542. *Infra-red Absorption of the Carbonyl Group. Part I. Diacyl Peroxides, Per-esters, and Per-acids.*

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Infra-red carbonyl absorption frequencies are reported for 18 symmetrical diacyl peroxides, six unsymmetrical diacyl peroxides, five per-esters, and perbenzoic acid. Characteristic carbonyl frequencies are given for diacyl peroxides and per-esters. Correlations are established between carbonyl frequencies of these compounds, and those of the corresponding acids, and also with Hammett's σ factors and thus with decomposition rates of benzoyl peroxides.

Although peroxides are of considerable interest in catalysed polymerisation and in the autoxidation and degradation of rubber, comparatively little infra-red or Raman work has been reported on them. In particular the O–O stretching frequency (ν_{O-O}) has not been assigned with certainty, although it has been variously and tentatively assigned by Shreve, Heether, Knight, and Swern (*Anal. Chem.*, 1951, **23**, 282) and Leadbeater (*Compt. rend.*, 1950, **230**, 829). There is, moreover, some reason to consider that there should be no very characteristic ν_{O-O}, caused by interaction with the adjacent ν_{O-O}. Unless the C–O–O angle is nearly 90°, considerable interaction of vibrations is to be expected (Herzberg, "Infra-red and Raman Spectra of Polyatomic Molecules," Van Nostrand, 1945, p. 199). A second difficulty is that, in hydrogen peroxide, the only peroxide for which a definite assignment has been made, the O–O stretching vibration has a weak infra-red absorption (Giguere, *J. Chem. Physics*, 1950, **18**, 88), which suggests that it may also be weak in other symmetrical peroxides; it is seldom possible to obtain simple peroxides of sufficient purity to justify the assignment of weak absorptions.

For a structural diagnosis of the benzoyl and acetyl derivatives of 1-hydroxy*cyclo*hexyl 1-hydroperoxide carried out for Dr. W. Cooper (*J.*, 1951, 1340) characteristic carbonyl frequencies ($\nu_{C=O}$) were established for diacyl peroxides and per-esters, and differentiated from those of other carbonyl compounds. In the course of this work, marked correlations were observed between $\nu_{C=O}$ values of corresponding diacyl peroxides, per-esters, and acids. These, together with the work of Flett (*Trans. Faraday Soc.*, 1948, **44**, 767) on the relationship of $\nu_{C=O}$ and reaction rates of a series of benzoic acids, suggested that similar relationships might exist in the case of peroxides, and this would shed some light on relative strengths of peroxide bonds.

EXPERIMENTAL.

Apart from those which were commercially available, all the diacyl peroxides and per-esters were prepared by Dr. W. Cooper. The only evidence of purity of the diacetyl peroxide was the simplicity of its spectrum. Perbenzoic acid as prepared contained some benzoic acid which was mainly removed by two short-path vacuum distillations with a Washburn molecular still. Other reference compounds used were of normal laboratory standard. The carbonyl absorption is sufficiently strong that no interference was experienced from impurities, other than compounds either possessing, or hydrogen-bonded with, carbonyl groups.

TABLE I.

Symmetrical diacyl peroxides (aliphatic).

$\nu_{C=O}$ (cm.$^{-1}$).

	Solvent.	*A.*	*B*	Mean.	Split.	F_I.
Acetyl	CCl_4	1820 ± 1	1796 ± 1	1808 ± 1	24 ± 2	6470
Butyryl	—	1816 ± 4	1784 ± 2	1800 ± 3	(32 ± 6)	6570
Octanoyl	—	1812 ± 1	1786 ± 1	1799 ± 2	26 ± 3	6610
Lauroyl	CCl_4	1811 ± 1	1786 ± 1	1798·5 ± 1	25 ± 2	—
Myristoyl	CCl_4	1811 ± 1	1785 ± 1	1798 ± 1	26 ± 2	—
Palmitoyl	CCl_4	1812 ± 1	1786 ± 1	1799 ± 1	26 ± 2	—
Stearoyl	CCl_4	1811 ± 1	1786 ± 1	1798·5 ± 1	25 ± 2	—

Average split (excl. butyryl), 25·3 cm.$^{-1}$.

