capronitrile: ir (CS_2) 3500, 2950, 1715 (CO_2H), 1275, 965, 740 cm^{-1}.

ε-Caprolactone, 2-cyclohexenone, and 2-chlorocyclohexanone were commercially available.

Glpc Retention Data.—On a DC Hyvac silicone grease on Chromosorb P column, retention times, *R*, relative to 2-chlorocyclohexanone follow: cyclohexanone, 0.45; 4-chlorocyclohexanone, 1.15; ε-caprolactone, 1.65; 3-chlorocyclohexanone, 1.9; 2,2-dichlorocyclohexanone, 2.0. 2-Cyclohexenone and 4-chlorocyclohexanone in our product mixtures were better separated by 1,2,3-tris(2-cyanoethoxy)propane on Chromosorb P (*R* 0.45 and 1.45, respectively).

Reaction of Cyclopentanone with Hypochlorous Acid.—The retention time of δ-valerolactone was determined with a sample made by oxidizing cyclopentanone (1 g) with *m*-chloroperbenzoic acid (2.06 g) in chloroform (25 ml) for 2 days at room temperature. The ir of the lactone compared well with the published[12] spectrum. No indication of a peak with this retention time was observed upon glpc analysis of the products of reactions between cyclopentanone (0.1 mol) and aqueous hypochlorous acid (0.4 mol) at pH 6 which were allowed to proceed until the active chlorine disappeared. The products were not identified.

Reaction of Cyclohexanone with Hypochlorous Acid.—To 400 ml of 5.2% aqueous sodium hypochlorite (0.28 mol) was added enough glacial acetic acid to bring the pH to 4.6 ± 0.1 (about 55 ml). Cyclohexanone (7.5 g, 0.076 mol) was added and the mixture was stirred at room temperature, protected from light, until a negative test for active chlorine was obtained with starch–iodide paper (20–60 hr). The mixture was extracted with chloroform and the chloroform extracts were washed with 5% sodium bicarbonate. In one experiment the bicarbonate washings were acidified and extracted with chloroform, from which a little 6-chlorohexanoic acid (0.1%) was obtained as the methyl ester by evaporation, treatment with diazomethane, and glpc collection. The original chloroform extract was concentrated and analyzed by preparative glpc, usually with ethyl phenylacetate as an internal standard. All major and most of the minor products were identified by comparing their glpc retention times and ir spectra with those of authentic samples. A few experiments were run at other pH values between 2 and 7 and the products were examined mainly for ε-caprolactone, none of which was ever detected. Several tests of the effect of irradiation with 3000–4000-Å light at various temperatures were done. The reaction vessel was cooled with ice–water in a Pyrex dewar for the runs at 2°. Reproducibility was poor, especially in the dark reactions, and the erratic material balances suggest that a variable amount of polymeric material was usually formed; this was not investigated.

Glpc analyses of "typical" runs for unchanged cyclohexanone (**6**), 4-chlorocyclohexanone (**7**), 2-chlorocyclohexanone (**8**), 2-cyclohexenone (**9**), and 2,2-dichlorocyclohexanone (**10**) are given in Table I.

TABLE I

REACTION OF CYCLOHEXANONE WITH HYPOCHLOROUS ACID AT pH 4.6

Conditions[a]			Conversions,[b] %				
	Temp, °C	Time, hr	**6**	**7**	**8**	**9**	**10**
Dark	25	60	18	10	8.9	0.0	0.0
Dark	25	21	92	1.3	3.5	0.0	4.3
Dark	30	18	53	22	6.2	9.3	Trace
3500 Å	40	0.5	15	14	3.0	14	0.0
3500 Å	47	0.83	21	12	4.0	14	0.0
3500 Å	2	2	61	10	1.4	9.8	0.0
3500 Å	2	4	64	9.0	2.1	12	0.0

[a] The time is that for disappearance of active chlorine. [b] Conversions into ε-caprolactone and 3-chlorocyclohexanone were 0.0 under all conditions tried.

