

PYROLYSIS KINETICS AND MECHANISMS FOR POLYCYCLIC PERHYDROARENES BEARING LONG N-ALKYL CHAINS

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ABSTRACT

A set of long-chain polycyclic n-alkylperhydroarenes was pyrolyzed neat at temperatures between 400 and 475°C. The disappearance of these compounds typically followed first-order kinetics. The pyrolysis of a perhydroarene with an n-carbon containing n-alkyl chain generated numerous primary products. The primary products with the highest initial selectivities were generally the perhydroarene plus an α -olefin with n carbon atoms, the methylene perhydroarene plus an n-alkane with n-1 carbon atoms, and a polycyclic mono-olefin plus an n-alkane with n carbon atoms. The kinetics data from this investigation were used to test a structure-reactivity correlation in the literature for the pyrolysis of saturated cyclic compounds and to update it so that it becomes consistent with the kinetics of long-chain n-alkylperhydroarenes.

INTRODUCTION

Naphthenic (perhydroarene) moieties decorated with n-alkyl substituents exist in heavy hydrocarbon resources such as coal, heavy oils, and asphaltenes. Additionally, these types of chemical structures are present in the endothermic jet fuels being developed for the next generation of high-performance jet aircraft. Given the presence of these structures in these materials, which experience elevated temperatures of around 400°C during their processing or use, it is clear that information about the thermal decomposition of saturated cyclic compounds with alkyl substituents at temperatures around 400°C would be useful.

Until very recently, the literature was limited to kinetics data at a single temperature (700K) for 28 saturated cyclic compounds (six were polycyclic), most of which bore short chains (Fabuss et al., 1964) and more extensive kinetics data and mechanistic information for a single one-ring compound, tridecylcyclohexane (Savage and Klein, 1988; Mushrush and Hazlett, 1984). Indeed, prior to the publication of our group's recent work (Humburg and Savage, 1996; Mizan et al., 1997), the literature provided no information about the pyrolysis kinetics, pathways, or mechanisms for any polycyclic perhydroarenes bearing a long (> C₄) n-alkyl chain. This lack of information about the behavior of polycyclic n-alkylperhydroarenes and previous results showing that the pyrolysis of other polycyclic hydrocarbons led to products that differed from those of their single ring analogs (Savage et al., 1989; Virk et al., 1979) motivated the investigations with n-alkyl-substituted polycyclic perhydroarenes.

EXPERIMENTAL

The model compounds were obtained from the Thermodynamics Research Center at Texas A & M University, Pfaltz and Bauer, TCI Organics, and Wiley Organics. All chemicals were used as received. All pyrolyses were conducted neat in batch microreactors fashioned from a nominal 1/4 inch stainless steel Swagelok port connector and two caps. We loaded between 10 and 40 mg of the reactant and about 10-15 mg of biphenyl (an internal standard) into each reactor, and these quantities were weighed to within ± 0.1 mg. The loaded reactors were placed in a fluidized sand bath maintained at the desired pyrolysis temperature. When the desired batch holding time had elapsed, the reactors were removed from the sand bath, and the reaction was quenched by immersing the reactors in water at room temperature. The reactors were then opened and their contents retrieved by repeated additions of methylene chloride. The reaction products were identified and quantified via capillary-column gas chromatography with either a mass spectrometric or flame-ionization detector. Product molar yields, calculated as the number of moles of product formed divided by the number of moles of reactant initially loaded into the reactor, were obtained from the chromatographic analysis using experimentally determined detector response factors. Additional details about the experimental methods appear in the literature (Humburg and Savage, 1996; Mizan et al., 1997).

RESULTS AND DISCUSSION

This section summarizes the experimental results obtained from n-alkylperhydroarene pyrolysis. These results were used to determine the reaction rate law and to develop the reaction network for neat pyrolysis.

Pyrolysis Kinetics

The objectives of the kinetics analysis were to determine the global reaction order (m) and Arrhenius parameters (A, E) for the power-law rate expression in Equation 1 that best describes n-alkylperhydroarene disappearance.

$$\text{rate} = kC^m = A \exp\left(\frac{-E}{RT}\right)C^m \quad (1)$$

The parameters in the rate law were determined by examining the results of numerous experiments at different temperatures, holding times, and initial concentrations. First order kinetics

gave an adequate description of the kinetics for each compound examined in detail. Our previous reports (Humburg and Savage, 1996; Mizan et al., 1997) provide the experimental data and the details of the kinetics analysis for 9-dodecylperhydroanthracene (DDPA) and 1-undecylperhydronaphthalene (UPN). Additionally, Table 1 provides new kinetics data for the pyrolysis of nine other n-alkylperhydroarenes.

