

CHARCOALS AS CATALYST SUPPORTS IN THE TRAPPING OF METHYLRADIOIODIDE(131)

Victor R. Deitz
Naval Research Laboratory
Washington, D. C. 20375

INTRODUCTION

Commercial solid adsorbents are used in the nuclear industry as final back-up beds to conventional chemical processes for waste disposal and as a solid sink for the permanent retention of nuclides. Several important features are novel to the nuclear applications. First, the waste products are present in extremely low magnitudes; the concentration unit of ppb is considered to be high. It is well known that many adsorption isotherms measured for different charcoals in the conventional concentration ranges actually cross over when the data are extended to lower values. Such behavior has complicated the selection of the adsorbent when it is based only on conventional testing procedures.

A second factor is the design of an installation for operating periods of one to three years without adsorbent replacement. Thus, a qualification acceptance test of a new material must be supplemented by some knowledge of satisfactory performance after a year or more service. The adsorption process must operate in polluted environments that may be local to nuclear power sites; the process is thus vulnerable to the vagaries of air pollution.

This paper is restricted to the use of a base charcoal as a catalyst support in the trapping of methylradioiodide. While the base charcoal alone may be adequate for removing elementary iodine, the trapping of organic iodides in air flows of high humidity require impregnated materials. Several new impregnations have been examined and some of the results are presented. The evaluation was made with methylradioiodide(131) as the test gas in specified air flows having a contact time of 0.25 seconds and a test bed of 2-inch diameter and 2-inch height. The prehumidification was 16 hours at 96 RH (1).

Charcoal Impregnations

A charcoal and the impregnation must combine to realize the following objectives: (a) the efficiency in trapping organic iodides must be above 99% in air flows at high relative humidity, (b) the product must have good thermal stability in order to minimize the desorption of any iodine product, (c) the impregnated charcoals must possess particle integrity in specified particle ranges against excessive dust formation, (d) the charcoal must be compatible with a high pH of the impregnating solutions, and (e) the product must retain efficiency in the presence of local air pollutants.

Iodine in its various chemical compounds can have oxidation states I, I₀, I⁺¹, I⁺⁵, and I⁺⁷. When alkaline solutions of these salts (for example KI and KIO₃) are mixed, the solution then contains intermediate oxidation states due to several well known disproportionation reactions (2). A number of such solution mixtures have been impregnated on charcoals (3) and the total iodine content varied from 1 to 3 wt.% of the dry charcoal. A second component, a high flash point amine, such as hexamethylene-tetraamine (HMTA), was added after the oxyiodine salts. Solution concentrations were adjusted so that the charcoal retained a dry appearance after the 2-stage impregnation.

Results

A few of the many values obtained in independent runs for the penetration of methyl iodide are given in Table 1. When paired with suitable base charcoals, excellent trapping can be obtained. The coal base charcoals appear to be better than coconut and wood charcoals for the designated impregnations.

Table 1: Penetration of Methyl Iodide Using Impregnations of Oxyiodine Salts

	Source	Impregnation	Penetration(%)
207A	Coal	KI, KIO ₃ , HMTA	0.21,0.21,0.38 0.35,0.22,0.25
MBV	Coal	I ₂ ,KI,KOH, HMTA	0.51,0.30,0.43 0.30,0.29,0.29
CHR-76108	Coal	KI,KIO ₃ , HMTA	0.56,0.74,0.32 0.51,0.37,0.71
337	Pet.Coke	KI _x	0.73,0.44,1.10 2.08,1.09,0.72
G-210	Coconut	KI,KIO ₃ , HMTA	3.92,3.27,4.21 1.56,2.06,3.0
GX-202	Wood base	KI,KIO ₃ , HMTA	1.62,1.18,1.04 1.38,2.34,1.5
G-212	Coconut	I ₂ ,KOH, HMTA	4.9,4.0,5.0 4.6,2.4,4.7

Thermal Stability

Thermal analyses of several impregnated charcoals have been made in a temperature gradient of 5°/min and the CO, CO₂, I₂ and organic iodides have been monitored. The results indicate rather complex chemical reactions that release both elementary iodine and volatile organic iodides at temperatures well below the ignition of the charcoals. The spontaneous ignition of the impregnated charcoals appears to be of secondary importance in the nuclear applications.

