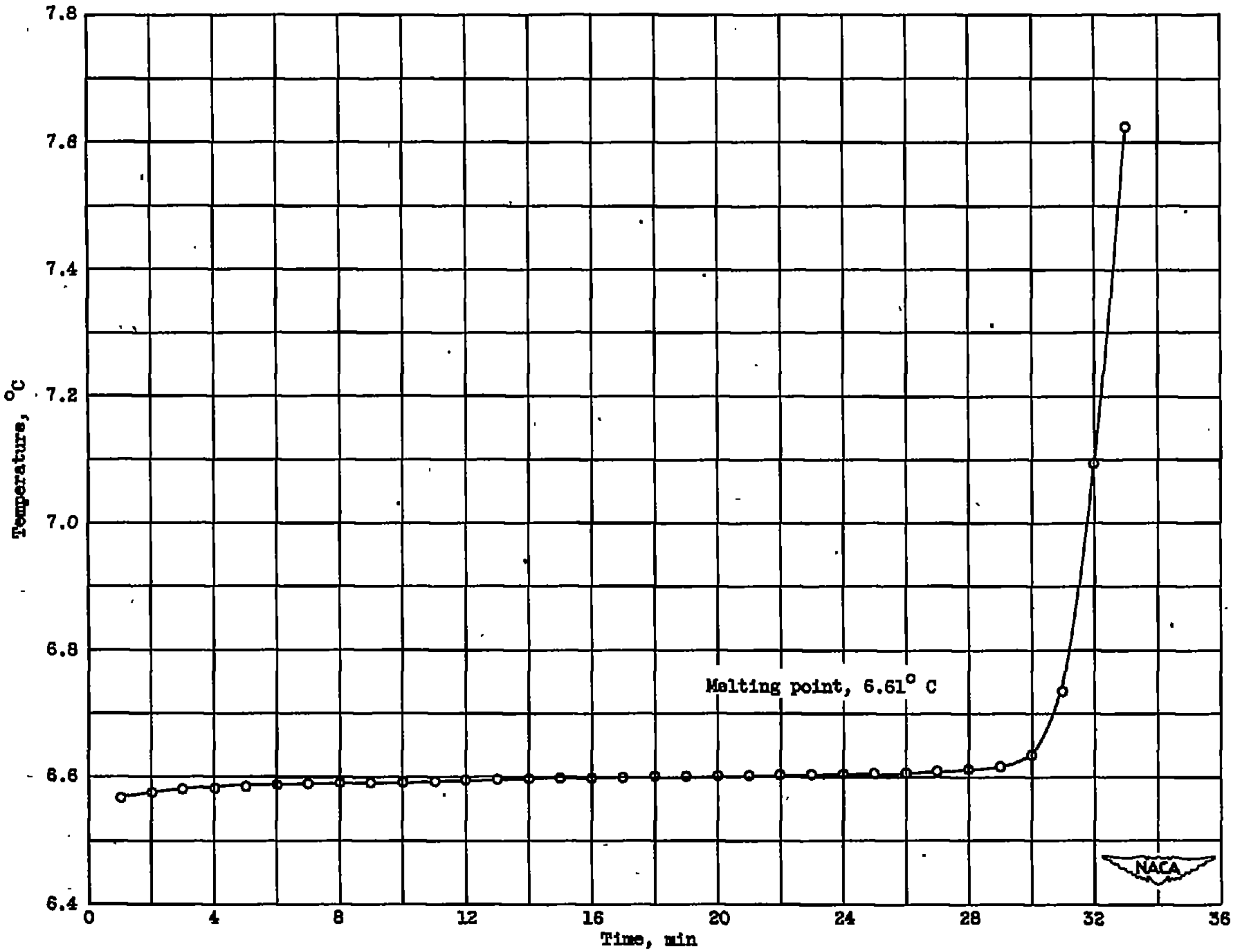
