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SPECTROSCOPIC DETERMINATION OF PEROXY COMPOUNDS DURING PHOTOCHEMICAL OXIDATION

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1. PHOTOCHEMICAL OXIDATION OF HYDROCARBONS

Many investigations of the thermal and photochemical oxidation of organic compounds indicate that the initial stages involve formation of peroxy compounds — hydroperoxides and photo-oxides — in which two oxygen atoms are linked together[1-5]. The peroxy compounds, containing the $-O-O-$ link, then decompose exothermally forming free atoms and radicals, which are the cause of the chain character of the subsequent stages of the oxidation.

Spectroscopic investigation of the peroxy compounds requires that they should be produced in greater quantities in the reaction mixture, which can be achieved mainly in photochemical oxidation reactions which take place at fairly low temperatures. Thermal oxidation involves a considerably more rapid decomposition of the intermediate reaction products, so that their concentration in the reaction mixture is insignificant. Also, a thermal process does not allow selective supply of energy to one of the reaction components. With activation by light it is possible to raise the oxidisable molecule to an excited state without affecting the intermediate and final reaction products. The photochemical oxidation is initiated by light (principally ultra-violet), which acts either directly on the oxidisable organic molecule or on a sensitiser, the latter oxidising the organic compound under the influence of visible light quanta. The path of the sensitised reaction is naturally of the greatest interest, since reaction is then effected by a small quantum, as in photosynthesis.

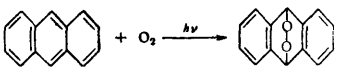
Photochemical oxidation under ultra-violet radiation has been investigated with di- and poly-olefines[6-9], alcohols[10], acetaldehyde[11,12], paraldehyde[13], propionaldehyde[12], butyraldehyde[14], benzaldehyde[15-18], acids[19], the aromatic hydrocarbons toluene[20-23], xylene[20,24], isopropylbenzene[20,25-27], and ethylbenzene[27], decalin, methylcyclohexane, 2,7-dimethyloctane, butylbenzenes and other compounds[5], dioxan[28], cyclohexene[29,30], and terpinolene (*p*-mentha-1,4(8)-diene)[31].

In all these researches the reaction kinetics and the chemical properties of those intermediate and final reaction products isolated were investigated, and on this basis mechanisms were suggested for the oxidation of organic compounds in which the initial stage is assumed to be radical formation by loss of hydrogen from the hydrocarbon. Hydroperoxides are then formed as a result of two bimolecular chain processes:

$$RH + h\nu \rightarrow R + H,$$
$$R + O_2 \rightarrow RO_2,$$
$$RO_2 + RH \rightarrow ROOH + R \text{ etc.}$$

Several organic compounds and dyes, however, absorb oxygen on prolonged or intense illumination of their solutions, peroxides — photo-oxides — being formed[32-50]. The formation of photo-oxides was first noted by Dufraisse and coworkers[32-45] in the case of the bright red hydrocarbon rubrene, solutions of which are rapidly decolorised with loss of fluorescence on exposure to sunlight or artificial light in the presence of oxygen. The colourless photo-peroxide, which is deposited on evaporation, decomposes at 180°, giving the original hydrocarbon and oxygen. Photo-oxides of other simple cyclic compounds can be obtained in a similar way. Benzene does not form a photo-oxide, but several furan and thiophen derivatives and terpenes do so, exhibiting great reactivity at the 1,4-positions. The photo-oxides of the simplest heterocyclic compounds are unstable at room temperature, and can be isolated only at low temperatures, *e.g.* the photo-oxide of 1,3-diphenylisobenzofuran.

The most stable photo-oxides are formed by polycyclic aromatic compounds — anthracene, naphthacene, pentacene, and other compounds containing an anthracene nucleus:



Other polycyclic hydrocarbons, containing the naphthalene or phenanthrene nucleus, do not yield photo-oxides. Acridine forms no photo-oxide, but dibenzacridine does, because it contains an anthracene nucleus.

The formation of photo-oxides from polycyclic aromatic compounds is associated with the higher reactivity of the *meso* positions, to which oxygen is added as a bridge lying outside the plane of the molecule (transannular peroxides), the angle between the *meso* carbon atoms and the $-O-O-$ bridge being 118°, which is somewhat larger than in peroxides (100°–105°). There is consequently some strain in transannular peroxides, but it is not very great since the heat of formation of photo-oxides is low.

The reactivity of the *meso* carbon atoms depends on the substituents, especially those in the *meso* position. Thus

alkyl or phenyl groups, and especially methoxy groups, facilitate addition of oxygen. Cyano groups, halogens, and oxygen completely suppress it.

The nature of the solvent is of fundamental importance to the formation of photo-oxides. Thus anthracene gives photo-oxides readily in carbon disulphide and chloroform, but only slowly in benzene and hexane, in which anthracene dimers are obtained simultaneously.

All photo-oxides of aromatic compounds decompose on heating, but the amount of oxygen evolved depends on the structure of the original hydrocarbon. The photo-oxides of anthracene and naphthacene decompose explosively at about 120° without liberation of oxygen, but that of 9,10-diphenylanthracene evolves up to 98% of its combined oxygen when heated to 80°. The evolution of oxygen is accompanied by bright luminescence (chemiluminescence). Thermal decomposition of this photo-oxide, as well as that of 1,4-dimethoxyanthracene, apparently takes place by a cyclic electron transfer mechanism[51]:

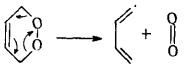


Photo-oxides are not formed in the dark. Their formation requires the action of light, which raises the hydrocarbon molecule first into an excited singlet state, which is then converted, in the presence of oxygen, into a triplet (biradical) state with subsequent addition of the paramagnetic oxygen molecule:

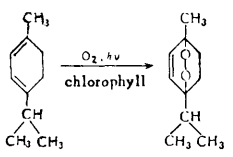
$$A + h\nu \rightarrow A^* \xrightarrow{O_2} \cdot A \cdot$$

$$\cdot A \cdot + {}^3O_2 \rightarrow \cdot A \cdot {}^3O_2 \rightarrow \cdot A - O_2 \cdot$$

Comparatively little work has been done on sensitised oxidation of organic compounds. Photosensitised oxidation of unsaturated hydrocarbons containing the allyl group yields hydroperoxides by a different route from the direct photo-oxidation of mono-olefines.

