pure methane and with methane diluted about 1:1 with nitrogen and with steam, were shown in Table IV and plotted in Fig. 4. A straight line was drawn through the four points for pure methane decomposition; the three points with nitrogen fell reasonably close to this line and the two almost identical points with steam fell on the line. Since the first-order "constants" for pure methane over this range of contact times increased some 36%, these plotted results were quite interesting because they indicated a first-order decomposition. It may be noted in Table IV that the percentages of acetylene in the exit gas for the same percentage of methane decomposed were not very different for these various cases. One possible way the observed results may be explained was by assuming that, in the rate of decomposition of methane, the effect of surface and of acetylene depended on the concentration of methane to the first power; the acetylene and surface may be to any power. Kassel[4] has already shown the homogeneous decomposition to be first order at somewhat lower temperatures.

Acknowledgments.—I should especially like to thank Dr. R. A. Friedel and his group, including Mr. A. G. Sharkey, Jr., Mr. C. R. Humbert, Mrs. G. Bloom, and Miss H. R. Borgman, for their kindness in analyzing the off-gas from each run with the mass spectrometer. I should like to express my appreciation to Dr. Helmut Pichler for illuminating discussions of the results, and to Dr. H. H. Storch, chief of the synthetic liquid fuels research program, for his encouragement during this research. Mrs. Norma Golumbic read the manuscript critically and made many valuable suggestions.

Summary

The decomposition of methane has been studied in a porcelain tube at temperatures between 1007 and 1075°. The following observations were made:

1. Within this range the first-order reaction constants increased with increasing decomposition.
2. There was a catalytic effect of acetylene, probably homogeneous, which accounts for (1), since the percentage of acetylene increased with increasing percentage of decomposition.
3. There was probably no effect of ethylene on the decomposition of methane.
4. There was a large catalytic effect of surface in the early stages of the reaction which disappeared by the time 30% of the methane was decomposed.
5. No induction period was found.
6. In the early stages of the decomposition, 50% nitrogen or steam in the entering gas resulted in about the same percentage of decomposition of the methane for equal contact time.

PITTSBURGH, PENNSYLVANIA RECEIVED APRIL 11, 1947

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

The Effect of Activator Concentration on the Infrared-Sensitive Phosphor, Strontium Sulfide–Samarium, Europium[1]

BY KENNETH F. STRIPP AND ROLAND WARD

The recognition by Urbach[2] that the double activator principle permits long storage of energy in infrared-sensitive phosphors at room temperatures led to the development of his Standard VI phosphor. This material was originally prepared by heating a mixture containing approximately 70% strontium sulfide, 25% strontium sulfate and 5% calcium fluoride to which samarium and europium salts had been added. It has been shown[3] that the strontium sulfate and calcium fluoride constitute the flux for this phosphor and that the sulfate may cause some oxidation to occur.

In attempts to simplify the composition of these phosphors, it was found that satisfactory fluxing could be obtained with strontium chloride. The only complication which this flux may cause is the introduction of chloride ions. The lattice constants from pure strontium sulfide and from strontium sulfide fluxed with strontium chloride were the same within experimental error, indicating a very limited solubility of the chloride in the sulfide. The luminescent characteristics of phosphors prepared in this way appeared to be much more consistent than those obtained by the Lenard procedure so that it was thought worthwhile to undertake a more critical determination of the optimum concentrations of the activators.

Experimental

(a) The Preparation and Measurement of Samples.—Pure strontium sulfate obtained by precipitation from purified strontium nitrate solution[4] was reduced to the sulfide by heating in silica glass boats to constant weight in a stream of dry hydrogen or hydrogen sulfide. The products were white powders which showed neither fluorescence nor phosphorescence on exposure to ultraviolet radiation.

Strontium chloride solution was purified by a procedure

---

(1) This work was carried out at the Polytechnic Institute of Brooklyn under Contract NObs 28370 with the Bureau of Ships.

(2) F. Urbach, D. Pearlman and H. Hemmendinger, *J. Optical Soc. Am.*, **36**, 372 (1946).

(3) W. Primak, R. K. Osterheld and R. Ward, THIS JOURNAL, **69**, 1283 (1947).

