$C_2H_7O^+$ Potential Surface and Ion−Molecule Association between H_3O^+ and C_2H_4

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The $C_2H_7O^+$ potential surface has been explored using the G2 procedure. Four stable structures were identified: protonated ethanol, $C_2H_5OH_2{}^+$, protonated dimethyl ether, $(CH_3)_2OH^+$, and the electrostatic complexes $C_2H_4\cdots H\cdots OH_2{}^+$ and $CH_3{}^+\cdots HOCH_3$. Experiments conducted using a selected ion flow tube identify the $H_3O^+\cdot C_2H_4$ product of the ion−molecule association reaction $H_3O^+ + C_2H_4$ as $C_2H_5OH_2{}^+$, protonated ethanol. Rate coefficients and branching ratios are reported for reactions of the $C_2H_7O^+$ ions—$H_3O^+\cdot C_2H_4$ formed in the reaction of $H_3O^+ + C_2H_4$, $C_2H_5OH_2{}^+$, and $(CH_3)_2OH^+$—with acrylonitrile and 2-fluorotoluene.

Introduction

Ethanol is one of the molecules observed in interstellar clouds, and although it is not found in cold, dark clouds, it is present in appreciable abundances in regions where stars are formed.[1−3] Model calculations have used a variety of reactions, both gas phase and heterogeneous reactions on grain surfaces, as sources of C_2H_5OH in the interstellar medium.[3−5] Among the gas phase reactions considered in the models are the following ion−molecule association reactions:

$$CH_3{}^+ + CH_3OH \rightarrow (CH_3)_2OH^+ + h\nu \qquad (1a)$$

$$\rightarrow C_2H_5OH_2{}^+ + h\nu \qquad (1b)$$

$$H_3O^+ + C_2H_4 \rightarrow C_2H_5OH_2{}^+ + h\nu \qquad (2)$$

C_2H_5OH has been assumed in the models to be formed from $C_2H_5OH_2{}^+$ in a dissociative recombination reaction.

$$C_2H_5OH_2{}^+ + e \rightarrow C_2H_5OH + H \qquad (3)$$

Several stable isomers of $C_2H_7O^+$ are possible, and it is not certain which isomeric species or mixture of species might be produced from an ion−molecule association process. Likely stable isomers of association reactions coincide with valleys on the $C_2H_7O^+$ potential surface and include $C_2H_5OH_2{}^+$ (protonated ethanol), $(CH_3)_2OH^+$ (protonated dimethyl ether), $C_2H_4\cdots H\cdots OH_2{}^+$, and $CH_3{}^+\cdots HOCH_3$ (electrostatic-type complexes). Jarrold *et al.*[6] examined the collision-induced dissociation (CID) spectra of $C_2H_5OH_2{}^+$ and $(CH_3)_2OH^+$ and concluded that the association product of reaction 1 has predominantly the $(CH_3)_2OH^+$ structure while the product of reaction 2 has mainly the $C_2H_5OH_2{}^+$ structure.

In this study we have probed the structure of the $C_2H_7O^+$ ion formed in the termolecular analogue of reaction 2 by examining its proton transfer reactions using a selected ion flow tube (SIFT) with the neutral reagents 2-fluorotoluene and acrylonitrile. The technique has been used previously to probe the structures of several other products of ion−molecule association.[7,8] We have also undertaken ab initio calculations of the $C_2H_7O^+$ energy surface to assist in the interpretation of our experiments.

Experimental Section

The experiments reported here were carried out using the SIFT at Canterbury University operating at room temperature (300 ± 5) K as described previously.[9] The $C_2H_7O^+$ ions examined in this work were produced in the following ways. The product ion of the association reaction 4b, which we designate $H_3O^+\cdot C_2H_4$, was formed in the flow tube by injecting H_3O^+ into a stream of C_2H_4 introduced at the first inlet port.

$$H_3O^+ + C_2H_4 \rightarrow C_2H_5{}^+ + H_2O \qquad (4a)$$

$$\xrightarrow{M} H_3O^+\cdot C_2H_4 \qquad (4b)$$

Sufficient C_2H_4 was added to remove >99% of the H_3O^+ ion signal. In the process, $C_2H_5{}^+$ produced in reaction 4a was completely converted into predominantly $(C_2H_4)_2H^+$ and $C_5H_9{}^+$, neither of which reacted further with 2-fluorotoluene and CH_2CHCN.

