Tetrahedron, 1960, Vol. 8, pp 350 to 355 Pergamon Press Ltd. Printed in Northern Ireland

FURTHER CONSIDERATIONS ON OXIDATIVE PROCESSES

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(*Received* 5 *September* 1959)

Abstract—Refuting recent criticisms by Russell, modification of the currently accepted mechanism of formation of benzyl chloride from toluene is introduced and current interpretation of the reactivity of carbonyl compounds is broadened. The results of the photochemical interaction of benzophenone, isopropyl alcohol, and nitric oxide are shown to accord with classical as against the hydrogen-abstraction theory of oxidation. Supplementary discussion of the behaviour of ethers, amines and paraffins is also contributed.

THE author's recent criticism[1] of the hydrogen-abstraction theory of oxidation has evoked renewed advocacy by Russell[2] of a version originally formulated by Russell and Brown[3] to cover the results of studies of competitive photohalogenation of toluene and cyclohexane at 80°.

In the first place, then, it must be emphasized that any such version is philosophically objectionable since it clearly assumes an essential difference between the courses of oxidation of inorganic and organic substances. Secondly, and consistently with this, the considerations by which Russell seeks to sustain his views are fallacious.

The admittedly generally accepted view that the side-chain photohalogenation of toluene proceeds directly and, apart from inductive effects, independently of the nucleus, is doubtful. It ignores the warning, to be derived from Faraday's ancient observation of the photochemical formation of hexachlorides from benzene,[4] that a similar reaction may occur with toluene. The cogency of this is supported by photo displacement from bromobenzene[5] and *p*-bromotoluene[6] of bromine by chlorine. The formation of *p*-chlorobenzyl bromide in the second case indicates displacement of atomic bromine. Similar results follow the chlorination of boiling *p*-bromotoluene[7] so that the observation by Asinger[8] of displacement of bromine from 3-chloro-5-bromo-toluene[9] at 180–190° is significant as evidence that the reaction depends, not on a simple replacement resulting from directive substitution, but on decomposition of an additive product. In fact α-benzene hexachloride melts with decomposition;[10] further, Barton *et al.* showed such decomposition of 1,2-dichloro-, 1,1,2-trichloro-, and 1,1,2,2-tetrachloro-ethanes to involve formation of atomic chlorine.[11] Similarly the writer, apropos of the thermal decomposition of tolane tetrachloride,[12] noted the

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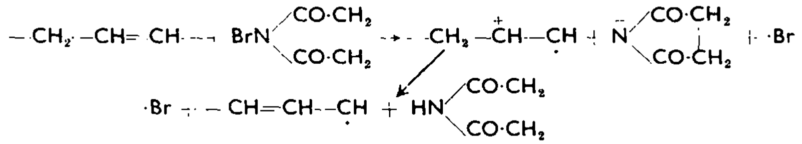
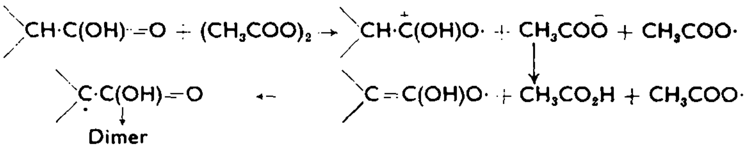
[1] J. Kenner, *Tetrahedron* **3**, 78 (1958).
[2] G. A. Russell, *Tetrahedron* **5**, 101 (1959).
[3] G. A. Russell and H. C. Brown, *J. Amer. Chem. Soc.* **77**, 4578, (1955).
[4] M. Faraday, *Ann. Chim. Phys.* (2) **30**, 274 (1825); H. P. Smith, A. A. Noyes and E. T. Hart, *J. Amer. Chem. Soc.* **55**, 4444 (1933).
[5] A. Eibner, *Ber. Dtsch. Chem. Ges.* **36**, 1230 (1903).
[6] O. Sprek, *Monats.* **11**, 431 (1890).
[7] G. Errera, *Gazz.* **17**, 202 (1887).
[8] F. Asinger, *Monats.* **64**, 153 (1934).
[9] cf. C. Walling and E. A. McElhill, *J. Amer. Chem. Soc.* **73**, 2927 (1951); B. Miller and C. Walling, *Ibid.* **79**, 4187 (1957).
[10] F. E. Matthews, *J. Chem. Soc.* **59**, 166 (1891); J. Meunier, *Ann. Chim. Phys.* (6) **10**, 234 (1887).
[11] D. R. Barton *et. al.*, *J. Chem. Soc.* 148, 155, 165, (1949).
[12] J. Kenner and E. Witham, *J. Chem. Soc.* 1960 (1910).

