Aromatic Hydroxylation by $O(^3P)$ Atoms on γ-Radiolysis of Liquid Carbon Dioxide Solutions of Alkylbenzenes

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Summary Hydroxylated products have been produced by the attack of $O(^3P)$ atoms, generated by γ-radiolysis of liquid CO_2, on alkylbenzene at the following sites: aromatic methine carbon, aromatic ring carbon bearing a substituent accompanied by 1,2-shift of the substituent (NIH shift) or removal of the substituent, and alkyl substituent.

REACTIONS of O(^3P) atoms with organic compounds have been studied extensively in the gas phase,[1] but rather less in the liquid phase.[2–5] Recently, aromatic hydroxylation by the oxygen atom transfer reaction of aromatic amine N-oxides has been investigated as a model for the reaction of mono-oxygenase enzymes.[6,7] It is not certain whether or not the oxidizing species in the photolysis of the N-oxides are oxygen atoms. We have already reported the reaction of O(^3P) atoms, produced by γ-ray-induced dissociation of CO_2 into CO + O, with hydrocarbons (alkane, alkene, and alkyne).[2]

We have now applied a similar procedure to aromatic hydrocarbons and observed the occurrence of the NIH shift,[8] which is known to be a characteristic rearrangement for aromatic hydroxylation by mono-oxygenase enzymes.

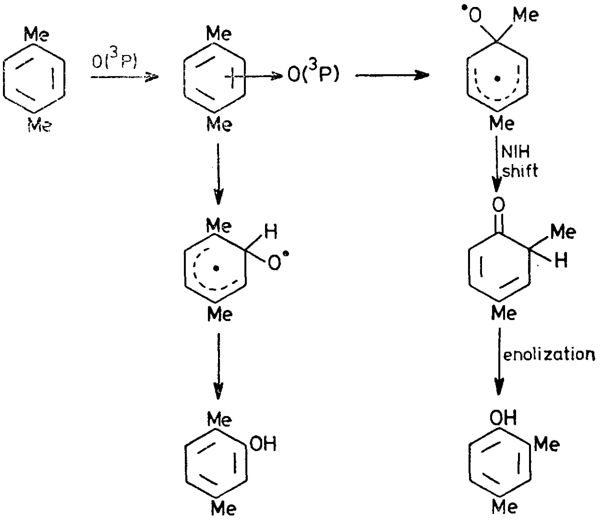
γ-Radiolysis of liquid CO_2 (1·4 mol) in the presence of aromatic hydrocarbons (0·1—0·2 M) was carried out in a stainless steel autoclave (65 ml) using a ^{60}Co source at 0 °C for 1 h.†

The results (Table) indicate that the hydroxylation of aromatic hydrocarbons by O(^3P) atoms can be classified into four types: (i) hydroxylation of the aromatic methine carbon to produce the corresponding phenols (main reaction), (ii) hydroxylation of the aromatic ring at the 1-position accompanied by 1,2-shift of the methyl group, the NIH shift (in the case of *o*- and *p*-xylene, and 1,2,3-trimethylbenzene), (iii) hydroxylation of the aromatic ring with removal of the substituent (in the case of 1,2,3-trimethylbenzene), and (iv) hydroxylation of the alkyl substituent (in the case of ethylbenzene and *o*-, *m*-, and *p*-xylene).

The total G-value (molecule/100 eV) of hydroxylated products depends on the substrate. The maximum G-value, 4·6, for *m*-xylene, indicated that the most of the O(^3P) atoms produced were trapped, because G(CO), and therefore accordingly G(O), has been reported to be 3·5–5·0 on γ-radiolysis of liquid CO_2.[9]

The relative rate constant, k_{rel}, was determined by measurements on competitive reactions, between two aromatic hydrocarbons for O(^3P) atoms (Table). The k_{rel} values decrease with increasing ionization potential of aromatic hydrocarbons, indicating that O(^3P) atoms are electrophilic and that the transition state for the reaction is predominantly charge-transfer in character. In addition, the dependence of k_{rel} on ionization potential and the products obtained in this study are similar to results obtained in gas-phase studies,[1,10] which is consistent with the oxidizing species being O(^3P) atoms.‡

