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Reactions of Oxo-derivatives of Furan with Hydrogen Peroxide and Peroxy-acids

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The reactions of furan oxo-compounds with hydrogen peroxide and with peroxy-acids are surveyed, different views on the reaction mechanism are discussed, and modern concepts are explained. Possible practical applications of the process are shown. Comparison with the oxidation of aromatic compounds under similar conditions indicates several specific features of the process in the furan series. The bibliography contains 160 items.

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I. INTRODUCTION

The oxidation of oxo-derivatives of furan by hydrogen peroxide and peroxy-acids yields such valuable products as furancarboxylic, oxo, and dibasic acids, lactones [1-14], peroxides of carbonyl compounds of the furan series, furyl formate, its homologues, and derivatives, and also unsaturated lactones [6,8,15-18]. However, by no means all potentialities of this process have been realised. The reaction is extremely sensitive to the nature of the solvent used, the temperature, and the proportions, concentration, and structure of the reactants. This enables its direction to be controlled, and provides ready methods for obtaining new compounds [8,17,18].

II. DEVELOPMENT OF IDEAS ON THE REACTION OF FURAN OXO-COMPOUNDS WITH HYDROGEN PEROXIDE AND PEROXY-ACIDS

The prospect of utilising the reactions of furan oxo-compounds with hydrogen peroxide has been established only during recent decades. For a long time investigators were unable to isolate any products other than maleic and succinic acids [3,7,9,19-23] because of the absence of systematic work, although these acids are formed as a result of fundamental changes in more valuable oxo-acids and lactones [4,5].

The reaction of 2-furaldehyde with 3% hydrogen peroxide in the presence of iron(II) sulphate was first accomplished in 1899 by Cross et al. [19], who postulated the formation of hydroxo-2-furaldehyde and hydroxyfuran-2-carboxylic acid. Neither they nor subsequent investigators were able to isolate these products, and later an error in identifying the latter was demonstrated. The mechanism of the reaction was not considered. Succinic, maleic, and fumaric acids have since been isolated (in 20-50%, 10-40%, and 2-25% yields respectively) from the oxidation of 2-furaldehyde by hydrogen peroxide in water [1,3,9,20-23]. Several workers have reported the formation of formylacrylic acid, either detected qualitatively or isolated as the unpurified product in yields up to 25%. [1,23] Formic acid was formed in all cases. Pyromucic acid could be obtained only when furaldehyde was oxidised with hydrogen peroxide in pyridine [2,24].

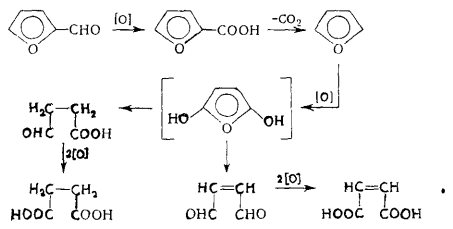
Very little information is available on the oxidation of furan oxo-compounds by peroxy-acids. The action of Caro's acid on 2-furaldehyde yields succinic and formic acids [25]. Oxidation by aliphatic and aromatic peroxy-acids gives a mixture of maleic, formic, formylacrylic, and succinic acids in proportions varying with the conditions [7,26,27]. Hydroxy-lactones may also be formed [26]. Marked resinification accompanies oxidation by peroxy-acids. In isolated cases succinic acid is not detected when 2-furaldehyde is oxidised by peracetic acid, but only formylacrylic, maleic, and fumaric acids [28]. A similar result has been obtained in the oxidation of 2-acetylfuran. A mixture of γ-oxovaleric and 4-oxopent-2-enoic acids is formed by the oxidation of 5-methylfuran-2-al by peracetic acid [28]. Furancarboxylic acids were not found among the oxidation products from carbonyl derivatives with peroxy-acids, but aldehydes gave the theoretical yield of formic acid, and ketones similarly formed acetic acid.

Some authors consider that the initial attack by hydrogen peroxide on 2-furaldehyde takes place at the furan ring [1,19,29], and others at the aldehyde group [22,23]. Salchinkin [22] supposes that the oxidant is active oxygen formed from hydrogen peroxide, which oxidises the furaldehyde at the carbonyl group to pyromucic acid, and the latter then undergoes decarboxylation to furan. Conversion of this product into the hypothetical furandiol is followed by the formation of malealdehyde and succinaldehyde, and finally maleic and succinic acids (Scheme 1). Only these acids were isolated among the products included in Scheme 1. No other evidence was given.

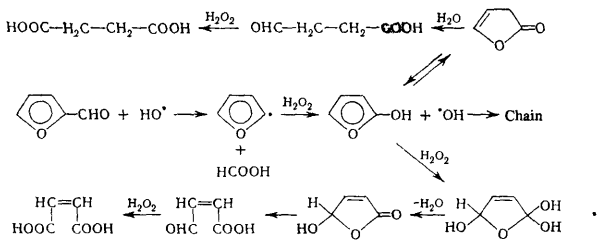
An alternative mechanism also involving the carbonyl group as the reactive centre entails oxidation by the hydroxyl radical (Scheme 2) [23]. Pyatnitskii and Lapkova suppose [23] that the reaction passes by a homolytic chain

mechanism through furanol and its tautomeric form (crotonolactone), which are converted into the β-formyl acids and then oxidised to maleic and succinic acids. The only evidence given in support of this scheme comprises isolation of the dibasic acids and the qualitative detection of 4-oxobut-2-enoic acid.

Scheme 1

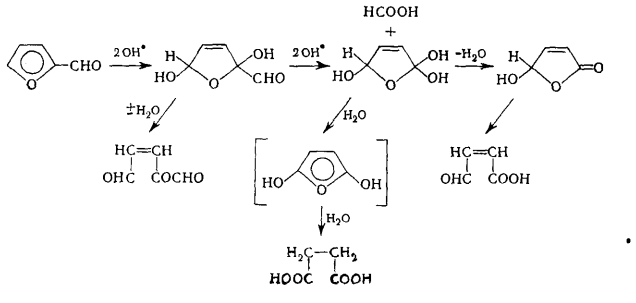


Scheme 2



Clauson-Kaas and Fakstorp[29] regard the interaction of 2-furaldehyde with hydrogen peroxide in alcoholic solution containing added osmium tetroxide as starting at the diene system of the furan ring, without indicating whether the mechanism is homolytic or heterolytic (Scheme 3). The mechanism suggested by Kallay[1] differs only in preliminary protonation of the heterocycle at the oxygen atom followed by ring opening and subsequent cyclisation. This assumes that the radical reactions of hydroxylation of the ring are coupled with the ionic reactions of its opening.

Scheme 3



No detailed consideration has been given to the mechanism of the oxidation of furaldehyde by peroxy-acids. It was suggested[26] that opening of the furan ring begins with formation of an unstable oxide involving one of the double bonds, while formic acid is obtained as a result of detachment of the aldehyde group; no information was given on the structure of the oxide or the mechanism of the process.

No proofs were given of the reliability of the mechanisms suggested for the oxidation of furaldehyde by hydrogen peroxide and peroxy-acids. They are inconsistent with modern views on the reactions of carbonyl compounds with these reagents, and do not take into account the formation and transformation of organic peroxy-compounds[30-32]. Nor are the schemes consistent with available information on the structure and reactivity of furan oxo-compounds and hydrogen peroxide; the mechanism is not related to the structural features of the reactants or the reaction conditions.

