[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

Exchange Reactions of $SnCl_4$ with HCl and Organic Chlorides

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Rapid exchange of chlorine occurs between HCl and solid, liquid or gaseous $SnCl_4$ in Pyrex or quartz vessels. The rate of the surface-catalyzed exchange between the vapors can be decreased by fluorocarbon coatings or treatment of the surface with chlorine. CH_3Cl, *sec*-C_4H_9Cl, CCl_4 and CH_3CCl_3 do not exchange chlorine with $SnCl_4$ in several hours at 200° in the vapor state or when frozen out with $SnCl_4$ and melted. $(CH_3)_3CCl$ exchanges rapidly with liquid $SnCl_4$ and also at a readily measurable rate in the vapor phase both at 25 and 190°.

Introduction

Previous studies[1-3] in this Laboratory have demonstrated that solid aluminum chloride can exchange chlorine with gaseous organic chlorides and catalyze Friedel–Crafts alkylation reactions between gaseous reactants. In the present work we have investigated the occurrence of similar exchange reactions with $SnCl_4$ (m.p. −33.3°, b.p. 113°) which can be studied readily in the liquid and gas as well as with the solid phase.

Experimental

Reagents.—The HCl used contained HCl^{36}[4] which was prepared from its water solution by drying over P_2O_5 and passing through a P_2O_5 column on a vacuum system. The radioactive HCl was mixed with tank HCl (Matheson), which was passed through the same P_2O_5 column.

Bakers "C.P. analyzed anhydrous" $SnCl_4$ was distilled through a P_2O_5 column on the vacuum system and stored in the system. $SnCl_4$ slowly attacks silicone and fluorocarbon stopcock greases. Dry air was admitted to the $SnCl_4$ when it was necessary to regrease the stopcocks. Occasionally the $SnCl_4$ was distilled into a new flask on the system, the first and last fractions being discarded. Radioactive $SnCl_4$ was prepared by the exchange between HCl^{36} and liquid stannic chloride.

All the organic chlorides were distilled on the vacuum system through a P_2O_5 column. Methyl chloride, Matheson Co., and 1,1,1-trichloroethane, Dow Chemical Co., were used without further purification. The 2-chlorobutane, Matheson Co., was purified by stirring with concd. H_2SO_4 and fractional distillation. Mallinckrodt, "sulfur free," CCl_4 was purified by photochlorination and distillation. Eastman Kodak Co., white label, *t*-butyl chloride was passed through a silica gel column and then distilled.

Reaction Mixtures.—For gas phase experiments 300–500 ml. flasks of known volume, attached to the vacuum line through a stopcock, were used as reaction vessels. $SnCl_4$ was admitted to a known pressure of 5.53 mm. by opening stopcocks connected to the $SnCl_4$ reservoir which was held at 0°. After closing the stopcocks and evacuating the connecting tubing, a metered amount of the other reactant, HCl or organic chloride, was condensed in a small volume section of tubing between two stopcocks at the entrance to the reaction vessel. The entrance stopcock was then opened and the reactant allowed to rush in, the usual HCl pressure in the reaction mixture being about 18 mm. The reactants could be separated after as little as ten seconds of reaction by opening the stopcock to the separation trap. Reaction mixtures involving organic chlorides which did not exchange readily with $SnCl_4$ were prepared by freezing both reactants directly into the reaction flask.

Following each experiment with $SnCl_4$ and HCl the reactants were remixed, the exchange was allowed to go to completion in a Pyrex vessel, and the specific activity of the HCl was redetermined. From the latter value and the known amount of HCl used, it was possible to calculate the amount of $SnCl_4$ which had been in the reaction mixture. The results agreed well with those predicted from the vapor pressure and volume measurements, when glass surfaced reaction vessels were used, but were high when fluorocarbon, polyethylene or Teflon surfaces were used.

