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Studies in Chemical Ionization Mass Spectrometry. Secondary Alcohols with Isobutane

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Abstract: The major ions of the characteristic isobutane CI mass spectra of secondary alcohols can be accounted for in large part by the initial formation of a $(M + t\text{-}C_4H_9)^+$ association complex that is relatively long lived, but not always readily detectable. This complex may dehydrate to give $(M + 39)^+$, eliminate C_4H_8 to provide $(M + 1)^+$, eliminate C_4H_{10} to afford $(M - 1)^+$, or eliminate C_4H_9OH to give $(M - 17)^+$. Experiments with labeled secondary alcohols show that significant amounts of hydrogen atom scrambling occur in the $(M + 57)^+$ ions in these decompositions.

In an earlier report on the isobutane chemical ionization (CI) mass spectra of a number of saturated monohydroxylic alcohols, Field noted the presence of $(M + 57)^+$ and $(M + 39)^+$ ions, as well as very abundant alkyl ions, $(M - OH)^+$, and small amounts of $(M - 1)^+$ and $(M + 1)^+$ ions.[1] Separate mechanisms were suggested by Field to account for the formation of each of these ions.[1] We now wish to present evidence which suggests that in (at least) secondary alcohols these ions result in large part from the decomposition of a sometimes observable common intermediate $(M + t\text{-}C_4H_9)^+$ association complex.

Experimental Section

All chemical ionization spectra were obtained with a (Du Pont) CEC 21-110B mass spectrometer that had been modified for high-pressure operation.[2] Samples were introduced into the source region of the mass spectrometer by a direct insertion probe or through a variable leak from a heated glass oven.

The perdeuterated isobutane employed was obtained from Merck Sharp and Dohme of Canada. A high-pressure mass spectrum (P = 0.8 Torr) of this gas contained ions from m/e 29 to 140. The observed *tert*-butyl ions were $C_4H_9{}^+$ (6.1% of total ionization), $C_4H_8D^+$ (1.8%), $C_4H_7D_2{}^+$ (0.9%), $C_4H_6D_3{}^+$ (0.7%), $C_4H_5D_4{}^+$ (0.7%), $C_4H_3D_6{}^+$ (0.9%), $C_4H_2D_7{}^+$ (3.7%), $C_4HD_8{}^+$ (10.5%), and $C_4D_9{}^+$ (38.8%).

Cyclohexan-*1-d*-ol was prepared by lithium aluminum deuteride reduction of cyclohexanone employing an aqueous work-up procedure. Similarly, 2-adamantan-*2-d*-ol was prepared from adamantanone. Mass spectral analysis indicated that the cyclohexan-*1-d*-ol contained 86.3% d_1 and the 2-adamantan-*2-d*-ol, 96.3%. Cyclohexan-*2,2,6,6-d*$_4$-ol was obtained from the lithium aluminum hydride reduction of cyclohexan-*2,2,6,6-d*$_4$-one, which was prepared from cyclohexanone by repeated base-catalyzed equilibration with deuterium oxide. Mass spectral analysis showed that this labeled cyclohexanol contained 7.0% d_0, 2.1% d_1, 4.2% d_2, 11.9% d_3, 60.1% d_4, and 14.7% d_5. All samples were purified by glpc.

Results and Discussion

The isobutane CI data obtained in this study and those previously reported by Field[1] for a typical secondary alcohol, cyclohexanol, are compared in Table I. Although there are obvious differences in the relative abundances of the ions, the major ions observed are the same. Particularly striking are the $(M + 39)^+$ and the $(M + 57)^+$ ions. Field accounted for these ions by the formation of association complexes of the alcohol with the $C_3H_3{}^+$ and $t\text{-}C_4H_9{}^+$ ions of the isobutane plasma.[1] Alternatively, the $(M + 39)^+$ ion

Table I. Isobutane CI Spectra of Cyclohexanol

	% ionization $(100I_i/\sum_{\text{sample}} I_i)$		
Ion	70° [a]	110° [a]	180° [b]
M − 19	1.1	1.2	1.0
M − 17	22.8	39.9	65.8
M − 1	6.0	4.5	10.0
M + 1	9.2	7.0	7.2
M + 39	3.8	3.7	3.1
M + 57	23.6	13.7	2.3
2M + 1	6.3	3.4	

