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The Oxidation of Iodide to Iodine on Boron Phosphate

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The oxidation of iodide by boron phosphate (BP) in nonaqueous solvent is shown to increase with phosphorus/boron (P/B) ratio for unpretreated BP, and for a tiven P/B ratio, to decrease with pretreatment temperature. Measurements of concentrations of acidic sites suggest that the weaker acidic sites would be more active in this process in BP.

INTRODUCTION

The characterization of real surfaces, and in particular those possessing catalytic properties, is a problem rendered particularly difficult as a consequence of the geometric and energetic heterogeneity of such a surface. As a consequence, those interested in such real surfaces have had to be content, at least to this date, with measurements of the surface properties by indirect methods. The use of "probe molecules," either interacting with the surface physically or chemically, has yielded substantial information in surface chemistry and heterogeneous catalysis. In this laboratory, krypton (*1*) and argon (*2*) have been used as physical probes, and water (*3*, *4*), ammonia (*5*), diphenylethylene, tetraphenylethylene, perylene (*6*, *7*), formic acid (*8*, *9*), ethanol (*10*), and propanol (*11*) have been used as chemical probes in elucidating the surface and catalytic properties of boron phosphate. Such experiments together with infrared spectroscopy (*12*, *13*) have shown, among other things, the acidic nature of the surface of boron phosphate, and the properties of the Lewis and Brønsted acid sites evidently present.

Recently, Flockhart *et al.* (*14*, *15*) have published the results of an interesting study of silica–alumina using the oxidation of iodide to iodine as a probe reaction. As pointed out by Flockhart and co-workers, the oxidizing properties of silica–alumina and alumina surfaces have been studied previously [see, for example, Refs. (*16*–*20*)]. Both Mellor *et al.* (*18*) and Fiedcrow and co-workers (*19*) have found that iodide is oxidized to iodine in aqueous solution, the experiments of the former being done with silica–alumina, while those of the latter employed alumina. These workers suggested that the sites on which hydrocarbons such as perylene or anthracene are oxidized may also be those which are catalytically active for the oxidation of iodide ions. Flockhart and co-workers (*20*) had earlier found that the activity of such surfaces for the oxidation of hydrocarbons decreased in the presence of water vapor. In their most recent study on this topic, Flockhart *et al.* (*14*) found that the production of iodine from iodide in aqueous solutions, and in benzene solutions of tetramethylammonium iodide, is catalyzed by activated silica–alumina, but not by either pure alumina or pure silica, and they relate such activity to the Brønsted acidity of the catalysts, which is suggested to be regenerated, in the presence of water, as the oxidation continues.

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Since the presence of acidic sites on boron phosphate has been demonstrated previously, and some similarities with alumina and silica–alumina catalysts have been observed *(10–13)*, it seemed both interesting and worthwhile to investigate the catalytic properties of boron phosphate for the oxidation of iodide to iodine, and to attempt to provide a correlation with some of the results obtained previously in our laboratory.

EXPERIMENTAL METHODS

Samples of boron phosphate were prepared by the method described previously *(8)*, and such samples, prior to any thermal treatment, are designated as "not pretreated." A variety of molar ratios of phosphorus/boron (P/B), as calculated from the initial amounts of reactants used, was employed in the preparations.

Tetramethylammonium iodide (BDH chemicals) anhydrous sodium thiosulfate (reagent grade), potassium iodide, and potassium iodate (Baker Chemicals Co.) were used without further purification. Benzene (A.R.) was stored over Drierite. The concentration of sodium thiosulfate solution was found by standardizing against potassium iodate solution and was checked every 2 weeks.

The oxidation of iodide was carried out in brown glass bottles with screw caps fitted with Teflon gaskets at three different temperatures, 20, 35, and 50°C. For the determination of the rates of reaction, four solutions each containing 0.4 g of tetramethylammonium iodide and 100 ml of dried benzene were prepared. Aliquots of approximately 0.3, 0.4, 0.5, and 0.6 g of boron phosphate were weighed and introduced into these benzene solutions. Five milliliters of each of these solutions was pipetted out at various times, normally every 2 days, and were titrated with sodium thiosulfate of appropriate concentration. Allowance for the removal of these 5 ml aliquots was made in the calculations.

