

Thermolysis of 2,2-Diphenylpropane and 4-Cumyl Phenol

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ABSTRACT

The thermal reactivity of 2,2-diphenylpropane is relevant to the stability of a broad class of polymers which are made using bisphenol A. Consequently, the pyrolysis of 2,2-diphenylpropane and 4-cumyl phenol, its analog containing a hydroxy substituent, have been studied at 450 and 500°C. 2,2-DPP is observed to react to 1,1-diphenylethane, 1,1-diphenylethylene, toluene, ethylbenzene, 2-phenyl propene diphenylmethane, benzene and cumene. 4-Cumyl phenol reacts to an analogous spectrum of products, but at faster reaction rates indicating activation by the hydroxy substituent. A free-radical mechanism consistent with experimental results has been proposed herein together with the associated rate parameters for elementary steps.

INTRODUCTION

Polymer thermal stability is important for purposes of recycling and in regards to degradation during end-use applications and high temperature processing. A broad class of these polymers (e.g., polycarbonate, polysulfone, polyarylate, polyetherimide) are prepared using bisphenol A, and therefore the thermal reaction of materials containing this moiety are of interest.

This reactivity can be probed directly in experiments with the polymeric materials themselves. These experiments can provide much relevant but system-specific information. A second, complementary approach is in experiments using pure component, model compounds, which provide a great deal of fundamental information about the reaction pathways, kinetics and mechanisms. This information can be used in the prediction of the reaction of polymeric materials beyond the range of experiments with the actual polymers.

In this work we follow the second tact to study the reactivity of materials containing the isopropylidene linkage. We present results of pyrolysis experiments of 2,2-diphenylpropane [2,2-DPP] and its hydroxy substituted analog, 4-cumyl phenol [4-CP].

The reaction pathways and kinetics of 2,2-diphenylpropane have not been thoroughly studied. Previous experimental work [1] indicates the bond homolysis activation energy as $E_a=65.7$ kcal/mol and $\log_{10}A=15.7$. Pryor, Gleicher and Church [2] studied ring ozonation of 2,2-DPP at 25°C. Duty, Geier and Harwood [3] demonstrated resistance of 2,2-DDP to oxidation by dichromate when reacted in an aqueous solution at 250°C and 18 hrs. Schanne and Haenel [4] used potassium to cleave the phenyl ring to form benzene and 2-phenylpropane by what they propose to be a radical ion mechanism. Golden [5] irradiated 2,2-DPP at 1000 megarads using electron beam radiation. The reaction products were primarily methane and hydrogen, with little CO , CO_2 and hydrocarbon gases found.

Herein we extend this previous literature through more comprehensive study of the reaction pathways, kinetics and mechanisms for the pyrolysis of 2,2-diphenylpropane and 4-cumyl phenol.

EXPERIMENTAL SECTION

2,2-DPP and 4-cumyl phenol were pyrolysed at 450°C and 500°C for batch holding times of 2-120 min. Initial concentrations were nominally 60 mM.

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Materials

2,2-DPP was obtained from Aldrich and subsequently distilled and collected at 113–117°C and 3 mm Hg. 4-Cumyl phenol was obtained from Aldrich and recrystallized before use. Dibenzyl ether, used as an external standard for GC analysis, was obtained from Aldrich. Gold band ampules (Wheaton) were used to fabricate batch reaction vessels.

Procedure

The reactors were loaded by weight with a typical charge of 25 mg of reactant. One reactor was prepared for each desired reaction time. The ampules were purged with argon to avoid oxidation and then immediately sealed using a propane/O₂ flame. These reactions were then immersed into a constant-temperature, fluidized sand bath (Techne) for the desired reaction time. The reaction was quenched by immersion in a cold, room-temperature fluidized sand bath. Reactors were checked for leaks by weighing both before and after reaction.

Reactant conversion and product yields were quantified by use of the external standard, dibenzyl ether, added to the reaction mixture after reaction. All materials were then recovered in methylene chloride. Analysis was performed by GC (Hewlett-Packard 5880) equipped with an FID to quantify yields and GC/MSD (Hewlett-Packard 5890 GC/H-P 5970 MSD) to identify products.

