

OXIDATION OF BENZENE AND CYCLOHEXANE IN $\text{CH}_3\text{CN}-\text{H}_2\text{O}$ BY MEANS OF XeO_3 AND XeF_2

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Xenon compounds XeO_3 and XeF_2 in aqueous acetonitrile efficiently hydroxylate benzene on heating (the reaction is accelerated by CrO_3), and XeF_2 in $\text{CH}_3\text{CN}-\text{H}_2\text{O}$ also oxidizes cyclohexane with the formation of cyclohexanol and cyclohexanone.

The oxidizing abilities of xenon compounds are used in organic chemistry to carry out the widest variety of reactions (see, for example, [1-6]). Most often used in XeF_2 , which either fluorinates substrates or causes their oxidative coupling. In his work, we investigated the thermal and photochemical reactions of the replacement of hydrogen atoms in alkanes and arenes by oxygen-containing groups. For this purpose, we used the oxygen-containing derivative, XeO_3 and the fluoride, XeF_2 . Both compounds are oxidants in aqueous acetonitrile. It is known [7] that XeO_3 and XeF_2 in the presence of water decompose with the formation of a whole series of products: HO^\cdot radicals, hydrogen peroxide, molecular oxygen, XeO , and superoxide ion. It can be assumed that these products will efficiently hydroxylate alkanes and arenes.

We have found that heating a solution of XeO_3 in aqueous acetonitrile in the presence of benzene leads to the hydroxylation of the latter, while the curve of phenol accumulation has a marked induction period (Fig. 1). It is of interest that this period can be significantly reduced by the addition of a catalytic amount of CrO_3 to the solution. The hydroxylation of benzene by xenon trioxide can be induced not only by heating, but also by irradiation with light at room temperature (Fig. 2). The addition of CrO_3 here, also accelerates the reaction somewhat.

Xenon difluoride in aqueous acetonitrile also proves to be an efficient agent for the hydroxylation of benzene (Fig. 3). The buildup of phenol takes place with a short induction period. The initial rate of the reaction depends strongly on the concentration of water in the solution. Thus, the yield of phenol (the concentration produced after 1 h) changes in the following manner.

water concentration, M	4.6	9.3	18.6
phenol concentration, M	0.5	3.3	5.8

Since the rate of hydrolysis of XeF_2 in aqueous acetonitrile solution also increases with increasing H_2O concentration [8], these data can be considered to show that the hydroxylating species arises during the hydrolysis of XeF_2 . Cyclohexane under these conditions is oxidized much more slowly than benzene, giving cyclohexanol and cyclohexanone. On the addition of CrO_3 to the solution, the rate of oxidation begins to rise somewhat, but the total yield after 4-5 h remains approximately unchanged. Additions of FeCl_3 and KVO_3 change the selectivity of the process somewhat, but the overall rate decreases.

Thus, XeO_3 and XeF_2 in a $\text{CH}_3\text{CN}-\text{H}_2\text{O}$ mixture efficiently hydroxylates arenes and also oxidizes alkanes.

In considering the mechanism of the oxygenation of hydrocarbons, it can be suggested that the active species in these reactions is an oxo derivative of xenon, for example, a $\text{Xe}=\text{O}$ species. In the reaction of this species with arenes, the first step could be an epoxidation at the "double" bond followed by conversion of the epoxide to a phenol.

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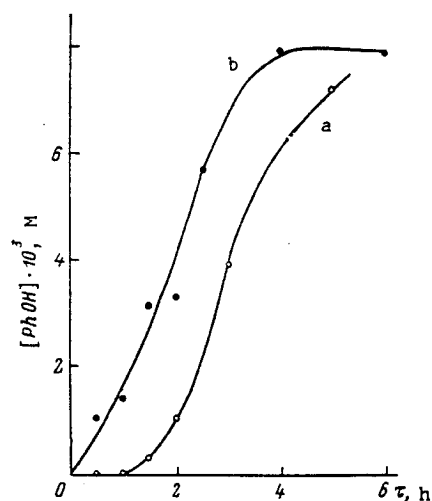


Fig. 1

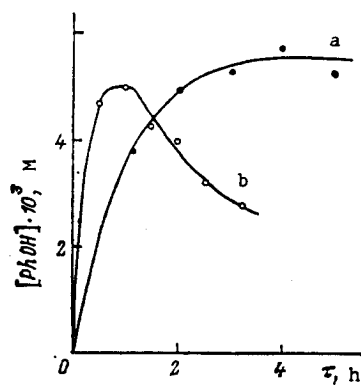


Fig. 2

Fig. 1. a) Rate curve of phenol buildup in the oxidation of benzene (0.73 M) in an acetonitrile-water mixture (3.8:1 by volume) by xenon trioxide (8.5×10^{-3} M) at 64°C ; b) the same with the addition of 1.6×10^{-4} M CrO_3 .

