UDC 547.582.1 : 543.422.4

72. **Shigeru Yoshida** : Infrared Spectra of Benzoyl Halides and their Substituted Derivatives.*[1]

(*Takamine Research Laboratory, Sankyo Co., Ltd.**[2])

Studies on the infrared spectra of the chlorides of aromatic carboxylic acids are limited to those of Flett.[1] In an earlier paper, the present author reported the CH out-of-plane vibration and extra bands of the esters and chloride of benzoic acid, and their *para*-substituted derivatives.[2] During the course of this work, it was noticed that benzoyl halides and their substituted derivatives exhibited a characteristic, strong absorption besides the extra band and that the C=O stretching vibration was split into two in most of these compounds. These points were examined in detail in the present series of work, the results of which are reported herein. After this work was presented at the Symposium,*[1] a report appeared which discussed in part absorption of benzoyl chloride[3] and the conclusions drawn were the same as the present one.

Experimental Results

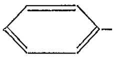
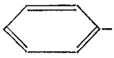
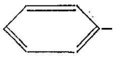
The Carbonyl Stretching Vibrations

(1) Benzoyl Halides

As will be clear from Table I and Fig. 1, there are two absorptions in the region of C=O stretching vibration. The absorption in the lower frequency region shifts to a lower wave number as the halogen atom changes from chlorine to bromine to iodine, as in benzoyl chloride, bromide, and iodide, and intensity of the absorption becomes weaker, the absorption of benzoyl iodide at 1698 cm^{-1} being especially weak. Since this absorption in benzoyl iodide is very labile, it may be due to the C=O stretching vibration of benzoic acid, formed by the decomposition of benzoyl iodide. In fact, infrared spectrum of benzoyl chloride added with a small quantity of benzoic acid exhibits a third absorption at 1695 cm^{-1},[4] but such an assumption is denied from the following point.

As will be described later, the characteristic, strong absorption of benzoyl halides is the in-plane bending vibration of ring C-H at 1170～1160 cm^{-1} and a strong absorption appears at 1160 cm^{-1} in benzoyl iodide. The in-plane bending vibration band of ring

Table I. Benzoyl Halides (cm^{-1})

Compound	Phase	ν_{CO} region bands		$\nu_{\text{C-}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{-}}$	δ_{CH} in	$\nu_{\text{-C-X}}$	δ_{CH} out-of-plane	Extra band
 -COCl	(l)	1779(s)	1739(s)	1203(s)	1174(s)	870(v.s)	775(s)	682(s)
	(CS$_2$)	1773(s)	1736(s)	1202(s)	1172(s)	870(v.s)	772(s)	682(s)
 -COBr	(l)	1779(s)	1701(m)	1195(s)	1171(s)	848(v.s)	768(s)	683(s)
	(CS$_2$)	1779(s)	1701(m)	1195(s)	1171(s)	850(v.s)	766(s)	681(s)
 -COI	(l)	1764(s)	1695(m)	1188(s)	1160(s)	828(v.s)	762(s)	677(s)
	(CS$_2$)	1761(s)	1698(w)	1186(s)	1161(s)	830(v.s)	762(s)	679(s)

l : liquid, CS$_2$: CS$_2$ solution, 0.1 mm. cell

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*[1] Paper presented at the 6th Symposium on Infrared and Raman Spectra, Chemical Society of Japan, Tokyo, October 14, 1959.

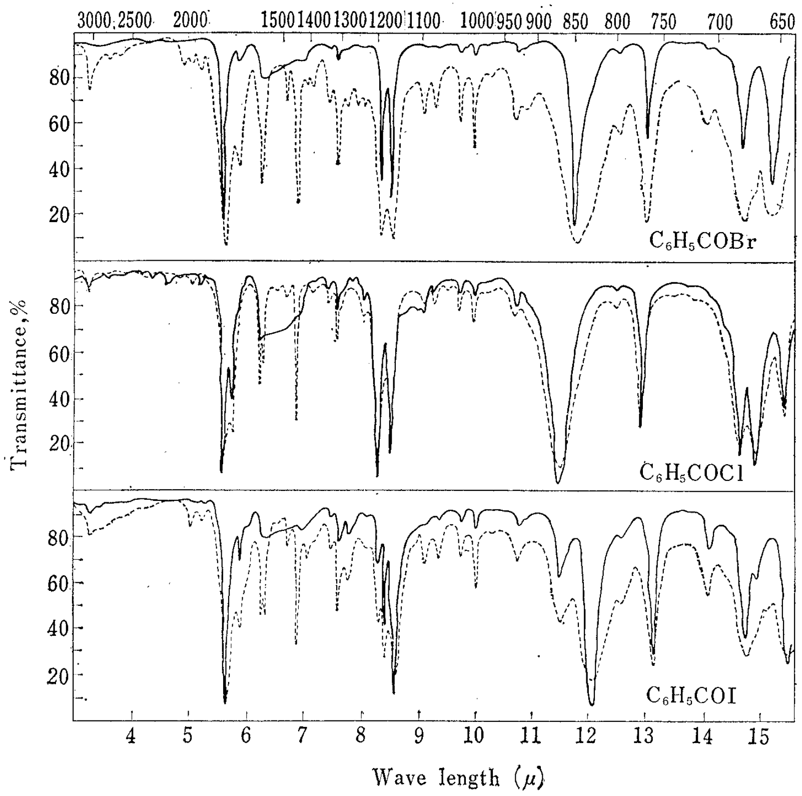
*[2] Nishi-shinagawa, Shinagawa-ku, Tokyo (吉田　茂).

1) M. St. C. Flett : Trans. Faraday Soc., **44**, 767 (1948).

2) S. Yoshida : This Bulletin, 8, 389 (1960).

3) *a*) R.N. Jones, *et al.* : Can. J. Chem., **37**, 2007 (1959); *b*) R.A. Nyquist, W.J. Potts : Spectrochim. Acta, **7**, 514 (1959).

4) R.N. Jones, *et al.* : Can. J. Chem., **37**, 2020 (1959).



9 o D

Fig. 1. Infrared Spectra of Benzoyl Halides

—— liquid
------ CS_2 solution, 0.1 mm. cell

C-H of benzoic acid it not so strong and, in order for benzoyl iodide to show medium intensity absorption at 1698 cm^{-1} (Fig. 1 and Table I), as in liquid, there must be a fairly large quantity of benzoic acid present. Consequently, it is impossible to think that the absorption at 1160 cm^{-1} would appear in such a strong intensity and, moreover, there is almost no characteristic absorption of benzoic acid. From these facts, the absorption at 1698 cm^{-1} is considered to be a characteristic absorption of benzoyl iodide.