Similarly, hydroperoxides have been obtained by the photosensitised oxidation of benzaldehyde in the presence of benzophenone, acetophenone, and other substances[52], in the oxidation of tetralin[5,53], ethyl alcohol[54,55], propyl alcohol[55,56], in the presence of benzophenone, anthraquinone and its derivatives as sensitisers, and in the oxidation of cyclohexene, *p*-phenylenediamine, and *p*-tolylenediamine in the presence of various dyes[57,58]. Chlorophyll and its analogues cause photo-oxidation of a variety of compounds — benzidine, carotene, xanthophyll, allylthiourea, amines, phenylhydrazine, pyruvic, oleic, and ascorbic acids, etc. (see the survey in ref. 59 and also refs. 60–65).

Some organic compounds with a conjugated diene structure, such as, for example, ergosterol and various sterol derivatives, form peroxides as well as hydroperoxides on photosensitised oxidation. The sensitisers used are chlorophyll, Eosin, and Methylene Blue[66-71]. This method has been used to synthesise many substances which had not been prepared in other ways. An example is the photosynthesis of ascaridole from α-terpinene (*p*-mentha-1,3-diene):



2. SPECTROSCOPIC INVESTIGATION OF PEROXY COMPOUNDS

Spectroscopic investigations of peroxy compounds have been carried out mainly in the infra-red, as they do not possess any characteristic absorption in the ultra-violet and visible regions.

Up to 1951 there were very few papers on the Raman or infra-red spectra of inorganic or organic peroxides. Frequencies of 870–880 cm^{-1} were ascribed to vibration of the –O–O– link in hydrogen and deuterium peroxides[72-75], and the value 882 cm^{-1} to the peroxy group vibration in five alkyl and acyl peroxides and hydroperoxides[76,77].

These data are clearly insufficient for the detection of organic peroxy compounds in a reaction mixture. Moreover, absorption in the region of 880 cm^{-1} is not an unambiguous indication of the presence of an –O–O– group, but may be caused by vibrations of other atoms, mainly the corresponding vibrations of the molecular skeleton, as the presence of vibrational bands characteristic of the –O–O– group in peroxides has been regarded as improbable. Symmetrical vibrations of the C–O–O–C chain do not produce a great change in the dipole moment, so that the corresponding infra-red bands will be weak. In this chain, furthermore, the masses and the force constants for the –O–O– group are very similar to the values for the C–O and C–C groups, so that appearance of a band typical of the –O–O– group is improbable. However, the definiteness of the characteristic band will depend on the angle between successive bonds in the molecular chain. If it is about 90°, transfer of vibrational energy from one bond to another will not take place, so that the characteristic bands will be clearly defined[78].

X-Ray analysis of hydrogen peroxide and dimethyl peroxide shows that the atoms of the H–O–O–H and C–O–O–C chains do not lie in one plane, and that the –O–O– group forms an angle of 100°–105° with H or C.[72-75,79-81] The –O–O– group may therefore be expected to possess a characteristic band. The presence of the light hydrogen atom at the end of the C–O–O–H chain in hydroperoxides must increase the probability of development of a characteristic band. Theoretical calculation of the vibrations in a model system X–O–O–X with X of different masses [from 15 (CH_3) to infinity] showed that the X–O and O–O vibrational frequencies vary within the comparatively narrow limits 819–985 cm^{-1} for O–O, 978–1082 cm^{-1} for ν_s(X–O) and 824–1044 cm^{-1} for ν_a(X–O).[81]

In order to establish exact rules governing the effect of the peroxy groups in the C–O–O–H and C–O–O–C chains on the infra-red spectra, the spectra of some organic hydroperoxides and peroxides, and also of related compounds, were studied[82,83]. This analytical procedure is, of course, applicable only to compounds containing many atoms, since otherwise the character of the vibrations will depend greatly on the actual number of atoms. Furthermore, assignment of an absorption band to a definite atomic vibration is to some extent arbitrary, as all the other atoms in the molecule will affect this vibration to different extents.

As an example, let us examine the infra-red absorption spectra of isopropylbenzene hydroperoxide and bisisopropylbenzene peroxide, and also, as compounds of related structure, the spectra of dimethylphenylmethanol and isopropylbenzene (see Figs. 1 and 2). Careful examination of these spectra shows that the hydroperoxide possesses

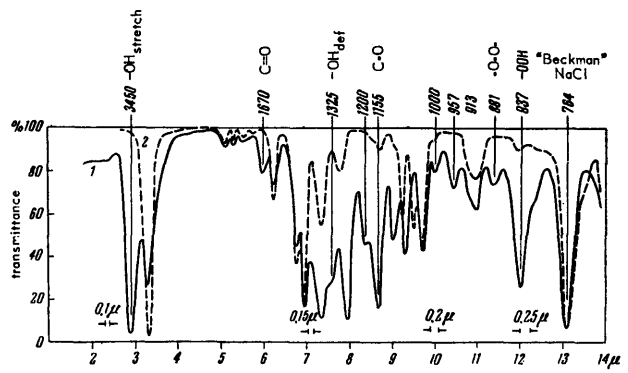


Fig. 1. Infra-red absorption spectra of:
1) isopropylbenzene hydroperoxide (liquid layer 0.02 mm);
2) isopropylbenzene (liquid layer 0.02 mm).

