taking the same readings on the right-hand capillary and making the same calculations as when the condensable vapor is absent.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE JOHNS HOPKINS UNIVERSITY]

THE INFRA-RED ABSORPTION SPECTRA OF ORGANIC CARBONATES[1]

BY FREDERICK K. BELL[2]

RECEIVED AUGUST 1, 1928 PUBLISHED NOVEMBER 6, 1928

Introduction

There are few instances in which an acid, the metallic salts of which are available in large crystals, also yields a series of well-defined organic salts or esters. These conditions are fulfilled, at least partially, by carbonic acid. A number of inorganic carbonates are found in nature in crystals of sufficient size to permit cutting, polishing, etc., for optical examination. Similarly a considerable number of esters of carbonic acid have been prepared and are described in the literature.

In a rather recent paper Schaefer and his co-workers[3] have measured the infra-red absorption spectra between 1.0 and 17.0μ of six inorganic carbonates: $MgCO_3$, $CaCO_3$, $CaMg(CO_3)_2$, $FeCO_3$, $BaCO_3$ and $PbCO_3$. In view of this work it seemed to the present author that a similar examination of a series of organic carbonates would yield results of particular significance and interest. The absorption spectra of such a series of compounds might be expected to offer also further information concerning the $C{=}O$ bond, which is surely among the most common linkages of organic compounds. The organic carbonates also represent one of the numerous series of compounds of organic chemistry which are especially suited for spectroscopic study of a systematic nature, one part of the molecule remaining unchanged as different hydrocarbon residues are introduced.

It is with these ideas in mind that the infra-red absorption spectra of seven organic carbonates have been examined between 1.0 and 12.0μ. The results of these examinations are presented and discussed in this paper.

Experimental

A detailed description of the experimental method employed in the present work has been given elsewhere.[4] The preparation of the absorption cells, however, has been altered. All cells were prepared from polished plates of rock salt.

[1] In memory of Ira Remsen.

[2] Grafflin Scholar.

[3] Schaefer, Bormuth and Matossi, *Z. Physik*, **39**, 648 (1926).

[4] F. K. Bell, THIS JOURNAL, **47**, 2194 (1925).

The cleaved plates were first ground on emery cloth until all irregularities of the cleaved surface had disappeared. The grinding was then continued on a coarsely sanded glass plate (treated with crocus and water) until all of the deep emery scratches were removed. As the next step, the plates were polished on a cotton cloth which was stretched over a suitable plane surface and then treated with crocus and moistened with water. This procedure was repeated using jewelers' rouge instead of the crocus. The final polishing was accomplished in a similar manner using jewellers' rouge and 95% alcohol.

The construction of the absorption cell was carried out as previously described, but it was soon evident that the cement used could not contain much water. Thus, Le Page's glue, which was found to be quite satisfactory for cementing cells of cleaved plates, was entirely useless for present purposes. Similarly, a litharge–glycerol paste was found to contain sufficient water to ruin the polished surfaces. The cement finally used was DuPont Household Cement. The solubility of this material in certain non-aqueous solvents offers an important advantage in that cells may be readily taken apart for cleaning and repolishing without damage to the plates.

Three different cells were used in the study. No cell was used a second time until it had been taken apart, cleaned, repolished and cemented together again. A number of check experiments were made which failed to reveal any measurable variations due to differences in the cells. It therefore appears that this cell error which existed in the author's previous work has been eliminated, at least in relation to the other sources of error in the experimental method. The use of polished cells was prompted by a desire to reduce losses in the intensity of the transmitted radiation and to obtain some basis for a closer comparison of the intensity of absorption bands in different compounds. It is believed that the results obtained have entirely justified this point of view.

The carbonates selected for examination are the following: dimethyl, diethyl, dipropyl, dibutyl, di-*iso*butyl, di-*iso*-amyl and diphenyl. All of these substances were obtained from the Eastman Kodak Company and were used as received without any attempt at further purification. Diphenyl carbonate was examined in the molten state at 50°. All of the other carbonates selected, being liquids, were examined in the usual manner at room temperature. The thickness, T, of the absorption cell was 0.025 mm. in each case.

