462. *The Infrared Absorption of ^{18}O-Labelled Benzoic Acid, Benzoyl Chloride, and Methyl Benzoate.*

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The infrared absorptions of ^{18}O-labelled, monomeric benzoic acid, benzoyl chloride, and methyl benzoate ($Ph{\cdot}C^{18}O{\cdot}^{16}OMe$), of about 90 atom % ^{18}O, have been measured in the 3700—670 cm.$^{-1}$ region in comparison with the absorptions of the corresponding normal compounds. The molar extinction coefficients of the $C{=}^{18}O$ stretching bands of benzoic acid and methyl benzoate, as well as the respective relative integrated absorption intensities, were found to be considerably lower than the corresponding coefficients and intensities of the normal compounds. The decrease in each case seems to be more than can be expected on the basis of the change in frequency only. The splitting of the benzoyl chloride C=O band was found to persist in the spectrum of the labelled compound and was shown to be the result of Fermi resonance.

It was shown recently [1] that the absorption intensity of the X=O group stretching bands (X = C or P), in a number of compounds, is changed appreciably when ^{18}O is substituted for ^{16}O. This effect is by far stronger than could be expected from the usual isotope effect [2] on the intensity of infrared bands, and its origin is as yet unclear. It seemed therefore interesting to investigate the infrared spectra of more compounds, of various classes, containing such groups labelled with ^{18}O and to compare them with the spectra of the corresponding normal substances. This has now been done for [$^{18}O_2$]benzoic acid, [^{18}O]-benzoyl chloride, and methyl [*carbonyl*-^{18}O]benzoate, the results being reported below.

^{18}O-*Labelled Benzoic Acid.*—When carbon tetrachloride solutions of benzoic acid were examined it was found that even solutions as dilute as 0·029 g./l. (0·0002M) are still mainly dimeric. In the case of normal benzoic acid the CO stretching bands are then located at 1739 (due to the monomer) and 1690 cm.$^{-1}$ (stronger; due to the dimer). In the case of $Ph{\cdot}C^{18}O_2H$ of about 90% purity these bands appear at 1707 and 1670 cm.$^{-1}$ respectively. The isotopic difference of 32 cm.$^{-1}$, observed in the C=O stretching frequency of monomeric benzoic acid dissolved in carbon tetrachloride, can be compared with the difference of 29 cm.$^{-1}$ in the analogous case of benzophenone [1a] and the value of 24 cm.$^{-1}$ for benzamide.[1c] That this difference amounts only to 20 cm.$^{-1}$ in the case of dimeric benzoic acid (in CCl_4) is probably the result of the greater participation of other groups, besides the C=O group, in the 1690—1670 cm.$^{-1}$ dimer vibration.

In order to compare the absorption intensity of the pure monomeric [^{18}O]benzoic acid CO band with that of the normal monomer, dilute solutions of these substances in chloroform were prepared. In this solvent benzoic acid is already practically fully dissociated in concentrations of about 0·06 g./l. and only one CO band appears then in the infrared spectrum. This behaviour is due to the tendency of chloroform to form hydrogen-bonded solvates [3] with proton acceptors (such as substances containing carbonyl groups) which stabilise the monomeric form. The CO frequency of normal benzoic acid under these conditions was found at 1715 cm.$^{-1}$ and that of [^{18}O]benzoic acid at 1688 cm.$^{-1}$. The somewhat lower difference between the isotopic monomeric frequencies in chloroform (27 cm.$^{-1}$) than in carbon tetrachloride (32 cm.$^{-1}$), although at the limit of the experimental error, seems to be real and to reflect a stronger chloroform-solvation effect on the normal monomer (—24 cm.$^{-1}$) than on the ^{18}O-labelled one (—19 cm.$^{-1}$). A similar phenomenon

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[1] Halmann and Pinchas, *J.*, 1958, (*a*) 1703, (*b*) 3264; (*c*) Pinchas, Samuel, and Weiss-Broday, *J.*, 1961, 1688.