[a] The ion intensities reported are corrected for ^{13}C isotope. The reproducibility of the percent ionization is ±10% of the reported values. Pressure of isobutane is 0.6 Torr. [b] Reference 1; pressure of isobutane is 0.5 Torr.

could result from the loss of water from the initially formed $(M + t\text{-}C_4H_9)^+$ complex

$$\begin{tikzcd}
M \arrow[r, "C_3H_3^+"] \arrow[dr, "t\text{-}C_4H_9^+"'] & (M + 39)^+ \\
 & (M + 57)^+ \arrow[u, "-H_2O"']
\end{tikzcd}$$

High-resolution experiments show that the $(M + 39)^+$ ion is a single chemical species of elemental composition corresponding to $(M + C_4H_9 - H_2O)^+$ and *not* $(M + C_3H_3)^+$. The agreement between the experimental and theoretical masses is ±0.003 amu. Because of the difference in mass between $(M + C_4H_9 - H_2O)^+$ and $(M + C_3H_3)^+$, 0.0363 amu, a hypothetical doublet of these two species could have been resolved easily. No detectable amount of $(M + C_3H_3)^+$ was present. A metastable transition was also observed for the loss of water from the $(M + 57)^+$ ion.

Recently, Field et al. have noted that the major reaction that occurs with isobutane and t-$C_5H_{11}OH$ is the formation of an addition ion, $C_9H_{20}OH^+$, which dissociates rapidly to give $(C_9H_{19}^+ + H_2O)$ and $(C_5H_{11}^+$ + neutral products).[3] However, in the earlier study by Field on the isobutane CI of alcohols, neither $(M + C_4H_9)^+$ nor $(M + C_4H_9 - H_2O)^+$ ions were reported for the tertiary heptyl, octyl, and nonyl alcohols which were examined.[1]

In an effort to determine the origin of the hydrogens lost in the elimination of water from $(M + t\text{-}C_4H_9)^+$, labeled secondary alcohols were examined.[4] In cyclohexan-*1-d*-ol the average ratio of $(M + 57 - HDO)^+/(M + 57 - H_2O)^+$ is 0.17 (range 0.06-0.22), i.e., ca. 15% of this reaction proceeds by a process which involves the α hydrogen. In 2-adamantan-*2-d*-ol ca. 5% of the elimination of water occurs by loss of the α hydrogen. Although interpretation of the isobutane CI spectrum of cyclohexan-*2,2,6,6-d_4*-ol is complicated by the presence of significant amounts of the lesser deuterated species, it is clear that the ratio of $(M + 57 - HDO)^+/(M + 57 - H_2O)^+$ is significantly greater than 1. Therefore it is apparent that the dehydration of $(M + 57)^+$ does not occur through a single intermediate involving only the hydrogens of a specific carbon atom.

Previously, it has been proposed that the formation of $(M - 1)^+$ ions in the methane[5] and isobutane[1] CI spectra of alcohols occurs by hydride abstraction from the α carbon by $C_4H_9^+$. We have observed a metastable transition for the process $(M + 57)^+ \rightarrow (M - 1)^+$. Consequently, at least part of the $(M - 1)^+$ ions formed must result from the elimination of C_4H_{10} from a $(M + t\text{-}C_4H_9)^+$ intermediate complex.

In contrast to the earlier proposals concerning the mode of formation of $(M - 1)^+$ ions,[1,5] Dzidic and McCloskey have reported that in the methane CI spectrum of 1-decan-*1,1-d_2*-ol only 10% of the hydrogens are removed from the α carbon (for statistically random abstractions, 9.5% would be expected).[6] This behavior was attributed to internal solvation of the hydroxyl group by the polymethylene chain; hence a number of non-α hydrogens would be available when attack by the reagent ion occurs at the hydroxyl substituent. Such internal solvation is not possible in cyclohexanol. The CI spectrum of cyclohexan-*1-d*-ol indicates neither specific abstraction of the α deuterium nor random attack at the other carbon atoms. The ratio of $(M - H)^+/(M - D)^+$ is 0.45 ± 0.12. The $(M - H)^+$ ion is not very abundant (5.6%) in the methane CI spectrum of cyclohexanol. In the isobutane CI spectrum of cyclohexan-*1-d*-ol, the ratio of $(M - H)^+/(M - D)^+$ is 0.08 (range 0.04-0.2), i.e., 93% of the hydrogen abstracted from cyclohexanol in forming $(M - 1)^+$ ions originate from the α carbon.