The spectrophotometer used was a standard single-beam Grubb–Parsons instrument with sodium chloride prism; 0·1-mm. slits were used, except with Nujol mulls, for which larger slits were used. All spectra were plotted as percentage transmissions, and absorption frequencies were corrected for the atmospheric-water absorption at 1699·5 cm.$^{-1}$. Sharp absorptions could be read to about 1 cm.$^{-1}$, and estimated errors are given in the results (Tables I—IV). These estimates of accuracy are applicable within the series of results in this paper, but a small systematic error may arise from possible inaccuracies of the calibration curve. To minimise solvent shifts, carbon tetrachloride (" AnalaR ") was used where possible.

TABLE II.

Symmetrical diacyl peroxides (aromatic).

$\nu_{C=O}$ (cm.$^{-1}$).

	Solvent.	*A.*	*B.*	Mean.	Split.	F_I.*	σ.
Phthaloyl	Nujol	1805 ± 2	1783 ± 2	1794 ± 2	22 ± 4	4000	—
	Dioxan	1800 ± 5	1784 ± 2	1792 ± 4	26 ± 7	—	—
p-Nitrobenzoyl	$C_2H_4Cl_2$	1799 ± 2	1779 ± 1	1789 ± 2	20 ± 3	4640	0·778
	CCl_4	1804 ± 1	1782 ± 1	1793 ± 1	22 ± 2	—	—
m-Nitrobenzoyl ...	$C_2H_4Cl_2$	1800 ± 2	1777 ± 1	1788·5 ± 2	23 ± 3	4690	0·710
m-Chlorobenzoyl ...	,,	1797 ± 2	1773 ± 2	1785 ± 2	24 ± 4	5200	0·373
p-Iodobenzoyl	,,	1792 ± 2	1771 ± 1	1781·5 ± 2	21 ± 3	—	0·276
p-Bromobenzoyl ...	,,	1793 ± 1	1771 ± 1	1782 ± 1	22 ± 2	5420	0·232
p-Chlorobenzoyl ...	,,	1787 ± 2	1765 ± 1	1776 ± 2	22 ± 3	5500	0·227
p-Fluorobenzoyl ...	,,	1789 ± 1	1768 ± 1	1778·5 ± 1	21 ± 2	5280	0·062
Benzoyl	CCl_4	1792 ± 1	1771·5 ± 1	1782 ± 1	20 ± 2	5690	0
	$C_2H_4Cl_2$	1789 ± 2	1767 ± 1	1778 ± 2	22 ± 3		
	$CH_3{\cdot}NO_2$	1788 ± 2	1766 ± 1	1777 ± 2	22 ± 3		
p-Toluoyl	$C_2H_4Cl_2$	1785 ± 2	1763 ± 2	1774 ± 2	22 ± 4	5960	−0·170
p-Methoxybenzoyl	,,	1780 ± 2	1758 ± 2	1769 ± 2	22 ± 4	6120	−0·268

Average split, 22 cm.$^{-1}$.

* For definition of F_I see p. 2461.

TABLE III.

Mixed or unsymmetrical benzoyl peroxides.

$\nu_{C=O}$ (cm.$^{-1}$).*

	A.	*B.*	Mean.	Split.
Acetyl benzoyl	1811 ± 1	1779 ± 1	1795 ± 1	32 ± 2
Benzoyl stearoyl	1811 ± 2	1786 ± 1	1798·5 ± 2	25 ± 3
Benzoyl *p*-nitrobenzoyl	1797 ± 1	1773 ± 1	1785 ± 1	24 ± 2
Benzoyl *m*-nitrobenzoyl	1796 ± 2	1771·5 ± 1	1784 ± 2	24·5 ± 3
Dibenzoyl phthaloyl	1801 ± 1	1776 ± 1	1788·5 ± 2	25 ± 3
Adipyl dibenzoyl	1808 ± 2	1775 ± 1	1791·5 ± 2	33 ± 3

* All these were determined in CCl_4 solutions.

TABLE IV.

Per-esters and per-acid.

