

Guidance for Thermal Stability of Common Oilfield Chemicals

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ABSTRACT

The application temperature for oilfield chemicals often exceeds 120°C (248°F). This temperature is important because it is the threshold for the thermal breakdown of many oilfield chemicals. The breakdown of oilfield chemicals used to treat problems such as corrosion, scale, oil-water separation, bacterial corrosion, etc. can create additional problems if they are applied at temperatures greater than their breakdown temperatures. The breakdown products can cause gunking and in some cases the breakdown products can be corrosive to mild steel. This paper explores the high temperature thermal stability of several common families of molecules including amines, quaternary amines, phosphate esters, alkylthiols, imidazolines, and polymers at temperatures above and below this key temperature and provides data which describes why this temperature is a hard limit for many oilfield chemicals. Guidance is provided for personnel incorporating chemical treatment in their oilfield systems. This guidance will help identify system components or locations where thermal breakdown should be studied before implementing a chemical program.

Key words: oilfield chemicals, imidazolines, phosphate esters, phosphonates, amines, quaternary amines, thermal stability, thermal breakdown.

INTRODUCTION

As oilfield technologies have advanced, they have made high temperature (HT) reservoirs more accessible. HTs make the application of chemical more difficult because chemical instability at HT restricts what intermediates will work in these environments and the safety and complexity of HT testing further adds to the challenge.

HTs in oilfield applications are often found at bottomhole conditions. Operators often apply chemical at the bottom of the well to protect the tubing or casing from corrosion or scaling, but bottomhole temperatures can exceed 230°C in some cases. Electric submersible pump applications exacerbate this problem because they can add 10 to 20°C locally to the local temperature. HTs can also be found in geothermal applications and solvent regeneration systems like glycol and glycerin regeneration loops, as well as heat exchangers common to HT gas operations. Flowline applications can exceed 120°C in fields with extremely high bottomhole temperatures or in gas systems where compression is employed. Other HT industries are discussed in the literature.¹

There are hundreds of references in the literature that discuss HT applications with chemical inhibition. While authors often publish the development of products or intermediates for HT applications, the underlying mechanisms for chemical instability at HT are rarely discussed.²⁻⁸ Despite the utility and ubiquity of oilfield chemicals, only a few oilfield literature references discuss the mechanisms of chemical thermal breakdown in detail.⁹⁻¹³ These references refer to scale inhibitors (SIs) but the mechanisms should extend to other oilfield chemicals as well. The general thermal breakdown mechanisms agreed upon in these references are 1) radical attack via oxidation, and 2) deactivation of the functional groups by HT reactions such as hydrolysis. Only one reference was found which studied actual breakdown products of SIs which seemed to support hydrolysis and free radical attack.⁹

The neat stability of hydrocarbons is often very high, meaning that the native molecules are stable in the absence of external reactions. Therefore, the proposed mechanisms of free radical attack and hydrolysis are probably valid as general thermal breakdown mechanisms for all chemistries used in the oilfield. Studies show hydrocarbon stability temperatures greater than 238°C with many compounds reaching stability temperatures greater than 475°C.¹⁴⁻¹⁶ The chemistries discussed in these references maintain their neat molecular integrity above 300°C. Thermal degradation via free radical attack or hydrolysis is a kinetic phenomenon and as such it can be slow or fast at any temperature but like many chemical processes thermal degradation is typically accelerated at higher temperatures. These reactions can also be catalyzed by acid or base as well as metals in solution.^{17,11} There are many more references that describe the neat stability of oilfield-like chemicals. Many research studies have investigated quaternary amines and others have looked at amides, pyridiniums, phosphate esters, and polymers.^{18-21,22,23,24,25} All of these studies confirm that acid or base catalyzed hydrolysis is a key degradation mechanism for thermal decomposition.