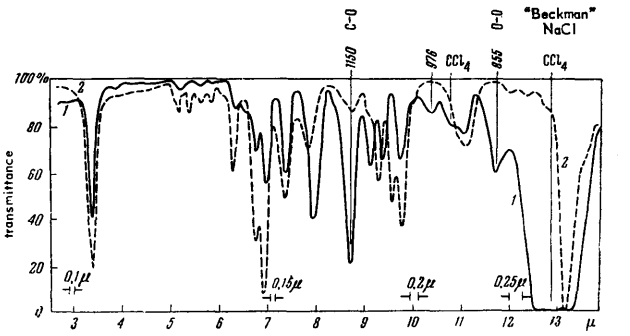
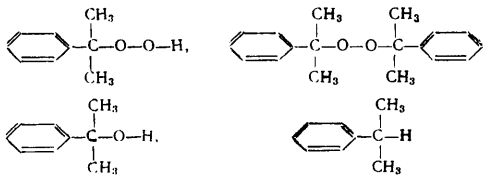


Fig. 2. Infra-red absorption spectra of a saturated solution of bisisopropylbenzene peroxide in CCl_4 and of isopropylbenzene.

an intense absorption band at about 837 cm^{-1}, which is absent in the peroxide.



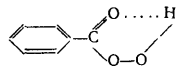
Consequently this band cannot be assigned to the O–O group, but to vibration of the C–O–O–H chain as a whole. The frequencies 855 cm^{-1} for the peroxide and 881 cm^{-1} for the hydroperoxide must be ascribed to the stretching vibration of the O–O group. The first three compounds have a common absorption band at 1150–1160 cm^{-1}, which must be assigned to the ν_{CO} stretching vibration[83]. The hydroperoxide and the alcohol contain an OH group, which has a stretching vibration ν_{OH} at 3450 cm^{-1} and a deformational vibration δ_{OH} at 1325 cm^{-1}.[84] It is difficult to interpret some of the other bands, which are apparently due to vibrations of the $C_6H_5C(CH_3)_2$ nucleus, which depend on the substituents. These conclusions were later confirmed by comparing some synthetic peroxides and hydroperoxides with substances of similar structure[82,83].

The infra-red spectra therefore show clearly several absorption bands due to vibrations of the C–O–O–H chain:

δ_{COOH} 835 cm^{-1},
ν_{O-O} 880 cm^{-1},
ν_{C-O} 1150 cm^{-1},
δ_{OOH} 1325 cm^{-1},
ν_{OH} 3450 cm^{-1}.

The peroxide chain C–O–O–C shows stretching vibration frequencies ν_{O-O} at 855 cm^{-1} and ν_{C-O} at 1150 cm^{-1}.

Benzaldehyde hydroperoxide, which is prepared from benzoyl peroxide[85], shows two new absorption bands in the infra-red spectrum, at 852 and 893 cm^{-1}, which are absent from the spectra of benzaldehyde itself and benzoic acid[86]. These frequencies belong to the C–O–O–H chain. However, the band with a maximum at 852 cm^{-1} is much weaker than with other hydroperoxides. According to experimental[82,83,87] and published data on the presence of an intramolecular hydrogen bond in the hydroperoxides of acids[79,80,88-91], it must be supposed that benzaldehyde hydroperoxide has the following structure



In the infra-red spectra of hydroperoxides, the frequencies relating to the O–O vibration and that of the C–O–O–H chain have not yet been separated. Thus, for example, for four hydroperoxides and two peroxides[91], two absorption bands (a strong one at 840 cm^{-1} and a weak one at 880 cm^{-1}) were assigned to ν_{O-O}. Very similar conclusions were reached in an investigation of the infra-red absorption spectra of tertiary peroxides and hydroperoxides[92,93] and of 32 organic peroxides and hydroperoxides[81]. Absorption at 840 cm^{-1} is due to hydroperoxides, but that at 880 cm^{-1} [81,91-93] and 890 cm^{-1} [94] is due to peroxides. With acyl peroxides 840–842 cm^{-1} is given for ν_{O-O}.[95]

More definite conclusions were reached from an investigation of the infra-red spectra of a homologous series of sixteen alkyl hydroperoxides[96]. All of them were found to give a strong absorption band in the range 810–830 cm^{-1}, while those of normal hydrocarbons containing an odd number of carbon atoms showed one band at 815 cm^{-1}, and those with an even number a double band at 825 and 805 cm^{-1}. Hydroperoxides of secondary and tertiary hydrocarbons contain only one band in the above spectral range. In addition, all the hydroperoxides have a weak band in the range 850–870 cm^{-1}, where some alcohols absorb, but in this case too the absorption due to the hydroperoxide can be distinguished. More precise conclusions confirming the group (ν_{O-O}) and chain ($\delta_{C-O-O-H}$) vibration frequencies were not reached in this work. However, an analysis of all these spectra shows that a quite distinct set of frequencies characteristic of the hydroperoxide and peroxide groupings can be found. The values for the set of vibration frequencies of the C–O–O–H and C–O–O–C chains agree well with our previous conclusions.

