Metal-catalysed Organic Photoreactions. Evidence for the Long-range Electron-transfer Mechanism in the Uranyl- or Iron(III)-catalysed Photoreactions of Olefins

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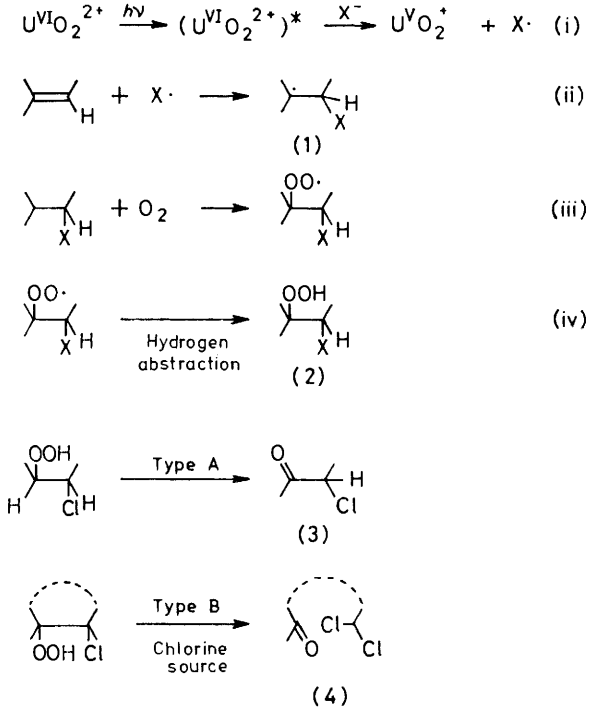
A scheme involving interligand electron transfer from the electron-donating ligand (OH^- or Cl^-) to molecular oxygen through the metal ion and olefin molecule is proposed for the metal-catalysed photo-oxidation of olefins. The scheme is verified for the uranyl-catalysed photochemical formation of bromohydrins from olefins and various polyhalogenated compounds by correlation of the reactivities and product ratios with the half-wave reduction potentials of the polyhalogenated compounds.

DYE-SENSITISED photo-oxidation and autoxidation are two of the major types of photo-oxidation of olefins, and have been interpreted as involving reaction of singlet oxygen and radical initiation, respectively.[1] Recently several papers on photo-oxidation involving novel mechanisms have been published. Photo-oxidations sensitised by dicyanoanthracene,[2] α-diketones,[3] or Lewis acids [4] are examples. Sensitisation by dicyanoanthracene has been reported to involve a donor (olefin) radical cation and a sensitiser radical anion which subsequently reduces oxygen to superoxide.[2] Other reactions involving electron-transfer sensitisation have also been reported.[5]

In connection with our study on the catalytic effects of metal compounds upon organic photoreactions, we have reported the photo-oxidation of olefins in the presence of uranyl acetate [6] or iron(III) chloride [7] in pyridine solution, which produced β-hydroxy-hydroperoxides (2; X = OH) or chlorinated ketones [(3), Type A, from mono- and di-substituted olefins, or (4), Type B, from tri- and tetra-substituted olefins], respectively. We proposed a common mechanism for both reactions comprising (i) metal-catalysed photochemical formation of hydroxyl radical or chlorine atom (X·) from hydroxide or chloride ion, respectively, (ii) addition of the species X· to the olefin so as to produce a regiochemically more stable intermediate (1), (iii) coupling of the intermediate with molecular oxygen, and (iv) hydrogen abstraction (Scheme 1). When X = OH, the product is isolated as the β-hydroxy-hydroperoxide, while, when X = Cl, the product further decomposes into chlorinated ketones in two ways (Types A and B) depending on the substitution pattern of the starting olefin. In some cases the intermediate β-chloro-hydroperoxides (2; X = Cl) were isolated.[8]

