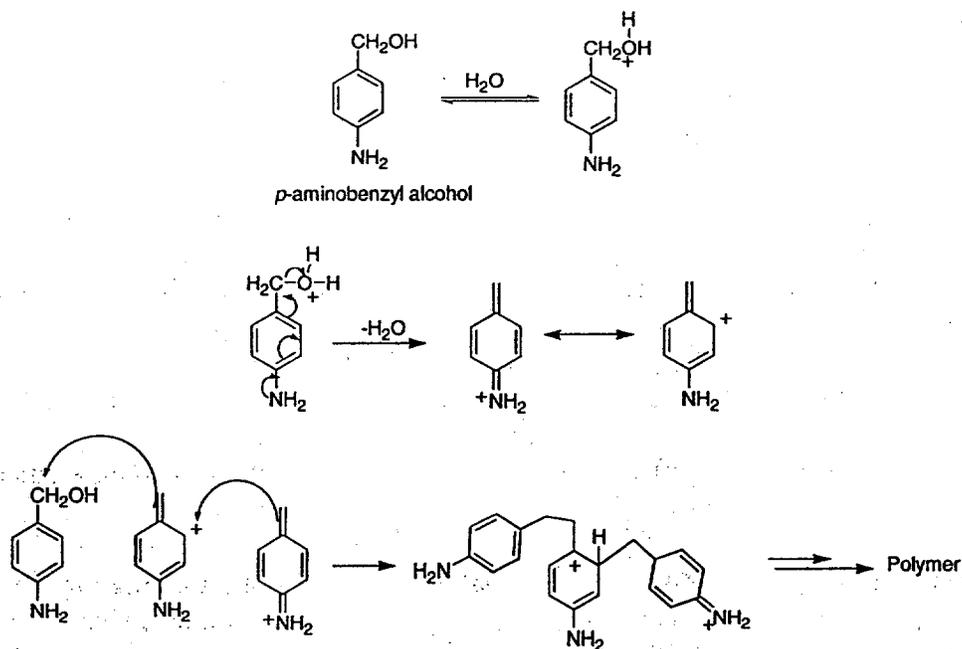


**Unsuitable Substrates.** It is noteworthy that many substituted benzyl alcohols were found not suitable for this study, as summarized in Table S1, because they were water-insoluble or because they showed competing reactivity. For example, halogenated benzyl alcohols were not suitable because they were not soluble in D<sub>2</sub>O.<sup>21</sup> Numerous other substituted benzyl alcohols were also insoluble in water. To increase solubility, a common practice is to add co-solvent. For substituted benzyl alcohols, a solvent mixture of 50% water, 50% alcohol is typically employed.<sup>5</sup> However, this solvent mixture is obviously not practical for studying the rate of H/D exchange in an alcohol substrate. We found that the use of solvent mixtures containing D<sub>2</sub>O and non-interacting co-solvents such as THF or DMSO, in concentrations up to 75% D<sub>2</sub>O /25% co-solvent (v/v), did not dissolve the substrates.

While polar substrates can be used to impart solubility in water, coordination of polar functional groups to the catalyst is a concern. Coordination of the functional group in preference to the alcohol would deactivate the catalyst. Therefore, benzyl alcohols with sulfoxide or carboxylic acid groups were not suitable substrates. *m*-Nitrobenzyl alcohol was unsuitable because it formed an insoluble precipitate upon heating. This is not unexpected because molybdocenes can react to form nitro, nitrito, and nitrate-derivatives.<sup>22</sup> Likewise, amino-substituted alcohols were unsuitable. Primary amines were found to be unreactive,<sup>3</sup> and aromatic amines complexed with the catalyst. (We found that the aromatic hydrogens in 3,5-diaminobenzyl alcohol underwent H/D exchange, a result most easily interpreted if the amine functionality complexes to the catalyst.<sup>23</sup> This result is also consistent with reports that aromatic amines are more likely to form complexes with molybdocenes than aliphatic amines.<sup>24,25</sup>)

Some substrates underwent competing side reactions before H/D exchange, making them unacceptable for kinetic studies. For example, *p*-ammonium benzyl alcohol at neutral pH contains small amounts of *p*-aminobenzyl alcohol, which activates electrophilic substitution leading to substrate polymerization (Scheme 3).