(4) A. L. Smith, R. D. Rosenstein and R. Ward, *ibid.*, **69**, 1725 (1947).

similar to that described for strontium nitrate.[4] The strontium chloride hexahydrate was crystallized from this solution and dried at 200° to give the anhydrous salt. The most satisfactory weight proportion of base and flux for our purpose was found to be 100 strontium sulfide to 12 strontium chloride. The samples were prepared as previously described for the selenide phosphor.[4] When the fired samples were split open it was observed that a thin layer at the surface which had been exposed during the fluxing operation was noticeably different in optical properties from the fracture surface. This was shown later to be due to oxidation at the surface of the sample which might be attributable to the effect of traces of moisture adsorbed on the sample during its preparation, or to oxygen in the nitrogen stream. Since neither of these factors could conveniently be brought under strict control it was decided to split the fired sample and measure the brightness of the fracture surface. With some practice it is possible to obtain reasonably plane fracture surfaces and in most cases both halves of the sample were measured. Preliminary experiments indicated that after heating for one and one-half hours at 1050° very little change occurred in the brightness of the fracture surfaces and that during this period the variable outer layer did not penetrate deeply into the sample.

The apparatus used to measure the brightness of the phosphors under constant I. R. stimulation is shown in Fig. 1. The stimulating light source (L) is a 6 volt, 3 c. p. lamp run from a 6-volt constant voltage transformer. The light passes through a ground glass (G) and through a Corning 2540 infrared filter (F) to be reflected by a mirror (M) to the surface of the phosphor sample (P). The light emitted by the phosphor is measured by the phototube multiplier (T). A calibrating light (a 6 volt, 3 c. p. tungsten lamp) was run off the same transformer as the stimulating light (L). It was placed directly above the aperture for the phosphor in a box in which a small pinhole covered with opalescent glass permitted the light to fall on the phototube multiplier. To take a calibrating reading the phosphor was replaced by a piece of ground glass which was illuminated by the light from the pinhole. To make sure that readings on different samples were strictly relative, this was done at the beginning and end of every set of readings. It was fairly easy to obtain brightness measurements on duplicate samples which agreed within 5%. Two minutes of exposure to the filtered light of a 60-watt tungsten lamp at a distance of 8 inches was the standard excitation given all phosphor samples. The filters were Corning Aklo and Blue-Green each about 5 mm. thick. The phosphorescence was measured up to five minutes after excitation at which time the phosphor was stimulated by infrared. The increment in emission was taken as the Brightness. At five minutes after excitation the phosphorescence (Background) of most samples was usually less than 10% of the Brightness except for those with low samarium concentrations in which it rose as high as 40%. The Brightness is given in galvanometer divisions.

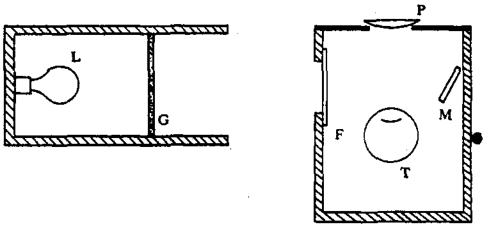

Fig. 1.—Apparatus for measuring the brightness of infrared-sensitive phosphors under constant infrared stimulation.

(b) The Effect of Addition of Oxide upon the Brightness of the SrS(Sm,Eu) Phosphor.—The first experiments were carried out using lithium fluoride as flux. Samples of composition $100SrS + xSrO(0.017\ Eu, 0.02\ Sm)9\ LiF$ were prepared as described above. The numbers refer to parts by weight. The amount of strontium oxide (x) consciously added to the mixture ranged from 0 to 10. The stimulated brightness of these samples as a function of added oxide is shown in curve 1, Fig. 2. It can be seen that maximum brightness is reached at 3% added oxide and the further increase in oxide concentration leads to a decline in brightness. This is similar to the results reported for the strontium selenide phosphor.[4]

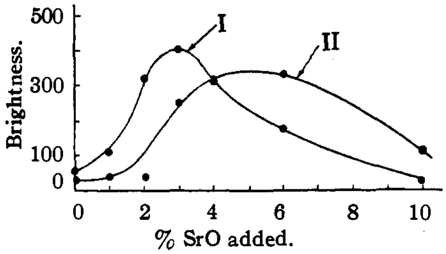

Fig. 2.—The effect of addition of oxide upon brightness: I, SrS(0.2 Sm, 0.017 Eu) 9 LiF, X SrO; II, 90 SrS:10 CaS(0.02 Sm, 0.017 Eu) 9 LiF, XSrO.

