ORGANIC AND BIOLOGICAL CHEMISTRY

[CONTRIBUTION FROM COATES CHEMICAL LABORATORIES, LOUISIANA STATE UNIVERSITY]

Complexation of Cyclic Olefins with Aqueous Silver Ion and with Molecular Iodine[1,2]

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Equilibrium constants for formation of olefin π-complexes with aqueous silver ion and with iodine have been evaluated. The olefins included cycloalkenes, methylenecycloalkanes and bicyclic olefins. The formation constants for silver ion complexes show more dependence on ring size than do those for iodine complexes and, except for the constants for methylenecycloalkanes which are little different from one another, are in the same order as the estimated relative strains in the olefins. Unlike other dienes, which form both 1-to-1 and 1-to-2 olefin–silver ion complexes, norbornadiene appears to form only a 1-to-1 complex.

Studies of alicyclic compounds have been fruitful in elucidating effects which in general are significant in substitution,[4] elimination[5] and carbonyl addition[4] reactions. Few studies of the reactivities of cyclic olefins have been described, however. We have undertaken a systematic study of reactions of cyclic olefins with a view toward unveiling details of olefin reactions in general as well as effects of ring size on such systems. The close resemblance between structures postulated for π-complexes derived from olefins and for transition states or intermediates in addition reactions[6] suggests that studies of the complexes may be helpful in understanding details of addition reactions. Some of our initial investigations were described in a previous publication.[7] All of the initial results have been checked and new complexes have been studied. The olefins used as donor species were cycloalkenes (ring sizes C_5 through C_8), methylenecycloalkanes (ring sizes C_4 through C_7), norbornene, bicyclooctene and norbornadiene. Acceptors were aqueous silver ion and molecular iodine.

The silver ion complexes were studied by distribution of olefin between carbon tetrachloride and aqueous silver nitrate (usually 1 *M* solutions). Equilibrium concentrations of olefin in the wet CCl_4 phase were evaluated by use of characteristic absorption bands in the near-infrared region. This method requires less olefin than is needed for the previously employed titration analysis, is more convenient and is at least equally precise. The difference in concentrations of olefin in the CCl_4 phase equilibrated with aqueous silver nitrate and that equilibrated with aqueous potassium nitrate was attributed to complex formation. Concentrations of uncomplexed silver ion and of complex in the aqueous phase could be computed. Equilibrium constants were calculated for the reaction

$$\text{olefin}(CCl_4) + Ag^+(H_2O) \rightleftharpoons \text{Complex}^+(H_2O)$$

The iodine complexes in 2,2,4-trimethylpentane were studied in the conventional manner by ultraviolet spectrophotometry.[8] The appearance of an absorption maximum near 300 mμ for solutions of olefin and iodine is associated with π-complex (charge-transfer complex) formation. The equilibrium constant for complex formation with each olefin was obtained graphically from the variation of the apparent extinction coefficient at the complex absorption maximum with mole fraction of olefin in the solution.

Experimental

Preparations of Materials.—Commercially available **cyclopentene and cyclohexene** were redistilled. **Cycloheptene** was prepared by acid-catalyzed dehydration of cycloheptanol. ***cis*-Cycloöctene** was prepared by partial hydrogenation of cycloöctatetraene, conversion of the crude cyclooctene to the olefin dibromide, and treatment of the bromide with zinc dust to regenerate *cis*-cycloöctene.[9] **Methylenecyclobutane** was prepared in the conventional manner from pentaerythrityl tetrabromide. All other **methylenecycloalkanes** were obtained by pyrolysis of the appropriate 1-methylcycloalkyl acetate.[10] **Norbornene** and **bicyclo[2.2.2.]-octene-2** were supplied by Dr. H. Walborsky and **norbornadiene** was supplied by Shell Chemical Co.; these samples were sublimed or distilled before use. Phillips 99.9% grade 2,2,4-trimethylpentane was shaken with concentrated sulfuric acid and then distilled. Analytical reagent grade silver nitrate, potassium nitrate, iodine and carbon tetrachloride were used without further purification.