RESULTS AND DISCUSSION

2,2-Diphenylpropane pyrolysis at 450°C was at holding times ranging from 2.0–120.0 minutes; reaction at 500°C was for holding times ranging from 5–60 min. The detailed product spectrum, shown in Table 1 as product molar yields vs. time, includes benzene, toluene, ethylbenzene, styrene, cumene, 2-phenylpropene, 1,1-diphenylethane, 1,1-diphenylethene and diphenylmethane. At 450°C, a 32% conversion of 2,2-DPP was observed at 120 min, where the products in most significant yields were 1,1-diphenylethane and 1,1-diphenylethene, followed by benzene, toluene and ethyl benzene.

The Delplot technique [6] is a data analysis approach which reveals reaction path information allowing discrimination between primary, secondary and higher order products. For example, in a first-rank Delplot, product selectivity (yield/conversion) is examined as a function of conversion. In extrapolation to zero conversion, primary products have finite y-intercepts, while that for higher order products goes to zero. In a second-rank Delplot (yield/conversion² vs. conversion), primary products diverge as $\chi \rightarrow 0$, while secondary products have finite intercepts.

First-rank Delplots for 2,2-DPP pyrolysis at 450°C indicate that all products except diphenylmethane, toluene, ethyl benzene and styrene were clearly primary. Delplots for 2,2-DPP pyrolysis at 500°C suggest all products but diphenylmethane to be primary. This may indicate that at 500°C the intermediates that lead to toluene, ethyl benzene and styrene may be very short lived.

4-Cumyl phenol was pyrolysed at both 450 and 500°C to final holding times of 101 and 60 min, respectively. Table 2 summarizes the reaction products, namely benzene, toluene, ethyl benzene, cumene, phenol, 2-phenylpropene, methylpropyl benzene, 4-methyl phenol, 4-ethyl phenol, 4-hydroxy diphenylmethane, 4-hydroxy-(1,1-diphenylethane) and 4-hydroxy-(1,1-diphenylethene). These are analogous to the products observed from 2,2-DPP pyrolysis. 4-hydroxy diphenylethane and 4-hydroxy diphenylethene were observed in the highest yields, with relatively large amounts of phenol. The first-rank Delplots for 4-cumyl phenol pyrolysis at 500°C suggest most products to be primary with the exception of methylpropyl benzene, 4-ethyl phenol and hydroxydiphenylmethane.

The foregoing information suggests the 2,2-DPP and 4-CP pyrolysis pathways to be straightforward. Primary pyrolysis provides most of the products, with secondary reactions accounting for only diphenylmethane (for 2,2-DPP) and methylpropyl benzene, 4-ethyl phenol, and hydroxy diphenylmethane (for 4-CP). Pseudo-first-order rate constants for the reaction of both 2,2-DPP and 4-cumyl phenol to their primary products are shown in Table 3. The suggested Arrhenius parameters (two temperatures only) for primary 2,2-DPP pyrolysis are also listed in Table 3. 4-Cumyl phenol pyrolysis was much faster than that of 2,2-DPP. For example, for reaction at 500°C and 60 min, the 4-cumyl phenol conversion was 93%, whereas only 80% conversion was observed for 2,2-DPP.

A set of elementary steps consistent with the observed product spectra is shown in Figure 1. For 2,2-DPP, initiation by unimolecular decomposition can proceed through fission of two different bonds, leading to

the production of either methyl and diphenyl ethyl radicals (which subsequently become methane and 1,1-diphenylethane following hydrogen abstraction) or to phenyl and isopropyl benzene radicals (similarly leading to benzene and cumene). The former is expected to be more facile since the controlling bond dissociation energy is ~66 kcal/mol, 14 kcal/mol lower than that of ~80 kcal/mol for the latter. Propagation is by hydrogen abstraction by any radical from 2,2-DPP. The thus-derived 2,2-DPP radical has two β -scission pathways available. One leads to a methyl radical and diphenylethane and has a lower heat of reaction than the second, leading to a phenyl radical and 2-phenyl propene. A thermodynamically favorable phenyl shift can ultimately lead to toluene and ethyl benzene. Termination is by combination of any two radicals. An analogous set of steps could lead to the observed 4-CP products.

In summary, the structure and thus-derived thermochemical properties of 2,2-DPP and 4-CP control their pyrolysis activity. No evidence for a significant kinetic chain was found. The main products all appear to be primary and are explained nicely by elementary steps in strict accord with thermochemical estimates.