Registry No.—Cyclobutanone, 1191-95-3; cyclohexanone, 108-94-1; 4-chlorocyclohexanone, 21299-26-3; 3-chlorocyclohexanone, 21299-27-4; 6-chlorohexanoic acid, 4224-62-8.

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Ion Radicals. XVIII. Reactions of Thianthrenium Perchlorate and Thianthrenium Trichlorodiiodide[1,2]

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The crystalline perchlorate and trichlorodiiodide of the thianthrene cation radical, $C_{12}H_8S_2{}^+ClO_4{}^-$, and $C_{12}H_8S_2{}^+I_2Cl_3{}^-$, have been prepared. With these salts it has been possible to study the reactions of the thianthrene cation radical with water, iodide ion, chloride ion, triphenylamine, and, to some extent, the vinyl monomers styrene, α-methylstyrene, ethyl vinyl ether, 1,1-diphenylethylene, acrylonitrile, and methyl methacrylate. Electron transfer to the thianthrene cation radical is facile, depending on the relative redox potentials of the cation radical and the other reactant. The reaction of the perchlorate salt with water has been studied in detail. The products are equal amounts of thianthrene and thianthrene 5-oxide. Kinetic work shows that the water reacts with the dication, formed by disproportionation of the cation radical, rather than with the cation radical itself. The longer known reactions of the thianthrene cation radical in sulfuric acid solution are now clearly understandable.

Cation radicals of thianthrene and similar compounds are usually obtained in concentrated sulfuric acid solution[4,5] although high-resolution esr spectra have been obtained recently with the nitromethane–aluminum chloride method at low temperatures.[6,7] Solid salts of the thianthrenium and similar cations are uncommon. Lucken has prepared thianthrenium perchlorate and pentachloroantimonate.[8] The latter has also been prepared by Kinoshita.[9] Both authors have discussed the

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esr spectra of the solid salts. Rundel and Scheffler[10] have prepared the perchlorate and fluoroborate. As far as we are aware these were hitherto the only solid thianthrenium salts known. Furthermore, the chemical properties of these salts have not been explored, attention having been confined to their spectroscopic properties. Indeed, knowledge of the chemistry of the thianthrene cation radical has been gained only in a speculative way from the behavior of its sulfuric acid solutions.[4] This situation is not much different from the general knowledge of cation-radical chemistry, the scarceness of which has been noted by Dewar, *et al.*,[11] Bawn, *et al.*,[12] Cauquis,[13] Ledwith,[14] and Fried and Schumm[15] in recent times.

In this paper we discuss the chemistry of a new salt, thianthrenium trichlorodiiodide, and the chemistry of the perchlorate.

Thianthrenium Perchlorate (1). Reaction of 1 with Water.—The mechanism of the reaction of a cation radical with water is of considerable interest. The reaction is likely to be encountered in most studies of cation-radical chemistry, and is a particular nuisance in electrochemical reactions.[16,17] Cauquis has represented two classes of reaction: one, for example, with the phenoxathiin cation radical giving phenoxathiin oxide; and the second, for example, with the dibenzodioxin cation radical giving dibenzodioxin and oxygen. The formation of phenoxathiin oxide is of particular interest because Cauquis has recognized that the over-all reaction could be composed of two elementary processes and proposes[18] either the reactions 1 and 2 or 3 and 4 as possible sequences. Ohnesorge[19] has interpreted the

$$2P\cdot^+ \rightleftharpoons P + P^{2+} \tag{1}$$

$$P^{2+} + H_2O \longrightarrow PO + 2H^+ \tag{2}$$

$$P\cdot^+ + H_2O \longrightarrow POH\cdot + H^+ \tag{3}$$

$$POH\cdot + P\cdot^+ \longrightarrow PO + P + H^+ \tag{4}$$

formation of 9-anthranol in the anodic oxidation of anthracene as involving the nucleophilic attack of water on the anthracene cation radical, which is analogous to the nucleophilic attack at the sulfur atom of the phenoxathiin cation radical ($P\cdot^+$) listed by Cauquis (eq 3).[18] It has been reported earlier that the pouring of sulfuric acid solutions of the thianthrene cation radical ($Th\cdot^+$) onto ice gives **2** and **3** as products, and two possibilities for their formation were noted. One of them is summarized in eq 5 and 6, while the other was analogous to eq 1 and 2.