	Solvent.	$\nu_{C=O}$ (cm.$^{-1}$).	Other $\nu\nu$.
tert.-Butyl peracetate	—	1783 ± 2	—
tert.-Butyl perbenzoate	—	1758 ± 2	—
Di-*tert.*-butyl perphthalate	CCl_4	1772 ± 2	—
" *tert.*-Butyl perphthalic acid "	Nujol	1771 ± 1	1705, 1685, 1674
(*tert.*-Butyl *o*-carboxybenzoyl peroxide)	Dioxan	1776 ± 1	1730 ± 1
" *tert.*-Butyl permaleic acid " (*tert.*-Butyl β-carboxyacrylyl peroxide)	Dioxan	1776 ± 1	1737 ± 3
Perbenzoic acid	CCl_4	1732 ± 1	1696 ± 2

RESULTS AND DISCUSSION.

Symmetrical Diacyl Peroxides.—All of these showed a pair of strong carbonyl absorptions, the stronger being rather sharper and at a lower frequency (Fig. 1). The seven aliphatic diacyl peroxides examined had absorptions at 1811—1820 and 1784—1796 cm.$^{-1}$ with an average split of 25·3 cm.$^{-1}$ (Table I). Eleven aromatic diacyl peroxides had absorptions at 1780—1805 and 1758—1784 cm.$^{-1}$, with an average split of 22 cm.$^{-1}$ (Table II). The intensities of the two bands observed are not dependent upon concentration and are not, therefore, connected with any form of association. Coupling between the identical characteristic stretching vibrations of the two carbonyl bonds causes a frequency splitting, and gives rise to a pair of absorptions on either side of the " free " or unperturbed frequency (Herzberg, *op. cit.*). The mean of the two observed frequencies gives the characteristic frequency (when the split is small), and the split is a measure of the efficiency of the coupling. Thus diacyl anhydrides show a similar pair of absorptions (Thompson, *J.*, 1948, 328) though with a larger split (average 65 cm.$^{-1}$) (Modest and Szmuszkovicz, *J. Amer. Chem. Soc.*, 1950, **72**, 577; Davison, unpublished work) resulting from the shorter coupling link. The carbonyl absorptions of anhydrides may also be differentiated from those of diacyl peroxides by their contours, the stronger and sharper absorption of the pair being at a higher frequency (Fig. 1).

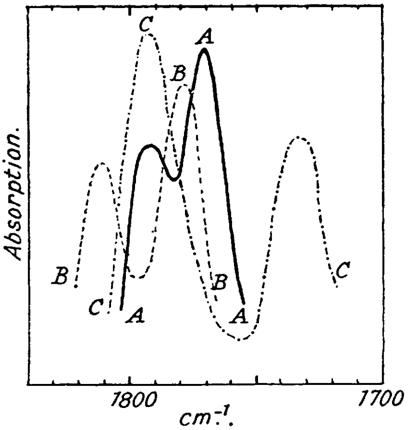
Correlations between $\nu_{C=O}$ of diacyl peroxides, per-esters, and per-acids indicate that this characterisation may need considerable extension towards higher frequencies. Linear extrapolation (Fig. 3) would lead to frequencies of 1867 and 1840 cm.$^{-1}$ for trichloroacetyl peroxide, but such extrapolation probably gives too high a frequency in these ranges.

Unsymmetrical Acyl Benzoyl Peroxides.—These similarly showed a pair of strong carbonyl absorptions of similar intensity and contour to those of the symmetrical compounds, but at 1796—1811 and 1771—1786 cm.$^{-1}$ (Table III). In unsymmetrical compounds R·O·OBz (where R is an acyl group) the two carbonyls will in general have different " free " or unperturbed frequencies. Thus acetyl benzoyl peroxide gives one absorption at 1811 cm.$^{-1}$, which can be assigned to the acetyl group (cf. 1808 cm.$^{-1}$, mean $\nu_{C=O}$ frequency of diacetyl peroxide), and one at 1779 cm.$^{-1}$ which is assigned to the benzoyl group (cf. 1782 cm.$^{-1}$, mean $\nu_{C=O}$ for dibenzoyl peroxide). In all these cases coupling causes some interaction and frequency splitting, which is greater when the " free " frequencies are closer. In this case a displacement of 3 cm.$^{-1}$ may be attributed to resonance splitting, and in the limiting case of dibenzoyl peroxide, coupling alone accounts for a split of 21 cm.$^{-1}$.