Discussion of the mechanism of the reactions between furan oxo-compounds and hydrogen peroxide or peroxy-acids cannot be based on any close analogy with corresponding reactions of aliphatic and aromatic aldehydes: the structure and the properties of furan systems are so specific that special consideration must be given even to whether the peroxide attacks the carbonyl group or the ring.

III. STRUCTURAL PECULIARITIES AND REACTIVITY OF FURAN OXO-COMPOUNDS AND HYDROGEN PEROXIDE

The reactions of 2-furaldehyde are often divided into aldehydic, diene, and ethereal.

The series of compounds—furan, 2-furaldehyde, and benzaldehyde—differ significantly in structure and properties. Thus no analogy is observed in the diene properties of furan and furaldehyde. Furan reacts with active dienophiles, whereas furaldehyde and other derivatives containing electron-accepting substituents (pyromucic acid, nitrofuran, etc.) do not react at all as dienes[33-38]. Furaldehyde itself is able to act as a dienophile[39]. Products of addition at the diene system of furaldehyde could not be isolated from the reactions of it and its derivatives with molecular oxygen even with active initiation by light[40-42,59].

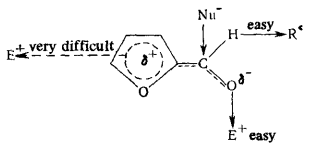
These facts are fully consistent with the view that oxygen adds only to those 1,3-dienes having enhanced electron density at the site of addition[43]. In furaldehyde, its homologues, and isomeric ketones the furan ring is conjugated with the carbonyl group, with displacement of electron density towards the latter. This is indicated by numerous data on the dipole moments[44,45], ultraviolet[6,46], infrared[6,47,48], proton magnetic resonance[48-50], and Raman[51] spectra, as well as the molecular exaltation. The infrared spectra show that the carbonyl group in furaldehyde lies in the plane of the ring owing to conjugation with the latter. The vector of the dipole moment is directed towards the carbonyl group with $\mu = 3.61$ D. The degree of conjugation between the π-bonds of the furan ring and the carbonyl group is clearly demonstrated by a comparison of the ultraviolet spectra of 2-furaldehyde and fur-2′-ylacetaldehyde, in which the carbonyl group is not conjugated with the ring ($\lambda_{max} = 277$ and 220 nm respectively). Calculation of the π-electron density shows considerable diminution in the ring and enhancement on the carbonyl oxygen in furaldehyde[52,53]. These facts are evidence of marked impoverishment of the electron density of the heterocycle and enrichment of the π-bond of the carbonyl group. This in turn strengthens the participation of p-electrons of the oxygen heteroatom in conjugation with the π-electrons of the ring. Hence the furan ring is more strongly aromatic in furaldehyde than in furan itself. This feature of the electronic structure of the furaldehyde molecule eliminates reactions involving the cyclic diene bonds, even with hydrogen peroxide. Thus Scheme 3 and

similar mechanisms[1,29] are inconsistent with modern views on the structure and properties of 2-furaldehyde.

Protolytic or hydrolytic cleavage of the furan ring by rupture of the C–O–C bond may be expected in systems containing hydrogen peroxide and especially its aqueous solutions. With regard to the acidophobic nature of furan compounds it is supposed that the cyclic oxygen atom forms a dative bond with the proton (oxonium ion) by means of the lone pair of electrons not involved in conjugation, which breaks down, and the ring is cleaved[54-56]. On the other hand, a vast amount of experimental work has been published indicating that electrophilic reagents do not attack the heteroatom but a cyclic carbon atom to form α-substituted furan derivatives[57]. The electron density on the cyclic oxygen atom is already low in the furan molecule, still lower in furaldehyde[52,53], and interaction with a proton cannot be ensured. The protonation of aromatic ethers involves the disruption of $p-\pi$ conjugation (E_{conj} = 8–12 kcal mole^{-1}), and occurs only if the energy of the resulting dative bond exceeds the conjugation energy[58]. Oxonisation is difficult with diphenyl ether, and is impossible at the heterocyclic oxygen atom in furaldehyde: this oxygen already possesses an oxonium character, and the energy of conjugation is very high.

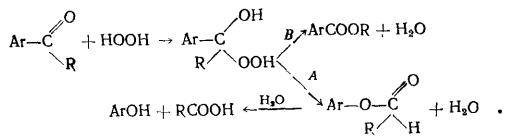
It has been proved experimentally that furaldehyde undergoes protonation not at the cyclic oxygen atom but throughout the conjugated system with formation of π-complexes[59,60]. This is consistent with the supposed π-functionality of the furan ring in complex formation[61]. In furaldehyde the end of the conjugated system having enhanced electron density is the aldehydic oxygen atom, to which a proton attaches in the limiting case. The protonation of furaldehyde by acids is accompanied by a strong bathochromic shift of the ultraviolet bands. Experiments suggest that electrophilic, nucleophilic, and radical reactions involve predominantly the aldehyde function, owing to the distribution of electron density in furaldehyde. Reaction will be favoured energetically if a stable transition state is established, in which the conjugation of the ring is preserved. The aldehydic carbon–hydrogen bond is less stable than a similar bond in the furan ring (70 and 103 kcal mole^{-1} respectively). Thus the direction of reactions in furaldehyde can be represented by Scheme 4, where R· is a free radical, E^+ an electrophilic species, and Nu^- a nucleophilic species. This scheme has been confirmed experimentally in the reduction[62] and the acetalation[63] of furan oxo-compounds. There are no grounds for supposing that reactions with hydrogen peroxide and with peroxy-acids will constitute exceptions.

Scheme 4



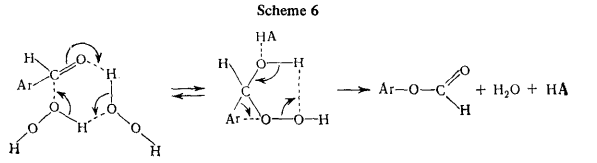
It does not follow that the reaction of furan oxo-compounds with these reagents will be analogous to that of the corresponding benzene derivatives, which also begins at the carbonyl group. Furaldehyde is more polar and more easily polarised than is benzaldehyde, as shown by the higher dipole moment and dielectric constant of the former. Experiment suggests that the π-electron system of the furan ring is more mobile than that of the benzene ring[44,46,64], which can be attributed to the presence of two oxygen atoms: the heterocyclic oxygen is a donor, and the carbonyl oxygen an acceptor, of electrons. As a result, the electron density and also the basicity of the ring are lower, while those of the carbonyl group are higher, than in benzaldehyde. On the other hand, furyl is more electronegative than is phenyl: the dissociation constant of pyromucic acid is 76.2×10^{-5}, tenfold that of benzoic acid (6.3×10^{-5}), which can be attributed to the weak aromaticity of furyl and its definite unsaturation. A significant difference in reactivity towards hydrogen peroxide and peroxy-acids should be observed between oxo-compounds derived from furan and benzene respectively. On the other hand, there are no grounds for supposing that these differences will be apparent in the direction of the early stages of interaction with the carbonyl group: only differences in reaction velocity are to be expected here.