$$TH\cdot^+ + H_2O \longrightarrow Th\ (\mathbf{2}) + H^+ + 0.5H_2O_2 \tag{5}$$

$$H_2O_2 + Th \longrightarrow ThO\ (\mathbf{3}) + H_2O \tag{6}$$

Work with **1** has now differentiated between these reaction sequences. Reaction in wet acetonitrile gave **2** and **3** in equal amounts (Table I). The reaction is second order in $Th\cdot^+$, and is described by eq 7 and 8. Two rate expressions can be derived from eq 7 and 8.

TABLE I

PRODUCTS OF REACTION OF THIANTHRENIUM PERCHLORATE (1) IN ACETONITRILE (AN) AND WATER

$[\mathbf{1}]_0 \times 10^3$, M	Solvent	Water added[b]	$[H_2O]_0/[Th^+]_0$	Products, %: **2**	**3**	**2/3**
1.84	AN[a]	0.270	2.81	49.6	50.4	0.99
7.51	AN[a]	0.355	10.3	48.8	51.2	0.95
6.55	AN[a]	0.660	19.4	49.9	50.1	0.99
15.7	H_2O[c]			83.3	16.7	5.0
5.78	H_2O			49.5	50.5	0.98

[a] "Dry" solvent. [b] Mole per cent in the AN. [c] Containing sodium iodide.

$$2Th\cdot^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Th + Th^{2+} \tag{7}$$

$$Th^{2+} + H_2O \xrightarrow{k_2} ThO + 2H^+ \tag{8}$$

One of them (eq 9) assumes a steady-state concentration of Th^{2+} while the other (eq 10) assumes rapid equilibration in eq 7, with constant K. In either case the

$$-d(Th\cdot^+)/dt = \frac{k_1[Th\cdot^+]^2}{(k_{-1}[Th]/k_2[H_2O)] + 1} \tag{9}$$

$$-d(Th\cdot^+)/dt = k_2K[Th\cdot^+]^2[H_2O]/[Th] \tag{10}$$

kinetics are second order in $Th\cdot^+$. By choosing a suitable ratio of $[H_2O]_0/[Th]_0$ in which $[H_2O]_0$ and $[Th]_0$ are severalfold larger than $[\mathbf{1}]_0$, the disappearance of $Th\cdot^+$ can be followed easily spectrophotometrically, according to the integrated expression in eq 11, in which

$$\frac{1}{A_t} - \frac{1}{A_0} = k_at \tag{11}$$

k_a is, for example, $k_2K[H_2O]/[Th]\epsilon d$. Here, ϵ is the estinction coefficient of **1** at the stipulated wavelength (546 mμ), d the cell width, and A the absorbance.

Kinetic results are given in Table II. Rates were followed conveniently when $[H_2O]_0/[Th]_0$ was in the 12–15 range. At a ratio of 30 the rate was too fast to follow, and at a ratio of 3 it was inconveniently slow. Plots of $1/A_t$ *vs.* t were linear (Figure 1). The linearity of these plots and also the effect of added Th on the rate are consistent with the steps in eq 7 and 8. By assuming that the equilibrium in eq 7 was rapidly reached, values of k_2K could be calculated and are given in Table II. The reasonably constant agreement among values is also consistent with the steps in eq 7 and 8. Thus, it is clear that the direct reaction of the thianthrene cation radical with water does not take place. We cannot say whether our finding will apply to the reactions of other cation radicals. One would expect that they apply to other sulfur-containing radicals, such as that of phenoxathiin. In general terms, how-

TABLE II

RATE DATA FOR THE DECOMPOSITION OF THIANTHRENIUM PERCHLORATE (1) IN WET ACETONITRILE

$[Th]_0 \times 10^3$, M	$[H_2O]_0 \times 10^2$, M	$[\mathbf{1}]_0 \times 10^4$, M	$[H_2O]_0/[Th]_0$	$k_a \times 10^2$, min^{-1}	Cor coeff	k_2K, $M^{-1}\,min^{-1}$
1.03	1.24	2.12	12.0	1.61	0.999	11.4
1.03	1.55	2.10	15.0	2.06	0.999	11.7
1.03	1.24	1.06	12.0	2.36	0.999	16.7
0	1.24	2.12		*a*		

[a] Too fast to measure.

