Summary

1. Methyl cyano-acetate can be added without difficulty to dimethyl glutaconate. The mode of addition is the same as that to any other α,β-unsaturated ester.

2. There is no appreciable difference in the ease with which cyano-acetic ester combines with the esters of the "normal" and labile forms of β-methylglutaconic acid; the addition product from both esters is the same, and the mode of addition is that of α,β-unsaturated esters.

3. The addition reactions of glutaconic acids cannot be properly used to support the view that the "normal" forms of these acids cannot be represented by conventional formulas.

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THE INFRA-RED ABSORPTION SPECTRUM OF MOLTEN NAPHTHALENE

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Introduction

In view of a proposed study of the infra-red absorption spectra of the naphthylamines and alkyl naphthylamines it seems particularly desirable that information concerning the absorption spectrum of naphthalene in this region be available.

Coblentz,[1] taking advantage of the high solubility of naphthalene in carbon tetrachloride, studied the absorption of the saturated solution between 2.0 and 5.0μ and found that the 3.25μ band of benzene was present, indicating that the vibration of the benzene nucleus in that region had not been disturbed by the naphthalene structure.

Stang[2] measured the absorption of solutions of naphthalene and several of its alpha and beta mono-derivatives in both carbon tetrachloride and carbon disulfide. These measurements extended from 2.7 to 10.0μ.

In studying the absorption of solid substances in the infra-red region two methods of procedure have been employed. Either a film of the solid substance or a solution of the solid in a suitable solvent may be used. In either case the absorption curves obtained leave much to be desired and this becomes at once apparent when such curves are compared with those obtained with pure liquids.

With solid films there is a considerable loss of energy due to scattering of light which, in effect, greatly reduces the resolving power of the optical

[1] Coblentz, *Carnegie Inst. Publ.*, **35**, 127 (1905).

[2] Stang, *Phys. Rev.*, **9**, 542 (1917).

system employed. Furthermore, such films are difficult to reproduce and the author's attempts to check such curves have been largely unsatisfactory.

The absorption curves of solids in solution also give a general impression of reduced resolution which depends, to a large extent, on the concentration of the solution. Carbon tetrachloride and carbon disulfide, by virtue of their unusual transparency to infra-red radiation, are the only liquids available for general use as solvents and their use is at once restricted to the relatively small number of organic compounds which are readily soluble in these liquids.

Perhaps the most serious complication in studying such solutions is the possible influence of the solvent on the absorption of the solute. Thus, Stang[3] found the benzene band at 3.25μ using a naphthalene solution in carbon tetrachloride. Using carbon disulfide as the solvent, this band appeared at 3.3μ. He attributes this shifting, which is well beyond the limit of his experimental error, to the influence of the solvent.

It occurred to the author that the field of infra-red spectroscopic investigation might be considerably extended by studying the absorption of solids in the molten state, in which case absorption curves could be obtained with the same degree of accuracy and reproducibility that is possible with substances which are liquids at ordinary temperatures. Regardless of the possible influence of temperature on infra-red absorption, such a procedure would at least furnish standardized and detailed data on a large number of substances hitherto uninvestigated.

It is the purpose of this paper to describe a very simple electrical device by means of which solid substances may be studied in the molten state. The absorption curve of molten naphthalene as obtained by means of this device will be discussed and directly compared with that of benzene, which has also been measured.

Experimental Part

Two similar pieces of 4.5 mm. ($^3/_{16}$ inch) Transite asbestos board, 5 cm. long and 2.5 cm. wide, as shown at A in Fig. 1, are drilled out at their centers yielding openings 4.5 × 12.5 mm. Along the long edge of each piece, holes of suitable size and at intervals of 3 mm. are drilled parallel to the short edges. These drillings are indicated by the horizontal dotted lines at A and the face of the long edge is shown at B. Resistance wire of the proper size is now woven back and forth through these drilled holes. The wire is started at the top of one piece of the Transite and, coming out at the bottom of this piece, it is continued directly to the bottom of the other piece. The two leads of this resistance unit appear at the top, one from the top of each piece.

The absorption cell is clamped between these two pieces so that the central openings of the latter, which permit the light to pass through the absorption cell, and the absorption chamber of the cell are in alignment. This heating unit, in series with a variable resistance, is connected with the lighting circuit.

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[3] Ref. 2, p. 546.

The temperature curve of the heating unit was obtained as follows. A hole having a depth and diameter sufficient to enclose the mercury bulb of a small thermometer was drilled into a rock-salt plate, somewhat thicker than the absorption cell, as shown at C in Fig. 1. This plate was clamped in the heating unit in the same position that was occupied by the absorption cell during a measurement. After the thermometer bulb had been inserted in the opening and with a definite setting of the variable resistance, the current was turned on and the temperature indicated by the thermometer was recorded at intervals. This procedure was repeated for a series of different resistance settings. In each case, the temperature reached a maximum value and remained constant within 5° over a period of some hours.