Scheme 3: Possible route of polymerization of *p*-aminobenzyl alcohol in aqueous solution.

3-Trifluoromethylbenzyl alcohol was found to activate the ring for nucleophilic attack. Other substrates, including 3-hydroxybenzyl alcohol and 3,5-hydroxybenzyl alcohol, which are very water soluble, undergo aromatic H/D exchange as the enolate of the alcohol is formed. In addition, the di-substituted alcohol has the potential to form a six-membered ring with the catalyst similar to that observed in ethylene glycol.<sup>6</sup> 4-Trifluoromethoxybenzyl alcohol undergoes hydrolysis and enolate formation. In summary, the necessary reaction conditions eliminated all of the alcohols in Table S1 except for the five reported in this study.

Table S1: Substrates Evaluated for Use in the Hammett Plot.

Substrate	Substituent	$\sigma_m$	$\sigma_p$	Solubility <sup>a</sup>	Reactivity
4-Chlorobenzyl alcohol	p-Cl		0.23	ns	-
4-Methoxybenzyl alcohol	p-CH <sub>3</sub> O		-0.27	ss	
4-Nitrobenzyl alcohol	p-NO <sub>2</sub>		0.78	ns	-
3-Nitrobenzyl alcohol	m-NO <sub>2</sub>	0.71		ss	Forms complex with molybdocene
3-Ammonium benzyl alcohol	m-NH <sub>3</sub> <sup>+</sup>	0.86		s	
4-Ammonium benzyl alcohol	p-NH <sub>3</sub> <sup>+</sup> /NH <sub>2</sub>		0.60/ -0.66	s	Electrophilic substitution leading to polymerization
3,5-Diaminobenzyl alcohol	m-NH <sub>2</sub>	2*-.16		s	Imido complexes and amine oxidation
3-Hydroxybenzyl alcohol	m-OH	0.12		s	enolate formation, aromatic H/D exchange
3,5-Dihydroxybenzyl alcohol	m-(OH) <sub>2</sub>	2*0.12		s	enolate formation, aromatic H/D exchange
3-Trifluoromethyl benzyl alcohol	m-CF <sub>3</sub>	0.43		ss	activates the ring for nucleophilic attack
3-Methoxybenzyl alcohol	m-OCH <sub>3</sub>	0.12		s	
Benzyl alcohol	H	0	0	s	
3-Methylbenzyl alcohol	m-CH <sub>3</sub>	-0.07		ss	
4-Trifluoromethoxy benzyl alcohol	p-OCF <sub>3</sub>		0.35	s	hydrolysis of substrate

<sup>a</sup>ns= not soluble, ss=slightly soluble, s=soluble

**Representative Rate Plots.** Included are representative concentration versus time plots for each substrate used. The curve shown is the first-order exponential decay.

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Figure S1: Reaction Rate of Benzyl Alcohol;  
Catalyst concentration is 0.0033M.