Structure-Reactivity Relations

The reaction kinetics for compounds in a single family can often be correlated using a structure-based reactivity index. Such structure-reactivity correlations are useful in computer models of the reactions of complex materials such as fossil fuels and for predicting the reactivity of compounds that have not been investigated experimentally. One needs a large set of reliable kinetics data to develop structure-reactivity correlations. Fabuss et al. (1964) provide data for the pyrolysis kinetics at 800°F (700K) of 28 saturated cyclic compounds that were either unsubstituted or bore short ($\leq C_4$) alkyl substituents. They correlated the disappearance kinetics using a "characterization number", n , as the reactivity index. The Fabuss et al. (1964) correlation is

$$k \text{ (hr}^{-1}\text{)} = 0.044 - 0.0114n + 0.0008n^2 \quad (2)$$

The characterization number can be determined by inspection of the structure of the compound, and it is based on group-additivity. The characterization number for decylcyclohexane, for example, is 49 (12 for the cyclohexane ring, plus 4 for each of the nine CH_2 group in the alkyl chain, plus 2 for the terminal methyl ring in the chain, and minus 1 for the one C-H bond in the ring structure replaced by an alkyl substituent). We note that the equation above shows 0.0114 as the coefficient for the second term, whereas the equation that appears in Fabuss et al. shows 0.114. We believe the equation in Fabuss et al. contains a typographical error because using 0.114 in Equation 2 leads to negative values for the rate constants.

In this report, we expand the existing database by providing new kinetics data (see Table 1) for the pyrolysis of long-chain and polycyclic perhydroarenes at 427°C. We can use the data in Table 1, along with that previously reported for tridecylcyclohexane, TDC, (Savage and Klein, 1988; Mushrush and Hazlett, 1984), undecylperhydronaphthalene, UPN (Mizan et al., 1997), and dodecylperhydroanthracene, DDPA, (Humburg and Savage, 1996) to assess the predictive ability of the Fabuss et al. (1964) structure-reactivity relation.

Figure 1 shows the correlation of Fabuss et al. along with our experimental data for 11 different long-chain n-alkylperhydroarenes. It is clear that the correlation fails to predict the kinetics for these compounds. Fabuss et al., to their credit, anticipated that the performance of their correlation would deteriorate as the length of the alkyl substituent exceeded four carbon atoms. Indeed, none of the compounds they pyrolyzed had characterization numbers that exceeded 40, and Figure 1 shows that the correlation performs poorly when extrapolated to these higher characterization numbers.

We next combined the kinetics data provided by Fabuss et al. with our more recent data for long-chain compounds to develop a new structure-reactivity relation that uses the characterization number as the sole correlating parameter. We fit the experimental kinetics data in Fabuss et al. along with our data for long-chain perhydroarenes to a quadratic equation of the form originally used by Fabuss et al. (Equation 2). The results from the non-linear regression showed that the uncertainty in the second parameter exceeded the value of the parameter itself. In fact, a value of zero was contained within the 95% confidence interval for this parameter. Consequently, we repeated the non-linear regression of the kinetics data, but with the statistically insignificant term set equal to zero. The resulting correlation is

$$k \text{ (hr}^{-1}\text{)} = -0.041 + 0.00035n^2 \quad (3)$$

The level of agreement between the new correlation and the experimental data is apparent upon inspection of Figure 2. We expect that the correlation of Equation 3 will provide reasonable estimates of the rate constants for long-chain alkylperhydroarenes. The only compound for which the correlation performs poorly is decylperhydroarene. The reason for this failure is not clear, and additional experiments with other polycyclic compounds are required to address this issue.

The structure-reactivity relation of Fabuss et al. qualitatively incorporates some fundamental aspects of hydrocarbon pyrolysis kinetics in their characterization number. For example, a CH_2 group adds more to the characterization number than does a CH_3 group, which is consistent with secondary C-H bonds being weaker and hence more reactive than primary C-H bonds. This correlation is empirical, however, because the relative contributions of the different structural groups were determined by fitting data rather than by building squarely upon the foundation of the governing reaction mechanism. The mechanism for the pyrolysis of saturated cyclic hydrocarbons is reasonably well established, and closed-form analytical rate expressions are available (Savage, 1990). A mechanism-based structure-reactivity relation has already appeared for n-alkylbenzenes (Savage and Korotney, 1990). Thus, the stage is now set for progress toward a mechanism-based structure-reactivity relation for long-chain n-alkylperhydroarenes.