[2] Crawford, *J. Chem. Phys.*, 1952, **20**, 977.

[3] Jones and Sandorfy in " Technique of Organic Chemistry," Interscience Publ., Inc., New York, 1956, Vol. IX, pp. 298—299.

was observed with normal and [^{18}O]benzamide[1c] where the isotopic CO frequency differences are 24 cm.$^{-1}$ in carbon tetrachloride and 20 cm.$^{-1}$ in chloroform.

These values for the CO vibration of benzoic acid compare favourably with the data published by Mecke,[4] *i.e.*, bands at 1757 and 1712 cm.$^{-1}$ for the vapour and at 1742 and 1695 cm.$^{-1}$ for a very dilute carbon disulphide solution.

The high dilution necessary, even in chloroform, to obtain the full disssociation of benzoic acid made it impossible to observe properly any other monomeric infrared absorption band.

The CO band absorption intensities in various solutions of the normal and the labelled acid are summarised in Table 1. The relative integrated absorption intensity of the band in each case was obtained by multiplying the apparent maximum molar extinction coefficient by the apparent half-width of the band.

TABLE 1. *The absorption intensity of the* CO *band in isotopic benzoic acids.*

Material	Concn.[a] (g./l.)	Optical density	Molar extinction coeff. (l. mole^{-1} cm.$^{-1}$)	Half-width (cm.$^{-1}$)	Relative integrated absorption (l. mole^{-1} cm.$^{-2}$)
Normal	0·036	0·232	393	49	19,300
Normal	0·0646	0·403	380	49	18,600
Normal	0·083	0·510	374	49	18,300
90 Atom % ^{18}O ...	0·0354	0·177	350[b]	48·5	17,000
90 Atom % ^{18}O ...	0·069	0·347	352[b]	49	17,200
90 Atom % ^{18}O ...	0·0712	0·360	354[b]	—	—

[a] The solvent is always chloroform, and the cell thickness 20 mm. [b] Corrected for the lower concentration of the labelled acid.

TABLE 2. *The infrared absorption bands of normal and* [^{18}O]*benzoyl chloride* (*cm.*$^{-1}$).

Normal compound				Normal compound			
Present work[a]	Rasmussen and Brattain[5]	Documentation of Molecular Spectra[6]	Labelled compound Present work[b]	Present work[a]	Rasmussen and Brattain[5]	Documentation of Molecular Spectra[6]	Labelled compound Present work[b]
3075w	3081w	*c*	3065w	1175s	1176m	1175[e]	1174vs
*1777*s[d]	*1773*m	1764[e]	1747s[d]	—	1102w		—
1736s	1736m	1721[e]	*1711*s	—	1079w		—
1595w	1599w		1597w	—	1028w		1027w
—	1586w		1582w	—	1003w		—
—	1493w		—	932w	936w		934w
1453w	1450m		1452m	875vs	876vs	871[e]	872vs[b]
—	1418w		—	801w[e]			801w[c]
—	1387w		—		833—714bs		777vs,[e] 769vs,[e]
—	1344w		1342w	774s[e]			758w[e]
1316w	1316w		1314w	690vs[e]	686s		691vs[c]
—	1304w		—	685vs[e]			685vs[e]
			1238vw	676vs[e]	674s	675[e]	676vs[e]
1203s	1204s	1205[e]	1199vs	671vs[e]			671vs[e]

[a] Unless otherwise stated, for a 3% concentration in CCl_4 in a 0·2 mm. cell. [b] Unless stated differently, for a 9% CCl_4 solution in the same cell. [c] Only the main frequencies are given. [d] The main component of the doublet is italicised. [e] Measured on a capillary layer of pure material. [f] Evidently, this number was intended by the misprinted value of 845, as can be seen from the curve.

