

be considered; pyrrole, one of the weakest acids, reacts rapidly, its donating ability being strong because of the N lone pair. Cyclopentadiene, the strongest acid,²⁴ shows no reactivity apparently because of its lack of donor properties.

One can conclude then that a 4-center transition state is in agreement with all of the available facts.

It is interesting that in Hawthorne's investigation⁷ of the acid hydrolysis of $(C_6H_5)_2BH \cdot NC_6H_5$ where boron is already coordinated with a donor, a 3-center transition state has been suggested. Similarly, Shore and Parry²⁵ have shown that NH_4X salts react slowly with many borohydrides, the reaction being *strongly* catalyzed by ammonia.

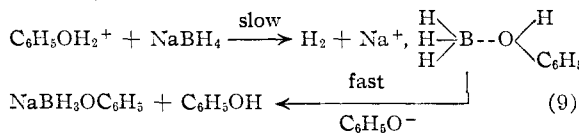
Obviously, both a proton donor and an electron donor seem to be necessary for such reactions to

(24) One referee has correctly pointed out that the greater reactivity of pyrrole or alcohols compared to that of cyclopentadiene might be due to the fact that in general N-H and O-H bond-breaking processes are rapid compared to C-H bond breaking. As indicated in the footnote to Table III we are currently measuring the rates of deuterium exchange in a series of weak acids, and cyclopentadiene exchange has been studied. If the N-H systems prove amenable to the same treatment this question may be answered.

(25) S. S. Shore and R. W. Parry, *J. Am. Chem. Soc.*, **80**, 8 (1958).

take place easily. These may be in one molecule of the attacking reagent (present work), in separate attacking reagent molecules (Shore and Parry²⁵) or distributed between the substrate (borohydride) and the attacking reagent (Hawthorne⁷).

Returning then to the problem of the detailed mechanism of the reaction between C_6H_5OH and $NaBH_4$, we can write



Whether the attack of phenoxide is on the B, followed by displacement, or involves proton abstraction is not known.

Acknowledgment.—The authors wish to thank the following for grants and fellowships which enabled the work to be carried out: Research Corporation; Office of Scientific Research, U. S. Air Force; and the Texaco Co. They also wish to thank Dr. M. F. Hawthorne and Dr. D. McDaniel for several valuable suggestions.

[CONTRIBUTION FROM RESEARCH AND DEVELOPMENT GROUP FRANKFORD ARSENAL, PHILADELPHIA 37, PA.; AERONAUTICAL RESEARCH LAB., WRIGHT-PATTERSON AIR FORCE BASE, OHIO AND THE RESEARCH DIVISION OF THE WYANDOTTE CHEMICALS CORP., WYANDOTTE, MICH.]

n-Alkyl Perchlorates: Preparation, Study and Stabilization

By JACK RADELL,¹ J. W. CONNOLLY AND A. J. RAYMOND

RECEIVED APRIL 22, 1961

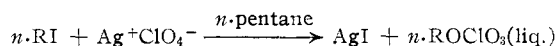
The previously unreported normal pentyl, hexyl, heptyl and octyl perchlorates were prepared from the corresponding alkyl iodide and silver perchlorate. The pure esters of perchloric acid were stabilized as the endocycle of a urea inclusion compound. The infrared spectra and some physical properties are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

Introduction

Covalent esters of perchloric acid have been reported² in the literature. These 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 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 alkyl perchlorates were prepared by the reaction



Commercially available "anhydrous" silver perchlorate required dehydration. This dehydration is necessary because covalent perchlorates are

(1) From the Frankford Arsenal and from whom reprints may be obtained.

(2) C. Hare and M. H. Boyle, *Phil. Mag.*, **19** (3), 370 (1841); K. A. Hofmann, A. Zedtwitz and H. Wagner, *Chem. Ber.*, **42**, 4390 (1909); L. Birckenbach and J. Goubeau, *Naturwissenschaften*, **18**, 530 (1930); J. Meyer and W. Spormann, *Z. anorg. u. allgem. Chem.*, **228**, 341 (1936); R. D. Stewart in J. C. Schumacher, "Perchlorates," Reinhold Publishing Corp., New York, N. Y., 1960, pp. 67, 214.

thermodynamically unstable to hydrolysis.³ All of the alkyl perchlorates prepared were explosive. The lowest molecular weight alkyl perchlorate was most sensitive to shock. Although the highest molecular weight 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 pentyl, 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 I. The pentyl 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 pentyl: 7.05–7.10, 4.09–

(3) J. Radell and J. W. Connolly, Papers and Summaries, International Symposium on Macromolecular Chemistry, The International Union of Pure and Applied Chemistry, Moscow, U.S.S.R., June, 1960, Section I, pp. 292–295; *J. Polymer Sci.*, **XLVIII**, 343 (1960).