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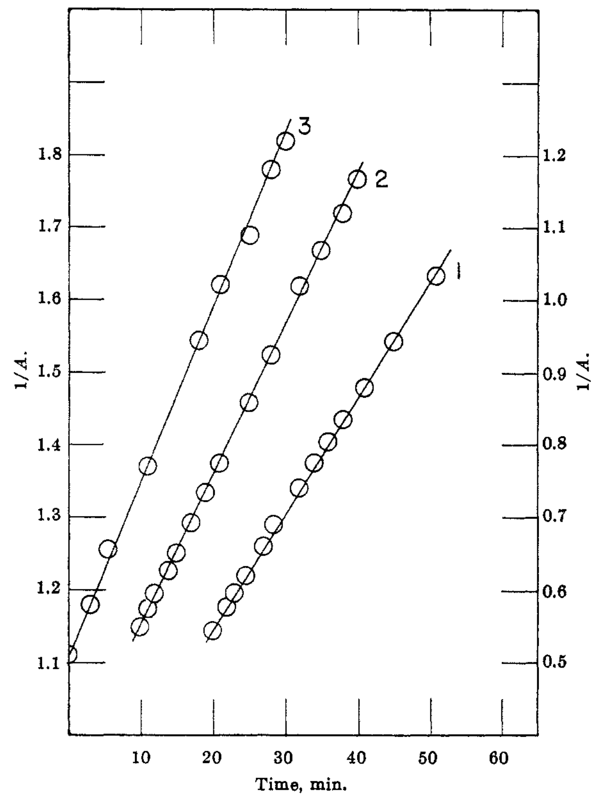

Figure 1.—Plot of $1/A_t$ *vs.* t for the disappearance of the thianthrene cation radical in aqueous acetonitrile. A is the absorbance at 546 mμ. The time scale for run 2 is shifted 10 min, and for run 1 20 min to the right. The $1/A_t$ scale for runs 1 and 2 are on the right and for run 3 on the left.

ever, it appears that the role of disproportionation in cation-radical reactions cannot be ignored.

Reaction of 1 with Halide Ion.—The results are given in Table III. Iodide ion reduces the cation radical effectively in a dry solvent. There is a competition in aqueous iodide solution between hydrolysis (presumably of the dication) and reduction. The reason for the high yield of **3** in the chloride ion experiment is not known since the solvent was dried carefully, but it is thought to be due to our inability to dry the lithium chloride (source of chloride ion) well enough. The formation of iodine and chlorine (albeit in small amount) is indicative of electron transfer from halide ion to the cation radical. The oxidation of chloride ion is not expected, and is not likely to proceed easily because of the closeness of the redox potentials: thianthrene, +1.35 V,[5] and chloride ion, −1.36 V,[20] *vs.* a normal hydrogen electrode. Two possible routes exist for the formation of 2-chlorothianthrene (ThCl, **4**), that is, eq 12 and 13–15. Each of these has been discussed earlier.[21]

Table III

Products of the Reaction of Thianthrenium Perchlorate (1) with Halide Ions

$[\mathbf{1}]_0 \times 10^2$, *M*	Halide ion (X^-)	$[X^-]_0 \times 10$, *M*	Solvent	Products, %[a] **2**	**3**	**4**	X_2	Recovery, %[b]
0.995	I^-	4.16	AN	85.8	0		88.3	85.8
3.70	I^-	4.14	Water	76.3	20.4		43.6	96.7
8.23	Cl^-	6.28	AN	46.8	32.9	0.3	9.2	80.1