presence of chlorine and formation of benzoyl chloride,[13] during the thermal decomposition of αα-dichlorobenzylphenyl ketone. There is thus every reason to suppose, subject to more detailed study, some occurrence of such reactions during photohalogenation of toluene at 80°. In this case, and since the same cannot apply to cyclohexane, the above mentioned formulation of Russell and Brown is based on the treatment as comparable of reactions essentially different.

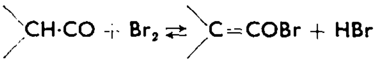
This also applies to Russell's comparative treatment of the photochalogenation of carboxylic acids and their reaction with acetylperoxide. This latter involves α-attack, followed by dimerization, and was attributed by Kharasch and Gladstone[14] and by Price and Moritz[15] to attack by methyl radicals derived from the peroxide. The reaction is, however, limited to the α-position and accordingly Occam's razor demands its consideration in this context. Now, in all cases of α-attack by a single molecule, whether of $>\!CH{-}\overset{|}{C}{=}O$ or of $>\!CH{-}\overset{|}{C}{=}C\!<$, one portion of it causes (1) electron disturbance of the carbonyl group or double bond, (2) removal of proton. The other portion then remains as an atom or radical which, if suitable, completes the process of α-substitution. Thus we have



The α-benzoxylation of olefins by benzoyl peroxide is accompanied by polymerization of the intermediate unsaturated radical.[16] Similarly the process of α-substitution is not completed when acetyl peroxide acts on carboxylic acids:—



It will be noted that molecular bromine does not meet the above conditions and its interaction with carbonyl compounds may be represented as follows:—



Thus α-substitution by bromine requires the auxiliary presence of acid or base.

In default, then, of satisfaction of the conditions necessary for α-substitution. e.g. by atomic chlorine, electrophilic attack must proceed by direct substitution, This probably also accounts for the methyl ketones obtained by Dakin from the action of hydrogen peroxide on ammonium carboxylates[18]:—

$$\begin{tikzcd}
X{\cdot}CH_2CH_2{\cdot}CO\bar{O} + 2{\cdot}OH \arrow[r] & X{\cdot}CHOH{\cdot}CH_2{\cdot}CO\bar{O} \arrow[d] \\
X{\cdot}CO{\cdot}CH_3 & X{\cdot}CO{\cdot}CH_2CO\bar{O} \arrow[l]
\end{tikzcd}$$

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[13] J. Kenner, unpublished observation.

[14] M. S. Kharasch and M. J. Gladstone, *J. Amer. Chem. Soc.* **65**, 15 (1942).

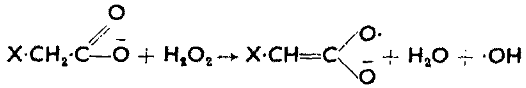
[15] C. C. Price and H. Moritz, *J. Amer. Chem. Soc.* **75**, 3686 (1952).

[16] cf. J. Kenner, *loc. cit.*

[17] A. Michael, *Ber. Dtsch. Chem. Ges.* **34**, 4028 (1901); M. S. Kharasch and H. C. Brown, *J. Amer. Chem. Soc.* **62**, 925 (1950).

[18] H. D. Dakin, *J. Biol. Chem.* **4**, 77, 91, 419 (1908); *Amer. Chem. J.* **44**, 41 (1910).

