Tetrahedron, 1958, Vol. 3, pp. 78–89. Pergamon Press Ltd., London

SOME MECHANISMS OF OXIDATION

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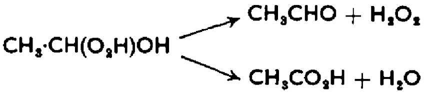
(*Received* 2 *December* 1957)

Abstract—The Haber–Willstätter hypothesis of oxidation is criticised as having no proper theoretical basis, and its experimental support by Bartlett and Nozaki is shown to be invalid. The general adequacy of the classical view of oxidation primarily by electron transference is maintained by reference to oxidations of paraffins, olefins, alcohols, ethers, amines, aldehydes and ketones.

WIELAND in 1912 inaugurated his studies of the formation of carbonyl from alcoholic groupings by catalytic removal of two hydrogen atoms.[1] Later he suggested that alcohol in the presence of "cellular catalysts" might yield the peroxy compound (I), from which either acetaldehyde or acetic acid could be derived:[2]



$$CH_3{\cdot}CH(O_2H)OH \begin{cases} \rightarrow CH_3CHO + H_2O_2 \\ \rightarrow CH_3CO_2H + H_2O \end{cases}$$

(I)

The nature of the initial activation process was not further specified, but Haber and Willstätter postulated the removal of a single hydrogen atom as the first step in the reaction:[3]

$$CH_3{\cdot}CH_2{\cdot}OH + \text{Enzyme} \rightarrow CH_3{\cdot}CHOH + \text{Monodesoxyenzyme} + H^+$$

Similarly they assumed direct formation of the radical $CH_3\dot{C}O$ in the oxidation of acetaldehyde and also extended their hypothesis of single hydrogen abstraction to purely chemical processes. It has since been adopted as a basis of interpretation of numerous kinetic studies, and Haber and Willstätter's consideration of the strength of the >C—H bond has been supplemented by emphasis on the greater strength of the —O—H bond, in justification of their hypothesis in regard to alcohol.[4,5,6]

Evidently, however, the arbitrary limitation of determining influence on a reaction to one of the participants is inadmissible. Thus, although, in accordance with bond-strength considerations, Partington observed constancy of rate of thermal decomposition in a series of paraffin hydrocarbons,[7] this was disturbed by the presence of a second reactant, so that Cullis and Hinshelwood recorded considerable variation of induction period in the low-temperature oxidation of such hydrocarbons.[8] Further, consistent application of the bond-strength criterion would require rupture of a >C—C< rather than of a >C—H bond. Although this has in fact been assumed

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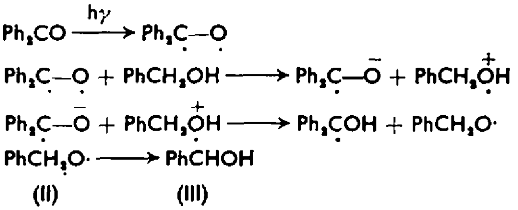
[1] H. Wieland, *Ber. Dtsch. Chem. Ges.* **45**, 484, 2606 (1912).
[2] H. Wieland, *J. Chem. Soc.* 1055 (1931).
[3] F. Haber and R. Willstätter, *Ber. Dtsch. Chem. Ges.* **64**, 2844 (1931); cf. J. Kenner, *Ibid.* **65**, 705 (1932).
[4] J. L. Bolland and H. R. Cooper, *Proc. Roy. Soc.* A **225**, 405 (1954).
[5] C. F. Cullis and E. J. Newitt, *Proc. Roy. Soc.* A **237**, 540 (1956).
[6] K. M. Bell and C. H. Tipper, *Proc. Roy. Soc.* A **238**, 265 (1956).
[7] R. G. Partington, *Disc. Faraday Soc.* **2**, 114 (1947).
[8] C. F. Cullis and C. N. Hinshelwood, *Disc. Faraday Soc.* **2**, 116 (1947).

by Hinshelwood and co-workers to occur in the thermal decomposition of diethyl ether,[9–16] another interpretation of this reaction will be suggested as preferable. Finally, it is clear that the bond-strength concept offers no guidance as to the particular site of reaction in a given molecule. In fact, its introduction seems most unfortunately to have diverted attention from the fundamental fact that chemical, as well as extra-nuclear physical, phenomena are primarily electronic and not atomic in character.

Again, although Haber and Willstätter's equation recognised in respect of the enzyme the classical conception of oxidation as a process of electron transference, this was evidently only secondary to hydrogen transference. Also, owing to the virtually non-polar character of $\equiv C{-}H$ bonds, the electron transference did not apply to the substrate; yet it is solely this aspect of the equation that has figured in the kinetic studies just mentioned. These have also been marked by neglect of any attempt to correlate their findings with either the relevant general data of chemistry or the classical electron-transference mechanism. In short, there has been consistent neglect of Occam's razor.

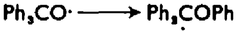
The photochemical oxidation of alcohol to acetaldehyde by excited benzophenone clearly involves electron transference, since the ketone is reduced to tetraphenylethylene glycol,[17] as is its unexcited form by metallic reagents. However, Bäckström noted an independent side-reaction in the presence of oxygen, which led to the formation of acetic acid, and so attributed his results to hydrogen abstraction[18] as envisaged by Haber and Willstätter. He did so the more readily since the formation of a mixture of di-,tri- and tetra-phenylethylene glycols by photolysis of a mixture of benzophenone and benzyl alcohol[19] clearly requires the formation of the two radicals $Ph\underset{\cdot}{C}HOH$ and $Ph_2\underset{\cdot}{C}OH$. This is, however, consistent with an electron transference mechanism if isomerisation of benzyloxy (II) to phenylhydroxymethyl radical (III) be assumed:



$$\begin{aligned}
&Ph_2CO \xrightarrow{h\nu} Ph_2\underset{\cdot}{C}{-}\underset{\cdot}{O}\\
&Ph_2\underset{\cdot}{C}{-}\underset{\cdot}{O} + PhCH_2OH \longrightarrow Ph_2\underset{\cdot}{C}{-}\overset{-}{O} + PhCH_2\overset{+}{\underset{\cdot}{O}}H\\
&Ph_2\underset{\cdot}{C}{-}\overset{-}{O} + PhCH_2\overset{+}{\underset{\cdot}{O}}H \longrightarrow Ph_2\underset{\cdot}{C}OH + PhCH_2O\cdot\\
&PhCH_2O\cdot \longrightarrow Ph\underset{\cdot}{C}HOH
\end{aligned}$$

