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### INTRAMOLECULAR EXCHANGE IN NIOBIUM AND TANTALUM PENTA-ALKOXIDES

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# INTRAMOLECULAR EXCHANGE IN NIOBIUM AND TANTALUM PENTA-ALKOXIDES

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Variable temperature proton magnetic resonance studies on dimeric niobium and tantalum penta-methoxides, -ethoxides and isobutoxides have been carried out. The activation energy for scrambling of the terminal and bridging alkoxy groups was found to be fairly constant (10 to 12 kcal mole<sup>-1</sup>) and the free energy activation  $\Delta G^\ddagger$  increased by small amounts as the degree of chain branching in the alkoxy ligand increased. For the tantalum derivatives the variation in entropy of activation was found to be quite dependent on ligand bulk, and it has been suggested that steric effects play an important role in the activation process. Terminal site scrambling was found to occur at a faster rate than terminal-bridging scrambling, as reflected in a lower activation energy. Some observations on chemical shifts of terminal and bridging sites are made, the importance of a neighbour-anisotropy effect being indicated.

## INTRODUCTION

Proton magnetic resonance spectroscopy has been used previously<sup>1</sup> to show that niobium and tantalum penta-alkoxides exhibit a dimeric bi-octahedral structure in solution, very similar to that of the corresponding penta-chloride.<sup>2</sup> Distinct proton resonances for bridging and terminal groups are observed near room temperature. In addition, the resonances of the terminal groups separate at lower temperatures into two equally populated sets, representing groups in the plane of the two bridges and the metal atoms, and those situated above and below this plane. Alkoxy groups with a high degree of chain branching, such as tertiary-butoxide, showed only the monomeric species in solution in accordance with Bradley's theory.<sup>3</sup> Monomer and dimer species could be identified in the nmr spectrum by their qualitative difference in rate of alcoholysis with the parent alcohol. The bridging and terminal groups scramble at rates accessible by the nmr method, and a preliminary survey together with detailed results for tantalum penta-methoxide was reported. These data showed that the scrambling is slower for the more highly branched alkoxy groups, which is at first surprising for an exchange believed to occur via a partial dissociation. Equilibria studies<sup>1</sup> on the partially depolymerized niobium and tantalum penta-isopropoxides gave an estimate of the enthalpy of an isopropoxy bridge in the region of 8 to 9 kcal mole<sup>-1</sup>, whereas the most rapidly

scrambling species (the penta-methoxides) gave an  $E_a$  value of around 10 kcal mole<sup>-1</sup>.

To investigate the energetics of the scrambling further, a more detailed investigation of the temperature dependent nmr spectra has been undertaken. The present results suggest that the differences in rate are dependent in large part on variations in the frequency factor,  $\log A_o$ , of the Arrhenius rate equation. Unfortunately, nmr kinetic data is noted for the large discrepancies in frequency factors which occur as a result of systematic errors. However, in a series of related systems it is likely that errors of a systematic nature would all be in the same direction and of similar magnitude, provided that data were obtained from the same region of the coalescence phenomenon, i.e. above, below or in the region of coalescence. It is therefore with this reservation in mind that the study was undertaken.

## EXPERIMENTAL

The alkoxides of niobium and tantalum were prepared from the penta-chlorides by established methods.<sup>4,5</sup> The solvent for the nmr experiment was chosen to minimize solvent effects which could lead to large temperature variations in chemical shift. The solutions were prepared in a dry-box under nitrogen using *n*-octane freshly distilled from sodium wire. Approximate concentrations between 0.05 and 0.1 molar were prepared in the nmr tube

using 0.5 ml of solvent. This was necessary in order to avoid the contact of the solution with more glass surfaces than absolutely necessary, since all of these materials are readily hydrolyzed. Initially, three concentrations between 0.05 and 0.5 molar were prepared, but no significant changes in rate could be detected. In the case of the pure tantalum penta-ethoxide, with TMS as reference, some broadening was observed which appeared to be due only to the viscosity of the sample. The results have been reported only for the dilutest solutions (0.05 to 0.1 M) with no exact concentration specified since the rates are concentration independent.