In Fig. 2, $\nu_{C=O}$ of peroxides R·O·OBz are plotted against their $\nu_{C=O}$ means and against the mean $\nu_{C=O}$ of peroxides R·O·OR. Where spectra were measured in ethylene dichloride, 4 cm.$^{-1}$ has been added to bring them into line with frequencies in carbon tetrachloride. Broken lines represent unperturbed frequencies (on the assumption that they are unaffected by replacement of Bz by R), and the chain line is the mean of these unperturbed frequencies. The full curves represent the form of theoretical interaction curves, fitted to the experimental points (Herzberg, *op. cit.*, Fig. 70, p. 216). With the exception of benzoyl stearoyl peroxide [shown thus ()], agreement is reasonable, and is consistent with resonance splitting and the assumption that the characteristic frequencies of the carbonyl groups are independent of the nature of the more remote acyl group. This assumption is consistent with the general decrease of influence with distance (cf. Watson, " Modern Theories of Organic Chemistry," O.U.P., 1941, p. 28) and direct spectroscopic evidence that carbonyl frequencies of esters are relatively independent of the nature of the alcoholic group (Hartwell, Richards, and Thompson, *J.*, 1948, 1436).

As discussed in the case of symmetrical peroxides, the characteristic frequencies of 1796—1811 and 1771—1786 cm.$^{-1}$ need some extension to allow for unsymmetrical peroxides such

FIG. 1.



A. Benzoyl peroxide. B. Acetyl benzoyl peroxide. C. Benzoic anhydride.

FIG. 3.

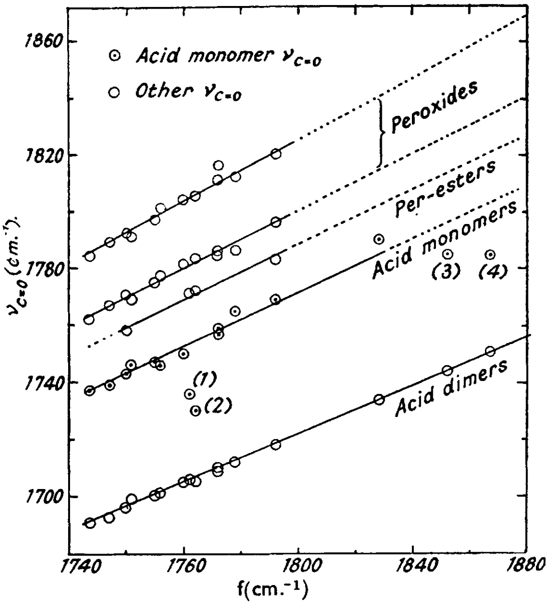
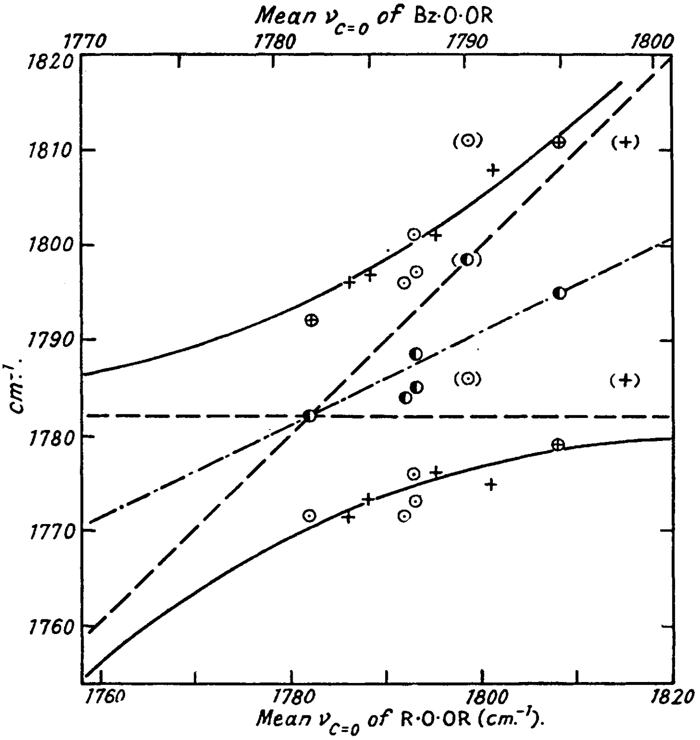


FIG. 2.



