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Organic Perchlorate Esters

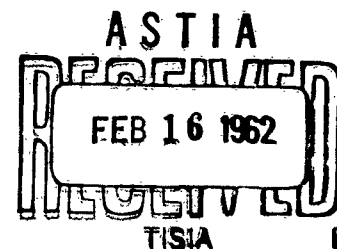
Jack Radell

Directorate of Materials and Processes

J. W. Connolly, Captain, USAF

Aeronautical Research Laboratory

MAY 1961



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Aeronautical Systems Division

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Organic Perchlorate Esters

Jack Radell

Directorate of Materials and Processes

J. W. Connolly, Captain, USAF

Aeronautical Research Laboratory

May 1961

Project No. 7360

Task No. 73607

Aeronautical Systems Division
Air Force Systems Command
United States Air Force
Wright-Patterson Air Force Base, Ohio

Foreword

This report was initiated in the Directorate of Materials and Processes, Deputy for Advanced Systems Technology, Aeronautical Systems Division, under Project No. 7360, "Chemistry and Physics of Materials," Task No. 73607, "High Energy Materials Phenomenon," with Dr. Jack Radell acting as project engineer. Part of this work was done by A. J. Raymond, Wyandotte Chemical Corporation, under USAF Contract No. AF 33(616)-5937, Project No. 3059, Task No. 30207, administered by Mr. C. C. Selph of Edwards Air Force Base, California.

Work reported was conducted from June 1960 to February 1961.

The authors gratefully acknowledge the assistance of Dr. L. A. Harrah, Physics Laboratory, Directorate of Materials and Processes, in interpreting the infrared spectra.

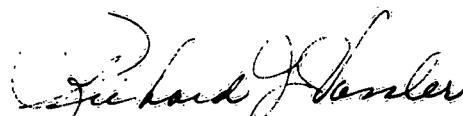
Abstract

The previously unreported *n*-amyl, *n*-hexyl, *n*-heptyl and *n*-octyl perchlorates were prepared from the corresponding alkyl iodide and silver perchlorate. The pure perchlorate esters were stabilized as the endocycle of a urea inclusion compound. The infrared spectra and some physical properties are reported for the *n*-alkyl perchlorates.

Publication Review

This report has been reviewed and is approved.

FOR THE COMMANDER:



RICHARD J. VOSSLER, Capt. USAF
Chief, Radiation Branch
Physics Laboratory
Directorate of Materials and Processes

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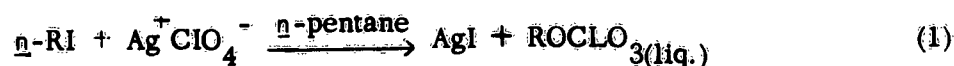
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Introduction

Covalent alkyl perchlorate esters have been reported¹ in the literature. The referenced and reported alkyl perchlorates are extremely unstable and treacherous to prepare. Because of the explosion hazard associated with these compounds, we undertook to stabilize these covalent perchlorates by trapping them as the endocycle (guest) in a urea inclusion compound. This approach was used because the highly oxidized urea molecule would be expected to act as a protective cover for the strongly oxidizing *n*-alkyl perchlorates.

Discussion

The *n*-alkyl perchlorates were prepared by the following reaction:



Commercially available "anhydrous" silver perchlorate required dehydration. This dehydration is necessary because covalent perchlorates are thermodynamically unstable to hydrolysis². All of the alkyl perchlorates prepared were explosive. The smallest alkyl perchlorate was most sensitive to shock. Although the highest alkyl perchlorate was least sensitive to shock after isolation, the higher temperatures required for distillation introduced a compensatory hazard.

The isolated perchlorates were treated with a urea-methanol solution. Crystalline urea inclusion compounds formed for the normal: amyl, hexyl, heptyl and octyl perchlorates.

The ease of formation of the urea inclusion compound was proportional to the chain length of the alkyl perchlorate. The resulting crystalline complexes had no apparent shock sensitivity in small quantities (ca. 0.5 g). The formation of the urea inclusion compound was unequivocally verified by the x-ray powder diffraction data in table 1. The amyl perchlorate inclusion compound is the least stable and most highly dissociated. The following spacings characteristic of urea inclusion compounds are consistently present for all of the perchlorates except the *n*-amyl: 7.05-7.10, 4.09-4.11, 3.83-3.85, 3.54-3.56, 3.37-3.39 and 2.60-2.61 Å. These spacings have been consistently found for urea inclusion compounds with various guest molecules.³ The spacing at 3.91-3.98 is an intense and reliable spacing for dissociated tetragonal urea. This data may be used to determine the relative stability of the inclusion compounds^{3,4}.

