

JUN 24

D6.3

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

TECHNICAL NOTE

No. 1021

THE SYNTHESIS AND PURIFICATION OF AROMATIC HYDROCARBONS

III - ISOBUTYL BENZENE, sec-BUTYL BENZENE

AND tert-BUTYL BENZENE

By C. M. Buess, J. V. Karabinos
P. V. Kunz, and L. C. Gibbons

Aircraft Engine Research Laboratory
Cleveland, Ohio



Washington
June 1946

N A C A LIBRARY
LANGLEY MEMORIAL AERONAUTICAL
LABORATORY
Langley Field, Va.



NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

TECHNICAL NOTE NO. 1021

THE SYNTHESIS AND PURIFICATION OF AROMATIC HYDROCARBONS

III - ISOBUTYLBENZENE, sec-BUTYLBENZENE

AND tert-BUTYLBENZENE

By C. M. Buess, J. V. Karabinos
P. V. Kunz, and L. C. Gibbons

SUMMARY

The syntheses of isobutylbenzene, sec-butylbenzene, and tert-butylbenzene in 11-gallon quantities are described. The sec-butylbenzene was prepared by reacting sec-butyl alcohol with benzene in the presence of aluminum chloride and anhydrous hydrogen chloride. The tert-butylbenzene was prepared in a similar manner without the use of hydrogen chloride. The preparation of isobutylbenzene involved the reaction of phenylmagnesium bromide with methallyl chloride to yield 2-methyl-3-phenyl-1-propene, which was partly rearranged to 2-methyl-1-phenyl-1-propene. Both olefins were isolated. The physical properties are tabulated and freezing curves are plotted for the five hydrocarbons.

INTRODUCTION

Isobutylbenzene, sec-butylbenzene, and tert-butylbenzene were synthesized and purified as part of a program involving the evaluation of aromatic hydrocarbons as antiknock components of aviation fuel at the NACA Cleveland laboratory. Each hydrocarbon was prepared and purified in an 11-gallon quantity. The synthesis and purification of n-butylbenzene (reference 1) and 1,2,4-trimethylbenzene (reference 2) have previously been reported from this laboratory.

Several methods for the synthesis of isobutylbenzene have appeared in the literature but much of the work is questionable because tert-butylbenzene is formed when benzene is alkylated with isobutyl alcohol or isobutyl chloride. Isobutylbenzene has been prepared by the Wurtz-Fittig method using either isobutyl bromide (reference 3) or isobutyl iodide (reference 4) with bromobenzene. Similarly, benzyl chloride was condensed with isopropyl iodide in

reference 5. Isobutylbenzene has also been prepared by the hydrogenation of the olefins obtained from the dehydration of the reaction product of benzylmagnesium chloride and acetone (reference 6). Because this method involves three steps, it was decided to investigate the two-step reaction between phenylmagnesium bromide and methallyl chloride and the subsequent hydrogenation of the reaction product.

The alkylation of aromatic hydrocarbons in the presence of various dehydrating agents has been described in many articles. sec-Butylbenzene has been synthesized from benzene and halides, alcohols, ethers, or esters containing active n-butyl or sec-butyl groups. When sec-butyl alcohol was reacted with benzene in the presence of anhydrous aluminum chloride and hydrogen chloride, sec-butylbenzene was prepared in 81-percent yield (reference 7). This method with slight adaptations was found to be suitable for large-scale synthesis.

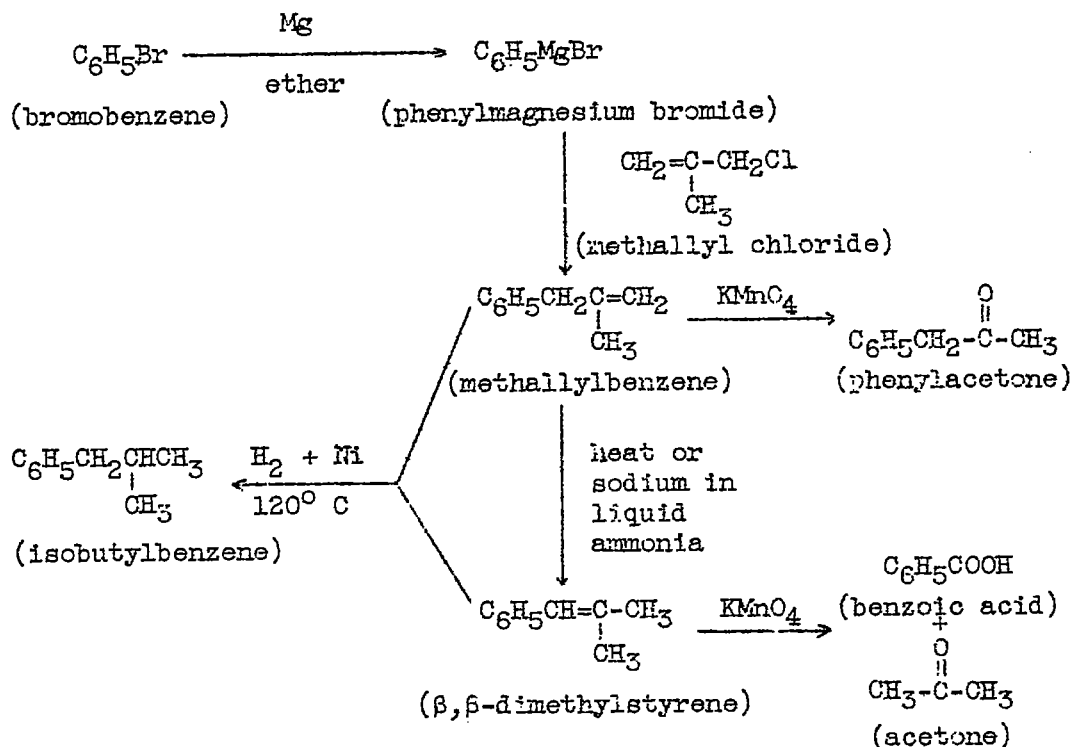
Similarly, tert-butylbenzene has been prepared by many alkylations. The method of reference 8 in which tert-butyl alcohol is condensed with benzene in the presence of anhydrous aluminum chloride in the molar ratio of approximately 1:5:0.5, respectively, was found to be very satisfactory.