Table 1 shows that while the value for the relative integrated absorption intensity of the carbonyl stretching frequency is 18,800 ± 500 units in the case of the normal acid, it decreases to 17,000 ± 400 units in the case of the fully ^{18}O-labelled benzoic acid. This decrease of about 10% seems to be more than can be expected from the usual isotopic effect on the intensity of infrared bands (which would seem to be about 3% since[1b] $1688^2/1715^2 = 0{\cdot}97$).

It is interesting that the ^{18}O-labelled benzoic acid behaves as do labelled benzophenone[1a] and triphenylphosphine oxide,[1b] which also show a decrease in the intensity

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[4] Mecke, "Documentation of Molecular Spectra Catalogue," Butterworths, London, 1958, compound cards nos. 3183, 3386.

of their X=^{18}O bands as compared with the normal intensity, and not as does [^{18}O]-benzamide [1c] which in carbon tetrachloride solution absorbs some 20% more than [^{16}O]benzamide while in chloroform solution its intensity is practically that of the normal amide.

[^{18}O]*Benzoyl Chloride.*—The infrared absorption spectrum of both normal benzoyl chloride and 89·9 atom % [^{18}O]benzoyl chloride was investigated for carbon tetrachloride solutions and, in the 830—670 cm.$^{-1}$ region, for undiluted capillary layers. The results are summarised in Table 2 where the literature data concerning the absorption of a 5% carbon tetrachloride solution of normal benzoyl chloride [5] and an undiluted capillary layer of it [6] are included for comparison. As can be seen from this Table the agreement between the present results for normal benzoyl chloride and the literature is very good although some weak bands reported by Rasmussen and Brattain [5] are missing for our chloride. This is, no doubt, partly a consequence of the somewhat lower concentration–cell thickness factor in the present work (3% × 0·2 mm.) relative to that in the case of Rasmussen and Brattain (5% × 0·15 mm.). It can also be noticed that a number of strong bands have now been shown to possess some structure.

When the spectrum of the labelled chloride is compared with that of the normal compound it is observed that the only real differences between them are in the *1777*, 1736, and 1203 cm.$^{-1}$ frequencies of the normal substance, their values in the case of the labelled modification being 1747, *1711*, and 1199 cm.$^{-1}$, respectively. Thus, only these frequencies (down to 670 cm.$^{-1}$) are connected with modes of vibration in which the oxygen atom participates considerably.

It is known that the C=O stretching band of aliphatic acid chlorides appears [7] at about 1800 cm.$^{-1}$ and it is equally well established that a phenyl ring conjugated with a carbonyl group usually decreases its otherwise expected frequency by about [8] 20—40 cm.$^{-1}$; hence the C=O stretching band of the normal benzoyl chloride must be expected to appear at about 1770 cm.$^{-1}$. The fact that two bands, at about 1777 and 1736 cm.$^{-1}$, appear in its spectrum in this region has been ascribed by Rasmussen and Brattain [5] to either a monomer–dimer equilibrium or the presence of some low-energy thermally excited level in the chloride.

It was, however, observed that changing the concentration from 0·03 to 0·006 g./l. did not change materially the intensity ratio of the two bands in the case of a cyclohexane solution. This ratio (of about 2 : 1) was also found to be practically constant when different solvents, such as cyclohexane, carbon tetrachloride, and acetonitrile, were used. It was finally established that varying the cell temperature from 20° to 60° had no measurable effect on the relative intensities of the bands. It is therefore clear that this doublet is the result neither of a monomer–dimer equilibrium (which should be affected considerably by changes in dilution and temperature) nor of a thermally excited level (which is more populated at higher temperatures, so that its effect is then more pronounced).

It seems that this doublet is due rather to Fermi resonance between the first overtone of the 875 cm.$^{-1}$ frequency and the fundamental C=O stretching frequency, which probably occur originally at about 1748 and 1765 cm.$^{-1}$, respectively. The higher frequency, being also the more strongly absorbed, thus appears to possess a higher contribution from the original C=O stretching vibration than the lower frequency which has a higher overtone character.