The lesser stability of the shorter endocycles was shown by the presence of appreciable amounts of dissociated urea in the x-ray powder diffraction patterns of the complexes of *n*-amyl and *n*-hexyl perchlorates. The longer endocycles, *n*-heptyl and *n*-octyl perchlorates were free of dissociated tetragonal urea. The relative intensity of the spacings for dissociated urea and inclusion compound is the basis of a method^{3,4} for estimating the relative stability of the inclusion compounds of a homologous series of complexing compounds. In table 1, we find that the intensity of certain complex spacings increases with increasing number of -CH₂- groups at: 4.07-4.11, 3.54-3.56 and 2.60-2.63. The *n*-amyl

perchlorate inclusion compound was the least stable and did not show the last spacing. On the other hand, the intensity of the line for dissociated urea at 3.97-4.01 increased with decreasing chain length. These results are consistent with those of other studies^{3,4,5}.

The cross-sectional diameter of a normal hydrocarbon (4.6 Å) seems to be close to the optimum for urea channel complex formation^{4,5b}. The measured maximum cross-sectional diameter of the *n*-alkyl perchlorate was approximately 5.3 Å under the following conditions: 1) The molecule was arranged in a planar zigzag conformation having the smallest maximum cross section. 2) The chlorine atom was tetrahedrally substituted. 3) The atomic radii used for the structure RCH_2OC10_3 were 1.3 Å for all the oxygen atoms, 1.5 Å for chlorine, 1.0 Å for hydrogen and 1.3 Å for carbon. The shortest hydrocarbon which formed a complex by this⁶ procedure was *n*-octane. However, the shortest *n*-alkyl perchlorate to form a complex was *n*-amyl with only 5 methylene groups.

The infrared spectra of the capillary liquid film samples of all the *n*-alkyl perchlorates except amyl are shown in figure 1. The *n*-amyl perchlorate spectrum was not run because of its extreme instability. A comparison of absorption bands associated with the perchlorate function are listed in table 2 for perchloric acid, perchloryl fluoride, perchloryl

benzene and our *n*-alkyl perchlorates, $R-O_3C-\overset{\overset{O}{\parallel}}{\underset{\underset{O}{\parallel}}{C}}$. The C1-O asymmetric stretching gave a doublet for the *n*-alkyl perchlorates and perchloric acid. A single band was obtained for perchloryl fluoride and perchloryl benzene although the latter probably has an unresolved doublet. In the case of the C-O₁ stretching and to a lesser extent the C1-O₁ stretching there is an increase in the absorption frequency with decreasing mass of the alkyl group. The C1-O₁ band is also present in perchloric acid while the C-O₁ stretching is present in the alkyl perchlorates only.

The infrared spectra of the alkyl perchlorates were compared before and after complex formation to show that the endocyte was unaltered. These spectra were made of the pure liquid perchlorates and the nujol mull of the crystalline urea complexes of the perchlorates. The spectra of the complexes were in each case compared with the spectra of the nujol mull of urea. The following absorption peaks were absent from the urea spectrum but appeared in the spectra of the perchlorate inclusion compounds: 1235, 1270, 1118 and 917 cm^{-1} . All other peaks were present in both the urea and inclusion compounds' spectra. The following pairs of absorption bands appear in the spectra of the *n*-alkyl perchlorate complexes and the pure *n*-alkyl perchlorate respectively: 917 and 925, 1118 and 1120, 1235 and 1220, 1270 and 1270 cm^{-1} .

In the preparation of a nujol mull of an *n*-alkyl perchlorate urea inclusion compound, it is possible that the nujol may replace the perchlorate as the endocyte in the inclusion compound. This does not complicate the situation because we only want to show that the endocyte of the inclusion compound was a perchlorate.

Sufficient data is available (see table 3) for determining the molecular refraction for *n*-hexyl and *n*-octyl perchlorates only. Using the Lorentz and Lorenz equation the values obtained for the molecular refraction of the *n*-hexyl and *n*-octyl perchlorates were 55.48 and 66.88 respectively. If we subtract the refractivity value for $n-C_6H_{13}$ (28.86)¹⁰ and

$n\text{-C}_8\text{H}_{17}$ (38.14)¹⁰ from 55.48 and 66.88 respectively, we obtain values of 27.62 and 28.74 for the refractivity of the perchlorate group in the two separate compounds. No value for the refractivity of the perchlorate group in a covalent perchlorate ester has been found in the literature.