DISCUSSION OF SYNTHESSES

The procedure described herein for the preparation of isobutylbenzene involves the preparation of methallylbenzene (2-methyl-3-phenyl-1-propene) from phenylmagnesium bromide and methallyl chloride. It was noted, however, that either on distillation of the reaction product at atmospheric pressure or on treatment with small amounts of sodium in liquid ammonia to remove the last traces of halogen, varying quantities of β,β -dimethylstyrene (2-methyl-1-phenyl-1-propene) were obtained. Both olefins were purified by fractional distillation under vacuum and their constants are recorded in table I. The structures of these olefins prepared by the rearrangement of neophyl chloride (1-chloro-2-methyl-2-phenylpropane) has been previously established in reference 9. Ozonolysis of methallylbenzene gave phenylacetone and formaldehyde, and the same procedure applied to β,β -dimethylstyrene resulted in the formation of benzaldehyde and acetone. These observations have been confirmed by the isolation of phenylacetone from methallylbenzene and of benzoic acid and acetone from β,β -dimethylstyrene by permanganate oxidation.

The last traces of halogen were removed from the olefins by azeotropic distillation with cyclohexanol or by treatment with sodium in liquid ammonia. After the removal of halogen, the olefins were readily hydrogenated in the presence of U.O.P. nickel catalyst.

The reactions are illustrated as follows:



When benzene is alkylated with *n*-butyl alcohol or *sec*-butyl alcohol, *sec*-butylbenzene is produced. Because *sec*-butyl alcohol gave good yields, the reaction with *n*-butyl alcohol was not investigated. The yield of the monosubstituted product is quite sensitive to the molar ratio between alcohol and aluminum chloride and the ratio shown in the experimental details gives nearly the maximum yield of *sec*-butylbenzene. A small amount of di-*sec*-butylbenzene was also obtained; the boiling point of this material was 235° C 760 mm and the refractive index n_D^{20} was 1.487.

The use of ferric chloride as well as aluminum chloride in the preparation of *tert*-butylbenzene was investigated with good results; because the amount of ferric chloride required for a comparable yield is nearly twice the amount of aluminum chloride needed, aluminum

chloride was used exclusively in the large-scale preparation. A small amount of p-di-tert-butylbenzene was also obtained under the conditions used; the melting point of this substance was 77.5°-78.0° C.

Because the density and refractive index of isobutylbenzene and sec-butylbenzene increased on standing due to oxidation, the physical constants were taken immediately after distillation. The physical constants of all hydrocarbons are shown in table I.

EXPERIMENTAL DETAILS

Isobutylbenzene. - The apparatus used for this synthesis was the same as that described in reference 1. In a 100-gallon reactor 9.74 kilograms (400 moles) of magnesium turnings was covered with 10 gallons of dry ethyl ether. A 2-mole preparation of phenylmagnesium bromide and a 2-kilogram quantity of bromobenzene was added to the mixture to start the reaction. After the initial reaction subsided, reflux was maintained by the addition of 60.5 kilograms (a total of 400 moles) of bromobenzene dissolved in 10 gallons of ether. A 36.5-kilogram quantity of methallyl chloride dissolved in 10 gallons of ether was added in a period of 8 hours; the mixture became quite pasty. It was then hydrolyzed by the slow addition of 35 gallons of 10-percent hydrochloric acid. The acid layer was drawn off and the ether-hydrocarbon layer was washed successively with water, 5-percent sodium bicarbonate solution, and finally water. After the ether was distilled from the reaction mixture, about 15 gallons of crude product remained, 6 gallons of which was distilled with 1 gallon of ethanol and 1 gallon of cyclohexanol in a fractionating column of approximately 40 theoretical plates. The last traces of halogen came off in the cyclohexanol fractions; a mixture of methallylbenzene and β,β -dimethylstyrene was obtained. A sample of methallylbenzene (n_D^{20} 1.5083) was purified by fractional distillation in a glass-helix packed column at reduced pressure. The physical constants are recorded in table I and a freezing curve is shown in figure 1.