The absorption of C=O stretching vibration in the higher frequency in benzoyl halides is the stretching vibration of C=O and that in the lower frequency is considered to result from the Fermi resonance between the over-tone of the stretching vibration of $-\overset{\parallel}{C}-X$ (X=halogen atom) appearing at 870~830 cm^{-1}, as will be described later, and C=O stretching vibration. The difference between the mean value (ν_1) of two absorptions in the C=O stretching vibration region and the double volume of the absorption (ν_2) at 870~830 cm^{-1} is shown in Table V. This difference becomes greater as the compound changes from benzoyl chloride to benzoyl iodide. For the Fermi resonance to occur, the absolute value of this difference is important and its plus (+) or minus (−) is not a great matter. In general, the Fermi resonance seems to become weak in benzoyl halide derivatives when the absolute value of the difference becomes above 50.

Splitting of the carbonyl absorption into two generally appears in conformational isomers[5] and due to dependence on Fermi resonance of C=O stretching vibration with over-tone of a lower-lying fundamental vibration.[4,6] When there are solvent- and temperature-dependent spectral changes, this splitting is thought to be due to conformational isomers. According to the studies made by the present author[*3] and that of

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[*3] Measurements were made in dioxane, acetonitrile, CS_2, CCl_4, and $CHCl_3$, but details will be omitted since the solvent effect was clarified by the work of Jones.[4]

5) H. H. Morris, R. A. Young, Jr.: J. Am. Chem. Soc., **79**, 3408 (1957); H. O. Hause, J. W. Blaker: *Ibid.*, **80**, 6389 (1958); H. Shindo: This Bulletin, **8**, 33 (1960).

6) P. Yates, L. L. Williams: J. Am. Chem. Soc., **80**, 5896 (1958).

Jones,[4] solvent and temperature effects were observed with benzoyl chloride. Results of these experiments seem to indicate that this splitting of the carbonyl band is due to conformational isomers but such conformational isomers cannot be considered in benzoyl chloride. Kohlrausch and others had pointed out that this phenomenon in benzoyl chloride is due to the association of two molecules by the hydrogen bonding between the carbonyl and benzene ring favored by the value of electronegative affinity of the chlorine atom.[7] At present, however, this hypothesis of Kohl raush is thought to be unlikely. In spite of the fact that $\Delta^2\beta$-butenolide studied by Jones, *et al.* shows temperature, solvent, and concentration effects, the splitting of its carbonyl band is thought to be due to the Fermi resonance and not to conformational isomers. Similarly, the splitting of the carbonyl band in benzoyl chloride seems more appropriate to be considered as due to the Fermi resonance.

(2) *para*-Substituted Benzoyl Halides

The carbonyl stretching vibration bands of these compounds are shown in Table II and in Fig. 2 and 3, from which it will be seen that all absorptions of *para*-substituted benzoyl chlorides in the C=O stretching region are split into two. Origin of the absorptions at 1730 and 1704 cm^{-1} respectively in *p*-nitrobenzoyl chloride and bromide is still obscure. If they are due to the presence of *p*-nitrobenzoic acid, they should appear in

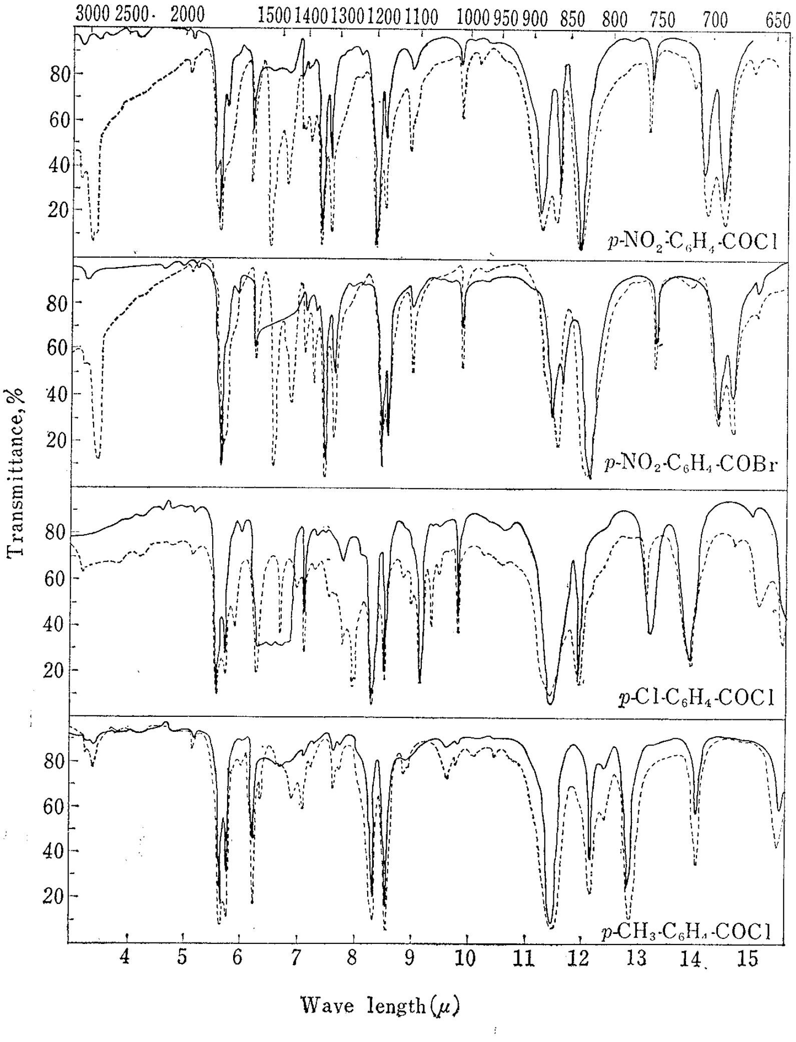

Fig. 2. Infrared Spectra of *para*-Substituted Benzoyl Halides

—— Nujol or liquid
------ CS$_2$ solution
1.0 mm. cell

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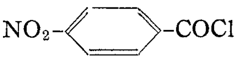
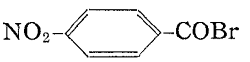
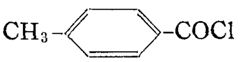
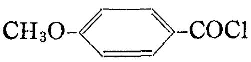
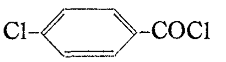
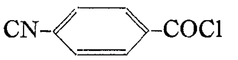
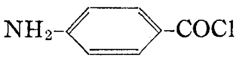
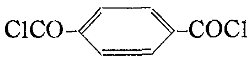
[7] L. Kabonec, K. W. F. Kohlrausch: Z. physik. Chem., 38, 96, 119 (1937); E. Herz, L. Kabonec, K. W. F. Kohlrausch: Sitzber. Akad. Wiss. Wien, Math.-naturw. Kl., Abt. [IIb], **152**, 65 (1943); cf. I. Cooke, *et al.*: Helv. Chim. Acta, **37**, 1280 (1954).