Analysis of the pure alkoxides was carried out by ignition to the oxide after hydrolysis and precipitation by aqueous ammonia. The filtrate and washings from the precipitation were tested to ensure the absence of chloride. A satisfactory metal analysis together with the correct nmr integration of the alkoxy protons was considered adequate characterization<sup>6</sup> of these well-known materials.

The nmr spectra were obtained on a Varian A-60 spectrometer. Temperature measurements were made by measuring chemical shift differences of ethylene glycol or methanol samples supplied by Varian. Theoretical line shapes were calculated from the Gutowsky-Holm equation<sup>7</sup> for two single resonances in the ratio 1:4. Perturbations of bridging exchange by the additional exchange of terminal sites was ignored on the grounds that the lifetime of any individual terminal site is not more than a twentieth of that of a bridging site. Likewise terminal-terminal exchange was examined without reference to bridging exchange, for here the lifetime of a bridge is very long compared to the rate of terminal exchange. A program of the basic equation was set up and to this was added searching routines to characterize the line shapes. This was later simplified considerably by directly plotting lineshape using a Hewlett-Packard 2114A computer and 7200A graphic plotter, which was programmed to reproduce the nmr frequency and intensity scale. Natural linewidths for the exchanging peaks were obtained from the appropriate  $\alpha$ -proton linewidth of the parent alcohol, acidified to remove coupling with the hydroxyl proton. This effective measure of  $T_2$  includes field inhomogeneity and additional broadening due to second order coupling which is unresolved. The homogeneity was reproduced for each run using the internal TMS reference peak shape as criterion. Chemical shifts were taken from TMS in the usual manner. Where the  $\alpha$ -proton resonance appears as a multiplet due to coupling,

the spectra were reproduced by superimposition of pairs of calculated peaks at the appropriate intensities and chemical shifts. It was found that in most cases this had little effect on the rates much faster or much slower than that for coalescence, but a marked effect near coalescence. Due to the characterless shape of the resulting peak in the region of coalescence, the errors in rate become quite large, and this region is best avoided where possible.<sup>8</sup>

Population and lifetime for two sites are given by  $P_a/P_b = \tau_a/\tau_b$ . For bridging exchange the population ratio is 1:4 and hence the reduced lifetime  $\tau = \tau_a\tau_b/(\tau_a + \tau_b)$  represents 0.8 times the bridge lifetime. For terminal-terminal exchange the populations of each site are equal and the lifetime of a site is thus 2 tau. Plots of  $\log(\text{rate})$  versus  $(T^\circ\text{K})^{-1}$  give the Arrhenius activation energy  $E_a$  and frequency factor  $\log A_o$  for the rate process involved. Activation entropy  $\Delta S^\ddagger$  can be related to  $\log A_o$  by the expression

$$A_o = .k_B T . h^{-1} . e^{1-\Delta S/R}$$

where  $k_B$  is the Boltzman constant and  $h$  is Planck's constant.

Free energy calculations at a given temperature  $\Delta G_T^\ddagger$  are given by

$$\Delta G^\ddagger = 2.303RT \log(k_B T/kh)$$

where  $k$  is the measured rate at temperature  $T^\circ\text{K}$ .

## RESULTS

Chemical shifts have been reported for the tantalum and niobium alkoxides elsewhere.<sup>1</sup> In all cases the  $\alpha$ -protons of the alkoxy groups are shifted downfield of those in the parent alcohol. Both bridging and terminal resonances have been observed for the methoxides, ethoxides, isobutoxides and isopropoxides, but not for the neopentyloxides. Distinct terminal sites have only been observed for the methoxides, ethoxides and isobutoxides. Typical spectra are shown in Figure 1 for these three derivatives of niobium. Spectra of tantalum isopropoxide<sup>9</sup> and tantalum ethoxide<sup>10</sup> have been previously published. The  $\alpha$ -protons of the neopentyloxide exhibit a single sharp resonance which is temperature invariant.

