The effects of HCl, H_2O, KCN and KOH are at once evident on this scheme. The fact that the colored product is regenerated upon reillumination of partially decolorized solution is understandable when it is realized that the carbinol now undergoes photolysis reproducing the colored compound. We assume that Reaction I is instantaneous. (We have no evidence of an intermediate compound formed in Reaction Ia.) Reaction III may be slow or moderate, while IV is known to be comparatively slow from measurements with the pure carbinol. Reactions II plus IV were found to be fast compared to the time of measurement if hydrochloric acid was used during the photolysis. The dark reaction had a positive temperature coefficient.

Stability of Solutions

Neutral alcoholic (95%) solutions of malachite green oxalate and crystal violet chloride faded when stored in glass bottles. The former faded much more rapidly than the latter. Reliable color standards were obtained by addition of hydrochloric acid (in slight excess) to solutions of malachite green carbinol and crystal violet chloride. The mechanism proposed above affords a satisfactory explanation of the fading.

Solubilities

The solubility of the purified leucocyanide in ethyl alcohol (95%) was determined at several temperatures using precautions to approach equilibrium from over- and under-saturation. The rate of solution was slow. The solubility at 24.5° was 3.1×10^{-3} g. mole per liter. The concentration of the solution after saturation at 24.5° and after standing for five days at 0° in contact with the solid was 1.6×10^{-3} g. mole per liter. The concentration of leucocyanide in an absolute alcohol solution, originally 1×10^{-3} g. mole per liter, was 8.6×10^{-4} after remaining five days at −78° in contact with solid. (The solubility of crystal violet leucocyanide in ethyl alcohol (95%) at 24.5° was found to be 9.3×10^{-5} g. mole per liter, about 50% greater solubility than reported.[4])

Summary

The absorption spectra of the malachite green and crystal violet series have been presented and discussed. A study was made of the fading of the compound formed by photolysis of the leucocyanides, and of salts of malachite green. On the basis of these experiments a new mechanism for the "dark reaction" is proposed, in which the hydrolysis of the photo-compound is given the primary importance.

The solubility of malachite green leucocyanide was found to be about thirty times as large as that of crystal violet leucocyanide, a property indicating its preference for use in actinometry.

CAMBRIDGE, MASS. RECEIVED MARCH 6, 1935

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 348]

A Precision Actinometer for the Ultraviolet Region (Including an Exact Test of the Einstein Equivalence Law)

BY LOUIS HARRIS AND JOSEPH KAMINSKY

The coloration produced on illumination of alcoholic solutions of crystal violet leucocyanide by ultraviolet light has been proposed[1,2] as the basis of quantitative measurements of ultraviolet energy. We[3] have found that malachite green leucocyanide possesses some important advantages over crystal violet leucocyanide for use in actinometry. Our results indicate that an alcoholic solution of malachite green leucocyanide is admirably suited for a precision actinometer for the spectral region between 3340 and 2480 Å. The fact that malachite green leucocyanide is thirty times[3] more soluble than crystal violet leucocyanide (at 25°) permits a shorter cell length to be used and a certainty of 99.9% absorption. Furthermore, the correction for inner filtration by the photo-compound of the former is less than that by the photo-compound of the latter. The colorimetric measurements can be made more accurately for the green dye. Standard solutions

---

[1] Weyde, Frankenburger and Zimmermann, *Naturwissenschaften*, **18**, 206 (1930).

[2] Weyde and Frankenburger, *Trans. Faraday Soc.*, **28**, 561 (1931).

[3] Harris, Kaminsky and Simard, THIS JOURNAL, **57**, 1151 (1935).

of the green dye[3] (prepared from the carbinol) are not so susceptible to changes of transmission in the visible with varying acid content as the corresponding solutions of violet dye. In addition greater intensities may be measured with the more soluble salt.