The absorption spectra obtained are shown graphically in Figs. 1 to 7 by means of the customary wave length–percentage transmission curves.

Discussion

The dimethyl ester is the only carbonate of the present study the infrared absorption of which has been previously described in the literature. A comparison of Coblentz'[5] curve for this substance with that shown in Fig. 1 demonstrates clearly the influence of the polished cell. Coblentz, using a cell made from cleaved plates of rock salt, employed a cell thickness of 0.01 mm. and his curve indicates a higher degree of general opacity than the present curve in which the cell thickness is 0.025 mm. In comparing the two curves it should also be noted that there is a difference in the resolving power of the optical systems employed in each case.

All of the compounds examined display a marked uniformity in general transparency as shown in Figs. 1 to 7 and it is to be recalled that one

[5] W. W. Coblentz, *Carnegie Inst. Publ.*, No. 35, **1905**, p. 65.

aryl compound (diphenyl carbonate) is included. The regions between 1.0 and 3.0μ and between 3.6 and 5.0μ are particularly striking in this respect. A considerable increase in the thickness of the absorbing layer is undoubtedly necessary for a closer examination of these two transparent regions.

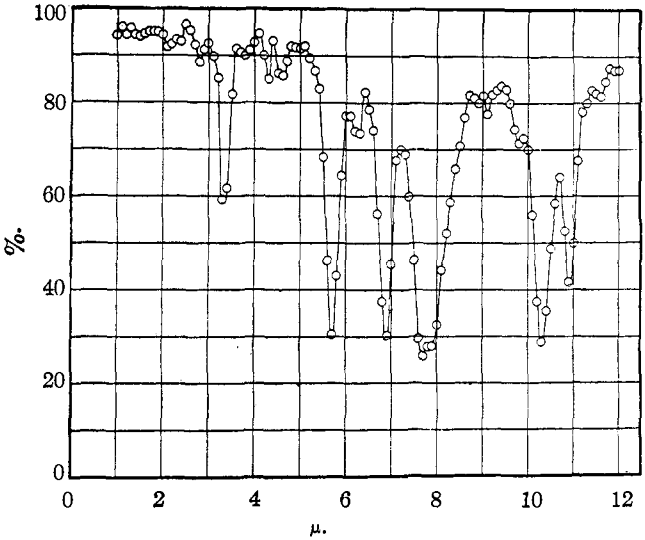

Fig. 1.—Dimethyl carbonate, T = 0.025 mm.

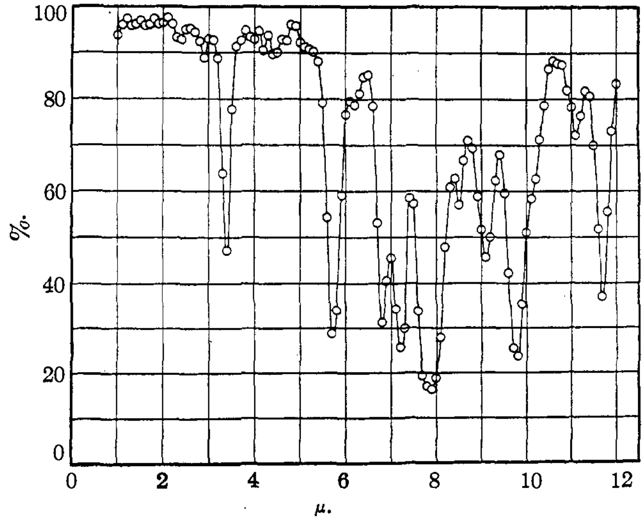

Fig. 2.—Diethyl carbonate, T = 0.025 mm.