The products of reaction 4 were first established by Bohme and Mackay[10] and also by McIntosh *et al.*[11] Our measurement of the rate coefficient for the reaction ($k = 8.4 \times 10^{-11}$ cm^3 s^{-1}) and of the branching ratio ($H_3O^+\cdot C_2H_4$ = 30%) at 0.35 Torr of helium is in reasonable agreement with the earlier measurements when allowance is made for the different bath gas pressures between different experiments. (McIntosh *et al.*[11] report a rate coefficient of 1×10^{-10} cm^3 s^{-1} with a branching ratio of 60% adduct at a helium pressure of 0.45 Torr.) Our measurement is also in excellent agreement with that given in the accompanying paper by Matthews *et al.* of $k = 7.8 \times 10^{-11}$ cm^3 s^{-1}.[12]

The $C_2H_5OH_2{}^+$ ion was generated in the ion source by initial electron impact on C_2H_5OH, followed by H atom abstraction (reaction 5).

$$C_2H_5OH^+ + C_2H_5OH \rightarrow C_2H_5OH_2{}^+ + C_2H_5O \qquad (5)$$

Alternatively $C_2H_5OH_2{}^+$ was formed in the flow tube by injecting H_2CN^+ into the helium carrier gas and adding C_2H_5OH at the first neutral inlet. This prevents any breakup from $C_2H_5OH_2{}^+$ that occurs during the injection process. A similar technique was used to produce the $(CH_3)_2OH^+$ ion by subjecting

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$(CH_3)_2O$ to electron impact in the ion source and, after mass selection, injecting $(CH_3)_2OH^+$ into the flow tube.

All reagents were obtained from commercial sources. A trace of the radical inhibitor, 4-methoxyphenol, was added to acrylonitrile to prevent polymerization in the absence of oxygen.

Results

SIFT Experiments. We examined the reactions of three $C_2H_7O^+$ isomers ($H_3O^+{\cdot}C_2H_4$, $C_2H_5OH_2^+$, and $(CH_3)_2OH^+$) with the reagents 2-fluorotoluene, C_7H_7F, and acrylonitrile, CH_2CHCN. We also examined the reaction of $H_3O^+{\cdot}C_2H_4$ with CH_3OH. These three reagents were selected on the basis of their known proton affinities (PAs) which are (in kJ mol^{-1}) C_7H_7F (PA = 782); CH_2CHCN (PA = 794), and CH_3OH (PA = 761).[13] The following results were obtained:

$$H_3O^+{\cdot}C_2H_4 + CH_3OH \rightarrow \text{adduct} \quad (1.0) \tag{6}$$

$$k = 6.9 \times 10^{-10}\ \text{cm}^3\ \text{s}^{-1}$$

$$H_3O^+{\cdot}C_2H_4 + C_7H_7F \rightarrow C_7H_8F^+ + C_2H_5OH \quad (0.65) \tag{7}$$

$$\rightarrow \text{adduct} \quad (0.35)$$

$$k = 5.4 \times 10^{-10}\ \text{cm}^3\ \text{s}^{-1}$$

$$H_3O^+{\cdot}C_2H_4 + CH_2CHCN \rightarrow CH_2CHCNH^+ + C_2H_5OH \quad (0.40) \tag{8}$$

$$\rightarrow \text{adduct} \quad (0.60)$$

$$k = 3.2 \times 10^{-9}\ \text{cm}^3\ \text{s}^{-1}$$

$$C_2H_5OH_2^+ + C_7H_7F \rightarrow C_7H_8F^+ + C_2H_5OH \quad (\sim 0.70) \tag{9}$$

$$\rightarrow \text{adduct} \quad (\sim 0.30)$$

$$k = 4.3 \times 10^{-10}\ \text{cm}^3\ \text{s}^{-1}$$

$$C_2H_5OH_2^+ + CH_2CHCN \rightarrow CH_2CHCNH^+ + C_2H_5OH \quad (0.50) \tag{10}$$