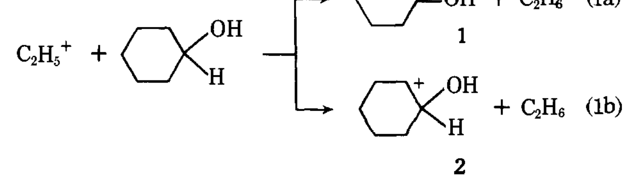
An alternative explanation to the "internal solvation" suggestion for the differences in the origins of the hydrogens lost in the formation of $(M - H)^+$ in the isobutane and methane CI mass spectra of secondary alcohols follows from a consideration of the thermochemistry of the competitive hydride transfer reactions. The pertinent thermochemical data for cyclohexanol are summarized in Table II and similar considerations should apply for any secondary alcohol.

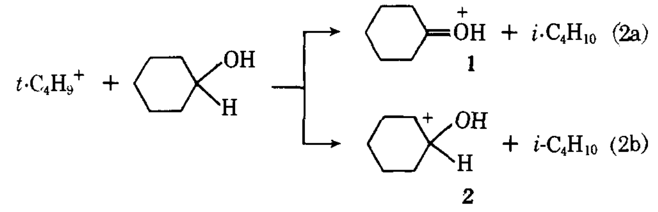
Table II. Thermochemical Data for Cyclohexanol[a]

Ion (HX^+)	$\Delta H_f(HX^+)$	H^-A-$(HX^+)^b$	X	$PA(X)^c$
$C_2H_5^+$	219	273	C_2H_4	159
i-$C_3H_7^+$	190	248	C_3H_6	181
i-$C_3H_7^+$	192^d	250	C_3H_6	179
sec-$C_4H_9^+$	183^d	247	1-C_4H_8	183^e
sec-$C_5H_{11}^{+f}$	171	239	1-C_5H_{10}	190^e
sec-$C_5H_{11}^{+f}$	173	241	1-C_5H_{10}	188^e
sec-$C_5H_{11}^{+f}$	174	242	1-C_5H_{10}	187^e
sec-$C_6H_{13}^{+f}$	170	243	1-C_6H_{12}	186
c-$C_6H_{11}^+$	183	246	c-C_6H_{10}	181
c-$C_6H_{11}^+$	187	250	c-C_6H_{10}	177
c-$C_6H_{11}^+$	181^g	244^g	c-C_6H_{10}	183^g
t-$C_4H_9^+$	167^d	233	1-C_4H_8	195
c-$C_6H_{10}OH^+$	108	211	c-$C_6H_{10}O$	204^h
c-$C_6H_{11}OH_2^+$	99		c-$C_6H_{11}OH^i$	197^j

