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REACTIONS BETWEEN  $Pb^{2+}$  AND  $(I^- + I_3^-)$  IN  
ACIDIC SILICA GELS<sup>1</sup>

PHILIP F. KURZ

*Battelle Memorial Institute, Columbus, Ohio 43201*

ABSTRACT

In this work it was found that reactions between  $Pb^{2+}$  and  $(I^- + I_3^-)$  in acidic silica gels are limited to the formation of  $PbI_2$  from  $Pb^{2+} + 2 I^-$  and from  $Pb^{2+} + 2 I_3^-$ , the latter occurring with the coincident formation of  $I_2$  crystals. There was no evidence of pseudomorphic conversion of  $I_2$  to  $PbI_2$ , even by the presence of large excesses of  $Pb^{2+}$ , in contrast to reactions in acidic gels between excess  $Hg^{2+}$ ,  $Ag^+$ , or  $Tl^+$  and  $I_2$ , in which instances these metal cations convert  $I_2$  pseudomorphically to the respective iodides. When a deficiency of  $Pb^{2+}$  existed, there was no zone separation of  $PbI_2$  and  $I_2$ , as occurs with  $HgI_2$ ,  $AgI$ , or  $TlI$  and  $I_2$  in metal-ion deficient systems, and the distributions of  $PbI_2$  and  $I_2$  crystals were random.

Reactions between  $Pb^{2+}$  and  $I^-$  in acidic and slightly basic silica gels have been described by Holmes (1917, 1934). In sufficiently acidic gels, Holmes found that the normal iodide,  $PbI_2$ , formed, whereas in only slightly acidic and in basic gels, a basic iodide resulted, presumably  $Pb(OH)I$  or  $PbI_2 \cdot PbO$ . Holmes (1917, 1934)

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<sup>1</sup>Manuscript received August 15, 1964.

also describes the formation of  $\text{HgI}_2$  in gels. The present investigator has repeated and extended Holmes' work and has found that, when acidic silica gels containing  $(\text{I}^- + \text{I}_3^-)$  are reacted with excess  $\text{Hg}^{2+}$ ,  $\text{Ag}^+$ , or  $\text{Tl}^+$ , all of the iodine, as well as all of the iodide, is converted to the respective heavy-metal iodide (Kurz, 1966 and unpublished results). With excess  $\text{Hg}^{2+}$  crystals of red  $\text{HgI}_2$ , some of which are pseudomorphs, are the single visible, ultimate reaction product in a slightly cloudy but otherwise colorless gel, indicating the absence of  $\text{I}_3^-$  and  $\text{I}_2$ .

Similarly, with excess  $\text{Ag}^+$ , yellow microcrystals of  $\text{AgI}$  and larger yellow pseudomorphs originally formed as  $\text{I}_2$  are the sole visible end products in an otherwise color-free gel. With excess  $\text{Tl}^+$ , glistening clusters of lemon-yellow needles and long, lustrous black needles coexist in an otherwise color-free gel at the conclusion of the reaction. The yellow needles presumably are  $\text{TlI}$ , and the black needles probably represent a higher-valence thallium iodide. In  $(\text{I}^- + \text{I}_3^-)$ -bearing gel systems treated with only enough  $\text{Hg}^{2+}$  or  $\text{Ag}^+$  to react with the excess  $\text{I}^-$  and to rob  $\text{I}_3^-$  of its  $\text{I}^-$ , crystals of  $\text{HgI}_2$  and  $\text{I}_2$  or of  $\text{AgI}$  and  $\text{I}_2$ , respectively, form in distinctly separate zones in the gel and coexist permanently. The metal halide crystals form nearest the gel surface and the  $\text{I}_2$  crystals are segregated in the zone farthest from the gel surface. The gel background and the supernatant liquor are light yellow brown in color and probably represent aqueous media saturated with  $\text{I}_2$ .

Reactions between  $\text{Pb}^{2+}$  and acidic gels containing  $(\text{I}^- + \text{I}_3^-)$  were investigated because lead is another heavy metal whose iodide, like  $\text{HgI}_2$ ,  $\text{AgI}$ , and the thallium iodides, is relatively insoluble in water. As mentioned above, it has been known for many years that crystals of  $\text{PbI}_2$  can be grown in acidic silica gels using  $\text{I}^-$  as the internal reagent and  $\text{Pb}^{2+}$  as the external reagent, or vice versa. Both methods were tried before reacting  $\text{Pb}^{2+}$  with  $(\text{I}^- + \text{I}_3^-)$ , to which no reference has been found.

When  $(\text{I}^- + \text{I}_3^-)$ -bearing gels were reacted with  $\text{Pb}^{2+}$  supplied from a supernatant solution of lead nitrate, interesting and, in the light of earlier experience with  $\text{Hg}^{2+}$  and  $\text{Ag}^+$ , somewhat unexpected results were obtained.