It now appears, however, that this scheme is not fully satisfactory in view of the following points. First, when the uranyl acetate-catalysed reaction is carried out in the absence of molecular oxygen, starting material is recovered with no observable products identified. Similarly, in the iron(III) chloride-catalysed reaction without oxygen, cyclo-octene gives only a small amount of 1,2-dichloride [7] as a major product along with starting material. Referring to Scheme 1, some products from the intermediate radical (1) should be formed even in the absence of molecular oxygen. Minisci and Galli [9] reported on the iron(II)-catalysed *non*-photochemical formation of α-amino-ketones by the reaction of olefins with *N*-chloroamines and molecular oxygen, and proposed essentially the same mechanism as in Scheme 1 (X = NR_2). In contrast to our results, however, their reaction proceeded well in the absence of oxygen to produce β-chloroamines, through chlorine abstraction by the intermediate radical corresponding to (1). It is thus evident that molecular oxygen plays an important role in



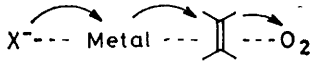
SCHEME 1

the initiation of our reactions. Secondly, our reactions were not affected by radical scavengers such as tri-t-butylphenol or di-t-butyl nitroxide, thus eliminating the possibility of intervening free-radical species. It would thus be reasonable to assume that the species X was activated and reacted with the olefin within the co-ordination sphere of the metal ion.

An alternative mechanism involving electron-transfer

sensitisation, as proposed earlier,[2,5] can be considered in place of steps (i) and (ii). This would involve electron transfer from the olefin to the metal compound with concomitant formation of the cation radical of the olefin. Subsequent coupling of the radical cation with a nucleophile (OH^- or Cl^-) would similarly lead to formation of the regiochemically more stable radical (1). The scheme, however, suffers in our opinion from the following defects. The present reactions are notable in that there exists a rigid correlation between the kinds of metal ion and species to be activated (ligand specificity).* Thus, the formations of β-hydroxy-hydroperoxides in the $UO_2Cl_2 \cdot nH_2O$-catalysed system and chlorinated ketones in the $FeCl_3 \cdot nH_2O$-catalysed system are quite specific, with no evidence of the alternative combination of catalyst and product being observed. This fact indicates that uranyl ion activates only the hydroxy-group (from water), while iron ion activates only chlorine (from chloride), even when both ligands are present in the reaction system. The scheme involving electron-transfer sensitisation would not account for this ligand specificity.

We now propose a scheme involving interligand electron transfer from the ligand X to molecular oxygen through the metal ion and olefin molecule, as shown in Scheme 2. A similar sheme has been tentatively pro-



SCHEME 2

posed for the $TiCl_4$-catalysed photoreactions of ketones with methanol,[10] and we would like to term this mechanism a long-range electron-transfer mechanism. Once the ligand X is furnished with radical character through the electron transfer, it adds to the olefin, and successive (or probably simultaneous) coupling of the resulting radical with oxygen anion radical followed by protonation completes the reaction to give the β-substituted hydroperoxides (2). It is conceivable also that compounds possessing electron-withdrawing character could induce the same type of reaction as oxygen does. We have now observed that bromotrichloromethane initiates a photoreaction to produce bromohydrins *via* catalysis by uranyl acetate. When a solution of 2-methylbut-2-ene and bromotrichloromethane in pyridine containing an equivalent amount of uranyl acetate was irradiated with Pyrex-filtered light, two bromohydrins, (5) and (6), and the bromotrichloromethyl derivative (7) were isolated.