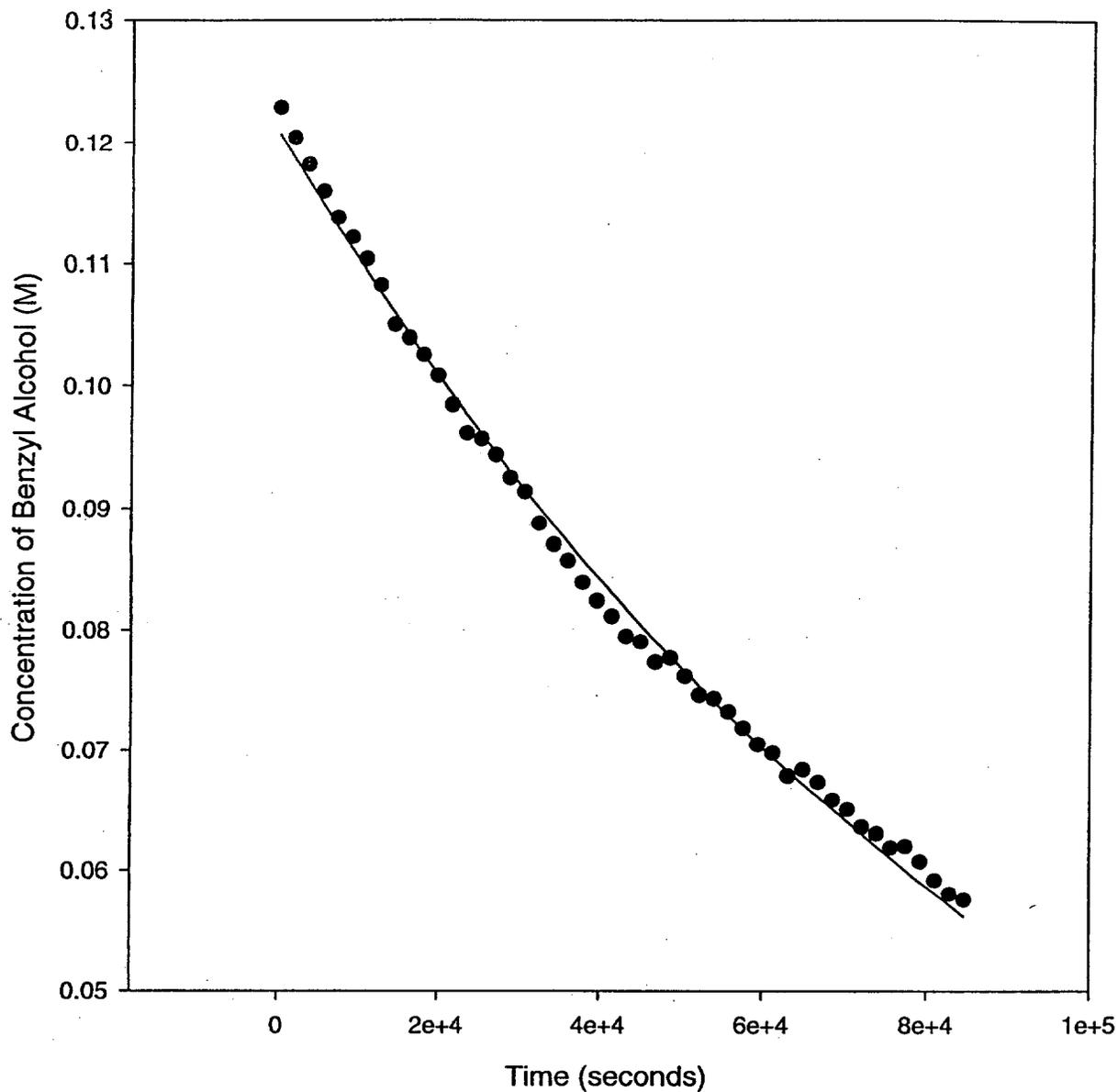


Figure S2: Reaction Rate of 3-Methoxybenzyl Alcohol;  
Catalyst concentration is 0.0033M