Pyrolysis Products, Network, and Mechanism

The neat pyrolysis of n-alkylperhydroarenes led to numerous reaction products, and the product spectrum comprised n-alkanes, 1-alkenes, perhydroarenes substituted with alkyl or alkenyl chains, and partially hydrogenated arenes. Our work with these compounds showed that a perhydroarene with an n-carbon-containing alkyl substituent pyrolyzed to form three pairs of major

primary products and numerous minor primary products. This network is illustrated in Figure 3 for UPN. The major primary product pairs are the perhydroarene plus a C_n olefin (decalin plus undecene for UPN), the methylene perhydroarene plus a C_{n-1} alkane (methylene decalin plus decane for UPN), and a cyclic olefin plus a C_n alkane (octahydronaphthalene plus undecane for UPN).

Although the identities of the three major primary product pairs are analogous for the different n-alkylperhydroarenes, the relative abundances of these products differ for the different compounds. The ring-containing products from the neat pyrolysis of the 2- and the 3-ring compounds were, in order of decreasing selectivity, the cyclic olefin, the methylene perhydroarene, and the perhydroarene. The pyrolysis of DPP, a 4-ring compound, on the other hand, led to the perhydroarene being the most abundant product, followed by the methylene perhydroarene and the cyclic olefin. The product spectrum from DPP more closely resembled that of an alkylcyclohexane, wherein the major primary pyrolysis products are cyclohexane, methylene cyclohexane, and lesser amounts of cyclohexene and methylcyclohexane. This comparison of the major primary products from neat pyrolysis of 1-, 2-, 3-, and 4-ring n-alkylperhydroarenes shows that an analogous set of three major product pairs forms in all cases. The compound-to-compound differences involve only the relative abundance of these different product pairs. This similarity in the reaction network suggests a corresponding similarity in the underlying reaction mechanism. Thus, the free-radical reaction steps advanced previously for 1-, 2-, and 3-ring alkylperhydroarenes (Savage and Klein, 1988; Humburg and Savage, 1996; Mizan et al., 1997) appear to be general.

SUMMARY AND CONCLUSIONS

This paper provides a summary of results from the pyrolysis of long-chain polycyclic n-alkylperhydroarenes. The neat pyrolysis typically follows first-order kinetics. The reaction network for n-alkylperhydroarenes includes parallel primary reactions to form an α -olefin plus the perhydroarene, an n-alkane plus the methylene perhydroarene, and an n-alkane plus a polycyclic mono-olefin. The numerous minor primary products were other n-alkanes, α -olefins, alkylperhydroarenes, and alkenylperhydroarenes. The arene and methylarene appeared as products at the more severe reaction conditions.

Kinetics data for the pyrolysis of n-alkylperhydroarenes revealed that the correlation of Fabuss et al. (1964) cannot be extrapolated to predict the reactivity of long-chain and polycyclic perhydroarenes. Equation 3 provides a new correlation, based on the Fabuss et al. characterization number, that is consistent with both their data and that reported herein. This correlation can be used to predict the kinetics of a wide variety of saturated cyclic compounds.

REFERENCES

- Fabuss, B. M.; Kafesjian, R.; Smith, J. O.; Satterfield, C. N. Thermal Decomposition Rates of Saturated Cyclic Hydrocarbons. *Ind. Eng. Chem. Proc. Des. Dev.* **1964**, *3*, 248.
- Humburg, R. E.; Savage, P. E. Pyrolysis of Polycyclic Perhydroarenes 1. 9-n-Dodecylperhydroanthracene. *Ind. Eng. Chem. Res.* **1996**, *35*, 2096.
- Mizan, T. I.; Savage, P. E.; Perry, B. Pyrolysis of Polycyclic Perhydroarenes 1. 1-n-Undecylperhydronaphthalene. *Energy Fuels* **1997**, *11*, in press.
- Mushrush, G. W.; Hazlett, R. N. Pyrolysis of Organic Compounds Containing Long Unbranched Alkyl Groups. *Ind. Eng. Chem. Fundam.* **1984**, *23*, 288.
- Savage, P. E. Pyrolysis of a Binary Mixture of Complex Hydrocarbons: Reaction Modeling. *Chem. Eng. Sci.* **1990**, *45*, 859.
- Savage, P. E.; Jacobs, G. E.; Javanmardian, M. Autocatalysis and Aryl-Alkyl Bond Cleavage in 1-Dodecylpyrene Pyrolysis. *Ind. Eng. Chem. Res.* **1989**, *28*, 645.
- Savage, P. E.; Klein, M. T. Asphaltene Reaction Pathways: 4. Pyrolysis of Tridecylcyclohexane and 2-Ethyltetralin. *Ind. Eng. Chem. Res.*, **1988**, *27*, 1348.
- Savage, P. E.; Klein, M. T. Asphaltene Reaction Pathways: 5. Chemical and Mathematical Modeling. *Chem. Eng. Sci.* **1989**, *44*, 393.
- Savage, P. E.; Korotney, D. J. Pyrolysis Kinetics for Long-Chain n-Alkylbenzenes: Experimental and Mechanistic Modeling Results. *Ind. Eng. Chem. Res.* **1990**, *29*, 499.
- Virk, P. S.; Korosi, A.; Woebcke, H. N. Pyrolysis of Unsubstituted Mono-, Di-, and Tricycloalkanes. In ACS Advances in Chemistry Series; Oblad, A. G., Davis, H. G., Eddinger, R. T., Eds.; American Chemical Society: Washington, DC, 1979; Vol. 183, p. 67

