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Size Dependence of Chemical Reactivity of Gaseous Metal Clusters, A New Mechanistic Probe

by

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May 17, 1993

SIZE DEPENDENCE OF CHEMICAL REACTIVITY OF GASEOUS METAL CLUSTERS, A NEW MECHANISTIC PROBE[(a)]

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1. Introduction

The determination of the mechanisms of chemical reactions leading to the formation of different types of materials is one of the principal occupations of many chemists today. To accomplish this, the dependence of the observed transformation is studied as a function of a number of intensive variables such as temperature, pressure, concentration of reactants as well as the Hydrogen ion concentration of the solution. In this account, we summarize recent studies in which the observed changes of the chemical reactivity of gaseous niobium clusters with size was used as a new degree of freedom that assists in deducing the mechanism of the chemical reactions studied.

2. Methodology

The clusters are made by techniques similar to those used by Smalley and his group,[1] utilizing laser evaporation-supersonic expansion techniques. The 355 nm harmonic of a YAG pulsed laser is used to evaporate Nb atoms from a rotating rod, followed by the opening and closing of a pulsed nozzle with 3-5 atm backing pressure of helium gas. The

collision with the expanding helium atoms cools off the hot Nb atoms, and the unidirectional expansion greatly reduces the spread in the velocity distribution of the expanding gases of helium and its Nb vapor content. This greatly reduces their translation (as well as rotational and to a lesser extent, their vibrational) temperature. Collision between the cold Nb atoms leads to their clustering. The gas mixture passes through a reactor in which dilute mixtures of different reagents in Helium gas is introduced. The gases are then expanded to eliminate further collisions and passed through a skimmer to select the clusters and their products moving along the expansion axis. This leads to the laser focus of the ionization region of a laser time-of-flight mass spectrometer. The ionization laser operates at 193 nm, which is capable of one-photon ionization of all the niobium clusters and their products. This eliminates the need for focusing the laser and thus avoiding nonlinear processes. This, together with the fact that Nb has only one isotope (which simplifies the observed mass spectrum) makes Nb clusters well suited for studies in which laser mass spectrometric techniques are used for detection.

3. Size Dependence of Stereochemical Specificity[2]

From molecular beam studies,[3] it is known that in the reaction between metal atoms (M) like Ba or Sr with Halocyanide (X-CN), MCN is formed with a higher cross section than MX. This is attributed to the stereospecificity of the reaction. The reaction involves an impulsive collision which gives rise to the product formed. Thus if the metal atom collides with the CN end of the molecule, MCN is formed with high probability due to the high exothermicity of the reaction. The formation of metal halide, MX, is not as exothermic. Upon the collision of the metal atom with the halogen end of the XCN

molecule, the probability of product formation is not as high. The question thus arises, what would happen in a reaction between the XCN molecule and a sufficiently large metal cluster (large compared say to the size of the BrCN molecule) and polarizable enough to form a complex to act as an intermediate for the reaction? Would this diminish or eliminate the stereochemical specificity observed in the monomer reaction?

The reaction of BrCN was studied[2] with Nb and its clusters. The ratio of the mass peak intensity of Nb_xCN to that of Nb_xBr is determined and plotted as a function of x as shown in Figure 1. If one draws a smooth curve (to remove the fluctuations observed in the ratio for clusters of small size, resulting most likely, from variation in the ionization cross sections), one reaches the conclusion that, indeed, the stereochemical selectivity, as measured by the deviation of the mass peak ratio from unity, is diminished rapidly. Thus while this ratio is near nine for the reaction with the niobium dimer, it falls rapidly to a constant value of 2 for $x \geq 7$. It should be remembered, however, that this is the mass peak intensity ratio of $Nb_xCN^+/NbBr^+$, which is related to the product [NbCN]/NbBr] ratio by the ratio of ion yields from the corresponding neutrals. Thus the final value of 2 (instead of unity) observed for this ratio at $x \geq 7$ might be a measure of the ionization yield ratio for the two kinds of compounds. The photodissociation of the M_xX cluster might explain the larger value of the observed $Nb_x(CN)^+/Nb_xX^+$ intensity ratio.

The above conclusion is readily explained. For small x, the collision is of the impulsive type. Thus the outcome would depend on which end of the BrCN molecule the metal atom or dimer or small cluster collides with. As the cluster size increases, complex formation would result, irrespective of which end of BrCN the cluster collides. This leads

to a loss of the stereochemical specificity observed in the reaction between the metal and its small clusters with XCN.