When similar experiments were tried using strontium chloride as flux, it was found that in general the addition of 1% strontium oxide led to a decrease in brightness and that with 2% oxide the brightness was reduced to a very low value. By using smaller increments of added oxide, however, a measurable maximum in brightness was usually obtained.

Several typical brightness *vs.* oxide plots are shown in

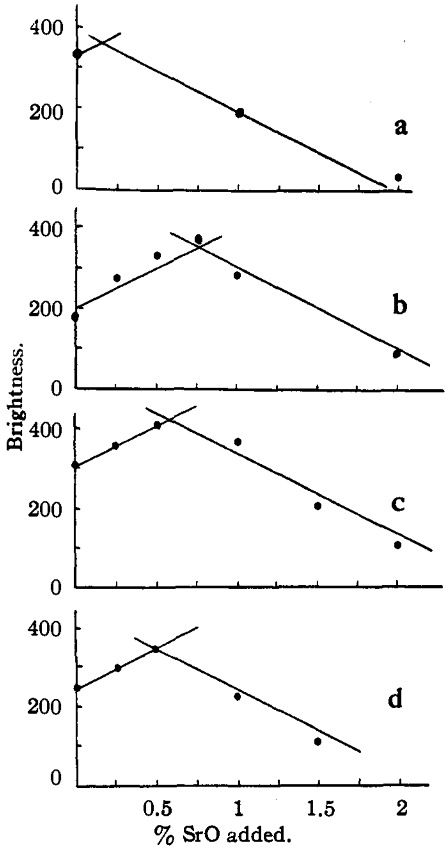

Fig. 3.—The effect of addition of oxide upon brightness: 100 SrS(0.02 Sm, 0.017 Eu) 12 $SrCl_2$, XSrO.

Fig. 3. The strontium sulfide represented in Fig. 3(a) is the same as that used with the lithium fluoride flux (Fig. 2). It was prepared by reduction of strontium sulfate with hydrogen. Fig. 3(b) represents another batch of strontium sulfide prepared by the same procedure while Fig. 3(c) was obtained by use of a sample of strontium sulfide prepared by heating the sulfate in hydrogen sulfide. Straight lines with the same slopes have been drawn rather arbitrarily through the experimental points. The point of intersection of these lines lies within 10 Brightness units of 380, which is about the maximum value obtained with lithium fluoride.

It appeared reasonable to suppose that the relative position of the maxima is indicative of the relative amount of oxide in different samples of strontium sulfide. Thus, Fig. 3(a) represents a sulfide which contains about 0.75% more oxide than represented by Fib. 3(b).

Many attempts were made to prepare a sample of strontium sulfide completely free from oxide. One of these involves the reaction between anhydrous strontium chloride and dry hydrogen sulfide. Under suitable conditions this reaction can be carried essentially to completion and the only impurity which should be present is strontium chloride. The oxide–brightness curve for strontium sulfide prepared in this way is shown in Fig. 3(d). It differs very little from the others.

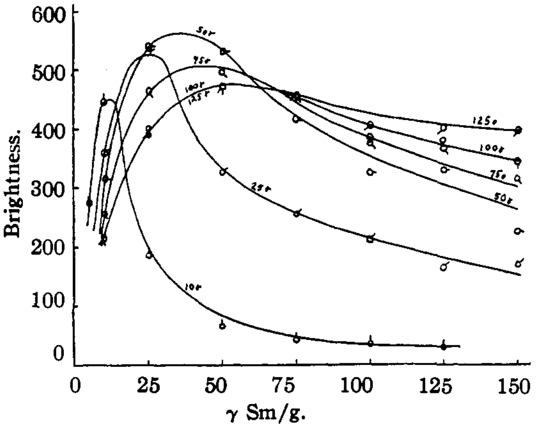

Fig. 4.—Variation of brightness with samarium concentration, SrS(XSm, Eu) 12% $SrCl_2$: ϕ, 10γEu; ♂, 25γEu; ⊸, 50γ Eu; ⍺, 75γEu; ♀, 100γEu; ρ, 125γEu.