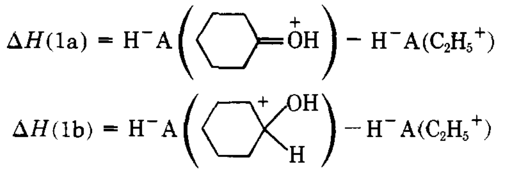
[a] Unless specifically noted, all thermochemical data are from: J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.*, No. 26 (1969). All values are in kcal/mol. [b] Hydride affinity, $H^-A(HX^+) \equiv \Delta H_f(HX^+) + \Delta H_f(H^-) - \Delta H_f(H_2X)$. [c] Proton affinity, $PA(X) \equiv \Delta H_f(X) + \Delta H_f(H^+) - \Delta H_f(XH^+)$. [d] F. P. Lossing and G. P. Semeluk, *Can. J. Chem.*, 48, 955 (1970). [e] If the neutral is a 2-alkene, rather than a 1-alkene, then the proton affinity is 2 kcal/mol lower (average of cis and trans isomers). [f] In view of the observations of Lossing and Semeluk (footnote *d*), the pentyl and hexyl ions have been assigned secondary structures. No attempt is made to differentiate the isomeric secondary ions. [g] Value obtained by assuming that there is no strain in the cyclohexyl ion and by assigning a value of 244 kcal/mol (average of the values for butyl, pentyl, and hexyl ions) to the hydride affinity of the cyclohexyl ion. The proton affinity of cyclohexene calculated from this assumed value of the hydride affinity of the cyclohexyl ion is 183 kcal/mol. This value is in good agreement with the values of the proton affinities of 2-butene, 2-pentene, and 2-hexene. [h] The proton affinity of cyclohexanone is reported to be 204 kcal/mol: B. L. Jelus, Ph. D. Thesis, University of Cincinnati, 1972. The $(M - H)^+$ ion for cyclohexanol is presumed to be the same as O-protonated cyclohexanone. [i] The heat of formation of cyclohexanol is estimated to be −70 kcal/mol by the method of S. W. Benson, "Thermochemical Kinetics", Wiley, New York, N. Y., 1968. [j] From the data of J. Long and B. Munson, *J. Am. Chem. Soc.*, 95, 2427 (1973), it is estimated that the proton affinity of cyclohexanol or of a secondary alcohol containing more than five carbon atoms is 197 kcal/mol.

Consider the alternative hydride abstractions of α and β hydrogens from cyclohexanol by the $C_2H_5^+$ ion in methane (eq 1a and 1b, respectively) and the t-$C_4H_9^+$ ion in isobutane (eq 2a and 2b, respectively). The heats of reaction for the hydride abstraction reactions can be expressed as differ-





ences between the hydride affinities of the reactant and product ions, $H^-A(X^+)$



As abstraction of the α hydrogen gives protonated cyclohexanone (**1**), reactions 1a and 2a are both exothermic, by −62 and −22 kcal, respectively. It is assumed that the hydride affinities of the ions obtained by abstraction of one of the β, γ, or δ hydrogens from cyclohexanol are all approximately the same and that each is approximately the same as the hydride affinity of the unsubstituted cylohexyl ion. Thus, if the hydride affinity of **2** is 244 kcal/mol, then reaction 1b is exothermic by 29 kcal, but reaction 2b is *endothermic* by 11 kcal. Consequently, both reactions 1a and 1b are expected to be rapid[7] and it is not surprising that there is no specificity for the abstraction of the α hydrogen in the methane CI spectra of alcohols. In contrast, although reaction 2a is exothermic, reaction 2b is endothermic. As endothermic ion-molecule reactions are generally slow under chemical ionization conditions, it follows that hydride abstraction by $t\text{-}C_4H_9^+$ should be highly specific for the α hydrogen. Similar conclusions should follow for other secondary alcohols. Although the $(M - H)^+$ ions of primary alcohols are protonated aldehydes, similar conclusions should also result for primary alcohols.

The dominant ion in the isobutane CI spectra of aliphatic alcohols with five or more carbon atoms is the $(M - 17)^+$ ion.[1] Field suggested that this ion might result from either protonation of the alcohol by $t\text{-}C_4H_9^+$ followed by dehydration or by an abstraction reaction, but was unable to distinguish between the two mechanisms.[1]

The heat of reaction for proton transfer from $t\text{-}C_4H_9^+$ to cyclohexanol (eq 3) can be calculated from the data of

$$t\text{-}C_4H_9^+ + c\text{-}C_6H_{11}OH \longrightarrow c\text{-}C_6H_{11}OH_2^+ + i\text{-}C_4H_8 \quad (3)$$

Table II: $\Delta H = PA(i\text{-}C_4H_8) - PA(c\text{-}C_6H_{11}OH) = -2$ kcal. The heat of reaction for the decomposition of protonated cyclohexanol to cyclohexyl ions and water (eq 4) can

$$c\text{-}C_6H_{11}OH_2^+ \longrightarrow c\text{-}C_6H_{11}^+ + H_2O \quad (4)$$

also be calculated from the data of Table II: $D(C_6H_{11}^+ - OH_2) = +24$ kcal. Dissociative proton transfer from $t\text{-}C_4H_9^+$ to cyclohexanol, the sum of eq 3 and eq 4, is therefore endothermic by 22 kcal and the reaction should be slow. A similar argument can be made for the corresponding process for all secondary alcohols.