Table II. *para*-Substitutud Benzoyl Halides

Compound	Phase	CO region bands			$\nu_{\mathrm{C-\overset{O}{\overset{\|}{C}}-}}$	δ_{CH} in	$\nu_{\mathrm{-C-X}}$	δ_{CH} out-of-plane	Extra band
	(N)	1789(m.sh)	1764(s)	1727(m)	1193(s)	1166(s)	890(s)	838(v.s)	760(m)
	(CS_2)	1792(m)	1767(s)	1730(w)	1193(s)	1166(s)	891(s)	838(v.s)	756(m)
	(N)	1773(s)	1757(m)	1704(w)	1192(s)	1170(s)	867(s)	831(v.s)	756(m)
	(CS_2)	1783(s)	1754(m)	1704(w)	1190(s)	1170(s)	861(s)	828(v.s)	754(m)
	(l)	1775(s)	1739(s)		1203(s)	1171(s)	874(v.s)	824(s)	780(v.s)
	(CS_2)	1776(s)	1742(s)		1202(s)	1171(s)	874(v.s)	824(v.s)	780(v.s)
	(l)	1776(s)	1742(s)		1214(s)	1168(s)	874(v.s)	840(s)	781(m)
	(CS_2)	1776(s)	1745(s)		1211(s)	1164(s)	874(v.s)	839(s)	781(m)
	(l)	1783(s)	1742(s)	1695(m)	1200(s)	1174(s)	876(v.s)	838(s)	761(m)
	(CS_2)	1783(s)	1742(s)		1199(s)	1174(s)	876(v.s)	837(s)	756(m)
	(N)	1773(s)	1745(s)		1236(s)	1170(s)	895(s)	852(s)	763(m)
	(CS_2)	1793(s)	1754(s)		1229(s)	1168(s)	878(s)	847(s)	758(m)
	(l)	1786(s)	1745(s)		1203(s)	1178(s)	880(s)	853(s)	758(m)
	(CS_2)	1786(s)	1748(s)		1199(s)	1179(s)	878(s)	852(s)	762(m)
	(N)	1783(sh. s)	1773(s)	1727(s)	1196(s)	1171(sh. w)	865(s)	855(v.s)	692(w)
	(CS_2)	1783(s)	1773(s)	1736(s)	1193(s)	1168(w)	855(s)	846(v.s)	694(m)

N : Nujol, l : liquid, CS_2 : CS_2 solution, 0.1 mm. cell

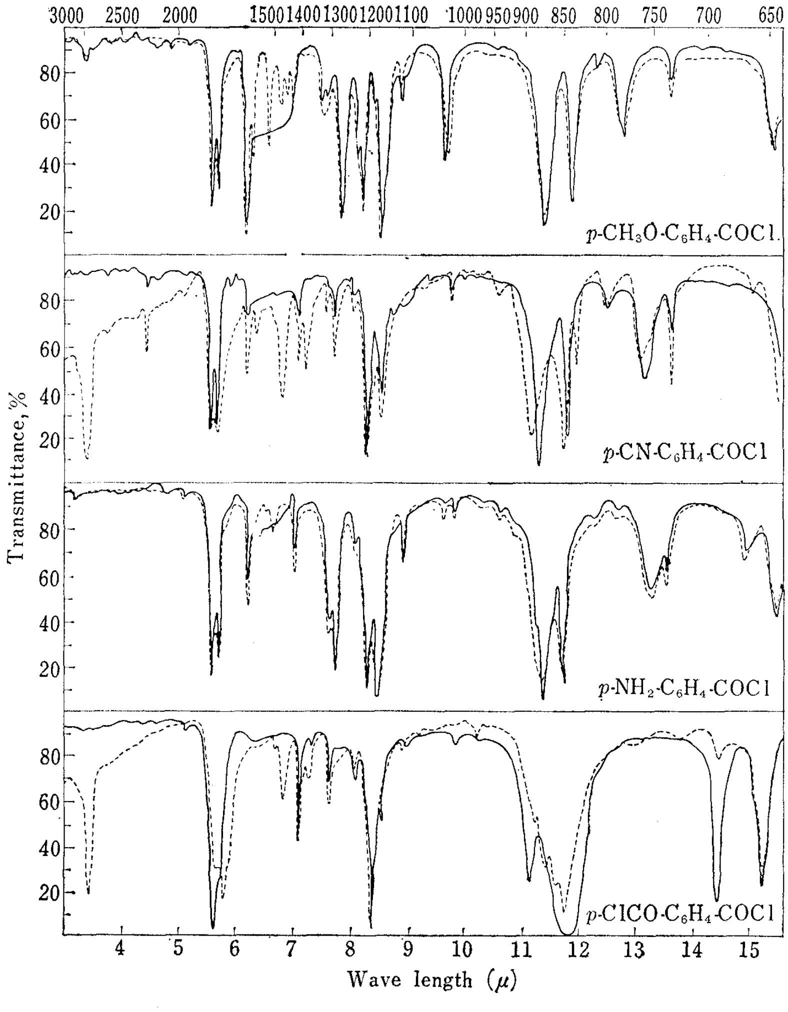


Fig. 3. Infrared Spectra of *para*-Substituted Benzoyl Chlorides

—— Nujol or liquid
------ CS_2 solution, 0.1 mm. cell

the same wave number in both compounds. Consequently, one of the three peaks in *p*-nitrobenzoyl chloride and bromide would be due to the Fermi resonance and the one should probably be interpreted as due to association between chlorine or bromine atom and the oxygen atom in the nitro group. In the case of *p*-chlorobenzoyl chloride in liquid, the absorption at 1695 cm^{-1} is not present in its spectrum in carbon disulfide solution so that it must be due to the presence of *p*-chlorobenzoic acid. In the case of terephthaloyl dichloride, two of the three absorptions are thought to be due to this C=O stretching absorption and the remaining one to the Fermi resonance of the $-\overset{\|}{C}-Cl$ overtone and carbonyl absorption, to be described later. As will be clear from Table V, the difference between ν_1 and $2\nu_2$ is generally below $+50$ and this fact suggests the occurrence of the Fermi resonance.

(3) *ortho*-Substituted Benzoyl Chlorides

The carbonyl stretching frequencies of these compounds are shown in Table III and Fig. 4. There are also two absorptions in the C=O stretching region in *ortho*-substituted benzoyl chlorides.