Thus on the basis of investigations by the present author and published data it can be accepted that these chains are

quite specific in their vibrations and that the corresponding absorption bands must always be situated within a definite spectral range. The C–O–O–H group, which possesses the most characteristic vibrations owing to the presence of a hydrogen atom in the chain, has the following frequencies: 840, 870, 1150, 1325, and 3450 cm^{-1} †.

The characteristic intense band in the range 800–840 cm^{-1} is conventially denoted as $\delta_{C-O-O-H}$, since it is difficult to assign this band to any definite vibration in the chain. It is obviously of interest to examine theoretically the specificity of the above frequencies of the hydroperoxy group. To simplify the problem, we have calculated the vibration frequencies taking as a model for this group a four-atom molecule[97,98] with the structure illustrated in Fig. 3.[79,80] However, this calculation required a knowledge of the vibration frequencies for deuterated hydroperoxides. The infra-red absorption spectrum of the deuterated (70–75%) hydroperoxide of isopropylbenzene showed not only the characteristic bands of the C–O–O–H chain, which, apart from the ν_{O-O} and γ_{C-O} frequencies, were greatly diminished in intensity, but also two new absorption bands at 2550 cm^{-1} (ν_{OD}) and 995 cm^{-1} (δ_{OD}). Owing to the presence of deuterium at the end of the chain, the O–O vibration frequency was somewhat displaced, its value being 885 cm^{-1} instead of 881 cm^{-1}.

Analysis of the above sets of frequencies for the non-linear chains C–O–O–H and C–O–O–D suggests that they are incomplete and should contain six frequencies. The δ_{COO} frequency, which should be about 600 cm^{-1}, is absent. Further examination of isopropylbenzene hydroperoxide in the infra-red between 700 and 400 cm^{-1} showed that it has an intense absorption band at 585 cm^{-1}, which was assigned to δ_{COO}. The intense band at 840 cm^{-1}, which had earlier been identified with δ_{COOH}, must be assigned to oscillation of the dihedral angle κ between the COO and OOH planes.

After the mechanical problem of the vibrations of free COOH and COOD chains had been solved, the vibration frequencies were assigned as shown in Table 1, which includes also the experimental frequencies. The agreement between calculated and observed frequencies is quite good, which again confirms the specificity of the set of frequencies for the hydroperoxide chain. Furthermore, the energy of activation of reactions involving hydroperoxides of benzene derivatives is independent of the length of the radical, indicating that the electron shell of the hydroperoxide chain remains unchanged in structure; this is shown by the constancy of the vibration frequencies.

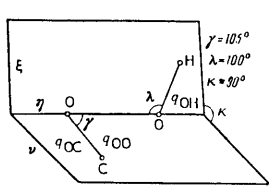


Fig. 3. Geometrical structure of the COOH chain.

† These values are correct in the absence of an intramolecular hydrogen bond.

TABLE 1. Calculated and observed vibration frequencies of the COOH and COOD chains (cm^{-1}).

COOH			COOD		
bonds and angles	calculated	observed	bonds and angles	calculated	observed
COO	586	585	COO	549	—
κ	834	840	κ	680	—
O—O	886	880	O—O	873	855
C—O	1156	1155	OOD	997	995
OOH	1321	1325	C—O	1156	1155
O—H	3450	3450	O—D	2539	2550

However, no calculation was made of the vibration modes or of the intensity of the absorption bands for the COOH chain, which would make it possible to obtain additional information about its structure and permit a more precise assignment of the observed absorption bands. With this aim the COOH (COOD) frequencies were calculated taking account of the vibration modes and the displacement of all the atoms during them, on the basis of which an approximate estimate of the intensities has been made[98] (see Table 2).

The calculated intensity distribution for the absorption bands in the spectrum of the COOH chain agrees well with the experimental values. This again points to the invariability of structure of the COOH chain in different compounds (constancy of its potential and electrical fields). As regards intensity, the most characteristic vibrations will be those of frequency 1322 cm^{-1} (variation of the OOH angle) and the stretching vibration of the OH bond with a frequency of 3450 cm^{-1}, since they are governed by the change in the λ and q_{OH} parameters, and the corresponding force constants will depend little on the remainder of the COOH chain. The 834 cm^{-1} vibration will be quite characteristic in intensity, giving an absorption band of high intensity due to variation in the dihedral angle κ.

The intensities of the remaining vibrations of the COOH chain will be considerably less characteristic, since they depend on the hydroperoxide radical owing to the fact that the COO angle γ will be determined to a greater extent by the nature of the radical.

The 886 cm^{-1} vibration frequency of the O–O group is characteristic of the COOH chain, since it is dependent not only on the stretching vibration of the O–O group but also

TABLE 2. Frequencies and intensities of vibrations of the COOH chain.

Assignment of bands to corresponding parameters (see Fig. 4)	Frequencies, cm^{-1}	Theoretical intensity	Relative intensity	
			calculated	observed
γ, κ	586	medium	4.3	11
κ	834	strong	9	9.5
γ, q_{OO} κ	886	weak	1.2	1.2
q_{CO} γ	1156	very strong	—	—
λ	1322	strong	9	9.5
q_{OH}	3450	very strong	—	—

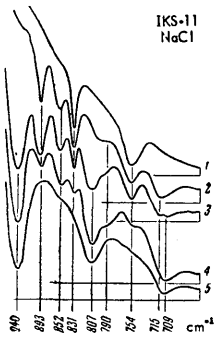


Fig. 4. Infra-red absorption spectra of films at -180°:
1) benzaldehyde; 2) product of photo-oxidation after 40 min at +15° (first fraction, sublimed after 1–2 min); 3) product of photo-oxidation after 40 min at + 15° (second fraction sublimed after 50–60 min); 4) product of photo-oxidation at -50°; 5) benzoic acid.