α-Attack also occurs and may supply the hydroxyl radicals requisite for the β-oxidation:



$$X\cdot CH_2\cdot C(=O)-\bar{O} + H_2O_2 \rightarrow X\cdot CH{=}C(O\cdot)(\bar{O}) + H_2O + \cdot OH$$

Similarly it appears that the attack of alcohols by hydroxyl is not limited to the hydroxy group or adjoining carbon atom.[19] The work of Westheimer[20] has illustrated the dual character required of reagents for the oxidation of alcohols.

The evidence adduced by Bridge and Porter,[21] of hydrogen-abstraction in the oxidation of alcohols by excited quinones also requires consideration. The reaction is not, as might be inferred from the title of their paper, limited to quinones and dyes, for Ciamician and Silber[22] recorded its occurrence with excited ketones and with benzaldehyde. Moreover the relative simplicity of the monocarbonyl compounds renders them more suitable than quinones for study of the essential mechanisms involved. Accordingly the oxidation of isopropyl alcohol by benzophenone, as recorded by Ciamician and Silber, was studied more closely by Bäckström[23] and formulated as follows:—

$$Ph_2CO + h\nu \rightarrow Ph_2\underset{\bullet}{C}-\underset{\bullet}{O}$$

$$Ph_2\underset{\bullet}{C}-\underset{\bullet}{O} + Me_2CHOH \rightarrow Ph_2\underset{\bullet}{C}OH + Me_2\underset{\bullet}{C}OH$$

$$2Ph_2\underset{\bullet}{C}OH \rightarrow (Ph_2\underset{\bullet}{C}OH)_2$$

$$2Me_2\underset{\bullet}{C}OH \rightarrow Me_2CHOH + Me_2CO.$$

The products are tetraphenyl-glycol and acetone and Bäckström was thus constrained to postulate dismutation of $Me_2\underset{\bullet}{C}OH$. Although such a change has been recorded in the case of sodium diphenyl ketyl:[24]

$$2Ph_2\underset{\bullet}{C}ONa + 2H_2O \rightarrow Ph_2CO + Ph_2CHOH + 2NaOH$$

it only occurs under alkaline conditions.[25] The formation of tetraphenyl-glycol in Bäckström's experiment shows the absence of conditions for dismutation and his formulation thus to be unacceptable. By contrast, the classical mechanism, involving contemporaneous electron and proton transference meets the experimental facts quite satisfactorily:

$$Ph_2\underset{\bullet}{C}-\underset{\bullet}{O} + Me_2CHOH \rightarrow Ph_2\underset{\bullet}{C}OH + Me_2CHO\cdot$$

$$Ph_2\underset{\bullet}{C}-\underset{\bullet}{O} + Me_2CHO\cdot \rightarrow Ph_2\underset{\bullet}{C}OH + Me_2CO\cdot$$

More recently, Bäckström *et al.*[26] have performed the same reaction in presence of nitric oxide, observing extensive formation of isopropyl nitrite, as would be anticipated if isopropoxy radical were an intermediate product. They were, however, unwilling to accept this interpretation because the products also included equimolecular quantities of nitrogen and nitrous oxide. Further, however, benzophenone was recovered unchanged and acetone was also produced. At least a qualitative

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[19] cf. *Nature, Lond.* **182**, 366 (1958).

[20] F. H. Westheimer, *Chem. Res.* **45**, 419 (1949); F. Holloway, M. Cohen and F. H. Westheimer, *J. Amer. Chem. Soc.* **73**, 65, (1951).

[21] N. K. Bridge and G. Porter, *Proc. Roy. Soc.* A **244**, 259, (1958).

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

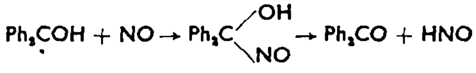
[23] H. L. J. Bäckström, *Svedberg Memorial Vol.* 456, (1944).