The temperature dependence of the line shapes have been used to obtain kinetic data from which thermodynamic parameters can be obtained. Arrhenius plots for the methoxides, ethoxides and

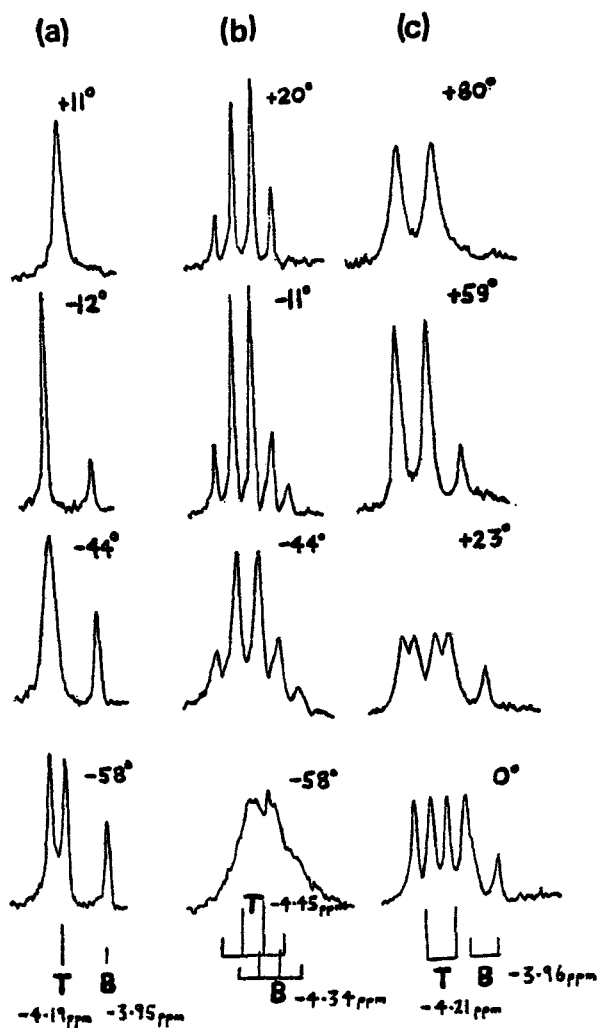


FIGURE 1 Typical nmr spectra. (a) Niobium penta-methoxide, (b) Niobium penta-ethoxide,  $\text{OCH}_2$  protons only, (c) Niobium penta-isobutoxide,  $\text{OCH}_2$  protons only.

isobutoxides are shown in Figure 2. The measurements were made over as wide a temperature range as possible, being limited by solubility problems and accuracy of line shape reproduction. Thermodynamic parameters derived from the best fit straight lines are given in Table I. These data are for the rate process causing bridging and terminal alkoxy group exchange. In the case of the isopropoxides, data over a temperature range could not be obtained, partly because of the slow rate of exchange and partly because of the dissociation of the dimer at elevated temperatures. However, it is

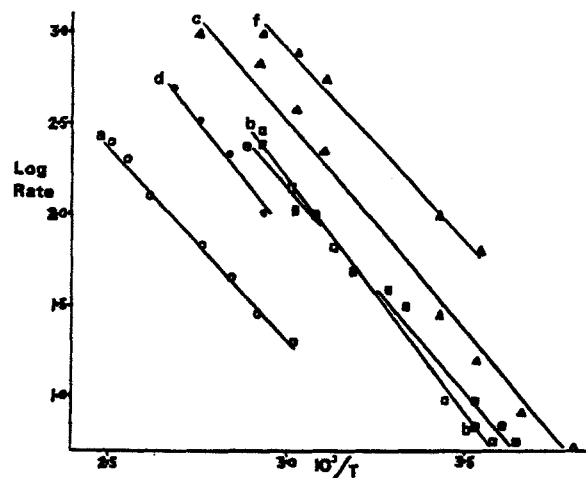


FIGURE 2 Arrhenius plot of rate data. (a) Tantalum penta-isobutoxide. (b) Tantalum penta-ethoxide. (c) Tantalum penta-methoxide. (d) Niobium penta-isobutoxide. (e) Niobium penta-ethoxide. (f) Niobium penta-methoxide.

possible to estimate a minimum  $\Delta G_T^\ddagger$  value for comparative purposes.

The errors quoted are at least twice as large as those obtained from a simple least squares analysis of the linear plots. They were obtained by considering the errors in the first and last points of each plot, and range of possible slopes drawn through these errors. Since it is being assumed that a linear Arrhenius plot should be obtained, and since the simple least squares analysis has a large dependence on the first and last points for determination of the slope, it seemed reasonable to stress the errors in these points.