Olefin–Silver Ion Complexes: General Procedure.—In these studies, concentrations of olefin in CCl_4 solutions were determined spectroscopically. Standard curves (optical density *vs.* concentration) were prepared from near-infrared spectra obtained with solutions containing known, weighed amounts of olefin in CCl_4 solvent saturated with water. The spectra were obtained with a Beckman DK-1 spectrophotometer; the region used was 1650–2700 Å. From several characteristic absorption bands recorded for each olefin, three sharp and relatively intense ones were chosen for linear plots of optical density *vs.* concentration.[11] Duplicate determinations were practically indistinguishable. The use of three wave lengths and standard curves for each olefin provided good internal checks on the method.

Distributions of olefin between CCl_4 and aqueous $AgNO_3$ or KNO_3 solutions were carried out in flasks immersed in a bath whose temperature was maintained constant within

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(2) Reported in part at the Southeastern Regional A. C. S. Meeting, Durham, N. C., November, 1957, and in part at the 133rd A. C. S. Meeting, San Francisco, Calif., April, 1958.

(3) Celanese Fellow, 1955–1956.

(4) H. C. Brown, J. H. Brewster and H. Shechter, THIS JOURNAL, **76**, 467 (1954), and references cited there.

(5) J. Weinstock, R. G. Pearson and F. G. Bordwell, *ibid.*, **78**, 3468, 3473 (1956).

(6) R. W. Taft, Jr., and co-workers, *ibid.*, **74**, 4372 (1952); **77**, 1584 (1955); **78**, 5807, 5811, 5812 (1956).

(7) J. G. Traynham and M. F. Sehnert, *ibid.*, **78**, 4024 (1956).

(8) H. A. Benesi and J. H. Hildebrand, *ibid.*, **71**, 2703 (1949).

(9) A. C. Cope, A. W. Pike and R. Spencer, *ibid.*, **75**, 3212 (1953).

(10) (a) J. G. Traynham and O. S. Pascual, *J. Org. Chem.*, **21**, 1362 (1956); (b) W. Bailey, J. J. Hewitt and C. King, THIS JOURNAL, **77**, 357 (1955).

(11) Although the absorption bands probably are associated with carbon–hydrogen bonds, we have not attempted to make assignments. A few measurements indicated that solutions of alkanes and alkyl halides in wet CCl_4 can be analyzed equally satisfactorily. After our work using this method of analysis was well under way, a detailed paper describing near-infrared spectrographic analysis of CCl_4 solutions of fatty acids and some related substances was published (R. T. Holman and P. R. Edmondson, *Anal. Chem.*, **28**, 1533 (1956)).

0.02°. A mixture of 10 ml. of olefin–CCl_4 solution (0.1–0.9 *M*) and 25 ml. of aqueous KNO_3 (1 *M*) was stirred for one hour. The phases were allowed to separate and 2 samples were withdrawn from the CCl_4 phase with a pipet. The olefin concentration in each sample was determined by comparison of its spectrum with the standard curves described above. The distribution then was carried out with another 10-ml. sample of the same olefin–CCl_4 solution and 25 ml. of aqueous $AgNO_3$ (1 *M*). The difference in concentration of olefin in the CCl_4 phase equilibrated with $AgNO_3$ solution and that equilibrated with KNO_3 solution was attributed to complex formation. Equilibrium concentrations of complex and of uncomplexed silver ion in the aqueous phase were computed. Equilibrium constants and thermodynamic functions for the reaction

$$\text{olefin}(CCl_4) + Ag^+(H_2O) \rightleftharpoons \text{complex}^+(H_2O)$$

are given in Table I. The values for K_{eq} are averages obtained with several duplicate experiments with different sets of solutions. Except for those indicated, the deviations for any average K_{eq} were less than ±2%.

TABLE I

OLEFIN–SILVER ION COMPLEX FORMATION

Olefin	Temp., °C.	K_{eq} l./mole	Rel. K_{eq}, 25°	$-\Delta H°$, kcal./mole	$-\Delta S°$, e.u.
Cyclopentane	25	0.119	23.6	6.63	26.5
	5	.266			
Cyclohexene	25	.0184	3.65	5.74	27.2
	5	.0369			
Cycloheptene	25	.0212	4.21	6.49	29.4
	5	.0466			
cis-Cycloöctene	25	.00504	1.00	4.11	24.8
	5	.0083[b]			
Methylenecyclobutane	25	.0900	17.9	4.04	18.4
	5	.147[b]			
Methylenecyclopentane	25	.0670[c]	13.3	3.31	16.5
	5	.100			
Methylenecyclohexane	25	.0598[d]	11.9	3.11	16.0
	5	.0872[e]			
Methylenecycloheptane	25	.0725[f]	14.4	3.21	16.1
	5	.107			
Norbornene	25	.268	53.2	6.68	25.0
	5	.603			
Bicycloöctene	25	.0955	18.9	4.94	21.2
	5	.174			
	32	.355			
Norbornadiene	25	.572	114	11.18	38.7
	20	.755[b]			
1-Methylcyclohexene[a]	25	.00827	1.64	...	..