In addition, separate experiments were performed to measure the total amount of iodine produced in 10 days at 60°C. Solutions for these experiments were prepared by adding 0.1 g of tetramethylammonium iodide to 20 ml dried benzene. Subsequently a weighed amount of boron phosphate of approximately 0.5 g was added. After 10 days the iodine contents of these benzene solutions were determined by titration with sodium thiosulfate solution of appropriate concentration. The amount of iodine remaining on the surface of boron phosphate after the 10 days was estimated by first separating the solid

TABLE 1

Surface Areas ($m^2 g^{-1}$) of Boron Phosphate Samples as Function of Composition (P/B) and Pretreatment Temperature

Pretreatment		Phosphorus/boron (moles/moles)							
Temp (°C)	Time (hr)	1.00	1.10	1.22	1.25	1.29	1.32	1.35	1.40
20[a]	—	14.1	9.1	12.4	11.9	8.1	9.4	5.1	5.0
100	24	—	—	—	—	—	11.5	8.4	—
150	24	—	—	—	14.1	—	10.8	6.9	—
200	21	14.9	11.8	9.6	13.4	8.0	10.3	8.1	6.7
300	16	15.5	14.2	17.5	15.8	11.9	16.5	10.1	31.4
400	12	13.2	18.2	19.6	22.8	22.8	30.5	14.4	21.2
500	12	11.2	22.1	9.6	27.0	19.9	26.9	22.7	18.2

[a] Not pretreated.

TABLE 2

Rate (mole m^{-2} hr^{-1}) of Oxidation of Iodide on Boron Phosphate Samples as Function of Composition (P/B) and Pretreatment Temperature

temp (°C)		Phosphorus/boron (moles/moles)		
Pretreatment	Reaction	1.10	1.22	1.29
200	20	4.6×10^{-9}	9.4×10^{-9}	1.5×10^{-8}
	35	6.4×10^{-9}	1.4×10^{-8}	2.7×10^{-8}
	50	1.2×10^{-8}	2.8×10^{-8}	6.9×10^{-8}
300	20	6.3×10^{-9}	6.2×10^{-9}	1.6×10^{-8}
	35	8.9×10^{-9}	8.3×10^{-9}	2.7×10^{-8}
	50	1.1×10^{-8}	1.2×10^{-8}	3.1×10^{-8}
400	20	5.8×10^{-9}	4.6×10^{-9}	8.2×10^{-9}
	35	7.7×10^{-9}	6.1×10^{-9}	9.5×10^{-9}
	50	9.6×10^{-9}	7.5×10^{-9}	1.1×10^{-8}
500	20	3.2×10^{-10}	8.4×10^{-10}	6.9×10^{-10}
	35	9.0×10^{-10}	1.5×10^{-9}	1.1×10^{-9}
	50	3.3×10^{-9}	3.4×10^{-9}	2.0×10^{-9}

phase from the liquid phase, followed by titration of both the liquid and solid phases with sodium thiosulfate solution.

Surface acidities of the samples of boron phosphate were found by titration with 0.01 *M* *n*-butylamine solution in dried benzene in the presence of a series of Hammett indicators.

RESULTS AND DISCUSSION

A summary of the various samples of boron phosphate together with their BET surface areas as obtained in the "not pretreated" form and after heating in vacuum (10^{-3} Torr) at various temperature is contained in Table 1.

On addition of a sample of boron phosphate to a benzene solution of tetramethylammonium iodide, a noticeable color change occurred in the solution after an initial period of time during which the rate was decreasing. The apparently slow reaction in which iodine was liberated continued at a constant rate for a period of at least 20 days. In the absence of boron phosphate, no observable color change in the solution or detectable amount of iodine was observed in the same period of time.

Rates of production of iodine per unit area, as taken from the linear portion of the graphs of iodine produced versus time, calculated at three temperatures, 20, 35, and 50°C, for samples of boron phosphate of three different compositions, pretreated at four different temperatures, are given in Table 2. In general, the rates can be seen to decrease as the pretreatment temperature increases and increase as the P/B ratio increases. A sample of boric acid was found to produce no significant amount of iodine when contacted with a solution prepared in the same way as described previously.