Materials.—The materials used have been described.[3]

Apparatus.—The light of a quartz-mercury vapor lamp, operated from a motor generator set, was focused on the slit of a Leiss monochromator. The lamp was maintained over ten-hour intervals at constant (within 1%) energy output in the ultraviolet. Both entrance and exit slits of the monochromator were set at 0.2 mm. width and 5.0 mm. height at all wave lengths except at 3130 Å. where 0.10 and 0.15 mm. slit widths were used. Spectrograms of the light emerging from the exit slit (taken with an auxiliary spectrograph) showed negligible amounts of false light for each wave length. Many of the errors inherent in the usual thermopile–galvanometer system were eliminated by the experimental arrangement. An excellent survey of the field has been given.[4] The effects of diverging light were eliminated through conversion from a surface to line thermopile (Kipp micro-thermopile) by means of a narrow slit close to the surface and through the use of an additional quartz lens to focus the light from the monochromator, so that the light just failed to fill the narrow (1 mm. wide) thermopile slit. The carefully prepared bismuth-black thermopile surface was assumed to eliminate any selectivity with wave length and the reflection loss was assumed to be negligible. Micrometer screw adjustments on the thermopile shield box permitted fine adjustment of the thermopile in 3 orthogonal directions. The thermopile was connected with an L. & N. H. S. galvanometer having a sensitivity of 0.2 microvolt per mm. at 1 meter, while the readings could be made to 0.2 mm. with the scale at a distance of 5 meters. No quartz window, which would have introduced corrections, was employed before the thermopile. The reaction cell was in the form of a parallelepiped $1.01 \times 2.03 \times 3$ cm. (inside dimensions) with the edges fused together. Transmission measurements of the five fused quartz faces were made before the cell was assembled and were in agreement with the transmission of the assembled cell. The Bausch and Lomb Duboscq colorimeter was fitted with a micro-attachment. Using the necessary precautions, an accuracy of 1% was obtained in determining concentrations of the dye (and of the photo-compound) between 1.0×10^{-6} and 5.0×10^{-5} g. moles per liter.

Experimental Procedure

After the lamp had reached a steady state, the energy was measured with the thermopile–galvanometer system. An alcoholic (95%) solution of malachite green leucocyanide (3.02 cc.) was then placed in the reaction cell, which was maintained in a definite position in a cell holder by means of 2 springs and 2 milled brass uprights. The cell was arranged so that the light beam entered at normal incidence. One or two drops (0.01 cc. per drop) of 3 *N* hydrochloric acid were added to eliminate the dark reaction.[3] Tank nitrogen, first bubbled through alcohol (95%), was passed through a fine tapered quartz capillary (placed in the solution outside of the light beam) to obtain efficient stirring. The solution was illuminated for a definite time interval, four to twenty minutes. At the end of the exposure, some of the photolyzed solution was transferred to one micro-cup of the colorimeter. To the other cup was added a standard dye solution containing an amount of acid equivalent to that present in the photolyzed solution. After some preliminary measurements, it was found best to wait approximately five minutes after exposure before analyzing colorimetrically. Three measurements were made and the results averaged.

Corrections.—The largest correction was due to the reflection loss at the first air–quartz surface for perpendicular incidence. The transmissions of the fused quartz plates (all of which had the same transmission) used for the reaction cell were determined with the aid of a quartz photoelectric cell, connected with a direct current amplifier and galvanometer used in conjunction with the above monochromator.

TABLE I

TRANSMISSIONS

Wave length in Å.	Number of plates	Average transmission
2537	1	0.871
2537	2	0.760 ($\sqrt{0.760}$ = 0.872)
2654	1	0.890
2654	2	0.803 ($\sqrt{0.803}$ = 0.896)
2967	1	0.901
2967	2	0.821 ($\sqrt{0.821}$ = 0.906)
3130	1	0.902 ± 0.005
3130	2	0.821 ($\sqrt{0.821}$ = 0.906)
3660	1	0.909

In addition to the reflection loss at the air–quartz surface, a correction of 0.4% was made for the reflection loss at the first quartz–alcohol surface.