TABLE 3. Vibration frequencies of the COOC chain in photo-oxides of anthracene and its derivatives from infra-red absorption spectra

Photo-oxide of	Frequency, cm⁻¹	
	—O—O—	C—O (?)
Anthracene	894	1245, 1260
9-Methylanthracene	890	1230, 1246
9, 10-Dimethylanthracene	888	1246, 1258
9, 10-Diphenylanthracene	888	1260

to an equal extent on variation in the parameters γ and κ‡. It will be weak in intensity and not very specific. The intensity of the absorption band at 586 cm^{-1} must be the most sensitive to the hydroperoxide radical, which may explain the considerable discrepancy between the intensity calculated for the COOH chain and that determined experimentally for isopropylbenzene hydroperoxide.

In addition to the peroxy compounds considered above — hydroperoxides and peroxides — other peroxy compounds are known, the photo-oxides or so-called transannular peroxide of polycyclic aromatic hydrocarbons, which were considered earlier. It is supposed that in these compounds the oxygen bridge lies outside the plane of the molecule. It has also been suggested, however, that photo-oxides are hydroperoxides or hydroxy compounds[99]. In order to clarify the structure of photo-oxides and also to discover the frequencies characteristic of the COOC chain, measurements were made at -180° of the infra-red absorption spectra of sublimed films of four photo-oxides of anthracene and its derivatives, and also of the original hydrocarbons[100]. These spectra do not contain the absorption band of the OH group, and hence they are not hydroperoxides or hydroxy compounds. It can be concluded that the photo-oxides contain an oxygen bridge characterised by the COOC chain vibration frequencies given in Table 3.

The presence of an oxygen bridge in photo-oxides is known to affect the ultra-violet absorption spectrum, which is situated at shorter wavelengths than for the hydrocarbon. This is due to the breakdown of conjugation between the two benzene rings. Photo-oxides also show some differences from the hydrocarbons in their infra-red absorption spectra, the bands relating to the corresponding deformation vibrations of the C—H groups of the aromatic ring, for example, being displaced considerably towards higher frequencies in the transannular peroxides. Similarly, the absorption bands of the peroxy group ν_{O-O} and ν_{CO} have rather higher frequencies than those observed with organic peroxides. This increase in frequency must be ascribed to a change in the angle between the O—O group and the plane of the anthracene molecule (118°)[32] compared with that observed in peroxides (100°–105°)[81]. Thus the specific vibrations of the COOC chain are present also in photo-oxides.

3. USE OF INFRA-RED SPECTROSCOPY TO STUDY THE MECHANISM OF PHOTO-OXIDATION

Peroxy compounds are determined by many chemical reactions based on the fact that one oxygen atom (the available oxygen) of the peroxy group takes part in oxidising reactions[5].

The most widely used and most sensitive methods for the quantitative determination of organic hydroperoxides are the iodometric and the stannometric methods. The former is based on the liberation of iodine from acid solutions of potassium iodide by peroxy compounds. In the latter method the quantity of stannous chloride necessary to decompose the peroxide is determined. Chemical methods enable the presence of peroxy compounds in the reaction mixture to be determined with great accuracy, but the peroxides themselves are thereby destroyed.

Infra-red spectroscopy has undoubted advantages over chemical methods for the investigation of photo-oxidation, in spite of its considerably lower sensitivity, since it permits observation of changes in molecular structure during oxidation, and detection of the formation and decomposition of intermediate peroxy products directly in the reaction mixture, without disturbing the normal course of the reaction. We can take as example the photo-oxidation of benzaldehyde[86,101], a reaction which has been most studied by other methods, and also the oxidation of isopropylbenzene.

The photo-oxidation of benzaldehyde has been investigated in the overtone region and in that of the fundamental vibration frequencies; these complement one another very well. The absorption spectra of oxidised benzaldehyde in the near infra-red (as compared with the unoxidised compound) indicate that the aliphatic CH group has disappeared [the absorption bands at 7940 cm^{-1} ($3\nu_{CH\ aliph}$) and 5650 cm^{-1} ($2\nu_{CH\ aliph}$) are missing], and that an OH group has appeared [absorption band at 6920 cm^{-1} ($2\nu_{OH}$) and 6950 cm^{-1} ($2\nu_{OH...}$)]. The bands due to the CH groups of the benzene ring [6020 cm^{-1} ($2\nu_{CH}$) and 8790 cm^{-1} ($3\nu_{CH}$)] do not change. A study was then made of films of products of the photo-oxidation of benzaldehyde (oxidised both at +20° and at -50°) sublimed

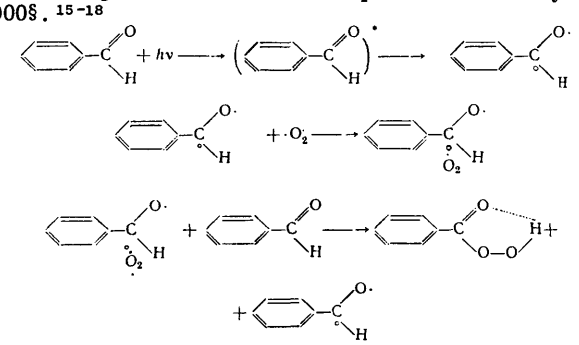
‡ With peroxides, which contain the COOC chain, vibrations of the same frequency will very probably include changes in the O—O bond length and in the COO angles.

on to an aluminised mirror cooled in liquid air. Measurements were made between 700 and 950 cm^{-1}, where there is no overlapping of the absorption bands due to the initial, intermediate, and final reaction products[86].