In the region between 8.0 and 12.0μ marked differences occur in the absorption to such a degree that no difficulty would be encountered in differentiating between the various carbonates examined. However, between 3.0 and 8.0μ pronounced similarities appear. The C—H band at 3.4μ and bands at 5.7μ and 6.9μ are sharply defined in each curve. A broad region of absorption occurs in each spectrum at 7.8μ and the curve for di-*iso*butyl carbonate (Fig. 5) indicates the presence of two bands in this region. A weak absorption appears in the region of 6.2μ

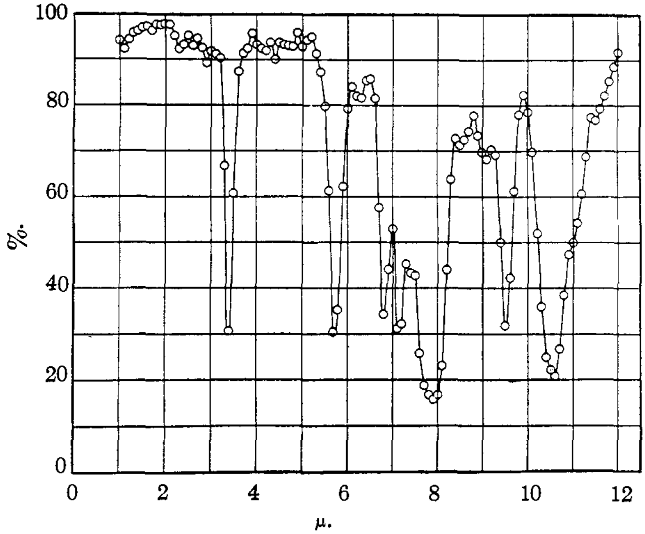

Fig. 3.—Dipropyl carbonate, $T = 0.025$ mm.

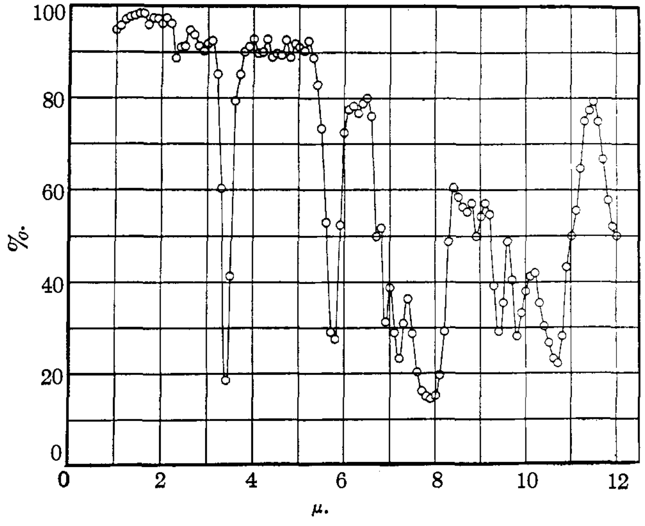

Fig. 4.—Di-*n*-butyl carbonate, $T = 0.025$ mm.

for each of the alkyl carbonates and in interpreting the more marked absorption in diphenyl carbonate (Fig. 7) at that wave length it is to be remembered that benzene derivatives have a characteristic absorption at 6.25μ.

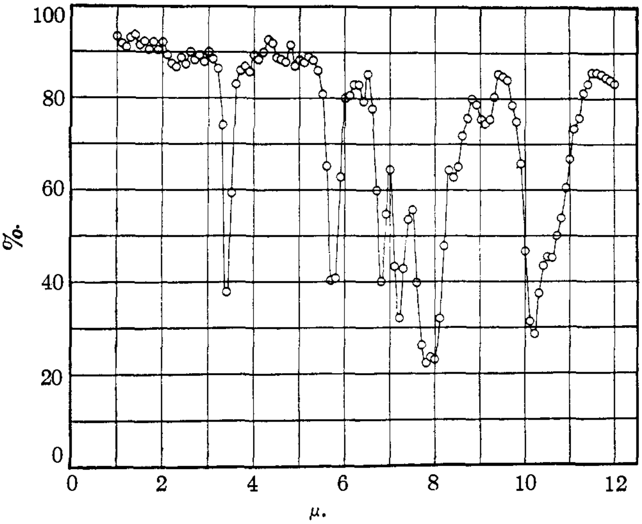

Fig. 5.—Di-*iso*butyl carbonate, $T = 0.025$ mm.