Separation Procedures.—CH_3Cl is volatile at −80° and was readily separated from $SnCl_4$ by passing through a trap at this temperature. The other organic chlorides except *t*-butyl were separated from $SnCl_4$ by freezing the reaction mixture into a trap containing degassed H_2O, melting, and distilling through P_2O_5 after the $SnCl_4$ had been hydrolyzed. Since *t*-C_4H_9Cl exchanges chlorine rapidly with liquid stannic chloride and with the HCl solution produced in the above separation, its mixtures with $SnCl_4$ were separated by bubbling through degassed water on the vacuum system. No method was found for separating gaseous mixtures of $SnCl_4$ and HCl without the occurrence of exchange in the separation process. In the most satisfactory methods found, the gases were either passed through a trap at −80° where the $SnCl_4$ condensed and the HCl passed through, or the mixture was frozen down with liquid air and the temperature then raised to −80° to allow the HCl to be taken off. Following carefully controlled procedures it was possible to obtain reproducibly a separation induced exchange which lay within the ranges of 65–75% and 40–50%, respectively, for the two methods.

Counting.—Following separation from the $SnCl_4$, the HCl or organic chloride was transferred on the vacuum line to the annular jacket of a glass walled solution-type Geiger counter. A manometer allowed the pressure of the gas in the annulus to be measured for the purpose of comparing specific activities of different samples. In the experiments with organic chlorides, where the $SnCl_4$ was separated by reaction with water, the water solution was removed from the system and counted. An experimentally determined conversion factor was used for comparing gas counting rates with solution counting rates. The initial specific activity of HCl samples was determined by counting them prior to exchange. When the activity was initially in $SnCl_4$, the specific activity of the latter was determined by counting HCl which had been equilibrated with it, since $SnCl_4$ would react with Hg in the manometer.

Results

Exchange of HCl with Solid $SnCl_4$.—Table I gives data for a typical experiment which demonstrated that chlorine exchanges rapidly between HCl and solid $SnCl_4$ at temperatures of −78 and −58°. The rate of transfer of radioactivity at a given temperature falls off with successive exposures because of the approach of the specific activity of the surface layers to that of the gas. After the rate has fallen off in this manner, it can be increased by melting and refreezing the $SnCl_4$. By comparing the alternate runs of Table I, made at two temperatures, it may be estimated that the temperature coefficient corresponds to an activation energy of about 3 kcal./mole.

Exchange of HCl with Liquid $SnCl_4$; Solubility of HCl in $SnCl_4$.—The solubility of HCl in $SnCl_4$ was determined by measuring the pressure exerted by a known amount of HCl metered into a flask of

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[1] C. H. Wallace and J. E. Willard, THIS JOURNAL, **72**, 5275 (1950).

[2] M. Blau and J. E Willard, *ibid.*, **73**, 442 (1951); **75**, 3330 (1953).

[3] M. Blau, W. T. Carnall and J. E. Willard, *ibid.*, **74**, 5762 (1952).

[4] Oak Ridge National Laboratories, Isotopes Catalog, item Cl 36-P (1952).

TABLE I

EXCHANGE OF HCl WITH SOLID $SnCl_4$ AT −78 AND −58°

4.1×10^{-4} mole HCl (40 mm. pressure); 3.4×10^{-4} mole $SnCl_4$ frozen on bottom of 135-ml. reaction flask, same solid surface throughout run; successive 10-second exposures of the same sample of HCl with *ca.* 30 min. between exposures.

T, °C.	Spec. act.[a] of HCl	Exchange, % of equilibrium	−log (1 − F)[b] Total	Δ
	9650	0.0		
−78	8840	9.8	0.045	0.045
−57	8010	21.0	.102	.057
−78	7680	25.6	.128	.026
−58	7100	33.4	.176	.048
−78	6830	37.1	.201	.025
	2200	100.0		

[a] Counts/min. per 10 cm. pressure of HCl in counting tube. [b] F is the fraction of equilibrium transfer of Cl^{36} from HCl to $SnCl_4$.

known volume containing a known amount of $SnCl_4$. The Henry's law constants are $6.6 \pm 0.5 \times 10^{-5}$ and $5.2 \pm 1 \times 10^{-5}$ mole fraction per mm. pressure at 0 and 27°, respectively.