Scheme 5



The oxidation of oxo-derivatives of benzene by hydrogen peroxide can be represented[30-32,65-69] by Scheme 5: hydrogen peroxide adds at the carbonyl group to give a hydroxy-hydroperoxide[67,69], whose formation in the aromatic and aliphatic series has been demonstrated by isolation or spectroscopically[70-73]. The resulting peroxide undergoes an intramolecular Baeyer–Villiger rearrangement[74], which is substantially accelerated by acids. In the case of benzaldehyde the rearrangement leads either to an ester (hydroxyphenyl formate) or to benzoic acid. Rearrangements of this type are widespread. Discussion of the mechanism of the formation and rearrangement of peroxides in the oxidation of aromatic and aliphatic oxo-compounds by hydrogen peroxide and peroxy-acids has considered as intermediate stages heterolysis[30,66,67,75-78], homolysis[79-81], or activated complexes[67,75-78]. A mechanism involving the molecular formation and rearrangement of hydroxy-hydroperoxides has the most convincing theoretical and experimental support[31,82-84]. Reactions of this type (Scheme 6) involve a continuous transition from the initial to the final state without formation of kinetically independent ions or radicals. This is due to the wave properties of electrons, the high polarity and the polarisability of bonds in oxo-compounds and peroxides, and the far greater instability of activated bonds in transition complexes in comparison with ordinary bonds[85-91].

Scheme 6



Transition states are usually regarded as stable five- or six-membered cyclic complexes [31]. An important part in these processes is played by acids, which largely polarise carbonyl and peroxide bonds, thereby promoting the formation and transformation of the transition complexes [31]. Arguments in support of molecular mechanisms do not exclude the probability of complete ionisation, adequate reasons for which have been given for the stage of peroxide formation [75], and this probability is increased by the effect of strong acids and bases.

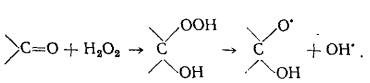
Irrespective of whether the hydroxy-hydroperoxide undergoes rearrangement by an ionic or by a molecular mechanism, it involves migration of one of the groups (Ar or R in Scheme 5) to the peroxide oxygen atom of diminished electron density. Migration of a hydrogen atom or the group R yields benzoic acid or its ester (Scheme 5*B*); that of aryl residues yields phenyl esters (Scheme 5*A*), which are then hydrolysed to phenols and acids. The relative migratory power of the groups varies in the sequence [30,68]

$$HOC_6H_4 > MeC_6H_4 > H > Ph > ClC_6H_4 > NO_2C_6H_4 > Me\ .$$

Similar data are not available for furan derivatives.

The main product of the oxidation of benzaldehyde is benzoic acid, in conformity with the greater ease of displacement of hydrogen than of phenyl. The simultaneous formation of small quantities of phenol and formic acid indicates the significance of the migration of phenyl. Electron-accepting substituents strongly impede such migration, and oxidation goes solely towards formation of benzoic acids. Electron donors, on the other hand, facilitate the formation of phenyl formates, and oxidation occurs very readily [30]. These results, as well as investigations using an oxygen isotope [92], have shown the untenability of the mechanism [93] of direct hydroxylation of the benzene ring by hydroxyl radicals. In the oxidation of salicylaldehyde by hydrogen peroxide the carbonyl group is the reactive centre, and a molecular activated complex is formed in which the *o*-phenoxy-group can easily migrate to an oxygen atom. As a result, the main oxidation product is catechol [92], whereas 3,5-di-t-butylbenzaldehyde yields the corresponding dialkylphenol and formic acid [94].

It is quite important to discuss the possible modes of breakdown of hydrogen peroxide in considering the mechanism of the oxidation of oxo-compounds. Some authors suppose that oxidation is effected by the cation HO^+ formed from hydrogen peroxide [95,96], but this is not supported by isotopic investigations [97-100]. The existence of an independent species HO^+ is improbable [101]. According to Denisov [102] ketones promote the homolysis of hydrogen peroxide:



It has been suggested [103] that radicals are formed in oxidations catalysed by certain strong acids in anhydrous medium:

$$H_2O_2 + H^+ \rightleftarrows H_3O_2^+ \xrightarrow{H_2O_2} H_3O^+ + HO^{\cdot} + HO_2^{\cdot}\ .$$

These processes are regarded as an exception to the general rule.

Oxo-compounds of low polarity in non-polar solvents, or in their absence under conditions of thermolysis, photolysis, or radical initiation, are able to react with hydrogen peroxide also by a homolytic mechanism [101]. In polar media (water, alcohols, organic acids, etc.), however, the mechanism is heterolytic [101,104]. Such a path is energetically more favourable, since solvation of the polar hydrogen peroxide molecule (μ = 2.13 D and ϵ = 73.1) [101,105] and its decomposition products greatly diminishes the energy of rupture of the bonds. Aqueous solutions of hydrogen peroxide have an acid reaction [101,105,106]:

$$H_2O_2 + H_2O \rightleftarrows H_3O^+ + HO_2^-.$$

Acid dissociation predominates over other types of breakdown [106] and increases with rise in temperature and increase in the hydrogen peroxide concentration of the solutions up to 80%. This compound also undergoes autoprotolysis:

$$H_2O_2 + H_2O_2 \rightleftarrows H_3O_2^+ + HO_2^-.$$

The degree of dissociation of hydrogen peroxide is determined by the nature of the solvent, the acidity of the medium, and the basicity of the substrate.

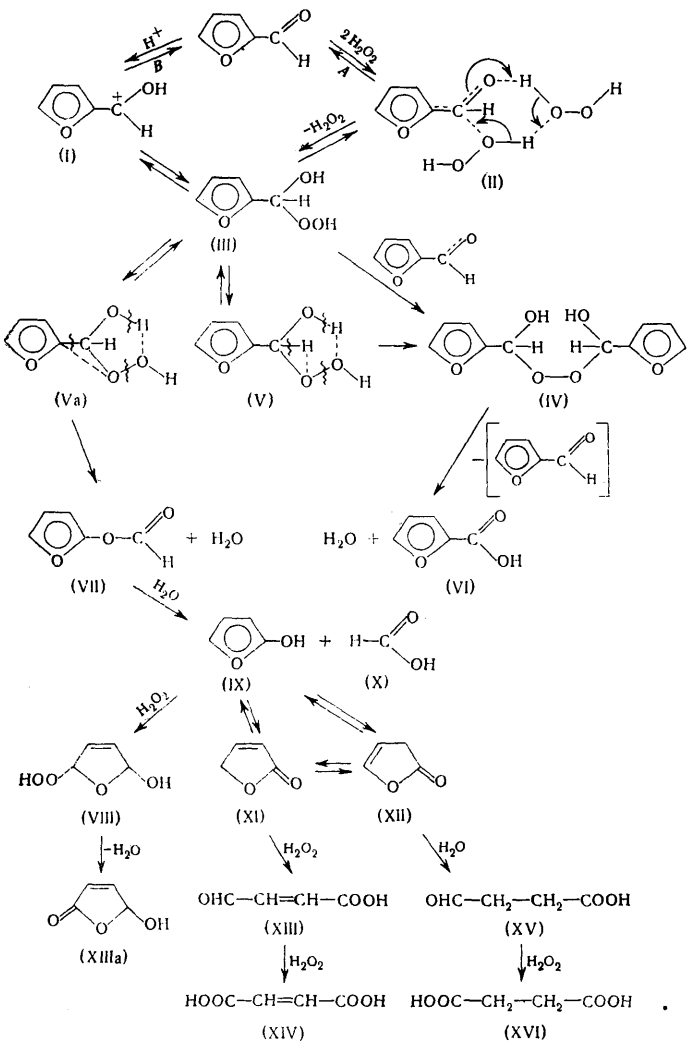
The high polarity and the polarisability of aromatic and especially furan oxo-compounds, their basicity due to the carbonyl group, the polar media used, and the relatively low temperatures—all these factors show that the reactions with hydrogen peroxide and peroxy-acids take place by a heterolytic or molecular mechanism. Either the hydrogen peroxide anion HOO^- or the molecule as a whole can act as nucleophilic reagent at the carbonyl group; it is also the proton donor.