Although part of the halogen was removed by heating with sodium hydroxide in ethanol, it was necessary to remove the last traces with sodium in liquid ammonia or by azeotropic distillation. A 1-gallon sample of the hydrocarbon mixture was placed in a 12-liter, three-necked flask, fitted with a Dry-Ice-acetone condenser and stirrer, and 4 liters of anhydrous ammonia was added followed by thinly sliced sodium metal until a Beilstein test for halogen was negative on a small hydrolyzed sample. Then 2 liters of water was slowly added until all the sodium had reacted and the aqueous ammonia layer was discarded. The hydrocarbon layer was washed with dilute hydrochloric acid, sodium bicarbonate solution, and water and dried

by passing it through a column of activated alumina at room temperature. The refractive index n_D^{20} of the 1-gallon sample was raised from 1.510 to 1.535 by this treatment, which indicates partial isomerization to β,β -dimethylstyrene.

A 2-liter sample of the hydrocarbon mixture treated with sodium and liquid ammonia was then distilled at reduced pressure and about 80 percent of this material distilled at 69.0°C at 12 mm and had a refractive index n_D^{20} varying from 1.5400 to 1.5406. A freezing curve (fig. 2) indicated high purity of the sample having a refractive index n_D^{20} of 1.5406. The total yield of the olefins varied from 45 to 53 percent.

Oxidation of 13.2 grams of the olefin with a refractive index n_D^{20} of 1.5406 with 31.6 grams of potassium permanganate in 150 cc of water resulted in a 74-percent yield of benzoic acid with a melting point of 122°C . The mixed melting point with an authentic sample of benzoic acid was unchanged. Acetone was recovered as the 2,4-dinitrophenylhydrazone in a 16-percent yield with a melting point of $123^\circ\text{-}124^\circ\text{C}$ after one recrystallization from alcohol. These data agree well with those in reference 10 and indicate that the olefin is β,β -dimethylstyrene.

Oxidation of a 2-gram sample of the olefin with a refractive index n_D^{20} of 1.5083 with 4 grams of potassium permanganate in a 50-percent aqueous acetone solution yielded an oil (1.0 gram; refractive index, n_D^{20} 1.515). After recrystallization from aqueous alcohol it gave a semicarbazone with a melting point of $186^\circ\text{-}187^\circ\text{C}$. The melting point of the semicarbazone of phenylacetone is reported as $186^\circ\text{-}187^\circ\text{C}$ in reference 7 indicating that the olefin is methallylbenzene.

The hydrogenations were conducted in the manner described in reference 1. In a typical run, 12.9 kilograms of a mixture of the olefins containing 5 percent by weight of U.O.P. nickel hydrogenation catalyst were hydrogenated at $120^\circ\text{-}140^\circ\text{C}$ until no more hydrogen was consumed. The benzene ring was hydrogenated at 170°C . The hydrogenated material was then subjected to careful fractionation in a column of approximately 100 theoretical plates; pure isobutylbenzene was obtained. The yield from the hydrogenation was nearly quantitative. The physical constants are listed in table I and the freezing curve is shown in figure 3.

sec-Butylbenzene. - A 35-kilogram quantity of benzene was placed in a 30-gallon glass-lined reactor equipped with separatory funnel, gas inlet tube, agitator, thermocouple, water-cooled jacket, condenser, and aspirator. The anhydrous aluminum chloride (6.17 kg) was added to the benzene, and hydrogen chloride gas was bubbled through the suspension for 30 minutes with stirring. A 5.7-kilogram quantity of benzene was mixed with 5.06 kilograms of sec-butyl alcohol and this solution was slowly added through the separatory funnel. As soon as the reaction became vigorous, the reacting mixture was cooled to 13° C by running cold water through the jacket. The alcohol solution was completely added in 3 hours after which the mixture was stirred for 10 hours and then allowed to stand over night. Dilute hydrochloric acid was added until the aluminum hydroxide from the benzene complex was completely dissolved. The hydrocarbon layer was then washed once with 5-percent sodium bicarbonate solution and twice with water. The layer was dried by passing it through an activated alumina tower and the sec-butylbenzene was fractionated in a 70 theoretical-plate column. An 80.2-percent theoretical yield (based on sec-butyl alcohol) was obtained. The best sample was obtained by refractionation. The freezing curve on sec-butylbenzene could not be brought to thermodynamic equilibrium despite repeated attempts. A melting curve as well as the freezing curve is therefore shown in figure 4.