It should be noted that the C=O stretching vibration in *ortho*-substituted compounds is in a higher wave-number region than those of *meta*- and *para*-substituted benzoyl chlorides. This is thought to be due to the steric hindrance of a substituent in the *ortho*

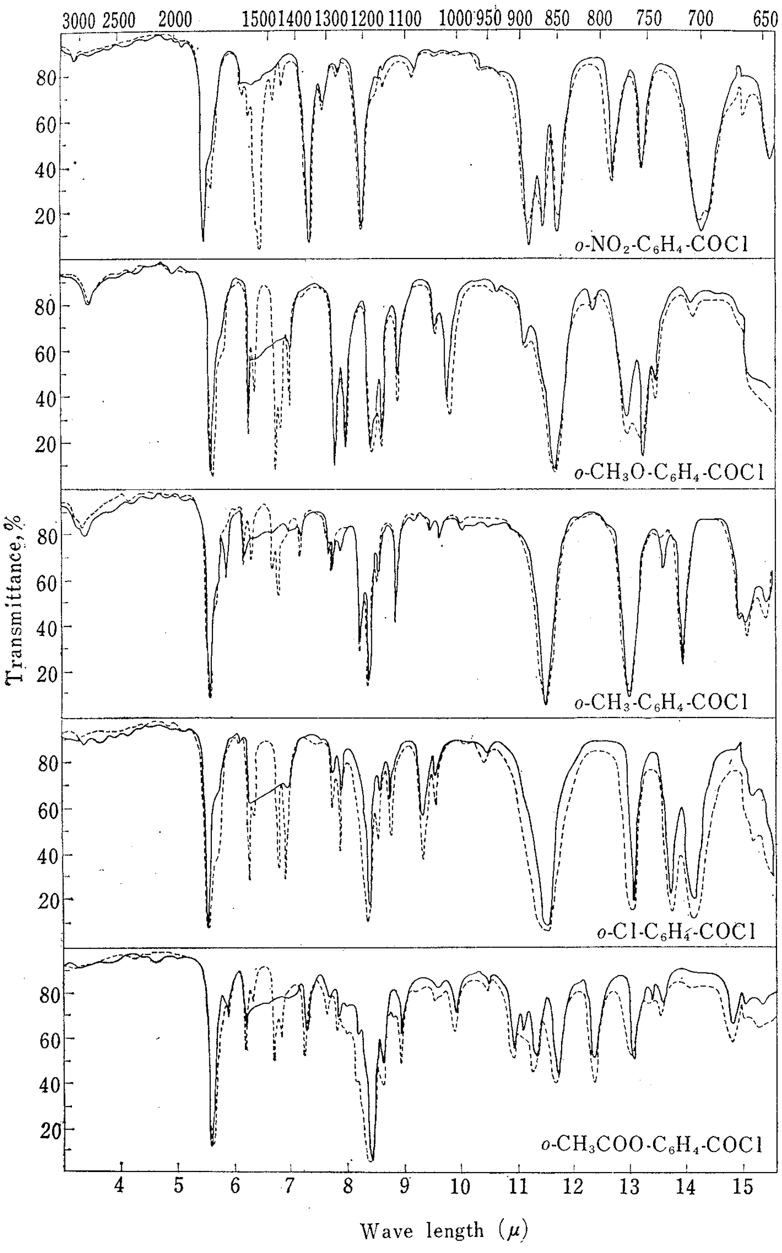
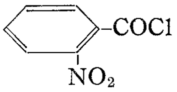
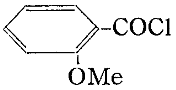
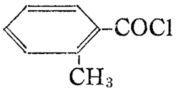
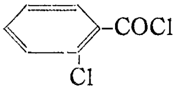
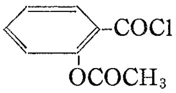


Fig. 4. Infrared Spectra of *ortho*-Substituted Benzoyl Chlorides

—— liquid
------ CS$_2$ solution, 0.1 mm. cell

Table III. *ortho*-Substituted Benzoyl Chlorides

Compound	Phase	ν_{CO} region bands		$\nu_{C-\overset{\overset{O}{\|}}{C}-}$	δ_{CH} in	ν_{-C-Cl}	δ_{CH} out-of-plane
	(l) (CS_2)	1805(s) 1805(s)	1773(s) 1767(s)	1203(s) 1202(s)	1170(w) 1164(w)	867(s) 868(s)	787(s) 784(s)
	(l) (CS_2)	1786(s) 1792(s)	1736(sh. s) 1736(sh.m)	1190(s) 1190(s)	1167(s) 1167(s)	858(v. s) 860(v. s)	773(s) 775(s)
	(l) (CS_2)	1783(s) 1779(s)	1748(m. sh) 1739(m)	1208(m) 1208(m)	1188(s) 1186(s)	867(v. s) 868(v. s)	769(s) 768(s)
	(l) (CS_2)	1792(s) 1795(s)	1751(sh. m) 1742(sh. m)	1190(s) 1189(s)	1166(m) 1160(m)	864(v. s) 864(v. s)	765(s) 762(s)
	(l) (CS_2)	1776(s) 1786(s)	1695(w) 1695(w)	1220(m) 1220(m)	1160(m) 1159(m)	855(m) 851(m)	765(m) 763(m)

l: liquid CS_2: solution, 0.1 mm cell

position, which makes it impossible for the benzoyl ring and the carbonyl group to take a coplanar position and the resonance between the benzoyl ring and carbonyl group decreases.

As will be seen from Table V, the difference between ν_1 and $2\nu_2$ is small, being less than 50, but some of the bands are not clearly split into two, as in *para*-substituted derivatives.

(4) *meta*-Substituted Benzoyl Chlorides

As shown in Table IV and in Figs. 5 and 6, the absorption of these derivatives in the C=O stretching region is split into two but one of them is weak in intensity or appears as a shoulder, and is not clear as in the foregoing compounds. As will be seen from Table V, the sign of the difference between ν_1 and $2\nu_2$ is minus (−), reverse of the signs of benzoyl halides and their *ortho*- and *para*-substituted derivatives. The origin of the absorption at 1825 cm^{-1} in *meta*-substituted benzoyl chloride is obscure and this absorption was excluded from the calculation of ν_1 of these compounds.