A correction was made for the average amount of light absorbed by the photo-compound. At each wave length, except at 3342 Å., the effective length of the leucocyanide solution necessary to absorb 99.9% of the incident radiation was calculated from the concentrations and extinction coefficients. Using this length, the absorption by the photo-compound at the end of the exposure was calculated from its concentration (colorimetrically determined) and extinction coefficients. By averaging this absorption with the absorption at the start (by the photo-compound), which is zero, a correction factor was calculated for the average absorption by the photo-compound during the photolysis. A small correction was also necessary for the slight amount of colored substances present in the leucocyanide solution to which acid had been added just before exposure. This and the preceding correction, collectively, were of the order of 1 to 2%. For wave lengths greater than 2537 Å., the absorption by the alcohol (95%) was determined and found to be negligible. At 2537 Å. a correction factor for the absorption by the alcohol was determined for a solution containing 10^{-3} g. mole per liter of the leucocyanide and was found to be 1.004, and for 5×10^{-4}, 1.007. At 2482 Å. the correction factor was 1.018 for 5×10^{-4} g. mole per liter.

Blanks.—By means of blank determinations, no chemical change caused by the extraneous light in the room was de-

---

[4] Leighton and Leighton, *J. Phys. Chem.*, **36**, 1882 (1932).

tected for the intervals of photolysis employed. An effective demonstration of the absence of false light was obtained when no measurable galvanometer deflection could be obtained on placing the leucocyanide solutions used in the quantum yield determinations in front of the thermopile.

Calculation of the Quantum Yields

The following constants and variables were used in the calculation of the quantum yields (Φ)

a = concentration in g. mole per liter of the photo-compound as determined with standard solutions of dye prepared from carbinol
b = the correction factor for the absorption by the photo-compound of concentration a
l = liters of solution employed for each photolysis (0.00302)
N = Avogadro's number = 6.063×10^{23}
h = Planck's constant = 6.554×10^{-27} erg sec.
c = velocity of light = 3.00×10^{10} cm. per sec.
d = galvanometer deflection in cm.
t = time of photolysis in sec.
r = 1 − fraction of light absorbed (fraction of light absorbed = $^1/_2$ measured absorption of the first quartz plate in air, plus the reflection loss at the first quartz–alcohol surface)
f = calibration factor in ergs per second per cm. deflection
λ = wave length in cm.

$$\text{Therefore } \Phi = \frac{a \times b \times l \times N \times h \times c}{d \times t \times r \times f \times \lambda}$$

Data

The calibration of the thermopile–galvanometer system was carried out against standard lamps C-112 (old) and C-203 (new) previously calibrated by the Bureau of Standards. Sufficient measurements were taken to enable the use of only the more accurate values obtained for 0.300 and 0.350 ampere passing through the lamps. The value of f was found to be 5.359 ± 0.016 erg per second per cm. deflection.

Quantum Yields

TABLE II

(3.02 cc. of solution photolyzed)

