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Short Communication

A new low temperature process for coal desulfurization

M. RAVINDRAM
Department of Chemical Engineering, Indian Institute of Science, Bangalore 560 012, India.

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Abstract

A number of processes have been proposed to remove sulfur from coal. N-Chloro-P-toluene sulfonamide sodium salt (Chloramine-T) and related compounds are reported to have unique activity towards a wide range of organic sulfur compounds. The ability of these compounds to act as a source of i) halonium cations, ii) hypohalite species and iii) N-anions forms the basis of a new low temperature process for coal desulfurization.

Preliminary experimental results indicate that substantial organic sulfur reductions could be achieved by reacting high sulfur coals at low temperatures with aqueous chloramine-T solutions.

Key words: Coal, desulfurization.

1. Introduction

The ever increasing demand for energy, shortage of petroleum resources, inherent problems associated with nuclear power and lack of appropriate finished technology for biomass utilization have all created a situation wherein coal is expected to provide a sustainable source of energy at least for the immediate future. However, utilization of coal in an environmentally acceptable manner necessitates beneficiating coal primarily to reduce the sulfur and ash levels while at the same time preserving its heating value. During the last decade several coal desulfurization processes have been proposed.

It is reported in literature that n-halogeno-n-metallo reagents commonly known as chloramines, possess unique reactivity towards a wide range of sulfur compounds, particularly organic sulfur compounds. In view of the similarity of some of the organic sulfur compounds to those present in coal, chloramines could be expected to provide a method for coal desulfurization. However, these have not so far been employed for coal desulfurization.

2. Experimental results

The present investigation was undertaken to demonstrate the activity of chloramine-T for coal desulfurization. In order to verify whether it selectively removes organic sulfur, a variety of coal containing essentially organic sulfur was selected for the study. As is evident from the coal characteristics listed in Table I, this particular coal contains 89.5% organic sulfur, 6.2% pyritic sulfur and 4.3% sulfate sulfur in a total sulfur content of 2.5% (on dry weight basis). Details of sulfur estimation and other experimental procedures are described elsewhere[1].

Experiments were conducted in a laboratory batch slurry reactor. The reactor was kept in a water bath provided with thermostatic control. The reactor was charged with 2g (-100+200 Tyler Mesh) of coal and the required amount of chloramine-T solution. The reaction mixture was kept under stirring for a know amount of time at the desired temperature. After the reaction, the contents were filtered and the coal sample was washed with methanol and water. The sample was dried before analyzing for total sulfur.

From the test results presented in Table II, it is evident that 25-38% sulfur reductions were achieved under the conditions employed. Since both the pyritic and sulfate sulfur contents

Table I
Coal characteristics

	Per cent sulfur content (Dry weight basis)		
Total	Pyritic	Sulfate	Organic (By difference)
2.5039	0.1606	0.1082	2.2351
2.5068	0.1492	0.1074	2.2502
2.4961	0.1516	0.1090	2.2355
Av. 2.5023	0.1538	0.1082	2.2403
Per cent of total	6.2	4.3	89.5

	Proximate analysis		
Moisture	9.88%	Volatiles	36.35%
Fixed carbon	42.74%	Ash	11.03%

* High sulfur Assam coal obtained from Regional Research Laboratory, Hyderabad, India.

Table II
Coal desulfurization — Test results

Coal : 2g
Coal/Chloramine-T : 1/3.5
Hydrochloric acid concentration : 0.6 N
Liquid/Solids : 175/1
Coal size : —100+200 Tyler Mesh
Stirrer speed : 2640 RPM

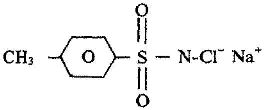
Reaction time (hr)	Reaction temperature (° C)	% Sulfur removed
1.5	33.0	25.9
3.0	33.0	31.1
1.5	47.5	30.3
3.0	47.5	38.1
1.5	62.5	26.3
3.0	62.5	30.8

put together add up to only 10%, it is apparent that considerable organic sulfur removal takes place. As can be expected, the extent of desulfurization was found to increase with increasing time of reaction and reaction temperature. However, at the highest temperature investigated sulfur removal was found to decrease. The reacted coals did not show any significant changes in pore, structure or heating value compared to the original coal.

In view of the demonstrated activity of chloramine-T for coal desulfurization, it may be interesting to examine the chemistry and reactivity of chloramine-T.

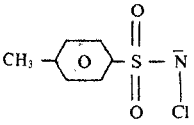
3. Reactions of chloramines with organic sulfur compounds

Chloramine-T, N-chloro-P-toluene sulfonamide sodium salt (I), is the first to be synthesized and studied in detail. More recently, a series of alkylsulonamide derivatives are developed.



