Gas-Phase Complexation of Polyethers with Halide Ions

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Gas-phase complexes of halide anions with a variety of crown ethers and acyclic analogs are formed by ion-molecule reactions in the chemical ionization source of a triple-quadrupole mass spectrometer. The ether complexes of iodide, bromide, and chloride dissociate on collisional activation by cleavage of the halide-ether electrostatic hydrogen bonds, resulting in the formation of bare halide anions. By contrast, the fluoride complexes dissociate by loss of HF, which may occur in conjunction or sequentially with losses of ethylene oxide units. This dissociation behavior is similar to that observed for collisionally activated dissociation of $[M - H]^-$ ions of the crown ethers and suggests that the fluoride ion is capable of promoting an intramolecular proton abstraction within the $[M + F]^-$ complex. This type of dissociation chemistry is only observed for the fluoride ion complexes, and the fluoride ion is the most basic of all the halides. The kinetic method was used to establish orders of relative halide binding strengths, and the trends for the chloride and bromide affinities were 12-crown-4 < triethylene glycol dimethyl ether < 15-crown-5 < tetraethylene glycol dimethyl ether < 18-crown-6 < 21-crown-7 < tetraethylene glycol < pentaethylene glycol < 1,4,7,10,13-pentathiacyclopentadecane. (*J Am Soc Mass Spectrom* 1993, 4, 242-248)

Negative ion chemical ionization involving electron or halide attachment processes has proved useful for selective, sensitive analysis of compounds of biological and environmental importance [1]. There have been numerous fundamental studies of halide attachment to organic molecules in the gas phase [2-9] because halide ions have well-defined sizes and thermochemical properties, as shown in Table 1. For example, structural effects on the hydrogen bonding energies of halide complexation to various organics have been evaluated by equilibria measurements performed in a high-pressure mass spectrometer [2-4]. Chloride binding energies to alcohols, ketones, amines, and other simple organic substrates were measured by chloride transfer equilibria in an ion cyclotron resonance mass spectrometer [5, 6], and it was found that binding energies varied from 14 to 26 kcal/mol, depending on the nature of the substrate. From these studies and from theoretical reports [7], it was concluded that chloride binds with less covalent character than the fluoride ion and that chloride promotes more favorable multiple hydrogen bonding interactions because of its bulkier size. The fluoride ion binds by stronger and therefore shorter hydrogen bonds, which causes entropic constraints on multiple bonding. In general, the halide binding strength of an organic compound is directly related to the gas-phase acidity of the

organic substrate [5, 6], a property that determines the capability for hydrogen bond donation. In another recent study, it was further demonstrated that more acidic organics formed stronger halide complexes in the gas phase [8]. Of particular relevance to the present study, it was also shown that simple monoethers typically did not form $[M + Br]^-$ or $[M + I]^-$ ions [8], presumably because of the low acidities of ethers, which disfavored the formation of hydrogen bonding interactions needed to effectively attach the halide ion. Finally, a recent theoretical study of $H_2O \cdots F^-$ and $H_2O \cdots Cl^-$ complexes reported the halide-hydrogen bond energies as 25.4 kcal/mol for the fluoride complex and 13.2 kcal/mol for the chloride complex [9].

Our interest in halide attachment ionization of polyethers stems from several sources. First, the understanding of halide attachment reactions to complex biological molecules, such as antibiotics, may allow the design of selective ionization reactions that afford relevant structural details of large molecules, many of which contain multiple basic and acidic functional groups. Second, several classes of antibiotics [12], such as the alborixins and dianemycins, have polyether skeletons, which suggests that their underlying structures may be conveniently modeled by polyethers, such as polyethylene glycols and crown ethers. In fact, various polyethers have been the subject of many studies of host-guest chemistry in solution [13-22], some of which have been undertaken specifically to model selective metal binding of antibiotics. In particu-

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Table 1. Ionic radii and thermochemical properties of halides

Halide ion	Radius ^a (Å)	Electron affinity ^b [X] (eV)	Gas-phase acidity ^b [HX] (kcal/mol)
F ⁻	1.33	3.399	371.8
Cl ⁻	1.81	3.617	333.7
Br ⁻	1.95	3.365	323.9
I ⁻	2.20	3.059	314.6