Exchange between terminal positions has already been reported for the tantalum penta-methoxide.<sup>1</sup> In Table II values of  $\Delta G_{T_c}^\ddagger$  have been listed, being estimated from the coalescence temperatures  $T_c$  and the chemical shifts. In none of the cases other than the reported methoxide was it possible to follow the temperature variation of line shape with any degree of confidence.

## DISCUSSION

Downfield shifts of metal-alkoxy  $\alpha$ -proton resonances relative to the parent alcohol appear to be the general rule. In the present compounds the chemical shifts between monomer, polymer, free alcohol and

TABLE I

Thermodynamic parameters for bridge-terminal exchange

Derivative	Coalescence temp. $T_c$ °C	$\Delta G_{340}^\ddagger$ kcal mole <sup>-1</sup>	$E_a$ kcal mole <sup>-1</sup>	log $A_0$	$\Delta S^\ddagger$ cals deg <sup>-1</sup> mole <sup>-1</sup>
Nb(OMe) <sub>5</sub>	11 to 19	15.3 ± 0.1	9.5 ± 1	9.15 ± 0.65	-18 ± 3
Nb(OEt) <sub>5</sub>	48 to 58	16.4 ± 0.1	10.5 ± 1	9.07 ± 0.65	-18.5 ± 3
Nb(OBu <sup>t</sup> ) <sub>5</sub>	70 to 80	16.9 ± 0.1	11.5 ± 2	9.39 ± 1.3	-17 ± 6
Ta(OMe) <sub>5</sub>	35 to 40	15.9 ± 0.1	10.4 ± 0.5	9.42 ± 0.3	-17 ± 1.5
Ta(OEt) <sub>5</sub>	38 to 48	16.4 ± 0.1	11.9 ± 1	9.97 ± 0.65	-14.5 ± 3
Ta(OBu <sup>t</sup> ) <sub>5</sub>	75 to 85	17.8 ± 0.1	10.0 ± 1	7.90 ± 0.65	-24 ± 3
Nb(OPr <sup>i</sup> ) <sub>5</sub>	above 0	min. $\Delta G_{273} = 14$ kcal mole <sup>-1</sup>			
Ta(OPr <sup>i</sup> ) <sub>5</sub>	above 60	min. $\Delta G_{333} = 16$ kcal mole <sup>-1</sup>			

TABLE II

Thermodynamic parameters for terminal-terminal exchange

Derivative	Coalescence temp. $T_c$ °C	$\Delta G_{T_c}^\ddagger$ kcal mole <sup>-1</sup>	$E_a$ kcal mole <sup>-1</sup>	log $A_0$	$\Delta S^\ddagger$ cals deg <sup>-1</sup> mole <sup>-1</sup>
Nb(OMe) <sub>5</sub>	-45 ± 0.5	12.1 ± 0.1	insufficient range		
Nb(OEt) <sub>5</sub>	-60	11.5 ± 0.3	—	—	—
Nb(OBu <sup>t</sup> ) <sub>5</sub>	5 to 15	15.5 ± 0.3	—	—	—
Ta(OMe) <sub>5</sub>	-28 ± 0.5	13.0 ± 0.1	8.6 ± 0.5	8.79 ± 0.45	-20 ± 2
Ta(OEt) <sub>5</sub>	-30 to -20	13.0 ± 0.3	—	—	—
Ta(OBu <sup>t</sup> ) <sub>5</sub>	25 to 35	16.5 ± 0.3	—	—	—

second versus third row element resembles those of the Group IVA alkoxides.<sup>9</sup> Rationalization of these shifts is uncertain, although it is clear that they are not consistent with simple  $\sigma$ -inductive effects at the  $\alpha$ -protons. Typically for the dimer species the downfield shift is 0.79 to 0.88 ppm for niobium and 0.86 to 0.97 ppm for tantalum derivatives. The monomeric isopropoxides both occur at around 0.66 ppm downfield of the free alcohol. The neopentyloxide of tantalum exhibits a difference shift in the range of a dimer species, yet otherwise appears to behave as a monomer. Another puzzling feature of these shifts is the relative values for terminal and bridging groups. The bridge  $\alpha$ -protons lie upfield of the terminal groups for the methoxides, ethoxides and isobutoxides (Figure 1) by 0.1 to 0.25 ppm, but downfield in the case of the isopropoxide<sup>9</sup> by 0.5 ppm. Only the latter is in the correct direction for a  $\sigma$ -inductive effect. Values of  $J_{C13H}$  for the  $\alpha$ -protons, obtainable from the natural abundance proton