The photo-oxidation product of benzaldehyde shows a diminution of the bands at 754 and 831 cm^{-1} belonging to benzaldehyde, and the appearance of bands due to the hydroperoxide, κ 852 cm^{-1} and ν_{O-O} 893 cm^{-1}, as well as 715 and 790 cm^{-1} (see Fig. 4). At the same time bands arise with frequencies of 709, 807, and 940 cm^{-1}; these belong to benzoic acid, which is clearly produced in the second fraction of the photoproduct. Hence it can be concluded that the first fraction of the product photo-oxidised at +20° contains benzaldehyde and the hydroperoxide as the most volatile compounds, and that the second fraction contains also benzoic acid. In the photo-oxidation of benzaldehyde at -50° the reaction mixture contains mainly the hydroperoxide, since the absorption bands κ 582 cm^{-1} and ν_{O-O} 893 cm^{-1} are observed.

It was noted earlier that with hydroperoxides containing no intramolecular hydrogen bond the κ absorption band is always more intense than the ν_{O-O} band, whereas the opposite is true with benzaldehyde hydroperoxide, whether prepared from benzoyl peroxide or obtained by photo-oxidation. This indicates that benzaldehyde hydroperoxide contains an intramolecular hydrogen bond. It was also observed that the relative intensities of these absorption bands differ somewhat with specimens prepared by different methods. In fact, the intensity ratio is almost identical for the hydroperoxide prepared from benzoyl peroxide and for that obtained by photo-oxidation at -50°. However, the intensity ratio is considerably larger for the hydroperoxide formed at +20°, indicating a decrease in the proportion of COOH chains while the number of peroxy O–O groups is maintained. It follows that the products of the photo-oxidation of benzaldehyde at +20° contain a peroxide with the COOC chain in addition to the hydroperoxide. This peroxide is very probably a benzaldehyde hydroxyperoxide, formed by reaction between the hydroperoxide and the benzaldehyde.

On the basis of the above experimental results and also of published data[15-18,52,102,103], the following mechanism may be suggested for the photo-oxidation of benzaldehyde. A benzaldehyde molecule, after absorbing a quantum of ultra-violet radiation, passes into a reactive (triplet-biradical) state and adds on another valency-saturated molecule, oxygen, to form an active intermediate peroxide (moloxide), which on collision with a normal (unexcited) benzaldehyde molecule is converted into the hydroperoxide with simultaneous formation of an excited benzaldehyde molecule. The resulting chain reaction has a quantum efficiency of 10 000§. [15-18]

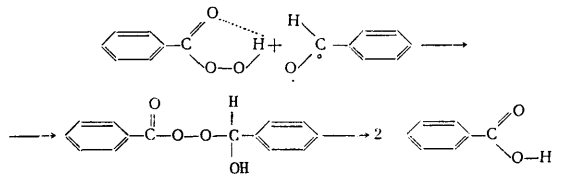


§ Circles and dots denote unpaired electrons with opposite spins.

The first stage in this scheme is confirmed by the absorption and emission (fluorescence? (Ed. of Translation)] spectra of benzaldehyde[103-105]. Benzaldehyde vapour, and also its solutions at -180°, give a discrete emission spectrum in the visible region, in which the characteristic vibration frequency of the carbonyl group, 1730 cm^{-1}, stands out; this belongs to the ground state of the molecule (1710 cm^{-1} in the infra-red spectrum). If the double bond in the C=O group were retained in the excited benzaldehyde molecule, the ultra-violet absorption spectrum of benzaldehyde vapour should, like the emission spectrum, give a frequency close to 1730 cm^{-1}. Actually, the absorption spectrum of benzaldehyde vapour shows only the frequencies 200, 950, 1200, and 1309 cm^{-1}; the first two are due to the benzene ring, and the latter represent vibration frequencies of the carbonyl group in the excited state[107,108]. Since the vibration frequencies of the CO group in alcohols, ethers, and acids usually have values[84] of 1100–1300 cm^{-1}, the excited carbonyl group of benzaldehyde, with frequencies of 1200 and 1309 cm^{-1}, can be represented as a C=O group with, as it were, one of the bonds broken. This electron transition can be treated more exactly as the transfer of one of the lone pair $2p$ electrons of the oxygen atom to an anti-bonding excited π^* orbital of the $\rangle C=O$ grouping[108-111]. In this way the vibrational structure of benzaldehyde, studied in both absorption and emission, confirms the formation of a biradical after absorption of a quantum of ultra-violet radiation.

The formation of a primary peroxide or moloxide of benzaldehyde with oxygen is proved by a study of the infra-red spectra of benzaldehyde adsorbed on sintered glass[112]. Ultra-violet irradiation in the presence of oxygen leads to increased absorption in the region corresponding to hydrogen bonds between the surface OH groups of the glass and the carbonyl; this is ascribed to formation of the moloxide, the latter possessing strong proton-accepting properties with respect to OH groups.

At room temperature the hydroperoxide reacts readily with the excited benzaldehyde molecules, which are present in excess, to form benzaldehyde hydroxyperoxide[5]; this is an unstable compound decomposing spontaneously to form two molecules of benzoic acid:



An investigation was also made of the sensitisation of the photo-oxidation of benzaldehyde with molecular oxygen, using as sensitisers derivatives of anthraquinone and acridine[100,112] whose optical properties had been studied earlier[113,114]. The changes taking place in the reaction mixture were recorded in the same regions of the infra-red spectrum. With some sensitisers — anthraquinone, 2-aminoanthraquinone, 3-aminoacridine, and 3,6-diaminoacridine — illumination of solutions of benzaldehyde, in the presence of oxygen, with visible light from the part of the spectrum where only the sensitiser absorbs, caused characteristic changes in the infra-red spectrum, indicating that oxidation of benzaldehyde was occurring. No changes in the infra-red absorption spectra were observed on illuminating either pure benzaldehyde solution or solutions containing 1-aminoanthraquinone or 1- or 2-aminoacridine.

