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KINETICS OF THE FORMATION OF $BaSnO_3$ FROM BARIUM CARBONATE AND TIN(IV) OXIDE OR OXALATE PRECURSORS*

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ABSTRACT

Various physical mixtures of $BaCO_3$ with SnO_2 react following rate laws determined by contracting geometry with an activation energy of 55–70 kcal/mole. Ba_2SnO_4 is an intermediate in the formation of $BaSnO_3$. In contrast, $BaSn(C_2O_4)_2 \cdot 0.5H_2O$ and $Ba_2Sn(C_2O_4)_4 \cdot 6H_2O$ decompose to yield an intimate mixture of highly reactive $BaCO_3$ and SnO_2 which subsequently reacts at a relatively low temperature to form $BaSnO_3$ directly, without intermediates, according to the second-order rate law, with a similar activation energy.

INTRODUCTION

Chemical reactions in the solid state are of considerable practical importance and interest. There is a constant effort to enhance the reactivity of solids in order to obtain more homogeneous products with reduced effort and expense. Therefore, an understanding of the kinetics and mechanisms by which two solids react to form a third is of considerable value.

The reaction of barium carbonate and tin(IV) oxide to form barium stannate, $BaSnO_3$, is particularly interesting. Wagner and Binder[1] used X-ray diffraction techniques to follow the reaction between an equimolar physical mixture of the two materials, and observed that Ba_2SnO_4 was formed as an intermediate in the course of the reaction. This reacted at higher temperatures with the unreacted tin(IV) oxide to form $BaSnO_3$.

Oxalate compounds of barium and tin can be precipitated from aqueous solution[2]. These compounds decompose in air to yield a mixture of barium carbonate and tin(IV) oxide, which reacts at higher temperatures to form $BaSnO_3$ without any evidence for the prior formation of Ba_2SnO_4. Neither investigation indicated the presence of BaO at any time and it is therefore concluded that the reactions involve direct interaction of barium carbonate and tin(IV) oxide with the concomitant evolution of

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CO_2. This fortunately enables the progress of the reaction to be followed by monitoring the weight loss due to the evolution of carbon dioxide.

The kinetics of this reaction were determined for several physical mixtures and the precipitated compounds, $BaSn(C_2O_4)\cdot 0.5H_2O$ and $Ba_2Sn(C_2O_4)_4\cdot 6H_2O$, in order to differentiate between the various reaction paths.

EXPERIMENTAL PROCEDURES

Reagent grade $BaCO_3$, BaC_2O_4, and SnO_2 were used. The specific surface areas determined by nitrogen absorption (BET technique) were 3.2, 0.6, and 3.5 m^2/g, respectively. $BaSn(C_2O_4)_2\cdot 0.5H_2O$ and $Ba_2Sn(C_2O_4)_4\cdot 6H_2O$ were prepared as described previously[2]. $BaSnO_3$ was prepared by calcination of $BaSn(C_2O_4)_2\cdot 0.5H_2O$ in air at 800°C. Its surface area was determined to be 10.4 m^2/g. Various carefully weighed mixtures of the above materials were made by light grinding in a mortar and pestal under methanol. Equimolar mixtures of $BaCO_3$ with each of SnO_2, and $BaSn(C_2O_4)_2\cdot 0.5H_2O$; and a mixture $2BaCO_3\cdot SnO_2$ were prepared. Similar mixtures were made substituting BaC_2O_4 for $BaCO_3$.

In order to reaffirm the difference in behavior between the coprecipitated oxalate compounds and the physical mixture, 1 g samples of the $BaCO_3\cdot SnO_2$ physical mixture and $BaSn(C_2O_4)_2\cdot 0.5H_2O$ were heated for thirty minutes in air at 100°C intervals from 500 to 1000°C. X-ray diffraction patterns were made of each sample using a GE-XRD-3 diffractometer and CrKα radiation.