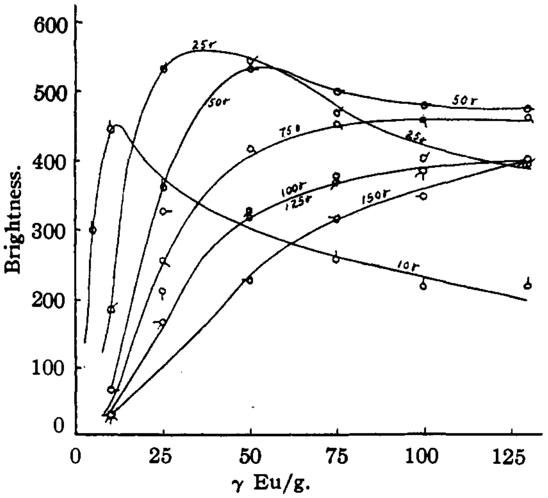

Fig. 5.—Variation of brightness with europium concentration, SrS(Sm, XEu) 12% $SrCl_2$: ϕ, 10γSm; ♂, 25γ Sm; ⊸, 50γSm; ⍺, 75γSm; ♀, 100γSm; ρ, 125γSm; ⊸, 150γSm.

A mixture of 90 parts of strontium sulfide to 10 parts calcium sulfide was tested in this way using lithium fluoride as flux. The results shown in Curve II, Fig. 2, indicate that much more oxide can be tolerated in this mixture. The maximum brightness is obtained with 5 to 6% oxide. With 0 to 2% oxide, phosphors of very low stimulability are formed. The lower value for the maximum brightness is probably to be attributed to the shift in emission color toward the red caused by the introduction of calcium.

(c) The Effect of Varying Concentrations of Samarium and Europium upon the Brightness of the Strontium Sulfide Phosphor using Strontium Chloride as the Flux.—Strontium chloride was chosen as the flux for this investigation. Strontium sulfide was prepared by reduction of the sulfate with hydrogen. Several batches were intimately mixed to give a sufficient quantity so that the entire investigation could be carried out with the same base material. No addition of oxide was made to the material to be used in the activator concentration experiments. A sample of the sulfide, however, was found to give a maximum in brightness upon the addition of about $^1/_3$ per cent. oxide.

Samples of composition $100SrS(xSm,0.001Eu)12SrCl_2$ were prepared where x varied from 0 to 125 γ per g. of strontium sulfide. The brightness under infrared stimulation of these samples was plotted as a function of the samarium concentration. This gave a curve which may be called a constant europium profile. Similar series of constant europium samples were prepared with 25, 50, 75, 100 and 125 γ of europium per gram of strontium sulfide. The results are shown in Fig. 4. Constant samarium profiles were also determined for the concentrations 10, 25, 50, 75, 100, 125 and 150 γ of samarium per gram of strontium sulfide.

From Fig. 4 we see that at 10 γ europium concentration the addition of samarium causes a very rapid rise in infrared sensitivity to a maximum value at about 10 γ samarium. Further addition of samarium causes a rapid decline in sensitivity. At progressively higher europium concentrations the maxima become broader and the sensitivity does not fall off so rapidly at higher samarium concentrations. There is also a shift in the position of the maxima toward higher samarium concentrations as the europium concentration increases. The brightness represented by the peaks of the profiles passes through a maximum in the 50 γ europium profile but appears to level off at the 100 γ europium profile.

In Fig. 5 which gives the constant samarium profiles it is shown that similar shifts in the maxima are obtained.

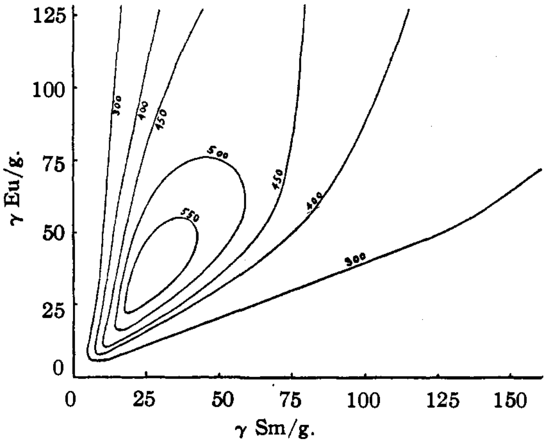

Fig. 6.—Brightness as a function of samarium and europium concentration: SrS(XSm, YEu)12% $SrCl_2$.