Thus published experimental and theoretical results on the structure and properties of oxo-derivatives of furan and hydrogen peroxide, as well as the reactions of the latter and of peroxy-acids with aromatic oxo-compounds, show that Schemes 1–3 have no basis in fact. They and similar schemes cannot be used to describe the mechanism of the reactions of 2-furaldehyde and other furan oxo-compounds with these reagents. They are inconsistent with the structure and properties of furan aldehydes and ketones and of hydrogen peroxide, disregard the vast amount of experimental information on the peroxide oxidation of benzaldehyde and its derivatives, and do not provide for the formation of intermediate peroxy-compounds. Other concepts have therefore been advanced, and confirmed experimentally, to explain the mechanism of the oxidation of furan oxo-compounds by hydrogen peroxide and peroxy-acids.

IV. CURRENT IDEAS ON THE MECHANISM OF OXIDATION OF FURAN OXO-COMPOUNDS BY HYDROGEN PEROXIDE AND PEROXY-ACIDS

The special features of the reactivity of furan oxo-compounds and hydrogen peroxide and the reactions of aromatic carbonyl compounds with this reagent and peroxy-acids are taken into account in Scheme 7. The oxidation of the furan derivatives is regarded as a consecutive reaction having an ionic–molecular mechanism [4,5,120,126]. Here the carbonyl group is attacked initially either by a hydrogen peroxide molecule (reaction *A*) or by a proton (*B*). The predominance of *A* or *B* is determined by the structure of the carbonyl compound and by the reaction conditions. An intermediate linear or cyclic complex (II) is quite probably formed by reaction *A*, and the protonated species (I) by reaction *B*. The common result of the first stage is formation of the α-hydroxy-hydroperoxide (III), which may be converted, perhaps via the complex (V), either into the furyl ester (VII) or into the $\alpha\alpha'$-dihydroxy-peroxide (IV) depending on the structure and the reaction conditions. The corresponding furancarboxylic acid (VI) might be formed from (III) or

Scheme 7



from (IV). These stages show an analogy with the mechanism of the corresponding reactions in the benzene series (Scheme 5).

Significant differences in reaction velocity and proportions of products can be expected between furan and benzene derivatives, because of the greater mobility of the π-electron system of the furan ring. The rate of rearrangement of the peroxide (III) into the ester (VII) should be far greater with furaldehyde than with benzaldehyde. Furthermore, the rearrangement is stimulated in the furan series by hydrolysis of the ester to furanol (IX) and formic acid (X). The reverse reaction is improbable in this case, since the products of hydrolysis—(IX), (XI), and (XII)—are converted irreversibly into acids—4-oxobut-2-enoic (XIII), maleic (XIV), γ-oxobutyric (XV), and succinic (XVI). In the case of benzaldehyde, its derivatives, and its homologues, compounds containing stable aromatic rings are formed at all stages, and reactions involving cleavage of the ring are not observed (Scheme 5).

The oxidation of furan oxo-compounds is accompanied by substantial variation in the stability of the heterocyclic ring in the initial and intermediate products (IX): its stability undergoes a marked decrease after removal of the electronegative carbonyl group. The intermediate furanol (IX), in which the stability of the ring should be significantly lower than in furan itself, can readily undergo transformation involving the diene system and with cleavage of the ring. This is consistent with its ready oxidation via the peroxide (VIII) to formylacrylic acid (XIIIa) and the tautomerisation into the lactones (XI) and (XII) of but-2- and -3-enoic acids. The oxidative and hydrolytic changes undergone by the lactones and the furanol yield 4-oxobut-2-enoic (XIII–XIIIa) and γ-oxobutyric (XV) acids, which are converted by excess of hydrogen peroxide into succinic, maleic, and fumaric acids. The mechanism of the changes undergone by furanol and its tautomeric forms will not be considered here.

1. Role of Complex Formation

Various factors can influence the redistribution of electron density in oxo-derivatives of furan; these produce significant changes in their reactivity. Thus the self-association of 2-furaldehyde and association in its binary systems with the solvent and with hydrogen peroxide cause significant polarisation of the carbonyl group and affect its reactions with this reagent and with peroxyacids. The tendency of furaldehyde to associate[108] is such that its molecules are associated even in benzene[109], although the interaction is then weaker than for ordinary hydrogen bonds. It is not associated in dilute (<0.02 M) solutions. The tendency of furaldehyde to associate is indicated by its abnormally high boiling point in comparison with furan and its great solubility in water, as well as by significant differences in the ultraviolet and infrared spectra in various solvents[60,107,110]. Its self-association and its association with the solvent have been confirmed cryoscopically[112–115]. Weak hydrogen bonds are formed with acetic acid, and stronger bonds with stronger acids[115,116]. Complex formation between furaldehyde and pyromucic acid has been detected polarographically[5]. With sulphuric acid furaldehyde and its derivatives form complexes, which are completely converted into the initial aldehydes when the solutions are diluted[5]. No common view is held on the structure of the complexes. There is no doubt, however, that interaction in furaldehyde–solvent systems does not involve the ring but the carbonyl group. This is indicated by the constancy of the νC : C band of the furan ring (1565 cm^{-1}) and the variation in the νC : O band in the infrared spectra of furaldehyde obtained in various solvents[107]. Comparison of the infrared spectra of furaldehyde and its solutions in non-polar and in polar solvents shows (Table 1) a change in the structure of the doublet at 1660–1690 cm^{-1} representing vibrations of the carbonyl group involved in hydrogen bonding.

Considerable shifts in the νC : O bands are also observed when water and hydrogen peroxide are dissolved in furaldehyde, indicating considerable association in the binary systems. These observations have also been confirmed by cryoscopic measurements: when increasing quantities of hydrogen peroxide are added to a solution of furaldehyde in benzene, the freezing-point depression diminishes, indicating the bonding of furaldehyde molecules by hydrogen peroxide molecules and their removal from solution as complexes[8,117]. Association is more marked with hydrogen peroxide than with water; this is confirmed by the greater solubility, exceeding that in water by a factor of ~3.5.[4]

The strong association in the furaldehyde–hydrogen peroxide system shown by the above facts is consistent with the assumed formation of the intermediate complex (II) (Scheme 7) governed energetically by the stability of the resulting ring. Although the structure of the complex is open to discussion, the fact of its formation is indisputable. Polarisation of the carbonyl group by the hydrogen peroxide molecule must be taken into account in connection with the mechanism of the oxidation of furan oxo-compounds, and by the acid molecule or the proton in acid catalysis [cation (I) in Scheme 7]. Subsequent stages of the reaction will be facilitated significantly by such activation of the molecule.

Table 1. Dependence of stretching frequencies $\nu_{C:O}$ of 2-furaldehyde[107] on nature of solvent.