With the data of Table II and $\Delta H_f(t\text{-}C_4H_9OH) = -75$ kcal/mol,[8] it follows that the abstraction of hydroxide from cyclohexanol by $t\text{-}C_4H_9^+$ (eq 5) is endothermic by 9 kcal. It

$$t\text{-}C_4H_9^+ + c\text{-}C_6H_{11}OH \longrightarrow c\text{-}C_6H_{11}^+ + t\text{-}C_4H_9OH \quad (5)$$

is somewhat disconcerting that this reaction is endothermic also; however, the combined uncertainty in the data is probably ca. 5 kcal. The analogous reaction should be endothermic for all secondary alcohols. Since the hydroxide abstraction reaction is ca. 15 kcal less endothermic than dissociative proton transfer, the activation energy for hydroxide abstraction should be lower and the rate of abstraction faster than the rate of dissociative proton transfer.

Although we have observed a metastable transition for $(M + 1)^+ \rightarrow (M - 17)^+$, and thus it is clear that some $(M - OH)^+$ ions are formed from $(M + H)^+$, it appears from the thermochemical arguments advanced that the majority of $(M - OH)^+$ ions result from the loss of $t\text{-}C_4H_9OH$ from the relatively long-lived $(M + t\text{-}C_4H_9)^+$ complex. Indeed, we have observed a metastable transition for the process $(M + 57)^+ \rightarrow (M - 17)^+$.

If the $(M - OH)^+$ ions were formed by a direct hydroxide abstraction analogous to the spectator stripping model[9] with no long-lived complex intervening, then any label present in the hydrocarbon portion of the alcohol would be completely retained in the alkyl ion. However, in both cyclohexan-*1-d*-ol and 2-adamantan-*2-d*-ol the ratio of $(M - 18)^+/(M - 17)^+$ is 0.04–0.05. This small, but nonzero, value suggests that the formation of the $(M - 17)^+$ ion involves an intermediate species of sufficient lifetime that some exchange can occur between the hydrogens on the α carbon and on the oxygen. Precise data are not available for cyclohexan-*2,2,6,6-d₄*-ol, but the ratios of the ion currents for *m/e* 83, 84, 85, 86, and 87 show that some exchange is also occurring from the β hydrogens. Moreover, although the spectra of $i\text{-}C_4D_{10}$ contain many impurity ions, it is clearly apparent that some transfer of deuterium occurs to the alkyl group of the alcohol. The ratio of $C_6H_{10}D^+/C_6H_{11}^+$ in the $i\text{-}C_4D_{10}$ spectrum of cyclohexanol is 0.11 ± 0.01, i.e., ca. 10% of the alkyl ions contain a deuterium from the reagent gas. In the $i\text{-}C_4D_{10}$ spectrum of $t\text{-}C_5H_{11}OH$, the ratio of $C_5H_{10}D^+/C_5H_{11}^+$ is 0.04.[3] Although it is possible that exchange could be occurring with the $(M - OH)^+$ ions and the reagent gas, we feel that these observations are best accounted for by exchange between C-bonded and O-bonded hydrogens in long-lived $(M + t\text{-}C_4H_9)^+$ ions.

The strong temperature dependence of the relative abundances of ions present in the isobutane CI spectra of secondary alcohols is apparent in Table I. As the temperature is increased, there is a marked decrease in the abundance of $(M + 57)^+$ ions and a substantial increase in the abundance of $(M - OH)^+$ ions. These observations are consistent with the thermally induced decomposition of $(M + t\text{-}C_4H_9)^+$ complex ions by a process which has an activation energy of a few kilocalories per mole.