Isothermal weight loss measurements were made using a Cahn RG microbalance. Samples were suspended in a small hemispherical platinum basket which

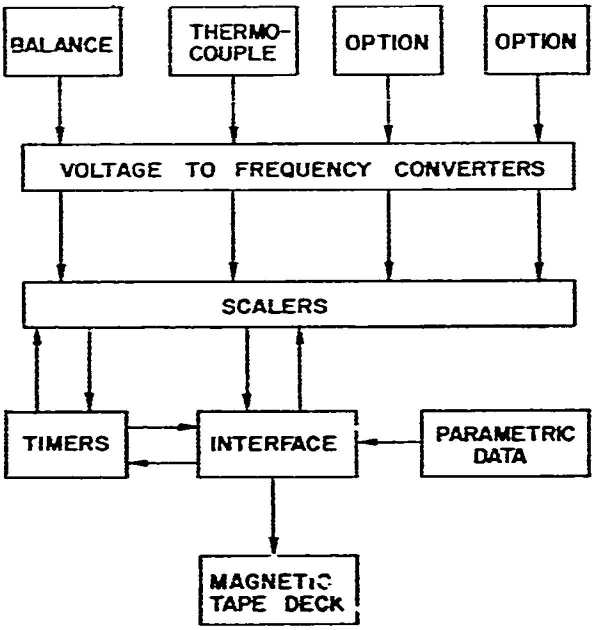

Fig. 1. Block diagram of the data collection system.

hung in a 0.75 in. i.d. fused quartz tube. A chromel–alumel thermocouple was positioned just under the basket. A clam shell furnace maintained at about 500°C was placed around the tube until the sample came to constant weight (approximately 20 mg). This served to convert the oxalates to carbonates. This furnace was then quickly replaced with a similar one controlled at the desired reaction temperature and data collection was begun. A flow of dry oxygen at about 1 cc/sec was maintained down the tube.

Fig. 1 is a block diagram of the data acquisition system. The system accepts up to four analog inputs. Only two were used here corresponding to weight and temperature. The voltages were converted to frequency using a Logical Data Model LDC-1248 converter which provided a wide selection of conversion rates. In this case the weight channel was 1 vdc = 10 kHz and the temperature channel was 0.1 vdc = 10 kHz. The four channels were simultaneously counted on four scalers (Harshaw Chemical Co., Model NS30A) for a predetermined interval set on the timer (Harshaw Chemical Co. Model NT-29). The magnetic tape interface (Harshaw Chemical Co., Model NE-25) served as the control center. In the automatic mode the data was scanned repeatedly at the preset time interval and placed on the magnetic tape along with channel identification numbers. The scalers were provided with an extra level of buffer storage so that the dead time was insignificant. A fifth channel could be created to insert a six-digit number for labeling or control purposes using a parametric data unit (Harshav· Chemical Co., Model NY-10). The data were stored on magnetic tape by means of a magnetic tape deck (Digital Data Co., Model 1337-556). The scalers,