[a] 1-Methylcyclohexene was included mainly to assist in the confirmation of identity of the methylenecyclohexane sample (see ref. 10a). The wide difference in the K_{eq} values for these two olefins is in the same direction as that found for retention times of the olefins on a glycol–$AgNO_3$ column in vapor chromatography,[12] and suggests that there was little, if any, contamination of the methylenecyclohexane sample by 1-methylcyclohexene. [b] Deviation ±2–3%. [c] Deviation ±0.0027. [d] Deviation ±0.0055. [e] Deviation ±0.0044. [f] Deviation ±0.0072.

Norbornadiene–Silver Ion Complex.—Because of the possibility of formation of 1:2 as well as 1:1 olefin–silver ion complexes with norbornadiene, the dependence of the apparent equilibrium constant on silver ion concentration was examined. The procedure was the same as that described above except that the aqueous phase contained both $AgNO_3$ and KNO_3. The total salt concentration was always 1 *M*; the $AgNO_3$ concentration was varied over the range 0.2–1 *M*. Temperatures below 20° could not be used because of the tendency for solid complex to separate from the liquid phases. There was no apparent change in K_{eq} with changes in $AgNO_3$ concentration, indicating absence of any 1:2 complex. Were both 1:1 and 1:2 complexes formed, the apparent K_{eq} would increase with increasing $AgNO_3$ concentration.[12,13]

When norbornadiene was added to 1 *M* $AgNO_3$ in the absence of CCl_4, a white solid precipitated. The solid complex was washed, dried and analyzed for silver content (thiocyanate titration). The silver analysis also indicated formation of a 1:1 complex. Calcd. for $C_7H_8{\cdot}AgNO_3$: Ag, 41.17. Calcd. for $C_7H_8{\cdot}2AgNO_3$: Ag, 49.96. Found: Ag, 41.82, 42.25, 42.45. The solid complex appeared to be stable when stored under nitrogen in a dark bottle, but it did turn dark when exposed to air and light. Slight loss of olefin through decomposition would result in a high silver analysis.

Olefin–Iodine Complexes.—Stock solutions containing known, weighed amounts of iodine and of olefin in 2,2,4-trimethylpentane were prepared. The concentration of iodine was approximately 10^{-4} *M*. The concentration of olefin was expressed as mole fraction and varied from 0.2 to 0.033.

Measured quantities of iodine solution and olefin solution were mixed and placed in a 1-cm. glass-stoppered silica absorption cell. In a companion cell was placed an iodine–2,2,4-trimethylpentane blank.[14] The solutions were compared in a Beckman DU spectrophotometer equipped with thermospacers through which was circulated water from a bath whose temperature was carefully controlled (±0.02°). After temperature equilibration of the cells in the spectrophotometer, the optical density of the solution containing both iodine and olefin was measured at the absorption maximum associated with complex formation. (The characteristic absorption maximum for each olefin was determined experimentally; these appeared near 300 mμ, a region in which neither olefin solutions nor iodine solutions absorbed significantly.) Several duplicate runs were made with each set of solutions. The optical densities of the solutions were shown to remain unchanged during the time required for spectrophotometric measurements.

Equilibrium constants for complex formation were obtained from observed variation of the apparent extinction coefficient at the absorption maximum with mole fraction of olefin in the solution. Equations used were[8,15]

$$Y = \frac{l[I_2]}{d}$$

$$Y = \frac{1}{(\epsilon_c - \epsilon_{I_2})K} \times \frac{1}{N_0} + \frac{1}{(\epsilon_c - \epsilon_{I_2})}$$

in which d is the net optical density of the complex solution at the characteristic absorption maximum, l is the length of the light path, $[I_2]$ is the total concentration of I_2 in the complex solution, ϵ_c is the extinction coefficient of the complex and ϵ_{I_2} is that of uncomplexed I_2 at the wave length used, K is the equilibrium constant for complex formation and N_0 is the mole fraction of olefin in the complex solution.

