Low Temperature Oxidation of Biphenyl in an Alumina Reactor: Possible Initiation by O_2 ($^1\Delta$)

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Abstract

Oxidation of biphenyl (as a prototype model compound for polychlorinated biphenyls) in an alumina reactor at 490°C yields the initial products dibenzofuran and benzaldehyde which have been confirmed in GC/MS studies. It is postulated that O_2 ($^1\Delta$) whose formation is catalysed by the reactor surfaces, initiates the reaction at this low temperature. Quantum chemical computations of the reaction potential energy surfaces suggest low energy pathways to the observed initial products.

Keywords: PCBs, PCDD/Fs, reaction potential energy surfaces, quantum chemistry

1. Introduction

Although it has been known for several years that combustion of polychlorinated biphenyls (PCBs) in accidental fires of electrical equipment and in municipal waste can lead to significant emissions of polychlorinated dioxins and dibenzofurans (PCCD/Fs), particularly the latter [1], understanding of the mechanism of the oxidation process is quite limited. Of particular uncertainty is the initiation of oxidation in the presence of air or oxygen. Most models for the oxidation assume that (an unspecified) initiation involving abstraction of a hydrogen atom on one of the benzene rings leads to a phenyl-type radical site at which ground state O_2 ($^3\Sigma_g$) undergoes addition. However, the C-H bond enthalpy in benzene is very large (113 kcal mol^{-1} at 298K) [2] and is estimated to be slightly higher (at 117 kcal mol^{-1}) in biphenyl, thus making abstraction of H by, e.g., ground state O_2 extremely unlikely at the low temperatures (300 - 500°C) at which conversion of PCBs to dioxins has been recorded [1].

In an attempt to unravel the mechanism we have studied the oxidation of the non-chlorinated prototype, biphenyl, in an alumina flow reactor in high purity synthetic air at temperatures from 450° to 700° C. Quantum chemical studies of the oxidation process have been used to elucidate possible mechanisms especially of initiation and initial product formation.

2. Methodology

2.1 Experimental Methods

Oxidative studies were carried out using a tubular reactor of alumina, 50 cm in length and 5.4 mm in internal diameter. Biphenyl was loaded inside a ceramic tube which was installed vertically in a vaporiser and heated at 150 °C to evaporate slowly under the flow of high purity synthetic air with a flow rate of 21.99 cm^3/min. Uniform mixing was achieved by a plug of pre-cleaned glass wool. The average biphenyl evaporation rate was measured as 0.211±0.007 mg/min. The volume of the reactor was adjusted by inserting two rods, 3.7 mm in outside diameter, from both ends of the tube to ensure that the vapour reaches the reaction zone rapidly, through the annulus between the rod and the alumina tube. Temperature ranged from 450 to 700 °C at atmospheric pressure. Reactor residence time was maintained at 5.0 s.

The reactor's exit was coupled with a chilled impinger containing dichloromethane (DCM) and acetone (AC) and with a trap of XAD-2 resin (approximately 180 mg) to intercept volatile organic compounds (VOC). The XAD-2 resin was desorbed using 2 mL of CS$_2$ solution in ultrasonic bath for 3 hours. The CS$_2$ extract required filtration prior to injecting into the Varian CP3800 GC and Varian 1200 QMS, the former equipped with a 30 m Varian VF-5ms column (0.25 mm i.d., 0.25 μm film thickness). Helium functioned as the carrier gas flowing at a constant rate of 1.0 mL/min. The temperature program of the GC oven commenced at 30 °C, held for 5 min, then followed an imposed temperature ramp of 5 °C/min up to 60 °C, held for 5 min, to conclude the heating at 260 °C at a rate of 15 °C/min.

FTIR has also been employed to study gaseous products emanating from the flow reactor.