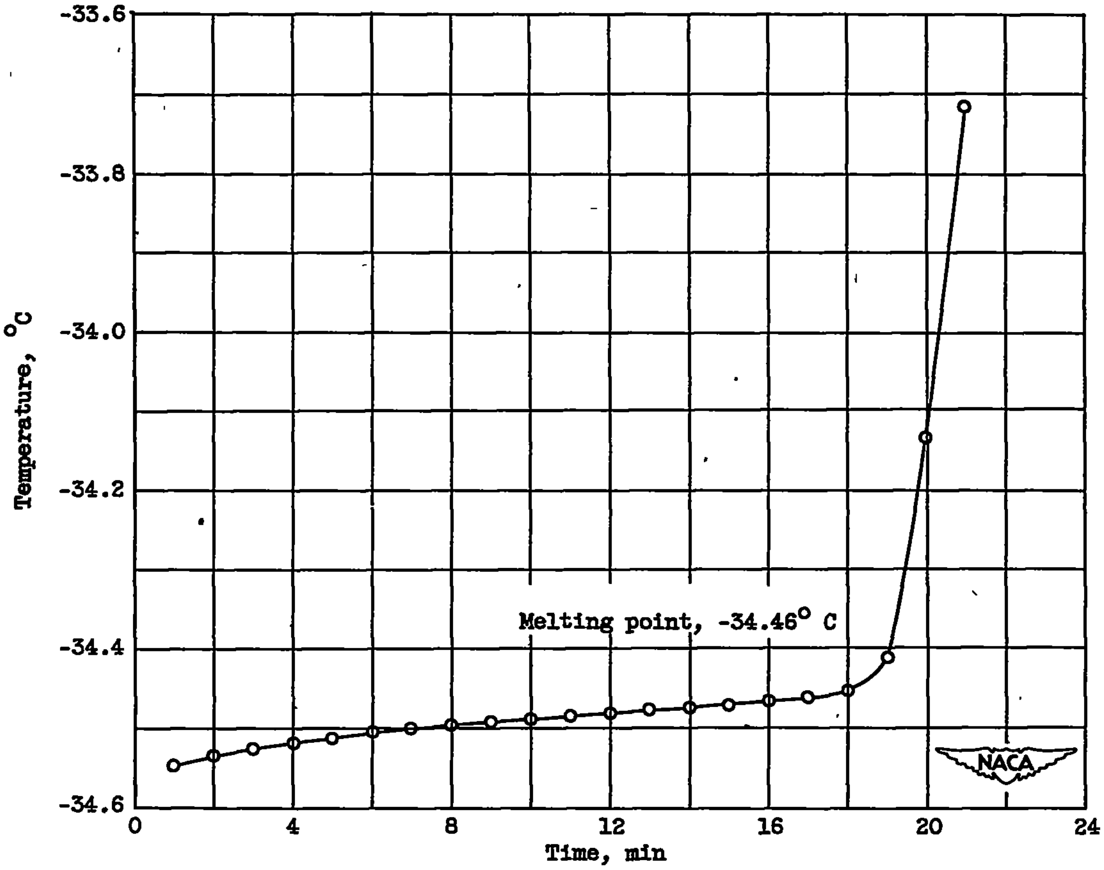