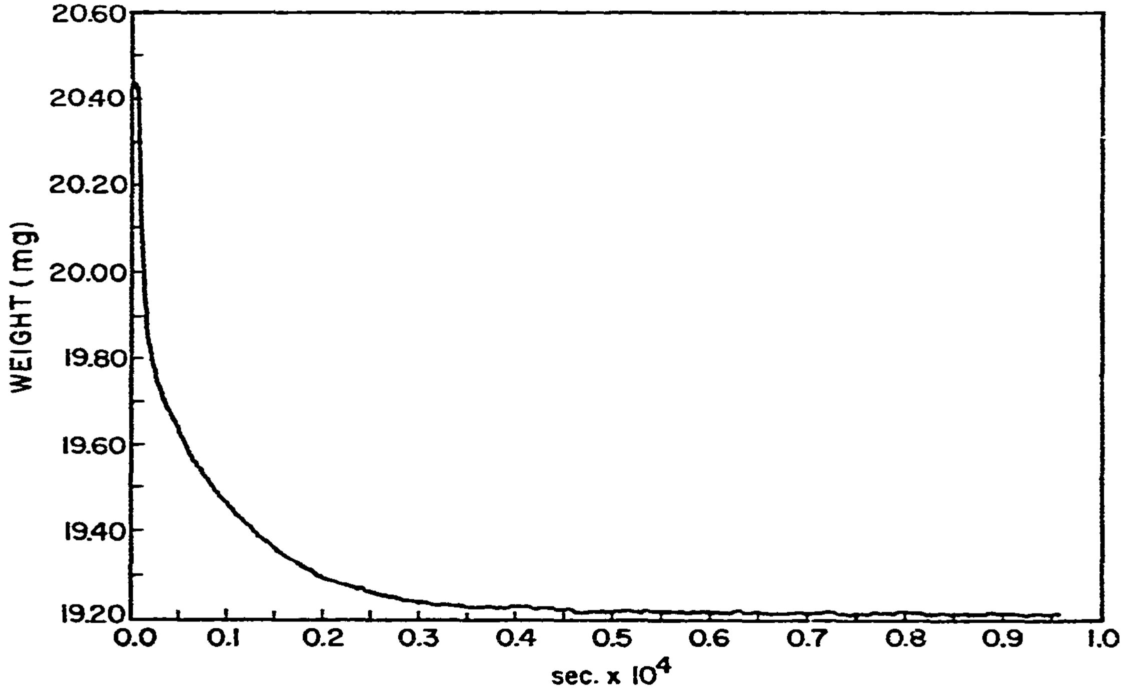

Fig. 2. Plot of weight *vs.* time for $BaSn(C_2O_4)_2 \cdot 0.5H_2O$ at 825°C, in dry O_2 (15-sec intervals).

timer, interface, and parametric data unit were all housed as a single standard NIM bin so that the total electronic units shown in Fig. 1, less the inputs, formed a compact package requiring only 25 in. of rack space.

