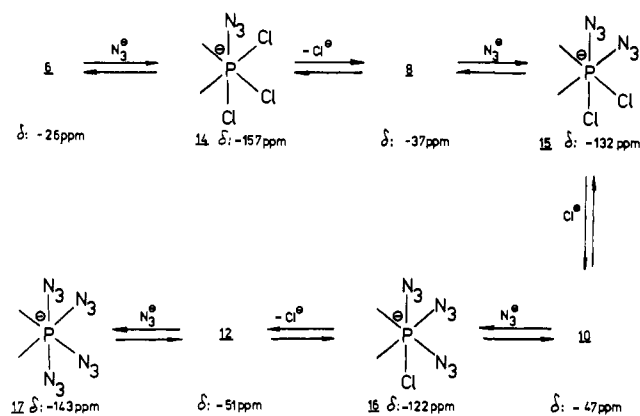


Scheme III



tropropane solution led to the adduct **2** as the major product, accompanied by some azidophosphorane **3**, unchanged chlorophosphorane **1**, and traces of compound **4**. A large increase in the amount of azidophosphorane **3**, formed by elimination of trimethylsilyl chloride, was observed on warming of the reaction mixture to -60°C . At this temperature **3** became the major product while **2** and **4** were minor components and the chlorophosphorane **1** disappeared. Reaction with 2 equiv of trimethylsilyl azide afforded **4** as the main product, which in turn was transformed into **5** by the action of N_3^- . The azidophosphorane **3**, prepared in an independent way by nucleophilic displacement of the chloride group in **1** by the action of benzyltri-*n*-butyl ammonium azide at -80°C in nitropropane, had the same ^{31}P NMR chemical shift and was transformed by the second equivalent of azide salt into the hexacoordinate salt **5**. The apparent equilibrium between **3** and **5** and between **3** and **4** was noted. These types of equilibria were observed by other investigators.⁷ The chemical shifts related to 85% phosphoric acid of compounds **2**, **4**, and **5** are in the high-field range of -90 ppm to -114 ppm, which must be associated with hexacoordinate phosphorus derivatives. The proposed zwitterion structures of **2** and **4** are analogous to those accepted for adducts of phosphorane amines.³

Reaction between *O*-phenylenetrichlorophosphorane **6** and 3 equiv of trimethylsilyl azide in ethyl chloride solution led to the hexacoordinate adduct **7** and traces of the pentacoordinate dichloroazidophosphorane **8**. After slow warming to -90°C , the amount of **7** determined by integration of the ^{31}P NMR signals decreased to 50% with parallel increase of the product **8** to 30%. Other components of the mixture were the diazide **10** (20%) and traces of the hexacoordinated diazide **9**. At -75°C , **7** (15%), **8** (15%), **9** (8%), **10** (60%), and the triazide **11** (9%) were all seen. After slow warming to room temperature the spectrum indicated further the azides **12** (80%) and **13** (20%). The full picture of the above reaction is presented in Scheme II.

The structural assignments from ^{31}P NMR spectroscopy were supported by evidence from nucleophilic displacement reactions between **6** and benzyltri-*n*-butylammonium azide, described in Scheme III. The addition of trimethylsilyl chloride did not affect the reaction picture. Therefore, the elimination of trimethylsilyl chloride in reactions $7 \rightarrow 8$, $9 \rightarrow 10$, and $11 \rightarrow 12$ is most likely irreversible.

Treatment of **6** with 3 equiv of benzyltri-*n*-butylammonium azide in nitropropane solution at -100°C results in the formation of the hexacoordinate phosphorus complex **14** (50%) accompanied by the hexacoordinate species **15** (20%) and **16** (10%) and phosphoranes **8** (10%) and **10** (10%). At -50°C the concentration of the intermediate **14** decreases while **15** and **16** increase with parallel formation of the phosphorane **12**. At -20°C the major product is **17**. Nucleophilic displacement of the chlorine atom by the azide anion in chlorophosphoranes

thus proceeds via individually distinct hexacoordinate species.

The experiments describing the effect of added reagents and temperature and solvent, while qualitative, are indicative of the occurrence of various possible types of equilibria. No attempts have been made at this stage to define these equilibria rigorously. Similar observations of discrete hexacoordinate species in the reaction involving trimethylsilyl azide and azide anion were made in the case of other halogenophosphoranes.