$$\rightarrow \text{adduct} \quad (0.50)$$

$$k = 3.2 \times 10^{-9}\ \text{cm}^3\ \text{s}^{-1}$$

$$(CH_3)_2OH^+ + C_7H_7F \rightarrow \text{adduct} \quad (1.0) \tag{11}$$

$$k = 1.9 \times 10^{-10}\ \text{cm}^3\ \text{s}^{-1}$$

$$(CH_3)_2OH^+ + CH_2CHCN \rightarrow \text{adduct} \quad (1.0) \tag{12}$$

$$k = 2.3 \times 10^{-9}\ \text{cm}^3\ \text{s}^{-1}$$

Branching ratios for the product channels are shown in parentheses following the stated channel, and the rate coefficients for each reaction are also given. Although the rate coefficients for adduct formation are presented as simple bimolecular processes, the adducts are undoubtedly formed via collisional stabilization of the $(AB^+)^*$ complex. The rate coefficient for adduct formation may therefore exhibit some sensitivity to pressure, although the rate coefficients observed in most of the reactions 6−12 suggest that collisional stabilization is approaching the pressure-saturation regime at our operating pressure of 0.35 Torr of helium bath gas.

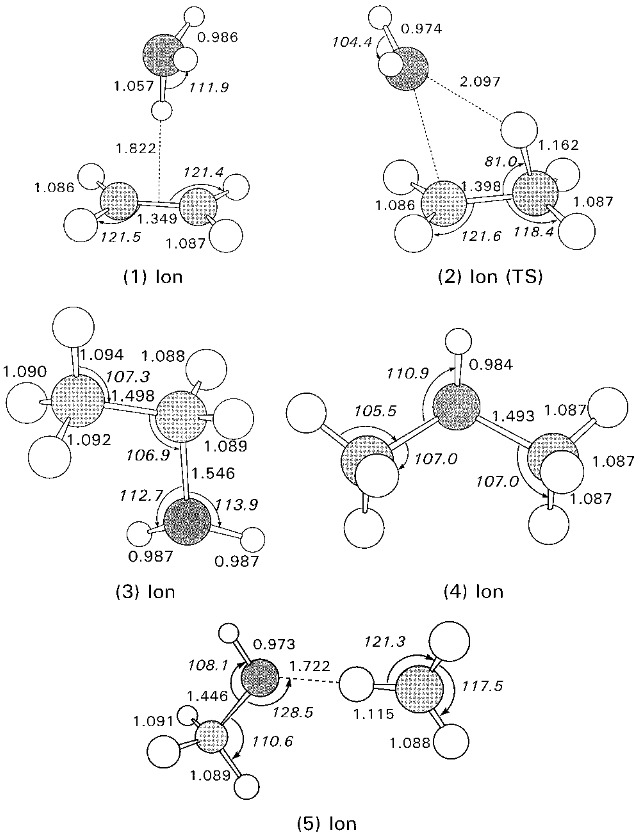

Figure 1. MP2/6-31G* optimized geometries for the designated $C_2H_7O^+$ species with bond lengths in Å and bond angles in deg.

We have presented the neutral products of $H_3O^+{\cdot}C_2H_4$ in reactions 7 and 8 as C_2H_5OH rather than $H_2O + C_2H_4$. Evidence presented in the Discussion section will show that the C_2H_5OH representation of the neutral product is a likely outcome in these two reactions.

A summary of the experimental results is presented in Table 1.

Ab Initio Studies. Two isomers of $C_2H_7O^+$, protonated ethanol, $C_2H_5OH_2^+$, and protonated dimethyl ether, $(CH_3)_2OH^+$, have been well characterized and identified experimentally as distinct isomeric species that retain their identifies under a wide range of conditions. Their enthalpies of formation have been determined.[13] Bouchoux and Hoppilliard in an ab initio study[15] characterized an electrostatic complex $C_2H_4{\cdots}H{\cdots}OH_2^+$ that is readily accessible from $C_2H_5OH_2^+$. Recently Audier *et al.*[16] also identified an electrostatic complex $CH_3^+{\cdots}HOCH_3$ formed from the association of CH_3^+ and CH_3OH, which they predicted to be separated by a small potential barrier from $(CH_3)_2OH^+$. In our calculations we identified four stable $C_2H_7O^+$ structures corresponding to minima on the potential energy surface using the G2 procedure.[17,18] These structures, in order of decreasing stability are: protonated ethanol, protonated dimethyl ether, and electrostatic complexes $C_2H_4{\cdots}H{\cdots}OH_2^+$, and $CH_3^+{\cdots}HOCH_3$. Our calculations of the $C_2H_7O^+$ potential surface are the first extended calculations of this surface at the G2 level of theory.