The results for the experiments in which a saturated benzene solution of tetramethylammonium iodine was contacted with a sample of boron phosphate for 10 days at 60°C are summarized in Fig. 1. In these experiments at 60°C only the total amount of iodine produced during the 10 days was measured. Figure 1 shows that such total amount of iodine decreases as the pretreatment temperature is increased, consistent with the evidence presented in Table 1. Unfortunately, however, the conclusions which can be drawn with respect to the variation with composition of the sample are not so unambiguous. In the case of the samples which had not been pretreated, the total amount of iodine produced per area, is, in general, larger for the samples of higher initial phosphorus content. However, as shown in Fig. 1, as the pretreatment temperature is increased,

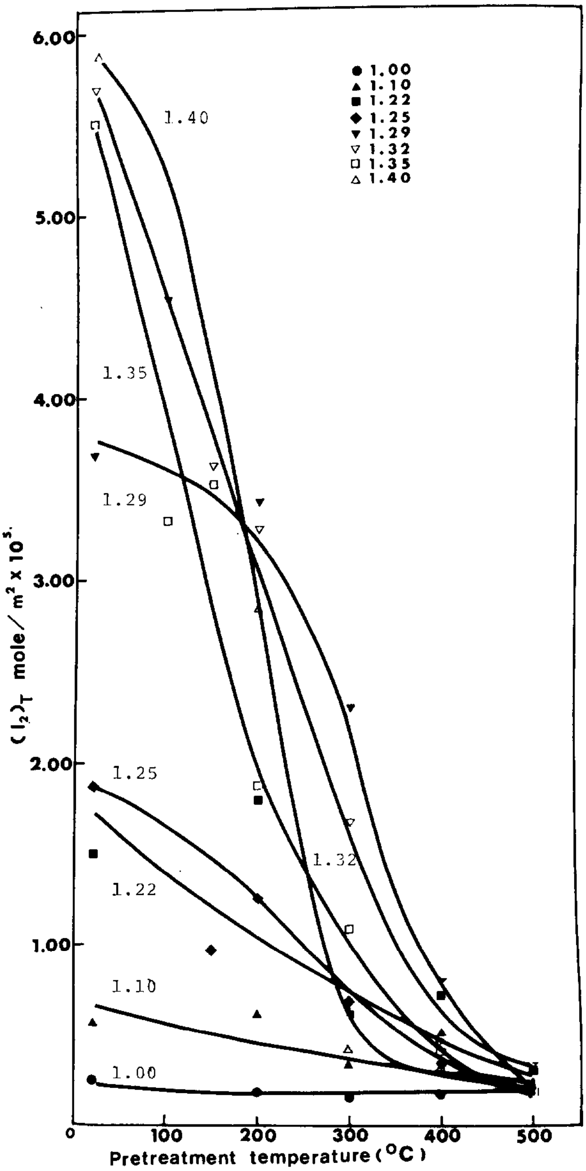

FIG. 1. Total iodine production with boron phosphate of various P/B in a saturated benzene solution of tetramethylammonium iodide at 60°C for 10 days, as a function of pretreatment temperature of the catalyst.

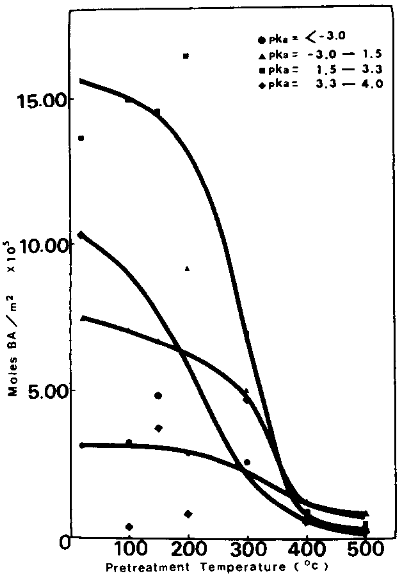

FIG. 2. Surface acid concentrations (moles butylamine/m²) for four pK_a ranges of a sample of BP with P/B equal to 1.32 pretreated at various temperatures.

the curves corresponding to the three samples of highest P/B values drop rapidly and cross the curves for the remaining P/B samples. If these three curves corresponding to the highest concentrations of phosphorus are ignored, then one can conclude, from the remaining data, that the total amount of iodine produced decreases with decreasing phosphorus content, no matter what the pretreatment temperature was. The behavior of these higher concentration samples, as evidenced in Fig. 1, does suggest that, as they are subjected to pretreatment, phosphorus (presumably in the form of P_2O_5) is lost, thereby reducing them in effectiveness in so far as iodine production is concerned to a level below those of initially lower phosphorus concentration. Presumably loss of phosphorus in whatever form would be accompanied by a loss in surface acidity.