4. Benzene Dehydrogenation:[4] Is there a size-threshold?

In the mass spectrum of the reaction products of Nb_x with benzene, two dominant types of products are observed, $Nb_x(C_6H_6)$ and $Nb_x(C_6)$. For small clusters, the $Nb_xC_6H_6$ mass peaks are intense. Furthermore, for x = 1 and 2, mass peaks for $Nb_x(C_6H_6)_2$ are also observed. At $x \geq 4$, the mass peaks resulting from $Nb_xC_6H_6$ are found to decrease while those due to Nb_xC_6 mass peaks increase. This suggests that these two species are produced from competing channels; the dehydrogenation of the $Nb_xC_6H_6$ leads to the formation of Nb_xC_6. Thus, as x increases above 4 the $Nb_xC_6H_6$ peak intensity decreases and that of Nb_xC_6 increases.

If one assumes that the ratio of the mass peak intensity of Nb_xC_6 to the sum of those for Nb_xC_6 and $Nb_xC_6H_6$ can be taken as a measure of the dehydrogenation probability of benzene on Nb_x clusters, the size dependence of the dehydrogenation process can be represented by Figure 2. This figure shows a threshold for the dehydrogenation process at x = 4 and a dehydrogenation probability with maxima at 5,6 and minima at 8 and 10. The minima corresponds well with the known high stability of Nb_8 and Nb_{10} clusters.

The sudden increase in the dehydrogenation probability at x = 4 or 5 could either be catalytic or thermodynamic in origin. If it is the latter, it suggests that a minimum number of niobium-carbide bonds are needed to be formed to drive the reaction. If it is the former, it suggests that a minimum number of Nb atoms are required to anchor the benzene ring for an effective activation of the carbon-hydrogen bonds. Theoretical

calculation might be able to distinguish between these two possibilities.

Other studies[5] have yielded two additional insights into the dehydrogenation process. In order to observe it on the time scale of our experiment (microseconds), the reagent is required to have at least one double bond. Furthermore, only the loss of an even number of hydrogen atoms is observed for the dehydrogenation of hydrocarbons. The former observation suggests a mechanism involving complex formation (with the π-electronic system of the double bonds). The latter observation suggests the formation and evaporation of molecular hydrogen.

5. Steric Effects due to Cluster Size[6]

The reaction of metal atoms with organic halides, e.g., CH_3Br, leads to the formation of a stable metal halide molecule (MBr):

$$RBr + M \rightarrow MBr + R$$

This is known as an abstraction type reaction.

Let us examine the bromine abstraction reaction between niobium clusters from two different organic reagents. In one, the bromine is not sterically shielded, e.g., CH3-CH2Br; the other is shielded as in CH3CHBr-CH3. The mass peak intensities of NbxBr are normalized to an NbI^+ peak in each spectrum produced from the reaction of Nb clusters with CH_3I which is added in the same amount in each experiment.

The results are shown in Figure 3. The reaction with both reagents gave the same yield of Nb_xBr from small clusters ($x < 5$), including the fluctuation resulting from the ion yield dependence on x for small x. For $x \geq 5$, the yield of Nb_xBr from $H_3C\text{-}CHBr\text{-}CH_3$ is reduced by ~20% when compared to that produced from the reaction with the less sterically

hindered reagent (CH_3CH_2-Br).

The above results strongly suggests that sterric hindrance depends not only on the structure of the organic reagent, but also on the structure and size of the metal cluster. At $x \geq 5$, the cluster size is such that these clusters become less efficient in abstracting the bromine from the sterrically hindered reagent than from the nonsterrically hindered bromide. Collisions between these clusters and the sterrically hindered side of the molecule leads to low yield of product.

6. Size Dependence of the Reactivity as a Monitor of the Reaction Mechanisms in Multiple Reactions[7]:

When more than one product is observed from the reaction of clusters with a certain reagent, the question is usually raised whether the reactions involved are competing with, or parallel to, one another. Using the change in the cluster size as an additional degree of freedom, one can distinguish between these two possibilities as shown below.