Slopes and intercepts of straight-line plots of Y against $1/N_0$ for each olefin were evaluated by the method of least squares and were used for calculations of K.

Data for iodine–olefin complexes are given in Table II. The values of K are averages of several determinations with deviations of about 1–2%. Attempts to measure K for norbornadiene were unsuccessful because of the slow separation of a white precipitate when 2,2,4-trimethylpentane solutions of iodine and norbornadiene were mixed.

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(12) E. Gil-Av, J. Herling and J. Shabtai, *Chemistry & Industry*, 1484 (1957).

(13) S. Winstein and H. Lucas, THIS JOURNAL, **60**, 836 (1938).

(14) Since nearly all the iodine is complexed in the solution containing olefin, the use of an I_2–solvent blank actually provides an overcorrection for iodine absorption. However the ϵ_{I_2} is so small in the region of 300 mμ (10–25 l./mole/cm.) that little difference was obtained in the value of K whether an I_2–solvent blank or an olefin–solvent blank was used. The use of an I_2–solvent blank was found to yield data which gave better straight-line plots. The equations are based on an I_2–solvent blank.

(15) J. A. A. Ketelaar, C. van de Stolpe, A. Goudschmidt and W. Dzcubas, *Rec. trav. chim.*, **71**, 1104 (1952). The value of K was unchanged by the use of the modified equation recommended by R. L. Scott, *ibid.*, **75**, 787 (1956).

TABLE II

OLEFIN–IODINE COMPLEX FORMATION

Olefin	λ_{max}, mμ	$10^{-4} \times \epsilon_c$, l./mole/cm.	Temp., °C.	K^b	Rel. K, 25°	$-\Delta H°$, kcal./mole	$\Delta S°$, e.u.
Cyclopentene	298	1.42	25	2.80	2.58	0.43	−0.6
			15	2.87			
Cyclohexene	302	1.40	25	3.30	3.04	2.18	+4.9
			15	3.75			
Cycloheptene	300	1.66	25	3.05	2.80	1.95	4.3
			15	3.42			
cis-Cycloöctene	295	8.34	25	1.09	1.00	0.48	1.4
			15	1.12			
Methylenecyclobutane	283	1.53	25	2.78	2.54	.84	0.8
			15	2.92			
Methylenecyclopentane	312	1.65	25	2.61	2.39	.96	1.3
			15	2.76			
Methylenecyclohexane	305	1.39	25	3.65	3.34	1.78	3.4
			15	4.05			
Methylenecycloheptane	317	2.05	25	2.67	2.45	2.88	7.7
			15	3.16			
Norbornene[a]	298	0.515	25	4.33	3.97	..	...

[a] These data obtained by Mr. James Eric Landry, single determination. [b] Reciprocal mole fraction units.

Discussion of Results

The formation constants for silver ion complexes of the cycloalkenes and bicyclic olefins are in essentially the same order as the estimated relative strains in the olefins (see Table I). The relative strains among these olefins were estimated from available thermochemical data.[7] Although small differences in entropy of reaction were found, the enthalpy factor appears to reflect the predominant effect. Only with norbornadiene and possibly with bicycloöctene does $\Delta S°$ seem sufficiently different from the others to be significant.

The formation constants for silver ion complexes of the methylenecycloalkanes show less dependence on ring size (Table I). The small differences which were found (ratio of extremes for K_{eq} about 1.5 to 1) do not appear to be simply related to the relative strain in the olefin in the way found for *endo*-olefins. The magnitude of these formation constants is about the same as that reported for the acyclic analog, isobutylene.[13] The $\Delta H°$ terms are somewhat less favorable than those for the more extensively complexed cycloalkenes, but the $\Delta S°$ terms are significantly more favorable (about 10 e.u. more positive).