It is interesting to compare these latter results with those of Flockhart and coworkers (*14*) on silica–alumina (~13% Al_2O_3), where the quantity of iodine produced increased as the activation temperature increased to 100°C. As the temperature was increased above 100°C the quantity of iodine remained constant at approximately 5×10^{-7} mole/m² of surface until the activation temperature was approximately 700°C, at which point it increased to approximately 8×10^{-7} mole/m² of surface. As the activation temperature was further increased to 1000°C, the iodine production rapidly fell to zero. In addition, the authors observed, with 100% silica, dehydrated at 550°C, no iodine production under similar experimental conditions as reported here. On addition of alumina, the iodine production increased to a maximum of approximately 5×10^{-6} mole iodine/g of catalyst, decreasing to zero at 80% alumina.

The results of the surface acidity measurements using *n*-butylamine are displayed for a sample of boron phosphate of P/B equal to 1.32 in Fig. 2. The molar quantities of *n*-butylamine required to complete the titration for each of four Hammett indicators, with values of pK_a equal to -3.0, $+1.5$, $+3.3$, and $+4.0$, were subtracted in turn to obtain the equivalent moles of acid for the ranges of pK_a less than -3.0, -3.0 to $+1.5$, $+1.5$ to $+3.3$, and $+3.3$ to $+4.0$. These concentrations are then plotted against pretreatment temperature to produce Fig. 2. As shown in Fig. 2, the apparent concentrations of acid sites with acid strengths in the various ranges appear to decrease as the pretreatment temperature increases, although in some cases rather substantial experimental error can be observed. Comparison of Figs. 1 and 2 shows that, as the iodine produced decreases with increasing pretreatment temperature, so also does the concentration of acidic sites.

The effect of varying the ratio of phosphorus to boron on the surface acidity and on the iodine produced can be seen from Fig. 3 which applies to samples of boron phosphate that were not pretreated. The