If the multiple products result from competing channels, i.e., result from complex formation that decomposes to give either one product or the other, one expects that as the size is changed, an increase in the mass peak intensity of one product should result in a decrease in the peak intensity of the other. This is shown in Figure 4 for the reaction of Nb_x with CO_2. In the reaction with small clusters, Nb_xO is observed. As the cluster size increases above $x = 4$, the Nb_xO mass peak intensity diminishes while that for Nb_xCO_2 increases. We believe[6] that the cluster first forms the complex (ONb_xCO) which is very hot due to the formation of the Nb-O and Nb-CO bonds and the absence of cooling collisions. As a result, the complex cools off by evaporating CO. As the cluster size increases, the

increase in the internal degrees of freedom is sufficient to absorb the amount of heat produced in the exothermic formation of the Nb-O and Nb-CO bonds and evaporation cooling is no longer needed.

If the multiple products result from different types of collisions, the cluster size at which a new channel opens up does not affect the probability of the product formation of the other product. An example of this mechanism is the reaction of Nb_x with R-CH=CHBr to give two products:

Nb_x + R-CH=CH-Br → Nb_xBr (bromine-abstraction)

→ Nb_xRC_2Br (addition-dehydrogenation)

Figure 5 shows the change in the relative yield of Nb_xC_3Br (top) and Nb_xBr (bottom) as a function of x for the reaction with two different unsaturated organic bromides (H_3C-CH=CHBr and H_2C=CHCHBr). As shown in the top part of the figure, at x = 6, the threshold of the dehydrogenation reaction (which requires complex formation with the π-electronic system of the organic reagent), no significant change is observed in the mass peak intensity of the abstraction reaction yield shown in the bottom of Figure 6. This suggests that bromine abstraction results from a different type of collision (impulsive type with the bromine atom) than the sticky type required for the complex formation with π-electronic system which give rise to the dehydrogenation process.

7. Conclusions:

In this article, the observed changes in the reactivity of niobium metal clusters of increasing sizes with different reagents are used as a new degree freedom to give us a better understanding of the mechanisms and the type of collisions leading to chemical reactions.

Several conclusions are reached: 1.) as the size of metal cluster increases, the type of collision leading to a certain chemical reaction changes from impulsive to an attractive type which leads to the formation of complexes as intermediates; 2.) For reactions producing more than one product, the observed changes or lack of changes in the amount of one product as the second begins to be produced as the cluster size increases could identify the mechanism of the reaction involved. For competing reactions, i.e., those produced from complex formation, a change is observed. However, for products produced from different types of collisions, no change in the amounts of one product is observed at the cluster size when the second one begins to be observed; 3.) If clusters are used as efficient catalysts for dehydrogenation reactions, the reagents are required to have at least one double bond; this suggests a π-complex formation as intermediate; 4.) dehydrogenation reaction on metal clusters is found to have a size threshold; 5.) Small clusters are more efficient in abstraction reactions of groups or atoms that are sterrically hindered. The maximum size of the cluster can efficiently give products depends on the sterrically hindered volume shielding the atom or group being abstracted by the metal cluster; 6) the reaction of niobium metal clusters, Nb_x, with CO_2 gives [(Nb_{x-1}) NbO] cluster and CO for small cluster sizes ($x < 5$) and [Nb_{x-2}NbO NbCO] cluster for larger clusters.

The fact that metal clusters are reactive chemicals offers not only new methodology to understand chemical reaction mechanisms, but also new routes in designing material synthesis. Once we understand how metal clusters react, using them for synthesis design of new material can be placed on a firm ground. The quantitative mechanisms of metal surface catalysis might also be understood.