The strong 875 cm.$^{-1}$ band must be attributed to the =C–Cl stretching vibration. This assignment is supported by the strong carbonyl chloride C–Cl band at about [9] 850 cm.$^{-1}$

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[5] Rasmussen and Brattain, *J. Amer. Chem. Soc.*, 1949, **71**, 1078.

[6] Collection of the British Ministry of Supply, ref. 4, no. 535.

[7] Ref. 3, p. 457.

[8] Ref. 3, pp. 448, 452, 454, 456.

[9] National Academy of Sciences–National Bureau of Standards, " Infrared Spectral Catalog," compound card no. 831.

and the intense bands at about 900 cm.$^{-1}$ of propionyl chloride,[10] butyryl chloride,[11] and adipoyl chloride.[12]

As mentioned, ^{18}O-labelled benzoyl chloride also shows such a doublet at 1747 and 1711 cm.$^{-1}$; in this case, however, the relative intensity of the two branches is inverted, the lower being now the stronger. It is clear that because of the isotopic exchange the original C=O stretching frequency is decreased here by about [1a] 30 cm.$^{-1}$ and occurs at approximately 1730 cm.$^{-1}$. The original overtone of the C–Cl band of the labelled chloride can be expected to be at about 1740 cm.$^{-1}$ ($= 2 \times 872$ — an anharmonicity correction), so again Fermi resonance between these two vibrations sets in; in this case, however, the lower frequency has a larger contribution from the C=O stretching vibration and is therefore absorbed more readily, giving rise to a stronger band. That the higher frequency of the [^{18}O]chloride appears already at 1747 cm.$^{-1}$, and not higher, seems to imply that its original position is really at about 1732 cm.$^{-1}$, the perturbation shift being about 15 cm.$^{-1}$ ($\sim$1730 — 1711). This means a higher anharmonicity term for the C–Cl group in the labelled compound than in the normal substance, the C–Cl overtone of which must be assumed to occur only at about 1748 cm.$^{-1}$ (since the Fermi resonance which increases so much the intensity of the normal overtone must have also affected appreciably its frequency and moved it considerably towards lower frequencies; if it then appears finally at 1736 cm.$^{-1}$ it must have been originally at a materially higher frequency).

The strong band which appears in the normal chloride spectrum at 1203 cm.$^{-1}$ and in the case of the labelled material at 1199 cm.$^{-1}$ is probably analogous to the $R\cdot CO\cdot R_1$ asymmetrical stretching band which appears in the neighbourhood of 1200 cm.$^{-1}$ in the spectra of ketones,[13,14] propionyl chloride [10] (1250 cm.$^{-1}$), butyryl chloride [11] (1220), adipoyl chloride [12] (1170), etc.

Since neither the 1777 nor the 1711 cm.$^{-1}$ band is due to a pure C=O stretching vibration it is not possible to learn much from a comparison of their absorption intensity. An estimate of this intensity which was however carried out gave the value of 322 l. mole^{-1} cm.$^{-1}$ for the molar extinction coefficient of the (normal) 1777 cm.$^{-1}$ band, and 228 units for the corresponding constant in the case of the 1711 cm.$^{-1}$ (labelled) band.

Methyl [carbonyl-^{18}O$_1$]*Benzoate*.—The infrared absorption of methyl [*carbonyl*-^{18}O$_1$]-benzoate (84 atom % of the C=O oxygen ^{18}O) was investigated in solution in carbon tetrachloride and compared with the absorption of the normal compound under the same conditions. The results are summarised in Table 3, together with other data on the infrared absorption of a pure (liquid) sample of normal methyl benzoate.[5,15]

It is evident from Table 3 that, when the somewhat different measurement conditions are taken into due account, the agreement of the present results for the normal methyl benzoate with those of the literature is generally good (especially with the D.M.S.[15] data).