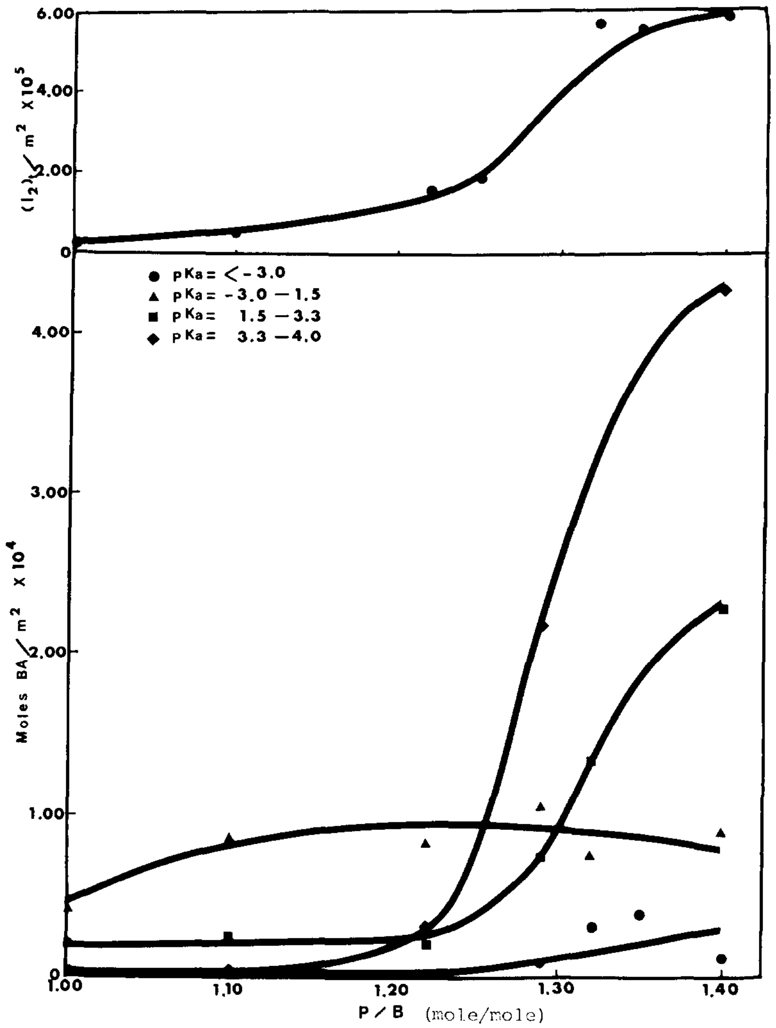

FIG. 3. Total iodine production and surface acid concentrations of unpretreated BP of various P/B.

upper curve of Fig. 3 shows the increase in the production of iodine as the molar P/B ratio is increased from 1.0 to 1.4 while the lower curve of Fig. 3 illustrates the change in the concentration of acid sites in the various ranges with the same P/B ratio. A number of interesting features can be observed. From Fig. 3 it appears that the increase in the concentration of acidic centers as the P/B ratio is increased must, in the range of P/B from 1.00 to 1.20, be attributed to the increase in number of sites with pK_a between -3.0 and $+1.5$. However, for P/B values between 1.2 and 1.4, the increase in concentration of acid must arise primarily from sites of pK_a greater than $+1.5$. It is then apparent that the effectiveness of the samples of boron phosphate with P/B ratios greater than 1.2 in the oxidation of iodide is in large part due to large numbers of relatively weak acidic sites, which, according to Fig. 2, suffer a much larger percentage reduction in number when the boron phosphate is pretreated.

If the oxidation of iodide occurs primarily at acidic sites on the surface of boron phosphate, then it seems reasonable to assume that iodide ions must initially chemisorb on such sites. The iodine produced then may remain chemisorbed on the surface or may desorb, possibly forming the triiodide (I_3^-) complex in solution. The results of experiments in which the solid and liquid phases were separated and the amounts of iodine in each phase were measured are shown in Fig. 4 in the form of total iodine (from both liquid and solid phases) as a function of the iodine measured in the solid phases. It can be observed that the total amounts of iodine plotted as a function of the quantities of iodine measured in the solid phase fall on the same curve for all samples of boron phosphate.

The simplest interpretation of such results is one in which the quantity of iodine measured in the solid phase is taken