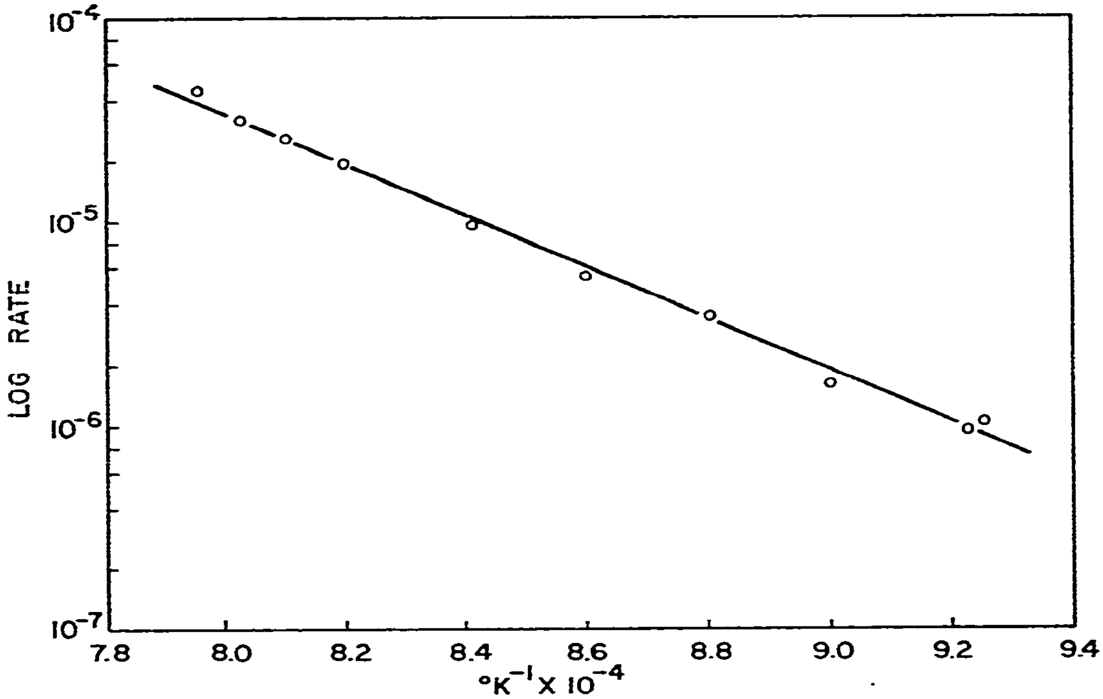

Fig. 3. Arrhenius plot for $2BaCO_3 + SnO_2$ in dry O_2. $\Delta H^* = 57.8$ kcal/mole and $A = 4.3 \times 10^5$.

The first step in data processing consisted of transferring the data from tape onto the disc storage of a Honeywell 635 computer in appropriate arrays corresponding to each channel. Computer-generated plots of each array as a function of time were made. Fig. 2 shows a typical weight *vs.* time plot. Subsequent data processing was as previously described[3]. Table I gives the functions of alpha used in the computer

TABLE I

KINETIC FUNCTIONS USED IN THE COMPUTER ANALYSIS

Name	*Function*[a]
Power law	α^n, $n = 1, 2, 1/2, 1/3, 1/4$
Contracting geometry	$1-(1-\alpha)^{1/n}$, $n = 2, 3$
Erofeev	$[-\ln(1-\alpha)]^{1/n}$, $n = 1, 1\frac{1}{2}, 2, 3, 4$
Diffusion controlled, 2D	$(1-\alpha)\ln(1-\alpha)+\alpha$
Diffusion controlled, 3D	$(1-2/3\alpha)-(1-\alpha)^{2/3}$
Jander	$[1-(1-\alpha)^{1/3}]^2$
Prout–Tompkins	$\ln[\alpha(1-\alpha)]$
Second order	$1/(1-\alpha)-1$
Exponential	$\ln \alpha$

[a] α = fraction reacted.