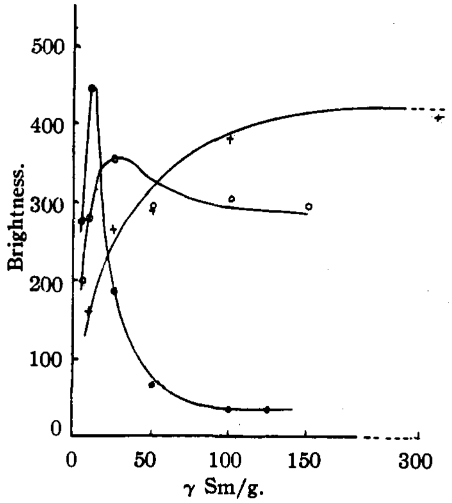

Fig. 7.—The influence of oxide upon the brightness of phosphors with varying samarium concentration, SrS-(XSm, 10Eu) 12% $SrCl_2$: ●, no SrO added; ○, 0.5%; +, 1%.

At the higher samarium concentrations no maxima were observed within the limits of europium concentrations used.

From Figs. 4 and 5 a contour plot was made of the brightness as a function of the samarium and europium concentrations. This is shown in Fig. 6 which indicates that at low concentrations of activators the optimum ratio of europium to samarium concentrations is about unity. Above 15 parts per million, however, this ratio increases and the brightest phosphors are those in which the europium concentration falls between 22 and 55 γ and the samarium concentration between 17 and 42 γ. If we were to assume that all of the activators entered the base material lattice and were uniformly distributed, the linear separation of activator ions in the maximum brightness region would be about 15 to 18 cation–cation distances. This must represent the minimum separation of the activator ions. The distribution coefficients of the activators between the flux and the strontium sulfide, however, are not at present known and an investigation of this problem is now being made. The increase of the europium to samarium ratio above unity at higher activator concentrations may be in

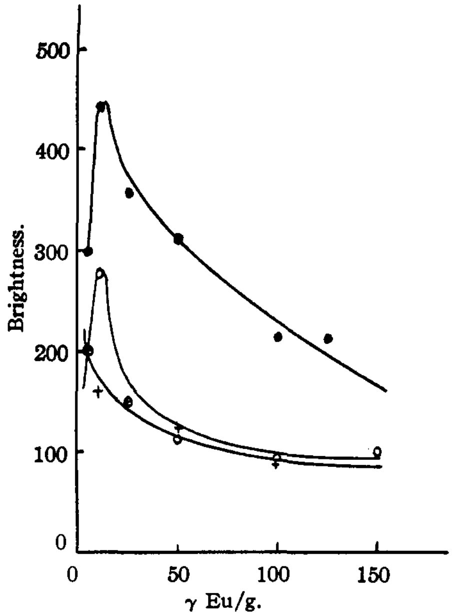

Fig. 9.—The influence of oxide upon the brightness of phosphors with varying europium concentration, SrS-(10Sm, XEu) 12% $SrCl_2$: ●, no SrO added; ○, 0.5%; +, 1%.

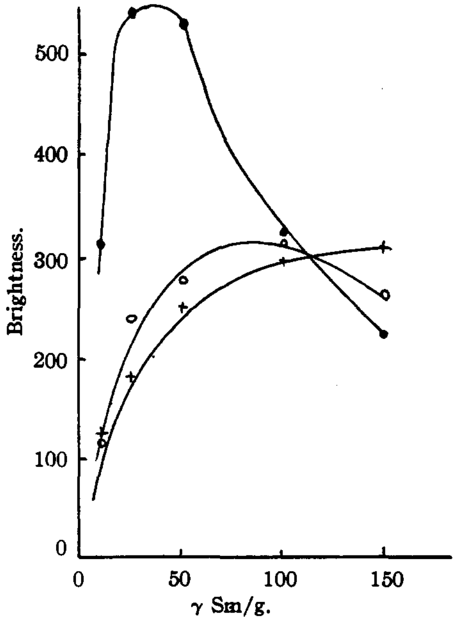

Fig. 8.—The influence of oxide upon the brightness of phosphors with varying samarium concentration, SrS-(XSm, 50Eu) 12% $SrCl_2$: ●, no SrO added; ○, 0.5%; +, 1%.