A comparison of the spectrum of the labelled compound with that of the normal ester shows that the significant differences between them are as follows: (*a*) the C=O stretching band appears at 1696 (C=^{18}O) as compared with 1727 cm.$^{-1}$; (*b*) the =C–OC asymmetrical stretching band [16] at 1277 cm.$^{-1}$ is decreased in the labelled compound to 1273 cm.$^{-1}$; (*c*) new bands appear at 1252, 758, and 702 cm.$^{-1}$ and a band at 822 cm.$^{-1}$ disappears in the isotope spectrum; (*d*) the second benzoate band [17] (at 1111 cm.$^{-1}$), which is probably due to a =C–OC symmetrical stretching vibration,[16] is moved to 1108 cm.$^{-1}$ and the band at 675 cm.$^{-1}$ is shifted to 671 cm.$^{-1}$.

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[10] Ref. 9, no. 1687.
[11] Ref. 9, no. 1689.
[12] Ref. 9, no. 1694.
[13] Ref. 3, pp. 507—508.
[14] Bellamy, " The Infra-red Spectra of Complex Molecules," Methuen & Co. Ltd., 2nd edn., London, 1958, p. 132.
[15] Collection of the Research Dept., Imperial Chemical Industries Limited, ref. 4, no. 1043.
[16] Ref. 3, p. 503.
[17] Ref. 14, p. 191.

The shift in the C=O frequency because of the isotopic substitution amounts thus to 31 cm.$^{-1}$, in good agreement with the value of 30 cm.$^{-1}$ observed by Braude and Turner [18] with labelled cinnamyl *p*-nitrobenzoate. The weak band observed in the case of the labelled ester at 1727 cm.$^{-1}$ belongs no doubt to the 16 atom % of normal ester present in it.

The appearance of the new bands and disappearance of the 822 cm.$^{-1}$ band seem to be due to a different rotational isomeric composition of the different isotopic modifications. Anyhow, the 1252 cm.$^{-1}$ band seems to be connected with some kind of =C–OC vibrations (in analogy with the 1277 cm.$^{-1}$ band), while the 822, 758, and 702 cm.$^{-1}$ bands appear to be a result of some out-of-plane C_{ar}–H bending vibrations similarly to the 800 cm.$^{-1}$ band of benzamide.[1c] The 675 cm.$^{-1}$ band (of the normal ester) must be ascribed to an out-of-plane CO_2 bending vibration, in analogy with the 667 cm.$^{-1}$ CO_2 bending frequency,[19] since it is affected considerably by the isotopic exchange. Ethyl acetate also shows a band in this vicinity [20] (at 630 cm.$^{-1}$), both monomeric and dimeric acetic acid show an absorption maximum at about [21] 670 cm.$^{-1}$, and even the dimer of fully deuterated acetic acid shows this band (at about 645 cm.$^{-1}$).

TABLE 3. *The infrared absorption bands of normal and* ^{18}O*-labelled methyl benzoate (cm.*$^{-1}$*).*

Normal compound			Labelled compound Present work [c]
Rasmussen and Brattain [5a]	Documentation of Molecular Spectra [15a]	Present work [b]	
3623w	—	—	—
3436w	—	—	—
3077w	3085	—	—
3040m	3060, 3040	3030w	3025w
2985w	2970	2950w	2960w
2874w	2870	—	2840w
2096w	~2080	—	—
1931w	~1924	—	—
1789w	~1786	—	—
1724s	1725	1727s	1727w
1684w		—	1696s
1650w	1645	—	—
1602w	1607	1602w	1603w
1590w	1585	~1590vw	~1585w
1495w	1496	~1490w	~1490w
1445s	1456, 1437	1455w, 1436w	1438m
1318m	1315	1314w	1313m
1282vs	1277	1277vs	1273vs
1220w	—	—	1252w
1195m	1190	1192w	1192w
1179m	1174	1177w	1177w
1161w		—	—
~1111vs	1108	1111m	1108s
1074s	1068	1069w	1070w
1028s	1025	1028w	1028w
1004w	1000	1006vw	—
969s	964	971w	969w
940m	932	934vw	934w
851w	~845	848vw	
825m	821	822m [a]	—
812w	804	808w [a]	808m [a]
762w	—	—	758w [a]
714vs	707	712vs,[a] 707vs [a]	713vs,[a] 707vs,[a] 702vs [a]
689m	685	686m [a]	686m [a]
676m	672	675m [a]	671m [a]