No.	Solvent	c, M	$\nu_{C:O}$, cm^{-1} [a]
1	None	—	1670 1630
2	Tetrachloro-methane	0.60 2.00	1690 1675
3	1,4-Dioxan	0.60	1685 1670 1635
		1.00	1685 1670
4	Diethyl ether	0.60	1685 1670 1635
		1.00	1685 1670
5	Water[b]	0.50	1680 1670
		6.00	1635
6	Hydrogen peroxide[b]	0.40	1680 1665
		0.80	1630
		4.00	1670 1635
		6.80	1680 1665
		7.90	1630

[a] The most intense band is underlined.
[b] Water and hydrogen peroxide in furaldehyde.

2. Role of Peroxy-compounds

The formation of peroxy-compounds was not even mentioned in the early papers on the oxidation of carbonyl derivatives of furan by hydrogen peroxide and peroxy-acids (Schemes 1–3). Various organic peroxides have since been detected among the products of the oxidation of furan aldehydes and ketones by hydrogen peroxide in the experimental verification of Scheme 7.[118,125] Originally only the total organic peroxides could be determined quantitatively, and the composition qualitatively[118,120-123].

For a long time it proved impossible to isolate the intermediate peroxy-compounds as individual species because of their tendency to detonate. They were stable in solution, but detonated on concentration (cf. the properties of the "active" and "inactive" forms of acyl hydroperoxides[126-130]). By the use of highly concentrated hydrogen peroxide under special conditions it has proved possible to prepare α-hydroperoxyfurfuryl alcohol (III)[18,126,131] and its ring-substituted nitro-derivative[16], which was stable unlike (III) but resembling other peroxides having electronegative substituents[119]. The synthetic compound (III) was identical with one of the peroxides detected among the oxidation products[120,126]. In the active period of oxidation in water the only intermediate peroxy-product is (III). The oxidation of furaldehyde in water involves intermediate formation of this peroxide. Formic, oxo, and furancarboxylic acids accumulate only after it has been transformed. During oxidation in anhydrous media (III) is accompanied by (IV), which predominates when the reaction is conducted in an alcohol[126].

The peroxide (III) is extremely unstable both in aqueous solution and in the crystalline state, decomposing with the formation of furaldehyde, hydrogen peroxide, the peroxide (IV), formylacrylic, maleic, formic, and pyromucic acids, and non-acidic products. The corresponding peroxide from nitrofuraldehyde is quite stable at +5°C, but when heated in water undergoes quantitative conversion into nitrofuran-2-carboxylic acid[18]. In aqueous solution this acid is accompanied by nitrofuranal and hydrogen peroxide. The formation of furaldehyde, its nitro-derivative, and hydrogen peroxide among the products from these hydroxy-hydroperoxides results from their dissociation into a furaldehyde and hydrogen peroxide. This process takes place both during the reaction and when samples of the oxidation products are diluted with water[8]. All the remaining products formed from (III) result from its conversion into (IV), (VI), and (VII). Conversion into furyl formate (VII) is assumed to involve a sextet rearrangement of the Baeyer–Villiger–Criegee–Waters type. Furancarboxylic acid can be formed not only from (III) but also by breakdown of the dihydroxy-peroxide (IV).[126,131] The direction of the rearrangement for furan hydroxy-hydroperoxides is determined by the structure. Electron-accepting substituents cause marked weakening of the π-donor properties of the furan ring, and its migration to the peroxide oxygen atom depleted in electrons becomes impossible. Hydrogen is then more mobile, and the hydroxy-hydroperoxide rearranges to the corresponding furancarboxylic acid (VI), perhaps via (V). Peroxides of furaldehyde itself, its homologues, and derivatives having electron-donating substituents rearrange preferentially into furyl formate (VII).

It is noteworthy that furancarboxylic esters are not detected among the oxidation products of acetylfuran and its derivatives[125]. Independently of the substituents in the furan ring, it obviously migrates in preference to the methyl group during the rearrangement, and furyl acetates are formed. A similar phenomenon has been observed among ketones of the benzene series[30,65,132]. Very small quantities of three further peroxides besides (III) and (IV) have been detected qualitatively in the aqueous oxidation products at the later stages of oxidation[8]. They have been regarded as formed from intermediate products—(IX), (XI)–(XIII), and (XV)—and could not be isolated or prepared in individual form.

Furoyl peroxide and hydroperoxide are not formed in the oxidation of oxo-derivatives of furan by hydrogen peroxide and peroxy-acids. Their presence could easily have been detected from their intense absorption maxima at 262 and 240 nm respectively[119,133], as well as by chromatography[119]. When furaldehyde is oxidised by hydrogen peroxide in water the products do not absorb in the range 240 to 265 nm; in anhydrous media a band is observed at 243 nm, which is due to pyromucic acid[17,126], formed only after breakdown of the organic peroxides.

In order to assess the mechanism of the action of hydrogen peroxide on oxo-derivatives of furan it is important to determine the kinetics of the stage in which peroxides are formed. Oxidation in water cannot be arrested at this stage [120,122,123]. Because water is present, the process goes so far as the formation of acids (Scheme 7), whose accumulation catalyses both the formation and the transformation of the peroxy-compounds, and the final content of organic peroxides is only 0.5–1 g-equiv. litre^{-1}. The kinetic curves representing their accumulation and conversion pass through three maxima. A similar pattern is observed in the oxidation by aqueous hydrogen peroxide of several furan aldehydes [120,124] (methylfuranal, 2-furaldehyde, and its amino- and halogeno-derivatives) and ketones [125] (acetylfuran and its derivatives).

In the absence of acids oxidation in anhydrous solvents ceases at the stage of formation of peroxy-compounds [111,120,126]. The rate constant for the consumption of furaldehyde corresponds to that for accumulation of the organic peroxide [120]. Oxidation in alcohol is a third-order reaction—of the first order with respect to furaldehyde and of the second order with respect to hydrogen peroxide [126]—which is consistent with formation of the hydroxy-hydroperoxide via the complex (II) involving three molecules. If formation of the peroxide is controlled by conversion of the transition complex, the overall process should be described by a third-order equation, as is the case. In the presence of acids the reaction is first order with respect to hydrogen peroxide, which confirms the catalytic role of hydrogen peroxide in the absence of acids.

The above results on the composition and reactions of the intermediate hydroxy-hydroperoxides in the action of hydrogen peroxide on furan oxo-compounds support Scheme 7. However, they still cannot indicate whether conversion of the oxo-compounds into peroxides takes place by a homolytic, heterolytic, or molecular mechanism.

Neither the changes undergone by furaldehyde and hydrogen peroxide nor the accumulation and transformation of organic peroxides and acids in this reaction are influenced by molecular oxygen [134]: the processes are identical in its presence and after it has been completely removed. Breakdown of the organic peroxides is not accompanied by the evolution of oxygen. These facts indicate that, as in most radical oxidations, molecular oxygen plays no part in the oxidation of furaldehyde and its derivatives by hydrogen peroxide. The formation of peroxy-acids and diacyl peroxides characteristic of radical processes is not observed [135,136]. In the autoxidation of furaldehyde, in which radical reactions predominate in the early stages, the initial products of the action of molecular oxygen are furoyl hydroperoxide and difuroyl peroxide [135,137], which are not formed in the oxidation of furaldehyde by hydrogen peroxide [4,126], as mentioned above.