(II) (III)

This change results in a condition of greater resonance and corresponds to that of triphenylmethoxy to diphenylphenoxymethyl radical[20]:



$$Ph_3CO\cdot \longrightarrow Ph_2\underset{\cdot}{C}OPh$$

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[9] C. N. Hinshelwood, *Proc. Roy. Soc.* A **114**, 84 (1927).

[10] C. N. Hinshelwood and P. J. Askey, *Proc. Roy. Soc.* A **115**, 215 (1927).

[11] P. A. K. Clusius and C. N. Hinshelwood, *Proc. Roy. Soc.* A **128**, 82 (1930).

[12] J. V. S. Glass and C. N. Hinshelwood, *J. Chem. Soc.* 1804 (1929); *Ibid.* 1815 (1929).

[13] P. A. K. Clusius, *J. Chem. Soc.* 2607 (1930).

[14] L. A. K. Staveley and C. N. Hinshelwood, *Proc. Roy. Soc.* A **154**, 335 (1936); *Ibid.* **159**, 192 (1937); *J. Chem. Soc.* 1568 (1937).

[15] J. R. E. Smith and C. N. Hinshelwood, *Proc. Roy. Soc.* A **180**, 242 (1942); *Ibid.* **183**, 37 (1944).

[16] C. N. Hinshelwood, *The Structure of Physical Chemistry* p. 420. Oxford (1951).

[17] G. Ciamician and P. Silber, *Ber. Dtsch. Chem. Ges.* **33**, 2911 (1900).

[18] H. L. J. Bäckström, *Svedberg Memorial Vol.* 456 (1944).

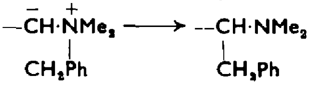
[19] W. D. Cohen, *Rec. Trav. Chim. Pays-Bas* **39**, 249 (1920).

[20] H. Wieland, *Ber. Dtsch. Chem. Ges.* **44**, 2550 (1911).

Similarly the trimethylene biradical, from electrolysis of potassium glutarate, at once isomerises to the more saturated propene[21]:

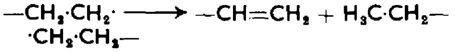
$$\bar{O}_2C(CH_2)_3C\bar{O}_2 \xrightarrow{-2e} 2CO_2 + [\cdot CH_2\cdot CH_2\cdot CH_2\cdot] \longrightarrow CH_3\cdot CH{=}CH_2$$

These changes can be regarded as radical analogues of the Stevens rearrangement[22]:



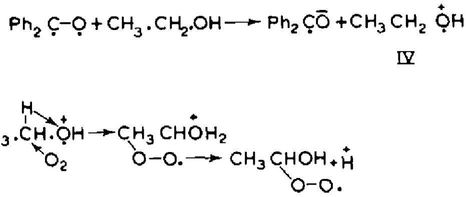
$$-\overset{-}{C}H\cdot\overset{+}{N}Me_2(CH_2Ph) \longrightarrow -CH(CH_2Ph)\cdot NMe_2$$

and illustrate the fact that, under a suitable impulse, radicals are liable to change like other electron-deficient systems. Thus radical disproportionation corresponds to the Hofmann degradation of organic kations:

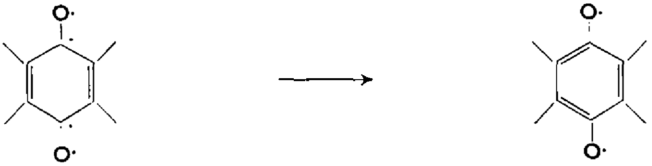


$$\begin{array}{l}-CH_2\cdot CH_2\cdot \\ \cdot CH_2\cdot CH_2-\end{array} \longrightarrow -CH{=}CH_2 + H_3C\cdot CH_2-$$

and the occurrence of Bäckström's side-reaction is attributable to a Wagner–Meerwein type of reaction of the positively charged hydroxyethyl radical (IV), resulting from attack of alcohol by excited benzophenone:

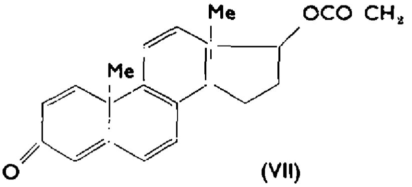


Excitation of quinone also can induce oxidation of alcohol to acetaldehyde,[23] whilst direct photochemical oxidation of the alcohol by oxygen to acetic acid and acetaldehyde occurs in the presence of anthraquinone or its sodium 2:6-disulphonate.[4] The previous detailed discussion[24] of this reaction, in refutation of its interpretation by Bolland and Cooper, was based on the biradical (V), assumed by them as intermediate and derived by aromatisation of the excited state (VI) of the quinone, but is clearly also applicable to this latter, with its higher oxidation potential and correspondence to the excited state of benzophenone:



(V) (VI)

Further, the concordance of the effects of protonic and of photoactivation of 1-dehydro-*O*-acetyltestosterone[25] (VII):



(VII)

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[21] B. L. Vanzetti, *Gazz. Chim. Ital.* **34** (II), 511 (1904).

[22] T. S. Stevens *et al.*, *J. Chem. Soc.* 2107, 2119 (1930); *Ibid.* 55, 69, 1926, 1932 (1932).