Bands in the 1200 cm^{-1} Region

As will be clear from Tables I～IV and Figs. 1～6, benzoyl halides and their *ortho*-, *meta*-, and *para*-substituted derivatives show two absorptions of very strong intensity in the region of 1200 cm^{-1}. The absorption in the lower frequency is thought to be the in-plane bending vibration of the ring CH. In general, benzene derivatives with a carbonyl group possess strong absorption of in-plane bending vibration of ring CH in this region. For example, this absorption appears at 1185 cm^{-1} in acetophenone,[8] at 1176 cm^{-1} in methyl, ethyl, propyl, and butyl benzoates,[9] and at 1175 cm^{-1} in butyl thiobenzoate.[3b] In analogy with these compounds, the in-plane bending vibration of ring CH in benzoyl halide derivatives is assumed to appear at around 1170 cm^{-1}.

Origin of the absorption in the higher frequency at around 1200 cm^{-1} in benzoyl halides has not been found in any literature. In acetophenone, antisymmetric stretching vibration of C-C-C in $\mathrm{C\text{-}\overset{\overset{O}{\|}}{C}\text{-}C}$ structure appears at 1270 cm^{-1} and this absorption is the strongest in the spectrum of acetophenone.[8] The absorptions of thiobenzoic acid esters and thiobenzoic acid are very similar to that of benzoyl chloride, according to the report

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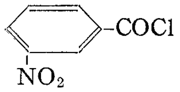
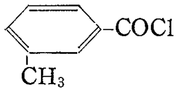
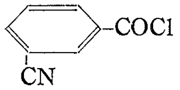
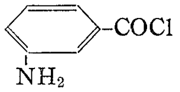
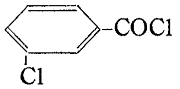
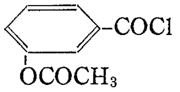
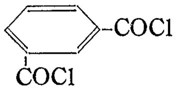
[8] Sadtler Card No. 3220.

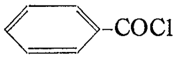
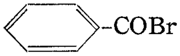
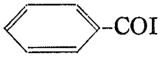
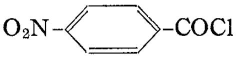
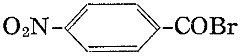
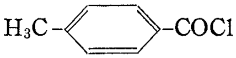
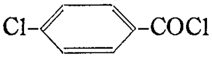
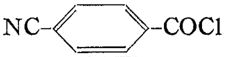
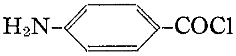
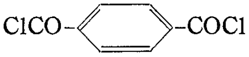
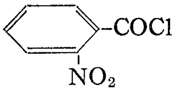
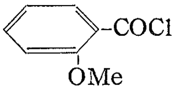
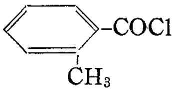
[9] S. Yoshida: Unpublished data.

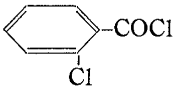
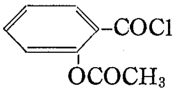
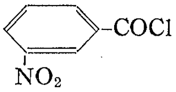
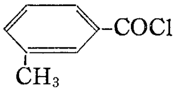
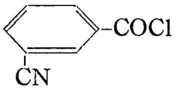
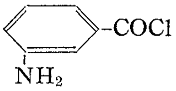
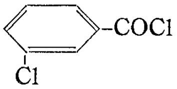
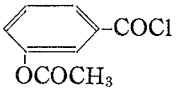
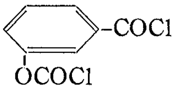
Table IV. *meta*-Substituted Benzoyl Chlorides

Compound	Phase	ν_{CO} region bands			$\nu_{C-\overset{O}{\overset{\|}{C}}-}$	δ_{CH} in	ν_{-C-Cl}	δ_{CH} out-of-plane	Extra band
	(l)	1792(m)	1757(s)		1202(s)	1167(w)	928(s)	813(m)	730(s)
	(CS$_2$)	1789(m)	1761(s)		1200(s)	1163(w)	927(s)	810(m)	729(s)
	(l)	1770(s)	1736(sh.m)	1695(sh.w)	1242(s)	1151(s)	929(s)	800(s)	768(s)
	(CS$_2$)	1772(s)	1733(m)	1695(w)	1241(s)	1149(s)	919(s)	803(s)	769(s)
	(N)	1783(s)	1733(sh.m)		1235(s)	1147(s)	929(s)	808(s)	747(s)
	(CS$_2$)	1776(s)	1730(m)		1232(s)	1147(s) 1142(s)	932(s)	800(s)	749(s)
	(l)	1764(s)	1692(w)		1195(s)	1143(s)	909(s)	805(s)	746(s)
	(CS$_2$)	1768(s)	1695(w)		1196(s)	1143(s)	912(s)	801(s)	747(s)
	(l)	1825(sh.m)	1761(s)	1730(sh.w)	1193(v s)	1162(m)	908(v.s)	796(s)	754(s)
	(CS$_2$)	1825(sh.m)	1770(s)	1742(sh.w)	1192(v s)	1163(m)	907(v.s)	792(s)	754(s)
	(l)	1776(s)			1239(s)	1140(m)	873(m)	809(m)	712(m)
	(CS$_2$)	1783(s)			1235(s)	1139(m)	870(m)	804(m)	710(m)
	(N)	1836(w)	1770(s)	1745(s)	1241(s) 1227(s)	1143(s)	850(s)	821(m)	733(m)
	(CS$_2$)	1818(sh.w)	1770(sh s)	1773(s)	1235(s)	1143(s)	857(s)	808(m)	734(m)

N : Nujol l : liquid CS$_2$: CS$_2$ solution, 0.1 mm. cell

Table V. Relationship between the Position of Carbonyl Bands and -C-X Stretching Bands that might enter into Fermi Resonance (cm^{-1})

Benzoyl halides	$\nu_1=1/2\cdot(\nu_A+\nu_B)$	ν_2	$2\nu_2$	$\nu_1-2\nu_2$
	1755	870	1740	+15
	1740	850	1700	+40
	1730	830	1660	+70
para-Substituted benzoyl halide				
	1780	891	1782	− 2
	1769	861	1721	+48
	1759	874	1748	+11
	1761	875	1750	+10
	1763	876	1752	+11
	1774	878	1756	+18
	1767	878	1756	+10
	1764	855	1710	+54
orthe-Substituted benzoyl chlorides				
	1786	885	1770	+16
	1764	860	1720	+42
	1759	868	1736	+23

	$\nu_1=1/2\cdot(\nu_A+\nu_B)$	ν_2	$2\nu_2$	$\nu_1-2\nu_2$
	1759	864	1728	+31
	1741	851	1702	+39
meta-Substituted benzoyl halides				
	1775	928	1856	−79
	1753	919	1838	−85
	1753	932	1864	−101
	1732	912	1824	−92
	1756	907	1814	−58
	1783	870	1740	+43
	1787	969	1938	−151