[a] Compounds **2**, **3** and **4** were determined spectrophotometrically after sepration by tlc. Iodine was titrated directly. Chlorine was determined iodimetrically after displacement into potassium iodide solution by nitrogen gas. [b] Based on $[\mathbf{1}]_0$.

$$Th^{2+} + Cl^- \longrightarrow ThCl\ (\mathbf{4}) + H^+ \qquad (12)$$

$$Th\cdot^+ + Cl^- \longrightarrow Th + Cl\cdot \qquad (13)$$

$$2Cl\cdot \longrightarrow Cl_2 \qquad (14)$$

$$Th + Cl_2 \longrightarrow ThCl + HCl \qquad (15)$$

Reaction of 1 with Triphenylamine.—Solutions of **1** and triphenylamine were prepared in dry acetonitrile in separate, degassed vessels connected by a break seal. The molar ratio of **1** to triphenylamine was 1.1/1.0. The **1** was then added in three increments to the triphenylamine, each addition causing a change in the color of the solution and esr spectrum. Thus the violet, five-line esr characteristics of **1** gave way to green-brown three-line esr, followed by blue-brown five-line esr, and finally intense blue single-line esr characteristics, with a *g* value of 2.0036. The changes in the esr spectrum are similar to those observed by Stamires and Turkevitch[22] in the reaction of iodine with triphenylamine and are attributable to both spin exchange and dimerization phenomena after the cation radical of triphenylamine has been formed.

Reaction of 1 with Vinyl Monomers.—Solutions of **1** in dry, degassed acrylonitrile were stable for months. In contrast, **1** rapidly disappeared in nitromethane solutions of styrene, α-methylstyrene, ethyl vinyl ether, and 1,1-diphenylethylene. The first three compounds were polymerized, and the last formed a dimer. As yet we do not know the nature of the polymers. The dimer obtained from 1,1-diphenylethylene was the head-to-tail dimer, 1,1,3,3-tetraphenyl-1-butene,[23] rather than the head-to-head product, 1,1,4,4-tetraphenyl-1,3-butadiene, recently obtained by Szwarc by one-electron transfer from 1,1-diphenylethylene to antimony pentachloride.[24] Traces of water in our systems may have hydrolyzed **1** (*via* the dication) and so procuced enough hydrogen ion to catalyze the head-to-tail dimerization. The same possibility may pertain to work with the polymerizable monomers, so that these systems must be reinvestigated. It is quite evident, however, that **1** does not initiate free-radical reactions. Thus, **1** did not polymerize acrylonitrile and methyl methacrylate. Only those monomers were affected which were capable of sustaining a positive charge.

Thianthrenium Trichlorodiiodide (5).—Compound **5** is prepared by mixing solutions of thianthrene and iodine chloride in dry carbon tetrachloride.[1b] The salt precipitates immediately as a black, crystalline solid. Although carefully purified iodine chloride was used it is probably sufficient to use iodine chloride containing a small excess of iodine (which suppresses iodine trichloride formation), since the iodine reacts with thianthrene only to form a weak 1:1 complex[25] and, therefore, does not interfere with the salt formation.

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Interhalogens act not only as oxidizing agents,[26] but also as electron acceptors in donor–acceptor molecular complexes.[27,28] Little is found in the literature, however, on the reactions between iodine chloride and organic sulfides. Complexes have been reported for trithiane and *p*-dithiane,[29] and for 1,4-selenothiane.[30] In the last case the iodine chloride is thought to complex at the selenium rather than at the sulfur atom. In the case of thianthrene the stability of the cation radical and the insolubility of the salt lead to the very rapid and facile formation of **5**, the stoichiometry of which is given in eq 16.

$$2C_{12}H_8S_2 + 6ICl \longrightarrow 2C_{12}H_8S_2{\cdot}^+ I_2Cl_3^- + I_2 \qquad (16)$$

Compound **5** is stable at room temperature over periods of several weeks. Slow decomposition occurs during long storage. The solid is paramagnetic, giving a single, broad esr signal with $g = 2.0084$. Saturated solutions in nitromethane and 1,2-dichloroethane (DCE) gave the well-known, five-line esr spectrum, and the characteristic visible spectrum, λ_{max} 546 mμ, of the thianthrene cation radical.[4]

Attempts to recrystallize **5** were unsuccessful. The reasons for this are the low solubility of the solid, its sensitivity to water, and its decomposition in solution. The products of decomposition were thianthrene (**2**), thianthrene 5-oxide (**3**), and 2-chlorothianthrene (**4**). The origin of the oxygen in **3** is believed to be the water which remained in some solvents in spite of attempts at removing it.