[24] E. Beckmann and T. Paul, *Liebigs Ann.* **266**, 1 (1891); W. Schlenk and P. Weickel, *Ber. Dtsch. Chem. Ges.* **44**, 1182 (1911); M. Gomberg and W. E. Bachmann, *J. Amer. Chem. Soc.* **49**, 236 (1926).

[25] W. E. Bachmann, *J. Amer. Chem. Soc.* **55**, 1179 (1932).

[26] H. L. J. Bäckström, A. Steneyr and P. Perlman, *Acta Chim. Scand.* **12**, 8 (1951).

explanation of these results is readily available as follows:



$$Ph_2\underset{\cdot}{C}OH + NO \rightarrow Ph_2C\begin{smallmatrix}OH\\NO\end{smallmatrix} \rightarrow Ph_2CO + HNO$$

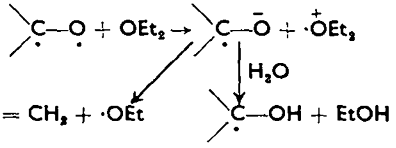
$$Me_2CHONO \rightarrow Me_2CO + HNO$$

Thompson and Dainton[27] found the photochemical decomposition of alkyl nitrites to proceed according to the second of these equations and to yield much nitrogen and nitrous oxide derived, as they suggest, from decomposition of HNO.

It can thus hardly be doubted that the above reactions simply depend on photostimulation of the normal electrophilic property of benzophenone and that a similar conclusion applies to the photochemical behaviour of ketones and quinones generally. Here it is significant that stimulation by appropriate substitution has a similar effect. Thus Braude *et al.*[28] found tetrachloro-*o*-quinone to oxidise unsaturated alcohols in the dark.

It thus appears that Bridge and Porter's experiments merely amount to illustration of the fact that extrusion of proton is contemporaneous with removal of an electron from the oxygen atom of an alcohol. Their repeated references to hydroxylation of quinones by alkali are also presumptive evidence of the attack of hydroxy-compounds by quinones through oxygen.[*]

The above conclusion in regard to the chemical behaviour of excited carbonyl compounds and quinones gives added significance to the other observations of Ciamician and Silber. Thus their observation that the reaction of moist ether with excited carbonyl compounds yields the same products as alcohol is readily explained:



From anhydrous ether condensation products, presumably of acetaldehyde and ethylene were obtained.

The cleavage of ethers by radicals either directly by use of t-butyl peroxide[29] or indirectly by a mixture of alkyl halide with the corresponding Grignard compound in presence of cobaltous chloride,[30][†] falls into the same category.

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[*] It must further be added that their experiments, though initiated to elucidate the mechanism of oxidative tendering of cellulose by anthraquinone dyestuffs, were mainly carried out with duroquinone. At the outset Cooper (private communication) reported this quinone not to exhibit the oxidative behaviour of the tendering quinones towards alcohol.

[†] The interpretation of the genesis of radicals in this manner [R. O. C. Norman and W. A. Waters, *J. Chem. Soc.* 1950 (1957)] requires revision as follows in the light of the formation of diphenyl from phenyl magnesium bromide by treatment with chromic [G. M. Bennett and E. E. Turner, *J. Chem. Soc.* 1057 (1914)] or cupric chloride [J. Krizewsky and E. E. Turner, *Ibid.* 559 (1919)]:—

$$RCl + CoCl_2 \rightarrow R\cdot + CoCl_3$$

$$RMgBr + CoCl_3 \rightarrow R\cdot + MgBrCl + CoCl_2$$

M. S. Kharasch and R. L. Huang, *J. Org. Chem.* **17**, 669 (1952)) have claimed the cleavage of ethers by the Grignard reagent and cobaltous chloride but a considerable excess of these reagents was used and M. S. Kharasch and Reinmuth, *Grignard Reactions of Non-metallic Substances*. Prentice-Hall, New York (1954) recognized the presence of perhaps 20 per cent of the original unused halide in Grignard reagents.