+ *Observed against mean* Bz·O·OR.
⊙ ,, ,, *mean* R·O·OR.
◐ *Mean* Bz·O·OR *against mean* R·O·OR.

——— *Unperturbed (theoretical).*
— — — — *Theoretical mean* Bz·O·OR.
— · — · — *Theoretical.*

as benzoyl trichloroacetyl peroxide which would be expected to show an absorption at 1782 cm.$^{-1}$ (benzoyl) and one at considerably higher frequency assigned to the trichloroacetyl group. As before, linear extrapolation suggests an upper limit to this at about 1854 cm.$^{-1}$.

Per-esters and Per-acids.—Esters of only five per-acids were available and these show a carbonyl absorption 1758—1783 cm.$^{-1}$ (Table IV), which probably extends over the wider range 1747—1820 cm.$^{-1}$. This characteristic frequency is clearly differentiated from that of normal esters (1715—1765 cm.$^{-1}$) (Thompson, *loc. cit.*) and has been used for the structural diagnosis of per-esters for Dr. W. Cooper (*loc. cit.*).

The general rise of 36 cm.$^{-1}$ from ester to per-ester suggested that perbenzoic acid should have a monomeric carbonyl absorption at about 1780 cm.$^{-1}$. At a dilution (about 0·003M.) at which some 30 carboxylic acids all showed measurable monomer absorptions (Davison, unpublished work), there was no evidence of a monomer–dimer pair of absorptions, a single absorption at 1732 cm.$^{-1}$ being observed, together with a hydroxyl absorption at 3250 cm.$^{-1}$ (cf. 3551 cm.$^{-1}$ for monomeric benzoic acid; Thompson, quoted by Flett, *loc. cit.*). This, together with the low m. p. of 41° (compared with 122° for benzoic acid), suggests that perbenzoic acid is normally monomeric and that the lower carbonyl and hydroxyl frequencies are due to intramolecular hydrogen bonding. Such chelation is dimensionally possible if the skew configuration of the peroxide bond is somewhat nearer to a *cis*-configuration in this molecule. It is hoped to investigate the spectrum and structure of perbenzoic acid in greater detail later.

FIG. 4.

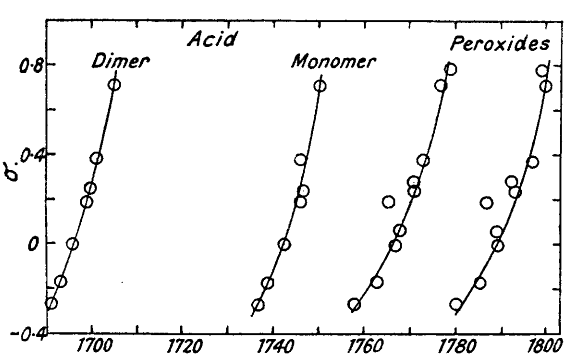
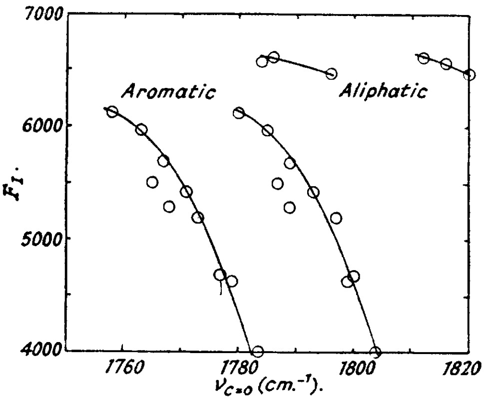


FIG. 5.