Formation of the $H_3O^+{\cdot}C_2H_4$ electrostatic π complex involves approach of the oxygen atom of H_3O^+ toward the midpoint of the C−C double bond with the formation of a hydrogen bond directed toward the center of the double bond (i.e. the most basic site). (See **1** in Figure 1.) The transition state between $H_3O^+{\cdot}C_2H_4$ and $C_2H_5OH_2^+$ resembles a loose association between a classical $C_2H_5^+$ ion and a water molecule. (See **2** in

TABLE 1: Reaction Rate Coefficients and Product Ratios with the Specified Reagent for the Three $C_2H_7O^+$ Ions: $H_3O^+{\cdot}C_2H_4$, Protonated Ethanol, $C_2H_5OH_2^+$, and Protonated Dimethyl Ether, $(CH_3)_2OH^+$

reactant	products	branching ratio	k_{obs} (10^{-9} cm^3 s^{-1})	k_{coll}[a] (10^{-9} cm^3 s^{-1})
		$H_3O^+{\cdot}C_2H_4$		
CH_3OH	adduct	1.0	0.69	2.1
C_7H_7F[b]	$C_7H_8F^+ + C_2H_5OH$[c]	0.65	0.54	1.9
	adduct	0.35		
CH_2CHCN	$CH_2CHCNH^+ + C_2H_5OH$[c]	0.40	3.2	3.8
	adduct	0.60		
		$C_2H_5OH_2^+$		
C_7H_7F[b]	$C_7H_8F^+ + C_2H_5OH$	~0.70	0.43	1.9
	adduct	~0.30		
CH_2CHCN	$CH_2CHCNH^+ + C_2H_5OH$	0.50	3.2	3.8
	adduct	0.50		
		$(CH_3)_2OH^+$		
C_7H_7F[b]	adduct	1.0	0.19	1.9
CH_2CHCN	adduct	1.0	2.3	3.8

[a] Reference 14. [b] 2-fluorotoluene. [c] See text for discussion.

TABLE 2: Calculated Enthalpies of Formation and Proton Affinities of C_2H_6O Isomers

	$\Delta_fH°$ (kJ mol^{-1})		E_{pa}/kJ mol^{-1}	
structure	calc[a]	exp[b]	calc[c]	exp
CH_3CH_2OH	−233.6	−234.7	780.4	788[b]
$(CH_3)_2O$	−190.2	−184.0	791.1	804[b]
$H_2O + C_2H_4$	−180.2	−189.5	767.5[d]	

[a] Calculated enthalpies of formation at 298 K at the G2 level of theory using $E_{G2}(C_2H_6O) - E_{G2}(H_2O) - E_{G2}(C_2H_4) = \Delta_fH°(C_2H_6O) - \Delta_fH°(H_2O) - \Delta_fH°(C_2H_4)$. Substitution of $\Delta_fH°(H_2O)$ and $\Delta_fH°(C_2H_4)$ from ref 13 yields $\Delta_fH°(C_2H_6O)$. [b] Experimental values are from ref 13. [c] Calculated proton affinities at 298 K at the G2 level of theory. [d] Calculated in the usual way using the equation $H_2O + C_2H_4 + H^+ \rightarrow H_3O^+{\cdot}C_2H_4$.

TABLE 3: G2 Energies and Relative Energies of $C_2H_7O^+$ Species at 298 K

		ΔE(G2)[a]	$\Delta_fH°$ (kJ mol^{-1})	
structure	E(G2)	(kJ mol^{-1})	calc	expt[b]
$H_3O^+ + C_2H_4$	−155.00200	0.0	657.4	642.3
$H_3O^+{\cdot}C_2H_4$	−155.03212	−79.1	563.2	
$C_2H_5OH_2^+$	−155.05385	−136.1	506.2	506.3
TS (2)	−155.02195	−52.4		
$(CH_3)_2OH^+$	−155.04141	−103.5	538.8	544.0
$C_2H_5^+ + H_2O$	−154.99953	6.5	669.4	660.2
$CH_3^+{\cdot}HOCH_3$	−154.94289	155.2	816.7	
$CH_3^+ + CH_3OH$	−154.91435	230.1	883.8	891.6

[a] Relative to $H_3O^+ + C_2H_4$. [b] Values from ref 13.