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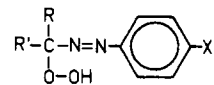
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Hydroxylation of Benzene with α -Azohydroperoxide. A Novel Route for Generation of Hydroxyl Radical and Its Reaction in Anhydrous Media

Sir:

Recently the importance of hydroxyl radical as an intermediate in many chemical and biological processes has been documented, while the reactions of hydroxyl radical with organic compounds have been studied extensively.^{1,2} In these cases, hydrogen peroxide or water is employed for a source of hydroxyl radical as demonstrated in the reactions with Fenton's reagent, radiation chemical techniques, and photochemical techniques,¹⁻⁴ which are, however, carried out usually under hydrous conditions. We now report that α -azohydroperoxide (**1**) can be another source of hydroxyl radical in anhydrous media, hydroxylating aromatic molecules to yield corre-



1a: R = Ph; R' = H; X = Br

1b: R = R' = CH₃; X = Br

1c: R = Ph; R' = H; X = CH₃

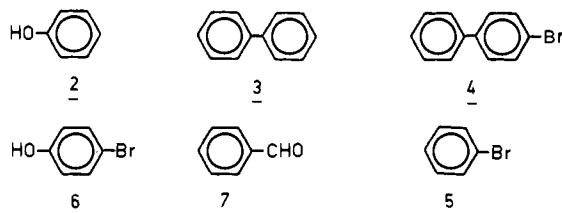
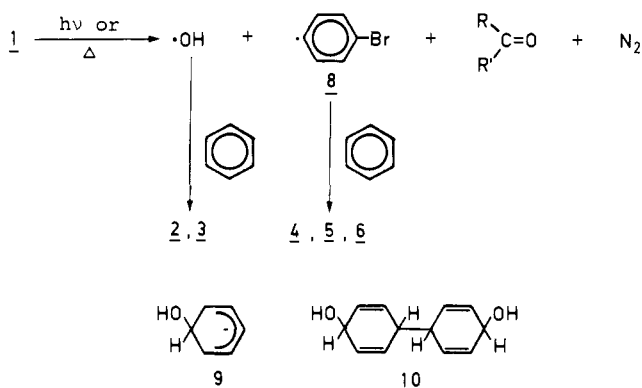


Table I. Photo- and Thermal Reactions of α -Azohydroperoxide (**1**)

run	1	conditions			yield, %, ^a of products							
		$h\nu^b$ or Δ^c	gas	solvent	2	3	4	5	6	7	11	12
1	1a	$h\nu$	Ar	benzene	23	3	86	3	3	65	<i>d</i>	<i>d</i>
2	1a	Δ	Ar	benzene	12	12	67	10	3	67	<i>d</i>	<i>d</i>
3	1a	$h\nu$	O ₂	benzene	52	0	34	trace	34	65	<i>d</i>	<i>d</i>
4	1b	$h\nu$	Ar	benzene	20	4	78	2	3	<i>d</i>	<i>d</i>	<i>d</i>
5	1b	Δ	Ar	benzene	6	11	38	38	4	<i>d</i>	<i>d</i>	<i>d</i>
6	1a	$h\nu$	Ar	<i>t</i> -BuOH	<i>d</i>	<i>d</i>	<i>d</i>	8	4	32	3	1
7	1a	Δ	Ar	<i>t</i> -BuOH	<i>d</i>	<i>d</i>	<i>d</i>	6	3	17	1	trace

^a Yields of the products based on **1** were estimated by GLC; phenolic compounds were analyzed after the treatment of the reaction mixture with hexamethyldisilazane. ^b Photolysis was carried out with a high pressure mercury lamp through a Pyrex filter under argon gas. ^c Thermal reaction was conducted under reflux. ^d Not corresponding to this reaction.

Scheme I

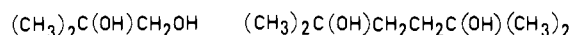
sponding phenols by either photolysis or thermolysis under anhydrous conditions without catalysts. The chemical reactivities of **1** differ considerably from those of the alkyl hydroperoxide.⁵ The α -azohydroperoxide⁶ is readily formed from the hydrazone by autoxidation and is known as a radical-chain initiator,⁷ but its hydroxylating property has received rather scant attention.

When a benzene solution (10^{-3} M) of α -azohydroperoxide **1a**⁶ possessing absorption maxima at 285 and 413 nm was irradiated with a high pressure mercury lamp through a Pyrex filter under argon gas for a few hours at 15 °C, phenol (**2**) was formed in 23% yield together with biphenyl (**3**), *p*-bromobiphenyl (**4**), bromobenzene (**5**), *p*-bromophenol (**6**), and benzaldehyde (**7**) (Table I, run 1). Phenol was also obtained, together with **3**, **4**, **5**, **6**, and **7**, when **1a** was heated in benzene under reflux under argon gas for several hours. Photolysis or thermolysis of **1b** in benzene under argon gas also gave phenol, together with **3**, **4**, **5**, and **6**. The results are summarized in Table I. Anisole was also hydroxylated to hydroxyanisole in 10% yield when **1a** was decomposed in anisole photochemically or thermally under argon gas. Photolysis of **1c** in *tert*-butyl alcohol gave **7** (20%) and *p*-cresol (2%).