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Figure Captions

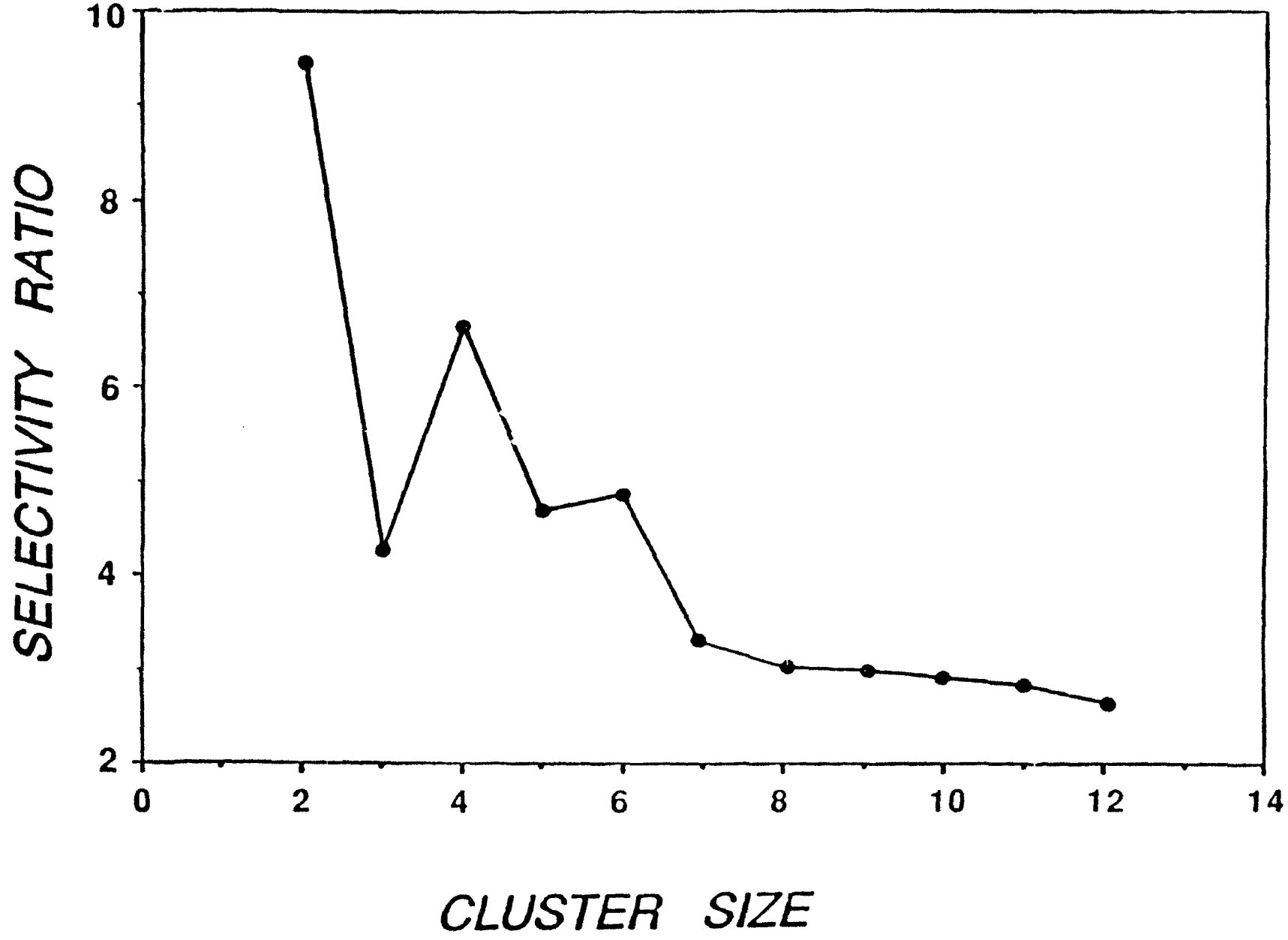
Figure 1: The decrease of the stereochemical specificity with cluster size in the reaction betweeen niobium clusters and BrCN. (At x = 7 it disappears.)

Figure 2: The observation of size threshold in the dehydrogenation of benzene by niobium clusters at x = 4).

Figure 3: The sterric hindrence dependence on the cluster size in its reaction with sterically hindered group (e.g., bromine). For $x \geq 5$, a large difference in the cross section is with C_2H_5Br and the more sterically hindered $CH_3CHBrCH_3$ molecule is observed.

Figure 4: An example of competing reactions: As the niobium size increases, the appearance of a new product (Nb_xCO_2) at x = 5 decreases the yield of the other (Nb_xO) in the CO_2 + Nb_x reaction with Nb_x.