tert-Butylbenzene. - The tert-butylbenzene was prepared in a reactor similar to that used for sec-butylbenzene. The aluminum chloride (8.46 kg) was covered with 31.8 kilograms of dry benzene. A mixture of 7.9 kilograms of benzene and 9.47 kilograms of tert-butyl alcohol was slowly added while the suspension was stirred. After the initial reaction began, as evidenced by the evolution of hydrogen chloride, the mixture was cooled to 17° C during the addition of the remainder of the benzene-alcohol solution. The addition required 4 hours. The mixture was hydrolyzed with 25 liters of water, and hydrochloric acid was added until all the aluminum hydroxide dissolved. The hydrocarbon layer was washed once with water, once with 5-percent sodium bicarbonate solution, and twice more with water. The hydrocarbon layer was then dried by passing it through an activated alumina tower, and after the benzene had been distilled the tert-butylbenzene was fractionated. The yield of tert-butylbenzene was 69 percent of the theoretical yield. The physical constants are shown in table I and the freezing curve is shown in figure 5. The properties of n-butylbenzene (reference 1) are included for purposes of comparison.

Aircraft Engine Research Laboratory,
National Advisory Committee for Aeronautics,
Cleveland, Ohio, January 2, 1946.

REFERENCES

1. Karabinos, J. V., and Lamberti, J. M.: The Synthesis and Purification of Aromatic Hydrocarbons. I - Butylbenzene. NACA TN No. 1019, 1946.
2. Ebersole, E. R.: The Synthesis and Purification of Aromatic Hydrocarbons. II - 1,2,4-Trimethylbenzene. NACA TN No. 1020, 1946.
3. Riess, Joh.: Ueber das Isobutylbenzol und Isobutylanisol. Berichte d. D. Chem. Gesellschaft, Bd. 3, Juli 25, 1870, Art. 221, pp. 779-782.
4. Wreden, F.: Die V. Versammlung russischer Naturforscher und Aertze in Warschau 31. Aug. - 9. Sept. 1876. Berichte 12. Sept. 21. d. D. Chem. Gesellschaft, Bd. 9, Art. 431, Okt. 23, 1876 pp. 1598-1607.
5. Köhler, H., and Aronheim, B.: Ueber eine neue Synthese des Phenylisobutans. Berichte d. D. Chem. Gesellschaft, Bd. 8, Art. 140, April 12, 1875, p. 509.
6. Brown, Weldon G., Mighton, Charles J., and Senkus, Murray: The Raman Spectra of Some Hydrocarbons Containing Tertiary C-D Linkages. Jour. Org. Chem., vol. 3, no. 1, March 1938, pp. 62-75.
7. Huston, R. C., and Kaye, I. A.: The Condensation of Some Secondary Aliphatic Alcohols with Benzene in the Presence of Aluminum Chloride. Jour. Am. Chem. Soc., vol. 64, no. 7, July 1942, pp. 1576-1580.
8. Huston, R. C., Fox, W. B., and Binder, M. N.: Condensation of Aliphatic Alcohols with Aromatic Compounds in the Presence of Aluminum Chloride. II. Tertiary Aliphatic Alcohols and Benzene. Jour. Org. Chem., vol. 3, no. 3, July 1938, pp. 251-260.
9. Whitmore, Frank C., Weisgerber, Cyrus A., and Shabica, A. C., Jr.: Formation of Cyclopropanes from Monohalides. IV. Some Reactions of 1-Chloro-2-methyl-2-phenylpropane (Neophyl Chloride). Jour. Am. Chem. Soc., vol. 65, no. 8, Aug. 1943, pp. 1469-1471.
10. Shriner, Ralph L., and Fuson, Reynold C.: The Systematic Identification of Organic Compounds. John Wiley & Sons, Inc., 1940, 2d ed., pp. 183, 221.

TABLE I - PHYSICAL CONSTANTS

Hydrocarbon	Source of constants	Freezing point (°C)	Boiling point at 760 mm (°C)	Index of refraction n_D^{20}	Density at 20° C (gram/ml)
2-Methyl-3-phenyl-1-propene	Cleveland laboratory	-33.96	175.8	1.5083	0.8821
2-Methyl-1-phenyl-1-propene	-----do-----	-50.60	187.7	1.5406	.9050
<u>n</u> -Butylbenzene	Referencel	-87.97	183.3	1.4899	.8601
Isobutylbenzene	Cleveland laboratory	-51.61	172.7	1.4862	.8525
<u>sec</u> -Butylbenzene	-----do-----	-75.68	173.4	1.4901	.8618
<u>tert</u> -Butylbenzene	-----do-----	-57.87	169.2	1.4925	.8662