2.2 Quantum Chemical Studies

All computations were carried out with the Gaussian 09 [3] suite of programs. Optimized geometries and zero point vibrational energies (ZPVE) were calculated at the B3LYP/6-31G(d) level of theory. Improved electronic energies were obtained by carrying out single point energy calculations using the large 6-311++G(3df,3pd) basis set. All energies, including barrier heights, have been evaluated at the B3LYP/6-

311++G(3df,3pd)//B3LYP/6-31G(d) level of theory. Stationary points located were either minima or transition states (TS) determined by an analysis of the vibrational frequency wherein a transition structure contains only one imaginary frequency along the specified reaction coordinate. Intrinsic reaction coordinate calculations (IRC) were performed to link reactants and products with their transition states. Where singlet biradicals were located, these were optimized using unrestricted methodology and tested for stability of the singlet wavefunction.

3. Results and Discussion

3.1 Experimental Results

As the reactor temperature was increased, products of the oxidation of biphenyl first appeared at 490°C. The two products identified in the GC/MS were dibenzofuran and benzaldehyde. These were both confirmed by injection of authentic standards. There were also traces of CO and CO_2 in the FTIR spectra at this temperature. At significantly higher temperatures benzene, phenol, styrene, benzofuran, indene and naphthalene started to form.

3.2 Quantum Chemical Results

Our principal motivation is to understand the mechanism of initiation of oxidation and of the formation of dibenzofuran, the protype of the PCDFs produced from PCBs together with the other initial product, benzaldehyde.

As outlined in the Introduction, the very large C-H bond enthalpy in biphenyl, together with a probable maximum A-factor for reaction with ground state O_2 of 6×10^{13} cm^3 mol^{-1} s^{-1} (estimated for benzene [4]) rule out any possibility of an initiation involving abstraction of a ring H to HO_2 at 490°C. The possibility of addition of O_2 ($^3\Sigma_g$) to a ring carbon bearing hydrogen or to a bridge C atom has been investigated by quantum chemical computation. It has not been possible to optimize any addition complex involving ground state O_2.

Aromatic hydrocarbons emitted to the atmosphere are principally destroyed through reaction with OH radicals which have a maximum concentration of about 2×10^7 molecules cm^{-3}, however, reaction half-lives are days or months and clearly any residual amount of OH radical present in a high purity synthetic air mixture is unlikely to oxidize biphenyl at 490°C in a 5 s residence time reactor.

In seeking a possible initiator of oxidation, we consider the nature of the reactor walls, constructed of alumina (with a small silica concentration). There have been several recent studies of the ability of surfaces such as zeolites, alumina, vanadia, etc to produce excited state O_2 ($^1\Delta$) in heated flows of oxygen at quite modest temperatures. Romanov et al [5] found that O_2 ($^1\Delta$) was produced by zeolite ZSM-5 surfaces at only 140°C. More recently, Krylova [6] observed the formation of O_2 ($^1\Delta$) from several types of alumina and silica surfaces heated to 180°C. Hence, we have made a quantum chemical investigation of initiation and subsequent reaction involving O_2 ($^1\Delta$) whose energy level lies some 23 kcal mol^{-1} above ground state O_2.

We have been successful in optimizing a singlet state O_2 adduct (II) of biphenyl (I). The structures of biphenyl and its adduct, together with all optimized equilibrium structures, are given in Fig. 1. The adduct has singlet biradical character and its wavefunction has been tested for stability. A reaction potential energy surface (PES) for further reaction of this adduct to form dibenzofuran has been developed and is shown in Fig. 2. The adduct first cyclizes to the endoperoxide (III) with a six-membered ring through a modest barrier of 20.7 kcal mol^{-1}. (All barrier energies are quoted for 0 K.) Rupture of the O-O bond leads to the diketo structure (IV). This is followed by the concerted double H atom transfer to form the dihydroxy intermediate (V). After two trivial torsions forming (VI) and (VII), water is eliminated from the two juxtaposed hydroxyl groups with concomitant cyclization to form dibenzofuran (VIII). This last process has a significant barrier of 66.2 kcal mol^{-1} but it should be pointed out that the entire reaction from II → VIII + H_2O has an overall barrier of only 31.1 kcal mol^{-1} and once surmounted, reaction to dibenzofuran can take place by chemical activation.