It was demonstrated that rapid exchange occurs between liquid $SnCl_4$ and dissolved HCl by observing the rate of decrease in specific activity of the latter when exposed to the liquid for periods of 10 to 40 sec. at −31°. This temperature, which is just above the melting point, was used in order to minimize the amount of $SnCl_4$ vapor removed from the reaction vessel when the HCl was removed by cooling an adjacent trap with liquid air. The observed exchange was corrected on the assumption that complete exchange occurred with the $SnCl_4$ which distilled over during the separation. The amount of $SnCl_4$ transferred in this manner was determined by dissolving in water and titrating with standard base. Results of such measurements are given in Table II. The rate of transfer of radioactivity may be seen to decrease with increasing time of contact between the reactants. This is probably due to the slowness of diffusion from the gas phase into the solution. The amounts of reactants and volume of the vessel were such that about 12% of the HCl would have been in solution at any instant if solubility equilibrium were achieved.

TABLE II

EXCHANGE OF HCl WITH LIQUID $SnCl_4$ AT −31°

$3.8 \pm 0.2 \times 10^{-4}$ mole HCl (40 mm. pressure); 150×10^{-4} mole $SnCl_4$ (1.7 ml. liquid on bottom of 135-ml. reaction flask with 9 $cm.^2$ surface exposed)

Reaction time, sec.	Spec. act. of HCl[a] Initial	After reaction	% exch.[b] on sepn.	% exch. during reaction time
10	11050	6730	17.9	25.9
40	6730	2730	26.3	52.3
20	13460	6530	17.3	41.2
40	6530	2730	19.8	49.1

[a] Counts/min. per 10 cm. pressure of HCl in counting tube. [b] Calculated on the assumption of complete exchange with the $SnCl_4$ carried over with the HCl when it was removed.

Exchange of HCl with Gaseous $SnCl_4$.—Approximately 150 determinations were made of the extent of exchange between gaseous $SnCl_4$ and HCl for the purpose of finding: (a) the method of separating the reactants which would give the minimum and most reproducible exchange on separation; (b) a reaction vessel with a surface which would not catalyze the exchange, and would therefore be satisfactory for a study of the kinetics of the homogeneous exchange. The tests, which are described briefly below, have led us to conclude that the magnitude of the exchange on separation and the uncertainties in seeking a non-catalytic surface are so great that it would not be rewarding to make kinetic studies. All the runs reported in this section were made with 5.5 mm. pressure of $SnCl_4$ and HCl pressure between 16 and 25 mm.

Using a Pyrex flask coated with Hooker Electrochemical Co. Fluorolube GR 660 (by thoroughly swabbing it over the surface) the total exchange in the reaction vessel and separation trap in a series of 10 sec. runs and one 60 sec. run was between 64 and 75%, while a value of 87% was obtained for a 240 sec. exposure. Experiments of this type established the fact that the homogeneous gas phase exchange reaction is not instantaneous, and made it possible to conclude that the exchange on separation by passing through a trap at −80° lay in the range of 65–75%. There was some indication that this value increased with repeated use of the separation trap, but was returned to its original value by flaming the trap under vacuum.

A reaction vessel consisting of a 540-cc. polyethylene bottle (mounted in a vacuum desiccator in such a way that equal pressure could be maintained on both sides while filling it from a vacuum line) gave results similar to those obtained with the Fluorolube surface, while a 300-cc. vessel machined from Teflon and having a Teflon stopcock and Teflon end-plates lubricated with Fluorolube never gave less than 86% total exchange.

In all runs in vessels coated with Fluorolube and also in the Teflon and polyethylene vessels the amount of $SnCl_4$ recovered from the reaction vessel was found to be from 12 to 25% higher than that calculated from the volume of the vessel and the vapor pressure of $SnCl_4$ at the temperature at which the liquid was held when the vapor was introduced. This effect, which was not observed in Pyrex or silica vessels, was undoubtedly due to "dissolving" of $SnCl_4$ in the surface. It made a quantitative interpretation of the exchange results over the organic surfaces impossible, since the $SnCl_4$ was present in two phases. If exchange of HCl did not occur with the "dissolved" $SnCl_4$ but only with that in the gas phase, the percentage exchange with the vapor in fluorocarbon coated vessels was actually 5–10% units higher than calculated.

In contrast to the results with organic surfaces, Pyrex and silica reaction vessels which had been treated by evacuation for several hours with intermittent flaming always gave complete exchange even in 10 sec. runs, thus indicating the ability of the latter surfaces to catalyze the reaction.