[27] H. W. Thompson and F. S. Dainton, *Trans. Faraday Soc.* **33**, 1546 (1937); cf. P. Gray and M. W. T. Pratt, *6th Symposium on Combustion* p. 183. Reinhold (1956).

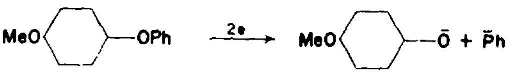
[28] E. A. Braude, H. P. Linstead and K. R. H. Wooldridge, *J. Chem. Soc.* 3070 (1956).

[29] R. L. Huang and S. S. Si-Hoe, *Proc. Chem. Soc.* 354 (1951).

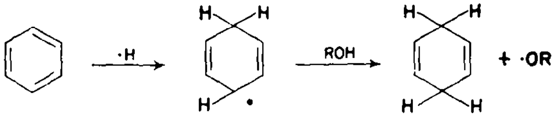
[30] M. S. Kharasch and R. L. Huang, *J. Org. Chem.* **17**, 669 (1952); R. L. Huang, *J. Chem. Soc.* 3084 (1954); R. L. Huang and S. S. Si-Hoe, *Ibid.* 3988 (1957).

The possibility that the thermal decomposition of ether also may be initiated at the oxygen atom[31] has been recognized by Freeman.[32] In fact this and the reactions just discussed correspond to the ionization of the sodium atom alternatively by heat or by electrophilic agents.

Here it must be pointed out that in direct contrast to the foregoing treatment of the reactivity of ethers, it has been suggested that they act as electron acceptors in reductive cleavage by a solution of sodium in ammonia.[33] This view, however, is not only suspect in the light of Occam's razor but also, in its application to the case of 4-methoxy-diphenyl ether,

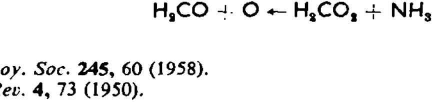


is at variance with the reducing power of hydroquinone monomethyl ether towards ammoniacal silver nitrate.[34] It would therefore seem that such metal-ammonia reductions must be attributed to atomic hydrogen, either actual or perhaps, in view of the colour changes noted in the reduction of naphthalene,[35] potential. The reduction of aromatic nuclei, acting as electron donors in covalent binding of hydrogen, should, as observed by Wooster,[36] be promoted by presence of an alcohol, acting as electron donor and source of proton:



The complete elucidation of the reduction process must, however, await that of the nature of metal-ammonia solutions and of the related mechanism of the action of $\overset{+}{H_3O}$ on metals.

The comparison of amines with alcohols and ethers in respect of oxidation[37] is further illustrated by the behaviour of triethylamine towards chloranil.[38] On the other hand, but without regard for organic-chemical data, Cullis *et al.*[39] have interpreted the thermal reaction of amines with oxygen in terms of hydrogen-abstraction. Yet the formulation of ammonia in 90 per cent yield in the early stage of reaction with methylamine at 350° surely points to a simple reaction involving transfer of hydrogen from carbon to nitrogen:



$$\begin{array}{c} H_3C{\cdot}NH_2 + O_2 \rightarrow H_2C{\cdot}\underset{\bullet}{N}H_2 + \bar{O}_2 \rightarrow H_2\underset{\bullet}{C}{\cdot}NH_3 + O_2 \\ \downarrow \\ H_2CO + O \leftarrow H_2CO_2 + NH_3 \end{array}$$