The formation of phenol even by the decomposition of **1b** in benzene indicates that phenol is originating from the solvent benzene. The distributions of the products **2**, **3**, **4**, **5**, and **6** in the photolyses of both **1a** and **1b** in benzene are nearly equal (see Table I, runs 1 and 4), implying that a common reactive species is involved in the reactions of both **1a** and **1b**. A plausible mechanism for the formation of phenol and several aromatic compounds is shown in Scheme I. According to this scheme α -azohydroperoxide (**1**) decomposes to form hydroxyl radical, aryl radical (**8**), carbonyl compound, and nitrogen upon photolysis or thermolysis. Once hydroxyl radical is formed, it is known to react with benzene to give phenol and biphenyl via the intermediate species **9** and **10**, followed by the subsequent oxidation or disproportionation and dehydration reactions, respectively (vide infra).⁸⁻¹⁰

The homolytic cleavage of the α -azohydroperoxide by

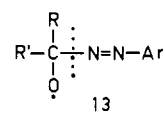
photolysis and thermolysis is supported by our observation that *p*-bromobiphenyl (**4**) and bromobenzene (**5**) are formed together with phenol in the reactions of **1a** and **1b** in benzene (see Table I). The formation of reactive hydroxyl radical in the reaction is in keeping with our following observation that photolysis of α -azohydroperoxide **1a** in anisole under argon gas afforded a mixture of positional isomers of hydroxyanisole¹¹ in which the ortho:meta:para ratio was 76:0:24. This ratio is in good agreement with that observed for the hydroxylation of anisole with hydrogen peroxide and ferrous ion (ortho:meta:para, 84:—:16),¹² in which a reactive species is hydroxyl radical, but differs from that observed for the hydroxylation with the H₂O₂-Fe³⁺-catechol reagent,¹³ in which the reactive species is postulated to be Fe⁺=O. In addition, when the reaction of **1a** with benzene was carried out in the presence of Me₂SO,^{14,15} the formation of phenol was suppressed. When **1a** was decomposed photochemically or thermally in *tert*-butyl alcohol under argon gas, 2-methyl-1,2-propanediol (**11**) and 2,5-dimethyl-2,5-hexanediol (**12**) were

**11****12**

obtained together with **4**, **5**, and **6** (Table I, runs 6 and 7). Incidentally these diols are known to be the products in the reaction of *tert*-butyl alcohol with Fenton's reagent.¹⁶

The amount of phenol was found to increase up to 52% when **1a** was photolyzed in benzene in the presence of oxygen (Table I, run 3). Oxygen is undoubtedly the acceptor of hydrogen from the intermediate species **9**.^{8-10,17} The intermediacy of hydroxycyclohexadienyl radical (**9**) and the role of oxygen as an oxidant in the formation reaction of phenol from benzene and hydroxyl radical generated from water by pulse radiolysis have first been demonstrated by Dorfman et al.⁸ In fact, biphenyl,⁸⁻¹⁰ which is a product of dimerization of **9** followed by **10**, was not formed in this case. The amount of hydroxyanisole also increased to 32% when the photolysis of **1a** in anisole was carried out in the presence of oxygen.

The thermal reactivity of α -azohydroperoxide differs considerably from that of alkyl hydroperoxide. For example, *tert*-butyl hydroperoxide generally decomposes thermally (~ 100 °C) in the liquid phase to give *tert*-butyl alcohol and molecular oxygen in quantitative yields,¹⁸ but no products due to hydroxyl radical,^{19,20} although in the vapor phase at 260 °C *tert*-butyl hydroperoxide hydroxylates cyclohexene to give cyclohexanol in low yield.²¹ In contrast, α -azohydroperoxide (**1**) decomposes thermally (~ 80 °C) to give carbonyl compound and several products formed in the reaction with hydroxyl radical. The alkoxy radical (**13**) initially formed from



1 may induce the facile β cleavage^{18,22,23} of the neighboring C–N bond shown by the dotted line and prevents the chain propagation process demonstrated in the decomposition reaction of *tert*-butyl hydroperoxide. This facile cleavage of **1** gives rise to carbonyl compound and hydroxyl radical in good yield.

tert-Butyl hydroperoxide reacts with benzene, for example, in the presence of a Lewis acid to give phenol.^{20,24} In the presence of aluminum chloride, *tert*-butoxy cation formed from the hydroperoxide by treatment with aluminum chloride reacts with benzene to give *tert*-butyl phenyl ether, which in turn affords phenol upon hydrolysis.²⁴ For comparison, the reaction of α -azohydroperoxide **1a** with benzene in the presence of aluminum chloride was examined. However, only a small amount of phenol (<4%) was obtained by this reaction.