The PES for formation of benzaldehyde from biphenyl + O_2 ($^1\Delta$) again commences from the adduct II as shown in Fig. 3. However, the adduct now forms an endoperoxide with a four-membered ring (IX) by addition to the adjacent bridge carbon. The barrier for formation of (IX) is 15.8 kcal mol^{-1}. Rupture of the O-O bond has a barrier of 29.4 kcal mol^{-1}. This produces (X) which has two epoxide rings on the same six-membered ring. Opening of one of the epoxide rings through a barrier of 55.4 kcal mol^{-1} leads to the ketone (XI). Rupture of the remaining epoxide ring (barrier 31.5 kcal mol^{-1}) produces the diketone (XII). A hydrogen shift with a barrier of 31.2 kcal mol^{-1} forms the intermediate (XIII). Finally, a second hydrogen shift from the adjacent carbon atom to the carbonyl hydrogen leads to cyclization of the side chain and fission into the five-membered cyclopentadienone ring and to benzaldehyde. The barrier for this process lies 58.7 kcal mol^{-1} above (XIII). The IRC potential energy surface for this reaction shows that after the hydrogen transfers to the carbonyl carbon, a metastable biradical intermediate forms in which the five- and six-membered rings are attached at the carbonyl carbon atom. This is not, however, a stable entity, i.e., a minimum, but appears as a point of inflection on the IRC energy surface. All attempts to optimize this
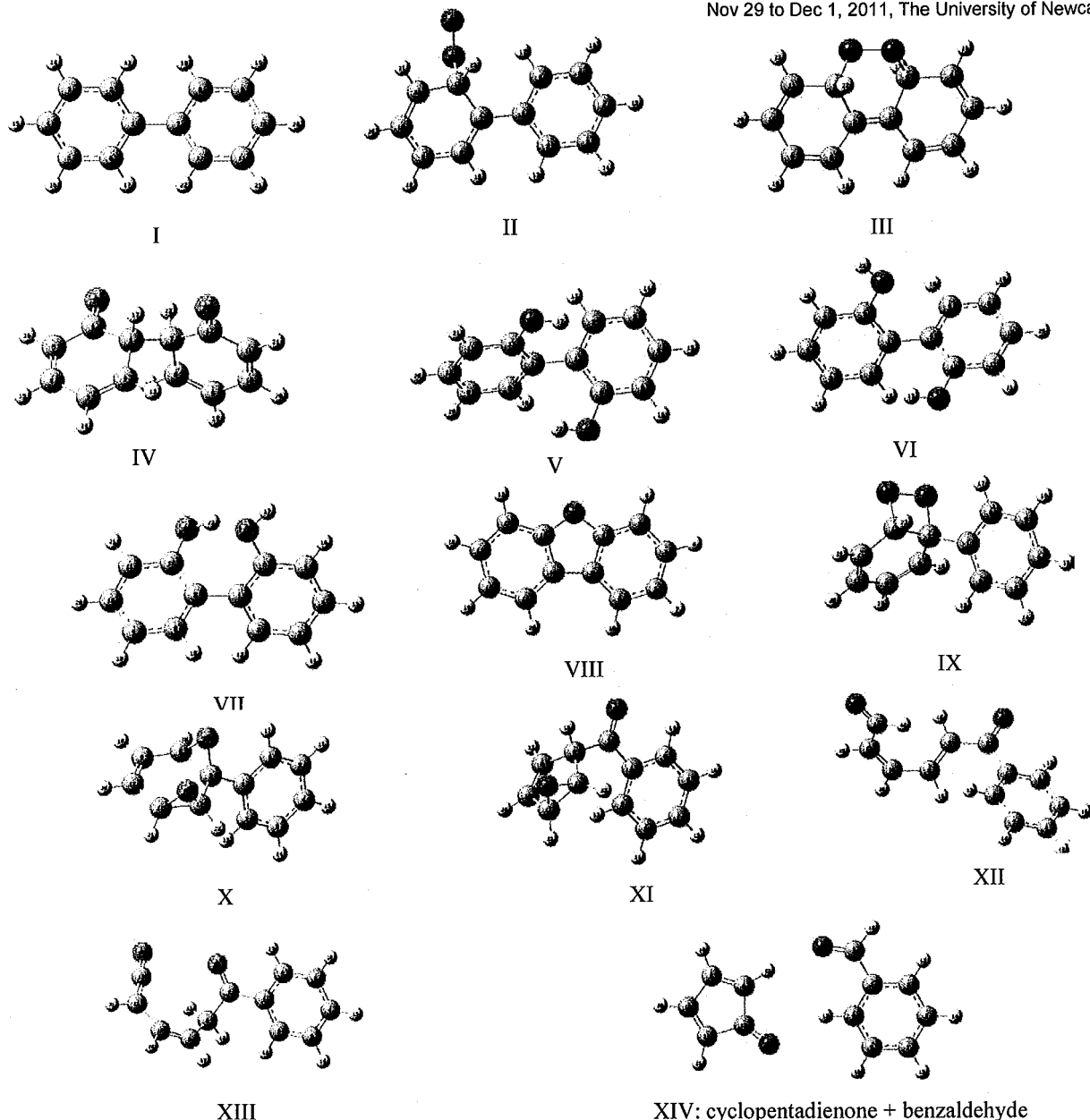
Fig. 1: Equilibrium structures on the reaction PESs to dibenzofuran and benzaldehyde