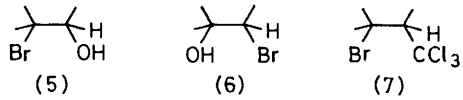
TABLE 1

Yields and ratios of the photoreaction products from 2-methylbut-2-ene [a]

Light	$CBrCl_3$ (M)	Additive (M)	Irradiation time (h)	Yield (%) (5) + (6)	Ratio (5) : (6)	Ratio (7) : [(5) + (6)]
Pyrex filtered [b]	0.04		1	37	4.0	0.26
Pyrex filtered [b]	0.04		4	34	3.5	0.24
Pyrex filtered [b]	0.04	Q [i] 0.004	2	35	4.3	0.12
Pyrex filtered [b]	0.04	HQ [j] 0.004	2	28	4.0	0.23
Pyrex filtered [b]	0.04	CuBr 0.004	2	32	3.5	0.08
Pyrex filtered [b]	0.04	CuCl 0.004	2	26	3.5	0.07
Pyrex filtered [b]	0.04	CuCl 0.01	2	26	4.0	0.02
Pyrex filtered [b]	0.02	H_2O 0.2	1	22	4.3	0.23
Pyrex filtered [b]	0.02	H_2O 2.0	1	24	4.0	0.21
Pyrex filtered [b]	0.4		1	36	3.5	0.70
Pyrex filtered [c]	0.01		1	25	3.8	0.13
265 nm [b,e]	0.04		2	20	4.6	0.24
313 nm [b,f]	0.04		3	35	3.8	0.32
>360 nm [d,g]	0.04		3	24	3.8	0.82
405 nm [d,h]	0.04		3	11	3.5	1.17

[a] Unless otherwise stated, a solution of olefin (0.02M) and uranyl acetate (0.02M) was used. [b] High-pressure mercury lamp (1 kW). [c] Olefin (0.01M). [d] Super high-pressure mercury lamp (500 W). [e] Solution filter [potassium iodide (170 mg) in water (100 ml), 8-mm thickness, ref. 11]. [f] Solution filter potassium hydrogenphthalate (500 mg) in water (100 ml), 8-mm thickness, ref. 11]. [g] Corning C. S. no. 0–52 filter. [h] Solution filter [I_2 (75 mg) in CCl_4 (10 ml), 1-cm thickness, ref. 11] and Corning C. S. no. 0–52 filter. [i] *p*-Quinone. [j] Hydroquinone.

Although the product (7) formed irrespective of the presence or absence of uranyl acetate, the acetate was necessary for the formation of the bromohydrins. The yields of bromohydrins under various conditions are



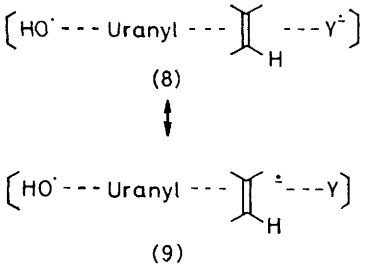
(5) (6) (7)

summarised in Table 1. Compound (7) must be a product of a radical reaction initiated by the trichloromethyl radical, because its yield was diminished by adding appropriate radical scavengers to the reaction system. The mechanism of bromohydrin formation can be as shown in Scheme 2, where bromotrichloromethane plays a role in withdrawing an electron with the resulting anion radical being the bromine source. As is evident from Table 1, the ratio of the two bromohydrins (5) : (6) was almost independent of the reaction conditions, while the total yield of bromohydrins (5) + (6) and the ratio (7) : [(5) + (6)] varied remarkably. This would indicate that both bromohydrins originate from a common intermediate.

In view of our long-range electron-transfer mechanism, we suggest that the intermediate could be represented as a resonance hybrid of structures (8) and (9), in which structure (8) tends to predominate as the electron-

* We use the term ' ligand ' tentatively for these species.

withdrawing abilities of Y become stronger. If the reaction proceeds from structure (8), a hydroxyl radical would attack the less substituted carbon of the olefin so as to produce the more stable radical intermediate,



leading to (5) as the final product. On the other hand, if the reaction proceeds from structure (9), the hydroxyl radical would attack the more substituted carbon of the olefin, which has more radical character than the less substituted carbon, and the product would now be (6). Thus, it should be anticipated that as the electron-withdrawing power of Y increases, structure (8) would predominate and the product ratio of (5) to (6) would be increased. At the same time, the overall reaction rate