I

These compounds are found to react with a surprising range of organic sulfur functional groups and thereby bring about an array of molecular transformations by virtue of their ability to act as a source of i) halonium cations; ii) hypohalite species and iii) N-anions which act both as bases and nucleophiles. The structure of chloramine-T is most commonly depicted as in (II)[2] and occasionally as in (III)[3]. Chloramine-T and other related compounds are strong electrolytes and oxidants in both acidic and basic media[4]. In aqueous solutions, chloramine-T is thought to exist in a complex series of equilibria[5].



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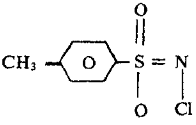
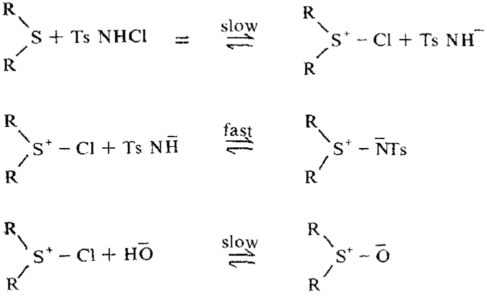


III

Chloramine-T reacts with a wide range of alkyl and aryl sulfides yielding the corresponding sulfimides[6,7]. These reactions are often carried in water or alcohol or a mixture of the two. It is generally observed that an equilibrium is established as given below:

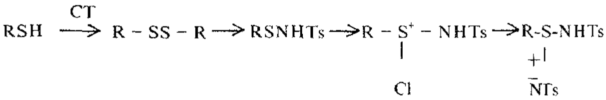
$$\text{Ts}\,\bar{\text{N}}\text{Cl} + \text{H}_2\text{O} \rightleftharpoons \text{Ts NHCl} + \text{H}\bar{\text{O}}$$



$$
\begin{aligned}
&{}^{R}_{R}\!\rangle S + \text{Ts NHCl} \;=\; \overset{\text{slow}}{\rightleftharpoons} \;{}^{R}_{R}\!\rangle S^+ - \text{Cl} + \text{Ts NH}^- \\
&{}^{R}_{R}\!\rangle S^+ - \text{Cl} + \text{Ts N}\bar{\text{H}} \;\overset{\text{fast}}{\rightleftharpoons}\; {}^{R}_{R}\!\rangle S^+ - \bar{\text{N}}\text{Ts} \\
&{}^{R}_{R}\!\rangle S^+ - \text{Cl} + \text{H}\bar{\text{O}} \;\overset{\text{slow}}{\rightleftharpoons}\; {}^{R}_{R}\!\rangle S^+ - \bar{\text{O}}
\end{aligned}
$$

The overal reaction was reported to be second order. Under acidic conditions, sulfoxides are oxidized by chloramine-T to the respective sulfones.

Chloramine-T (2 moles) reacts in alkaline solutions with thiols and disulfides forming the sulfimides as follows[8].



$$\text{RSH} \xrightarrow{\text{CT}} \text{R}-\text{SS}-\text{R} \longrightarrow \text{RSNHTs} \longrightarrow \text{R}-\underset{\substack{| \\ \text{Cl}}}{\text{S}^+}-\text{NHTs} \longrightarrow \text{R-}\underset{\substack{+| \\ \bar{\text{N}}\text{Ts}}}{\text{S}}\text{-NHTs}$$

Chloramine-T in strong acid media extracts sulfides, disulfides and other sulfur compounds[9]. Six moles of chloramine-T are required to convert aryl thiols to the corresponding sulfonic acids. Alkane thiols require higher concentrations of chloramine-T while 10 molar equivalents are needed for the oxidation of disulfides and other organic sulfur compounds. Reaction of chloramine-T with thiobenzophenone has indicated that it acts as a source of chloronium ions thereby affecting oxidative coupling of thiols[10]. Oxidative potentials of chloramine-T for organic and inorganic compounds have been reported. Chloramine-T oxidizes inorganic sulfur compounds in acid media to sulfuric acid[11-13]. Consequently, it is used as a powerful oxidizing agent for the quantitative estimation of hydrogen sulfide, thiosulfate, carbon disulfide, thiocyanate, bisulfite and other sulfur compounds.

From the foregoing discussion it is evident that chloramine-T could be a potential reagent for coal desulfurization as in fact been demonstrated by the test results. A recent publication[14] presents results on the effect of operating variables.

4. Conclusions

A majority of the existing coal desulfurization processes do not remove enough organic sulfur. It has been reported that chloramines react with a wide variety of organic sulfur functional groups and that these are also used for the quantitative estimation of several inorganic sulfur compounds. Laboratory exploratory studies were thus undertaken to verify the activity of chloramine-T for coal desulfurization.

Preliminary results demonstrate the desulfurization activity of chloramine-T in aqueous solutions at low temperatures. The method appears to hold promise for selective removal of organic sulfur. However, extensive parametric studies are needed to understand the mechanism of the reactions involved, establish optimum conditions of operation and evaluate the economics of the process.

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