National Advisory Committee
for Aeronautics

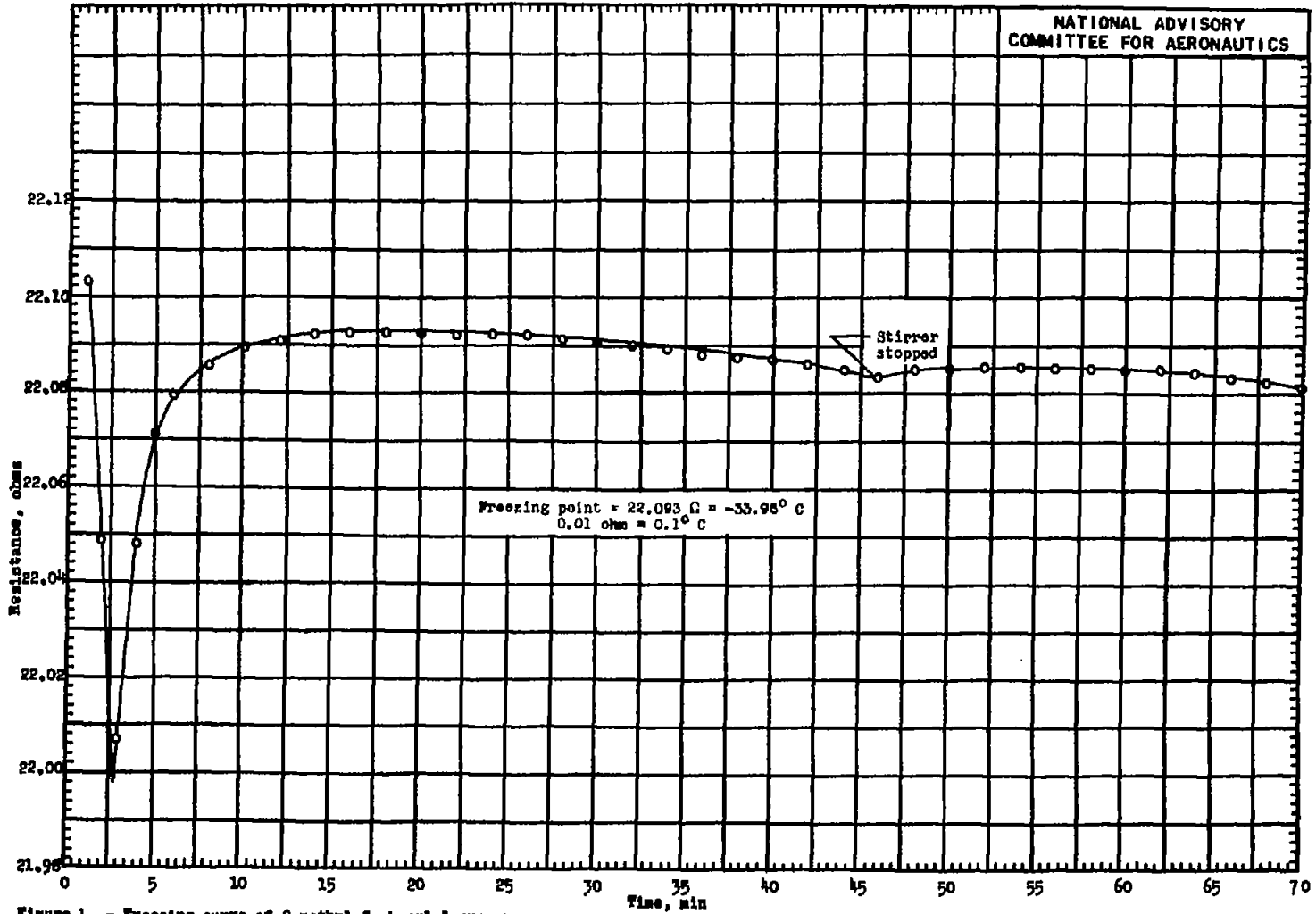


Figure 1. - Freezing curves of 2-methyl-3-phenyl-1-propene.