^aFrom crystal structures (Weast [10]).^bFrom Lias et al. [11].

lar, crown ethers afford a series of hosts with known cavity sizes that are suitable substrates for size-selective binding to a variety of guests. Some of the most simple model guests are those which have spherical shapes with well-defined diameters, such as alkali metal cations and halide anions. Numerous studies of solutions have evaluated the kinetics, selectivities, and binding energies of complexation of macrocycles with these guests [13-23]. Host-guest chemistry in solution is largely influenced by solvation effects because the specific host and guest are solvated to different extents depending on the nature of the solvent, and this competitive solvation ultimately affects the types and strengths of operative binding interactions. By contrast, host-guest complexation studies undertaken in the gas phase are not influenced by solvation effects, and such studies have recently proved to be experimentally plausible and of great intrinsic interest [24-28].

There have been several reports of host-guest chemistry of polyethers involving negative guest ions, including halide complexation in solution [16-23]. One of the first reports of complexation of negative ions was the observation of encapsulation of chloride ions by diazabicyclic ammonium ions (captapinands) in 1968 [16]. In later studies, it was shown that protonated nitrogen-containing cryptands enclosed halide ions by four $^+N-H \cdots X^-$ hydrogen bonding interactions, and size-selectivity of the various macrocyclic hosts was observed [17,18]. For example, depending on the arrangement of the bridges, certain cryptands demonstrated great selectivity for chloride complexation over bromide complexation, and this was attributed to topological effects [19]. More recently, Dye and co-workers [22,23] formed unusual alkali salts, $A^+ \cdot M \cdot A^-$, where A^+ and A^- are an alkali metal cation and anion, respectively, and M is a macrocycle, and demonstrated that crown ethers could also act as electrified (electron solvators). The structures of such salts consist of an alkali metal cation complexed inside the macrocycle with an alkali metal anion attached outside.

In the current work, the complexation of halide anions with a variety of crown ethers and their acyclic counterparts is examined in the gas-phase environment of a mass spectrometer. In an earlier study [29], negative molecular ions (albeit of low abundance) of

polyethers were formed by electron attachment negative ionization, and the collision-activated dissociation (CAD) spectra showed that such ions produced many structurally diagnostic fragment ions, more so than the CAD spectra of protonated polyethers. As a comparison and follow-up to the previous study, the present work describes the production of polyether-halide complexes, $[M + X]^-$, by ion-molecule reactions between selected ethers $[M]$ and halide ions $[X^-]$ generated from ionization of volatile halogenated solvents. The structures and orders of binding affinities of the resulting complexes are characterized by use of various CAD techniques, including the kinetic method [30]. The primary objectives were to determine whether complexes could be formed between the halide ions and the polyethers, whether there was evidence for any size effects in the binding affinities of the various crown ethers for different halides, and whether complexation with negative ions significantly altered the dissociation reactions of the polyether ions. It was also of interest to evaluate whether the cyclic polyethers demonstrated different affinities relative to their more flexible acyclic or substituted analogs.

Experimental

All measurements were performed with a Finnigan triple-stage quadrupole mass spectrometer (TSQ-70; Finnigan-MAT, San Jose, CA) equipped with a chemical ionization source. The negative ion chemical ionization mode was used. The samples were introduced by a direct insertion probe, and typical sample pressure was $1-3 \times 10^{-6}$ torr. A halogenated solvent or gas was introduced via a leak valve to a pressure of 4 torr in the source and used to generate halide anions $[X^-]$ by dissociative electron attachment. The halogenated reagents included CF_4 , CH_2Cl_2 , $CHCl_3$, CH_2Br_2 , and CHI_3 . Methane was admitted into the source to 2 torr to assist in the production of thermal electrons for negative ion chemical ionization of the halogenated reagents. Negative ions were formed by using a 70-eV electron beam at 200 μA . The source temperature was 50 °C. Under these conditions, the typical relative abundances of product ions formed were $[2M_1 + X]^- : [M_1 + X]^- = 1:100-10:100$, where M_1 represents any ether introduced into the source. Often, mixtures of two ethers were introduced to facilitate examination of complexes containing two different polyethers bound to a single halide ion (as described later for the kinetic method). The relatively high pressure of the chemical ionization source ensures that the complexes experience hundreds of collisions, and thus for the average ion, thermal equilibrium conditions are approached. Additionally, the complexes are most likely formed by gas-phase processes, but the possibility of formation of halide complexes on the probe with subsequent desorption cannot be eliminated.