Figure 5: An example of parallel reactions: As the cluster size increases, the appearance of a new product does not affect the yield of the other: the dehydrogenation top) vs bromine abstraction (bottom) reaction. As the dehydrogenation product is observed at x = 6 in the top figure, no effect is observed in the bromine abstraction product (Nb_xBr) in the bottom figure.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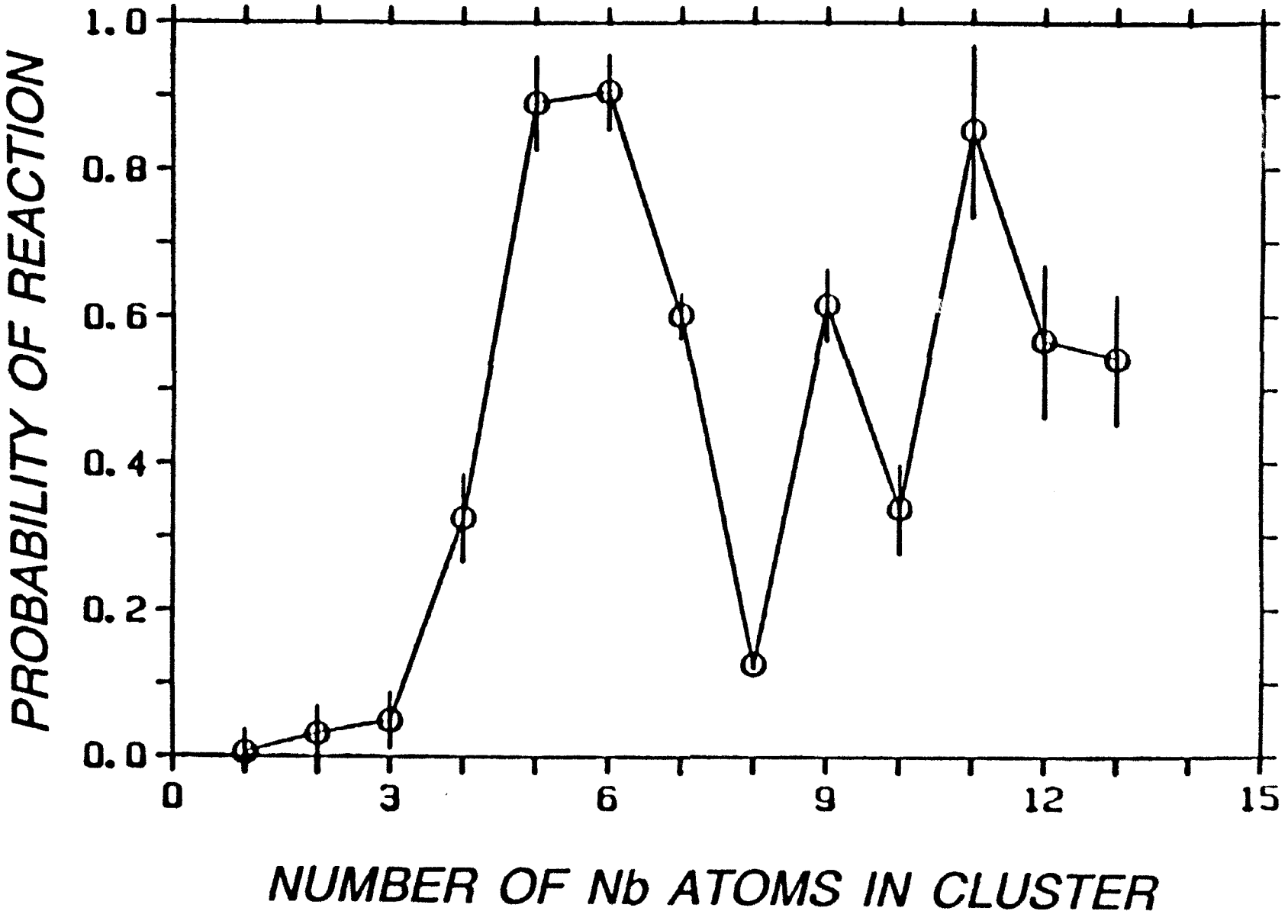