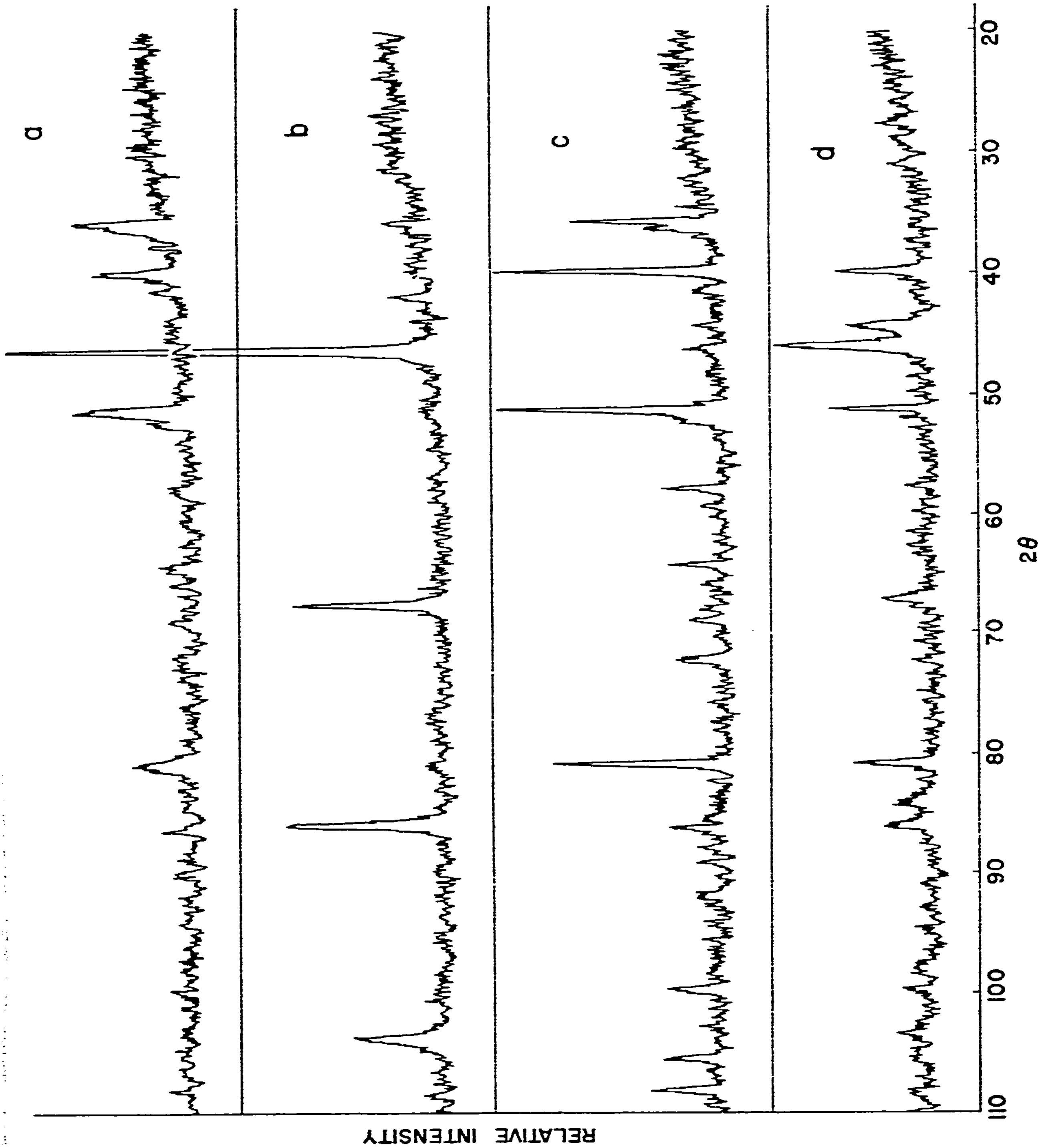

Fig. 4. X-ray diffraction patterns using CrKα radiation. a, $BaSn(C_2O_4)_2$ for 30 min in air, at 600 °C; b, $BaSn(C_2O_4)_2$ for 30 min in air, at 700 °C; c, $BaCO_3 \cdot SnO_2$ for 30 min in air, at 900 °C; d, $BaCO_3 \cdot SnO_2$ for 30 min in air, at 1000 °C.

analysis. A plot of the alpha function *vs.* time is linear for the appropriate rate law, and the standard deviation in alpha arising from the least squares fit of the experimental data to each equation is used as the determining factor for the selection of the applicable rate law or laws for each system.

The final stage of computer processing involved the determination of the activation energy and pre-exponential term from the Arrhenius equation. Fig. 3 illustrates a typical plot.

RESULTS AND DISCUSSION

Fig. 4 shows the relevant X-ray diffraction patterns. The oxalate compound decomposes to yield $BaCO_3$ and SnO_2 which react cleanly and quickly between 600° and 700°C to form $BaSnO_3$ without the formation of intermediate phases[2]. The $BaCO_3 \cdot SnO_2$ mixture, however, does not begin to react until above 900°C and the pattern at 1000°C clearly shows the presence of $BaSnO_3$, $BaSnO_4$, and SnO_2 indicating the presence of Ba_2SnO_4 as an intermediate phase.