The sensitising action is thus selective with respect to the anthraquinone and acridine derivatives. Comparison of the sensitisation by the above compounds with the strong quenching of their fluorescence by molecular oxygen and the occurrence in them of delayed fluorescence, indicating their possession of an adjacent triplet level, makes clear the interdependence of these phenomena.

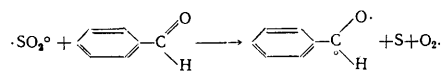
On the above basis the following mechanism may be imagined for the initial stages of the photosensitised oxidation of benzaldehyde[115]. On absorption of a light quantum the sensitiser (dye) passes into an excited state, and then into a metastable (triplet) state under the influence of a paramagnetic O_2 molecule:

$$S \xrightarrow{+h\nu} S^* \xrightarrow{O_2} \cdot S \cdot$$

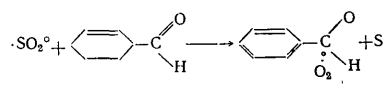
The biradical, *i.e.* the molecule in the triplet state, can add on oxygen, forming an unstable complex having the properties of a biradical:

$$\cdot S \cdot + {}^{\circ}O_2{}^{\circ} \longrightarrow \cdot S \cdot {}^{\circ}O_2{}^{\circ} \longrightarrow \cdot SO_2{}^{\circ} \cdot$$

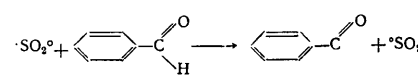
Sensitisation of the photo-oxidation of benzaldehyde is effected by this unstable complex of sensitiser and oxygen, *i.e.* the moloxide¶, which transfers the excitation energy to the oxidisable molecule or even dehydrogenates it[113 117 118] There will be a certain probability of energy transfer if the electronic level of the sensitiser is not lower than that of the oxidisable molecule. Consequently this process can take place only with anthraquinone:



The possibility of the simultaneous transfer of oxygen to the benzaldehyde is not excluded[66]:



where S represents a sensitiser molecule. In the case of derivatives of anthraquinone and acridine, however, dehydrogenation of the benzaldehyde molecule by the $\cdot SO_2{}^{\circ}$ is more probable:



This last process requires that the moloxides, and hence the sensitiser molecule, should possess proton-accepting properties, which is the case with most derivatives of anthraquinone and acridine[119,120].

Spectroscopic study of isopropylbenzene, its photo-oxidation products, and a preparation of its hydroperoxide between 4000 and 700 cm^{-1} shows that the photoproducts exhibit only the characteristic frequencies of the hydroperoxide group (see Fig. 5)[101-103]. Hence isopropylbenzene hydroperoxide is formed initially in the reaction mixture, by the following mechanism.

¶ A moloxide — an unstable complex of oxygen with a molecule of a substance in the triplet state — is formed also in the quenching of the fluorescence of anthraquinone, acridine, and their derivatives by molecular oxygen[114,115]:

$$A + h\nu \longrightarrow A^* \xrightarrow{O_2} \cdot A \cdot$$

$$\cdot A \cdot + {}^{\circ}O_2{}^{\circ} \longrightarrow \cdot A \cdot {}^{\circ}O_2{}^{\circ} \longrightarrow \cdot AO_2{}^{\circ} \cdot$$

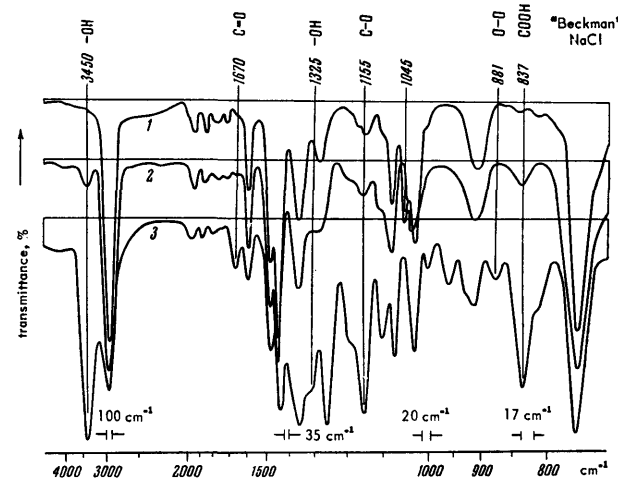
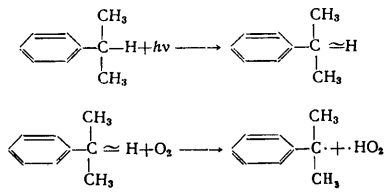


Fig. 5. Infra-red absorption spectra in relation to the photo-oxidation of isopropylbenzene:
1) isopropylbenzene; 2) oxidised isopropylbenzene;
3) isopropylbenzene hydroperoxide.