Although mechanistic details of the reaction with the α -azohydroperoxide found by this study have to be elucidated by further studies, we would like to stress that the α -azohydroperoxide exhibits interesting chemical reactivities differing from those of the alkyl hydroperoxide, generating hydroxyl radical which hydroxylates aromatic molecules under anhydrous condition without any catalyst. The reaction of α -azohydroperoxide with organic substrates can be achieved even by using longer wavelength light at low temperature.

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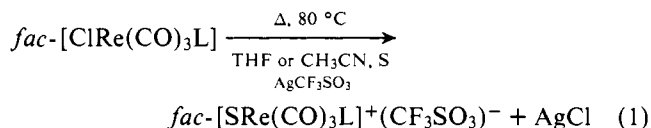
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Multiple Emissions from Rhenium(I) Complexes: Intraligand and Charge-Transfer Emission from Substituted Metal Carbonyl Cations

Sir:

Transition metal complexes that exhibit optically excited emission from two, non-equilibrated excited states are known,^{1–5} but factors controlling this important phenomena are not well understood. We report the synthesis and characterization of a set of Re(I) complexes where two emissions obtain and where systematic variation in charge density on Re(I) results in systematic variation in the energy of the ReLCT emissive state. Importantly, significant variation in charge density on Re(I) can be effected by variations in N-donor ligands other than L. The relative importance of ReLCT and intraligand, ³(π - π^*) emission can be manipulated in a controlled manner, depending on the energetic separation of the ReLCT and ³(π - π^*) states.

The Re(I) complexes studied were prepared according to



S = CH₃CN, PhCN, pyridine, piperidine

L = 2,2'-biquinoline, 1,10-phenanthroline

fac-[ClRe(CO)₃L] complexes were synthesized according to published procedures.^{1,6} Products are isolated as the CF₃SO₃⁻ salt by first filtering to remove the AgCl; solvent is removed by rotary evaporation. Products can be purified by crystallization from CH₃CN by addition of ether/*n*-pentane solution. Re(I) cations exhibit two bands in the CO stretching region of the IR, Table I, and ¹H NMR spectra for the complexes are consistent with the formulation *fac*-[SRe(CO)₃L]⁺. Elemental analysis (Alfred Bernhardt, West Germany) for S = CH₃CN or piperidine is satisfactory. Calcd for S = CH₃CN (found): C, 33.75 (33.92); H, 1.72 (1.87); N, 6.56 (6.40). Calcd for S = piperidine (found): C, 36.81 (36.74); H, 2.77 (2.75); N, 6.13 (6.29). Table I includes spectral data for the previously characterized⁶ neutral complexes *fac*-[ClRe(CO)₃L], for comparison.

The Re(I) cations exhibit detectable optical emission at 298 or 77 K in solution, Table I. Solution lifetimes at 298 K are $\sim 10^{-6}$ s, and the emission spectra are featureless and independent of the excitation wavelength (230–410 nm). The emission maximum for L = 2,2'-biquinoline is at lower energy than that for L = 1,10-phenanthroline, consistent with a CT emission associated with Re \rightarrow L direction in absorption. This ordering of energy is consistent with the previous assignments of MLCT bands.^{6,7} The difference in 2,2'-biquinoline and 1,10-phenanthroline rules out a ligand field assignment; the ligand field states would be at the same energy for these complexes, since the donor sphere is invariant. Consistent with a CT assignment, the emission maximums for the four cations for L = 1,10-phenanthroline are ordered as predicted from the CO stretching frequencies: CH₃CN \sim PhCN > pyridine > piperidine; that is, the complex exhibiting the lowest electron density (highest CO stretching frequency) on Re has the highest energy CT state, confirming the direction of the CT.

The emission of the various Re(I) species undergoes substantial changes upon cooling solutions of the complexes to 77 K. Generally, and as has been reported previously,^{1,6,8} the emission blue shifts and intensifies. For *fac*-[(CH₃CN)-Re(CO)₃(2,2'-biquinoline)]⁺ the featureless CT emission moves smoothly to the blue and intensifies as found⁶ for *fac*-[ClRe(CO)₃(1,10-phenanthroline)]. Except for *fac*-