

PHENOXYL AND CYCLOPENTADIENYL RADICALS FROM THE GAS-PHASE PYROLYSIS OF PHENOL

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Abstract

The formation of radicals from the gas-phase pyrolysis of phenol over a temperature range of 400-1000 °C was studied using the technique of low temperature matrix isolation-Electron Paramagnetic Resonance EPR (LTMI-EPR). Cooling the reactor effluent in a CO₂ carrier gas to 77 K produces a cryogenic matrix that exhibits complex EPR spectra. Annihilation procedures along with microwave power saturation experiments helped to clearly identify phenoxy and cyclopentadienyl radicals in the same temperature region. Conclusive identifications of these radicals were based on pure spectra of phenoxy and cyclopentadienyl radicals under the same experimental conditions generated from suitable precursors. Cyclopentadienyl is clearly the dominant radical at temperatures above 700 °C and is observed at temperatures as low as 400 °C. The low temperature formation is attributed to heterogeneous initiation of phenol decomposition under very low pressure conditions. The high cyclopentadienyl to phenoxy ratio was consistent with the results of reaction kinetic modeling calculations using the CHEMKIN kinetic package and a phenol pyrolysis model adapted from the literature.

Introduction

Phenol and substituted phenols play an important role in the combustion of aromatic compounds as they are typically the first oxidation product of an aromatic hydrocarbon^{1,2,6}. It is also known that homogeneous formation of non-chlorinated dibenzo-p-dioxins/dibenzofurans, DD/DF, and polychlorinated dibenzo-p-dioxins/dibenzofurans, PCDD/Fs, is governed by the concentration of chlorophenols and chlorobenzenes³⁻⁵. Phenol is also a likely reaction intermediate in the decomposition of hydroquinones and catechols that are formed in the combustion of tobacco and other biomass which are implicated as precursors in the formation of biologically active, semiquinone-type free radicals^{2,6}. Although the combustion and thermal degradation of phenol has been the topic of some research, its role in the formation of environmentally persistent free radicals (PFRs) has only recently begun to be explored⁷.

There are a few reports of the high temperature (~900 to 1200 K) pyrolysis of phenol. Generally the published results concern the nature of the initiation step. Some authors conclude that the hydroxylic hydrogen atom of the C₆H₅OH enol structure tautomerizes to form the C₆H₆O keto structure before decomposing into carbon monoxide and cyclopentadiene (C₅H₆)^{8,9}, the cyclopentadienyl radical, C₅H₅ (CPD), then being formed from the cyclopentadiene molecule⁹. It has also been proposed that the initiation step of the phenol decay is the formation of phenoxy (C₆H₅O + H) followed by the phenoxy decomposition into CPD and carbon monoxide¹⁰⁻¹².

At the present time, we are not aware of any published literature demonstrating direct experimental proof of formation of phenoxy or CPD radicals during phenol pyrolysis. Consequently identification of the exact nature of the radicals from phenol pyrolysis, their origin, their stability, and the potential health impacts of possibly environmentally persistent free radicals appears to be an increasingly important environmental issue.

Methods and Materials

We studied the thermal degradation of phenol under controlled conditions that allowed trapping of decomposition radical(s) under conditions that facilitated their identification. We employed the technique of the Low Temperature Matrix Isolation (LTMI) EPR¹³, in which phenol was pyrolysed in a low pressure reactor (0.1- 0.2 torr) that was directly connected to a liquid nitrogen-cooled cold finger situated within the EPR cavity of a Bruker EPR spectrometer. The experimental system was configured such that matrix isolation gases could be introduced to improve the quality of the resulting EPR spectra. In some experiments, gradual warming of the Dewar was employed to allow annealing of the matrix and annihilation of mobile or very reactive radicals. This resulted in production of cleaner, sharper spectra of single radicals under environmentally isolated conditions. These simple annealing experiments¹⁴ in conjunction with the LTMI EPR technique allowed the identification of phenoxy as well as CPD radicals in the complex mixture of radicals from pyrolysis of phenol over the surprisingly wide pyrolysis temperature range of 400 to 1000 °C.

Results and Discussion

The 77 K EPR spectra from phenol pyrolysis over the temperature range of 400 to 1000 °C before and after annealing, as well as total radical yields vs. temperature is presented in **Figure 1**. Annealing by slowly raising the matrix temperature resulted in well-resolved, identifiable spectra (spectra below the black curve, **Figure.1**). All annealed spectra over the temperature range of 700 to 1000 °C resulted in the generation of EPR spectra with 6 lines, hyperfine splitting constant ~ 6.0 G, $g = 2.00430$, and peak to peak width ~ 3 G that was readily assignable, based on comparison to the literature and theoretical calculations, as that of cyclopentadienyl radical.