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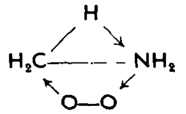
[31] J. Kenner, *loc. cit.*
[32] G. R. Freeman, *Proc. Roy. Soc.* **245**, 60 (1958).
[33] cf. A. J. Birch, *Quart. Rev.* **4**, 73 (1950).
[34] H. H. C. Hlasiwetz and J. Habermann, *Liebigs Ann.* **246**, 340 (1875).
[35] N. D. Scott, J. F. Walker and V. L. Hansley, *J. Amer. Chem. Soc.* **58**, 2442 (1935); W. Hückel and H. Bretschneider, *Liebigs Ann.* **540**, 157 (1939).
[36] C. B. Wooster, U.S. Pat. 2182242 (1938); A. J. Birch, *J. Chem. Soc.* 430 (1944).
[37] J. Kenner, *loc. cit.*
[38] D. Buckley, S. Dunstan and H. D. Henbest, *J. Chem. Soc.* 4880 (1957).
[39] C. F. Cullis and J. P. Willsher, *Proc. Roy. Soc.* A **209**, 218 (1951); C. F. Cullis and B. J. Waddington, *Ibid.* **244**, 110 (1958); **246**, 91 (1958); **248**, 316 (1958).

The occurrence of this series of electronic transferences in the gas phase is readily accommodated within the complex



This would also explain the transition from a slow induction period[40] by the genesis of atomic oxygen.

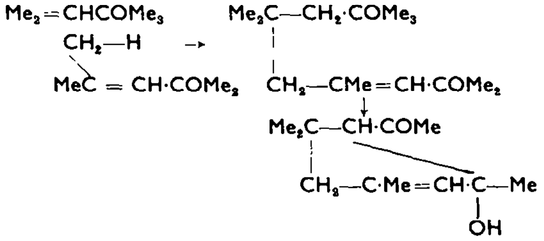
Ciamician and Silber also showed the oxidizing action of excited quinone to be effective in the cases of hexane and octane.[41] This evidence, together with that of charge-transfer between oxygen and paraffins[42] is in contrast with current neglect of the significance in this matter of electron-transference,[43] and accords with the scheme already advanced.[44]

$$\mathrm{RH} + \mathrm{O_2} \rightarrow \overset{+}{\underset{\bullet}{\mathrm{R}}}\mathrm{H} + \overset{-}{\mathrm{O}}_2 \rightarrow \underset{\bullet}{\mathrm{R}}\text{—H—O}_2 \rightarrow \mathrm{R}\cdot + \mathrm{HO_2}$$

Insistence on the diagnostic value of Occam's razor has pervaded the foregoing discussion and the earlier paper. Two instances of its more general application are therefore appended:—

(1). The apparently anomalous *meta*-chlorination of chloro-and bromo-benzenes above 450° [45] are probably attributable to isomerization of the normal *para*-product by hydrogen chloride. Baddeley and Kenner[46] demonstrated the conversion of *p*-di-n-propyl benzene into its *meta*-isomeride by aluminium chloride.

(2). Braude *et al.* regarded the dimerization of mesityl oxide in presence of lithium as "a novel type of diene addition.[47]" The first stage of the reaction is, however, evidently an expanded or vinylogous form of the Michael reaction, just as the latter is an expanded form of the aldol reaction:—



The second stage is a normal aldol reaction.

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[40] L. J. Jolley, *J. Chem. Soc.* 1957 (1934).
[41] G. Ciamician and P. Silber, *loc. cit.*; cf. N. K. Bridge and G. Porter, *loc. cit.*
[42] A. D. Munck and J. F. Scott, *Nature, Lond.* 177, 587 (1956); cf. D. F. Evans, *J. Chem. Soc.* 4229 (1957).
[43] e.g., C. F. H. Tipper, *Quart. Rev.* 11, 313 (1957).
[44] J. Kenner, *loc. cit.*; cf. A. D. Walsh, *Trans. Faraday. Soc.* **42**, 269, (1946).
[45] J. P. Wibaut, L. M. F. Lande and G. Wallagh, *Rec. Trav. Chim.* **51**, 381, 940 (1933); J. P. Wilbaut and M. van Loon, *Ibid.* **56**, 815 (1937).
[46] G. Baddeley and J. Kenner, *J. Chem. Soc.* 633 (1934).
[47] E. A. Braude, B. F. Gofton, G. Lowe, and E. S. Waight, *J. Chem. Soc.* 4054 (1956).