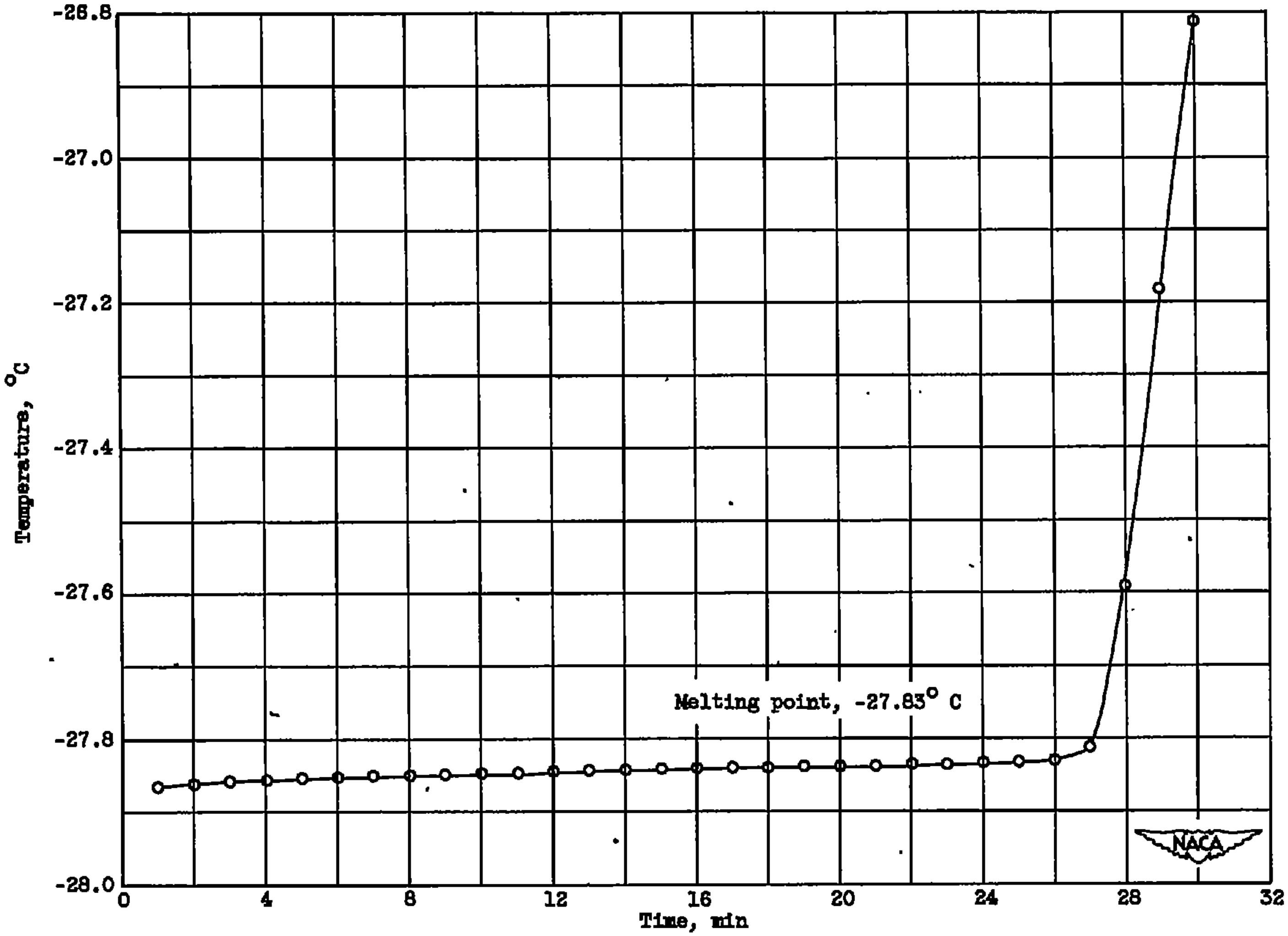