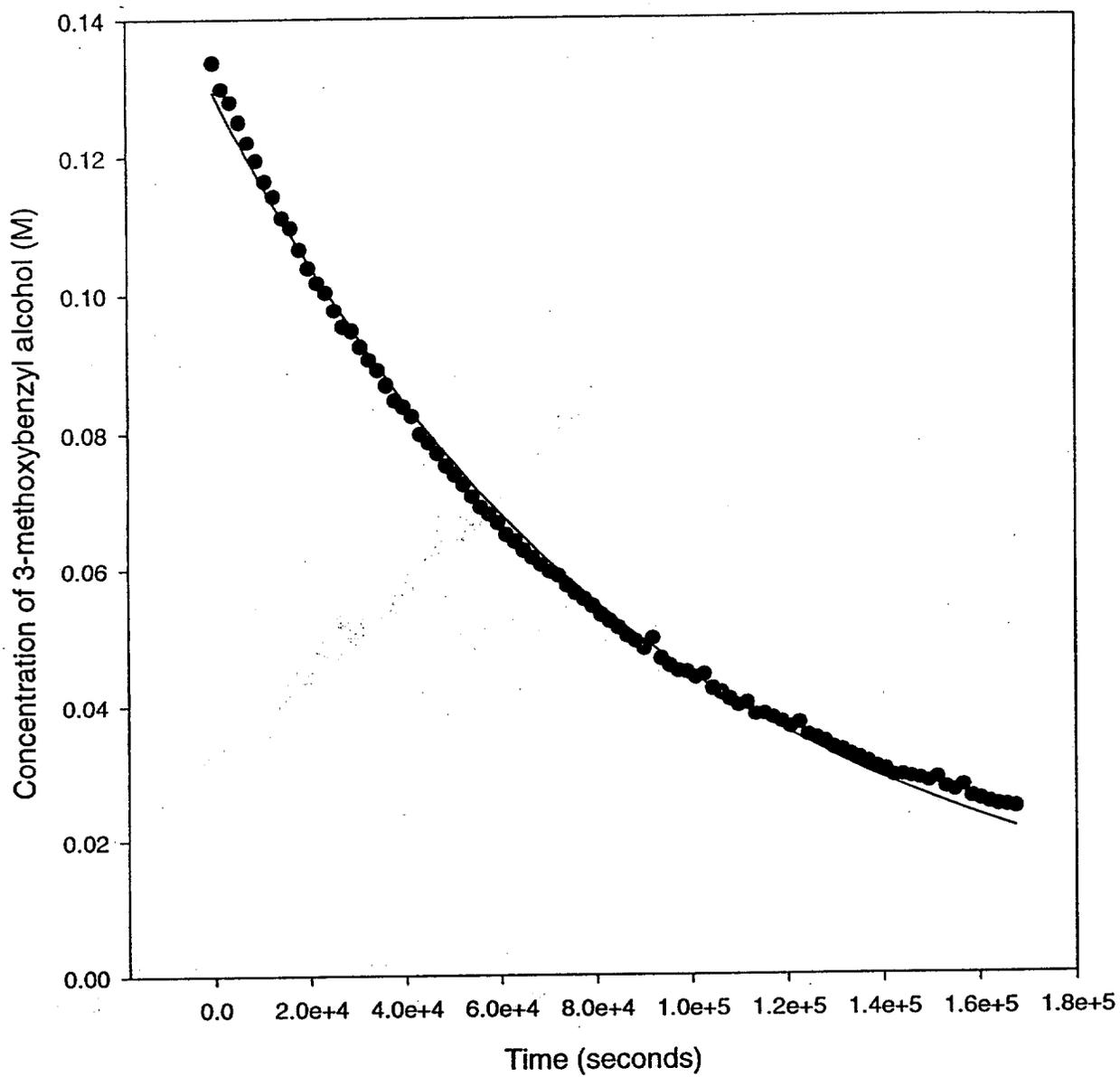


Figure S3: Reaction Rate of 3-Methylbenzyl Alcohol;  
Catalyst concentration is 0.0033M.