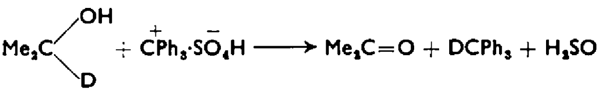
[23] G. Ciamician and P. Silber, *Ber. Dtsch. Chem. Ges.* **34**, 1530 (1901).

[24] J. Kenner, *Nature, Lond.* **179**, 142 (1957).

[25] H. Dutler, H. Bosshard and O. Jeger, *Helv. Chim. Acta* **50**, 494 (1957).

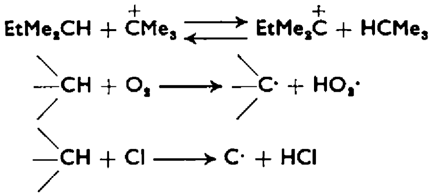
supports the view that the effect of excitation is simply to increase the oxidation potential of ketones and quinones rather than to modify their normal electrophilic reactivity to one of hydrogen abstraction, as assumed by Bäckström and by Bolland and Cooper. Indeed, it would seem axiomatic that the effect of access of energy to a given molecular system can, so long as it remains intact and able to revert to its unexcited state, alter its reactivity only intensively and not qualitatively.

The limitation of oxidative changes in alcohol to the $\rangle$CH— group adjoining the oxygen atom makes the probable participation of this as a source of electrons at once obvious. In the same way the oxidation of *iso*propyl alcohol by triphenylmethylsulphuric ester[26]:



$$\mathrm{Me_2C(OH)D} + \overset{+}{\mathrm{C}}\mathrm{Ph_3}\cdot\overset{-}{\mathrm{SO_4}}\mathrm{H} \longrightarrow \mathrm{Me_2C{=}O + DCPh_3 + H_2SO_4}$$

and similar reactions[26] also depend on electron transference from oxygen so that D is removed, not as atom, but as negatively charged ion. The analogous reaction with paraffins[27,28] constitutes the ionic counterpart of their attack by oxygen and by atomic chlorine:



$$\mathrm{EtMe_2CH} + \overset{+}{\mathrm{C}}\mathrm{Me_3} \rightleftarrows \mathrm{EtMe_2}\overset{+}{\mathrm{C}} + \mathrm{HCMe_3}$$
$$\rangle\mathrm{CH} + \mathrm{O_2} \longrightarrow \rangle\mathrm{C}\cdot + \mathrm{HO_2}\cdot$$
$$\rangle\mathrm{CH} + \mathrm{Cl} \longrightarrow \mathrm{C}\cdot + \mathrm{HCl}$$

In these reactions the reagent, whether atom, oxygen or kation must be electrophilic, since it first encounters the electronic system enveloping an assemblage of carbon nuclei and protons and the susceptibility of the system to demand is well known, e.g. from the phenomena of aromatic substitution. Then the instability of kations $\overset{+}{\mathrm{RH}}$, resulting from electron transference can induce a condition of hydrogen bonding leading to proton transference:

$$\mathrm{RH + X} \longrightarrow \overset{\cdot+}{\mathrm{RH}} + (\overline{\mathrm{e\text{-}X}}) \longrightarrow \mathrm{R\text{-}(eX)} \longrightarrow \mathrm{R\cdot + H(eX)}\ *$$

As already insisted, the hydrocarbon suffers no net electronic loss in this reaction and, for example, its oxidation only sets in when R· is attacked. Similar peripheral preliminaries must occur when radicals are employed, so that we have a further

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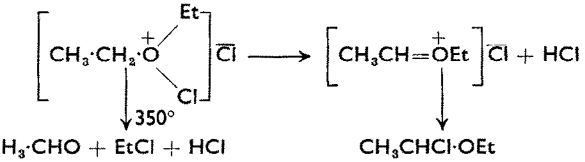
[*] This scheme covers the anti-knock properties of 2:2:4-trimethylpentane. Thus, although the optimum region for attack surrounds C2, no hydrogen is available here for completion of the change. Again, although C4 carries a hydrogen atom the tertiary radical $\mathrm{Me_3C.CH_2\underset{\cdot}{C}Me_2}$ resulting from attack should be relatively stable and experiment shows the corresponding olefin to be one product of oxidation of the pentane (F. F. Rust and Collamer, *J. Amer. Chem. Soc.* 76, 1055 (1954)). The photodecomposition of paraffins, now well recognised as involving $\rangle$C.H groups, is similarly attributable to preliminary ionisation to $\rangle\overset{+}{\mathrm{C}}\mathrm{H}$+e.

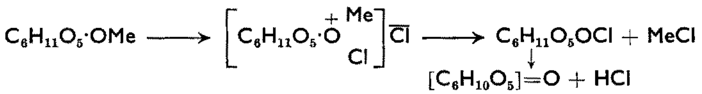
[26] P. D. Bartlett and J. D. McCollum, *J. Amer. Chem. Soc.* 78, 1441 (1956).
[27] P. D. Bartlett, F. E. Condon and A. Schneider, *J. Amer. Chem. Soc.* 66, 1531 (1944).
[28] H. Pines and R. Wacker, *J. Amer. Chem. Soc.* 68, 593, 599 (1946).

illustration of the significance of electron deficiency for the chemistry of radicals. The sharp differentiation of these from carbonium ions, fostered by the terms homolysis and heterolysis, is artificial and unjustifiable in principle.