Figure 1. - Time-temperature melting curve for 2-methyldiphenylmethane.



(a) Lower-melting modification.

Figure 2. - Time-temperature melting curve for 3-methyldiphenylmethane.



(b) Higher-melting modification.

Figure 2. - Concluded. Time-temperature melting curve for 3-methyldiphenylmethane.

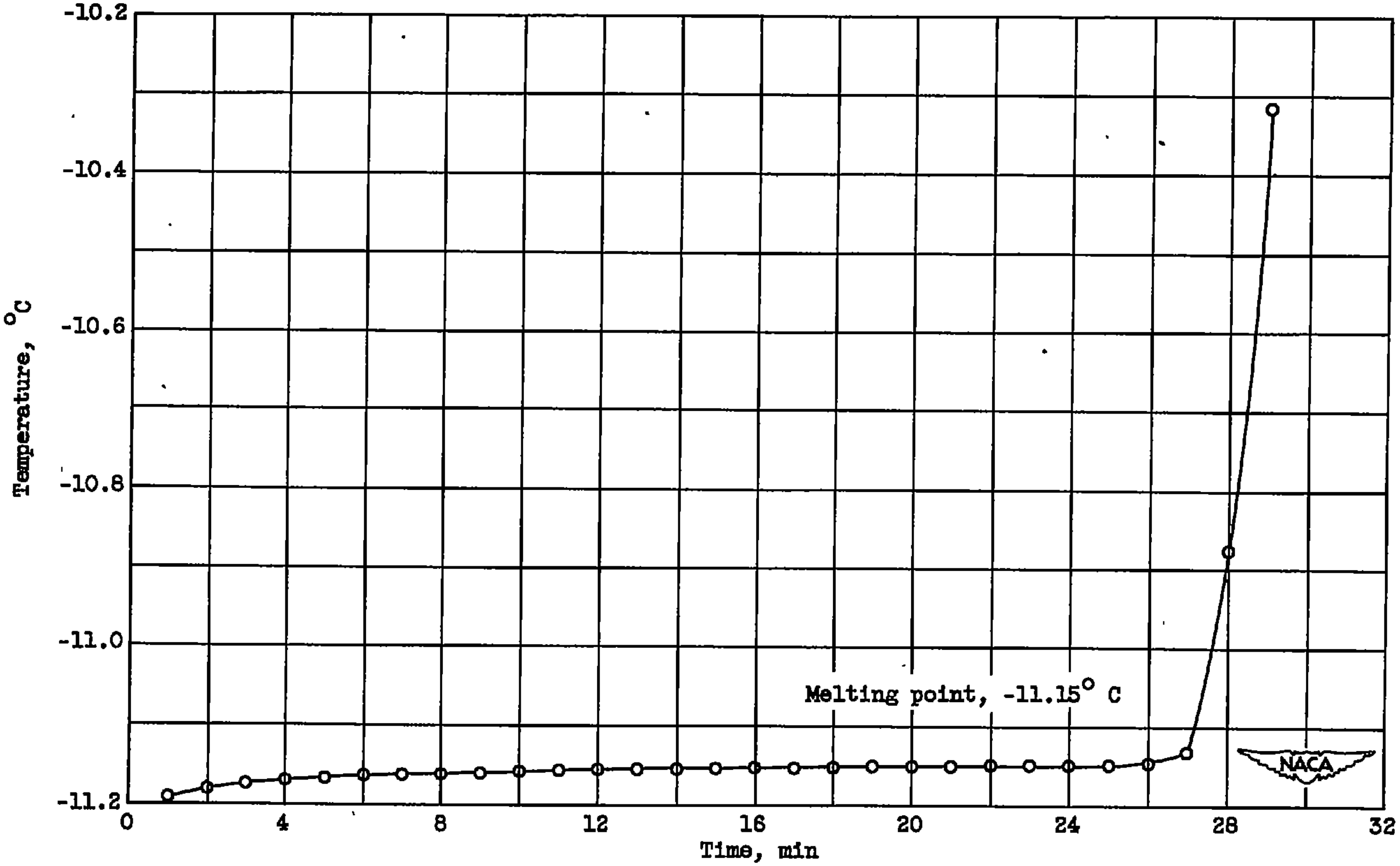


Figure 3. - Time-temperature melting curve for 2-ethyldiphenylmethane.