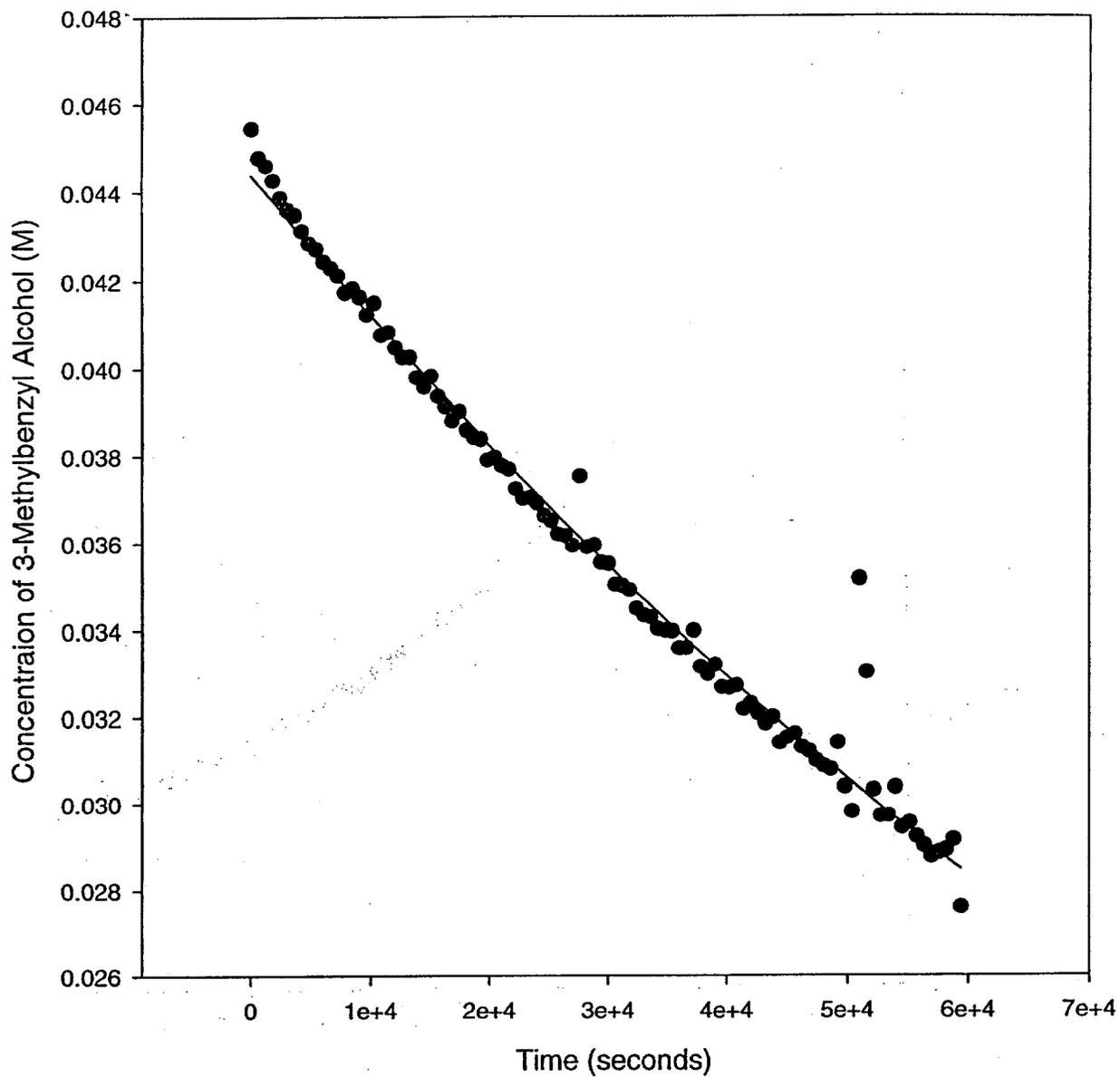


Figure S4: Reaction Rate of 4-Methoxybenzyl Alcohol;  
Catalyst concentration is 0.0033M.