[a] Measured on a pure liquid. [b] Unless otherwise stated, measured on a 0·016 g./ml. CCl_4 solution in a 0·2 mm. cell. [c] Unless stated differently, measured with a 0·055 g./ml. CCl_4 solution in a 0·2 mm. cell.

In spite of the other differences in the infrared spectrum of the labelled ester the decrease in the C=O frequency can no doubt be considered as the only really important one since it is the only change which affects a strong band by more than 5 cm.$^{-1}$. It seems therefore justified to ignore other frequencies in the spectrum when dealing, to a first approximation only, with the problem of the infrared absorption intensity of isotopic modifications of methyl benzoate. Only the absorption intensity of the C=O band of the methyl benzoates was therefore studied. The results of this study, which include the molar extinction coefficient, the band half-width, and the relative integrated absorption intensity in each case, are given in Table 4.

[18] Braude and Turner, *Chem. and Ind.*, 1955, 1223.

[19] Herzberg, " Infrared and Raman Spectra of Polyatomic Molecules," Van Nostrand Co. Inc., Princeton, N.J., 1945, p. 274.

[20] Ref. 9, no. 1366.

[21] Herman and Hofstadter, *J. Chem. Phys.*, 1939, **7**, 460.

TABLE 4. *The absorption intensity of the* CO *band in isotopic methyl benzoates.*

Material	Concn. (g./l. CCl_4)	Optical density [a]	Molar extinction coeff. (l. mole^{-1} cm.$^{-1}$)	Band half-width (cm.$^{-1}$)	Relative integrated intensity (l. mole^{-1} cm.$^{-1}$)
Normal	10·77	0·589	372	18·4	6800
Normal	7·42	0·438	401	17·9	7200
84 atom % $(C = O)^{18}O$	15·24	0·572	308 [b]	20·2	6200
84 atom % $(C = O)^{18}O$	10·94	0·424	318 [b]	19·8	6300

[a] In a 0·2 mm. cell. [b] Corrected for the content of the normal ester.

As seen from Table 4 the (apparent) molar extinction coefficient of the ester C=O band rises a little with dilution but is still definitely lower for the labelled (313 ± 10 units) than for the normal benzoate (387 ± 15 units). The relative integrated absorption intensity (obtained by multiplying the molar extinction coefficient by the corresponding band half-width) of the ^{18}O-labelled modification is again, as usual, appreciably lower than that of the normal compound. The decrease in integrated intensity, being about 11% (from 7000 ± 200 to 6250 ± 200 units), is in this case also several times that expected from the change in frequency [1b] only (about 3·5%), and methyl benzoate thus falls in line with benzophenone,[1a] triphenylphosphine oxide,[1b] and benzoic acid, leaving benzamide [1c] with its higher C=^{18}O absorption as an exception.

It is noteworthy that, as with triphenylphosphine oxide [1b] and benzamide [1c] dissolved in carbon tetrachloride, the half-width of the X=^{18}O stretching band (as measured in CCl_4) is about 10% bigger than that of the corresponding X=^{16}O band.