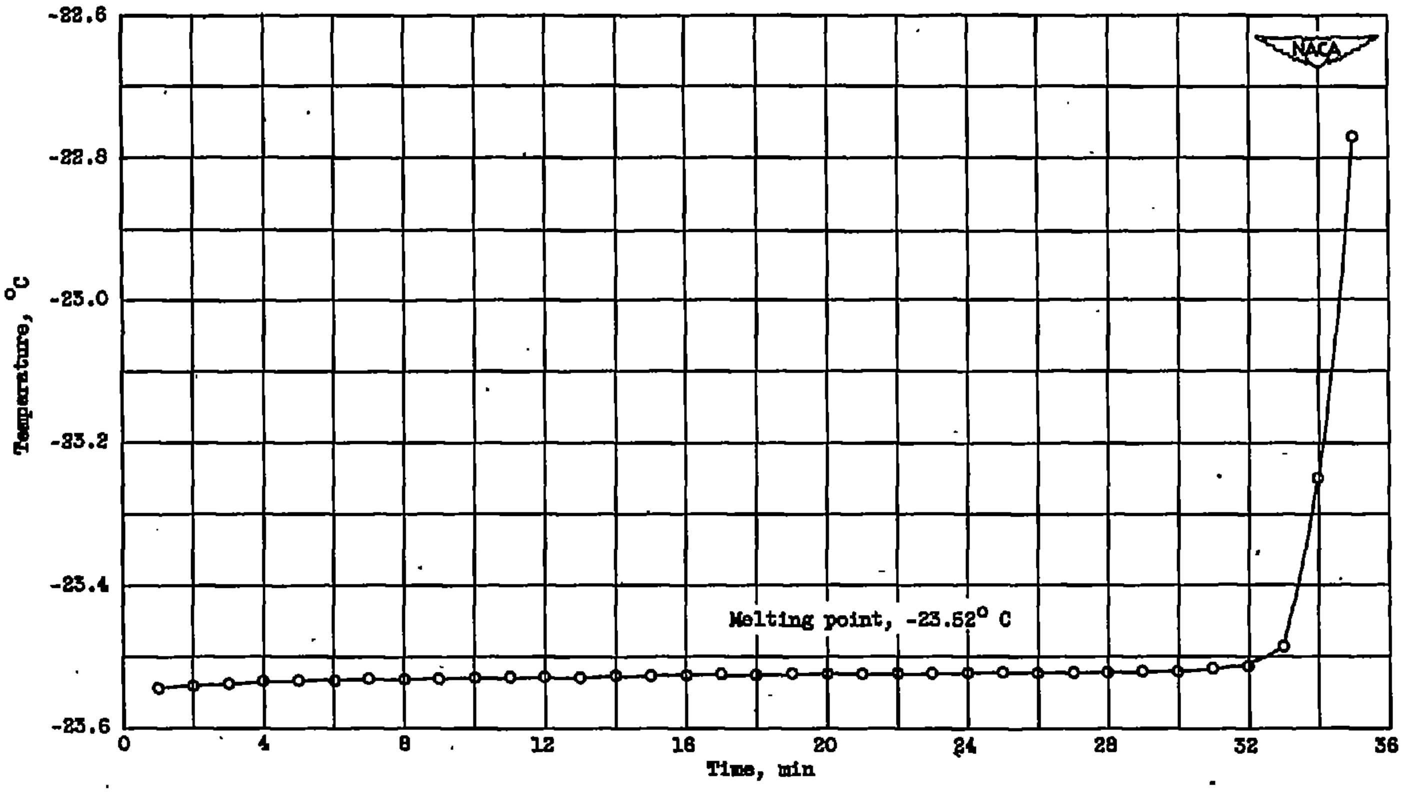


Figure 4. - Time-temperature melting curve for 4-ethyldiphenylmethane.