biradical intermediate were unsuccessful, leading invariably to optimization of the two separate entities - benzaldehyde and cyclopentadienone.

A transition state was also located for the initial addition of O_2 ($^1\Delta$) to biphenyl to form the adduct (II). However, the barrier for the addition to biphenyl cannot simply be obtained from the energy difference between the transition state and the reactants. Nor can we directly compute the energy difference between adduct and reactants. This is because the DFT method is not appropriate for computation of the energy of an excited state species such as O_2 ($^1\Delta$). Instead, we use isodesmic or isogyric work equations involving the species whose thermochemistry is not known but can be expressed in terms of reactants and products whose thermochemistry is accurately known from experiment.

For the enthalpy of formation, $\Delta_f H_{298}$, of biphenyl, we use the following work equation:

$$2C_6H_5CH_3 - C_2H_6 = C_6H_5\text{-}C_6H_5 \qquad (1)$$
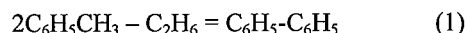
for which we compute the enthalpy of reaction at the level of B3LYP/6-311++G(3df,3pd)//B3LYP/6-31G(d) and use the experimental enthalpies of formation of toluene and ethane [2]. We thus obtain the value of $\Delta_f H_{298} = 43.3$ kcal mol^{-1} for biphenyl, a value which agrees well the experimental value of 43.5 ± 0.2 kcal mol^{-1} [2]. For the adduct (II) we use the work equation:

$$C_6H_7 + C_6H_6 + CH_3OO - CH_4 - H_2 = C_6H_5\text{-}C_6H_5OO \qquad (2)$$
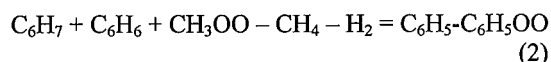
from which we obtain the value of $\Delta_f H_{298} = 54\pm2$ kcal mol^{-1}. From the experimental enthalpy of O_2 ($^1\Delta$) of

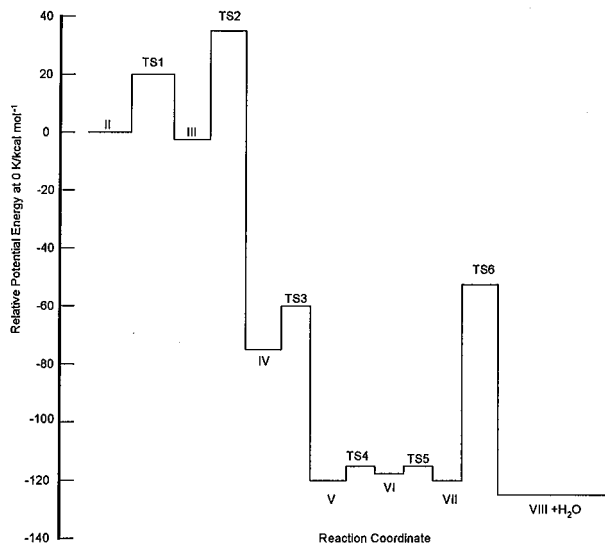Fig 2.: Reaction PES for formation of dibenzofuran

Fig. 3: Reaction PES for formation of benzaldehyde

22.5 kcal mol^{-1} [7] we then obtain the enthalpy of addition of singlet oxygen to biphenyl of -12 kcal mol^{-1}.