It was discovered, by chance, that Pyrex flasks which had been exposed to Cl_2 gas did not catalyze the exchange of HCl with $SnCl_4$ as readily as untreated flasks. The effect of the treatment wore off as successive runs were made but could be regenerated by a new Cl_2 treatment. For example, reaction flasks freshly treated with Cl_2 always gave between 76 and 83% exchange in each of the first two 10-second exposures. Subsequent 10-second exposures without Cl_2 retreatment gave greater than 84% exchange. Longer exposures gave generally greater amounts of exchange. It may be estimated from the data that the rate of exchange between 5×10^{-4} mole of HCl and 1.6×10^{-4} mole of $SnCl_4$ in a 500-ml. flask was at least ten times faster in an untreated Pyrex flask than in one freshly treated with chlorine.

Absence of Exchange between $SnCl_4$ and Four Organic Chlorides.—The data of Table III show that chlorine does not exchange between gaseous $SnCl_4$ and gaseous CH_3Cl, $CH_3CHClC_2H_5$, CCl_4 or CH_3CCl_3 either at room temperature or when held at 200° for several hours. CCl_4 likewise gave no exchange when mixed with liquid $SnCl_4$ for several hours, and all of the organic chlorides of Table III could be frozen down with $SnCl_4$ and subsequently thawed without giving appreciable exchange. The last experiment of Table III, where HCl was added to the reaction mixture, shows that this compound does not exchange with CH_3CCl_3 or form a complex with $SnCl_4$ which exchanges in the vapor phase.

TABLE III

ABSENCE OF EXCHANGE BETWEEN FOUR ORGANIC CHLORIDES AND $SnCl_4$ IN THE GAS PHASE

Reactants	Moles $\times 10^4$[a]	T, °C.	Reacn. time, min.	Exchange, %
$SnCl_4$	1.5	25	1000	0.0
CH_3Cl	8.8			
$SnCl_4$	1.5	200	196	0.3
CH_3Cl	8.1			
$SnCl_4$	1.0	112	240	0.0
sec-C_4H_9Cl	3.0			
$SnCl_4$	1.5	25	1000	0.5
sec-C_4H_9Cl	4.3			
$SnCl_4$	1.5	200	180	1
sec-C_4H_9Cl	4.5			
$SnCl_4$	1.5	25	1080	0.1
CCl_4	4.8			
$SnCl_4$	1.5	195	360	0.3
CCl_4	2.5			
$SnCl_4$	1.5	195	300	0.2
CH_3CCl_3	3.8			
$SnCl_4$	1.5	200	330	0.3
HCl	4.5			
CH_3CCl_3	2.9			

[a] In 500-cc. Pyrex reaction vessel.

Exchange between $SnCl_4$ and *t*-Butyl Chloride.—Over 70% exchange occurs between liquid $SnCl_4$ and $(CH_3)_3CCl$ in five minutes at 25°. A readily measurable exchange also occurs in the gas phase, as illustrated by the data of Table IV. Essentially all of the rather irreproducible exchange in the five minute runs was caused by the separation process. If the values for longer times are corrected for this induced exchange, and if it is assumed that the reaction is first order with respect to each of the reactants, it may be calculated that the rate constant at 25° is about 0.2 liter $mole^{-1}$ $sec.^{-1}$ in the unpacked vessel. In the unpacked vessel there was an increase in rate by a factor of two to four in going from 25 to 190° corresponding to an over-all activation energy of less than 3 kcal./mole. On changing to a reaction vessel packed with short pieces of Pyrex tubing, which increased the surface area about fivefold, there was an approximately threefold increase in the rate of exchange at 25°, but, on the basis of one experiment, less change in rate at 190°. These observations suggest the possibility of a homogeneous reaction with a low activation energy together with a surface-catalyzed reaction with a negative activation energy, the latter being important only at low temperatures.

Following experiments in the 190–195° range, the organic vapors separated from the $SnCl_4$ contained a gas with a lower specific activity than the $(CH_3)_3CCl$, which could be distilled slowly from the latter at −80° on the vacuum system. Infrared spectra of the mixture showed strong peaks corresponding to about 74% $(CH_3)_3CCl$ and 24% isobutene in the original mixture. The absence of characteristic peaks showed that there was less than 3% of 2-chlorobutane and less than 2% each of *trans*-2-butene, *cis*-2-butene, or 1-butene present. No more than traces of isobutene were observed in experiments at 25 or 113°. From the equilibrium constant[5] for the reaction $(CH_3)_3CCl \rightleftarrows i\text{-}C_4H_8 + HCl$ it may be calculated that there would be about 98% dissociation at equilibrium at 200° and 4% at 25° at the pressures used in these experiments.