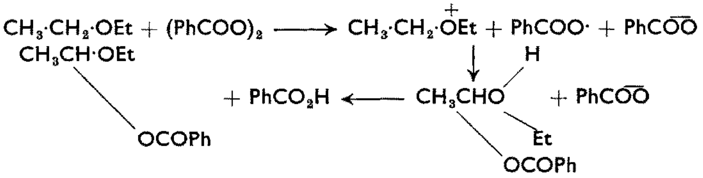
In ethers, as in alcohols, the oxygen atom is the seat of chemical reactivity. Thus the compound derived from ether by the action of chlorine at low temperature must be formulated[29] as $[\mathrm{Et_2\overset{+}{O}Cl}]\overline{\mathrm{Cl}}$. Under ordinary conditions this decomposes like other hypochlorites to yield chlorodiethyl ether[30] or, above 350°, acetaldehyde, ethyl and hydrogen chlorides[31]:



Similarly α-methylglucoside yields gluconolactone[32,33]:



The benzoylation of ethers by benzoyl peroxide[34] can be written:



(VIII)

This formulation also covers the formation of ethyl *n*- and *iso*-butyrates by action of the respective peroxides on ether[35]:

$$\mathrm{CH_3{\cdot}CH_2{\cdot}OEt + (C_3H_7COO{\cdot})_2 \longrightarrow CH_3CH_2\overset{+}{O}Et + C_3H_7COO{\cdot} + C_3H_7CO\overline{O}}$$
$$\downarrow$$
$$\mathrm{CH_3CHO + C_3H_7CO_2H + C_3H_7CO_2Et}$$

Again, autoxidation of ether leads essentially to equimolecular proportions of acetaldehyde and hydrogen peroxide (or their compounds) together with some acetic acid and a small proportion of formic acid.[36,37,38] Its photochemical oxidation by quinones also corresponds to that of alcohol.[23] This correspondence supports the view that the primary occurrence in the oxidation of alcohol is one of electron transference and that the accompanying loss of proton is consequential. Similarly the reduction of silver oxide by acyl diazoethanes in the presence of aniline, preliminary to rearrangement,[39] shows it to be unnecessary to assume with Newman

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[29] A. McIntosh, *J. Chem. Soc.* 789 (1905); O. Hassel, *Proc. Chem. Soc.* 250 (1957).

[30] O. Jacobsen, *Ber. Dtsch. Chem. Ges.* **4**, 215 (1871).

[31] H. P. Meissner and H. J. Schumacher, *Z. Phys. Chem.* A **185**, 457 (1940).

[32] A. Dyferman, B. Lindberg and D. Wood, *Acta Chim. Scand.* **51**, 253 (1951).

[33] N. Liehtin and J. Saxe, *J. Amer. Chem. Soc.* **77**, 1875 (1955).

[34] W. E. Cass, *J. Amer. Chem. Soc.* **69**, 500 (1947).

[35] M. S. Kharasch, S. S. Kane and H. C. Brown, *J. Amer. Chem. Soc.* **63**, 526 (1941).

[36] H. King, *J. Chem. Soc.* 749 (1929).

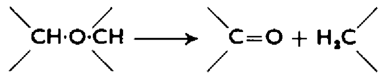
[37] N. A. Milas, *J. Amer. Chem. Soc.* **53**, 221 (1931).

[38] E. J. Orloff, *J. Russ. Phys. Chem. Soc.* **40**, 799 (1908).

[39] G. Baddeley, G. Holt and J. Kenner, *Nature, Lond.* **163**, 766 (1941).

and Beal[40] that the first step in the reaction with corresponding derivatives of diazomethane consists in removal of proton.

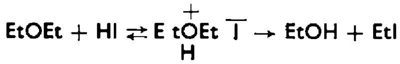
The thermal disproportionation of ethers into carbonyl derivatives and paraffins constitutes an intramolecular process of oxidation and reduction:



Hinshelwood and his collaborators have expressed the results of their kinetic study of this reaction in the following adaptation to the case of diethyl ether of the scheme put forward by Rice and Herzfeld for dimethyl ether[41]:

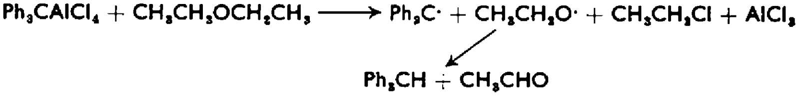
$$CH_3{\cdot}CH_2{\cdot}O{\cdot}C_2H_5 \rightleftarrows {\cdot}CH_2{\cdot}O{\cdot}C_2H_5 + {\cdot}CH_3$$
$${\cdot}CH_3 + CH_3{\cdot}CH_2{\cdot}O{\cdot}C_2H_5 \rightleftarrows CH_3{\cdot}CH_3 + {\cdot}CH_2{\cdot}O{\cdot}C_2H_5$$
$${\cdot}CH_2{\cdot}O{\cdot}C_2H_5 \rightleftarrows {\cdot}CH_3 + CH_3{\cdot}CHO$$
$${\cdot}CH_3 + {\cdot}CH_2OC_2H_5 \rightleftarrows CH_3{\cdot}CH_2{\cdot}O{\cdot}C_2H_5$$

They emphasise that this accords with the doctrine of maximum simplicity, but it clearly offends Occam's razor, a special form of the doctrine, since it does not accord with the general behaviour of ether, as illustrated by the foregoing and by its decomposition by hydrogen iodide into ethyl alcohol and ethyl iodide:



$$EtOEt + HI \rightleftarrows Et\underset{H}{\overset{+}{O}}Et\ \bar{I} \rightarrow EtOH + EtI$$

In this reaction the alkyl iodide corresponds to the alkyl hydride of the thermal reaction. If, then, in place of a co-ordinative sharing of the electronic system of the oxygen atom with proton, an electron transference could be achieved, formation of carbonyl derivative rather than of alcohol should ensue. This in fact occurs when ether is added to a cold solution of triphenylmethyl aluminochloride[41]:



$$Ph_3CAlCl_4 + CH_3CH_2OCH_2CH_3 \longrightarrow Ph_3C{\cdot} + CH_3CH_2O{\cdot} + CH_3CH_2Cl + AlCl_3$$
$$Ph_3CH + CH_3CHO$$

A similar reaction with chlorine above 350° has already been noticed.