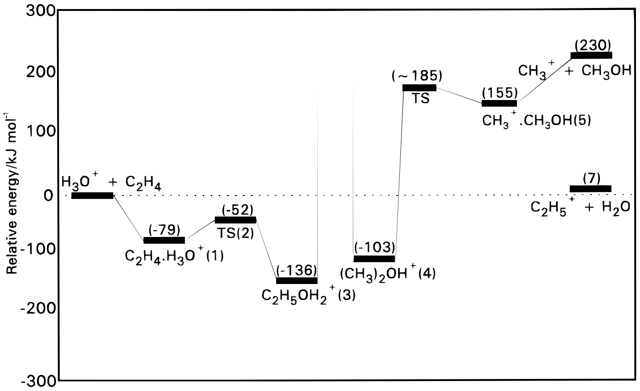

Figure 2. $C_2H_7O^+$ energy surface calculated using the G2 procedure. The energies are expressed in kJ mol^{-1} relative to $H_3O^+ + C_2H_4$ and are corrected to 298 K and for zero-point energy.

Figure 1.) Collision complexes with sufficient excitation energy may dissociate to $C_2H_5^+ + H_2O$ (reaction 4a): this proton transfer is calculated to be 7 kJ mol^{-1} endothermic. Complexes below this threshold can either dissociate back to reactants or be stabilized to form $C_2H_5OH_2^+$, which lies 136 kJ mol^{-1} below the reactants, $H_3O^+ + C_2H_4$. This mechanism supports the intuitive assumption that formation of $C_2H_5OH_2^+$ is more likely than $(CH_3)_2OH^+$ since the latter requires significantly more rearrangement.

In the reaction of CH_3^+ with CH_3OH, an electrostatic complex is formed with the CH_3^+ moiety attached by a H atom to the O atom of CH_3OH, with a binding energy of 75 kJ mol^{-1}. If the C−O bond distance is decreased, the energy of the system is raised until, at approximately R(C−O) = 2.6 Å, the CH_3^+ moiety is flipped to allow bonding between the C atom of CH_3^+ and the O atom of CH_3OH. The barrier between the $CH_3^+{\cdots}HOCH_3$ electrostatic complex and $(CH_3)_2OH^+$ is about 30 kJ mol^{-1}. An experimental investigation of the $CH_3^+ + CH_3OH$ reaction is presented in the accompanying paper by Matthews *et al.*[12]

A summary of some of the ab initio results showing the calculated proton affinities of the different C_2H_6O species is given in Table 2. Smith and Radom[18] have also calculated the proton affinity of $(CH_3)_2O$ using the G2 procedure as 792 kJ mol^{-1}.

The potential energy diagram relevant to the ion−molecule association reactions $H_3O^+ + C_2H_4$ and $CH_3^+ + CH_3OH$ incorporating our calculations is shown in Figure 2. The G2 energies of some of the ions and transition states on the $C_2H_7O^+$ surface are summarized in Table 3.

Discussion

The reaction chemistry summarized in Table 1 distinguishes clearly between the isomeric species, $C_2H_5OH_2^+$ and $(CH_3)_2OH^+$, on the basis of the different proton affinities of C_2H_5OH and $(CH_3)_2O$. Both ions exhibited near collision rate reactions with CH_2CHCN (PA = 794 kJ mol^{-1}), but protonated ethanol, $C_2H_5OH_2^+$, yielded a 50% proton transfer product channel whereas protonated dimethyl ether, $(CH_3)_2OH^+$, yielded only adduct. Both ions underwent slower reactions with 2-fluorotoluene (PA = 782 kJ mol^{-1}), but whereas $C_2H_5OH_2^+$ yielded a 70% proton transfer product channel and a faster reaction, no proton transfer was found for $(CH_3)_2OH^+$. These findings are in accord with the established proton affinities of C_2H_5OH (PA = 788 kJ mol^{-1}) and $(CH_3)_2O$ (PA = 804 kJ mol^{-1}).