In some of the spectra obtained, the isotopic ratios of the various halide complexes did not conform to

expected values (based on calculations of known natural isotopic abundances of the atoms). This anomaly was more noticeable in spectra of lower signal-to-noise ratio and under conditions in which lower resolution was used to enhance sensitivity. There appear to be two factors that contribute to the problem. First, under conditions of lower resolution, ion peaks separated by 1 Da are not adequately resolved, and thus quantitative isotopic abundances may be skewed (although qualitative comparisons of $[M + X]^-$ complexes versus dimer ions remain essentially correct). Second, and most important, the bar graph spectra generated from the data system did not adequately represent the spectral listing of individual ions. Thus, the fact that isotopic ratios were misrepresented on the bar graph printouts was predominantly an artifact of the print-out. For example, the bar graph spectra showed about half as many ion peaks as tabulated in the spectral listing. This problem was corrected by reconstructing mass spectra directly from the lists of ion peaks and abundances, as opposed to using the bar graph print-out spectra.

For the CAD spectra, the desired precursor ion was selected with the first quadrupole and passed into the collision quadrupole at an average collision energy of 10 eV in the laboratory frame. The collision gas pressure was typically 1.5 mtorr of argon. Experiments were done to estimate threshold dissociation energies by using less than 0.6 mtorr of argon and varying the collision energy from 0 to 5 eV [31]. No corrections for initial ion kinetic energies or kinetic energy calibrations were performed, so the threshold experiments provide only a qualitative estimate of energies. The experiments are qualitatively reproducible from day to day, although relative ion abundances of different fragment ions varied by as much as 25%. Absolute conversion of the selected adduct ion to the representative fragment ions was 10-25%. Typically, 10-100 spectra were averaged. All compounds except 21-crown-7 and perfluoro-15-crown-5 were obtained from Aldrich Chemical Co. (Milwaukee, WI) and used without further purification. The 21-crown-7 was obtained from Parish Chemical Co. (Orem, UT). The perfluoro-15-crown-5 was obtained from Professor Richard Lagow [32]. Purities were greater than 97%.

The kinetic method [30] was used to determine the relative halide affinities of the various ethers. This method involves forming an ion-bound adduct of two compounds, M_1 and M_2 , bound by a halide anion and designated as $[M_1 + X + M_2]^-$. The adduct is then energized above its dissociation threshold by low-energy collisional activation, and the abundances of the resulting fragment ions, such as $[M_1 + X]^-$ and $[M_2 + X]^-$, are measured. Based on the ratio of these abundances, the relative affinities for the X^- ion by each ether can be estimated. This sequence is repeated for many combinations of ethers to ultimately derive a complete scale of affinities. From reported electron affinities for oxygen-containing organic compounds [3],

the electron affinities of crown ethers are estimated as virtually negligible compared with any of the halogens (3.0-3.3 eV). Thus, the negative charge of the halide-polyether complexes is expected to be largely localized at the halogen atom. For a valid measurement of affinities, the adducts should dissociate by cleavage of only the weakest binding interactions (such as the hydrogen bonds that bind the halide ion to the ethers); the types of binding interactions must be similar for the different compounds involved; and the structures of the compounds studied must be similar. In the context of this study, these conditions are reasonably presumed to be satisfied. Equilibrium measurements of halide affinities of the polyethers were not feasible owing to the low volatility of some of the ethers, making accurate pressure measurements impossible.

The kinetic method was originally derived as a means of measuring proton affinities of related compounds [30, 33-36]. On the basis of our previous use of the kinetic method for determination of alkali metal ion affinities of crown ethers [26, 27], we have shown that the method may be used to estimate other types of ligand affinities of polyethers. Additionally, the experiments discussed herein demonstrate no dependence on the concentration of the polyethers in the ionization source, which suggests that the dissociation of the complexes truly reflects the intrinsic binding interactions and not simply the nature of the ion formation processes; however, it should be emphasized that for this study, only a qualitative order of affinities is established.