If dissociation equilibrium were established rapidly this would lead to rapid exchange between $SnCl_4$ and $(CH_3)_3CCl$, since HCl exchanges rapidly with $SnCl_4$. It may be calculated,[6] however, that with equilibrium at 98% decomposition, less than 0.1% exchange will occur through recombination in the time required for the 24% decomposition reported above. The contribution of the dissociation mechanism to the exchange observed in this work was therefore negligible.

Since HCl exchanges rapidly with $SnCl_4$, it was of interest to determine whether it also exchanges with $(CH_3)_3CCl$. A 12% exchange was observed in 276 min. at 25° in a 500-ml. reaction vessel containing 4×10^{-4} mole each of HCl and $(CH_3)_3CCl$. This was probably due completely to exchange on separation.

TABLE IV

EXCHANGE BETWEEN $SnCl_4$ AND $(CH_3)_3CCl$ IN THE GAS PHASE

All runs made in 500-ml. flasks with about 1.5×10^{-4} mole of $SnCl_4$ and 3×10^{-4} mole of $(CH_3)_3CCl$.

Time, min.	5	5	5	120	150	200	300	75
Temp., °C.	25	25	25	25	25	25	25	113
Exchange, %	17.5	10	26	41	68	82	73	52

			[a]				
Time, min.	45	60	10	30	30	30	30
Temp., °C.	190	195	25	25	25	25	190
Exchange, %	49	75	34	53	57	52	48

[a] These runs were made with a flask packed with glass tubing to increase the surface area by about fivefold.

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(5) G. B. Kistiakowsky and C. H. Stauffer, THIS JOURNAL, **59**, 165 (1937); D. Brearley, G. B. Kistiakowsky and C. H. Stauffer, *ibid.*, **58**, 43 (1936).

(6) R. A. Howald, unpublished.

Discussion

The exchange between hydrogen chloride and solid stannic chloride is much faster than the corresponding exchange with aluminum chloride.[3] This may be related to the existence of $SnCl_4 \cdot 2HCl$ as a stable crystalline solid[7] in contrast to the situation with $AlCl_3$ and HCl.[8]

The exchange between HCl and $SnCl_4$ in the vapor phase affords an interesting comparison to the exchange between HCl and Cl_2.[9] Both are rapid surface catalyzed exchange reactions over Pyrex or silica surfaces. Chlorine is a strong inhibitor of the HCl–$SnCl_4$ exchange; exposure to chlorine gas at low pressures (20 mm.) for an hour is sufficient to produce the effects reported here, and the rate of exchange rises only slowly over a period of several days with long periods of evacuation between runs. Conversely, we have found that complete exchange between HCl and Cl_2 is not attained in several hours in Pyrex reaction vessels which have been exposed to stannic chloride. This may be due completely to the dehydrating action of $SnCl_4$, as a similar effect is reported by Johnston and Walton[9] using B_2H_6. The most logical explanation of the effect of chlorine on vessels used for the HCl–$SnCl_4$ reaction requires extremely strong adsorption of Cl_2 on the Pyrex surfaces at the sites responsible for the HCl–$SnCl_4$ exchange.

The lack of exchange between $SnCl_4$ and most organic chlorides in the vapor phase is not surprising in view of the failure of exchange between CCl_4 and $AlCl_3$ vapor at 140°.[1] The occurrence of exchange with *t*-butyl chloride may be related to the ease of "carbonium ion" formation postulated from its reactivity especially in water solutions, but the relationship is not simple. The exchange does not proceed by recombination of HCl and isobutene, nor through a similar activated complex, since the activation energy for exchange is much lower than that for decomposition. No attempt was made to measure the amount of decomposition accurately, but there was a decrease in the rate of decomposition by a factor of at least five on decreasing the temperature from 190 to 110°.

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[7] A. Chretien and G. Varga, *Compt. rend.*, **201**, 1491 (1935).