satellites, are not significantly different from those of the parent alcohols<sup>11</sup>. Internal proton spin-spin coupling parameters are also indistinguishable from those of the free alcohols. It is thus plausible that the chemical shift differences are due almost entirely to changes in the shielding tensor arising from the magnetic anisotropy<sup>12</sup> of neighbouring groups, in particular the M-O-C bonding system. These effects would be dependent on local geometry which in turn would depend very much on the non-bonding interactions which are considered together as steric hindrance. Neighbour anisotropy has also been used to account for the chemical shifts in a series of alkylamide derivatives.<sup>13</sup> The effect most likely arises mainly in the M-O bond itself, and could be an indication of changing involvement of the oxygen lone pairs in the overall bonding scheme. It is interesting to note that in the aluminum alkoxides,<sup>14</sup> the aged isopropoxide species exhibits a downfield  $\alpha$ -proton bridging resonance at about

0.35 ppm from the terminal group. The  $\beta$ -proton resonances of the relevant alkoxy derivatives of niobium and tantalum, and the isopropoxy and tertiary-butoxy derivatives of aluminum,<sup>14</sup> all exhibit a downfield shift on bridging. It thus appears that the anisotropy effect does not extend much beyond the  $\alpha$ -protons of the alkyl chain.

The behaviour of the neopentyloxides is perplexing in that only a single  $\alpha$ -proton resonance is observed at all accessible temperatures, yet the tantalum derivative has been shown to be at least partially dimerized in solution.<sup>4</sup> A qualitative explanation is suggested on the basis of the observed chemical shift trends. From a steric viewpoint, the neopentyloxy group should be intermediate between an isobutoxy and isopropoxy group. The former has an upfield  $\alpha$ -proton bridge shift, relative to the terminal resonance, while the latter has a downfield shift. If these shifts are largely dependent on neighbour anisotropy effects, the neopentyloxy can be considered as at an intermediate point in which upfield and downfield effects cancel and cause accidental degeneracy of the bridging and terminal resonances. It does not seem necessary therefore at this point to emphasize any conflict between the previous molecular weight studies and the present nmr results. Perhaps a more detailed analysis of the chemical shifts using data from <sup>13</sup>C nmr might provide a better understanding of the anisotropic contributions, and lead to more precise information on the bonding and stereochemistry of these complexes.

The kinetic measurements, although subject to quite large errors, all suggest that differences in the energetics involved are all small. This includes the difference between corresponding niobium and tantalum derivatives. Equilibrium studies have indicated that tantalum forms stronger alkoxy-bridge derivatives than niobium, an energy difference of about half a kilocalorie per bridge being involved. The  $\Delta G_T^\ddagger$  values for the bridge-terminal scrambling process increase consistently with increasing bulk of the ligand. The  $E_a$  values follow a much less predictable trend, having a possible small maximum value for the ethoxide of tantalum. Niobium shows an increase of  $E_a$  from methoxide to ethoxide, with another increase for the isobutoxide. The error in the latter measurement is much larger due to the short temperature range over which this derivative could be examined. It is also noted that the value obtained exceeds that of the tantalum derivative, which is unusual. The frequency factors also show a trend in the tantalum derivatives which

matches that of the  $E_a$  values. A minimum value of  $\Delta S^\ddagger$  is observed for the ethoxide, which serves to cancel the effect of the maximum  $E_a$  value in determining the rate of scrambling. In the case of the niobium derivatives, no clear minimum value of  $\Delta S^\ddagger$  is indicated. Scrambling, particularly in a relatively inert solvent such as a saturated hydrocarbon, should be essentially a first order process and unimolecular. As such the associated entropy of activation should be small. However, large negative entropies of activation for ligand scrambling processes have been found to be a feature of alkoxy derivatives<sup>6</sup> and do not appear to be due to systematic errors in the nmr experiment or calculations.