Experimental

Dehydration of Silver Perchlorate - Commercial "anhydrous" silver perchlorate (25g) was added to 150 ml of benzene in a flask fitted with a Dean and Stark distilling receiver. The solution was refluxed until all water was azeotropically removed (four hours). The solution was cooled and treated with 100 ml of dry pentane. The precipitated silver perchlorate was filtered in a dry nitrogen atmosphere. The silver perchlorate was dried in a desiccator over phosphorous pentoxide at 1 mm for 24 hours leaving 21 g of anhydrous silver perchlorate.

Preparation of Alkyl Perchlorate - To a mixture of 50 ml of pentane and 0.1 mole of anhydrous silver perchlorate in a round bottom flask (fitted with a magnetic stirrer, reflux condenser, addition funnel and drying tube) was added dropwise with stirring at room temperature, 0.05 mole of n -alkyl iodide dissolved in 15 ml of n -pentane. An immediate yellow precipitate of silver iodide formed. The reaction mixture was stirred for four hours after the addition was completed. The solid silver iodide was separated from the n -alkyl perchlorate-pentane solution by filtering through an anhydrous sodium carbonate bed in a dry box under a nitrogen atmosphere. The silver iodide precipitate was washed with 50 ml of n -pentane. The n -pentane was evaporated at room temperature by passing dry nitrogen through the solution protected by a drying tube for two hours. This was either done immediately or the n -pentane solution was stored overnight over anhydrous sodium carbonate before filtering and concentrating. In this way about 90 percent of the n -pentane was removed. The remaining material in the flask was distilled under vacuum with a nitrogen capillary bleed after a small forecut of n -pentane was removed by using an eight inch Vigreux column. The yield in each case was between 90-95 percent based on the silver iodide precipitated. Recoveries were always appreciably less, ranging between 60-75 percent.

Although the thermal and drop weight stability for the perchlorates were not very reproducible, the results indicate the relative instability of these compounds. The compounds were detonated by a five kilogram weight dropped from a height of between 2 and 5 inches. The shorter perchlorates were most sensitive. The charring temperature of the perchlorates varied between 150 and 350°C. These values varied considerably but were generally proportional to the chain length of the n -alkyl group. The properties and analysis of the perchlorates are listed in table 3.

Perchlorate Analysis - The distilled n -alkyl perchlorates were analyzed by dissolving ca. 2g of n -alkyl perchlorate in 25 ml of concentrated aqueous ammonium hydroxide and 75 ml of 95 percent ethanol. The liquid was evaporated to near dryness and the residue was analyzed by the nitron method.¹¹

Urea Inclusion Compounds - The urea inclusion compounds of the n -alkyl perchlorate were prepared by a previously described procedure.⁴

Infrared Analysis - The liquid film infrared analysis of the liquid n -alkyl perchlorates was performed between sodium chloride windows on a Perkin Elmer Infracord. The crystalline urea inclusion compounds were examined as nujol mulls on a Perkin Elmer 21 instrument. The spectrum for n -amyl perchlorate was not measured because of its instability.

X-Ray Powder Diffraction Analysis - This was done by a previously described⁴ procedure.

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Table 1

X-Ray Powder Patterns of Urea Inclusion Compounds of <i>n</i> -Alkyl Perchlorates										
<i>n</i> -R	7.05-7.10 ^a	4.09-4.11	3.91-3.98	3.83-3.85	3.54-3.56	3.37-3.39	2.68-2.69	2.60-2.61		
C ₈ H ₁₇	0.06 ^b	1.00	0.05	0.12	0.84	0.34	0.05	0.12		
C ₇ H ₁₅	0.08	1.00	0.05	0.07	1.00	0.20	0.05	0.08		
C ₆ H ₁₃	0.08	0.96	0.09	0.05	1.00	0.23	0.08	0.19		
C ₅ H ₁₁		1.00	0.35		0.89		0.05	0.05		

^a Interplanar spacings in angstroms using CuK α radiation.^b Relative intensities; 1.00 being the strongest.

Table 2

Related Absorption Bands				
Description	Frequency (cm ⁻¹)			
	Ours	HOC10 ₃ ⁷	ClO ₃ F ⁸	C ₆ H ₅ ClO ₃ ⁹
Cl-O asymmetric stretching	1230,1260	1182,1312	1191	1315
Cl-O symmetric stretching	1035	1032	1075	1061
Cl-O, stretching	C ₆ H ₁₃ OC10 ₃ 709 C ₇ H ₁₅ OC10 ₃ 705 C ₈ H ₁₇ OC10 ₃ 704	738		
C-O, stretching	C ₆ H ₁₃ OC10 ₃ 1125 C ₇ H ₁₅ OC10 ₃ 1105 C ₈ H ₁₇ OC10 ₃ 1080			