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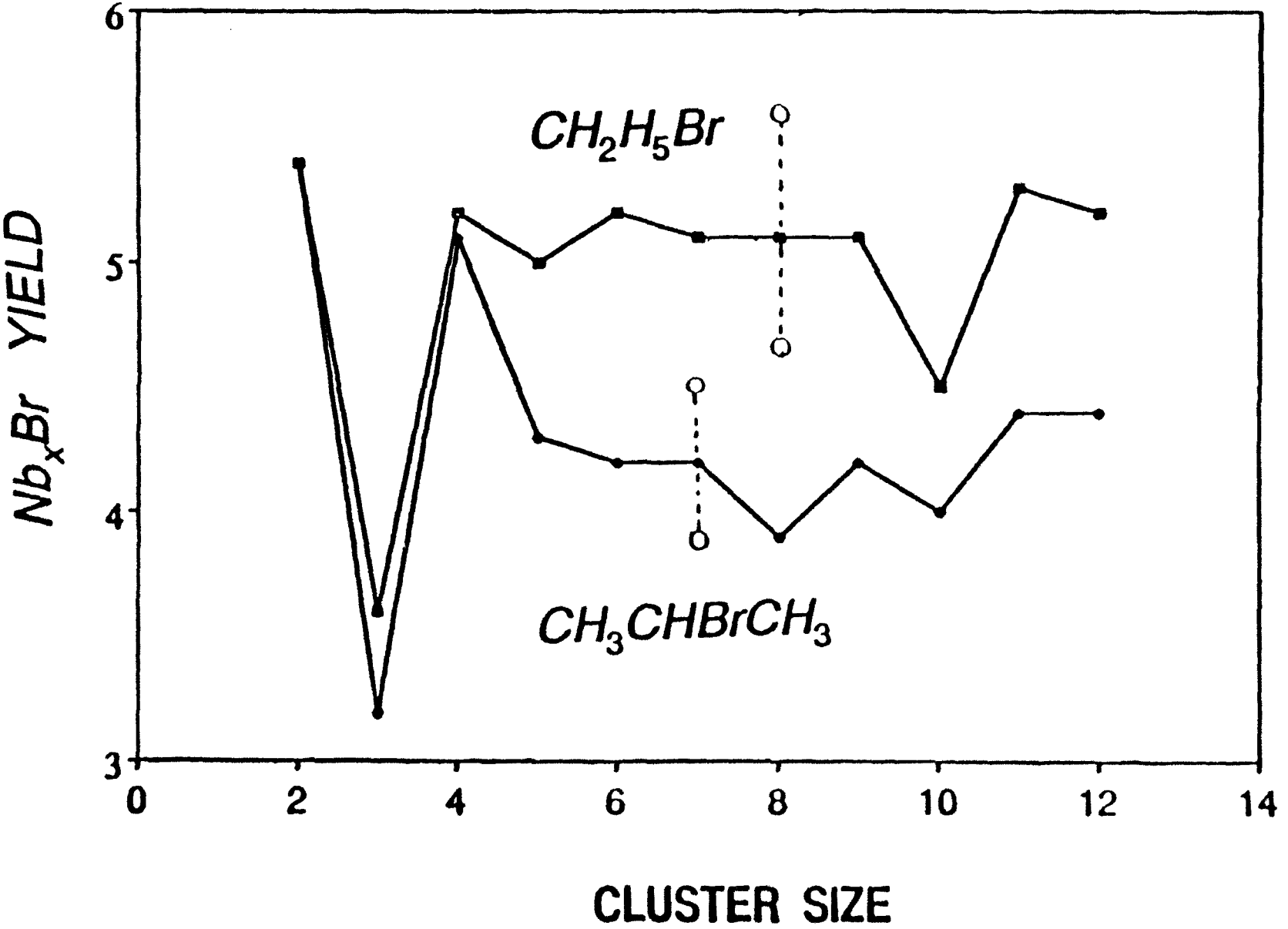
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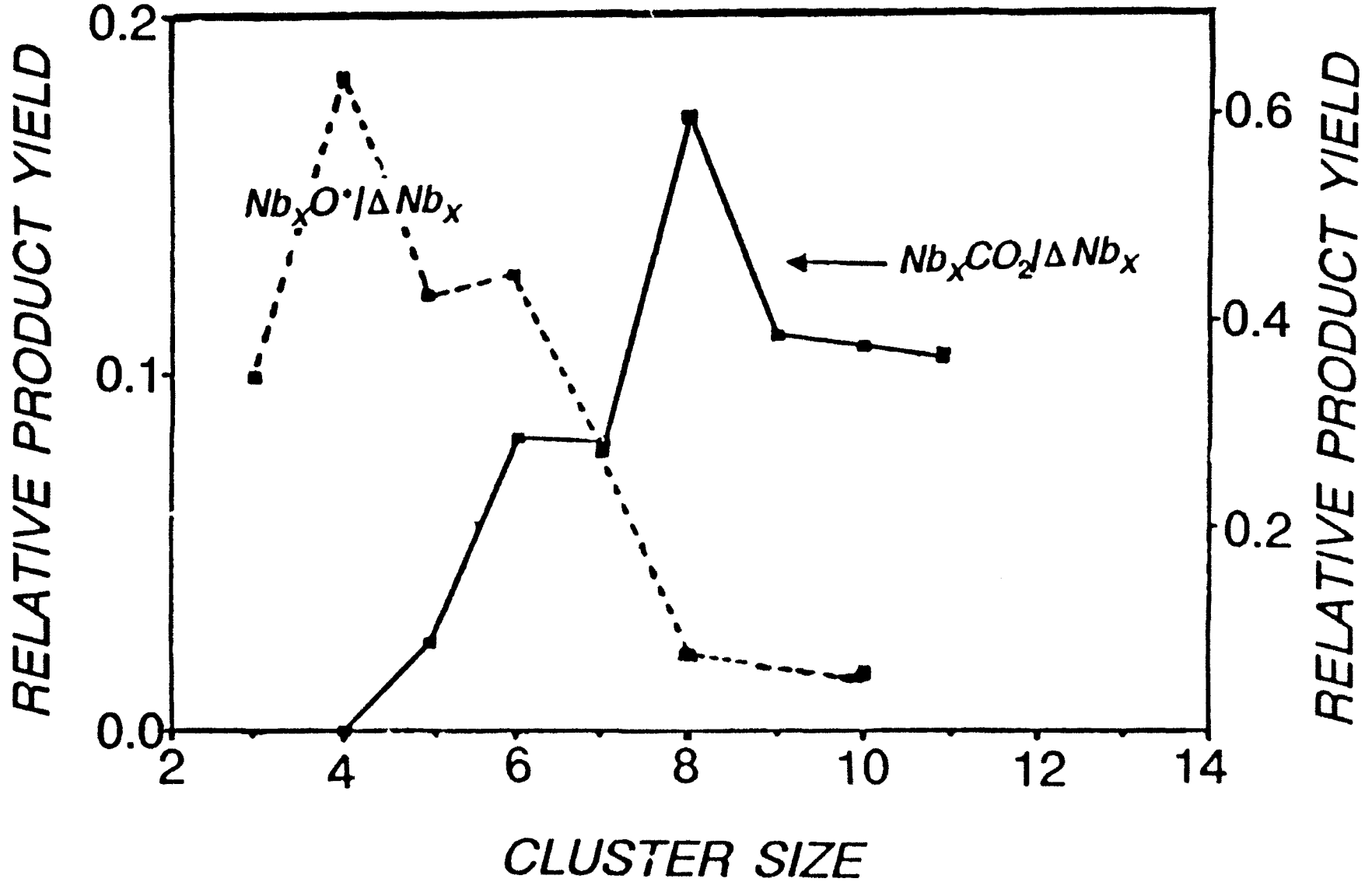