Reactions of 5 in Solution.—The reactions of **5** in various solvents, which were subjected to various drying procedures, were monitored by ultraviolet and visible spectroscopy. The visible spectroscopic data are given in Table IV. The pertinent data for solutions of iodine, iodine monochloride, and the ICl_2^- ion are also given. Initially the 546-mμ peak of the thianthrene cation radical was detectable in DCE and acetonitrile (AN). The 429-mμ peak of iodine chloride was also detected in DCE. The other initial maxima listed in Table IV (346–400 mμ) are believed to be due to charge-transfer interaction between thianthrene and iodine chloride. The charge-transfer band for the thianthrene–iodine system in carbon tetrachloride lies at 375 mμ.[25] The band for the thianthrene–iodine bromide system lies near 350 mμ.[31] These data lead us to the conclusion that the charge-transfer band for the thianthrene–iodine chloride system should lie in the same region but be shifted by the solvent.

TABLE IV

MAXIMA OF BANDS IN VISIBLE SPECTRA

	λ_{max}, mμ				
				5	
Solvent	I_2	ICl	ICl_2^-	Initial	Final
DCE	500	426	338	374, 429, 546	478
DBE	495	409		375	478
Benzene	500	495		400	500
AN	365, 462	358	336	346	None

The initial bands disappeared in time. In the solvents DCE, 1,2-dibromoethane (DBE), and benzene the visible spectrum corresponded finally with that of a solution of free iodine and thianthrene in the same solvents. The spectroscopic data indicate that **5** dissociates in solution and that reactions of the dissociated ions take place. Products are given in Table V.

TABLE V

PRODUCTS (%) OF REACTION OF 5 IN VARIOUS SOLVENTS

	$[\mathbf{5}]_0 \times 10^3$,	Products, %			
Solvent	*M*	**2**	**3**	**4**	Total
DCE	3.11	33.3	15.8	12.4	61.5
DBE	5.18	31.9	28.2	8.2	68.3
Benzene	12.5	25.4	68.2	4.1	97.6
AN	7.95	47.2	37.5	6.3	91.0
Cyclohexane	7.30	28.3	48.6	*a*	76.9
Water	*b*	7.5	74.6	*a*	82.1
Water (NaI)	*c*	62.9	10.9	*a*	73.8

[a] Not detected. [b] 192.1 mg of **5** triturated with 250 ml of water. [c] 105.3 mg of **5** tritutated with 100 ml of sodium iodide solution.

Chlorine was detected in the vapor above a solution of **5** in DCE and other solvents. The formation of thianthrene 5-oxide (ThO, **3**) in all cases is attributed to the hydrolysis of the dication (Th^{2+}), firm evidence for which was obtained with the perchlorate salt and is given earlier. All of the organic solvents listed in Table V were dried carefully before use, but we must presume that in spite of this the solvents contained enough water to produce the 5-oxide (**3**). Compound **5** was used in concentrations of the order of 10^{-3} *M*, and the concentration of the water remaining in the dried solvents may well have been of this order, too.

The reaction of solid **5** with water gave a large amount of **3**. Probably, the rapid hydrolysis of iodine chloride, resulting in the formation of an excess of an oxidant (HOI), initiated the formation of so much of **3**. Similar treatment of the perchlorate salt (Table I) did not give an excess of **3**. Furthermore, inclusion of iodide ion in water added to solid **5** suppressed the formation of **3**. Instead the major product was thianthrene (**2**). The added iodide ion was available for reduction of the cation radical, the dication, iodine monochloride, and any HOI produced by hydrolysis.