Unlike other dienes, which have been reported to form both 1:1 and 1:2 olefin–silver ion complexes,[13] norbornadiene appears to form only a 1:1 complex. Both K_{eq} and $-\Delta H°$ are higher than for any other olefin studied. The $\Delta S°$ term is less favorable than that with norbornene by about 14 e.u. The absence of any 1:2 complex formation may result either from overlapping of the orbitals of the silver ion with both π-clouds (silver ion located "under" the diene molecule; structure A), or from π-orbital overlap (homoallylic resonance[16]) with the silver ion located on one side of the diene in an *exo* configuration (structure B). Orbital overlap "under" the molecule in B with extensive polarization would make the cloud at the 5,6-position relatively positive and an unattractive bonding site for another silver ion. Because of the favorable geometry for overlapping of appropriate orbitals when silver ion is placed under the diene molecule, structure A would probably be favored *a priori*. However the stereochemistry of addition products reported by Winstein and Shatavsky[16] suggests that bromine approaches the diene from an *exo*-position. To the extent olefin–silver ion complexes may be assumed to resemble olefin–halogen complexes in gross structure, structure B is favored. The apparent presence of homoallylic resonance in the silver ion complex and its apparent absence in the ground state of the diene[17] strongly support the view that these complexes closely resemble the transition states or intermediates in olefin addition reactions.

Except for the two extremes (*cis*-cycloöctene and norbornene), the molar extinction coefficients of these olefin–iodine complexes and the K's for complex formation fall within a narrow range of values and do not provide a good test of any correlation between these two experimental constants.[18] There is a fairly good linear relationship however between ϵ_c and $1/K$ for all the olefins studied here.

The formation constants for the iodine–olefin complexes show less dependence on ring size than do those for silver ion–cycloalkene complexes (Table I). Both enthalpy and entropy factors seem to be important. The increase in both $-\Delta H°$ and $\Delta S°$ with increase in ring size among the methylenecycloalkanes is particularly interesting since no similar effect was found elsewhere in this study. Except for the positions of *cis*-cycloöoctene (the least extensively complexed olefin) and norbornene (the most extensively complexed olefin used with both silver ion and iodine), the order of the formation constants for the iodine complexes bears essentially no resemblance to the order for silver ion complexes. Indeed the K's for cyclopentene, cyclohexene and cycloheptene are in the opposite order in the two series. These differences in K for iodine complexes may be too small to be assigned any significance. However the lack of parallel trends among the silver ion complexes and the iodine complexes does seem significant.

In the absence of unfavorable steric factors, the stability constants for silver ion complexes and iodine complexes with aromatic hydrocarbons do exhibit parallel trends.[19a] In these aromatic complexes the silver ion is located above and between two carbon atoms of the aromatic ring[19b, 20] but the iodine molecule is centered on the axis of the aromatic ring.[19b] One might well expect even closer parallelism among the stability constants for the olefin complexes since both the silver ion and the iodine molecule must be located above and between the olefinic carbons. The lack of similar trends in the two series is striking and does not seem to be associated directly with steric effects. It may

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(16) S. Winstein and M. Shatavsky, *Chemistry & Industry*, 56 (1956).

(17) R. B. Turner, W. R. Meador and R. E. Winkler, THIS JOURNAL, **79**, 4116 (1957).

(18) M. Tamres, D. R. Virzi and S. Searles, *ibid.*, **75**, 4358 (1953), reported a linear correlation between ϵ and $1/\sqrt[3]{K}$ for iodine–polyalkylbenzene complexes.

(19) (a) L. J. Andrews, *Chem. Revs.*, **54**, 753 (1954); (b) p. 735; (c) pp. 764, 768.

(20) R. E. Rundle and J. H. Goring, THIS JOURNAL, **72**, 5337 (1950).

reflect that with these olefins the stability constants for silver ion complexes depend on ionization potential of the donor[19c] to a different degree or in a different way than do those for iodine complexes. Or the lack of parallel trends may indicate a difference in structure for the two types of complexes.

The silver ion–olefin complex has been described[21] in terms of some donation of electrons (charge-transfer) by overlapping of the occupied d-orbitals of silver ion with the unoccupied antibonding π-orbital of the olefin as well as charge-transfer by overlapping of the occupied π-orbital of the olefin with the unoccupied s-orbital of silver ion. Energy contributions from d-orbital overlapping are probably small compared with π-s-orbital overlapping.[22] One might well expect that this contribution would be considerably more important with silver ion, with its "exposed" d-orbitals, then with iodine molecule, with relatively unexposed d-orbitals. The p-orbitals of iodine do not have the appropriate geometry for overlap with the antibonding π-orbital of the olefin. Since the energy contributions from d-orbital overlap are expected to be small, they will become important or recognizable only when the contributions from π-s-orbital overlap become small. That is, this difference in structure for the two types of complexes may result in different orders for stability constants only among relatively weak donors. The olefins used in this study are weaker donors than are aromatic hydrocarbons.