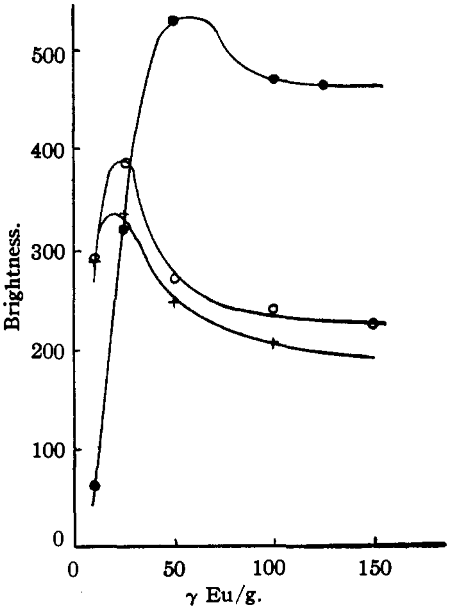

Fig. 10.—The influence of oxide upon the brightness of phosphors with varying europium concentration, SrS-(50 Sm, XEu) 12% $SrCl_2$: ●, no SrO added; ○, 0.5%; +, 1%.

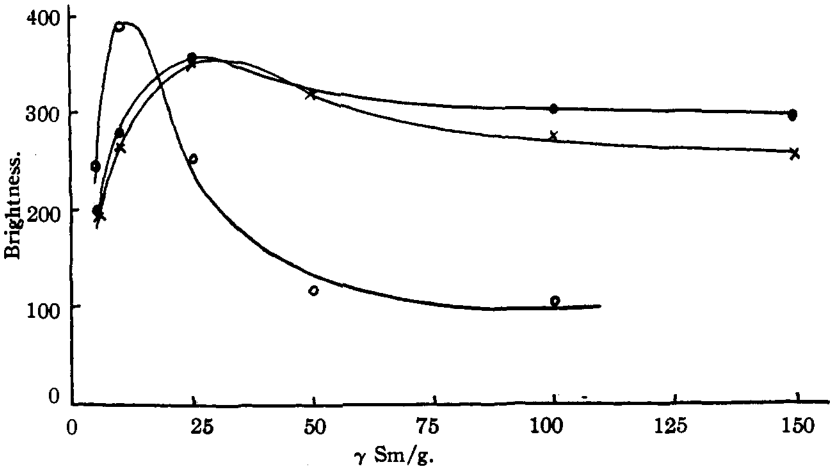

Fig. 11.—Brightness *vs.* samarium concentration for the surfaces of phosphor samples containing no oxide and for the fracture surfaces of samples containing oxide: O, inside and X, outside, no SrO added; ●, inside 0.5% SrO added.

part due to a difference in distribution coefficients of the two activators.

It should be noted that the measurement of brightness made here is the stimulated emission of the fully excited phosphor after the normal phosphorescence (or background) has decreased to a negligible value. The phosphors with low activator concentration showed a time lag in stimulation. The maximum brightness in these cases was recorded.

From the work of Urbach[2] it would seem likely that the samarium ion (auxiliary activator) provides the trapping states which lead to long storage of energy while the europium ion (the dominant activator) supplies the excited electrons. The stimulation involves the transfer of the trapped electrons to the conduction band whence they may return to the dominant activator ion with the emission of light or may return to a trap without the emission of visible radiation. From this model we would expect an increase in brightness with increasing samarium concentration up to the point at which the re-trapping of excited electrons predominates. This point appears to be reached at 40 to 50 γ of samarium or at a minimum lattice separation of 36 cation distances.

The effect of increasing the europium concentration beyond that required for maximum brightness is not so pronounced. With low samarium concentrations, however, it causes a definite decrease in brightness. This also would be predicted from the mechanism suggested above. Upon excitation of the phosphor the electrons from the europium are transferred to the conduction band. They may subsequently be trapped by the samarium or return to the europium, the latter giving rise to phosphorescence. Qualitatively, it would seem reasonable to suppose that fewer electrons would be trapped by the samarium when europium concentration is relatively high.