We have already commented on the origins of the initial and final absorption maxima of the solutions (Table IV). It should be noted that iodine chloride itself is not stable in solution. Slow decomposition in DCE and benzene led ultimately to the formation of iodine. Decomposition in certain solvents has also been noted by others.[32-34]

It is apparent that the reactions of the thianthrene cation radical are complicated by those of the $I_2Cl_3^-$ ion. Complications are not experienced with the use of the perchlorate.

Reactions of Thianthrene in Sulfuric Acid.—At the time of the discovery that thianthrene was converted into the cation radical quantitatively in 96% sulfuric acid it was also found that the pouring of such a sul-

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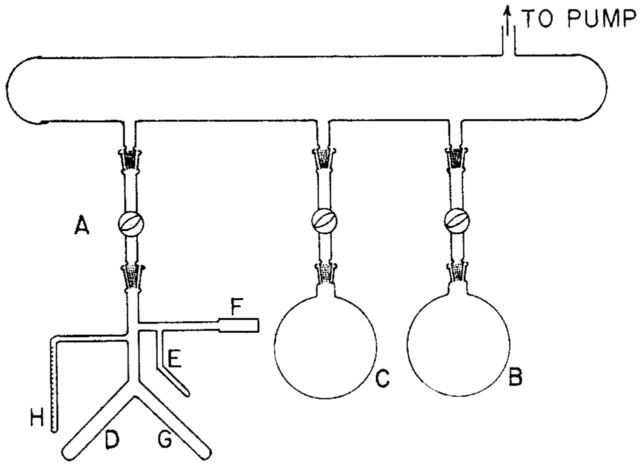

Figure 2.

furic acid solution onto ice gave almost equal amounts of thianthrene and thianthrene 5-oxide.[4] The mode of formation of the oxide was not known. It can be seen now that the most reasonable explanation involves the disproportionation of the cation radical in the aqueous sulfuric acid formed during contact with the ice.

Experimental Section

Spectra.—Visible and ultraviolet spectra were recorded with a Beckman Model DK-2A spectrophotometer. The far-infrared spectrum of **5** was recorded with a Beckman Model IR-11 instrument, using a Nujol mull between 0.5-mm polyethylene windows, and had broad maxima at 297 and 321 cm^{-1}. Esr spectra were recorded with a Varian Associates instrument, Model V4502. Field calibrations and g-value measurements were made with the customary frequency meters and counters, and the use of Fremy's salt in a dual-sample cavity.

Solvents were dried before use by distilling over phosphorous pentoxide through a 6-ft column. In certain experiments the solvents were redistilled *in vacuo* from other drying agents and a molecular sieve (see later).

Iodine chloride was prepared by the method of Buckles and Bader,[35] and had mp 27.5° and ϵ_{459} (CCl_4) 153 (lit.[25] mp 27.2° and ϵ_{460} 152).

Thianthrenium trichlorodiiodide (5) was prepared as described earlier.[1b]

Thianthrenium Perchlorate (1).—*Warning*: Although used without trouble for over 12 months, $Th\cdot{}^+ClO_4{}^-$ has proved to be extremely hazardous. A freshly made batch of 1–2 g exploded violently after being dried by suction and when being transferred to a petri dish from the sintered-glass filter. Explosion may have been initiated by the friction of transfer or by rubbing with a glass rod.

For some experiments the **1** was prepared by the method of Rundel and Scheffler.[10] Most of the work was carried out with **1** prepared as follows.[36] A solution of 0.5 g of **2** in 100 ml of carbon tetrachloride was added to a solution of 0.8 ml of perchloric acid (70%) in 50 ml of acetic anhydride and left overnight at room temperature. Dark, reddish brown crystals precipitated. These were filtered on sintered glass, washed with carbon tetrachloride, and dried under vacuum. The yield was generally greater than 90%. The value of ϵ_{546} (acetonitrile) was 8.5 × 10^3, which compares well with 8.9 × 10^3 obtained with thianthrene in sulfuric acid.[5] The five-line esr spectrum in acetonitrile had a g value of 2.0087.