Results and Discussion

Formation of Halide-Ether Complexes

The ethers of interest in this study included four cyclic ethers (12-crown-4, 15-crown-5, 18-crown-6, and 21-crown-7); four acyclic ethers (triethylene glycol dimethyl ether, tetraethylene glycol, pentaethylene glycol, and tetraethylene glycol dimethyl ether); one cyclic thioether (1,4,7,10,13-pentathiacyclopentadecane); and one perfluorinated ether (perfluoro-15-crown-5). An example of a negative ionization mass spectrum obtained for a mixture of two polyethers with chloroform as the reagent is shown in Figure 1. As illustrated, the chloride attachment ions $[M + Cl]^-$ are observed for both pentaethylene glycol and 1,4,7,10,13-pentathiacyclopentadecane, and various dimer ions are present. Exact quantitative comparisons of halide complexation on the basis of the abundances of the $[M + Cl]^-$ ions were not possible owing to the inability to precisely control the gas-phase concentrations of each ether and halogenated substrate; however, the relative orders of halide affinities were determined by application of the kinetic method to the CAD data obtained for the $[M_1 + X + M_2]^-$ complexes (as

Figure 1. Negative ionization mass spectrum of a mixture of pentaethylene glycol (5-GLYCOL) and 1,4,7,10,13-pentathia-cyclopentadecane (THIO-15-C-5) with chloroform as the reagent. The spectrum is reconstructed from a listing of ion intensities. The ion peaks labeled with an asterisk are attributed to ionization of the halogenated solvent and background impurities in the source.

discussed later). With the exception of the perfluorinated ether, reactions of each halide ion with each polyether in the chemical ionization source resulted in the formation of halide-ether complexes $[M + X]^-$ and dimers $[M + X + M]^-$. In contrast, the perfluorinated 15-crown-5 formed abundant complexes only with fluoride ions but not with any of the other halide ions. Instead of bromide, iodide, or chloride attachment complexes, abundant molecular radical anions of perfluoro-15-crown-5 are observed as products of the reactions between the bromide, iodide, or chloride ions and the perfluorinated substrate. Substitution of fluorine atoms in a crown ether results in a molecule that is more basic [37] and has a higher electron affinity than a hydrogenated crown ether [11], and thus the molecule is far more likely to undergo electron attachment than halide attachment. This preference for electron attachment of perfluoro-15-crown-5 is especially pronounced for complex formation involving the larger halide anions, which have lower electron affinities than the smaller charge-dense fluoride ion.

The formation of $[M - H]^-$ ions as a result of deprotonation of the ethers by the halide ions did not occur. Although the gas-phase acidities of crown ethers and related polyethers have not been measured, the gas-phase acidities of simple ethers have been reported [11]. For example, the gas-phase acidity of dimethyl ether is 407.4 kcal/mol and that of dimethyl sulfide is 393.5 kcal/mol [11]. The fluoride ion is the most basic of all the halides, and the proton affinity of F^- is 371.8 kcal/mol [11]. Thus, the observation of proton-transfer reactions between F^- and any of the ethers may be used to determine a lower bound on the gas-phase acidities of the ethers. Because $[M - H]^-$ ether ions are not observed from the reactions of the fluoride ion with any of the crown ethers, the gas-phase acidities of the crown ethers apparently are greater than 372 kcal/mol. Thus, the abstraction of a proton from a crown ether by a halide ion is an endothermic process but can be promoted by collisional activation, as shown later.

Collision-Activated Dissociation of the Halide-Ether Complexes

After formation of the halide complexes, each complex of interest was mass analyzed and passed into the second quadrupole of the triple-quadrupole mass spectrometer for CAD. Based on the fragment ions formed, some general structural characteristics are suggested. For each of the bromide, iodide, and chloride complexes, CAD resulted in the formation of only the bare halide ion. In no case was cleavage of the macrocyclic structure or formation of halide-attachment fragments observed, indicating that the halide-ether bonds are the weakest interactions in the complex. Typically, a relative kinetic energy of less than 1 eV (based on variable collision energy threshold dissociation experiments [30]) is needed to break the complex into its halide ion and ether constituents, and this value sets an upper limit on the strength of the binding interactions. This binding energy estimate is in qualitative agreement with halide binding energies determined for other organic substrates [3,7,8].