Mechanistic studies of phenol, as well as halogenated phenols, pyrolysis indicate that the first step in the pyrolysis involves the generation of a phenoxy radicals^{8,15-18}. Generally this is followed by expulsion of CO from the phenoxy radical to form CPD radical.

Further annihilation procedures, along with microwave power saturation experiments, resulted in identification of phenoxy radicals in the same temperature region. Conclusive identifications of these radicals were based on pure spectra of phenoxy and cyclopentadienyl radicals under the same experimental conditions generated from suitable precursors.

The principal conclusion from this work was that cyclopentadienyl is clearly the dominant radical at temperatures above 700 °C and is observed at temperatures as low as 400 °C. The high CPD to phenoxy ratio was a bit surprising in the light of the stability of phenoxy radical proposed in the literature^{11,19}.

To address this issue, we modeled our experimental data with a core phenol pyrolysis model from the literature⁹ using the CHEMKIN kinetic package and a perfectly-stirred, plug-flow reactor application (150 ppm phenol in flow of CO₂, total flow pressure 0.2 torr, contact time 4 ms). The modeling results are summarized in Table 1. Indeed at temperature >1073 K, as phenol decomposes, the model predicts a high CPD to phenoxy ratio.

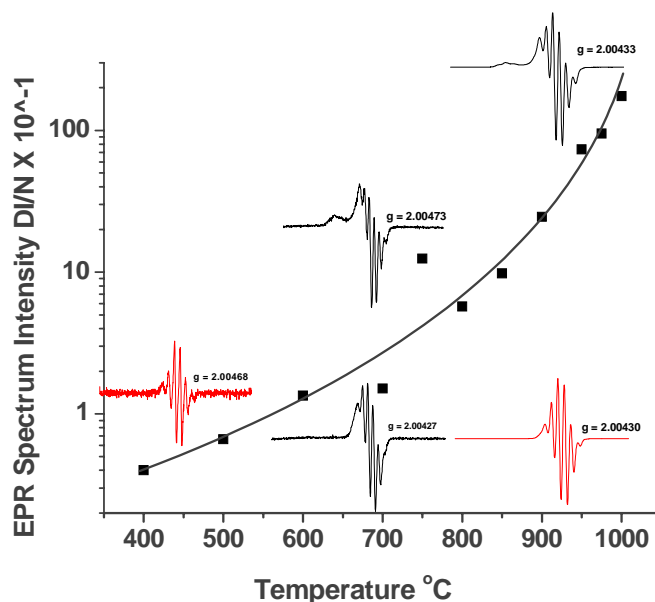


Figure 1. Temperature dependence of the total radical yields from the low pressure pyrolysis of phenol (0.2 torr). The DI/N value is the double integrated (DI) intensity of the EPR spectrum that has been normalized (N) to account for the conversion time, receiver gain, number of data points and sweep width [<http://www.bruker-biospin.com/winepr.html?&L=0>]. The representative EPR spectra of carbon dioxide matrix isolated radicals from the pyrolysis of phenol are depicted above the black curve (as un-annealed spectra at 77 K) and below the curve (as annealed spectra). Red spectra are pure EPR spectra of CPD. All spectra were registered at characteristic parameters; sweep width 200G, modulation amplitude 4G, time constant 5.12ms, microwave power 5mW.

Table 1.

CPD and Phenoxy concentrations (mole fractions) from the Phenol Reaction Kinetic Model*

	873 K	973 K	1073 K	1173 K	1273 K
C ₅ H ₅	0.64E-10	0.80E-07	0.12E-04	0.36E-03	0.38E-02
C ₆ H ₅ O	0.28E-08	0.28E-06	0.48E-05	0.18E-04	0.43E-04
C ₅ H ₅ /C ₆ H ₅ O	0.023	0.3	2.5	19.7	88.4
Percent consumption of C ₆ H ₅ OH	0.0	2.0	2.4	4.0	26.0

*Adapted from reference 9.

All of these results suggest that CPD radicals are the dominant persistent free radical formed from the low pressure pyrolysis of phenol.

Acknowledgements

The authors gratefully acknowledge the partial support of this research by NSF (Grant CTS-0317094) and Philip Morris USA.

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