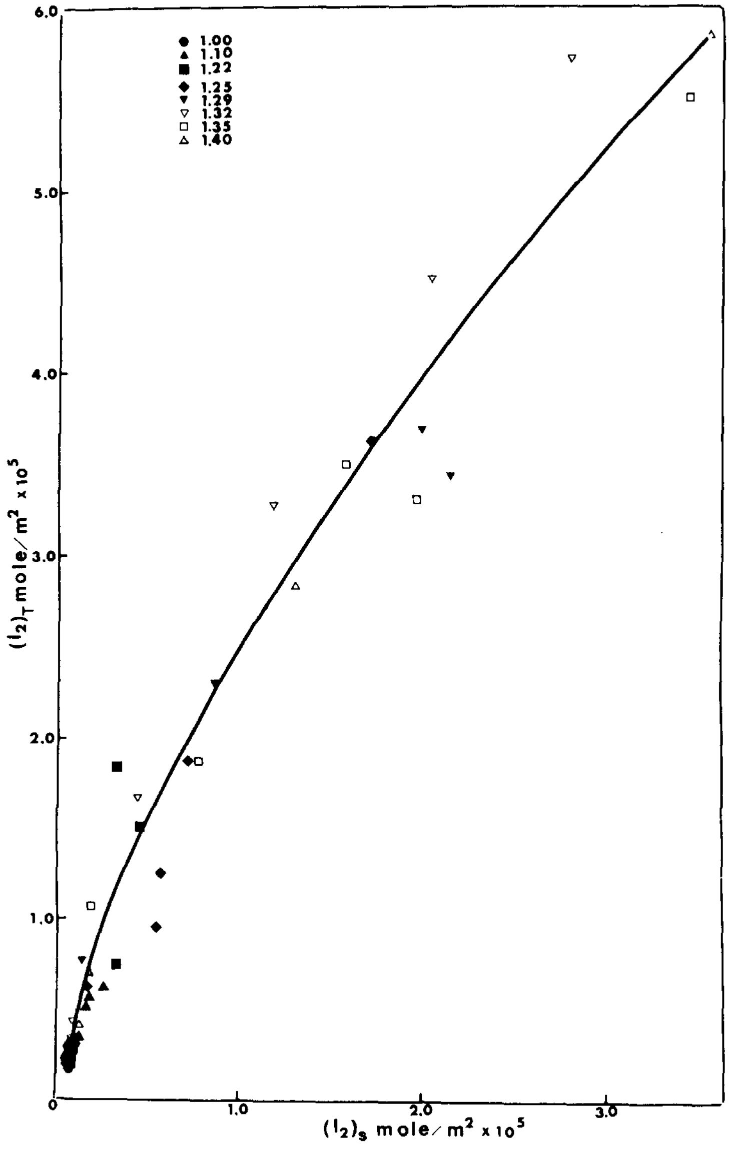

FIG. 4. Total iodine production vs iodine sorbed on BP for various P/B.

to represent the number of active sites. Of course this assumes that all the measured iodine was actually on the surface of the catalyst and none in the bulk, which is certainly not rigorously correct. However, within the confines of such an assumption, Fig. 4 can then be interpreted as representing the assumed equilibrium between iodine molecules in the liquid phase and those adsorbed on the solid, or alternatively can be taken as illustrating the manner in which the total amount of iodine varies with the number of sites active for the oxidation process. It is then interesting to compare the values of $(I_2)_s$ for boron phosphate of P/B equal to 1.32 with those for the surface acidity of the same sample given in Fig. 3. For example, a value of $(I_2)_T$ of 1.68×10^{-5} mole/m^2 corresponds to a value of $(I_2)_s$ of approximately 0.5×10^{-5} mole/m^2 (from Fig. 4). This was obtained with a 1.32 P/B sample of boron phosphate pretreated at 300°C. From Fig. 2 it can be seen that concentrations of acid sites in all the pK_a ranges fall in the region of 2×10^{-5} to 7×10^{-5}. Although the correspondence is not exact (nor would it be expected to be), nevertheless the orders of magnitude of $(I_2)_s$ and the numbers of acid sites agree reasonably well. Furthermore, measurements (*21*) with deuterium of the numbers of exchangeable hydrogen atoms on boron phosphate yield values up to 1.3×10^{-5} mole/m^2, of the same order of magnitude as the values found in the present work for $(I_2)_s$ but again smaller than the measured concentrations of acid sites. It is tempting to suggest, as concluded by Flockhart *et al.* (*14*), that this latter difference demonstrates that it is the Brønsted acidity which is important in the oxidation of iodide, since the butylamine titration method for measurement of surface activity cannot discriminate between Brønsted and Lewis acidity.

Some comments should be made on a possible mechanism for the catalyzed oxidation of iodide to iodine. As noted earlier no oxidation occurs in the absence of boron phosphate. Further, it is known that the oxidation occurs in an aqueous solution of potassium iodide containing sulfuric acid and exposed to air. These two observations provide additional support for the contention that the acidic sites on the surface of boron phosphate are active for the oxidation. Flockhart and co-workers (*14*) found that the sodium form of Y zeolite did not catalyze the oxidation of iodide, whereas the hydrogen Y zeolite possessed an activity as large as that measured with the silica–alumina. Since hydrogen Y zeolite heated below approximately 500°C shows substantial Brønsted acidity, while Na Y zeolite does not, no matter what the calcination temperature, they concluded that the sites active for the oxidation likely were of the Brønsted, rather than the Lewis type. While the present work demonstrates that acidic sites are responsible for the catalytic properties of boron phosphate in the oxidation of iodide, it does not provide evidence, except of an indirect nature, that such acidic sites are of the Brønsted and not of the Lewis type. However, the aforementioned results of Flockhart and co-workers (*14*) together with the observation (*11*, *12*) that the concentrations of Brønsted sites on boron phosphate decrease with increasing pretreatment temperature suggest that, as with silica–alumina, the active sites in the oxidation of iodide to iodine on boron phosphate are Brønsted acid sites.

ACKNOWLEDGMENT

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