Table 1: Rate Constants (in sec^{-1}) for Neat Pyrolysis of Long-Chain n-Alkylperhydroarenes at 427°C

Compound	$k \times 10^4$	95% C.I.
2-Octylperhydrochrysene (OPC)	2.97	1.64
9-Dodecylperhydrophenanthrene (9DPPH)	4.22	0.38
1-Dodecylperhydrophenanthrene (1DPPH)	3.73	0.78
1-Decylperhydroropyrene (DPP)	1.28	0.56
Tridecylcyclohexane (TDC)	2.90	0.86
Dodecylcyclohexane (DCC)	2.75	0.70
Decylcyclohexane (DC)	2.57	0.96
Heptylcyclohexane (HPC)	1.63	0.30
Hexylcyclohexane (HXC)	1.01	0.49

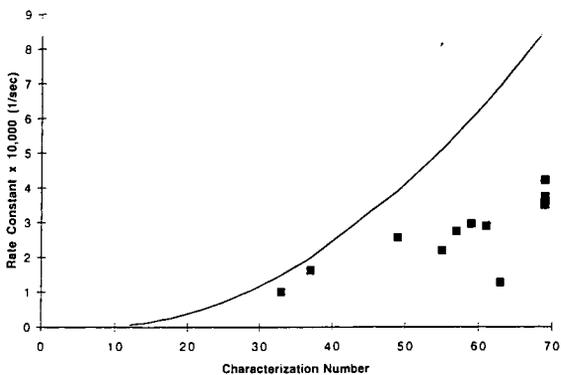


Figure 1: Structure-reactivity relation of Fabuss et al. (solid curve) and experimental data for long-chain n-alkylperhydroarenes (discrete points).

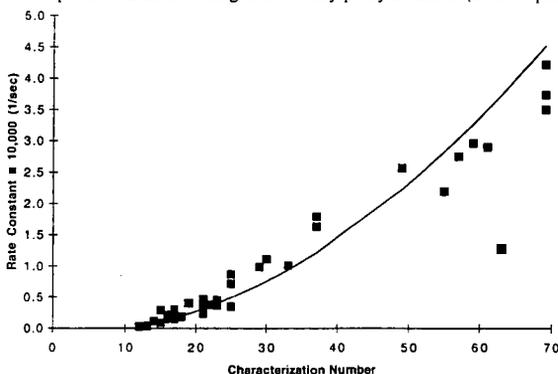


Figure 2: Updated structure-reactivity relation for saturated cyclic compounds.

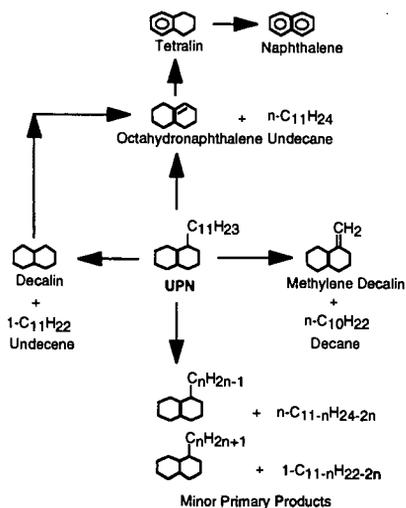


Figure 3: General reaction network for alkylperhydroarene neat pyrolysis.