Considering a possible route for the scrambling process, it seems reasonable to initially perturb a bridging link. This should contribute to  $E_a$  in such a way as to reflect the bridging strength which can be taken, from previous molecular weight studies,<sup>4,5</sup> to be  $\text{OEt} \sim \text{OMe} > \text{OBu}^i > \text{OPr}^i$ . The next step must involve the internal rotation or twisting of one of the metal-ligand systems relative to the other such as to bring a terminal alkoxy group into the bridge position. This is expected to be influenced mainly by steric interactions and should therefore contribute to  $E_a$  in the order of  $\text{OPr}^i > \text{OBu}^i > \text{OEt} > \text{OMe}$ . Thus if the activated state is a partially dissociated, distorted dimer, it is not inconceivable that the  $E_a$  values might remain nearly constant. The entropy term will likewise consist of two contributions. Excluding solvent effects, bridging dissociation should in itself cause an increase in the entropy of the activated state, if only a small one. However, as the bridge is broken, other non-bridging groups on the metal can tighten up and the subsequent increase in metal-oxygen vibrational frequency cause a loss in entropy. Also, increased solvation would cause a loss in entropy, although it is not possible to say whether the bridge-breaking process has any effect on solvation. Thus the initial step probably contributes little to the overall entropy change. The contribution from the twisting or partial reorientation of the alkoxy groups will probably have a negative entropy contribution since the minimum energy route will require some special orientation of the alkoxy group. This restriction would become more severe as the bulk of the alkoxy group increases. It is thus tempting to ascribe the negative entropy largely to the steric part of the activation step, and to suggest that increasing negative entropy and increasing steric hindrance go together. For tantalum a maximum

$E_a$  and minimum  $\Delta S^\ddagger$  occur for the ethoxide, indicating that the ethoxy group forms the strongest bridges. While this is not inconsistent with other evidence,<sup>15</sup> it is quite clear that neither  $E_a$  nor  $\Delta G^\ddagger$  is a reliable measure or even indicator of the strength of the alkoxy bridges in these complexes.

Terminal-terminal exchange is a much faster process, involving lower free-energies of activation.<sup>1</sup> A trend similar to that of bridge exchange is observed, the faster rates and lower  $\Delta G^\ddagger$  values being associated with the less bulky alkoxy derivatives. For tantalum penta-methoxide the  $E_a$  value is found to be about 2 kcal less than that for the bridge exchange, and the frequency factor is also slightly smaller. Again, for a process such as this large negative  $\Delta S^\ddagger$  values would not normally be expected. Here the activation step can be considered in terms of steric and electronic contributions. This has formerly been described<sup>1</sup> as a change from octahedral to trigonal prismatic coordination about one of the metal atoms, which has the effect of making all four terminal groups equivalent. Thus the energetics would reflect the difference in bonding energy between these two metal-ligand symmetries plus a steric barrier to ligand movement. The former would probably be small and fairly constant while the latter would be expected to increase with ligand bulk. This could help to explain the significant increase in the energy between the ethoxide and isobutoxide, since unlike the bridge exchange the two contributions would not be tending to cancel out. An alternative mechanism which would explain the rather large negative  $\Delta S^\ddagger$  value observed for the methoxide is a dissociative one in which an alkoxy group leaves a terminal position to form an ion pair with the parent alkoxide molecule. The observed energetics would not necessarily be inconsistent with such a mechanism, although solvent effects would be expected to be greater than they appear to be. In this connection it is interesting to note that addition of the parent alcohol has no effect on the exchange rates at room temperature, neither does the alcohol scramble with the alkoxy groups at rates accessible by nmr.

The isopropoxides and neopentyloxides are again unusual in that neither exhibits distinct terminal sites. Although this could be due to rapid exchange, it would be inconsistent for the isopropox-

ide. A qualitative view of the chemical shifts involved indicates that the difference between the terminal sites decreases as the bulk of the alkoxy group increases. Thus for tantalum the differences are;<sup>1</sup> OMe, 0.107 ppm; OEt, 0.103 ppm; OBu<sup>t</sup>, 0.058 ppm. The isopropoxide and neopentyloxide could therefore simply represent cases where this difference has approached zero, hence the lack of temperature dependent splitting would indicate nothing about the scrambling rates. However, until a more definite approach can be made as to the origins of the chemical shift differences, it is not possible to say whether the absence of terminal splitting is a structural or magnetic phenomenon.

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