In contrast, the $[M + F]^-$ complexes demonstrate strikingly different CAD behavior, as shown in Figures 2 and 3. Each of the simple crown ether-fluoride complexes dissociates by pathways that parallel ones observed from CAD of $[M - H]^-$ ions [29]. For example, as shown in Figure 2, the $[M + F]^-$ complex of 15-crown-5 dissociates by loss of HF to yield the $[M -$

Figure 2. CAD spectrum of (A) the $[M + F]^-$ complex and (B) the $[M - H]^-$ ion of 15-crown-5.

Figure 3. CAD spectrum of the $[M + F]^-$ (A) complex and (B) the $[M - H]^-$ ion of 1,4,7,10,13-pentathiacyclopentadecane.

$H]^-$ ion at m/z 219 and by losses of HF in conjunction with nC_2H_4O units, producing ions at m/z 131 and 87 ($n = 2$ and 3, respectively). The series of fragment ions observed at m/z 191, 147, 103, and 59 is attributed to the elimination of $[HF + CO + nC_2H_4O]$ in which $n = 0, 1, 2$, and 3, respectively. The other series of fragment ions observed at m/z 193, 149, 105, and 61 is suggested as due to the net loss of $[HF + C_2H_2 + nC_2H_4O]$ in which $n = 0, 1, 2$, and 3, respectively (see Figure 2a). The CAD spectrum of the $[M - H]^-$ ion for 15-crown-5 is shown in Figure 2b for comparison. None of the fragment ions shown in Figure 2a indicate retention of the fluoride ion by the dissociating ether. The $[M + F]^-$ complexes of the other crown ethers also dissociate by loss of HF in conjunction with pathways analogous to their $[M - H]^-$ ion counterparts [29], attributed to the types of neutral losses described above (i.e., $-HF$, $-[HF + nC_2H_4O]$, $[HF + CO + nC_2H_4O]$, etc.). For example, fragment ions common to most of the CAD spectra of the $[M + F]^-$ crown ether complexes include ions at m/z 59, 61, 87, 103, 105, 131, 149, and 193.

The $[M + F]^-$ complex of 1,4,7,10,13-pentathiacyclopentadecane dissociates by losses of $[HF + n(C_2H_4S)]$, where $n = 0, 1, 2$, or 3, giving the series of ions at m/z 299, 239, 179, and 119, respectively (see Figure 3a). This series duplicates the series of fragment ions generated from CAD of the $[M - H]^-$ ion of 1,4,7,10,13-pentathiacyclopentadecane (Figure 3b). These CAD patterns suggest that the $[M + F]^-$ complexes undergo intramolecular proton abstraction by the attached fluoride ion, resulting in an internally hot $[M - H]^-$ ion that then subsequently dissociates by cleavages of the polyether skeleton, such as by losses

of ethylene sulfide units. A proposed mechanism to account for this type of behavior is shown in Scheme I for the $[M + F]^-$ complex of 1,4,7,10,13-pentathiacyclopentadecane.

The ion observed in the CAD spectrum of the $[M + F]^-$ complex of 1,4,7,10,13-pentathiacyclopentadecane at m/z 79 may be attributed to $C_2H_4SF^-$. Although the identity has not been confirmed, this type of fragment ion would suggest that the thioether binds more strongly to the fluoride ion than do the oxy-crown ethers (which never showed retention of the fluoride ion on fragmentation). Finally, the $[M + F]^-$ complex of perfluoro-15-crown-5 dissociates directly by losses of $n(C_2F_3O)$ units, where $n = 1, 2, 3, \dots$, and this is similar to the way that the molecular radical anion, M^- , of perfluoro-15-crown-5 dissociates [29]. The attached fluoride ion always remains associated with the dissociating perfluoro-macrocyclic, suggesting that the fluoride ion is tightly bound.

From these CAD results, it is evident that the fluoride ion is sufficiently basic compared with the other halide ions (see Table 1 for the gas-phase acidities of HX) to promote very different types of complexation and dissociation chemistry than observed for the other halide ions. Theoretical studies [8] have demonstrated that the charge-dense fluoride ion binds with more covalent character than any of the other halide ions, so it is not unexpected that such differences would also be reflected in gas-phase polyether complexes as well.