What is also evident from the experimental studies is that the association adduct, $H_3O^+{\cdot}C_2H_4$, formed in reaction 4b is indistinguishable in our experiments from $C_2H_5OH_2^+$. The calculated G2 proton affinity of $(H_2O + C_2H_4)$ is 768 kJ mol^{-1}.

Our choice of CH_3OH (PA = 761 kJ mol^{-1}) as a neutral reagent for $H_3O^+ \cdot C_2H_4$ was influenced by this value. If the $H_3O^+ \cdot C_2H_4$ association ion product is the electrostatic ion, $C_2H_4 \cdots H \cdots OH_2^+$, identified in the ab initio studies, then proton transfer to CH_3OH might be expected. None was observed. Further, the rate coefficients and product distributions of the reactions of $H_3O^+ \cdot C_2H_4$ with C_7H_7F and CH_2CHCN are identical (within the experimental uncertainty) with those of $C_2H_5OH_2^+$ giving strong support to the identification of $H_3O^+ \cdot C_2H_4$ as $C_2H_5OH_2^+$. The transition state barrier between the two structures is only 27 kJ mol^{-1} relative to $C_2H_4 \cdot H_3O^+$ (Figure 2), and it is apparent that at the entrance level of $H_3O^+ + C_2H_4$ there is ample energy to overcome this small barrier and sample the surface above the $C_2H_5OH_2^+$ global minimum.

We conclude therefore that the experimental evidence supports the structure of the $H_3O^+ \cdot C_2H_4$ association adduct being $C_2H_5OH_2^+$. Although the accompanying paper of Matthews *et al.*[12] provides evidence for some fraction of the $C_2H_7O^+$ ion formed in the association reaction 4b being in the electrostatic form, some interconversion to $C_2H_5OH_2^+$ is possible. Our results from the product ratios of the two reagents studied (C_7H_7F and CH_2CHCN) do not allow us to state unequivocally that the electrostatic form is accessed. Two earlier studies also favor $C_2H_5OH_2^+$ as the structure of the $H_3O^+ \cdot C_2H_4$ adduct. Jarrold *et al.*[6] found supporting evidence from CID studies. Herbst *et al.*[19] compared the measured ternary reaction rate coefficient of reaction 4b with calculated values that were based on a designated structure of the $C_2H_7O^+$ product ion. They obtained satisfactory agreement between theory and experiment when they assumed an adduct structure of $C_2H_5OH_2^+$.

Conclusions

Proton transfer reactions can be used as a sensitive probe of structure.[7-9] We have utilized ab initio calculations of the $C_2H_7O^+$ energy surface and experimental observations of the proton transfer reactivity of the $C_2H_7O^+$ isomers, $C_2H_5OH_2^+$ and $(CH_3)_2OH^+$, to identify the $H_3O^+ \cdot C_2H_4$ product of reaction 4b as $C_2H_5OH_2^+$. Thus sources of C_2H_5OH in interstellar models utilizing the ion−molecule association reaction 2 remain valid although we note that the products of the subsequent ion−electron recombination reaction 3 have not yet been determined.

The observation of the endothermic proton transfer channel in reaction 4a ($C_2H_5^+ + H_2O$, $\Delta H° = +10.5$ kJ mol^{-1}),[13] which competes with formation of the $H_3O^+ \cdot C_2H_4$ adduct, shows that the exit channel from the $(H_3O^+ \cdot C_2H_4)^*$ complex to $C_2H_5^+ + H_2O$ is found before collisional stabilization can occur. In this work our measurement of the rate coefficient for endothermic proton transfer is 5.9×10^{-11} cm^3 s^{-1} at 0.35 Torr of helium. At 0.45 Torr of helium, McIntosh *et al.*[11] report a rate coefficient for proton transfer of 4.0×10^{-11} cm^3 s^{-1} and Bohme and Mackay[10] report a value of 6.3×10^{-11} cm^3 s^{-1} in a hydrogen carrier gas. The slight variation in rate coefficient in these three measurements is close to the experimental uncertainty. We conclude that the proton transfer channel takes place on a time scale that is much shorter than the time between collisions, *viz.* <125 ns, and proceeds independently of complex stabilization. The branching ratio is therefore expected to vary with pressure because of the variation in the termolecular rate.

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