(d) **The Effect of Addition of Oxide to Samples with Varying Samarium and Europium Concentrations.**—Three series of samples containing 10 γ of europium per gram of strontium sulfide were prepared with zero, one-half and one per cent. added oxide. In each series the samarium concentration ranged from 5 to over 100 γ. The stimulated brightness of these series as a function of samarium concentration is shown in Fig. 7. The results for a similar set of samples containing 50 γ of europium are presented in Fig. 8. These data show that at low samarium concentrations the addition of oxide causes a marked decrease in brightness while the reverse is true at higher samarium concentrations. The maximum in brightness, shown by the series containing no added oxide, is not so well marked in the series containing 0.5% oxide and does not appear when 1% oxide is added.

The influence of oxide additions upon the constant samarium profiles was also determined at 10 and 50 γ of samarium. The results given in Figs. 9 and 10 show that the addition of oxide causes increase in brightness only at low concentrations of europium with 50 γ of samarium. At high europium concentrations the addition of oxide causes a lowering of the brightness.

It should be noted that the most sensitive phosphor was produced without the addition of oxide. The effect of oxide in general appears to be most noticeable at high samarium and low europium concentrations.

An interesting observation was made by the comparison of the brightness values of the fracture surfaces of a series of constant europium phosphors to which 0.5% oxide had been added with the brightness values of the outside surfaces of a similar series to which no oxide had been added. The curves are shown in Fig. 11. The close correspondence between the 0.5% oxide series and the outside surfaces of the phosphors to which no oxide was added is a strong indication that the change occurring at the surface of the samples in heating is the introduction of a small amount of oxide.

(e) **The Effect of Oxide upon the Phosphorescence of Strontium Sulfide Activated with Europium.**—The light emission from the singly activated phosphor 100SrS(xEu)12SrCl$_2$ was measured as a function of europium concentration. The results shown in Fig. 12 indicate that there is a maximum at about 10 γ/g. of europium.

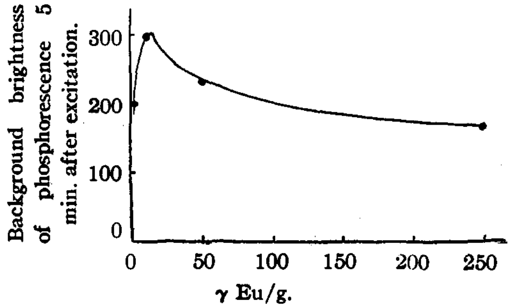

Fig. 12.—Phosphorescence of 100 SrS(Eu) 12SrCl$_2$ as a function of europium concentration.

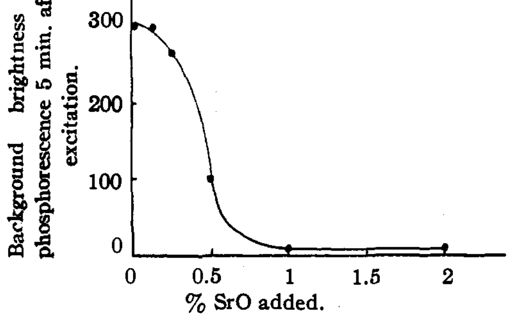

Fig. 13.—Phosphorescence of 100SrS(0.001Eu)12SrCl$_2$, XSrO as a function of oxide concentration.