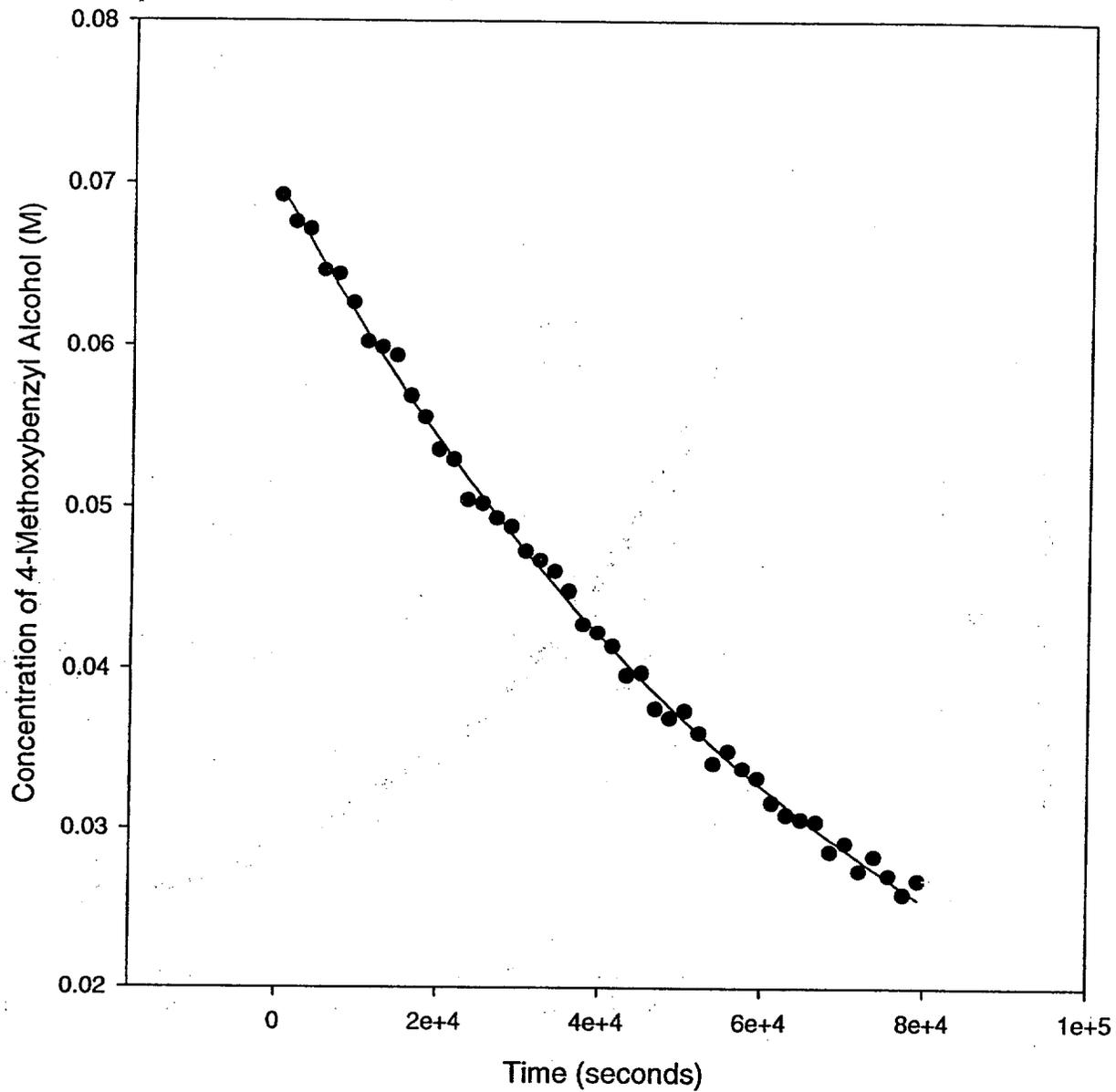


Figure S5: Reaction Rate of 3-Ammonium Benzyl Alcohol;  
Catalyst concentration is 0.0033M.