Number of run	Concn. of leucocyanide	Cm. deflection, d	Time in sec., t	Concn., a	Corr. factor, b	Φ	Av. Φ
				2537 Å.			
1	5.00×10^{-4}	6.73	600	1.39×10^{-6}	1.004	0.992	
2	5.00×10^{-4}	6.65	600	1.36×10^{-6}	1.004	.981	
3	5.00×10^{-4}	6.70	600	1.40×10^{-6}	1.004	1.002	
4	5.00×10^{-4}	6.52	600	1.35×10^{-6}	1.004	0.993	1.003 ±
5	5.00×10^{-4}	6.52	900	2.03×10^{-6}	1.006	.996	0.013
6	5.00×10^{-4}	6.65	1200	2.86×10^{-6}	1.008	1.032	
7	1.00×10^{-3}	6.61	1200	2.84×10^{-6}	1.004	1.026	
8	1.00×10^{-3}	6.64	900	2.11×10^{-6}	1.003	1.011	
9	1.00×10^{-3}	9.23	720	2.32×10^{-6}	1.003	1.000	
10	1.00×10^{-3}	9.62	727	2.43×10^{-6}	1.003	0.996	
				2654 Å.			
1	1.00×10^{-3}	6.63	1200	3.02×10^{-6}	1.002	1.022	
2	1.00×10^{-3}	6.63	1200	3.00×10^{-6}	1.002	1.015	
3	1.00×10^{-3}	6.63	600	1.46×10^{-6}	1.001	0.989	
4	5.00×10^{-4}	6.70	1200	2.97×10^{-6}	1.004	.997	
5	5.00×10^{-4}	6.69	600	1.50×10^{-6}	1.002	1.007	1.007 ±
6	5.00×10^{-4}	7.55	603	1.74×10^{-6}	1.002	1.030	0.012
7	5.00×10^{-4}	7.18	600	1.58×10^{-6}	1.002	0.988	
8	5.00×10^{-4}	7.32	600	1.65×10^{-6}	1.002	1.013	
9	5.00×10^{-4}	7.36	600	1.64×10^{-6}	1.002	1.000	
10	5.00×10^{-4}	7.34	1200	3.25×10^{-6}	1.004	0.996	
11	5.00×10^{-5}	7.44	600	1.66×10^{-6}	1.022	1.021	
				3130 Å.			
1	1.00×10^{-3}	6.53	540	1.52×10^{-6}	1.018	0.994	
2	1.00×10^{-3}	6.70	420	1.22×10^{-6}	1.015	.997	
3	1.00×10^{-3}	6.70	360	1.01×10^{-6}	1.012	.962	
4	1.00×10^{-3}	7.07	420	1.31×10^{-6}	1.016	1.014	0.995 ±
5	1.00×10^{-3}	7.04	360	1.067×10^{-6}	1.012	0.964	.018
6	1.00×10^{-3}	7.12	540	1.63×10^{-6}	1.021	.981	
7	1.00×10^{-3}	10.76	246	1.16×10^{-6}	1.012	1.004	
8	1.00×10^{-3}	9.745	487	2.08×10^{-6}	1.026	1.020	
9	1.00×10^{-3}	10.10	360	1.61×10^{-6}	1.020	1.023	

Some tentative values, not as accurate as the above, are presented next.

TABLE II (*Concluded*)

Number of run	Concn. of leucocyanide	Cm. deflection, d	Time in sec., t	Concn., a	Corr. factor, b	Φ	Av. Φ
				2482 Å.			
1	5.00×10^{-4}	3.31	915	1.063×10^{-6}	1.004	1.048	
2	5.00×10^{-4}	3.35	913	1.086×10^{-6}	1.004	1.058	1.046
3	5.00×10^{-4}	3.34	900	1.041×10^{-6}	1.004	1.033	
				2967 Å.			
1	5.00×10^{-4}	6.03	480	1.18×10^{-6}	1.017	0.991	0.994
2	5.00×10^{-4}	6.04	420	1.04×10^{-6}	1.015	.996	
				3342 Å.			
1	1.00×10^{-3}	3.32	1200	1.54×10^{-6}	$1.01 \div 0.842$	0.982	0.985
2	1.00×10^{-3}	3.35	1200	1.56×10^{-6}	$1.01 \div .842$	.987	

In none of the measurements was the shade of green of the photo-compound different from the shade of green of the standard dye solution. The temperature of the room during the period of measurements was between 26 and 29°. In all the runs at 2537 Å., as well as in run numbers 1 to 5 at 2654 Å., the length of the solution layer was 1.01 cm., while in all the other runs the length of the solution layer was 2.03 cm. At 3342 Å. the leucocyanide absorption was calculated from an accurate measurement with the photoelectric cell outfit. The transmission of the quartz plates of the reaction cell was not measured at 3342 Å. nor at 2482 Å. At the former wave length it was assumed to be the average of that at 3130 and 3660 Å., namely, 0.906. At 2482 Å. it was assumed to be 0.5% lower than the transmission at 2537 Å. Since in every run but one less than 1% of the leucocyanide was transformed, the effective length did not change by more than 1%.