Table I summarizes the composition of the gels and the concentrations of reactants used in these experiments. In one gel system, the amount of  $\text{Pb}^{2+}$  ultimately placed on the gel was only slightly in excess of that required to react

TABLE I  
Composition of gel systems for reactions between  $\text{Pb}^{2+}$  and  $(\text{I}^- + \text{I}_3^-)$

Sodium silicate solution		Acetic acid		Potassium iodide		Iodine (dissolved in KI)			Total $\text{I}^-$	Lead nitrate (external reagent)							
Undiluted silicate. <sup>a</sup> ml	Water, ml	$\text{OH}^-$ in silicate milli- equiv- alents	ml	N	Milli- equiv- alents	ml	N	Equiv- alents $\text{I}^-$	gm	Milli- equivalents $\text{I}_3^-$	2.7	Available as $\text{I}^-$ or in $\text{I}_3^-$ + potential (in $\text{I}_2$ ) milliequiv- alents	ml	N	Milliequivalents		
															Used	Excess avail- able $\text{I}^-$	Excess over total $\text{I}^-$
1.67	8.33	6.7	5	1.5	7.5	5	1	5	0.4	3.2	2.7	7.7	3 x 5	2	30	25	22.3
8.3	41.7	33.3	25	1.5	37.5	25	1	25	2.4	16.6	13.8	38.8	2 x 20	1	40	15	1.3
20.0	100.0	80.0	60	1.5	90.0	60	0.5	30	2.4	16.6	13.8	43.8	(1 x 16+ 3 x 10)	2	92	62	48.2

<sup>a</sup>Philadelphia Quartz Company's N Sodium Silicate ( $\text{SiO}_2/\text{Na}_2\text{O}=3.22/1$  by weight).

<sup>b</sup>Only 5/6 of  $\text{I}_2$  goes to  $\text{I}^-$  on hydrolysis and disproportionation.

with both the available  $I^-$  (present as  $I^-$  or complexed in  $I_3^-$ ) and the potential  $I^-$  (obtainable from  $I_2$  by promotion of its hydrolysis to  $I^- + IO_3^-$ ). In the other gel systems, approximately 2- to 4-fold excesses of  $Pb^{2+}$ , based on available plus potential  $I^-$ , were used.

The sketches in figure 1 show typical formations of  $PbI_2$  and  $I_2$  crystals in two of the gel-reaction systems described in table 1. In both gel systems, crystals of the two species coexisted permanently at the conclusion of the reaction and no indication of pseudomorphic formations of  $PbI_2$ , at the expense of  $I_2$ , was evident.

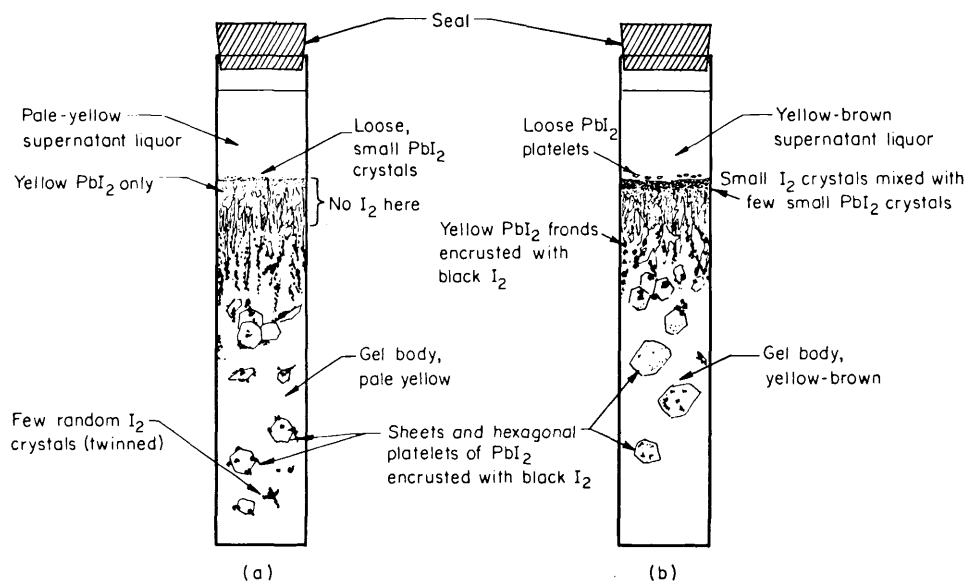


FIGURE 1. SKETCHES OF FORMATIONS OF  $PbI_2$  AND  $I_2$  IN ACIDIC ( $I^- + I_3^-$ ) -BEARING GELS REACTED WITH  $Pb^{2+}$

The first gel system described in table 1 initially contained 1.6 millimols of  $I_3^-$  (from  $I^- + I_2 \rightarrow I_3^-$ ) and 3.4 milliequivalents of excess  $I^-$ . It was reacted at approximately bimonthly intervals with three successive 5-ml portions of 2N  $Pb(NO_3)_2$  solution. Each 10-milliequivalent-portion of lead nitrate solution contained more than enough  $Pb^{2+}$  to react with all of the  $I^-$ , available plus potential, in the gel. The reaction:



is possible and occurs because the gel contains free  $I^-$ .