[8] H. C. Brown and H. Pearsall, THIS JOURNAL, **73**, 4681 (1951); R. L. Richardson and S. W. Benson, *ibid.*, **73**, 5096 (1951).

[9] W. H. Johnston and W. F. Libby, *ibid.*, **73**, 854 (1951); W. H. Johnston and J. R. Walton, unpublished.

[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Optical Studies of Cerous Solutions[1]

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A study of the near ultraviolet absorption spectra of aqueous solutions of cerous perchlorate together with perchloric acid and sodium perchlorate has revealed evidence for the existence of a $CeClO_4^{+2}$ complex, for two new absorbance peaks located at about 2010 and 2110 Å. and for an isosbestic point located at about 2790 Å. The difference between the extinction coefficients of the two cerous species is greatest percentagewise at the peak located at 2960 Å. where the complex appears to absorb about one third as much light as the uncomplexed cerous ion. The values of the thermodynamic constants of the reaction $Ce^{+3} + ClO_4^- = CeClO_4^{+2}$ at 25° are $\Delta F^0 = -2.6$ kcal., $\Delta H^0 = -11.8$ kcal., and $\Delta S^0 = -31$ e.u. The absorpton spectra, of the solutions consist of three groups of peaks whose strongest peaks are separated by 5700 cm.$^{-1}$ and are located at 2215, 2530 and 2960 Å. The peaks in each group are separated by about 2300 cm.$^{-1}$; the two new peaks are satellites of the peak at 2215 Å. The highest peak is at 2530 Å. and has one satellite which is located at 2390 Å. and is the next highest peak. The 2960 Å. peak is the lowest of all and has no satellite. Evidence also has been obtained for the existence of a cerous sulfamate complex, $CeSO_3NH_2^{+2}$, whose formation constant is about one-fifth of the value of the perchlorate complex.

Cerous perchlorate in water forms colorless solutions whose absorption spectra have been known for some time[2] to consist of a number of peaks that are located between 2215 and 2960 Å. The cerous species in these solutions have been assumed to exist only as completely hydrated cerous cations whose extinction coefficients depend only upon the wave length of the absorbed light. The present study was made to determine more about the nature of the cerous species, their extinction coefficients and the equilibrium constants of any reactions involving them.

Materials.—The solutions were made up from conductivity water and were free of impurities in excess of more than a few tenths of 1%. Especial care was taken to avoid traces of iron, ammonium salts, nitrates, chlorides and suspended material. None of the solutions exhibited the Tyndall effect. Acidities and ionic strengths were adjusted with stock solutions of J. T. Baker analyzed reagent grade perchloric acid and sodium perchlorate.

The cerous perchlorate was prepared from G. F. Smith reference purity ceric ammonium nitrate. This was done in the following way.

About 25 g. of ceric ammonium nitrate was dissolved in 20 ml. of water in a 210-cc. porcelain casserole; the mixture was heated to complete solution and filtered if not clear. About 50 ml. of concd. (12 *N*) HCl was added to the clear solution. The resulting solution was boiled to dryness and the residue was heated strongly until the evolution of red fumes ceased. The solid obtained in this way was crushed into a fine yellow powder while it was still hot and it was then reheated strongly until fuming ceased.

The powder was allowed to cool and then 50 ml. of concd. HCl was added to it whereupon the mixture was stirred to produce a fine suspension to which was added enough (about 35 ml.) 30% H_2O_2 without preservative, to produce a clear colorless solution of cerous chloride. Care was taken to add the hydrogen peroxide in small enough portions to prevent frothing over. The resulting colorless solution was carefully boiled down to fine dry white crystals.

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[1] Appreciation is expressed to the Charles F. Kettering Foundation and to the Godfrey L. Cabot Fund of M. I. T. for financial support. This is publication No. 56 of the M. I. T. Solar Energy Conversion Project.

[2] (a) D. C. Stewart A.E.C.D.-2389; (b) D. M. Bose and P. C. Mukherji, *Phil. Mag.*, **26**, 768 (1938); (c) D. M. Yost, H. Russell, Jr., and C. S. Garner, "Rare-Earth Elements and their Compounds," John Wiley and Sons, Inc., New York, N. Y.