Discussion of the Quantum Yield Determinations

The attempt was made to measure Φ as accurately as possible at 2537, 2654 and 3130 Å., in order to make an exact test of the Einstein equivalence law. The following factors were used in the calculation of the over-all error in these measurements. The errors of 0.2% in the calibration of the pipet and in the determination of the time are of no importance here. The errors in Φ at 2537 and 2654 Å. will be considered first. The concentration of the photo-compound was determined within 1%, the absolute energy to 1.4%, the galvanometer deflections to 0.5%, and the reflection losses to 1%. These are maximum values. The over-all error in absolute value of Φ (calculated by the method of partial errors) is 2.1% with a reproducibility of 1.3%. At 3130 Å. the inaccuracy of the colorimetric determinations is increased to 1.5%, because smaller amounts of photo-compound were formed on the average. The over-all error is 2.4%. Hence the equivalence law holds at these wave lengths within the experimental error.

At 2967 Å. the error is also about 2.5%, while at 2482 Å. it is about 3% because of the greater uncertainty in the reflection loss. At 3342 Å. the over-all error is slightly greater than 3% since an additional error of about 1.5% is introduced in the correction for the light transmitted by the solution.

Direct Comparisons with the Precision Actinometer

Direct comparisons were made against our precision actinometer to determine the effects of different factors on Φ. It did not vary with concentration over a 10-fold range at the two wave lengths tried. No measurable difference was found for the photolysis with stirring and without stirring for exposure periods up to eleven minutes for the intensities employed. (We would not advise, however, that stirring be dispensed with.) Results obtained with the macro-colorimeter were in agreement with those determined with the micro-colorimeter within the experimental error. The photolysis of the leucocyanide was tested at 2537 and 3130 Å. to determine whether the amount of photolysis was strictly proportional to the amount of light absorbed. The highest intensity was reduced by means of calibrated screens placed in front of the monochromator. The reciprocity law was found to hold within the experimental error of 2–3% over a 25-fold range of intensity. It was assumed to hold also at the other wave lengths used.

Ratio Method of Comparison

After it was found that the reciprocity law was valid, a null instrument was arranged which eliminated the effects of variations of the light source and difficulties inherent in the measurement of absolute energies. Alcoholic solutions of the malachite green leucocyanide were placed in two fused quartz cells of different volumes. The light beam, after passing through a lens beyond the exit slit of the monochromator, was divided into two beams of unequal intensity by means of a polished quartz plate mounted at an angle of approximately 45° to the direction of the original beam. The transmitted beam of greater intensity entered the cell with the larger volume of solution. The reflected beam entered the other cell at perpendicular incidence. The procedure consisted in exposing both solutions for a definite time, then analyzing colorimetrically. Corrections were then made as described above for the average amounts of light absorbed by the photo-compounds. The ratio of the equivalents of photo-compound formed in the two cases is equal to the ratio of the energies of the respective light beams incident on the alcoholic solutions (not on the quartz faces). The determination of Φ of another reaction, or the same reaction under different conditions, could then be calculated by use of this ratio. In practice, the precision actinometer solution was placed in one cell and the other solution, which absorbed completely, in the second cell. After the photolysis had proceeded sufficiently long the precision actinometer solution was analyzed colorimetrically and the correction for absorption by the photo-compound was applied. Then, by means of the predetermined ratio, the energy incident on the other solution studied was calculated. The chemical change in the second cell was determined and Φ calculated. Several runs with this ratio method yielded a precision of 1% and an accuracy of 3%.