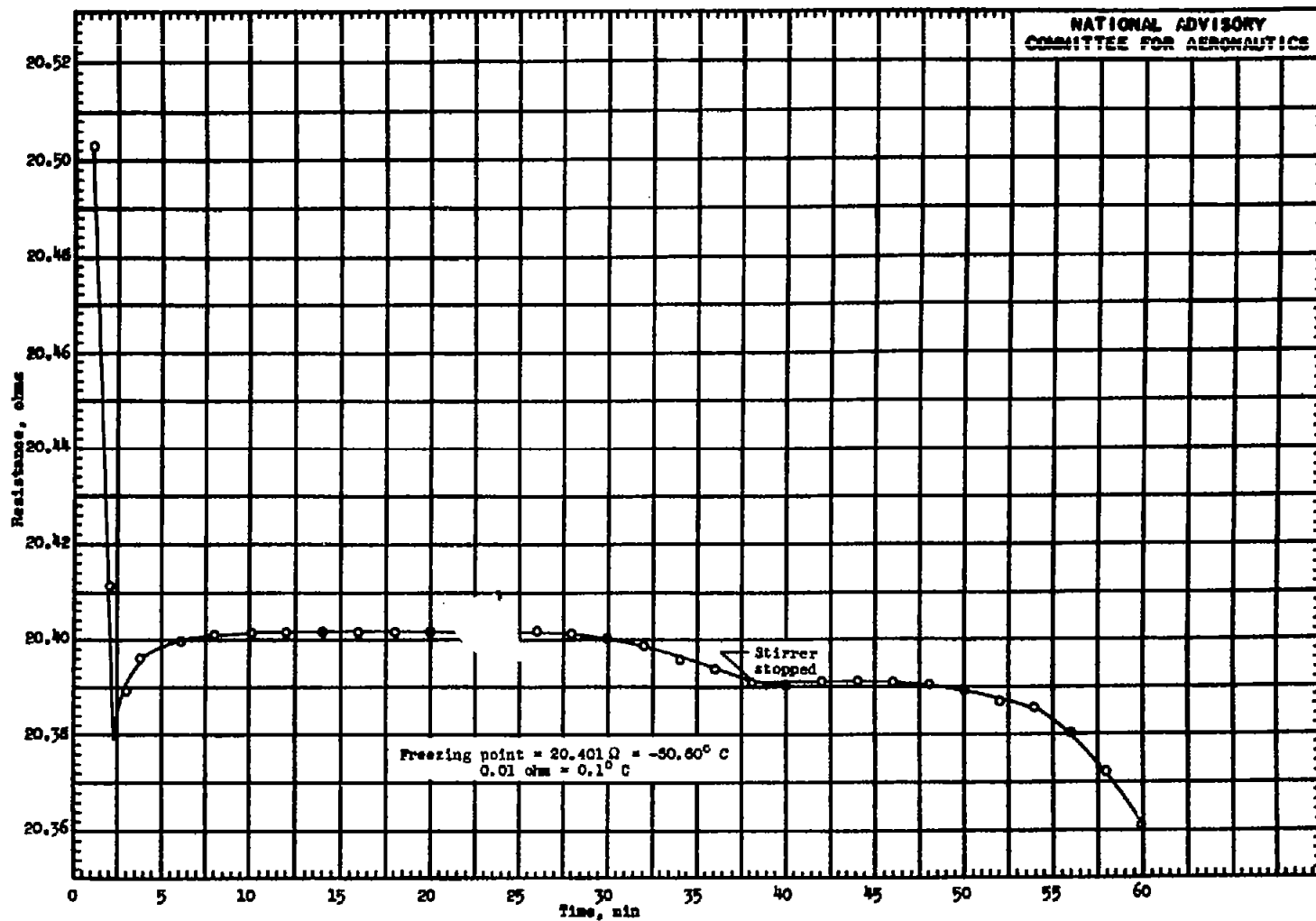


Figure 2. - Freezing curve of 2-methyl-1-phenyl-1-propene.