TABLE 2

Bromohydrin formation and half-wave reduction potential of polyhalogenated compounds

Polyhalogenated compound	Yield [a] (%) (5) + (6)	Ratio [a] (5) : (6)	Recovered olefin (%)	$E_{1/2}$ in DMF (V *vs.* s.c.e.)
$CBrCl_3$	31	3.8	36	−0.18
CBr_4	20	3.0	51	−0.31
CBr_3CN	18	3.0		−0.32 [b]
CBr_3COCBr_3	11 [c]	2.4 [c]		−0.30
$CHBr_3$	5	2.0	73	−0.48
CBr_2F_2	5	2.3	67	−0.66
CH_2Br_2	0		74	−1.48 [d]

[a] Irradiation time, 2 h. [b] Determined by a.c. polarography. [c] Irradiation time, 1 h. [d] Value from ref. 12 (in dioxan–H_2O, 8 : 2).

should increase with increasing electron-withdrawing power. We performed experiments on bromohydrin formation using various polyhalogenated compounds as the bromine source, and found that both the yield of bromohydrins [(5) + (6)] and the product ratio [(5) : (6)] correlated well with the reduction potentials ($E_{1/2}$) of the polyhalogenated compounds (Table 2). The results agree with our proposed mechanism and strongly support a long-range electron-transfer mechanism in the metal-catalysed photoreactions.

EXPERIMENTAL

Instrumentation and Product Identification.—Instrumentation and identification of products have been described previously.[6]

General Procedure for the Photoreaction of 2-Methylbut-2-ene with Bromotrichloromethane.—2-Methylbut-2-ene, uranyl acetate [$UO_2(OAc)_2 \cdot 2H_2O$], bromotrichloromethane, and additives were dissolved in pyridine (30—60 ml) at various concentrations as described in Table 1. The solution was irradiated in Pyrex or quartz tubes with a high-pressure mercury lamp [Ushio UM 1000 (1 kW)] or a super high-pressure mercury lamp [Ushio USH 500D (500 W)] through the filter described in Table 1 for 1—4 h. After the irradiation, the pyridine was removed *in vacuo*. The reaction products were extracted from the residue with chloroform, and the extract, after being dried over sodium sulphate, was passed through a Florisil column (6 cm, 5 g). The solvent was removed *in vacuo* from the eluate, and the yields of the products were determined by n.m.r. analysis on the residue, using 1,1,2,2-tetrachloroethane as an internal reference.

General Procedure for the Photoreaction of 2-Methylbut-2-ene with Polyhalogenated Compounds.—2-Methylbut-2-ene (42 mg), uranyl acetate (254 mg), copper(I) chloride (30 mg), and the polyhalogenated compound (2 mol. equiv.) were dissolved in pyridine–water (9 : 1 v/v; 30 ml), and the solution was irradiated in Pyrex tubes with a high-pressure mercury lamp [Ushio UM 1000 (1 kW)] for 2 h. After the irradiation, the reaction mixture was treated as described above.

Measurement of Half-wave Reduction Potential of Polyhalogenated Compounds.—Current–potential measurements of polyhalogenated compounds were performed against a saturated calomel electrode (s.c.e.) on a Yanagimoto P-8 Type DC-Polarograph equipped with three electrodes (mercury flow rate 9.25×10^{-4} g s^{-1}) at room temperature in dimethylformamide, using ammonium perchlorate (0.1M) as supporting electrolyte. The concentration of the samples was *ca.* 10^{-3}M. Nitrogen was bubbled through the solution before each measurement and over it during the measurement. An a.c. polarograph was used for the determination of the $E_{1/2}$ value of CBr_3CN because a clear wave was not obtained with a d.c. instrument.

The polarography experiments were carried out on an instrument in Professor T. Yoshida's group. Thanks are given to this group, particularly to Drs. S. Nakamura and T. Ohsaka for their assistance.

[9/693 *Received, 4th May,* 1979]

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