The reaction:



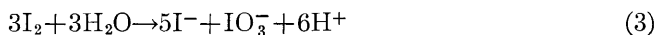
apparently occurs also because, in addition to golden-yellow hexagonal platelets of  $PbI_2$ , black, usually twinned crystals of  $I_2$  form as encrustations on the yellow fronds or hexagonal platelets of  $PbI_2$ . The black crystals are dispersed randomly on the yellow ones. In the presence of excess  $Pb^{2+}$ , as was used in this system, it is reasonable to believe that reactions (1) and (2) are essentially complete. Together they can consume 5 milliequivalents of  $Pb^{2+}$ , leaving an excess of 5 to

25 milliequivalents of  $\text{Pb}^{2+}$  (after first and third additions of  $\text{Pb}^{2+}$ ) to react with  $\text{I}^-$ , or  $\text{IO}_3^-$  that may form from  $\text{I}_2$  by hydrolysis. The background color of the gel and the supernatant liquor were light yellow brown, approximating the color of a saturated aqueous solution of  $\text{I}_2$ , after the first 10 milliequivalent portion of  $\text{Pb}^{2+}$  had reacted and paled only slightly as the second and third portions of  $\text{Pb}^{2+}$  were used. The only noticeable effect of using successive portions of  $\text{Pb}(\text{NO}_3)_2$  solution was to dissolve some of the  $\text{PbI}_2$  crystals initially formed near the top of the gel. This may have been a result of equilibration of  $\text{PbI}_2$  between the gel and the supernatant liquor which initially contained no  $\text{PbI}_2$ , but only  $\text{Pb}(\text{NO}_3)_2$ . It appears unlikely that the disappearance of some of the  $\text{PbI}_2$  was an acidification effect, because  $\text{PbI}_2$  crystals will form in gels prepared with glacial acetic acid (16N) and which are approximately 7N in acetic acid after neutralization of the silicate (Kurz, unpublished results).

The second gel system described in table 1 initially contained 8.3 millimols of  $\text{I}_3^-$  and 16.7 milliequivalents of uncomplexed  $\text{I}^-$ . It was reacted with two 20 ml portions of 1N  $\text{Pb}(\text{NO}_3)_2$ , added about 1 year apart. Reactions (1) and (2) apparently proceed in this system also, as indicated by the formation of crystals of  $\text{PbI}_2$  and  $\text{I}_2$ , which coexist in the gel as shown in figure 1. In this instance reactions (1) and (2) require 25 milliequivalents of  $\text{Pb}^{2+}$ . There was no excess  $\text{Pb}^{2+}$  until the second 20 milliequivalent portion of  $\text{Pb}^{2+}$  was placed on the gel. Yet, as evidenced by the formation of  $\text{I}_2$  during the first "half" of the reaction,  $\text{Pb}^{2+}$  successfully robbed  $\text{I}_3^-$  of its  $\text{I}^-$ . The background color of this gel system was a deep yellow brown, indicating the presence of  $\text{I}_3^-$ , as would be expected in the absence of excess  $\text{Pb}^{2+}$  addition. Likewise, as expected, the gel and supernatant assumed light yellow brown colors after the second 20-milliequivalent portion of  $\text{Pb}^{2+}$  had reacted.

Crystal distribution of both species is random in both gels. However, the bulk of the growth occurs in the half of the gel nearest the external reactant. This suggests that  $\text{I}^-$  and  $\text{I}_3^-$  migrate toward the supernatant source of  $\text{Pb}^{2+}$  faster than  $\text{Pb}^{2+}$  infuses into the gel.

It is apparent, because  $\text{I}_2$  coexists with  $\text{PbI}_2$  in the presence of large excesses of  $\text{Pb}^{2+}$ , that, unlike  $\text{Hg}^{2+}$  and  $\text{Ag}^+$  under similar conditions,  $\text{Pb}^{2+}$  does not promote reactions between  $\text{I}_2$  and  $\text{H}_2\text{O}$  which would produce  $\text{I}^-$  and  $\text{IO}_3^-$  as follows:



Hence, apparently only reactions (1) and (2) occur in  $(\text{I} + \text{I}_3^-)$ -bearing gels reacted with  $\text{Pb}^{2+}$ .

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