CLUSTER SIZE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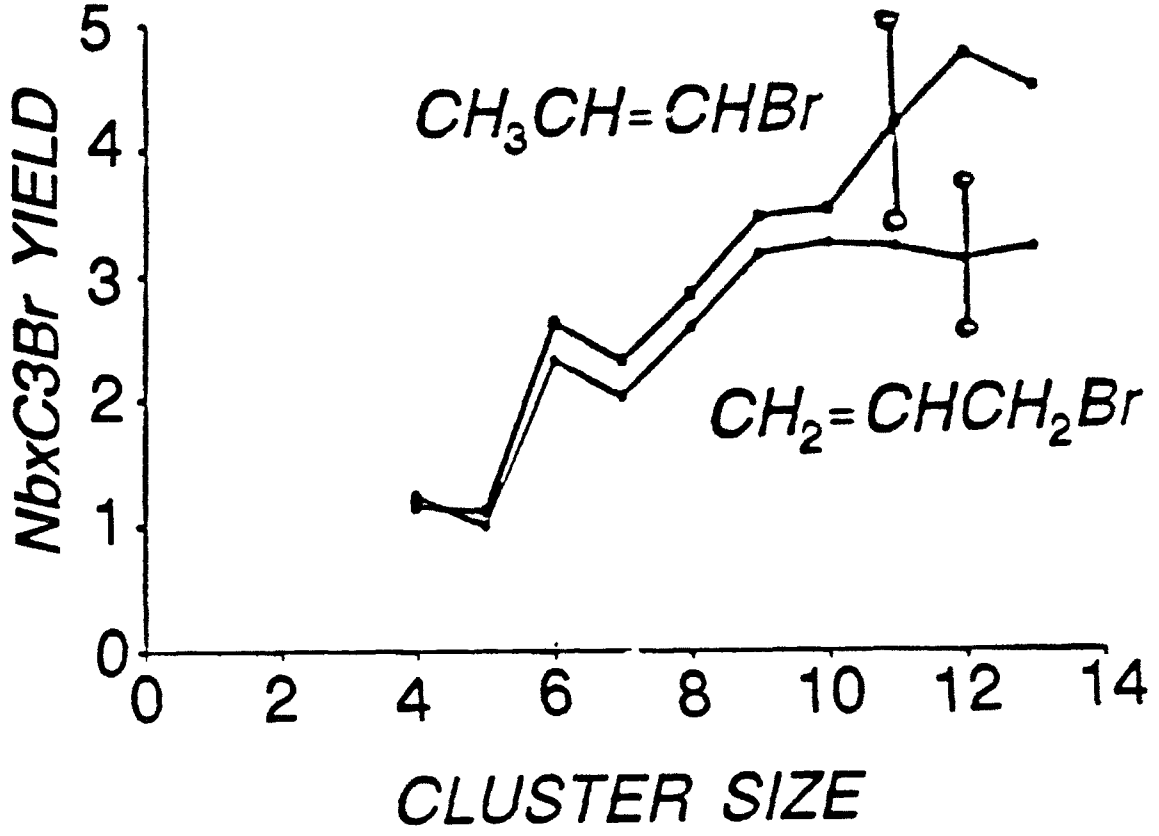
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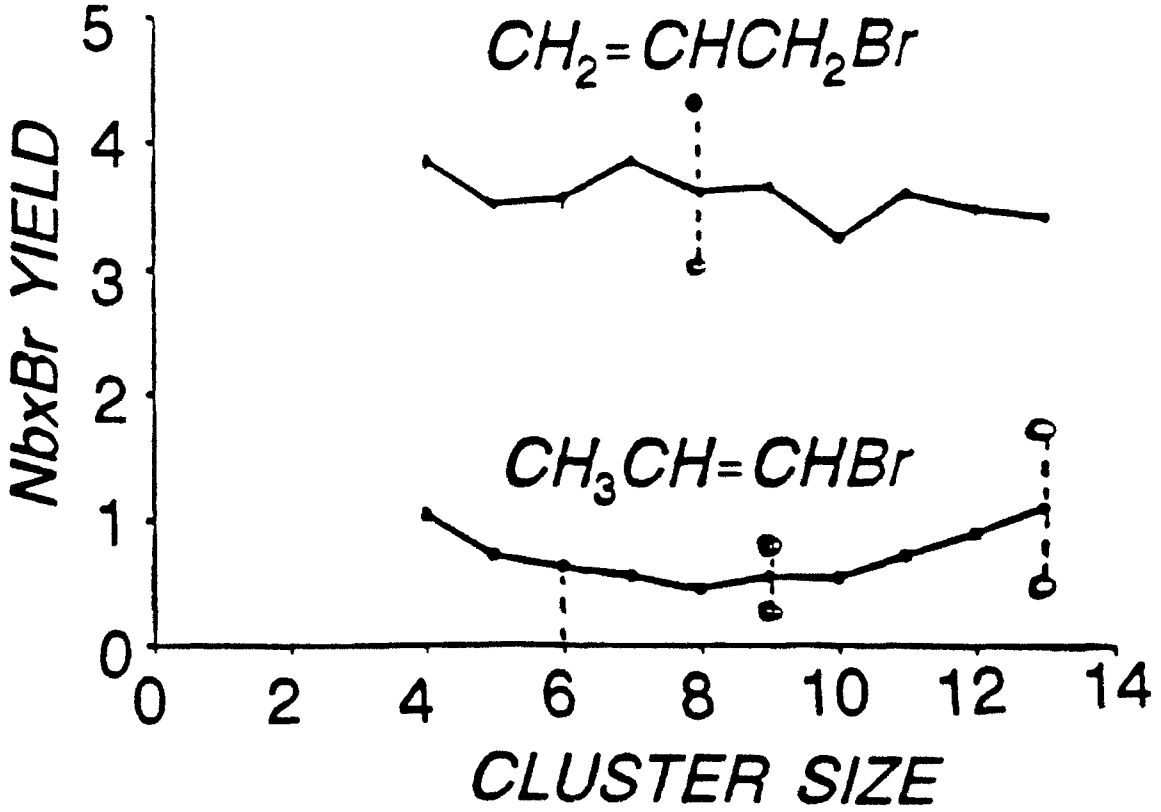
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