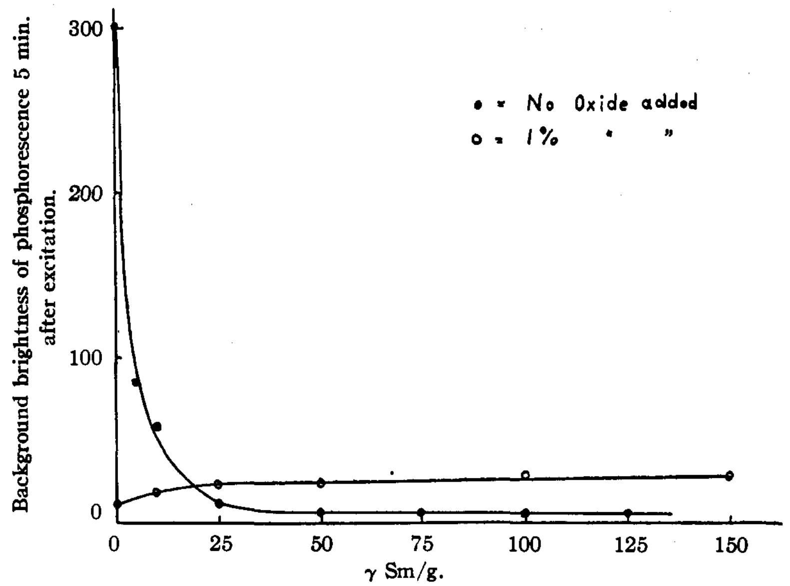

Fig. 14.—The phosphorescence of 100 SrS(0.001Eu, XSm) with and without the addition of oxide.

The phosphorescence was measured at one minute intervals after the phosphor had been fully excited. The data given represent the brightness at five minutes. From these results it would appear that the number of electrons which remain in the excited state is decreased by the addition of europium beyond 10 γ.

Samples of composition 100SrS(0.001Eu)12SrCl$_2$,xSrO where x varied from 0 to 2 were prepared and the phosphorescence measured as described above. The results, given in Fig. 13, show that the phosphorescence is lowered by a factor of one-third upon the addition of 0.5% strontium oxide and becomes practically zero at 1%.

The effect of the addition of samarium upon the phosphorescence of the europium phosphors 100SrS(xSm,0.001Eu)12SrCl$_2$ and 100SrS(xSm,0.001Eu)12SrCl$_2$·1SrO is shown in Fig. 14.

Unfortunately we have no theoretical interpretation of the peculiar influence of oxide upon the luminescent characteristics of the strontium sulfide phosphors. The measurement of brightness under infrared stimulation is obviously rather superficial. More fundamental information should be forthcoming from the measurement of light sum, quantum efficiency, photoconductivity, etc. Some preliminary investigations of these have been made.

The facts presented here, however, show clearly that impurities other than heavy metals may have profound effects on the behavior of these phosphors and that great care must be exercised in the preparation of samples.

Acknowledgments.—The authors wish to thank R. T. Ellickson and W. L. Parker for the construction of apparatus used in measuring the brightness of the phosphors.

Summary

A method is described by which reproducible measurements of the brightness of infrared sensitive phosphors can be made. The strontium sulfide–samarium, europium phosphor fluxed with lithium fluoride and with strontium chloride was shown to be affected by the addition of small quantities of strontium oxide. The presence of lithium fluoride or of calcium ions increases the tolerance of the phosphor toward oxide.

The dependence of the brightness of the phosphor upon the concentrations of samarium and europium, using strontium chloride as flux, was determined. It was shown that, at activator concentrations from 0 to 15 (γ) parts per million, the brightest phosphors are obtained with about equal concentrations of the two activators. At higher activator concentrations an excess of europium seems to be best. The brightest phosphors contain between 22 and 55 γ of europium and 17 and 42 γ of samarium per gram of strontium sulfide.

BROOKLYN, N. Y. RECEIVED JUNE 24, 1947

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Preparation of Optically Active Hydrocarbons by the Wurtz Reaction

BY R. L. LETSINGER

Of the attempts to prepare optically active hydrocarbons by the Wurtz reaction with secondary halides,[1,2] the only successful cases which have been reported are (a) the preparation of (+)2,3-diphenylbutane by the reaction of sodium with (−)1-chloro-1-phenylethane[3] and (b) the preparation of (−)3-methylnonane by the condensation of ethylsodium with (−)2-bromoöctane.[2] Even in these cases the yields were so low and the products so extensively racemized that the reactions are of little synthetic interest.

In the present paper it is shown that benzylsodium condenses with optically active 2-bromoöctane and 2-bromobutane to give good yields of the corresponding hydrocarbons and, furthermore, that in the reaction with 2-bromobutane a major portion of the optical activity is retained and an inversion of configuration probably occurs.

Hydrocarbon Preparation.—Data on the hydrocarbon syntheses are presented in Tables I and II. For comparative purposes, the reaction

(1) Gilman, "Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1943, p. 386.

(2) Brink, Lane and Wallis, THIS JOURNAL, 65, 943 (1943).

(3) Ott, *Ber.*, 61, 2124 (1928).