Hydroxylation of an equimolar mixture of benzene and [$^2H_6$]benzene under the present conditions and subsequent analysis of the phenols by mass spectrometry gave a value of 1·1 for the intermolecular hydrogen isotope effect, k_H/k_D. This small isotope effect shows that cleavage of aromatic C–H bonds does not occur in the rate-determining step of the hydroxylation. On the basis of these results, we suggest the pathway in the Scheme for the reaction of O(^3P) atoms with *p*-xylene as being typical.



SCHEME

TABLE. γ-Radiolysis of liquid CO_2 solutions of aromatic hydrocarbons

Substrate	k_{rel}[a]	Total G-value	Product (% relative yield)	% NIH shift of Me
Benzene	1·0	0·3	Phenol (100[b])	—
Toluene	3·2	2·0	*o*-Cresol (62); *m*- and *p*-cresol (37); phenol (1)	—
Ethylbenzene	3·9	2·7	*o*-Ethylphenol (52); *m*- and *p*-ethylphenol (41); MeCHPhOH (5); $PhCH_2CH_2OH$ (2)	—
t-Butylbenzene	6·7	2·3	*o*-t-Butylphenol (42); *m*- and *p*-t-butylphenol (56); phenol (2)	—
o-Xylene	7·5	3·1	3,4-Xylenol (52); 2,3-xylenol (35); 2,6-xylenol (7); *o*-$MeC_6H_4CH_2OH$ (6)	7
m-Xylene	20·8	4·6	2,4-Xylenol (61); 2,6-xylenol (32); *m*-$MeC_6H_4CH_2OH$ (4); 3,5-xylenol (3)	
p-Xylene	13·9	3·4	2,5-Xylenol (91); 2,4-xylenol (5); *p*-$MeC_6H_4CH_2OH$ (4)	5
1,2,3-Trimethylbenzene	19·5	2·2	2,3,4-Trimethylphenol (73); 2,6-xylenol (10); 3,4,5-trimethylphenol (9); 2,3,6-trimethylphenol (8)	8
1,3,5-Trimethylbenzene	38·0	4·0	2,4,6-Trimethylphenol (100)	c

[a] Relative rate constant of aromatic hydrocarbon to benzene. [b] *Ca.* 10—20% of unknown non-phenolic product was also obtained (mass spectra; *m/e* 110, 81, and 53). [c] Not detected.

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† Reactions were continued to <10% completion to investigate the reaction mechanism. The dose rate, measured with a Fricke dosimeter solution, was 2·2 × 10^{19} eV g^{-1} h^{-1}. The products were identified by comparison of g.l.c. retention times (Ucon Oil LB 550X, 3 m; Silicone DC 550, 9 m) and mass spectra (Hitachi RMS-4 (GC/MS) with those of authentic samples.

‡ γ-Ray induced oxidation of toluene in liquid CO_2 has been reported by Sato *et. al.*, but the oxidizing species causing hydroxylation were suggested to be anionic (K. Ishizaki and S. Sato, *Chem. Letters*, 1975, 123).

It is interesting that $\mathrm{O}(^3P)$ atoms cause an NIH shift of methyl groups in di- or tri-methylbenzene having *ortho*- or *para*-methyl substituents. This selectivity can be accounted for by the *ortho*- and *para*-orientation of $\mathrm{O}(^3P)$ atoms. The occurrence of an NIH shift of methyl groups in the gas-phase reaction of $\mathrm{O}(^3P)$ atoms with aromatic hydrocarbons[10] or in the photolysis of pyridazine *N*-oxide solution containing a polymethylbenzene has not been reported.[7]§

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§ The NIH shift of deuterium has been reported to occur in the photolysis of a solution of an aromatic *N*-oxide containing a monosubstituted benzene (ref. 6).

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