Similarly (VIII) is the benxoyl derivative of acetaldehyde alcoholate. We thus conclude that, in all probability, the course of the thermal decomposition is similar, the determinant initial thermal effect being disturbance of the electronic system of the oxygen atom somewhat as follows:

$$CH_3{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}CH_3 \overset{\text{heat}}{\rightleftarrows} CH_3{\cdot}CH_2{\cdot}\overset{+}{\dot{O}}{\cdot}CH_2{\cdot}CH_3 + e$$
$$\downarrow$$
$$CH_3{\cdot}CH_2{\cdot}O{\cdot} + {\cdot}CH_2CH_3$$
$$CH_3.CH_2{\cdot}O{\cdot} \rightarrow H + CH_3CHO$$
$$H + CH_3{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}CH_3 \rightarrow CH_3{\cdot}CH_2{\cdot}O{\cdot} + H{\cdot}CH_2{\cdot}CH_3$$

The particularly effective inhibitive action of nitric oxide is then expressed by the equations[42]:

$$CH_3{\cdot}CH_2{\cdot}O{\cdot} + {\cdot}NO \rightleftarrows CH_3{\cdot}CH_2{\cdot}O{\cdot}NO$$
$$CH_3{\cdot}CH_2{\cdot}O{\cdot}NO \rightarrow CH_3CHO + CH_3CH_2OH + NO$$

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[40] M. S. Newman and P. F. Beal, *J. Amer. Chem. Soc.* **72**, 5163 (1950).

[41] F. O. Rice and K. H. Herzfeld, *J. Amer. Chem. Soc.* **56**, 287 (1934).

[42] J. F. Norris, *Organic Synthesis* (Coll. Vol. I) p. 532. Wiley, New York (1941).

whilst the catalytic action of large concentrations of the gas is attributable to the reaction:

$$\mathrm{EtOEt + NO \rightleftarrows EtO\cdot + EtNO}$$

and that of hydrogen on low concentrations of the ether is perhaps due to the reaction:

$$\mathrm{EtOEt + H_2 \rightleftarrows EtO\cdot + H + ErH}$$

Although the course of the decomposition of dimethyl ether is clear cut, that of diethyl ether is less so owing to some diversion by the reaction (cf. Kenner[24]):

$$\mathrm{CH_3{\cdot}CH_2{\cdot}O\cdot \rightarrow \cdot CH_3 + CH_2O}$$

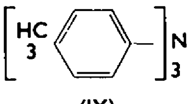
and its consequences.

The relationship of amines to alcohols and ethers renders their attack at the nitrogen atom by oxidising agents, e.g. chlorine, iodine, benzoyl peroxide[44] and acetyl peroxide[45], particularly significant for the present discussion:

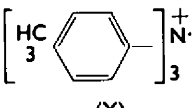
$$\mathrm{Et_2NH + (PhCOO)_2 \rightarrow Et_2NOCOPh + PhCO_2H}$$

$$\mathrm{2Ph_2NH + (CH_3COO)_2 \rightarrow Ph_2N{\cdot}NPh_2 + 2CH_3{\cdot}COOH}$$

Kern[45] and Horner and co-workers[46] have also contributed studies of the behaviour of etheric and amino compounds, particularly of dimethylaniline, towards dibenzoyl peroxide in terms of electron transference. The adequacy of this standpoint in respect of the behaviour of aliphatic amines and ethers towards the peroxide was also recognised by Bartlett and Nozaki, but they gave preference to that of hydrogen abstraction because they did not observe the blue coloration characteristic of the tri-*p*-tolylaminium radical (X) during the reaction of benzoyl peroxide with tri-*p*-tolylamine (IX) in benzene solution.[47]



(IX)



(X)

However, the observations of Wieland and Wecker[48] and of Weitz and Schwechten[49] demonstrate the exceedingly slight tolerance of the radical ion for its positive charge. There can thus be little or no prospect of the existence of the ion in the presence of the anion of a weak acid like benzoic acid and still less if the radical $C_6H_5COO\cdot$ is also present. Further, the triarylamines are themselves completely devoid of basic properties, owing mainly to steric inhibition of a tetrahedral configuration round the nitrogen atom. The planar configuration thus imposed is, however, favourable to

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[43] B. A. Gingras and W. A. Waters, *J. Chem. Soc.* 3508 (1954).

[44] St. Gambarjan, *Ber. Dtsch. Chem. Ges.* **42**, 4003 (1909); *Ibid.* **58B**, 1775 (1925); *Ibid.* **60B**, 390 (1927).

[45] W. Kern, *J. Makromol. Chem.* **1**, 209 (1948).

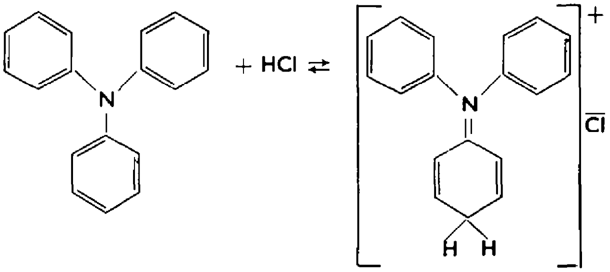
[46] L. Horner *et al.*, *Liebigs Ann.* **566**, 69 (1950); *Ibid.* **573**, 35 (1951); *Ibid.* **574**, 202, 212 (1951); *Ibid.* **579**, 175, 193 (1953); *Chem. Ber.* **85**, 804 (1952).

[47] P. D. Bartlett and K. Nozaki, *J. Amer. Chem. Soc.* **69**, 2299 (1947).

[48] H. Wieland and E. Wecker, *Ber. Dtsch. Chem. Ges.* **43**, 699 (1910).

[49] E. Weitz and H. Schwechten, *Ber. Dtsch. Chem. Ges.* **59**, 2307 (1926).

nuclear attack and these amines accordingly exhibit halochromy in benzene solution in the presence of hydrogen chloride; e.g.:



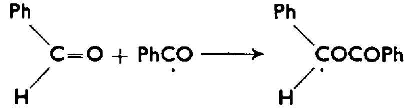
Similarly, no peroxide remained after a solution of tri-*p*-tolylamine (1·2 g) and benzoyl peroxide (4 g) in benzene (40 ml) had been boiled for 4 hr under reflux in a stream of nitrogen. After neutralisation with sodium hydroxide (18·6 ml) the separated benzene solution was evaporated. The filtered ethereal solution of the residue, after concentration and trituration with alcohol, yielded a vitreous product, apparently a mixture of isomeric tribenzoxy derivatives of tri-*p*-tolylamine [Found: C, 77·6; H, 5·37; N, 1·87. $C_{42}H_{33}O_6N_3$ (mol. wt. 675) requires C, 77·9; H, 5·1; N, 2·16 per cent]. It was easily hydrolysed by boiling alcoholic potassium hydroxide, (Calc. (OOC C_6H_5), 56·1. Found 56·0 per cent).