General Correlations of Carbonyl Frequencies.—Let us consider which correlations are likely to be of value. Empirical spectroscopic correlations which would permit the forecast of frequencies of compounds for which data are not available are of obvious value for identification and structural diagnosis. In Fig. 3, $\nu_{C=O}$ for peroxides, per-esters, and per-acids [$\nu_{C=O}$ for acids are from Flett (*loc. cit.*) and unpublished work in this laboratory] are plotted against an arbitrary parameter (f) which is, where applicable, the mean of the four frequencies for peroxide and acid. Where all four frequencies are not known, the parameter f is chosen to fit the available frequencies to their corresponding curves. Experimentally measured points fall on the straight lines within 3 cm.$^{-1}$ in most cases, and this is not greatly in excess of experimental errors. The biggest discrepancies are in the monomers of maleic (1), phthalic (2), dichloroacetic (3), and trichloroacetic (4) acids, the numerals in parentheses referring to points in Fig. 4. These will be dealt with in Part II. Flett (*loc. cit.*) has shown that a smooth relationship exists between reaction rates (measured by Hammett's σ factors) and $\nu_{C=O}$ for a series of benzoic acids, and has suggested the use of such curves to forecast reaction rates from the more readily obtainable spectroscopic measurements. In Fig. 4, $\nu_{C=O}$ for dibenzoyl peroxides are plotted against σ, together with Flett's results (*loc. cit.*) for the corresponding acids. The agreement is comparable with Flett's, as is of course to be expected from the correlations of Fig. 3. Since the only simple physical relationship between carbonyl frequency and reaction rates can be in the force constants of bonds whose fission is involved in the reaction, such relationships between carbonyl frequency and reaction rates can only be expected for simple reaction mechanisms. For structural diagnosis the method is first to decide the type of carbonyl compound (*e.g.*, from the number of carbonyl absorptions) and the value of f obtained from

Fig. 3 then assists in the identification of the acyl radical. Alternatively, if the nature of the acyl radical is known, $\nu_{C=O}$ for the corresponding acid fixes *f* and thus determines the type of carbonyl compound.

Cooper (*loc. cit.*) and Swaine, Stockmeyer, and Clarke (*J. Amer. Chem. Soc.*, 1950, **72**, 5426) have shown that there is a direct relation between the rate of decomposition of the peroxide and σ in the case of substituted benzoyl peroxides. A similar relationship must exist between $\nu_{C=O}$ and decomposition rates for these compounds.

There is considerable theoretical interest in correlating the strength of the C=O, C–O, and O–O bonds in diacyl peroxides. Such correlations would facilitate the search for the elusive ν_{O-O} absorption, and, more important, enable O–O bond strengths to be calculated from spectroscopic data. A direct measurement of either the C–O or the O–O strength from vibrational frequency appears impossible, since probably neither frequency is characteristic (*i.e.*, unaffected by small mass effects). The only other vibration which is characteristic is ν_{O-H} of the corresponding acid monomer, the accurate measurement of which requires a higher resolution than that of a sodium chloride prism, and for which few values are available. Thompson (quoted by Flett, *loc. cit.*) gives monomeric ν_{O-H} values for five benzoic acids, which bear a smooth relationship to both $\nu_{C=O}$ and free energy of ionisation ($F_I = \boldsymbol{R}T \ln K$, where K is the ionisation constant) of the corresponding acid.

A plot of carbonyl frequencies against F_I (Fig. 5) for a number of peroxides shows that aromatic peroxides fall on one curve, and aliphatic peroxides on another. (Ionisation data from "Int. Critical Tables," McGraw-Hill, N.Y., 1929, VI, p. 259 *et seq.*) This illustrates the fact that this completely empirical approach is only adequate within a class of similar compounds.

These correlations, *viz.*, between $\nu_{C=O}$ of peroxides and acids, and the strength of the hydroxyl bond as measured spectroscopically and by ionisation constants, show that a smooth relationship is to be expected between the strength of the O–O bond and $\nu_{C=O}$ within a series of similar compounds. In the case of the acid, a stronger carbonyl (*i.e.*, higher frequency) corresponds to a weaker O–H bond, and at first this may suggest that it corresponds to a weaker O–O bond. Walsh (*J.*, 1948, 331) has discussed the effect of electron shifts towards the peroxide bond, and considered that initially such a shift would strengthen the bond, but that still greater shifts towards the peroxide bond might result in a weakening of the bond. The matter is still further complicated by the fact that a steric effect which results in a twisting of the bond out of its most stable skew form would result in a weakening of the bond owing to repulsion of the lone-pairs. Thus, although in general a *smooth* relationship is expected betweeen carbonyl bond strengths and peroxide bond strengths, its form and even its sense cannot be readily predicted.

It is intended to examine the theoretical basis and limitations of these correlations in a second paper, which will also cover a larger range of carbonyl compounds.

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