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Table 1 - Product Molar Yields for Pyrolysis of 2,2-Diphenylpropane
Reaction at 450°C

Time (min)	0.00	2.00	5.00	10.00	15.00	20.00	30.00	45.00	60.00	120.00
2,2-DPP	1.0000	0.9715	1.0157	0.9604	0.9932	0.9124	0.9106	0.8427	0.8121	0.6812
Benzene	0.0000	0.0005	0.0012	0.0047	0.0067	0.0079	0.0094	0.0102	0.0125	0.0130
Toluene	0.0000	0.0004	0.0006	0.0027	0.0067	0.0104	0.0160	0.0202	0.0253	0.0383
Ethylbenzene	0.0000	<0.0001	<0.0001	0.0018	0.0042	0.0067	0.0103	0.0132	0.0173	0.0245
Styrene	0.0000	<0.0001	<0.0001	0.0006	0.0012	0.0018	0.0026	0.0032	0.0043	0.0052
Cumene	0.0000	<0.0001	0.0008	0.0026	0.0033	0.0037	0.0043	0.0046	0.0056	0.0060
2-PhenylPropene	0.0000	0.0004	0.0010	0.0032	0.0044	0.0051	0.0057	0.0061	0.0080	0.0071
DiPEthane	0.0000	0.0002	0.0017	0.0068	0.0122	0.0175	0.0262	0.0367	0.0542	0.0931
DP Ethylene	0.0000	0.0003	0.0014	0.0063	0.0124	0.0191	0.0295	0.0419	0.0668	0.0990
DPM	0.0000	<0.0001	0.0002	0.0003	0.0007	0.0009	0.0015	0.0021	0.0030	0.0073

Reaction at 500°C

Time (min)	0.00	5.00	15.00	45.00	60.00
2,2-DPP	1.0000	0.8872	0.6547	0.3302	0.2020
Benzene	0.0000	0.0131	0.0185	0.0237	0.0278
Toluene	0.0000	0.0176	0.0419	0.0823	0.1067
Ethylbenzene	0.0000	0.0122	0.0238	0.0393	0.0445
Styrene	0.0000	0.0035	0.0069	0.0107	0.0115
Cumene	0.0000	0.0061	0.0070	0.0087	0.0093
2-PhenylPropene	0.0000	0.0098	0.0120	0.0116	0.0109
DiPhenylEthane	0.0000	0.0334	0.0983	0.2070	0.2487
DP Ethylene	0.0000	0.0403	0.1274	0.2359	0.2582
DPM	0.0000	0.0013	0.0083	0.0414	0.0730

Table 2 - Product Yields for Pyrolysis of Cumyl Phenol
Reaction at 450°C

time/min	0.00	2.00	5.00	10.00	20.00	47.58	60.00	101.02
Cumyl Phenol	1.0003	0.8909	0.8753	0.8217	0.7247	0.614	0.5636	0.4699
benzene	0.0157	0.0150	0.0154	0.0157	0.0164	0.0191	0.0193	0.0242
toluene	0.0004	0.0009	0.0020	0.0043	0.0086	0.0183	0.0219	0.0402
et. benzene	0.0000	0.0003	0.0013	0.0031	0.0061	0.0129	0.0155	0.0297
cumene	0.0000	0.0015	0.0038	0.0076	0.0122	0.0232	0.0279	0.0469
phenol	0.0000	0.0030	0.0059	0.0148	0.0211	0.038	0.0472	0.0834
2pp	0.0000	0.0062	0.0088	0.0163	0.0197	0.0251	0.0283	0.0369
4mp	0.0000	0.0003	0.0012	0.0030	0.0062	0.0127	0.0154	0.0272
4ep	0.0000	<0.0001	0.0008	0.0024	0.0055	0.0113	0.0132	0.0218
HDPM	0.0000	<0.0001	<0.0001	<0.0001	0.0007	0.0029	0.0049	0.0124
hdpethane	0.0000	0.0005	0.0044	0.0108	0.0214	0.0493	0.0681	0.1145
hdpeithene	0.0000	0.0014	0.0063	0.0159	0.0329	0.0594	0.0707	0.0825