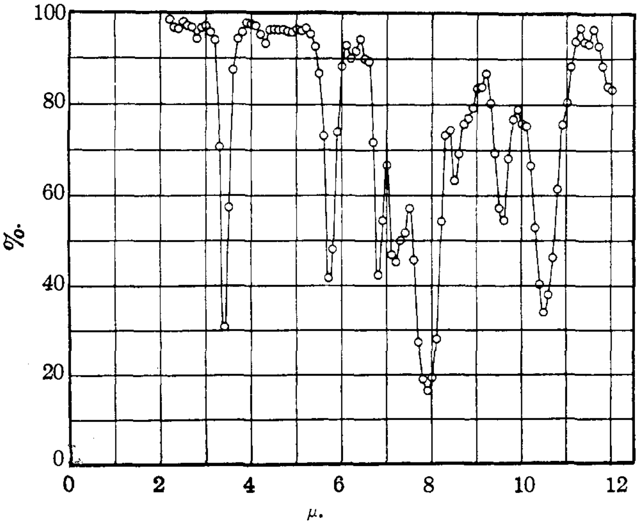

Fig. 6.—Di-*iso*-amyl carbonate, $T = 0.025$ mm.

Another region of interest is located at 7.2μ. In dimethyl carbonate (Fig. 1) no characteristic absorption occurs at that point, the transmission passing through a maximum; while in each of the other curves a well-defined minimum appears. This band, the location of which approximates that of the fourth member (at 7.0μ) of Ellis'[6] band series for the C—C linkage, may be regarded as characteristic of the C—C bond.

One of the components of the broad region at 7.8μ may be regarded as the 7.67μ band of methane, which Cooley[7] has examined with high dispersion. Dennison[8] regards this band as the result of one of the fundamental frequencies of the methane molecule. Similarly, the 6.8μ absorption band of the present curves corresponds to a frequency commonly attributed to one of the fundamental vibrations of the C—H pair. However, as will be noted below, another factor probably plays an important role in the absorption in this region.

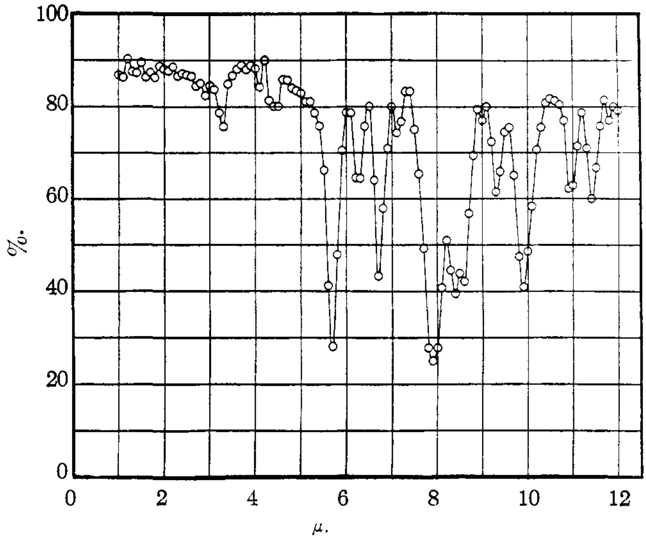

Fig. 7.—Diphenyl carbonate, $T = 0.025$ mm., temp. = 50°.

A well-defined absorption at 5.75μ which occurs with marked regularity in the spectrum of each of the compounds examined may be regarded as characteristic of the C═O linkage. A survey of the absorption spectra of the large number of compounds containing the C═O group which have been recorded in the literature lends support to this opinion. Even in the rather complicated molecules of some of the tropine alkaloids, which the author[9] has examined, this band was sharply resolved (at 5.8μ).

In comparing the absorption spectra of the organic carbonates with those of the inorganic carbonates as measured by Schaefer and his collabo-

---

[6] J. W. Ellis, *Phys. Rev.*, **27**, 309 (1926).

[7] J. P. Cooley, *Astrophys. J.*, **62**, 73 (1925).

[8] D. M. Dennison, *ibid.*, **62**, 84 (1925).