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BATON ROUGE, LA.

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[21] M. J. S. Dewar, *Bull. soc. chim. France*, **18**, C79 (1951).

[22] Qualitative estimate by Dr. S. P. McGlynn, Louisiana State University; private communication.

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMICAL ENGINEERING AND CHEMISTRY, UNIVERSITY OF FLORIDA]

Some New Sulfur-bearing Fluorocarbon Derivatives[1,2]

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Further studies involving sulfur-bearing organic materials by the electrochemical process in HF are herein reported. New starting materials such as trithiane, bis-1,2-meththioethane and dimethyl disulfide were investigated. Thioxane, studied previously, was investigated on a larger scale with some novel results, which cast some further light on the many ramifications of the process. Such new compounds as $CF_3SF_4CF_2SF_5$, $CF_3SF_4C_2F_4SF_5$, $(C_2F_4SF_4)_2$, $(CF_2SF_4)_3$ and $C_2F_5SF_4CF_3$ were isolated and identified and several reported compounds such as $C_2F_5OC_2F_4SF_5$, $\underline{C_2F_4OC_2F_4SF_4}$ and $SF_5CF_2SF_5$ were obtained with high purity and their simple properties are noted. Whenever it was feasible, the isolable products from the various investigations were purified by vapor phase chromatography and structures were confirmed by nuclear magnetic resonance (n.m.r.) spectral analysis.

Introduction

The electrochemical (Simons) process is one of the major methods for preparing certain types of fluorocarbon materials. Although it has definite limitations it also manifests definite preparatory advantages. The preparation, by this process, of several simple derivatives of SF_6 have been reported[3] in recent years. The purpose of this work was to determine the feasibility of preparing fluorocarbon sulfides with so-called "polyfunctional" character. However, it will be noted that although several products of this nature were isolated and identified, their yields were limited by the tendency of the process to fragment, regroup fragments, cyclize and decyclize the original chain structure.

Vapor phase chromatography and nuclear magnetic resonance spectroscopy have been used as extensively as possible for purity determinations and structure analysis. They have been most useful in conjunction with classical analytical methods, for confirming the character of the isolable products. However, they still manifest certain limitations as analytical tools which await the accumulation of the needed background data.

Experimental

The electrochemical unit used in this work was not unlike that described by Hoffmann and Simmons[3d] and designated by them cell C. There were only minor differences in design. The overhead condenser was cooled directly by an expanding refrigerant (Freon 12) from a standard refrigeration machine, and the superheat from this expansion was used to cool a water-bath in which the cell was immersed, before the gas was returned to the high pressure side of the compressor. In general, the condenser was maintained between −20 and −30° and the bath between 17 and 19°. The area of each electrode system was about 1,000 sq. cm.

Vapor phase chromatographic studies were made with a Perkin–Elmer Fractometer, model 154, using such stationary phases as are noted in the text. Bulk separations were performed in packed one inch tubes, 2 or 4 meters long, using

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[1] Presented in part at the Southeastern Regional Meeting of the American Chemical Society, Durham, N. C., Nov. 14–16, 1957.

[2] This work was supported by the Chemistry Branch, Office of Naval Research, and any or all of this paper may be reproduced for purposes of the United States Government.

[3] (a) A. F. Clifford, H. K. El-Shamy, H. J. Emeleus and R. N. Haszeldine, *J. Chem. Soc.*, 2372 (1953); (b) W. A. Severson, T. J. Brice and R. I. Coon, 128th Meeting A.C.S., Minneapolis, Minn., September 11–16, 1955, Div. Ind. & Eng. Chem., Fluorine Chem. Subdivision; (c) R. Dresdner, THIS JOURNAL, **79**, 69 (1957); (d) F. W. Hoffman, T. C. Simmons and co-workers, *ibid.*, **79**, 3424 (1957).