TABLE I

X-RAY POWDER PATTERNS OF UREA INCLUSION COMPOUNDS OF n-ALKYL PERCHLORATES

n-R	7.05	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 ₅ H ₁₁	0.06 ^b	1.00	0.05	0.12	0.84	0.34	0.05	0.12
C ₇ H ₁₅	.08	1.00	.05	.07	1.00	.20	.05	.08
C ₈ H ₁₇	.08	0.96	.09	.05	1.00	.23	.08	.19
C ₈ H ₁₇	..	1.00	.35	..	0.89	..	.05	.05

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

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.⁴ The spacing at 3.91-3.98 Å. is an intense and reliable spacing for dissociated tetragonal urea. These data may be used to determine the relative stability of the inclusion compounds.^{4,5}

The lesser stability of the lower molecular weight endocytos was shown by the presence of appreciable amounts of dissociated urea in the X-ray powder diffraction patterns of the complexes of pentyl and hexyl perchlorates. The higher molecular weight endocytos, heptyl and 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^{4,5} for estimating the relative stability of the inclusion compounds of an homologous series of complexing compounds. 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 (Table I). The pentyl perchlorate inclusion compound 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.⁴⁻⁶

The cross-sectional diameter of a normal hydrocarbon (4.6 Å.) seems to be close to the optimum for urea channel complex formation.^{5,6} The measured maximum cross-sectional diameter of the n-alkyl perchlorate was 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 RCH₂OCIO₃ 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 this⁷ procedure was n-octane. However, the shortest n-alkyl perchlorate to form a complex was pentyl with only five methylene groups.

The infrared spectra of the capillary liquid film samples of all the alkyl perchlorates except

(4) J. Radell and J. W. Connolly, Abstracts, 9th Annual Conference—Applications of X-Ray Analysis, Denver Research Institute—University of Denver, Denver, Colo., August 10, 1960; in W. M. Mueller, "Advances in X-Ray Analysis," Vol. IV, Plenum Press, New York, 1961, pp. 140-150. These reprints are available from J. R.

(5) J. Radell and J. W. Connolly, *J. Org. Chem.*, **25**, 1202 (1960).

(6) (a) J. Radell and P. D. Hunt, *J. Am. Chem. Soc.*, **80**, 2683 (1958); (b) J. Radell, J. W. Connolly and L. D. Yuhas, *J. Org. Chem.*, **26**, 2022 (1961).

(7) The shortest reported in the literature was n-hexane: E. V. Truter, "Wool Wax," Interscience Publishers, Inc., New York, N. Y., 1956, p. 212.

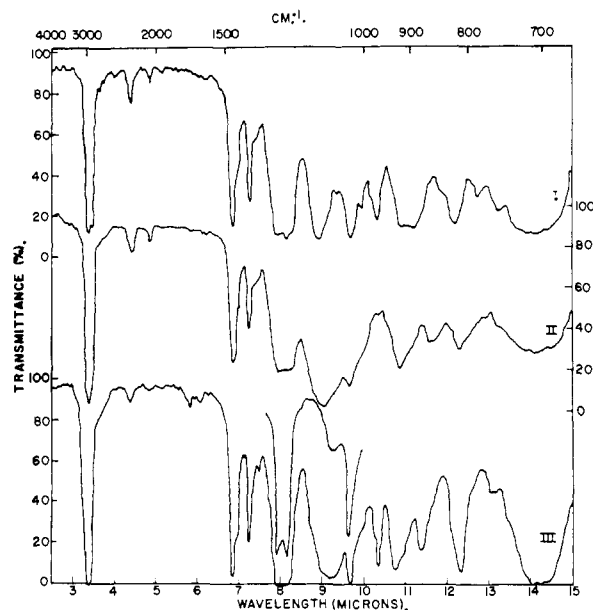


Fig. 1.—Infrared spectra of n-alkyl perchlorates: I, hexyl perchlorate; II, heptyl perchlorate; III, octyl perchlorate.

pentyl are shown in Fig. 1. A comparison of absorption bands associated with the perchlorate function is listed in Table II for perchloric acid, perchloryl fluoride, perchlorylbenzene and our

n-alkyl perchlorates, R-O₁-Cl $\begin{matrix} \diagup O \\ | \\ \diagdown O \end{matrix}$ O₁, designating the oxygen between the carbon and chlorine only.