The reacion is accelerated neither by ultraviolet nor by ultrasonic irradiation [4,123,140]. If the formation and transformation of the organic peroxides occurred homolytically, exposure would produce a marked change in its rate [136,138], but some specific effect on the direction of the process merely occurs. This ultraviolet irradiation increases the yield of 4-oxobut-2-enoic acid, and fumaric acid appears [4,123]. Treatment with ultrasonic vibrations results in considerable quantities of malic acid among the oxidation products [14,139,140], as a consequence of ultrasonic initiation of the breakdown of hydrogen peroxide and water with the formation of hydroxyl species [138]. If formation of the peroxide (III) had involved hydroxyl radicals or hydroxide ions, ultrasonic exposure should have intensified the process significantly, but this is not observed.

It is evident that neither molecular oxygen nor hydroxyl species are involved in the formation of (III). The oxidant giving the hydroxy-hydroperoxide must thus be the hydrogen peroxide molecule or ion H_2O_2 or OOH^- (Scheme 7). As the process exhibits no clear sign of a homolytic chain reaction, it cannot be regarded as a radical reaction. Furthermore, a heterolytic or molecular mechanism is suggested by many factors—those mentioned above together with the action of acids and water, the influence of the nature of the solvent, and the electronic effects of substituents in the furan ring.

In the oxidation of furan aldehydes and ketones by hydrogen peroxide the conversion of starting materials and intermediates becomes more intense as acids accumulate in the reaction mixture [4,6,122,123]. Neutralisation of the acids among the oxidation products slows the process down. The oxidation of oxo-derivatives of furan by hydrogen peroxide is evidently catalysed by the acids formed.

The addition of mineral and organic acids to the reaction mixture increases the rate of formation of peroxy-compounds, as can be assessed from the consumption of furaldehyde or acetylfuran. Acids also have a significant influence on the rate of subsequent stages (Scheme 7), as well as on the direction of the process [1,4,141]. Additions of formic, acetic, maleic, succinic, and sulphuric acids [4,6] all increase the consumption of furaldehyde or acetylfuran and hydrogen peroxide, and shorten or completely eliminate the induction period. The catalytic effect of the acid is greater the higher its dissociation constant:

sulphuric > maleic > formic > succinic.

The effect is greatest in the initial stages of the reaction. Such a strong effect of acids on the rate shows that the oxidation of furaldehyde and acetylfuran by hydrogen peroxide is ionic or molecular in character. Further evidence in support of this conclusion is the significant dependence of the rate and the direction of oxidation on the nature of the solvent [2,4,17,107,120,126,141,142].

The oxidation of furan oxo-compounds by hydrogen peroxide in anhydrous media or with a small water content differs significantly from oxidation in water: in the former case the reaction almost stops at the stage of formation of peroxides, and little or no acid is formed. As compared with water, alcohols, and organic acids, protophilic solvents (dioxan, oxolan, pyridine, ethers) slow down markedly the formation of hydroxy-hydroperoxides. Solvents having pronounced protogenic properties (formic and acetic acids) cause strong formation and transformation of (III) (Scheme 7). Initially reaction in alcohols is more intense than in water, after which it slows down. Small quantities of water have a peculiar effect: comparison of the consumption of furaldehyde and the accumulation of peroxides on oxidation in water and in aqueous ether shows that the presence of up to 5% of water in the reaction mixture accelerates the reaction in the initial period; higher water contents retard the process [142] (cf. Table 2).

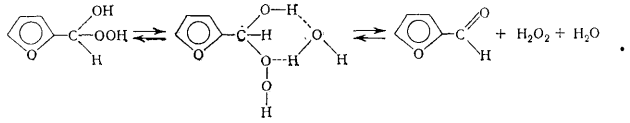
The action of water in the initial stage (Scheme 7) may be to affect either formation of the complex of furaldehyde with $2H_2O_2$ or the dissociation of (III) into furaldehyde and hydrogen peroxide. A high content of water in the oxidation products results in formation of a monohydrate of furaldehyde [107]. Competition in complex formation with furaldehyde between water and hydrogen peroxide molecules delays formation of a peroxide. A similar effect is possible in the presence of excess of water, because the dissociation of (III) into furaldehyde and hydrogen peroxide

is accelerated (Scheme 8). Small quantities of water activate the oxidation of furaldehyde by hydrogen peroxide, mainly by accelerating further transformations of the hydroperoxide (III).

Table 2. Effect of quantity of water on consumption of furaldehyde (Fu) on oxidation with 50% hydrogen peroxide ($Fu : H_2O_2 = 1 : 2.2$ at 22°C).

Solvent	$10^4 k_1$, min^{-1}
Water	≈0.00
Ether + 0.80% H_2O	21.4
Ether + 1.40% H_2O	34.6
Ether + 3.60% H_2O	59.8

Scheme 8



The nature of the solvent governs not only the rate but also the direction of the process. It has been shown above that the $\alpha\alpha'$-dihydroxy-peroxide (IV) is formed together with (III) in anhydrous and aqueous organic media. The nature of the conversion products of the peroxides varies in anhydrous media: thus the yield of the furancarboxylic acid (VI) is ~50% in alcohols, but only 2% in water[4,120,126]. This reaction is influenced by the polarity and the protophilic or protogenic character of the medium. Such a considerable solvent effect may be expected for ionic or molecular reactions[143]. The influence of solvents on radical reactions would be opposite to that found, since solvents capable of forming hydrogen bonds or π-complexes with radicals terminate the kinetic chain and lower the rate of oxidation[129,144,145]. In the present case alcohols and organic acids, which readily form hydrogen bonds, accelerate the oxidation of furan oxo-compounds by hydrogen peroxide.

A molecular or ionic mechanism is indicated not only by the above experimental results but also by the electronic effect of substituents in the furan ring on the rate and direction of the reaction. The effect on the rate has been assessed[120,124-126] by oxidising a series of aldehydes and ketones with a substituent—methyl, chloro, bromo, iodo, dialkylamino, hydroxymethyl, nitro—at position 5 in the furan ring. This series has the same reactive centre—the carbonyl group—and a variable 5-substituent. Conducting the reactions in a solvent containing a small quantity of water and at a relatively low temperature (30 to 40°C) enabled the process to be arrested at the stage of peroxide formation. The quantitative results given below relate to this particular stage. Its direction and mechanism were unaffected by the choice of solvent: in all cases the hydroxy-hydroperoxide (III) was formed with the substituent at position 5 in the heterocycle. Electron-donating substituents (methyl, dialkylamino) tend to increase the oxidation rate constant, whereas electron-accepting substituents (nitro, hydroxymethyl) tend to diminish the rate (Table 3). In contrast to methyl, hydroxymethyl retards oxidation[4]. Hydroxymethylfuraldehyde is oxidised rather more slowly than furaldehyde itself ($\tau_{1/2}$ = 63 and 55 min).

Table 3. Rate constants for the oxidation of 5-substituted furaldehydes[120] (aldehyde : H_2O_2 = 1 : 10 at 40°C) and acetylfurans[6] (ketone : H_2O_2 = 1 : 50 at 30°C) in aqueous dioxan.