The assumption by Haber and Willstätter of the radical $R\underset{\cdot}{C}O$ as the first step in the autoxidation of aldehydes has been widely adopted. It accords with the suggestion by Bodländer[50] that perbenzoic acid is an intermediate product in the autoxidation of benzaldehyde and with the demonstration by Baeyer and Villiger that benzoic acid results from interaction of the peracid with benzaldehyde.[51] The numerous kinetic studies supplementing this observation have frequently been based on the Haber–Willstätter standpoint. Bawn and his collaborators[65,66] have, however, recently abandoned their original formulation on these lines in favour of a process of electron transference, but left its precise mechanism indeterminate.

Since, now, the oxygen atom is the negative pole of the carbonyl group and reactive towards proton, it should be so towards other electrophilic reagents, including radicals. This is experimentally confirmed by genesis of the dibenzoates of the stereoisomeric hydrobenzoins in the reaction of benzaldehyde with di-*tert*.-butyl peroxide.[67] The radical (XI) must be the precursor of the isomers and equally

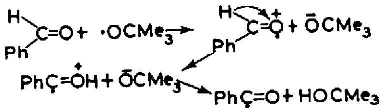
[50] G. Bodländer, *Ahrens Sammlung* 3, 470 (1899).
[51] A. von Baeyer and V. Villiger, *Ber. Dtsch. Chem. Ges.* 33, 858, 1560 (1900).
[52] M. Bodenstein, *Z. Phys. Chem.* 12B, 151 (1931).
[53] M. Bodenstein, *Rec. Trav. Chem. Pays-Bas* 59, 48 (1940).
[54] H. L. J. Bäckström, *Z. Phys. Chem.* 25B, 115 (1934).
[55] H. L. J. Bäckström, *J. Amer. Chem. Soc.* 49, 460 (1927).
[56] E. J. Bowen and E. L. Tietz, *J. Chem. Soc.* 234 (1930).
[57] H. J. Almquist and G. E. K. Branch, *J. Amer. Chem. Soc.* 54, 2293 (1932).
[58] C. A. McDowell and J. H. Thomas, *J. Chem. Soc.* 2208, 2217 (1949); *Ibid.* 1462 (1950).
[59] J. B. Farmer and C. A. McDowell, *Trans. Faraday Soc.* 48, 624 (1952).
[60] W. A. Waters and C. Wickham-Jones, *J. Chem. Soc.* 812 (1951); *Ibid.* 2420 (1952).
[61] J. R. Dunn, W. A. Waters and C. Wickham-Jones, *J. Chem. Soc.* 2427 (1952).
[62] R. F. Moore and W. A. Waters, *J. Chem. Soc.* 2432 (1952).
[63] H. R. Cooper and H. W. Melville, *J. Chem. Soc.* 1984, 1994 (1951).
[64] C. E. H. Bawn and J. B. Williamson, *Trans. Faraday Soc.* 47, 721, 735 (1951).
[65] C. E. H. Bawn and J. E. Jolley, *Proc. Roy. Soc.* A 237, 297 (1956).
[66] C. E. H. Bawn, T. P. Hobin and L. Raphael, *Proc. Roy. Soc.* A 237, 313 (1956).
[67] F. F. Rust, F. H. Seubold and W. E. Vaughan, *J. Amer. Chem. Soc.* 70, 3258 (1948).

must be derived from attack of the aldehyde through its oxygen atom by potential benzoyl radical:

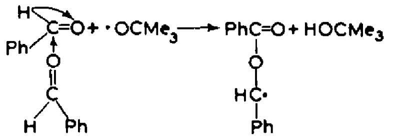


(XI)

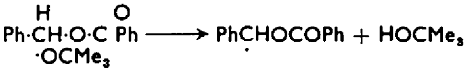
The occurrence of a similar attack of the aldehyde by *tert.*-butoxy radical (or by the methyl radical derived from it[68]) must then be accepted, and the formation of the benzoyl radical is readily expressed as the radical analogue of the Beckmann rearrangement:



This analogy requires, however, that the migration of hydrogen be accompanied by simultaneous entry of a radical or its equivalent. The PhCO radical is thus probably not involved as a separate entity, and the correct representation of the reaction is as follows:

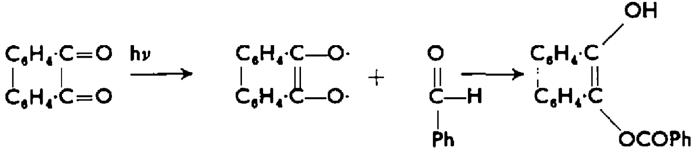


Mesoydrobenzoin is also formed by interaction of di-*t*-butyl peroxide and benzyl benzoate followed by dimerisation of a single form of (XI):

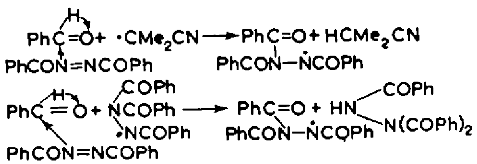


$$\mathrm{Ph{\cdot}\underset{\cdot OCMe_3}{\overset{H}{C}H}{\cdot}O{\cdot}\overset{O}{C}\;Ph} \longrightarrow \mathrm{Ph\underset{\cdot}{C}HOCOPh} + \mathrm{HOCMe_3}$$

Similarly, the formation of phenanthryl benzoate from irradiated phenanthraquinone and benzaldehyde[69,70] can be written:



Again, the reaction of benzaldehyde with azobenzoyl, is promoted by the radical derived from azo*iso*butyronitrile:[71]



This presumably also applies to the corresponding reaction with ethyl azocarboxylate,[72] and the relationship of these azo compounds to oxygen[71] renders their reactions particularly relevant to the oxidation problem. Again, it is confirmatory of the

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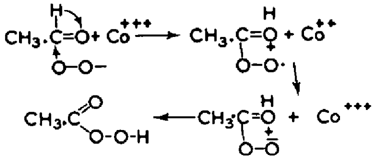
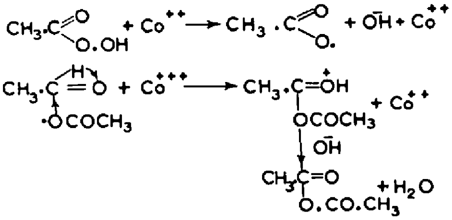
[68] N. A. Milas and D. M. Surgenor, *J. Amer. Chem. Soc.* **68**, 205 (1946).
[69] H. C. Klinger, *Liebigs Ann.* **249**, 143 (1888).
[70] R. F. Moore and W. A. Waters, *J. Chem. Soc.* 238 (1953).
[71] L. Horner and W. Naumann, *Liebigs Ann.* **587**, 81 (1954).
[72] K. Alder and T. Noble, *Ber. Dtsch. Chem. Ges.* **76**, 54 (1943).

foregoing interpretations of radical catalysis that cobaltic ion stimulates the autoxidation of acetaldehyde.[64] This reaction also can be represented without involving the free acyl radical, as follows:

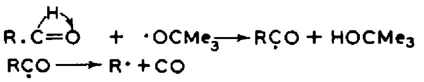


and the formation of acetic anhydride from acetaldehyde and peracetic acid, promoted by cobaltous ion, can be written:

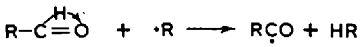


Corresponding formulations are applicable to retardation of benzaldehyde autoxidation by quinones (in biradical form), studied by Waters and his collaborators.[60,61,62]

The formation of (XI) is dependent on the resonance of the $Ph\underset{\cdot}{C}H$— grouping. Failing it, and in absence of oxygen, the resonance of carbon monoxide determines breakdown of the acyl radical, so that butylperoxide provokes the chain decomposition of aliphatic aldehydes.[73]



The recognised course of the subsequent reaction[74] can be similarly expressed:



The conversion of β-phenyl*iso*valeraldehyde by treatment with *tert.*-butyl peroxide into approximately equal proportions of *tert.*- and *iso*-butylbenzenes is due to migration of phenyl within the corresponding radicals.[75]

$$PhCMe_2CH_2CHO \rightarrow PhCMe_2\underset{\cdot}{C}H_2 + CO + H$$

$$PhCMe_2\underset{\cdot}{C}H_2 \rightleftarrows \underset{\cdot}{C}Me_2{\cdot}CH_2Ph$$

The small yields of the corresponding secondary alcohols occurring in these reactions would seem to be attributable to a reversal of the thermal decomposition of ketones followed by reduction:

$$R\underset{\cdot}{C}O + R\cdot \rightleftarrows R_2CO$$

The correspondence of the results of such thermal and of photal with those of the above radical excitations indicates that the former also arise from a disturbance at the oxygen atoms, such as already suggested in the case of ether.

The formation of benzoyl chloride by chlorination of benzaldehyde[76] is the

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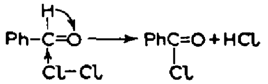
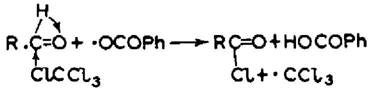
[73] F. F. Rust, F. H. Seubold and W. E. Vaughan, *J. Amer. Chem. Soc.* **70**, 4253 (1948).
[74] J. A. Leermakers, *J. Amer. Chem. Soc.* **56**, 1537 (1934).
[75] S. Winstein and F. H. Seubold, *J. Amer. Chem. Soc.* **69**, 2916 (1947).
[76] L. Wöhler and H. von Liebig, *Liebigs Ann.* **3**, 262 (1832).

earliest recorded instance of apparent hydrogen abstraction, and is also satisfactorily explained in terms of preliminary attack on the oxygen atom:



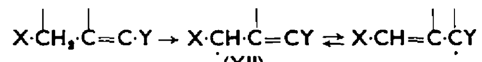
$$\mathrm{Ph{-}\underset{Cl-Cl}{\overset{H}{C}}{=}O \longrightarrow Ph\underset{Cl}{C}{=}O + HCl}$$

Similarly for chlorination by carbon tetrachloride in the presence of benzoyl peroxide:



$$\mathrm{R.\underset{ClCCl_3}{\overset{H}{C}}{=}O + \cdot OCOPh \longrightarrow R\underset{Cl + \cdot CCl_3}{C}{=}O + HOCOPh}$$

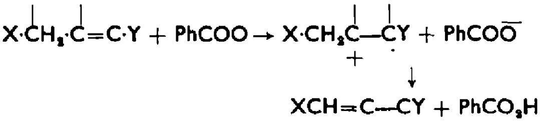
The α-oxidation of olefines depends on genesis of a mesomeric radical system (XII):



$$\mathrm{X{\cdot}\overset{|}{C}H_2{\cdot}\overset{|}{C}{=}C{\cdot}Y \rightarrow X{\cdot}\underset{\cdot}{C}H{\cdot}\overset{|}{C}{=}CY \rightleftarrows X{\cdot}CH{=}\overset{|}{C}{\cdot}\underset{\cdot}{\overset{|}{C}}Y}$$