Orders of Relative Halide Binding Affinities

To compare the relative halide binding energies of the crown ethers, the kinetic method [30] was applied to estimate the orders of halide affinities. An example of the method is shown in Figure 4 for the dissociation of a bromide-bound ether complex, and the relative orders for chloride and bromide affinities are shown in

Scheme I. Mechanism proposed for dissociation of the $[M + F]^-$ complex of 1,4,7,10,13-pentathiacyclopentadecane. CAD, collision-activated dissociation.

Figure 4. CAD spectrum of the bromide-bound complex of 15-crown-5 (15-C-5) and triethylene glycol dimethyl ether (3-GLYME).

Table 2. In general, the orders for chloride and bromide affinities are identical, with some variation in the relative differences. The iodide affinities are not shown because of the lack of sufficient replicate data. For the chloride and bromide affinities, the larger (more polarizable) crown ethers demonstrate higher halide affinities. The orders apparently reflect the availability of optimally positioned hydrogens for multiple bonding interactions and the polarizability of the ether. Compared with all of the polyethers, the pentathiacyclopentadecane showed the highest affinity for the halide ions, presumably because the sulfur atoms are more polarizable than the oxygen atoms and are thus better able to stabilize the negative polarization (due to halide attachment) of adjacent atoms. The glycols also formed abundant complexes, probably due to the enhanced acidities of the terminal hydroxyl groups, which afforded especially favorable hydrogen-donor binding sites.

Because of the involvement of covalent bonding on fluoride complex formation, the validity of the kinetic method is compromised for the fluoride complexes.

Table 2. Relative halide binding affinities of ethers,^a based on the kinetic method^b

Polyether	Cl ⁻	Br ⁻
12-C-4	1	1
Triglyme	2 (±15%)	2 (±10%)
15-C-5	5 (±15%)	6 (±20%)
Tetraglyme	50 (±20%)	50 (±25%)
18-C-6	100 (±25%)	100 (±25%)
21-C-7	2 × 10 ³ (±25%)	1 × 10 ⁴ (±25%)
Tetraglycol	8 × 10 ⁴ (±25%)	4 × 10 ⁴ (±25%)
Pentaglycol	8 × 10 ⁵ (±25%)	5 × 10 ⁵ (±25%)
Thio-15-C-5	8 × 10 ⁶ (±25%)	5 × 10 ⁶ (±25%)

^aListed after each compound, M, are the probabilities of dissociation of the halide-bound complex to form [M + X]⁻ relative to dissociation to form [12-C-4 + X]⁻, based on a series of overlapping peak height measurements to form a continuous ladder relative to the reference 12-crown-4 experimental values. Uncertainties shown in parentheses are based on replicate or triplicate measurements, rounded to nearest 5%; (C), crown.

^bSee text.

The fluoride ion attaches with more covalent character and in fact can bind strongly enough to induce proton abstraction and ring opening of the macrocycle (as shown in the CAD spectra discussed earlier). Thus, the assessment of fluoride binding affinities is at best speculative owing to the covalent nature of the interactions.

Conclusions

In contrast to simple acyclic monoethers, crown ethers form stable but loosely bound (< 1-eV binding energy) complexes with chloride, bromide, and iodide ions. They also form fluoride complexes that possess more covalent binding character. The formation of these halide complexes suggests that the conformation of the large, polarizable cyclic ethers or their polyether acyclic analogs permits effective hydrogen bonding between the halide and polyether that is not as favorable for the smaller ethers. The substitution of the oxygen atoms of the crowns by sulfur atoms greatly enhances the formation of the halide complexes, which demonstrates the influence of the electronic properties of the adjacent atoms on the binding affinities of the ethers. Finally, only the fluoride ion is sufficiently basic to bind with pronounced covalent character and thus induce intramolecular proton abstraction on collisional activation of the halide complex. The other halide ions are at least 38 kcal/mol less basic than the fluoride ion [11], and thus intramolecular proton abstraction by these halide ions is not promoted by collisional activation. This initial study suggests that the use of fluoride ions as chemical ionization agents (as an alternative to electron attachment negative ionization, which does not result in formation of very abundant negative molecular ions) may allow formation of stable polyether negative ion complexes that dissociate to form structurally diagnostic fragment ions.

Acknowledgments

The Welch Foundation (F-1155), ACS-PRF (22270-G5), and NIH (GM46723-01) are acknowledged for support of this work.

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