5-Substituent	Aldehydes			Ketones		
	$10^3 k$, min^{-1}	$\lg \frac{k}{k_0}$	σ	$10^3 k$, min^{-1}	$\lg \frac{k}{k_0}$	σ
I	9.90	−0.1209	0.276	6.20	0.3898	−0.130
Br	11.50	−0.0555	0.232	8.30	0.5160	−0.220
H	13.00	0.0000	0.00	2.52	0.000	0.000
Cl	15.00	0.0607	−0.227	63.60	1.4004	−0.240
Me	25.00	0.3010	−0.170	10.20	0.6055	−0.120
NMe_2	29.90	0.3617	−0.205	—	—	—

The oxidation of halogenated furan oxo-compounds follows a curious course in aqueous dioxan. That of ketones by hydrogen peroxide is accelerated by all the halogens examined at position 5 of the furan ring, with chlorine more effective than bromine, and iodine the least effective. Oxidation of the aldehydes is accelerated by chlorine, but somewhat retarded by bromine and iodine. All the halogens accelerate the oxidation of furaldehyde in anhydrous media[126]. The reason is that, during the reaction, the positive conjugation effect of the halogens becomes stronger in comparison with their negative inductive effect. This is already observed in the parent substance as a result of the strong acceptor properties of the carbonyl group. The ultraviolet and infrared spectra of substituted furan oxo-compounds provide convincing support[6]. Under the influence of the polarised carbonyl group the positive conjugation effect of the halogen increases many times during the reaction. Similar phenomena are observed in the electrophilic substitution of halogenated benzenes[143]. The greatest positive conjugation effect is found[146] with chlorine, and diminishes in the sequence Cl > Br > I; it is explained by the most favourable overlap of electrons in the $3p$ shell of chlorine with $2p$ electrons of carbon.

It is remarkable that this effect of halogens has not been observed among acetophenones: the rates of oxidation of p-chloro- and p-bromo-acetophenones by peroxy-acids are lower than those of acetophenone[147]. This shows that the transmissibility of electronic effects through the benzene ring differs from their transmissibility through the heterocyclic furan system: the π-electrons of furan are more mobile. A complete analogy cannot, of course, exist in the oxidation of benzene and furan carbonyl compounds by hydrogen peroxide and peroxy-acids.

The positive conjugation effect of halogens is more strongly developed in substituted acetylfurans than in furaldehyde and its derivatives, owing to the greater interaction of p-electrons of the halogens with those of the furan ring in ketones. The π-electron density of the furan ring is less displaced by the ketone group, being a weaker acceptor than the aldehyde group, and better conditions are created for interaction of electrons of chlorine and the ring. On the other hand, more intense polarisation of the carbonyl group is required during reaction with ketones

than with aldehydes, which tends to strengthen the positive effect of halogens. The difference in degree of conjugation of halogens in furan aldehydes and ketones develops mainly in the reactive state, since the infrared spectra indicate no special difference in the static state [6]. The effects of substituents are more strongly developed in the oxidation of furan aldehydes by hydrogen peroxide in aprotic solvents of low polarity (dioxan, oxolan), and are extremely slight in alcohol [126].

Migration of electrons towards the reactive centre—the carbonyl group—evidently governs the rate of oxidation of furan oxo-compounds by hydrogen peroxide. Hence the formation of (III) is a result of electrophilic attack, which apparently consists in protonation of the carbonyl group. Conjugation of π-electrons of the ring and the group diminishes the δ^+ charge on the carbonyl carbon, so that nucleophilic attack by such a weak nucleophile as hydrogen peroxide requires preliminary polarisation of the carbonyl by a proton. Hydrogen peroxide and the solvents used (water and alcohols) are extremely weak acids, which is responsible for the slowness of the electrophilic stage [143]. If the acidity of the solvent is closely similar to that of hydrogen peroxide, the solvent may act as protogenic substance, as in the oxidation of furaldehyde by hydrogen peroxide in water [142]. In less acidic media hydrogen peroxide acts as the acid [126].

The rate of oxidation is affected not only by substitution at the 5-position in the furan ring but also by change in the character of the side-chain containing the carbonyl group. Furylacrylaldehyde is oxidised very easily, but oxidation begins at the unsaturated side-chain, and the primary reaction products are furaldehyde and oxalic acid. The furaldehyde then undergoes conversion by the usual scheme [4]. This example clearly demonstrates that the oxidation of furan oxo-compounds containing electron-accepting substituents does not start at the furan ring, and that the ring is more stable than the double bond in the side-chain. Acetylfuran is oxidised considerably more slowly than is furaldehyde [125]: thus with 50% hydrogen peroxide at 60°C and the reactants in the proportions 1 : 2.5 furaldehyde is oxidised more rapidly than acetylfuran by a factor of 20 (the respective half-conversion times are 23 and 450 min). Substitution of the aldehydic hydrogen by methyl produces no great change in the distribution of electron density in the furan ring, as is indicated by the close similarity of the ultraviolet and infrared spectra of acetylfuran and furaldehyde [6,148]. The infrared spectra reveal no difference in position or intensity of the absorption bands due to stretching and deformation vibrations of the furan rings in aldehyde and ketone; appreciable differences are shown only by bands due to the carbonyl group.

The introduction of alkyl substituents increases the electron density on the carbonyl group and should thereby improve its sensitivity to electrophilic attack. This is accompanied by a diminution in the tendency of the carbonyl carbon to interact with nucleophilic reagents, owing both to electronic and to steric factors. The stage of hydroxy-hydroperoxide formation is limited by electrophilic attack with both aldehydes and ketones (Table 3). The unexpected sharp decrease in rate of oxidation with acetylfuran compared with furaldehyde can be explained if the formation of (III) is regarded as a termolecular reaction. The plausibility of this hypothesis has been demonstrated for furaldehyde [126]. The nucleophilic stage may be slower with ketones, resulting in a fall in the overall rate of oxidation. The electronic effects of substituents in the furan ring, like other factors, suggest an ionic or a molecular mechanism of the formation and transformation of hydroxy-hydroperoxides in the oxidation of furan oxo-compounds by hydrogen peroxide.

3. Furyl Formate and its Conversion Products

Furyl formate and the homologous acetate are intermediates in the oxidation of furaldehyde and acetylfuran by hydrogen peroxide (Scheme 7). They have been isolated individually, which convincingly proves the suggested rearrangement of the hydroxy-hydroperoxide (III) into (VII).

Formation of these compounds when furan oxo-compounds were treated with hydrogen peroxide and peroxy-acids had previously been ignored (Schemes 1–3), and no attempts had been made to isolate them from the oxidation products. Furyl formate (VII) was first isolated from the products of the oxidation of furaldehyde by hydrogen peroxide when they were evaporated down or at the start of vigorous reaction [15]. Furyl formate is comparatively easily hydrolysed to formic acid (X), the butenolides (XI) and (XII), and 4-oxobutyric acid (XV), and oxidised to 4-oxobut-2-enoic acid (XIII). [8,15] Accumulation and transformation of these products are observed in the oxidation of furaldehyde by hydrogen peroxide, which has been investigated quantitively [4,8,126]. The rate of accumulation of formic acid when furaldehyde is oxidised in water [120] clearly shows that intense formation of the acid ensues after considerable quantities of furaldehyde have been consumed. This is fully consistent with the characteristics of the consecutive reaction represented in Scheme 7.