Decomposition of 5 in Organic Solvents.—Enough **5** was weighed to give solutions in the millimolar range of concentration. Vigorous shaking was necessary to dissolve **5** quickly. A solution was kept for periodic recording of the absorption spectrum. When the peak of thianthrene cation radical in the visible range was no longer observed, the solution was streaked quantitatively on a tlc plate made from GF-254 silica gel (Brinkman). Thianthrene and 2-chlorothianthrene were separated clearly with cyclohexane (typical R_F values are 0.8 for 2-chlorothianthrene and 0.7 for thianthrene). Thianthrene 5-oxide remained at the origin and was developed later with benzene–ethanol (95:5 by volume). The bands of thianthrene and 2-chlorothianthrene were scraped off and leached with cyclohexane. Ethanol was used for thianthrene 5-oxide. Concentrations were then determined spectroscopically. The following extinction coefficients were used (all values are 10^4, M^{-1} cm^{-1}): thianthrene, 4.23 (258.7 mμ, cyclohexane); 2-chlorothianthrene, 4.48 (260.6 mμ, cyclohexane); thianthrene 5-oxide, 1.74 (239.3 mμ, ethanol).

Reaction of 1 and 5 with Water.—Both compounds gave a white precipitate when crushed under water. The white precipitate was filtered, washed, dried, and redissolved in acetonitrile for tlc separation and spectroscopic analysis as described above.

For the reaction of **1** with water in acetonitrile (Table I), a known amount of water was added to dry acetonitrile, and **1** was added. The disappearance of **1** was followed spectrophotometrically and when it was complete the solution was analyzed directly spectrophotometrically for thianthrene and thianthrene 5-oxide. The following extinction coefficients were used (all values × 10^4, M^{-1} cm^{-1}): thianthrene, 3.53 (256 mμ) and 1.69 (242.5 mμ); thianthrene 5-oxide, 0.82 (256 mμ) and 1.67 (242.5 mμ).

Kinetics.—The apparatus shown in Figure 2 was used. Acetonitrile, once distilled over phosphorus pentoxide, was placed over magnesium perchlorate in flask B. After degassing, some of the acetonitrile was distilled into C which contained freshly flamed molecular sieve (Linde, 4A). The acetonitrile in C was used for the kinetic work. A known amount of thianthrene was placed in D, and a known amount of **1** in E. A capillary containing a known amount of water was placed in G. The entire apparatus was evacuated on the diffusion-pump line, and solvent was distilled from C to E. The apparatus was tilted so as to transfer the solution of **1** from E to the cuvette F. The solvent was distilled back into C, leaving a film of **1** on the walls of F. Tube E was then removed by torch. Solvent was then distilled from C to H where its volume was measured. The measured volume was transferred to D to dissolve the thianthrene. The apparatus was then removed from the vacuum line above stopcock A. The solution of thianthrene was poured from D into G, and the capillary containing the water was broken by a magnet. The wet solution of thianthrene was transferred into F. The **1** dissolved very quickly and the disappearance of the cation radical was followed spectrophotometrically immediately at room temperature.

Reaction of 1 with Halide Ion and Triphenylamine.—All of the reactions were carried out on a vacuum line using two chambers connected by a break seal. A solution of **1** was prepared in one chamber and a solution of the reactant in the other. The solvent was acetonitrile which was dried and distilled as described in the kinetics section. Sodium iodide (Fisher) and lithium chloride (Baker-Adamson) were used. The lithium chloride was oven-dried. Iodine formed by reaction with potassium iodide was titrated directly at the end of the reaction. Chlorine formed by reaction with lithium chloride was carried by a stream of nitrogen into potassium iodide solution, also after the reaction was ended.

Registry No.—**1**, 21299-20-7; **5**, 12370-06-8.

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[35] R. E. Buckles and J. M. Bader, *Inorg. Syn.*, **9**, 130 (1967).

[36] See ref 8. We thank Dr. Lucken for informing us that the specification of chloroform as solvent in ref 8 is in error.