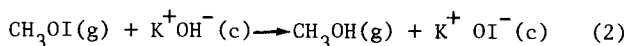
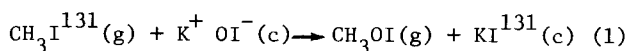
The iodine emission varies with both charcoal and the impregnation formulation. This behavior may best be seen when base charcoals are impregnated with only elementary iodine (0.5%). The rate of emission of iodine was first followed using a heating rate of 5°/min. by sampling the air flow (5 L/min) directly into the micro-coulombmeter and then in a repeat determination the rate was determined by sampling the air flow after it had passed through a quartz tube held at 700°C. Some typical results (Table 2) for three charcoals show the variation with both charcoal and temperature. Note that the iodine emission is a small fraction of the total iodine added to the charcoal, but, nevertheless, this is in the concentration range pertinent to a nuclear application.

Table 2: Rate of Iodine Emission
(nanomoles/minute)

Charcoal	I ₂ Added	Temp.	I ₂	Organic Iodide
177	25.6 mg	180°C	0.2	2.1
BPL 10X16	29.5	"	0.9	0.5
GX 32	17.2	"	5.7	2.5
177	25.6	200°C	0.4	4.6
BPL 10X16	29.5	"	3.7	1.5
GX 32	17.2	"	13.8	2.0

Trapping Mechanism

A reaction mechanism for CH₃I retention was devised as a guide to further research. The many combinations of the salts of iodine oxyacids used as impregnating solutions in the present study have one thing in common: in basic solutions it is possible to form the hyperiodite species. The formation is thermodynamically possible from calculated heats of formation. Postulating a small but finite concentration of OI⁻ in the boundary surface of a charcoal, the following trapping mechanism may occur:



The free energy change for the sum of these two reactions is -17.45 Kcal. A CH₃I molecule in approaching the OI⁻ species on the surface (Figure 1) is oriented with CH₃ towards the ion and I directed away. By means of a Waldon Inversion a transition state I is formed which readily is transformed into products II as indicated. A neighboring mobile OH⁻ surface group then rapidly forms the transition state II which results in the formation of III, CH₃OH and the original reactive OI⁻ species. A chain reaction is thus established with the following features:

1. The chain involves the regeneration of the active species OI⁻ and furnishes a stable sink for radioiodine, namely KI¹³¹.
2. The free energy change is favorable.
3. The charcoal support serves as a sink for the CH₃OH produced.
4. The mechanism accounts for high efficiency when the pH is high and a low efficiency observed when the pH is reduced.
5. The observed axial location of I(131) in the charcoal bed follows catalytic kinetics.(4)
6. Economical quantities of impregnants are employed.

One test for the reaction mechanism is the detection of methyl alcohol as a reaction product. Obviously, excess methyl alcohol will serve as a "poison" in the proposed mechanism.

The complete reaction mechanism is doubtlessly very complex. In some cases the adsorption process appears to dominate the trapping kinetics. However, in most cases, efficient trapping appears to occur via a catalytic process.

References

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Acknowledgement

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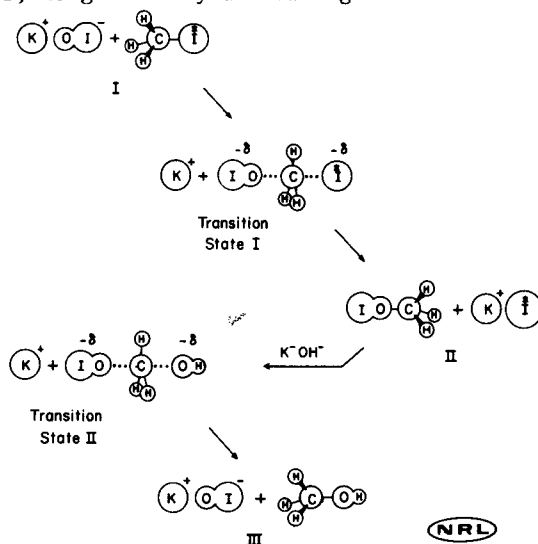


Fig. 1: A Mechanism for the Trapping of Methyl Iodide