Table 3

Properties and Analysis of η -Alkyl Perchlorates						
η -R	$^{\circ}\text{C.}$	B.p. Mm.	n_{D}^{25}	Chlorine, % Calcd.	Found	
C_5H_{11}	51.5	11	1.4042	20.79	19.93	
$\text{C}_6\text{H}_{13}^{\text{a}}$	52.0	4.5	1.4146	19.21	18.47	
C_7H_{15}	49-51	2.5	1.4170	17.85	17.47	
$\text{C}_8\text{H}_{17}^{\text{b}}$	55-60	1.5	1.4192	16.67	16.46	
a) d_4^{25} 1.11; b) d_4^{25} 1.070						

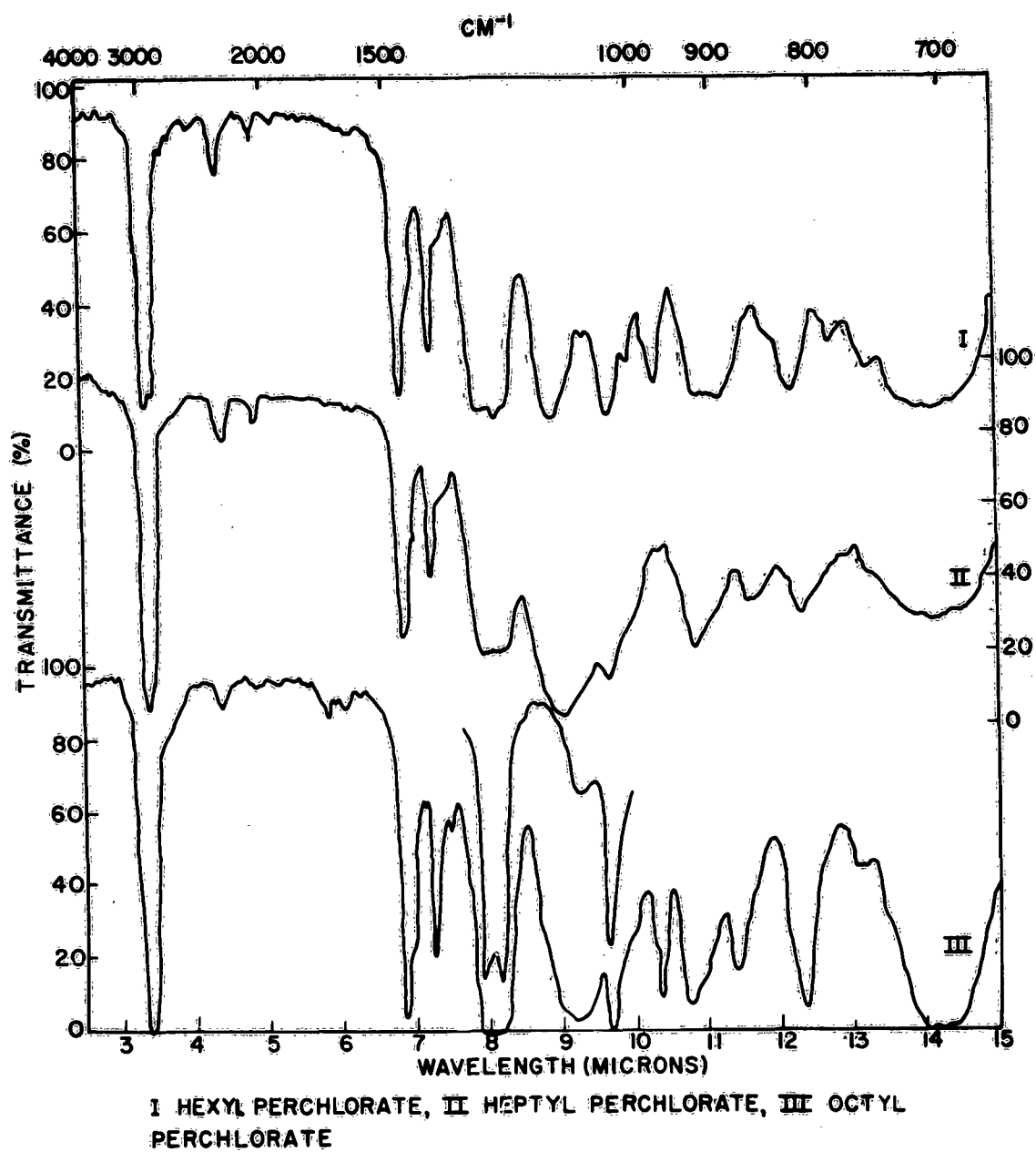


Figure 1: Infrared Spectra of n-Alkyl Perchlorates

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