Fig. 2. a) Rate curve of phenol buildup upon irradiation of a solution of benzene (0.64 M) and XeO_3 (7.4×10^{-3} M) in an acetonitrile-water mixture (4.6:1 by volume) with the total light from a high pressure mercury lamp at 20°C ; b) the same with the addition of 0.42×10^{-3} M CrO_3 .

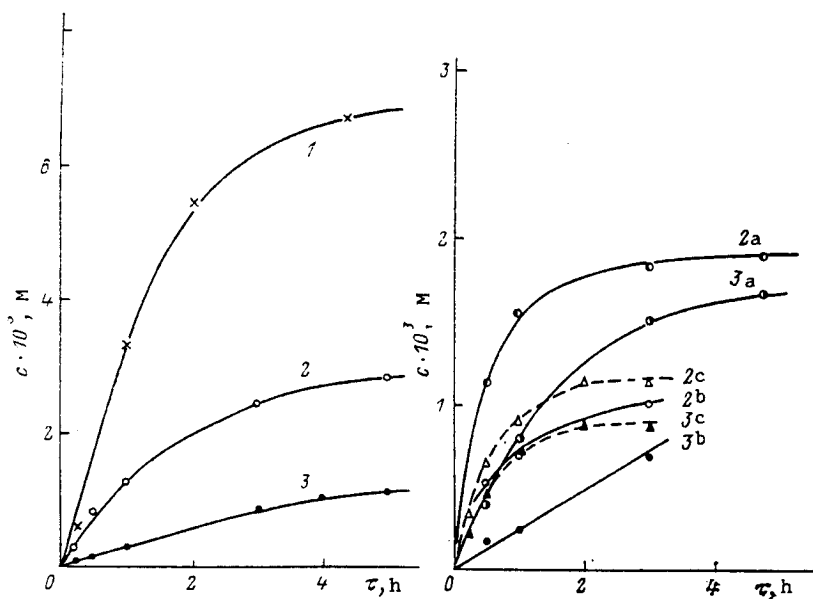
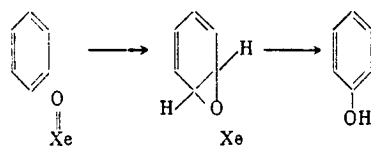
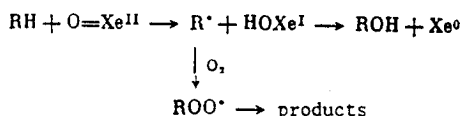


Fig. 3. Rate curve of buildup of phenol (1) in the oxidation of benzene (0.57 M) and buildup of cyclohexanol (2) and cyclohexanone (3) in the oxidation of cyclohexane (0.57 M) by xenon trifluoride (5×10^{-3} M) in acetonitrile containing 9.3 M water (61°C). 2a, 3a) With the addition of 0.41×10^{-3} M CrO_3 ; 2b, 3b) with the addition of 0.41×10^{-3} M FeCl_3 ; 2c, 3c) with the addition of 0.41×10^{-3} M KVO_3 .



Such a mechanism is assumed for the hydroxylation of arenes (and also the epoxidation of olefins) in living cells with the participation of cytochrome P-450 or in vitro with the use of iron porphyrin complexes as a catalyst [9, 10]. Usually this process is accompanied by an NIH shift [9, 10]. The suggestion of an initial epoxidation of arenes by a $Xe=O$ species is in accord with the fact that in the hydroxylation of phenol by means of XeF_2 in H_2O , p-hydroquinone is formed with a high degree of selectivity and is then oxidized to p-quinone [11].

The reaction of the $Xe=O$ species (as, apparently, the Fe^V oxoderivative in cytochrome P-450 and its models) with the saturated C-H bond in alkanes, can proceed by two paths. In the first path, an R^{\cdot} radical is formed which splits off the OH from $XeOH$; in the second, this radical reacts with the molecular oxygen existing in the solution.



EXPERIMENTAL

The amounts of cyclohexanol and cyclohexanone formed were determined on an LKhM-80-6 gas-liquid chromatograph (2000 \times 4 mm column packed with Inerton AW HMDS 0.25-0.315 mm support, 5% Carbowax-1500 stationary phase). The amount of phenol was determined by chromatographing a portion of the reaction solution on Silufol UV-254 plates (1:1 chloroform-hexane eluent), eluting the product band and measuring the absorption in the UV spectrum (UV-Vis Specord). The reactions were carried out in the air in thermostatted vessels equipped with reflux condensers with constant stirring by a magnetic stirrer. In the photochemical reactions, irradiation during stirring was carried out in a glass vessel equipped with a DRS-1000 (1000 W) high pressure mercury lamp.

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