One of the original references for the free radical attack and hydrolysis mechanisms shows that antioxidants used to prevent UV breakdown of polymers also work to prevent thermal

breakdown.²⁶ Later research on polymer degradation showed that inclusion of additives in a polymer can change the thermal gravimetric analysis (TGA) curves of polymers, and in some case increasing the breakdown temperature.²⁷ This phenomenon is described in a theory by Leffler as the isokinetic relationship.²⁸ Empirical data shows that the activation enthalpy ($\Delta H^\ddagger$) and activation entropy ($\Delta S^\ddagger$) are often highly correlated to temperature. A large enthalpy of activation often accompanies a large entropy of activation. Leffler devised Equation 1 to describe this relationship. Since Equation 2 describes the relationship of the activation free energy ($\Delta G^\ddagger$) to activation enthalpy and activation entropy, it follows that Equation 3 is the isokinetic relationship expressed in terms of activation free energy.

$$\Delta H^\ddagger = \Delta H_0^\ddagger + \beta \Delta S^\ddagger \quad (1)$$

$$\Delta G^\ddagger = \Delta H^\ddagger - T \Delta S^\ddagger \quad (2)$$

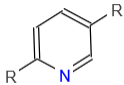
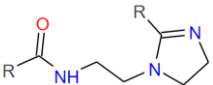
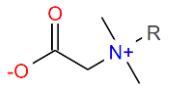
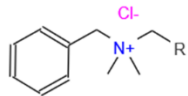
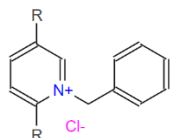
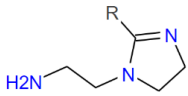
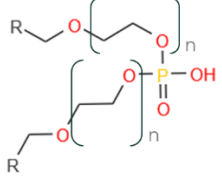
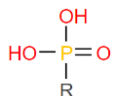
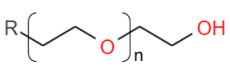
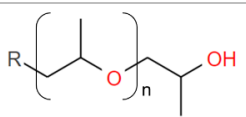
$$\Delta G^\ddagger = \Delta H_0^\ddagger - (T - \beta) \Delta S^\ddagger \quad (3)$$

Equation 3 shows that when $T = \beta$ the $\Delta G^\ddagger = \Delta H_0^\ddagger$ making the rate and equilibrium constants the same. The mysterious 120°C threshold for thermal breakdown could be related to the β temperature for radical attack or hydrolysis. Matsumoto showed that changing the surfactants and catalysts used for hydrolysis of p-nitrophenyl esters could be used to modify the β for this reaction.²⁹ This work is significant because it indicates that some chemistries that fail at high temperatures may benefit from the perfect selection of surfactants. While work on the isokinetic relationship is not discussed directly in the results of this paper, it is still an important point for guiding future work related to high temperature stability.

The general structures of the families discussed in this paper are show in Table 1.

This paper is not intended to be a comprehensive treatment of the subject of thermal stability. Instead, this work is an attempt to bridge the knowledge gap and provide general guidance on temperature stability of some of the families used in oilfield chemistry. The hope is that technology related to thermal stability is advanced with reference to oilfield chemical applications.

Table 1: General structures of some of the chemical families discussed in this publication.

Chemical Family	Structure	Notes
Amines	$R-NH_2$	R = alkyl C1 to C25+
Alkylpyridines		R = various including methyl, ethyl, butyl, could include alkene, imine
Alkylthiols	$R-SH$	R = C8 to C25+
Amido imidazolines		R = alkyl, typically natural fatty acids sources (C8 to C25+)
Betaine		R = alkyl groups C8 to C25, can include heteroatoms
Quaternary amines		- Alkyldimethyl benzylammonium chloride quat - ADBAC quat - R = alkyl C8 to C25+
		- Alkylpyridine quat - R = various including methyl, ethyl, butyl, could include alkene, imine
Imidazolines		R = alkyl, typically natural fatty acids sources (C8 to C25+)
Phosphate esters		- Ethoxylated - n = 2 to 25+
Phosphonates		R = alkyl groups C8 to C25 often containing heteroatoms
Polymers		- Ethoxylated - R = resins, phenols, alkyl groups (C8 to C25) - n = 2 to 25+
		- Ethoxylated - R = resins, phenols, alkyl groups (C8 to C25) - n = 2 to 25+