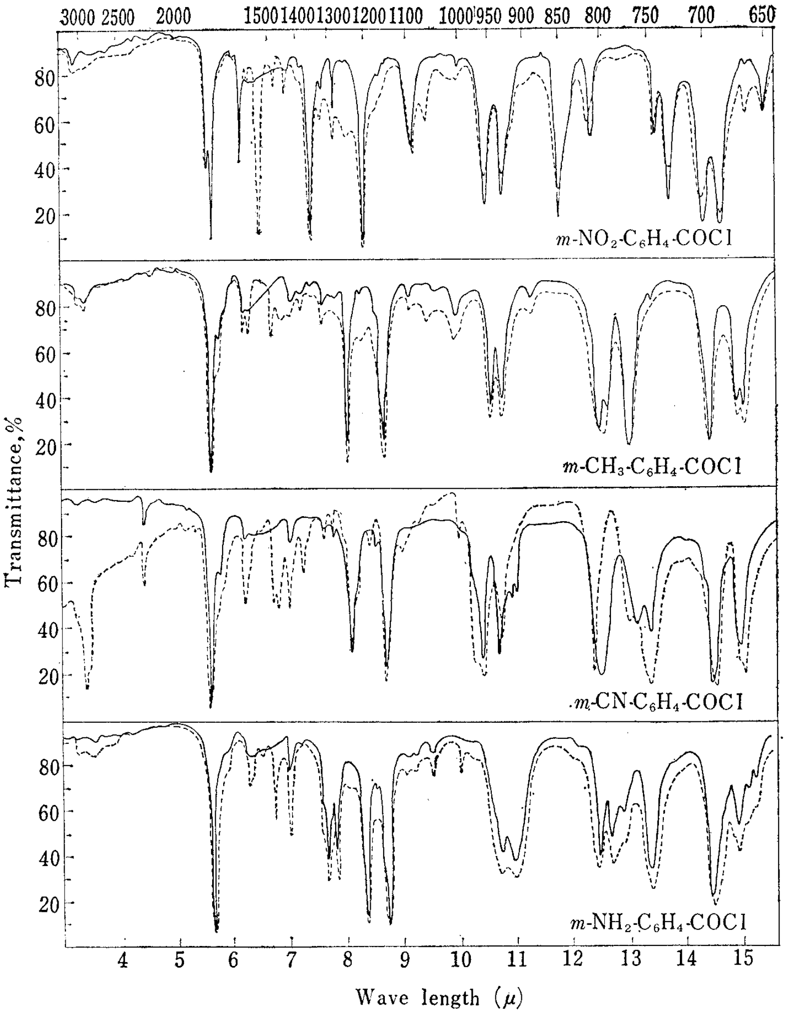


Fig. 5. Infrared Spectra of *meta*-Substituted Benzoyl Chlorides

—— Nujol or liquid
------ CS_2 solution, 0.1 mm. cell

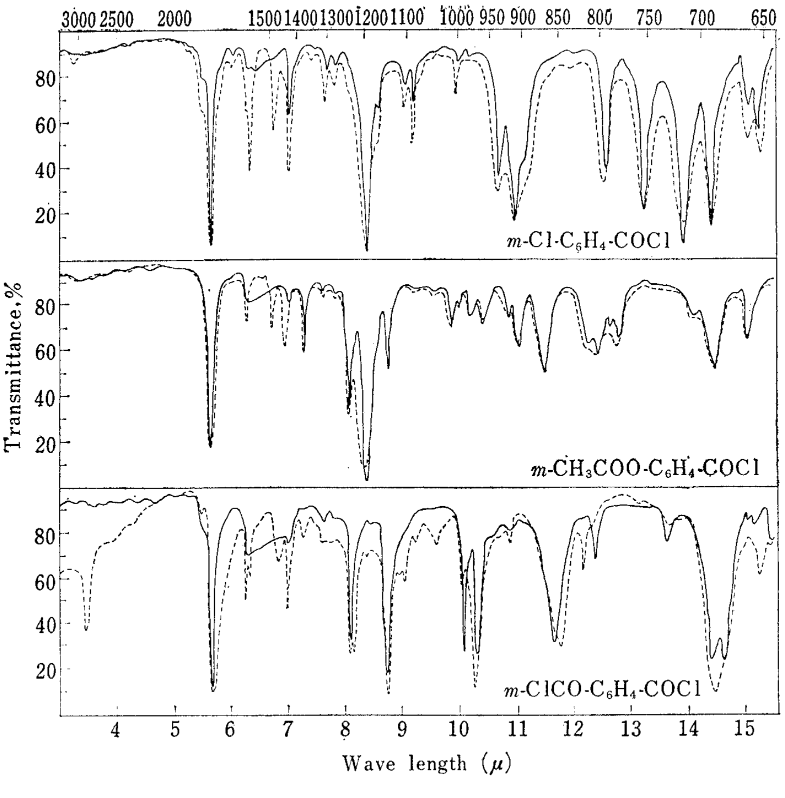


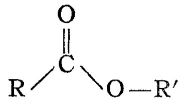
Fig. 6. Infrared Spectra of *meta*-Substituted Benzoyl Chlorides

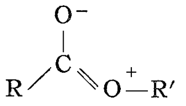
—— Nujol or liquid
------ CS_2 solution. 0.1 mm. cell

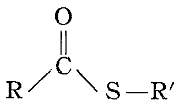
of Nyquist and Potts.[3b] The absorption of butyl thiobenzoate at $1200\,cm^{-1}$ is assigned to the $-C-\overset{\|}{C}-$ stretching vibration in the $-C-\overset{\overset{O}{\|}}{C}-S-$ structure. In analogy with these compounds, the absorption of benzoyl halide derivatives at around $1200\,cm^{-1}$ may be assigned to the $-C-\overset{\|}{C}-$ stretching vibration in the $C-\overset{\overset{O}{\|}}{C}-X$ structure. However, data in Table I indicate that the $-C-\overset{\|}{C}-$ streching vibration band shifts 1202 to a lower frequency 1186 cm^{-1} as the negativity of the halogen atom decreases from chlorine to bromine to iodine and the in-plane bending vibration of the ring CH shifts correspondingly to a lower frequency from 1172 to $1161\,cm^{-1}$. Consequently, the $-C-\overset{\|}{C}-$ stretching vibration and ring CH in-plane bending vibration in benzoyl halides are considered to be coupled to each other.