The ultraviolet absorption of the labelled methyl benzoate (in ethanol) was also measured and was compared with that of the normal compound. Both spectra were found to show absorption maxima at the same wavelengths, *i.e.*, at 2290 and 2730 Å. However, while the molar extinction coefficient at the first maximum was practically identical in both cases (11,700 ± 150 units in the normal ester, 11,400 ± 200 in the labelled one) it was appreciably different at the second wavelength, being 827 ± 12 units in the normal case and 898 ± 9 units for the isotopic modification. The results reported here for the normal coefficients are in good agreement with those of Ungnade and Lamb [22] (11,000 and 830 units, respectively).

Since the 2730 Å band is due to an $n \rightarrow \pi^*$ C=O transition [23] this difference in its intensity † seems to suggest that the transition moment of this group is somewhat different in the two isotopic modifications.[24] A similar phenomenon, although in the other direction, was observed with the 2530 Å band of benzophenone.[25] These results are in accordance with the other discrepancies in physical properties of isotopic pairs, mentioned above.

EXPERIMENTAL

[$^{18}O_2$]*Benzoic Acid.*—Benzonitrile (8·7 g.) was sealed in a borosilicate tube with water highly enriched in oxygen-18 (40 ml.) and saturated with dry hydrogen chloride. The tube was heated at 100° for 20 hr. After cooling, the water was distilled off and the solid dried *in vacuo* and extracted with dry ether. On recrystallising from ether, [$^{18}O_2$]benzoic acid, m. p. 122°, was obtained in 95% yield. The acid, analysed for its isotopic oxygen content by the method of Anbar and Gutmann,[26] was found to contain 90·0 atom % of oxygen-18.

[^{18}O]*Benzoyl Chloride.*—This compound was prepared by the method of Bender and Ginger [27]

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† Since this ester also shows (ref. 22) a shoulder at about 2810 Å it is impossible to evaluate precisely the integrated absorptions of the 2730 Å band and one must compare the molar extinction coefficients instead, assuming the band form to be only little affected by the isotopic exchange.

[22] Ungnade and Lamb, *J. Amer. Chem. Soc.*, 1952, **74**, 3789.
[23] See, *e.g.*, Ito, Inuzuka, and Imanishi, *J. Amer. Chem. Soc.*, 1960, **82**, 1317.
[24] Ref. 19, p. 261.
[25] Halmann and Pinchas, *J.*, 1960, 1246.
[26] Anbar and Gutmann, *J. Internat. Radiation Isotopes*, 1959, **3**, 233.
[27] Bender and Ginger, *J. Amer. Chem. Soc.*, 1955, **77**, 348.

in which [$^{18}O_2$]benzoic acid (5 g.) was heated with an excess of thionyl chloride (8 ml.) at 100—110° until no further hydrogen chloride was evolved. On fractional distillation, [^{18}O]benzoyl chloride, b. p. 196—198°, was obtained in 90% yield.

On isotopic oxygen analysis the benzoyl chloride was found to contain 89·9 atom % of oxygen-18.

Methyl [carbonyl-$^{18}O_1$]*Benzoate.*—[^{18}O]Benzoyl chloride (2 g.), prepared as above, was dissolved in anhydrous methanol (4 ml.) and boiled gently for 3 hr. until all the hydrogen chloride was driven off.

On fractional distillation at atmospheric pressure methyl [^{18}O]benzoate, b. p. 199—200°, was obtained in quantitative yield. The isotopic oxygen analysis gave 42·0 atom % of oxygen-18, the carbonyl oxygen containing 84 atom % of oxygen-18 and the alkoxy-oxygen being of normal abundance.

Optical Measurements.—The infrared measurements were carried out with a Perkin-Elmer, model 12 C, spectrophotometer equipped with a sodium chloride prism.

The absorption intensity measurements of isotopic pairs of compounds were all made in the same cell and at least in duplicate runs. Their mean result was used in the calculation. Blank measurements on the pure solvent in the same cell were run before each solution measurement.

The ultraviolet measurements were made with a Beckman DU spectrophotometer.

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