[9] F. K. Bell, *J. Pharm. Exptl. Therap.*, **29**, 533 (1926).

rators[3] it must be noted that the inorganic carbonates were examined as plates of 0.1 mm. thickness in comparison with the 0.025 mm. thickness used in the present study. Furthermore, the difference in density between these two types of carbonates must be considered.

In interpreting their experimental findings, Schaefer and his co-workers were guided by several factors: (1) the carbonates are characterized by five fundamental frequencies corresponding to (approximately) 7μ, 14μ, 30μ, 60μ and 90μ; (2) the CO_3 ion is characterized by four "inner" vibrations, according to Bresters[10] and Kornfeld,[11] at (approximately) 7μ, 11μ, 14μ and 8μ, which is the calculated wave length for an inactive frequency; (3) a combination of an inactive and an active frequency may result in an active frequency.

Between 2μ and 9μ the absorption of the inorganic carbonates is similar for each carbonate and this region, in which the influence of the metallic ion is apparently negligible, is regarded as the region of activity of the "inner" vibrations of the carbonate ion. A broad region of total absorption occurs at 7μ in each case and the authors have determined the location of the minimum by calculation from the first harmonic at approximately 3.5μ and checking this value against the reflection spectrum in the region of 7μ. Having determined the location of this 7μ band (frequency ν_1), the location of the inactive frequency (ν_0) was calculated from the absorption at 3.9μ, regarding this band as the resultant of the combination $\nu_1 + \nu_0$. The wave length corresponding to this combination lies between 9 and 10μ. The 14μ (frequency ν_2) and 11μ (frequency ν_3) bands were definitely resolved. The authors thus determined the location of the four fundamental frequencies (ν_0, ν_1, ν_2, ν_3) for each carbonate. Other bands occurring between 2μ and 9μ are then satisfactorily accounted for as resulting from combinations of two or more of these four fundamental frequencies.

Difficulties are encountered at once in attempting to apply a similar method of analysis to the present curves. The relatively inactive metallic ions of the inorganic carbonates have been replaced by hydrocarbon radicals which are known to display characteristic absorption between 2μ and 9μ. Furthermore, the intensities of these hydrocarbon bands are relatively much greater than those of the carbonate ion. Thus the intensity of the 3.5μ (first octave of the 7μ band) band of the carbonate ion as shown in the absorption of the inorganic carbonates is not sufficiently great to affect the location of the 3.4μ of the C—H pair in the present curves. Likewise, the presence of the 3.9μ band of approximately the same intensity as that of the 3.5μ band cannot be detected in the spectra of the organic carbonates.

---

[10] C. I. Bresters, *Z. Physik*, **24**, 324 (1924).

[11] H. Kornfeld, *ibid.*, **26**, 205 (1924).

Another factor to be noted is that a number of the characteristic carbonate bands are located near or superpose characteristic C—H bands, for example, 3.5μ, 7μ and 14μ; so that both the location and intensity of the absorption bands of the organic carbonates are to be interpreted with caution.

The 5.75μ band of the present curves approximates, in location, a similar band which occurs in the inorganic carbonates, thus affording additional evidence that this band is characteristic of the C=O linkage. Schaefer and his collaborators regard this band as resulting from the combination $\nu_1 + \nu_0 - \nu_2$ (see above). As has been noted already, the broad region at 7.8μ of the organic carbonates has one component corresponding to the 7.67μ C—H band. Another component of this region may be located at 7.9μ. This band cannot be regarded as characteristic of the C=O linkage since an absorption of comparable intensity does not occur at that wave length in the spectra of the inorganic carbonates. It is suggested that this band is a combination band resulting from a combination of frequencies characteristic of the C—H and C=O linkages.