The first stage in the photo-oxidation of isopropylbenzene is a "loosening" of the C–H bond owing to the increase in vibrational energy due to the absorbed ultra-violet quantum. The direct splitting off of hydrogen atoms under the influence of ultra-violet radiation (the 313 mμ mercury line) is improbable for energetic reasons. Thus after absorption of the quantum, the isopropylbenzene molecule will possess a greater proton-donating tendency, which will aid the splitting off of hydrogen by an oxygen molecule to form radicals, which then propagate the chain oxidation:



Energetically, this reaction mechanism is quite possible. The energy of formation of the HO_2 radical from H + O_2 is equal to 47 kcal[121-124], and hence an additional energy of ~ 50 kcal is necessary for rupture of the CH bond (~ 90 kcal); this can be provided by the storage of vibrational energy in the molecule, rather more than half the energy of the 313 mμ quantum being required.

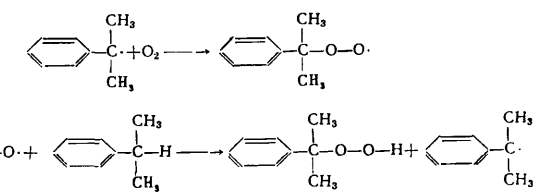
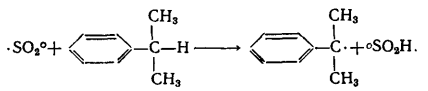


Photo-oxidation of isopropylbenzene sensitised by anthraquinone and 2-aminoanthraquinone also leads to the formation of the hydroperoxide[113]. The moloxide (biradical complex of a sensitiser molecule with oxygen)

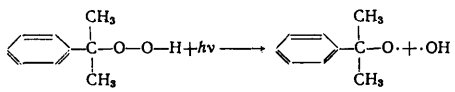
causes dehydrogenation of the hydrocarbon with formation of the corresponding radical, which propagates the chain reaction:



Isopropylbenzene hydroperoxide, being a stable intermediate in the oxidation, may, however, undergo decomposition under the influence of ultra-violet radiation (253.7 mμ) forming the end products of the photochemical reaction.

Measurements between 800 and 3000 cm^{-1} have shown that the photodecomposition products of isopropylbenzene hydroperoxide have an absorption spectrum identical with that of dimethylphenylmethanol[125] (see Fig. 6). It was therefore concluded that this is the main product of the decomposition of the hydroperoxide. The only important difference in the spectra is the appearance of a weak band at 1700 cm^{-1} in that of the photodecomposition product, obviously due to the stretching vibration of the C=O bond of the carbonyl group. The feeble intensity of this band indicates that the concentration of the compound containing the carbonyl group is low; it is apparently a subsidiary product of the photodecomposition.

The first stage in the photodecomposition of the hydroperoxide is the rupture of the weakest O–O bond[5,127,128] with the formation of two radicals:



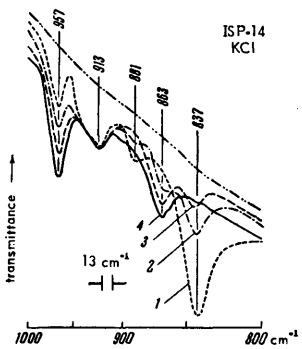
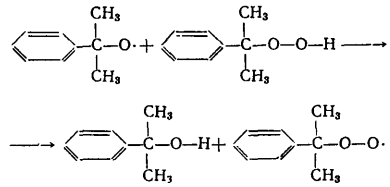
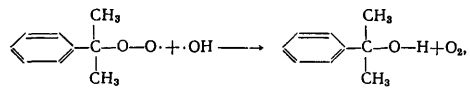


Fig. 6. Change in infra-red spectrum of isopropylbenzene hydroperoxide during photodecomposition:
1) before irradiation; 2)–4) after 3, 10, and 40 min irradiation (881 cm^{-1} relates to γ_{O-O}, 837 cm^{-1} to κ, and 863 cm^{-1} relates to the C–OH group of dimethylphenylmethanol).

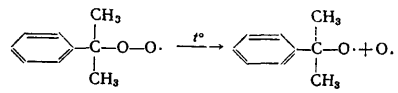
These react with hydroperoxide molecules present in excess, yielding the main product of the photodecomposition, dimethylphenylmethanol:



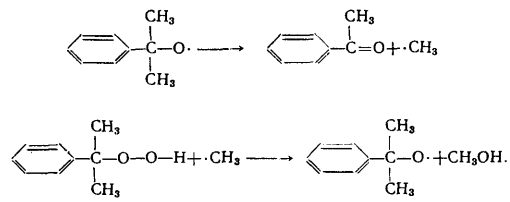
The peroxy radical either reacts with OH radicals (in the liquid phase):



or else liberates atomic oxygen (in the gas phase):



The radicals arising in the first stage can, apart from reacting with hydroperoxide molecules, yield small quantities of subsidiary products[130]:



The sensitised photodecomposition of isopropylbenzene hydroperoxide in the visible region of the spectrum also yields dimethylphenylmethanol, as is proved by the infra-red absorption spectra. However, the initial mechanism of the photodecomposition is different. For instance, the action of ferrocyanide as sensitiser involves an electronic mechanism, *i.e.* electron transfer from the iron cation to the hydroperoxide, leading to rupture of the O–O group[112]. Dye and pigment sensitisers probably dehydrogenate the hydroperoxide molecule with formation of a peroxy radical[112,131].

Thus the infra-red spectra of the reaction mixture in direct and sensitised photo-oxidation of hydrocarbons allow us to assess the changes taking place in molecular structure during the reaction and to detect intermediate peroxy compounds (hydroperoxides) from the appearance of a series of absorption bands having characteristic frequencies. With the unstable hydroperoxides we can also establish the subsequent course of the reaction leading to formation of the final stable products. This applies both to the direct and sensitised photochemical decomposition of hydroperoxides. Spectroscopic data enable the mechanism of the above reactions to be determined more exactly, especially the initial stages, in which radicals and biradicals play the main part.

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