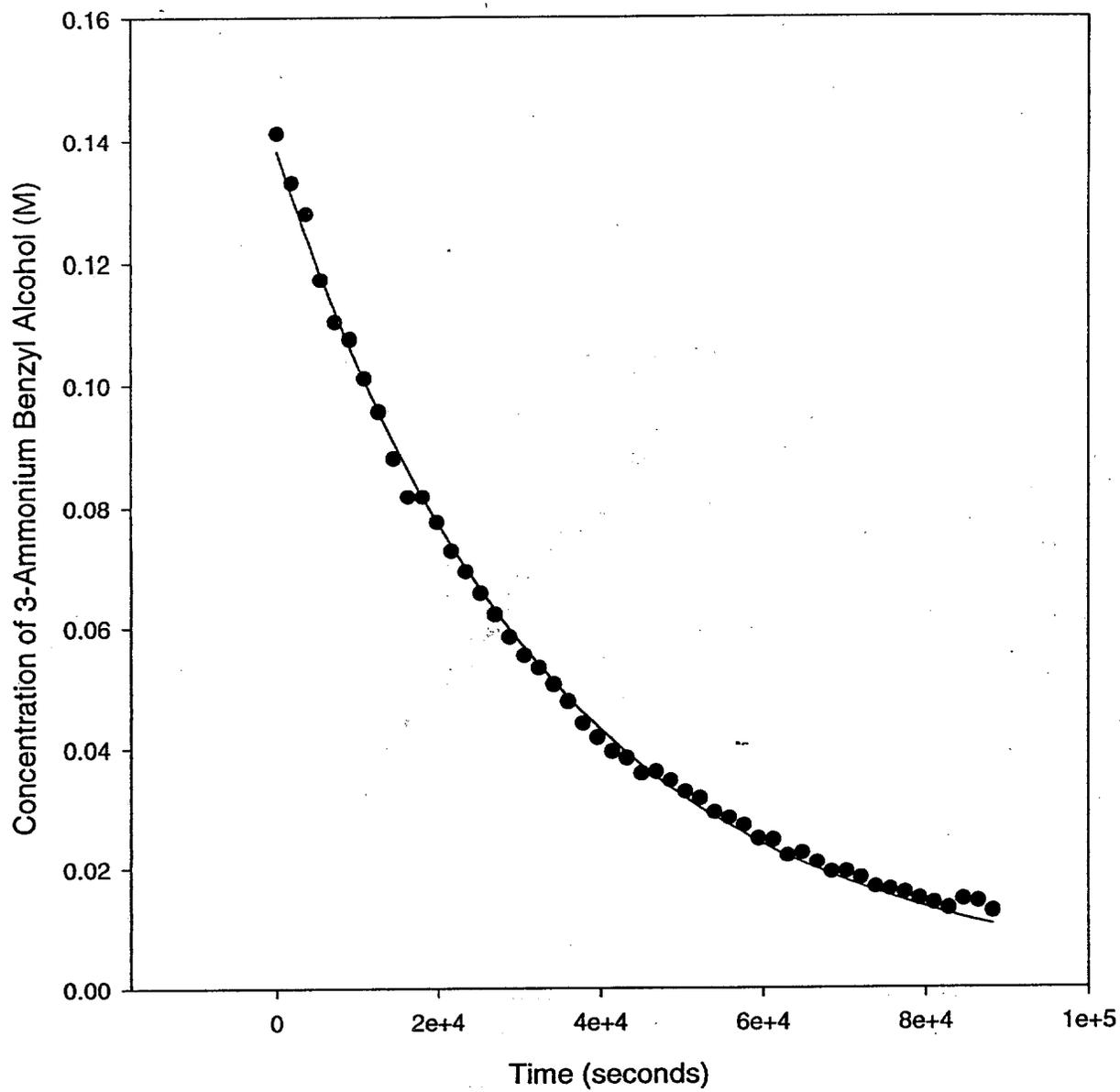
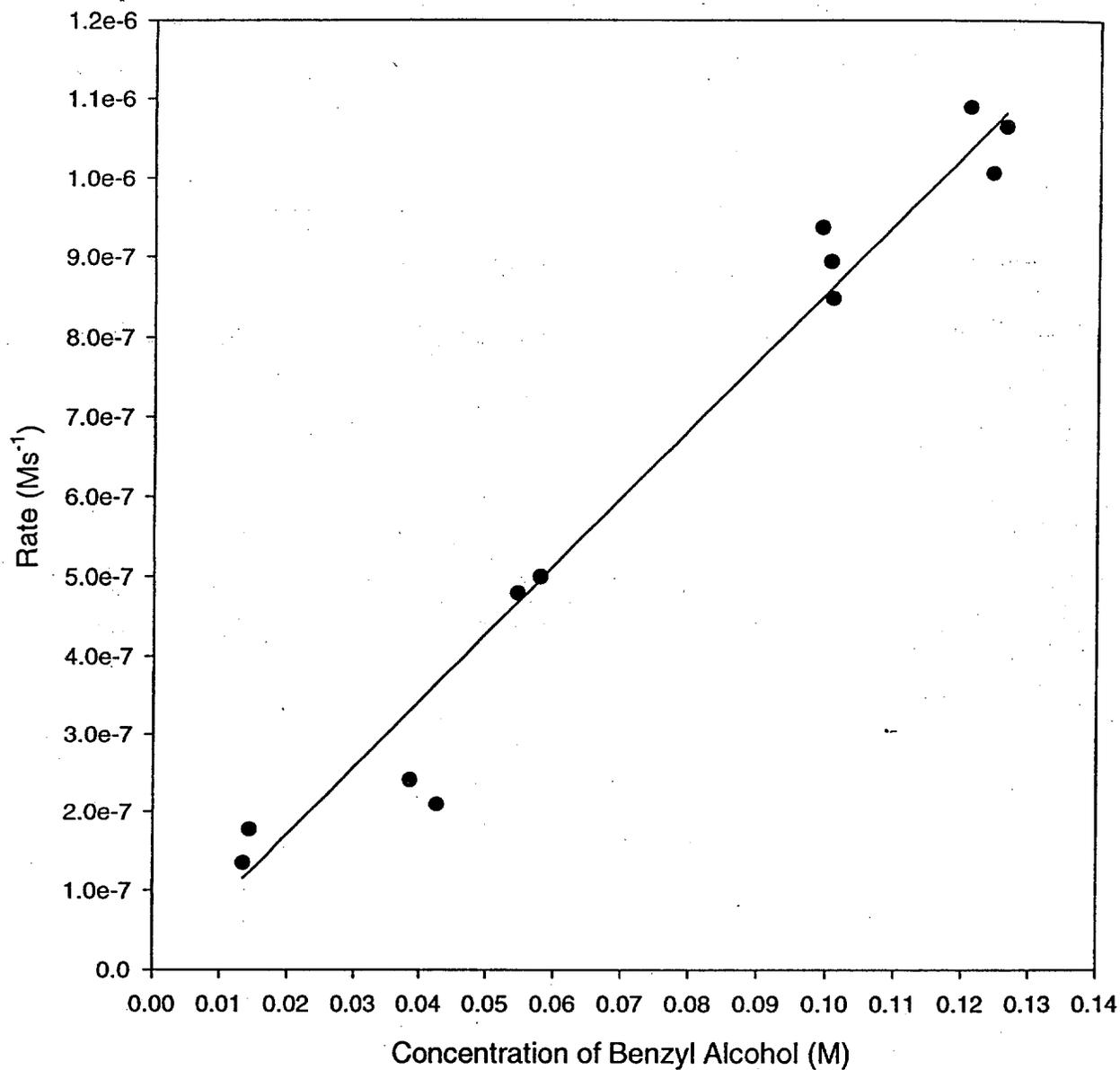


Figure S6: Plot of Rate versus Initial Substrate Concentration for Substrate Inhibition Studies.



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