Concerning the adequacy of this temperature calibration, it will be sufficient to note that Coblentz[4] was unable to detect any effect on the absorption due to a temperature rise of 20°. In Coblentz' experimental method it was desirable to have the light source close to the absorption cell, resulting in a considerable temperature rise of the latter. In this way he was able to study several low-melting solids in the molten state, for example, thymol, phenol and menthol and he points out that it was thus possible to examine these compounds "which as solids would have been too opaque because of their scattering effect."

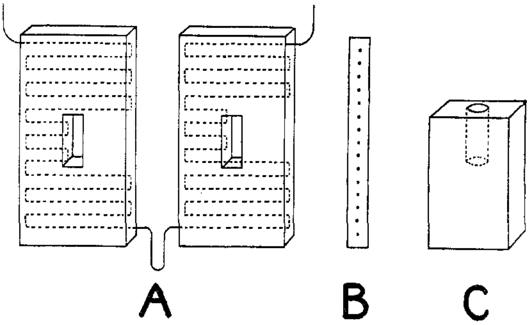

Fig. 1.

The absorption spectra of a large number of solid compounds have been determined in the molten state by means of this heating device and, although the highest temperature required was 175°, it is believed that the upper practicable limit is considerably beyond this temperature.

In general, the temperature employed was at least 10° above the melting point of the substance under examination in order to preclude the possibility of any temporary crystallization due to temperature variation. For example, in working with naphthalene, which melts at 80°, the temperature was maintained at 95°.

All other details concerning the experimental method and procedure in the determination of infra-red absorption spectra have been fully given in a previous communication.[5]

The specimen of naphthalene which was examined in the present study was imported and was designated "Zu Molekulargewichtsbestimmung." The specimen of benzene was likewise imported and was labeled "Aus Benzoesäure."

The absorption curves of these two substances are shown in Fig. 2. As is customary, wave lengths in microns have been plotted as abscissas

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[4] Ref. 1, p. 106.

[5] Bell, This Journal, 47, 2194 (1925).

against the percentages of transmission as ordinates. The cell used for naphthalene gave a layer thickness of 0.20 mm. and the temperature was 95°. The benzene layer had a thickness of 0.25 mm. and the examination was, of course, carried out at room temperature.

Discussion

The absorption of benzene has been previously determined by Coblentz[6] in the region from 1.0 to 15.0μ, and a comparison of his curve with that shown in Fig. 2 reveals a very satisfactory agreement. The resolving power of the optical system employed in the present investigation is somewhat higher than that obtained by Coblentz with his smaller spectroscope which he used in the case of benzene, so that it is not surprising that several absorption bands have been resolved which Coblentz' curve does not show.

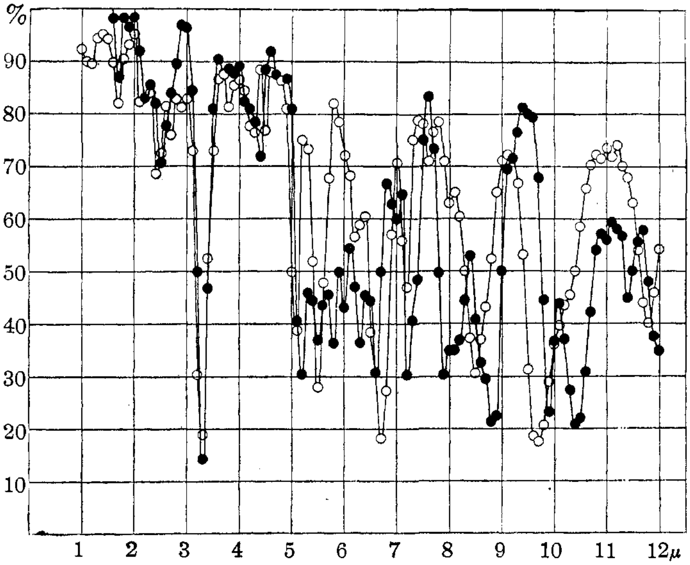

Fig. 2.—Circles, benzene; T = 0.25 mm. Dots, naphthalene; T = 0.20 mm. Temperature, 95°.

The present benzene curve shows a rather complex structure in the shorter wave lengths as far as 5.0μ. The band obtained by Coblentz in the region of 5.3μ has been resolved into two sharp bands at 5.1 and 5.5μ. The shallow band at 6.2μ was resolved by him in the examination of a thin layer of benzene and he has pointed out the particular significance of this shallow band in that it appears very strongly in certain benzene derivatives.[7]

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[6] Ref. 1, p. 76.

[7] This is shown very clearly in the present author's curves of the anilines, Ref. 5, p. 2201 and following.