TABLE II
RELATED ABSORPTION BANDS

Description	Frequency, cm. ⁻¹			
	n-RO ₁ ClO ₃	HOClO ₃ ^a	ClO ₃ F ^b	C ₆ H ₅ ClO ₃ ¹⁰
Cl-O ₁ asymmetric stretching	1230, 1260	1182, 1312	1191	1315
Cl-O ₁ symmetric stretching	1035	1032	1075	1061
Cl-O ₂ stretching	C ₆ H ₅ OCIO ₃ , 709 C ₇ H ₁₅ OCIO ₃ , 705 C ₈ H ₁₇ OCIO ₃ , 704	738
C-O ₁ stretching	C ₆ H ₅ OCIO ₃ , 1125 C ₇ H ₁₅ OCIO ₃ , 1105 C ₈ H ₁₇ OCIO ₃ , 1080

The Cl-O asymmetric stretching gave a doublet for the n-alkyl perchlorates and perchloric acid. A single band was obtained for perchloryl fluoride and perchlorylbenzene although the latter probably has an unresolved doublet. In the case of the C-O₁ stretching and to a lesser extent the Cl-O₁ stretching there is an increase in the absorption frequency with decreasing mass of the alkyl group. The Cl-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 ester was unaltered. These

(8) O. Redlich, E. K. Holt and J. Bigeleisen, *J. Am. Chem. Soc.*, **66**, 13 (1944).

(9) D. R. Lide, Jr., and D. E. Mann, *J. Chem. Phys.*, **25**, 595 (1956).

(10) C. E. Inman, R. E. Oesterling and E. A. Tyczkowski, *J. Am. Chem. Soc.*, **80**, 5286 (1958).

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 alkyl perchlorate complexes and the pure 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 alkyl perchlorate urea inclusion compound, it is possible that the Nujol may replace the perchlorate as the enclosed material in the inclusion compound. This does not complicate the situation, since the only purpose was to show that the inclusion compound involved a perchlorate.

Sufficient data are available (Table III) for determining the molecular refraction for *n*-hexyl

TABLE III

PROPERTIES AND ANALYSES OF *n*-ALKYL PERCHLORATES

<i>n</i> -R	B.p.		n_D^{25}	Chlorine, %	
	$^{\circ}\text{C}$.	Mm.		Calcd.	Found
C_6H_{11}	51.5	11	1.4042	20.79	19.93
$\text{C}_8\text{H}_{18}^a$	52.0	4.5	1.4146	19.21	18.47
C_7H_{15}	49-51	2.5	1.4170	17.85	17.47
$\text{C}_8\text{H}_{17}^b$	55-60	1.5	1.4192	16.67	16.46

^a d_{25}^{25} 1.11. ^b d_{25}^{25} 1.070.

and *n*-octyl perchlorates only. By use of the Lorentz and Lorenz equation the values obtained for the molecular refraction of the hexyl and octyl perchlorates were 55.48 and 66.88, respectively. If we subtract the refractivity value for *n*- C_6H_{13} (28.86)¹¹ and *n*- C_8H_{17} (38.14)¹¹ 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 (25 g.) 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 (4 hours). The solution was

(11) A. L. Vogel, "Practical Organic Chemistry," Longmans, Green and Co., New York, N. Y., 1954, p. 900.

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 phosphorus pentoxide at 1 mm. for 24 hours leaving 21 g. of anhydrous silver perchlorate.

Preparation of Alkyl Perchlorates.—To a mixture of 50 ml. of pentane and 0.1 mole of anhydrous silver perchlorate in a r.b. 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 4 hours after the addition was completed. The solid silver iodide was separated from the solution of alkyl perchlorate in pentane 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 pentane. The solvent was evaporated at room temperature by passing dry nitrogen through the solution protected by a drying tube for 2 hours. This was either done immediately or the solution was stored overnight over anhydrous sodium carbonate before filtering and concentrating. In this way about 90% of the solvent was removed. The residue was vacuum distilled with a nitrogen capillary bleed using an 8-inch Vigreux column. The yield was 90-95% based on silver iodide. Recoveries ranged between 60-75%. A safety shield was used to protect the operator from the distilling apparatus and Dry Ice trap.

Although the thermal and drop weight stabilities 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 5 and 12.7 cm. The lower molecular weights perchlorates were most sensitive. The charring temperatures of the perchlorates varied between 150 and 350 $^{\circ}$. These values varied considerably but generally were proportional to the chain length of the *n*-alkyl group. The properties and analysis of the perchlorates are listed in Table III.

Perchlorate Analysis.—The distilled alkyl perchlorates were analyzed by dissolving ca. 2 g. of alkyl perchlorate in 25 ml. of concentrated aqueous ammonium hydroxide and 75 ml. of 95% ethanol. The liquid was evaporated to near dryness and the residue was analyzed by the nitron method.¹²

Urea Inclusion Compounds.—The urea inclusion compounds of the alkyl perchlorate were prepared by a previously described procedure.⁵

Infrared Analysis.—The liquid film infrared analysis of the liquid 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 was done by a previously described⁶ procedure.

Acknowledgment.—The authors gratefully acknowledge the assistance of Dr. L. A. Harrah in interpreting the infrared spectra.

(12) W. W. Scott, "Standard Methods of Chemical Analysis," 5th Edition, D. Van Nostrand Co., Inc., New York, N. Y., 1925, Vol. II, p. 1677.