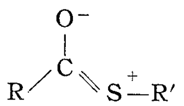
Stretching Vibrations of $-\overset{\|}{C}-X$ (X=Halogen Atom)

Benzoyl halides and their *ortho*-, *meta*-, and *para*-substituted derivatives all have strong absorption in the region of $920\sim830\,cm^{-1}$. This absorption is the strongest and broad in benzoyl halides and their *ortho*- and *para*-substituted derivatives, and is most characteristic, except in *meta*-substituted derivatives. This absorption is generally considered to be that of the stretching vibration of C–X. The C–Cl stretching vibration of acetyl chloride appears at $590\,cm^{-1}$[10] and the strongest absorption in benzoyl chloride appears at $870\,cm^{-1}$. If this absorption at $870\,cm^{-1}$ in benzoyl chloride is taken as that of the C–Cl stretching vibration, there arises the question of why the absorption of acetyl chloride at $590\,cm^{-1}$ has shifted to such a high frequency in benzoyl chloride. In esters and thioesters, the following two resonance forms are thought to be present.[3b,11]

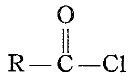

(I)

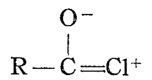

(II)


(III)


(IV)

In thioesters, (IV) is thought to be comparatively more important than the ester resonance form. In analogy with esters and thioesters, acid chlorides are also thought to have the following two resonance forms.


$R-\overset{\overset{O}{\|}}{C}-Cl$
(V)


$R-\overset{\overset{O^-}{|}}{C}=Cl^+$
(VI)

If the resonance form of (V) is the main one in acetyl chloride and the resonance form of (VI) is the main one in benzoyl chloride, the shift from $590\,cm^{-1}$ to a higher frequency of $870\,cm^{-1}$ may be explained as the increased double bond characters of the C–Cl bond. The C=O stretching vibration does not shift very much to a lower frequency, from $1800\,cm^{-1}$ of actyl chloride to $1773\,cm^{-1}$ of benzoyl chloride. Main contribution of resonance form of (VI) is convenient for the interpretation of the C–Cl absorption but not so for carbonyl absorption. However, the fact that the C–Cl bond in benzoyl chloride has increased ionic nature than that in acetyl chloride can be presumed from the value of eQq of quadrupole resonance.[12] This value of eQq of benzoyl chloride is

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[10] R.S. Rasmussen, R.R. Brattain: J. Am. Chem. Soc., **71**, 1073 (1949); B.P. Susz, J.J. Wuhrmans: Helv. Chim. Acta, **40**, 971 (1957); K.W. Kohlrausch: "Ramanspektren," Leipzig, (1943).

[11] R.B. Barnes, R.C. Gore, V. Liddel, V.Z. Williams: "Infrared Spectroscopy." Reinhold, New York (1944).

[12] P.J. Bray: J. Chem. Phys., **23**, 703 (1955).

of eQq of benzoyl chloride is 29.93 MC, which smaller than that of around 35 MC in usual acid chlorides, and this is considered to indicate the increased ionic property of the C-Cl bond. It would be more convenient to consider that, instead of a resonance form like (Ⅵ), the π-electron of the benzene ring causes C-Cl to become polar and does not affect the bond order of C=O to such a great extent. Absorptions of C-Cl, C-Br, and C-I in benzoyl chloride, bromide, and iodide are present respectively at 870, 850, and 830 cm^{-1}, there being less shift to the lower frequency than the usual C-X bond from chlorine to iodine atom. From such a consideration, there is still a doubt about assigning these absorptions to the C-X stretching vibration, although there is a great difference between the C-F and C-Cl absorptions.[13] It may therefore be concluded that the strong, characteristic absorption in the region of 920~830 cm^{-1} is due to C-X stretching vibration. In *ortho*- and *para*-substituted derivatives, such absorption is present in the region of 890~850 cm^{-1}, but there is no absorption in this region in *meta*-substituted derivatives and the absorption is shifted to the region of 990~950 cm^{-1}, with weaker intensity than those of *ortho*- and *para*-substituted derivatives. It is still unknown why this occurs in *meta*-substituted derivatives. This absorption appears in especially high frequency of 970 cm^{-1} in *m*-phthaloyl chloride. In addition, the presence of an absorption of similar strong intensity in slightly higher frequency region than that of C-Cl is the characteristic in *meta*-substituted derivatives in general and the origin of this absorption is also obscure.

Ring C-H Out-of-plane Bending Frequencies

CH bending frequencies of benzoyl chloride and its *para*-substituted derivatives were discussed in detail in the previous report[2] and some supplementary data are given in Tables I and Ⅱ. The CH bending absorptions of *ortho* and *meta* derivatives are indicated in Tables Ⅲ and Ⅳ. In *meta* derivatives, this absorption is present at around 800 cm^{-1}, while it is near 770 cm^{-1} in *ortho* derivatives.

Extra Bands

Detailed discussions were given in a previous paper[2] regarding extra bands and will be omitted here. Extra bands of benzoyl chloride and its *para*-substituted derivatives were reported in the previous report.[2] The extra band is not present in the *ortho*-substituted derivatives because there is no coplanarity of the benzene ring and CO-Cl group due to *ortho* substituent. In *meta*-substituted derivatives, the extra band is present in the region of 770~710 cm^{-1}, as shown in Table Ⅳ.

Absorptions below the Extra Band

Absorptions of several compounds were measured to 400 cm^{-1} in KBr and the data are given in Table Ⅵ. Assignment of these absorptions has not been made.

Summation Bands of CH Out-of-plane Bending Frequencies

These bands are given for benzoyl chloride and bromide in Fig. 7 and Table Ⅶ. Calculation of the assignment of CH bending frequencies according to the method of Kakiuchi[14] give the values of 937 cm^{-1} for b, 994 cm^{-1} for c, and 978 cm^{-1} for e, while the observed values are 772 cm^{-1} for a, 932 cm^{-1} for b, 1001 cm^{-1} for c, and 986.2 cm^{-1} for e. The shape of summation bands is very similar to that of methyl benzoate.[15]

The summation bands of *para*-substituted derivatives are given in Fig. 8 and Table Ⅷ. In these compounds, one strong absorption in the region of 1946~1919 cm^{-1} is characteristic.

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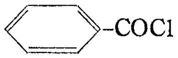
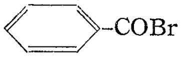
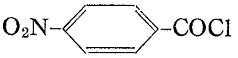
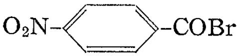
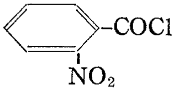
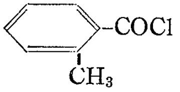
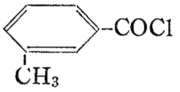
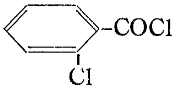
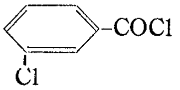
13) C-F stretching vibration in benzoyl fluoride is at around 1000 cm^{-1} (cf. F. Seil, J. Langer; Chem. Ber., **91**, 2553 (1958)).