The furanol (IX) formed by the hydrolysis of (VII) is too unstable to be detected among the oxidation products [54]. For this reason furanol has not yet been prepared in any other way. However, its stable tautomers—the butenolides (XI) and (XII)—have been isolated in large quantities [8,57]. Products of the extensive transformation of furanol—4-oxobutyric and 4-oxobut-2-enoic acids—are formed in this reaction [1,10,12,126]. Accumulation of the aldehydic acids suffers a delay, the maximum occurring only after 2 h, when the furaldehyde is almost completely exhausted. The oxo-acids formed undergo vigorous oxidation to succinic and maleic acids (XVI) and (XIV), which have been isolated from the oxidation products [1,3,14,17]. The same acids are formed when furaldehyde is oxidised by peroxy acids [26,28], which indicates the same mechanism of oxidation as with hydrogen peroxide.

Furyl acetate could not be isolated from the products of the oxidation of acetylfuran by hydrogen peroxide, because it is oxidised much more rapidly than the initial ketone [149]. However, its formation and transformation during the reaction have been demonstrated qualitatively [149–154]. The processes occurring in the oxidation of acetylfuran are analogous to the hydrolytic and oxidative changes undergone by furyl formate (VII) and shown in Scheme 7, except that hydrolysis of furyl acetate yields acetic acid. These results show that rearrangement of the peroxide (III) into (VII) does actually take place.

Formation and transformation of the peroxides have been most fully studied in the complicated consecutive reaction of furan oxo-compounds with hydrogen peroxide. The occurrence of the remaining stages has been proved by the products, but their mechanism has not been investigated in detail. This is due to the peculiarities of the reaction: when oxidation occurs in water, individual stages cannot be isolated, nor can autocatalysis by the resulting acids be taken into account; in anhydrous media

the reaction effectively ceases at the stage of peroxide formation. The rate of conversion of (III) could not be estimated because of the accumulation of other peroxides. In view of the properties of (III), however, the process can be regarded as fairly rapid [18]. It is strongly exothermic [155].

Thus the regularities found in the reaction and the intermediate and final products identified permit Scheme 7 to be accepted as soundly based both theoretically and experimentally for the oxidation of furan oxo-compounds by hydrogen peroxide. It is very useful to estimate the activation parameters of the reaction in order to interpret its mechanism.

V. ACTIVATION CHARACTERISTICS OF THE PROCESS

The thermal effects of individual stages and of the overall oxidation of furaldehyde by hydrogen peroxide have been found by calculating the energies of formation of the products on the basis of approximate additivity [120,156,157]. The conjugation energy of furaldehyde and other furan compounds has been taken into account at the stage of their transformation [48,53]. The method used is arbitrary, since it allows for neither the complete interaction of atoms in the molecules nor the effects of the medium. However, the results are useful for estimating the thermal effects.

Table 4 shows that the oxidation of furaldehyde by hydrogen peroxide is exothermic, which has been confirmed experimentally [3,123]. The greatest quantity of heat is evolved during the conversion of peroxy-compounds [155], which is consistent with the results in Table 4 (stages *2*, *5*, and *8*). Calculation of the thermal effects shows the largest consumption of energy at stages *3*, *4*, and *6*. However, the experimental conditions require the significant corrections to be made to these results. Excess of water in the oxidation products, catalysis by the accumulating acids, and conversion of the reaction products in the later stages (*4*–*8*) promote ready hydrolysis of furyl formate when the process is conducted in water. This explains the low yields when furyl formate is isolated. The limiting stage in processes *1*–*8* is most probably formation of the hydroxy-hydroperoxide (stage *1*).

Table 4. Energies of formation of molecules and heats of oxidation of furaldehyde by hydrogen peroxide.

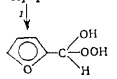
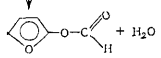
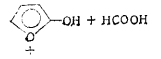
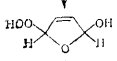
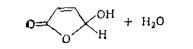
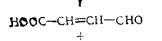
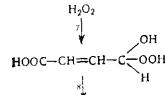
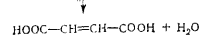
Stage	Energy of formation, kcal mole^{-1}	Heat of reaction, kcal mole^{-1}
	1121.0	
H_2O_2	240.2	
1		−15.1
	1376.3	
2		−50.0
	1188.0+238.2	
+ H_2O	238.2	
3		+54.0
	991.2+381.0	
+ H_2O_2	240.6	
4		+23.5
	1208.3	
5		−88.1
	1058.2+238.2	
6		+23.0
	1035.2	
+ H_2O_2	240.6	
7		−16.7
	1292.5	
8		−88.1
	1142.4+238.2	
	total	−157.5

Table 5. Activation parameters [120,126,158] of the oxidation by hydrogen peroxide of furaldehyde (Fu) (30% H_2O_2 with Fu : H_2O_2 = 1 : 15) and acetylfuran (AF) (50% H_2O_2 with AF : H_2O_2 = 1 : 3).

Activation parameter	Furaldehyde in		Acetylfuran
	water	alcohol	
Apparent activation energy E, kcal mole^{-1}	11.4	20.5	21.9
Pre-exponential factor A at 60°C, s^{-1}	$8.5 \cdot 10^{-5}$	$7.4 \cdot 10^{11}$	$5.1 \cdot 10^{11}$
Free energy of activation $\Delta G^{\neq}$ at 60°C, kcal mole^{-1}	24.7	24.7	25.7
Enthalpy of activation $\Delta H^{\neq}$ at 60°C, kcal mole^{-1}	10.7	19.8	21.2
Entropy of activation $\Delta S^{\neq}$ at 60°C, cal deg^{-1} mole^{-1}	−41.3	−14.6	−13.7

The experimental activation parameters of such complicated reactions as the oxidation of furan oxo-compounds by hydrogen peroxide (Table 5) apply in effect to the limiting stage of the process. As shown above, in water this is the stage of conversion of the carbonyl compound into a hydroxy-hydroperoxide. Oxidation in an anhydrous medium ceases at the first stage. The comparatively low activation energies are consistent with thermochemical calculations (Table 4) and the observed exothermic character of the process. The high activation energy for acetylfuran in comparison with furaldehyde corresponds to the above features of its oxidation. The lower activation energy of oxidation in water than in alcohol is consistent with the above role of water in the reaction. The experimental enthalpies of activation are closely similar to those calculated for the first stage in Scheme 7 (Table 4).

The low values of the pre-exponential factor (according to collision theory $A \simeq 10^{13}$ s^{-1}) suggest that the molecules are in contact and that the transition state is polar. The considerable degree of order of the transition state with loss of its rotational and translational degrees of freedom, as well as its polarity, is confirmed by the negative entropy of activation, which is possible in a system having a cyclic activated complex [159].

The autocatalytic character of the process is confirmed by the low entropy of activation [160]. The conclusion that, when oxidation takes place in water, the active stage is catalysed by acids accumulating during the reaction is supported by the identity of the activation energies for the oxidation of acetylfuran with and without acid catalysis [6], as well as by the lower activation energy in water than in alcohol (Table 5). Like the other experimental results cited, the activation parameters indicate that the action of hydrogen peroxide on furan oxo-compounds involves a transition complex and is autocatalytic.

Thus the investigations surveyed above indicate that the mechanism of the reaction of furan oxo-compounds with hydrogen peroxide and peroxy-acids represented by Scheme 7 is soundly based both experimentally and theoretically. The regularities elucidated in its occurrence and the effects of various factors permit this complicated consecutive and parallel process to be controlled with the aim of obtaining the most important products [1-18].

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