The transition state for addition of O_2 ($^1\Delta$) was found to have a reverse barrier of 0.7 kcal mol^{-1} at the B3LYP/6-31G(d) level of theory but became -0.02 kcal mol^{-1} using the extended basis set, suggesting that it is not a discrete transition state and that the exothermic addition is barrierless.

Concerning the pathway to benzaldehyde and cyclopentadienone, it should be noted that the latter product has not so far been detected in the reaction products. However, cyclopentadienone is a very reactive species and under our conditions might well rapidly decarbonylate leading to the traces of CO and light hydrocarbons observed in products especially as the reactor temperature is increased.

4. Conclusions

The experimental observation of dibenzofuran and benzaldehyde as initial products of oxidation of biphenyl in an alumina flow reactor at 490°C can be explained via two mechanisms possessing low overall activation energies initiated by addition of excited state O_2 ($^1\Delta$) whose formation is catalyzed by the reactor walls. Addition to form a singlet state adduct is exothermic and the reaction proceeds on the singlet reaction surface as the peroxy adduct cyclizes to a six-membered or four-membered endoperoxide. In the case of the first endoperoxide which symmetrically bridges the two biphenyl rings, O-O fission leads, via series of rearrangements of modest activation energies, eventually eliminating water to form dibenzofuran.

The four-membered endoperoxide ring is attached to a single ring in biphenyl. After O-O fission a structure containing two epoxide groups is formed and
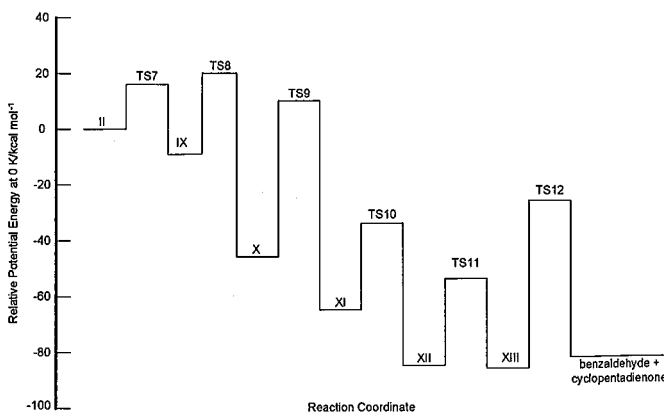
after several reaction steps also of modest activation energies eventually fissions to benzaldehyde and cyclopentadienone.

6. References

[1] O. Hutzinger, G.C. Choudhry, R. Chittim, L.E. Johnson, Environ. Heath Perspect. 60 (1985) 3-9.

[2] P.J. Linstrom and W.G. Mallard, Eds.,NIST Chemistry WebBook, NIST Standard Reference Database Number 69, National Institute of Standards and Technology, Gaithersburg MD, 20899, http://webbook.nist.gov, (retrieved August 31, 2011).

[3] Gaussian 09, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel et al, Gaussian, Inc., Wallingford CT, 2010.

[4] T. Asada, N. Fujii, Proc. Int. Symp. Shock Tubes & Waves, 8 (1971) 1-12.

[5] A.N. Romanov, M. Ya. Bykhovskii, Yu. N. Rufov, V. N. Korchak, Kinet. Catal. 41(6) (2000) 861-865.

[6] I.V. Kylova, Russ. J. Phys. Chem. 81 (1) (2007) 19-23.

[7] R. Boodaghians, P. Borrell, Photochem. Photobiol. 35 (1982) 411-412.