The curve for molten naphthalene at 95°, which is also shown in Fig. 2, agrees favorably with those obtained by Stang using carbon tetrachloride and carbon disulfide solutions. As might be expected, many of the finer details of the structure of the absorption curve are missing from Stang's results.

A comparison of the benzene and naphthalene curves reveals a striking similarity in the general transparency of these two substances to infra-red radiation, particularly when it is remembered that the naphthalene layer had a thickness of 0.20 mm. and that of the benzene was 0.25 mm.

The coincidence of the deep benzene band at 3.3μ with a correspondingly deep band in naphthalene confirms the results obtained by Stang and by Coblentz, both of whom used a carbon tetrachloride solution.

The absorption curves of benzene and naphthalene show a marked similarity in the region of the shorter wave lengths as far as 5.5μ. A shallow but well-defined band appears in both curves at 1.7μ as well as in the regions of 2.2 and 2.5μ. As has been previously noted, the characteristic benzene band has been found at 3.3μ in both compounds. There is an indication of the 3.8μ band of benzene at 3.9μ in naphthalene. The 4.25μ band of benzene is apparently present but has not been resolved in the naphthalene curve. The 5.1μ band of benzene appears at 5.2μ in naphthalene and both substances have a band at 5.5μ.

The 6.25μ band of benzene appears at 6.3μ in naphthalene and is considerably deeper in the latter compound, which is in accord with Coblentz' observation previously mentioned. Aside from the coincidence of the 7.2μ band in both substances there is a decided dissimilarity beyond 5.5μ, which becomes more pronounced as the longer wave lengths are approached.

It can hardly be regarded as surprising that the 3.25μ band of benzene which has been identified in numerous benzene derivatives of more or less complex structure occurs also in naphthalene since, according to the conception of the structure of naphthalene, it may be regarded as resulting from an *ortho* disubstitution of benzene. That this disubstituent happens to be a benzene ring would rather lead one to predict a greater similarity between the infra-red absorption of benzene and naphthalene than between that of benzene and other types of *ortho* disubstituted derivatives of benzene. It is believed that the curves obtained for benzene and naphthalene are in accord with this suggestion.

Summary

1. A simple electrical heating device for the examination of the infra-red absorption of solids in the molten state has been described.

2. By means of this device the infra-red absorption spectrum of molten naphthalene at 95° has been determined as far as 12.0μ. The absorption spectrum of benzene has also been examined in the same region.

3. A comparison of these absorption spectra reveals a pronounced similarity in the region of the shorter wave lengths as far as 5.5μ and beyond this point shows increasing dissimilarity as the longer wave lengths are approached.

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THE REACTION BETWEEN ORGANIC PEROXIDES AND ORGANOMAGNESIUM HALIDES

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In connection with studies on the relationship between chemical constitution and antiseptic action, an investigation has been made of the reaction between some typical organic peroxides and the Grignard reagent. Reaction does not take place with every peroxide, and the rate of reaction varies appreciably with different peroxides. The following is a general expression of the course of reaction.

$$\mathrm{ROOR} + \mathrm{R'MgX} \longrightarrow \mathrm{ROR'} + \mathrm{ROMgX} \qquad (1)$$

Wuyts[1] has reported an analogous reaction between disulfides and the Grignard reagent. Studies have been made on the reaction between hydrogen peroxide and organomagnesium halides. Oddo[2] obtained a variety of alcohols from the reaction between a concentrated hydrogen peroxide solution in water and alkylmagnesium halides. Durand and Naves[3] obtained an 80% yield of phenylhydroxylamine from the reaction between bromomagnesium aniline ($C_6H_5NHMgBr$) and hydrogen peroxide. Inorganic peroxides with phenylmagnesium bromide give phenol in a yield smaller than that obtained from dry oxygen.[4]

With equivalent molecular quantities of dibenzoyl peroxide and RMgX compound the splitting reaction represented in (1) takes place. When an excess of Grignard reagent is used the phenyl benzoate that is first formed undergoes the normal reaction of esters and RMgX compounds and a tertiary alcohol[5] is formed, namely, triphenyl carbinol. Gelissen and Hermans[6] found recently that a small amount of phenyl benzoate

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[1] Wuyts [*Bull. soc. chim.*, **35**, 166 (1906)] predicted a like reaction with diselenides and also probably with peroxides.

[2] Oddo and Binaghi, *Gazz. chim. ital.*, [II] **51**, 343 (1921); **54**, 193 (1924); *C. A.*, **18**, 3166 (1924).

[3] Durand and Naves, *Compt. rend.*, **180**, 521 (1925).

[4] Unpublished results of work by Agnes Wood.

[5] Although good yields of tertiary alcohols are obtainable, the reaction merits little consideration from a synthetic viewpoint. Unpublished results show that acid chlorides, from which peroxides are prepared either directly or indirectly, give better yields of tertiary alcohols when treated with RMgX compounds.

[6] Gelissen and Hermans, *Ber.*, **58**, 285 (1925).