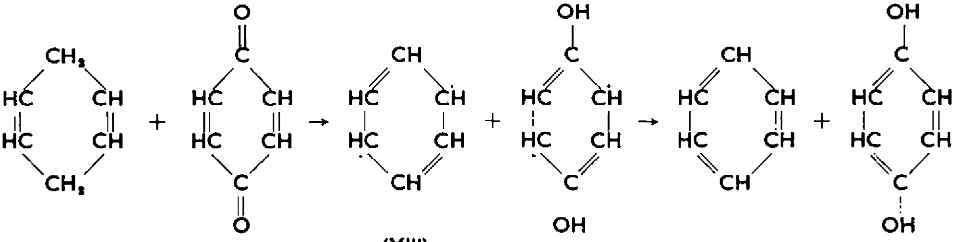
(XII)

and it is currently assumed that this arises from direct removal of a hydrogen atom.[77,78] This contravention of Occam's razor is the less acceptable since Kharasch, Engelmann and Mayo pointed out that the point of initial attack of olefines by atomic bromine is that carbon atom of the double bond with the greater electron availability.[79] Similarly propylene is more reactive towards atomic hydrogen than ethylene, and *iso*propyl predominates very largely over *n*-propyl radical in the product, whilst hydrogen abstraction is a very subordinate process.[80,81] The same would be expected of attack by a radical or of photochemical excitation. We then have a normal process of oxidation by electron transference, yielding radicals that combine with benzoxy radical to form the final product,[82] e.g.:



$$\begin{array}{l}\mathrm{X{\cdot}\overset{|}{C}H_2{\cdot}\overset{|}{C}{=}C{\cdot}Y + PhCOO \rightarrow X{\cdot}CH_2\underset{+}{\overset{|}{C}}{-}\underset{\cdot}{\overset{|}{C}}Y + PhCO\bar{O}} \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\downarrow \\ \qquad\qquad\qquad\qquad\quad \mathrm{XCH{=}C{-}CY + PhCO_2H}\end{array}$$

Experimental investigation of the reaction is complicated by chain polymerisation through the radical intermediate, but this is eliminated in the study of *cyclo*hexa-1:4-diene,[83] since the intermediate biradical (XIII) at once suffers aromatisation. The oxidation is ideally achieved by a molecule of quinone lying above and parallel to the plane of the diene ring:



(XIII)

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[77] Cf. J. L. Bolland, *Quart. Rev.* **3**, 1 (1949).

[78] Cf. L. Bateman, *Quart. Rev.* **8**, 147 (1954).

[79] M. S. Kharasch, H. Engelmann and F. R. Mayo, *J. Org. Chem.* **2**, 288 (1937).

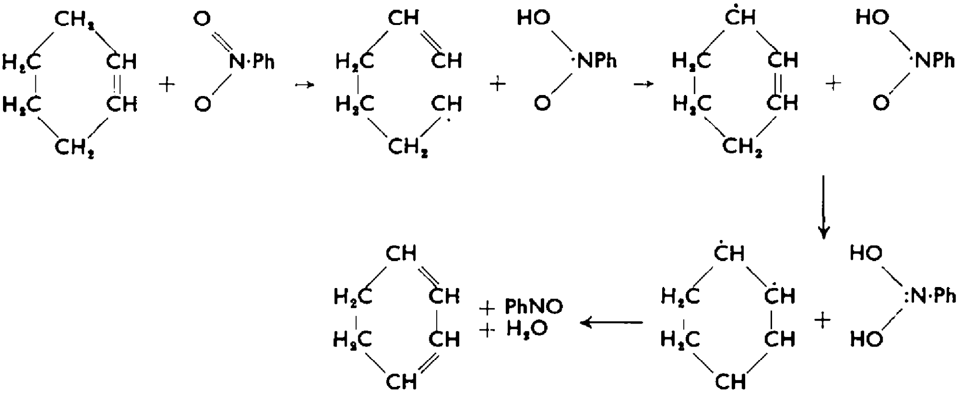
[80] J. N. Bradley, H. W. Melville and J. C. Robb, *Proc. Roy. Soc.* A **236**, 339, 455 (1936).

[81] B. de B. Darwent and R. Roberts, *Disc. Faraday Soc.* **14**, 55 (1953).

[82] Cf. E. H. Farmer, G. F. Bloomfield, A. Sundralingram and D. A. Sutton, *Trans. Faraday Soc.* **38**, 351 (1942).

[83] E. A. Braude, L. M. Jackman and R. P. Linstead *J. Chem. Soc.* 3548 (1954).

The reaction is favoured by polar solvents, proton activation and substitutional enhancement of the oxidation potential of quinone, but not by radical producing agencies. The unreactivity of *cyclo*hexa-1:3-diene is due to the unsuitable disposition of the seats of electron availability in the 1- and 4-positions in relation to the methylene groups. The initial stages of dehydrogenation of *cyclo*hexene by nitrobenzene in the presence of palladium[84] can be similarly represented with the plane of the nitro-group parallel to that of the olefinic system:



These several reactions thus conform to the respective general behaviours of olefines, quinones and nitro-compounds. A corresponding interpretation is applicable to the "allylic substitution" of olefines by maleic anhydride and by ethyl azocarboxylate[85,86,87,88] and the hypothesis of hydride-ion transference[84] should be discarded.

It will be seen that the catalogue of errors reviewed in the foregoing discussion derives not only from contravention of Occam's razor, but also from the fallacy that kinetic measurement can serve as a primary weapon of chemical investigation. The limitation of its legitimate use to that of a discriminant, auxiliary to purely chemical study, was accurately exemplified in the classical investigation of Lapworth,[89] which inaugurated the modern study of chemical mechanism.

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[84] E. A. Braude, R. P. Linstead and K. R. H. Wooldridge, *J. Chem. Soc.* 3586 (1954).

[85] K. Alder, F. Pascher and A. Schmitz, *Ber. Dtsch. Chem. Ges.* **76**, 27 (1943).

[86] K. Alder and H. Söll, *Liebigs Ann.* **565**, 57 (1949).

[87] K. Alder and H. Söll, *Liebigs Ann.* **565**, 73 (1949).

[88] K. Alder and A. Schmitz, *Liebigs Ann.* **565**, 99 (1949).

[89] A. Lapworth, *J. Chem. Soc.* 30 (1904).