Temperature Coefficients.—The temperature coefficients of the photolysis were determined by the ratio method. The solution, the temperature of which was varied, was cooled or warmed previous to photolysis and maintained at the desired temperature within a degree while the precision actinometer solution remained at room temperature. At the low temperatures, air was blown over the face of the cell to prevent condensation of water vapor. The following results were obtained

$$\text{at 2537 Å.:}\quad \begin{aligned} \Phi_{17^\circ+10^\circ}/\Phi_{17^\circ} &= 1.007\\ \Phi_{20^\circ+7^\circ}/\Phi_{7^\circ} &= 0.987\\ \Phi_{10^\circ+27^\circ}/\Phi_{27^\circ} &= 1.013 \end{aligned}$$

$$\text{at 3130 Å.:}\quad \begin{aligned} \Phi_{10^\circ+27^\circ}/\Phi_{17^\circ} &= 1.027\\ \Phi_{20^\circ+7^\circ}/\Phi_{7^\circ} &= 1.03\\ \Phi_{10^\circ+27^\circ}/\Phi_{27^\circ} &= 1.015 \end{aligned}$$

The temperature coefficients are essentially unity.[5]

With the aid of the ratio method, the effects of different conditions on Φ of the photolysis of the leucocyanide were redetermined and the results were found to be in good agreement with those obtained by the direct comparison method. In addition, Φ was the same in absolute as in 95% alcohol at 2537 Å.

Quantum Yield for the Photolysis of Monochloroacetic Acid.—This reaction has been carefully studied.[6] Using the precision actinometer the ratio method was applied to the redetermination of Φ at 2537 Å. We found $\Phi_{\text{Cl-HAc}} = 1.07$ (with an accuracy of 5.5%) for the 1 *N* acid, in good agreement with the published value. The difficulties of analysis for the small quantity of chloride are the cause of the greater inaccuracy in the case of the monochloroacetic acid.

Quantum Yields for the Photolysis of Crystal Violet Leucocyanide.—Quantum yields were redetermined by the ratio method and by direct measurement with the thermopile–galvanometer system. The results obtained, accurate to 3%, are as follows.

TABLE III

Wave lengths in Å.	Φ		
2537	0.99	1.00	1.02
2654	.99	1.01	
3130	.98		
2654	1.01 (by direct measurement)		

These values agree with those reported,[3] within their experimental error.

Summary

With the view of eliminating as many errors as possible by the proper experimental arrangement, a critical analysis was made of quantum yield measurements. The Einstein equivalence law has been found to hold for the photolysis of malachite green leucocyanide with an accuracy of 2.5% in absolute value and an average precision of 1.4% for three wave lengths. This accuracy is considerably greater than previously attained in such measurements. An actinometer using this solution is especially adapted for the measurement of very small light energies. A standard actinome-

---

(5) It may be mentioned that a qualitative experiment indicated that the quantum yield at −78° in absolute alcohol is the same as that at room temperature, and the dark reaction is very small.

(6) E. Rudberg, *Z. Physik*, **24**, 247 (1924).

ter employing this substance has been proposed and the effects of different conditions upon the behavior have been examined. A null method of comparison has been proposed and found satisfactory to 3% in absolute value. Other variations of the standard actinometer (as the temperature coefficients) were investigated with the aid of this null method. Other actinometers which used monochloroacetic acid and crystal violet leucocyanide were tested and found to be less desirable.

CAMBRIDGE, MASS. RECEIVED MARCH 6, 1935

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

Observations on the Rare Earths. XLIV. Preparation of Anhydrous Rare Earth Compounds by the Action of Fused and Solid "Onium" Salts on the Oxides

BY JAMES B. REED WITH B. S. HOPKINS AND L. F. AUDRIETH

Recent studies on the solubilities of rare earth compounds in non-aqueous solvents[1] and on the preparation of rare earth amalgams by electrolysis of non-aqueous solutions of their salts[2] have brought about the necessity of preparing anhydrous rare earth compounds, reasonably free from basic materials, and in considerable quantities. The compounds most extensively used in these studies are the halides which are exceptionally difficult to prepare in the anhydrous form. None of the many methods previously suggested for their preparation have proved entirely satisfactory when applied to relatively large quantities.