The reaction of the $BaCO_3$ and SnO_2 formed by the decomposition of the coprecipitated oxalate was best described by the second-order rate equation in every case. The initial formation of $BaSnO_3$ from $Ba_2Sn(C_2O_4)_4 \cdot 6H_2O$, $BaSn(C_2O_4)_2 \cdot 0.5H_2O$, and the mixtures of the latter with $BaCO_3$ or BaC_2O_4 gave the smallest standard deviation using the alpha function $[1/(1-\alpha)]-1$. The activation energies and pre-exponential terms derived from these data were 55–60 kcal/mole and 2×10^8–6×10^9, respectively. Second-order reactions are uncommon but not unreasonable for such solid phase reactions. Presumably the reaction is first order with respect to each of the reactants, $BaCO_3$, and SnO_2, leading to second-order behavior overall. Such behavior has been proposed[4] for the reaction of Bi_2O_3 and Fe_2O_3. The activation energy is not significantly different from the 60 kcal/mole reported for the decomposition of $BaCO_3$ in the absence of a reacting oxide[5]. The temperature of the decomposition however, is several hundred degrees lower.

The reactions of the physical mixtures which do not involve the coprecipitated compounds do not follow second-order kinetics at all. The contracting geometry models best describe their behavior in general. Those samples which utilized $BaCO_3$ follow contracting volume ($n = 3$) best, while those which started with BaC_2O_4 prefer the contracting area ($n = 2$) law. The activation energies are in the range of 55–70 kcal/mole, and the pre-exponential terms range from 4×10^5 to 8×10^8. The reactions to form Ba_2SnO_4 starting with coprecipitated oxalate, *i.e.*, the second step in the decomposition of $Ba_2Sn(C_2O_4)_4 \cdot 6H_2O$ and of the mixtures of $BaSn(C_2O_4)_2 \cdot 0.5H_2O$ with $BaCO_3$ and BaC_2O_4, also follow the contracting volume equation reasonably well and give Arrhenius parameters in the above range. Samples prepared with BaC_2O_4 always gave somewhat smaller values of the Arrhenius parameters than the comparable mixture prepared from $BaCO_3$.

As anticipated, the actual energetics of the reaction does not differ significantly between the mixture of $BaCO_3$ and SnO_2 prepared physically, and that resulting from the decomposition of a coprecipitated oxalate, as indicated by the insignificant variations in the activation energies. The several hundred degrees difference between the two reaction zones arises from the differences in the pre-exponential term and probably reflects the relative differences in particle sizes and contact areas. In the coprecipitated compound the barium and tin are mixed on an atomic scale. This, however, can not be maintained after decomposition, as shown by the presence of the X-ray diffraction patterns of $BaCO_3$ and SnO_2 in Fig. 4a. The breadth of the lines do indicate that the particles are small and no doubt strained with a high concentration of physical defects. The microhomogeneity of such a mix must also surely surpass that obtained by physical mixing. Consequently, this increased surface area and points of contact give rise to an almost homogeneous-type second-order reaction with a relatively high pre-exponential term. In contrast the physical mixture of the bulk materials is made up of coarser particles which are not nearly as intimately mixed. Their reaction is described by geometrical rate laws and is slower even though the same bonds are broken and formed during the reaction. The reaction also requires a longer diffusion path and thereby creates regions of Ba_2SnO_4.

CONCLUSIONS

Coprecipitated $BaSn(C_2O_4)_2 \cdot 0.5H_2O$ and $Ba_2Sn(C_2O_4)_4 \cdot 6H_2O$ decompose to yield intimately mixed highly reactive $BaCO_3$ and SnO_2 which subsequently reacts at a relatively low temperature. This reaction to form $BaSnO_3$ directly follows second-order kinetics with an activation energy of 55–60 kcal/mole. Physical mixtures of $BaCO_3$ and SnO_2 on the other hand do not react until much higher temperatures and follow geometrically controlled rate laws. The activation energy does not vary significantly and thus the difference is reflected in a lower pre-exponential term for the physical mixture. The relative inhomogeneity and longer diffusion paths also give rise to the formation of Ba_2SnO_4 as an intermediate.

ACKNOWLEDGMENTS

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