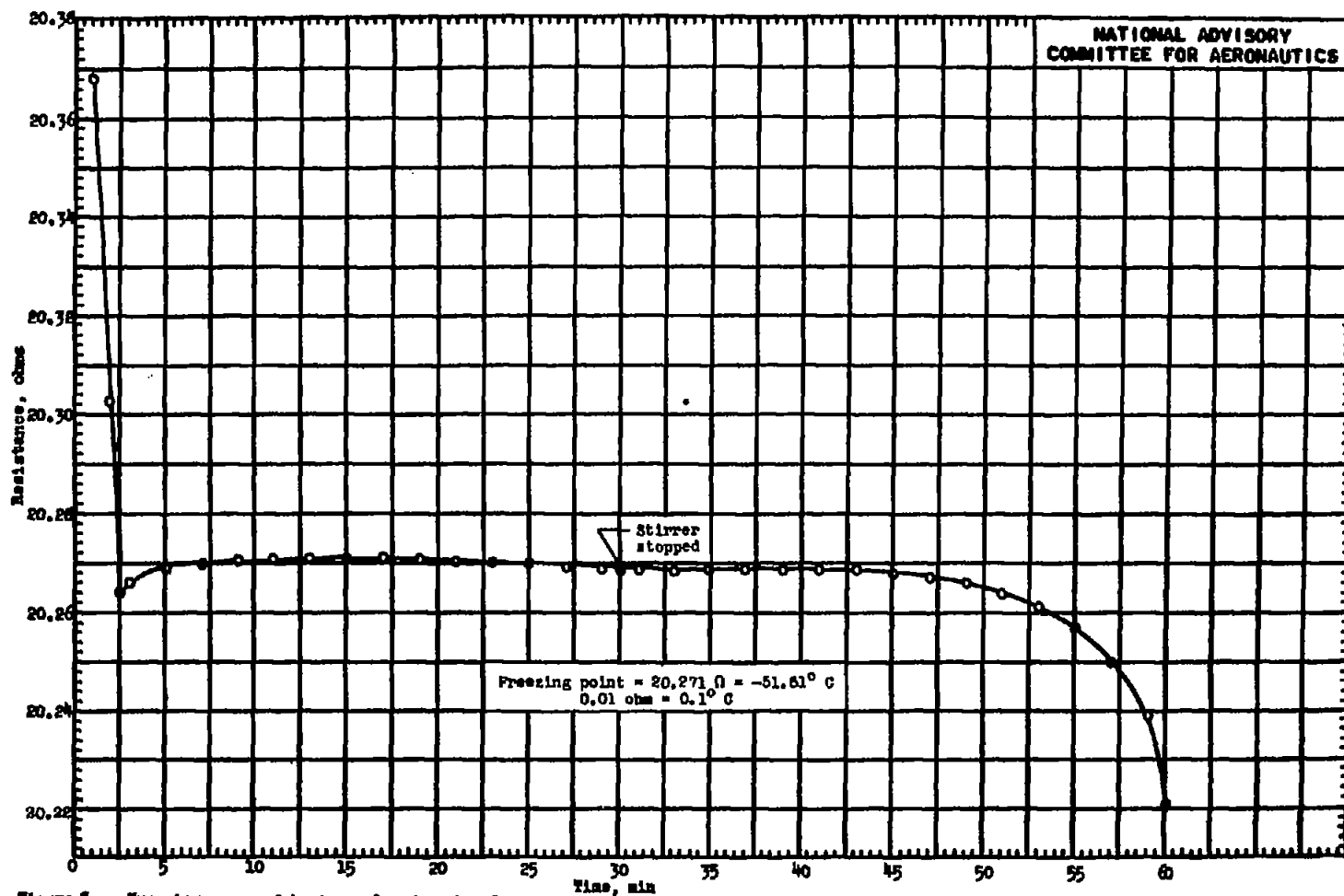


Figure 3. - Freezing curve of best sample of isobutylbenzene.