A consideration of the intensities of several of the more prominent absorption bands reveals some interesting relations. In Table I the transmissions (to the nearest per cent.) of the 3.4μ, 5.75μ, 6.8μ, 7.2μ and 7.85μ bands are given for each carbonate. It is at once seen that in the case of the normal alkyl hydrocarbon radicals the intensity of the 3.4μ band shows an increase with increase in molecular weight. Similar observations have been made by Henri and Bonino. Henri[12] examined a number of normal alcohols of the methane series. Although he failed to resolve the OH band at 3μ and the 3.4μ band, he found that the molecular coefficient of maximum absorption of the resultant band (at approximately 3.3μ) showed an increase with increase in molecular weight. By regarding this coefficient as an additive function and assigning values to the OH group and the CH_3 (or CH_2) group, he was able to obtain calculated values in good agreement with the observed data.

TABLE I

TRANSMISSION OF BANDS

	Transmission at				
	3.4μ	5.75μ	6.8μ	7.2μ	7.85μ
Methyl	0.60	0.30	0.30	absent	0.25
Ethyl	.47	.29	.31	0.26	.16
Propyl	.30	.30	.35	.31	.16
Butyl	.18	.28	.31	.24	.15
*Iso*butyl	.38	.40	.40	.32	.22
Iso-amyl	.30	.42	.42	.45	.16
Phenyl	.75	.28	.43	.74	.25

---

[12] V. Henri, "Études de Photochimie," Gauthier-Villars et Cie, Paris, 1919, p. 42.

Bonino[13] examined the absorption of several ketones containing only normal hydrocarbon residues of the methane series. He likewise found that the molecular coefficient of absorption of the 3.4μ band increased with increase in molecular weight. However, Bonino interpreted the intensity of the 3.4μ band as a function of the number of hydrogen atoms in the hydrocarbon radical and on this basis derived the empirical relation

$$\epsilon_2 = \epsilon_1 + C \log \frac{n_2}{n_1}$$

where ϵ_1 and ϵ_2 are the molecular coefficients of absorption and n_1 and n_2 are, respectively, the number of hydrogen atoms in the two homologs. By substituting the observed values of ϵ and the corresponding values of n, C was found to be a constant.

It is not necessary to express the absorption maxima of the present curves at 3.4μ in terms of the corresponding coefficients, in order to recognize at once that Bonino's empirical relation fails to hold; for it requires that the absorption maxima at 3.4μ should be the same for the butyl and *iso*butyl carbonates, since these two compounds contain the same number of hydrogen atoms. These two carbonates have approximately the same density and therefore the observed maxima are directly comparable and should be equal if Bonino's equation applies. The value for the dibutyl carbonate is approximately 0.19; that for the di-*iso*butyl carbonate is 0.38. The difference in these two values is, of course, far beyond the limit of experimental error. It is seen that the value of 0.38 falls between the values for ethyl and propyl carbonates. The value for di-*iso*-amyl carbonate is greater than that of the di-*iso*butyl carbonate and is approximately the same as the value for dipropyl carbonate.

A closer analysis of the intensity of the 3.4μ band would surely have to take into consideration the influence of the 3.5μ C═O band (as found in the inorganic carbonates). This influence should become more significant with decrease in molecular weight of the ester radical. The relative weakness of the 3.4μ band in dimethyl carbonate is striking, especially when it is considered that two methyl groups are present. Even more striking in this respect, is the aryl C—H band in diphenyl carbonate where the relative depth of the band is only ten percentage units.

The present curves, however, seem to show conclusively that the intensity of the 3.4μ band cannot be regarded merely as a function of the number of hydrogen atoms in the hydrocarbon radical, nor can it be regarded as a simple additive function depending upon the number of CH, CH_2 and CH_3 groups.

The intensities of the 6.8μ band, as shown in Col. 3 of Table I, are strikingly constant for the four normal esters. As has been noted above. this band, like the 3.4μ band, is regarded as resulting from one of the

---

[13] G. B. Bonino, *Gazz. chim. ital.*, **55**, 335 (1925).

fundamental vibrations of the C—H pair. It is therefore surprising that the intensity of this band fails to parallel the increase of that of the 3.4μ band with increase in molecular weight. This apparent discrepancy might be explained by assuming the presence of a carbonate band at 6.9μ (at 7.0μ in the inorganic carbonates) the intensity of which is considerably greater than that of the 6.8μ band. Thus in dimethyl carbonate the 6.8μ band would be expected to have a minimum intensity, which is probably less than that of the 3.4μ band. The location of the observed band (at 6.9μ) would therefore be that of the relatively more intense C═O band and the observed intensity would be the summation of the intensities of the 6.8μ and 6.9μ bands. The absorption of dibutyl carbonate (Fig. 4) may be interpreted to support this point of view. In this case the 6.9μ band has been definitely resolved and the 6.8μ band appears to have been shifted to the shorter wave length region as indicated by the poorly defined minimum near 6.7μ.