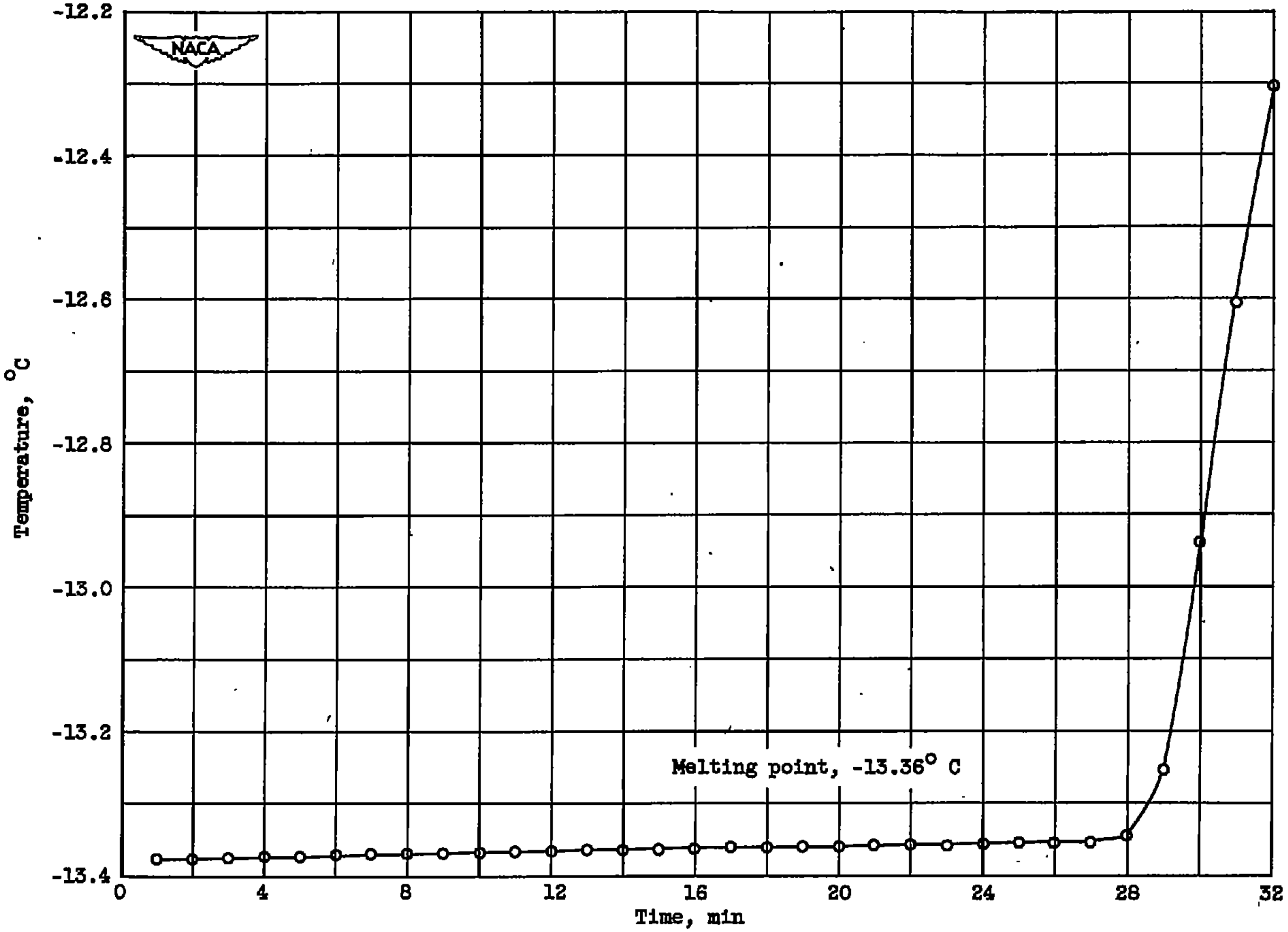


Figure 5. - Time-temperature melting curve for 4-isopropyldiphenylmethane.

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