Reaction at 500°C

time/min	0.00	5.00	15.00	30.00	45.00	60.00
Cumyl Phenol	1.0000	0.8222	0.5018	0.2472	0.1570	0.0665
benzene	0.0000	0.0020	0.0043	0.0068	0.0092	0.0127
toluene	0.0000	0.0085	0.0226	0.0429	0.0574	0.0852
et. benzene	0.0000	0.0058	0.0148	0.0303	0.0448	0.0665
cumene	0.0000	0.0109	0.0235	0.0352	0.0572	0.0569
phenol	0.0000	0.0148	0.0407	0.0760	0.1380	0.1737
2pp	0.0000	0.0178	0.0315	0.0398	0.0565	0.0536
methylpropbenz	0.0000	0.0021	0.0022	0.0028	0.0036	0.0038
4mp	0.0000	0.0062	0.0164	0.0307	0.0354	0.0512
hdpethane	0.0000	0.0329	0.0859	0.1400	0.1405	0.1390
hdpeithene	0.0000	0.0621	0.1390	0.1614	0.1387	0.1380

Table 3: Reaction Pathway Parameters; 2,2-Diphenylpropane and 4-Cumyl Phenol

a) 2,2-Diphenylpropane

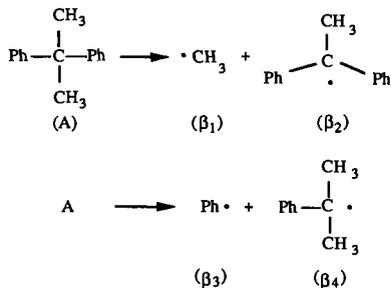
Reactant/Product	$k_1(450^\circ\text{C})$ [1/min]	$k_1(500^\circ\text{C})$ [1/min]	E_a [kcal/mol]	$\log_{10} A$
DPP	3.31E-03	2.61E-02	45.8	9.6
Benzene	1.86E-04	9.82E-04	37.0	9.2
Toluene	4.23E-04	3.33E-03	45.9	8.7
Ethyl Benzene	2.75E-04	1.53E-03	38.1	6.2
Styrene	6.94E-05	4.00E-04	38.9	5.8
Cumene	8.06E-05	6.16E-05		
2-Phenyl Propene	1.10E-04	4.21E-06		
1,1-DP Ethane	9.38E-04	8.02E-03	47.7	9.6
1,1-DP Ethene	1.04E-03	8.82E-03	47.5	9.6

a) 4-Cumyl Phenol

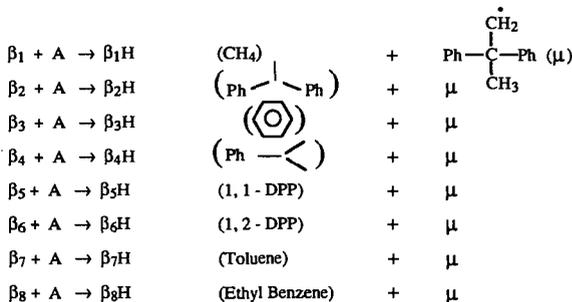
Reactant/Product	$k_1(450^\circ\text{C})$ [1/min]	$k_1(500^\circ\text{C})$ [1/min]	E_a [kcal/mol]	$\log_{10} A$
4-Cumyl Phenol		4.46E-02		
Benzene		1.07E-08		
Toluene		3.70E-03		
Ethyl Benzene		6.40E-04		
Cumene		2.98E-04		
Phenol		6.60E-03		
2-Phenyl Propene		2.82E-03		
4-Methyl Phenol		2.45E-03		
4-Hydroxy(1,1-DP Ethane)		6.24E-03		
4-Hydroxy(1,1-DP Ethene)		7.58E-03		

Figure 1
Elementary Steps for Reaction of 2, 2 - DPP

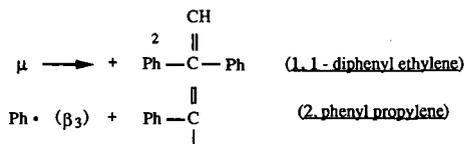
Bond Fission



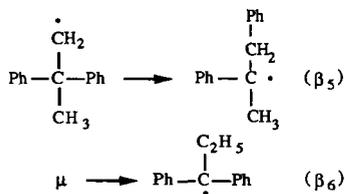
Hydrogen Transfer



β - scission



Radical Isomerization



Recombination

All combinations

Secondary Reactions