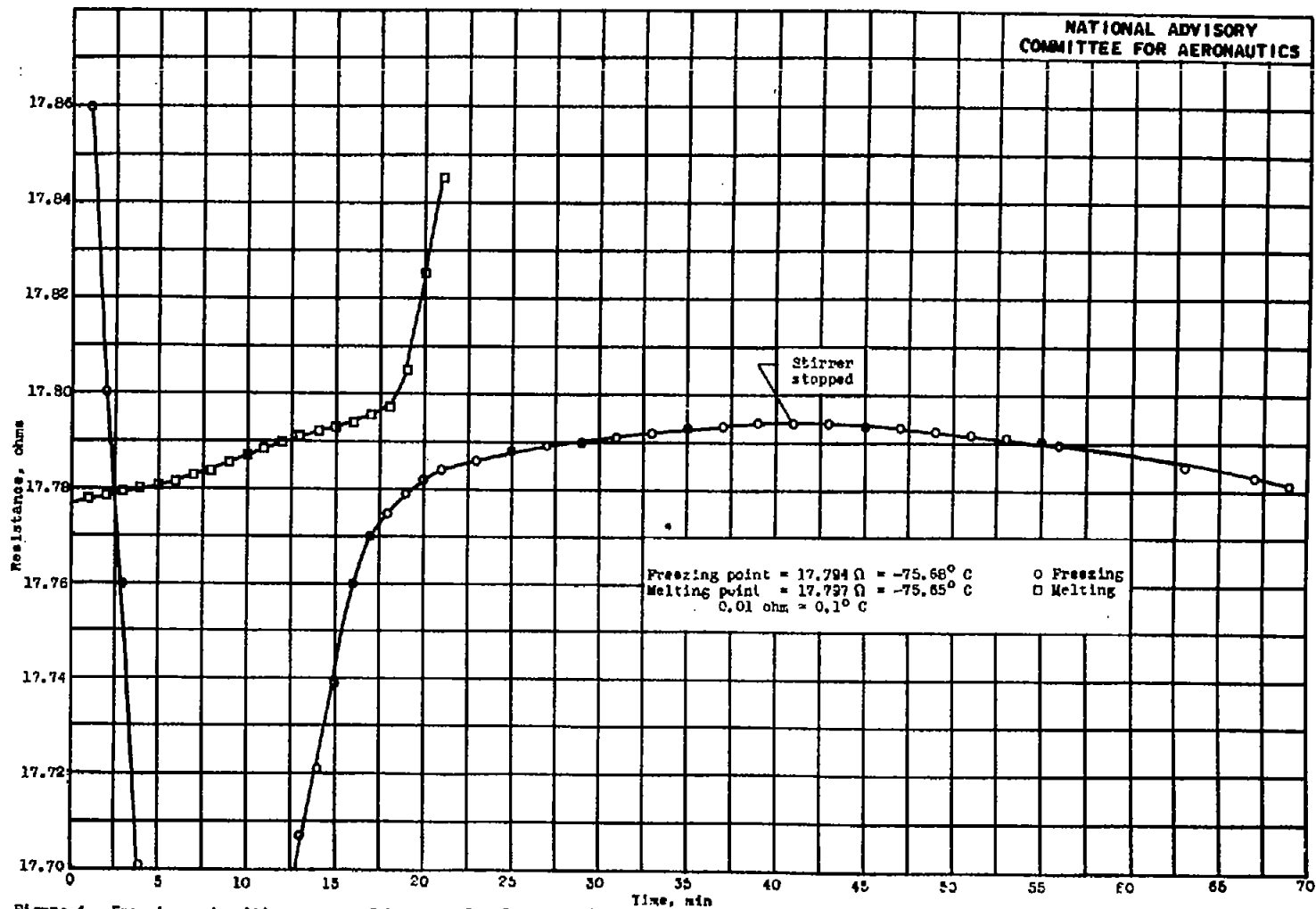
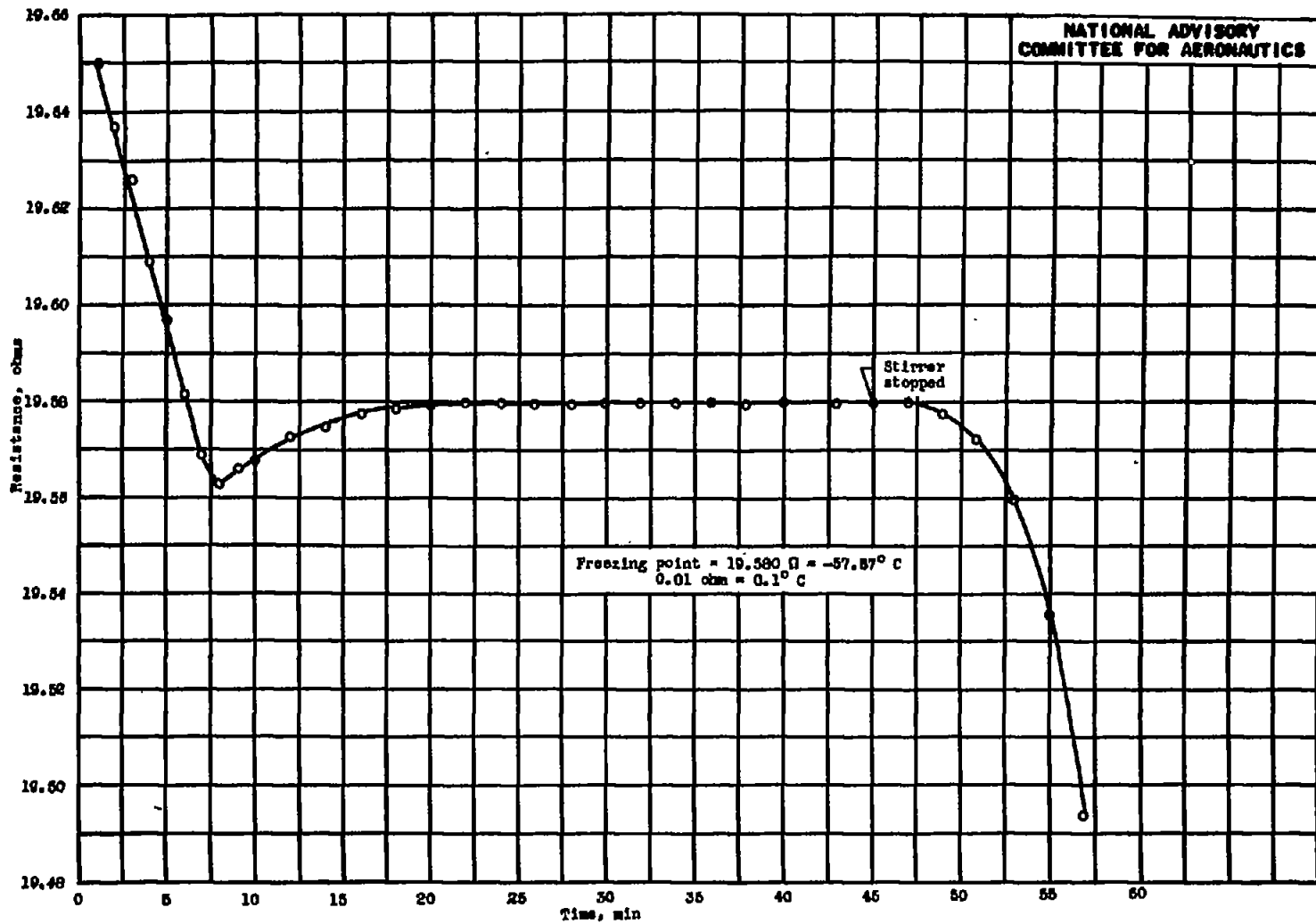


Figure 4.- Freezing and melting curves of best sample of sec-butylbenzene.

Figure 5.-Freezing curve of best sample of tert-butylbenzene.