14) Y. Kakiuchi : Nippon Kagaku Zasshi, **80**, 21, 28, 250 (1959).

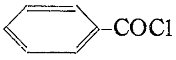
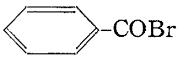
15) *Idem* : *Ibid*., **80**, 28 (1959).

Table VI. Absorption Bands below Extra Bands or CH Out-of-plane Bending Absorptions (cm^{-1})

	670(s), 648(s), 615(w), 503(br. w)
	680(s), 632(m), 614(w), 483(br. w)
	709(m), 691(s), 635(m), 557(m), 518(w. br)
	698(s), 686(s), 619(m), 550(m), 517(w. br)
	753(s), 700(s), 690(s), 641(s)
	714(m), 648(m), 614(s)
	716(s), 669(s. sh), 664(s), 647(s)
	693(s), 670(s), 665(s)
	725(s), 704(s), 655(m. sh), 640(s)
	714(s), 691(s), 661(w. br), 652(s)

Prism : KBr, Nujol.

Table VII. Summation Bands of Benzoyl Halides (cm^{-1})

		
$\alpha 1$	1988	1922
$\alpha 2$	1972	1969
$\beta 1$	1931	1929
$\beta 2$	1915	1911
$\gamma 1$	1883	

5% CCl_4 solution, 2.0 mm. cell

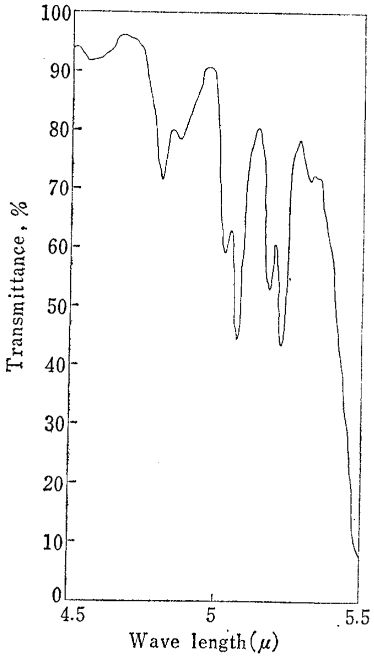
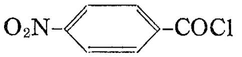
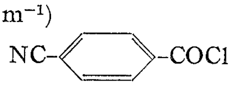
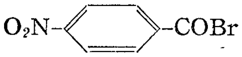
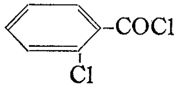
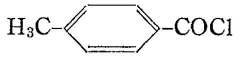
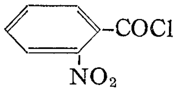
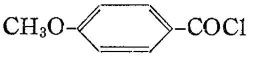
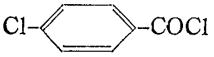


Fig. 7. Summation Bands of Benzoyl Chloride (5% CCl_4 solution, 2.0 mm. cell) →

Table VIII. Summation Bands of *para-* and *ortho-*Substituted Benzoyl Chlorides (cm^{-1})

		1946(s), 1908(w)		1942(s)
		1942(s)		1971(m), 1938(m)
		1931(s)		1981(m), 1948(m)
	1931(m. sh)	1919(s), 1905(w)		
	1976(w)	1927(s)		

4% CCl_4 solution, cell thichness, 20 mm.

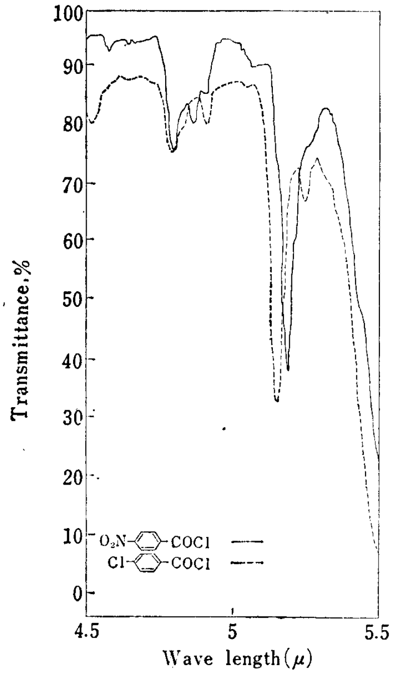


Fig. 8. Summation Bands of *para*-Nitro and Chloro-benzoyl Chloride (5% CCl_4 solution, 2.0 mm. cell)

700

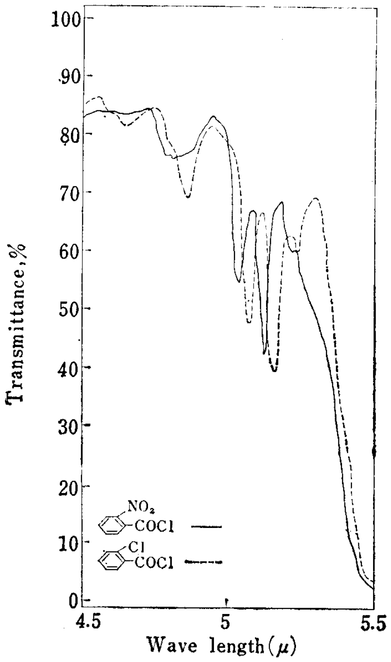


Fig. 9. Summation Bands of *meta*-Nitro and Chloro-benzoyl Chloride (5% CCl_4 solution, 2.0 mm. cell)

The summation bands of *ortho*-substituted derivatives are given in Fig. 9 and Table VIII, and the characteristic absorptions in these compounds are two bands at 1970~1980 and 1938~1948 cm^{-1}.

Experimental

All the compounds used here were synthesized by the method given in past literature and their infrared spectra were measured immediately after preparation. The spectra were measured with the Perkin-Elmer Spectrophotometer, Model 21. Conditions of the measurement are given with each Table and Figure.

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Summary

Infrared absorptions of benzoyl halides and their *ortho*-, *meta*-, and *para*-substituted derivatives were examined and following conclusions were drawn.

1) Absorptions of these compounds in the C=O region are mostly split into two. This is due to the Fermi resonance of the C=O stretching vibration and overtone of C-X (X= halogen atom) stretching vibration.

2) There are two strong absorptions in the region of 1240~1140 cm^{-1}. The absorption in the highere frequency is that of $-C-\overset{O}{\overset{\|}{C}}-$ stretching vibration and that in the lower frequency is the absorption of ring CH in-plane bending vibration.

3) In majority of compounds with the exception of *meta*-substituted derivatives, the -C-X (X=halogen atom) stretching vibration is the strongest absorption and is the most characteristic.

4) The summation bands are similar to those of benzoic acid esters.

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