It has been found that oxides of typical rare earth elements such as lanthanum, neodymium, samarium and yttrium dissolve in such fused salts as pyridine hydrochloride,[2d] ammonium nitrate,[2a] hydrazine hydrochloride, hydroxylamine hydrochloride, ammonium thiocyanate[3] and ammonium acetate.[4] They react with solid ammonium chloride, ammonium bromide and ammonium iodide. These reactions are all of the same general character and may be represented by the typical equation

$$La_2O_3 + 6NH_4Cl = 2LaCl_3 + 6NH_3 + 3H_2O$$

This reaction is readily understood if it is recognized that "onium" salts in the fused and solid states are acids according to the Brönsted definition.[5] In spite of the fact that water is one of the reaction products, the presence of excess ammonium chloride, by virtue of its acidic nature, prevents the hydrolysis of the lanthanum chloride. Hence, when carried out under proper conditions the above reaction and others of the same type may be used for the preparation of anhydrous rare earth compounds.

Experimental

Preparation of Anhydrous Rare Earth Chlorides.[6]—When ammonium chloride and oxides of the rare earth elements are mixed by grinding together in a mortar the odor of ammonia becomes distinctly noticeable, indicating that some reaction takes place even at room temperature. Up to a temperature of about 190° the reaction appears to be a very slow one, but above this temperature it proceeds vigorously. If twice the theoretical amount of ammonium chloride is used (for instance, 150 g. of NH_4Cl to 75 g. of Nd_2O_3) the reaction mixture soon becomes completely soluble in water.[7] A considerable portion of the

---

[1] Hopkins and Quill, *Proc. Nat. Acad. Sci.*, **19**, 64 (1933).

[2] (a) Audrieth, Jukkola, Meints and Hopkins, THIS JOURNAL, **53**, 1805 (1931); (b) Meints, Hopkins and Audrieth, *Z. anorg. allgem. Chem.*, **211**, 237 (1933); (c) Jukkola, Audrieth and Hopkins, THIS JOURNAL, **56**, 303 (1934); (d) Hopkins and Audrieth, *Trans. Am. Electrochem. Soc.*, **66**, 135 (1934).

[3] The resulting product composed of an intimate mixture of rare earth thiocyanate and excess ammonium thiocyanate is soluble in alcohol, acetone, pyridine and liquid ammonia.

[4] Lanthanum and neodymium oxides dissolve quite readily in fused ammonium acetate, whereas only incomplete reactions occur when the less basic rare earth oxides are employed. If these melts are heated in a vacuum at temperatures between 130–150° residues consisting essentially of the anhydrous acetates may be obtained.

[5] Audrieth and Schmidt, *Proc. Nat. Acad. Sci.*, **20**, 221 (1934).

[6] Various methods are listed in the literature for the dehydration of hydrated chlorides by heating in the presence of an excess of ammonium chloride. These procedures usually involve the addition of a large excess of ammonium chloride to a saturated solution of the chloride, after which the solution is evaporated to dryness and the mixture heated carefully by itself or in an atmosphere of hydrogen chloride. The method described by the authors not only eliminates this cumbersome procedure, but effects a considerable saving of time. The essential principle of preventing basic salt formation by the presence of the "onium" salt seems not to have been clearly defined heretofore and its elucidation (see Ref. 5) has enabled the authors to apply this method to the preparation of many other anhydrous chlorides.

It should be pointed out that Hodgkinson [*J. Soc. Chem. Ind.*, **33**, 445 (1914)] describes a method for the preparation of anhydrous chlorides, by mixing the oxides with a small excess of ammonium chloride and gradually dropping the mixture into a red hot crucible. Repeated trials of this method have shown that complete reaction is never obtained and that considerable loss of material is involved.

[7] In the case of cerium dioxide complete conversion to the chloride was not obtained.