The intensities of the 6.8μ band in di-*iso*butyl and di-*iso*-amyl carbonates are approximately equal, but their value is considerably less than those of the normal esters.

The 7.2μ and 7.8μ bands do not display any consistent variations in intensity in passing from one carbonate to another, as shown in Table I. In addition to being poorly defined, the region of 7.8μ is too opaque to reveal clearly any differences in intensity. Thinner layers of the absorbing substances must be employed in order to obtain a satisfactory analysis of this region.

A consideration of the intensity of the 5.75μ band as shown in Col. 2 of Table I offers a serious objection to the opinion, expressed above, that the 5.75μ band is due to the C═O pair. The intensity values for the four normal esters are practically equal. Since the densities of these substances are of the same order of magnitude, it is obvious that the molecular absorption coefficient at 5.75μ will show an increase with increase in molecular weight. However, if the 5.75μ band is due to the carbonate group, the molecular absorption coefficient should remain constant for each carbonate. The same reasoning may be applied to the case of the two *iso*-esters where, however, the intensity of the 5.75μ band, although the same for each of the two compounds, has a considerably smaller value than that of the normal esters.

It must also be noted that there is at least an approximate equality in the intensity values of the 5.75μ band and of the 6.8μ band in each of the compounds (with the exception of diphenylcarbonate), a condition which can hardly be regarded as coincidental.

The most obvious explanation of these observations is the assumption that another absorption band (perhaps due to the CH pair) occurs near the location of the C═O band, so that the intensity of the observed band at 5.75μ is that due to the superposition of two bands. However, little evidence can be found in support of this assumption.

The present study includes the examination of only two *iso*-esters and therefore offers little conclusive information concerning the absorption of that type of compound. From the above discussion, however, it is difficult to avoid the generalization that the normal esters and the *iso*-esters of carbonic acid form two distinct types of compounds in which the factors determining the intensities of the absorption bands characteristic of the C—H and C=O linkages are the same qualitatively but differ quantitatively for each type.

The absorption spectra of the organic carbonates offer a further indication, perhaps more clearly than previous work, of the definite possibilities of utilizing the intensity of characteristic absorption bands for purposes of identification. For example, it is readily seen that there would be no difficulty in differentiating between the four normal esters of carbonic acid by means of the intensity of the absorption at 3.4μ.

Summary

1. The absorption spectra of dimethyl, diethyl, dipropyl, dibutyl, di-*iso*butyl, di-*iso*-amyl and diphenyl carbonates have been examined between 1.0 and 12.0μ, using absorption cells made from polished rock salt plates.

2. These absorption spectra show a marked similarity in the number and location of absorption bands between 3.0 and 8.0μ; while no consistent variations or similarities can be detected in the region between 8.0 and 12.0μ.

3. The absorption spectra have been discussed in their relation to the results obtained by Schaefer and his co-workers in the examination of some inorganic carbonates.

4. An increase in the intensity of the 3.4μ band with increase in the molecular weight of the ester radical has been observed. However, the intensity values of the 3.4μ band in di-*iso*butyl and di-*iso*-amyl carbonates are not satisfactorily accounted for by the relations derived either by Henri or Bonino.

5. The intensity relations of the 5.75μ band in the various organic carbonates offer an important objection to the idea that the 5.75μ band depends solely on the presence of the carbonate group.

6. An analysis of the variations in intensity of characteristic absorption bands in the various organic carbonates indicates that the normal and the *iso*-esters may be regarded as two distinct types of carbonates.

BALTIMORE, MARYLAND