It should be noted that $(M + 39)^+$ ions, but not $(M + 57)^+$ ions, have been detected in the isobutane CI spectra of some esters.[10] Activation energies of 4–12 kcal/mol have been reported for the decomposition of $(M + H)^+$ ions in the isobutane CI spectra of these esters.[10]

If the $(M + 57)^+$ ions of the alcohols are formed as expected by attack at oxygen, then they are structurally the same as the $(M + H)^+$ ions of mono *tert*-butyl ethers. CI spectra of such *tert*-butyl ethers have not been reported for comparison with these data. However, the methane CI spectra of simple aliphatic ethers contain no ions corresponding to the loss of water from the $(M + H)^+$ ions. On the other hand, the spectra of some cyclic ethers, e.g., oxepane and 7-oxabicyclo[2.2.1]heptane, do contain $(M + H - H_2O)^+$ ions of reasonable abundance.[11]

Isobutane CI spectra have been reported recently for some lanthanide chelates, $L(fod)_3$.[12] Some unexpected ions were noted in these spectra which were postulated to occur by way of complex rearrangements of $(M + 57)^+$ intermediates leading to fluorinated isobutenes as neutral products.

Such $(M + 57)^+$ ions must also be relatively long lived in order for bond-breaking and bond-forming reactions to occur.

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Solute Structuring in Aqueous Lanthanum(III) Chloride Solutions

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Abstract: The structure of the average solute species in four concentrated aqueous $LaCl_3$ solutions, with and without hydrochloric acid, has been measured by X-ray diffraction. In each solution, La^{3+} has 8 ± 0.2 oxygen nearest neighbors with the average La–O distance being ca. 2.48 Å. The ion-pair La · · · Cl distance, ca. 4.7 Å, is easily identified in the atomic radial distribution functions of these solutions, particularly in the solution where the stoichiometric ratio of chloride-lanthanum is 6:1. Models have been proposed which are consistent with the ARDF's obtained.

The coordination chemistry of various lanthanides, particularly in solutions, is one of the frontier areas of chemical research. Studies designed to examine the structural details of various lanthanide complexes have been rather unproductive, to a large extent because the normal spectroscopic tools have not led to a thorough understanding of lanthanide–ligand interactions.

Raman studies of lanthanide complexes[1-3] in solutions have failed to yield direct information concerning lanthanide–ligand interactions. Though for many years visible spectroscopy was not thought to be a useful tool for studying these interactions, it has recently been reported that lanthanide–ligand interactions may be correlated with changes in molar absorptivity[4] and with small changes in the wavelength of maximum absorption.[5]

Stability constant studies have been numerous; but such studies, by their nature, do not provide a detailed knowledge of the coordination of the cation.

Several years ago Brady[6] examined a series of aqueous $ErCl_3$ and ErI_3 solutions with X-ray diffraction methods. He has reported that $Er(H_2O)_6{}^{3+}$ is the predominant species in each solution with the average Er–O distance being ca. 2.2 Å. He also has reported extensive Er · · · Cl ion pairing in these solutions.

We have examined a series of concentrated aqueous solutions of $LaCl_3$, with and without added hydrochloric acid, in an attempt to directly determine the following: (a) the average coordination number and the average coordination geometry of La^{3+} in each solution; (b) the average La–O and/or La–Cl bond distances in each solution; (c) how these parameters are affected by changing solution composition; and (d) the similarity between the coordination of La^{3+} in these solutions and in crystals, where the nearest neighbor coordination of La^{3+} ranges from six to ten.[7-21]

To this end we have examined the solutions described below by X-ray diffraction methods using Mo Kα radiation.

Experimental Section

Solutions were prepared by weight from predried anhydrous $LaCl_3$, 10 *N* hydrochloric acid and/or distilled water. Densities were measured with a specific gravity bulb. Solution compositions are shown in Table I. Each solution was loaded into a Teflon sample holder, which has a window covered by a 1.0-mil Mylar film, and an X-ray diffraction pattern was obtained using the reflection method.[22] Scattered intensities were collected using our θ-θ diffractometer as counts per preset time as a function of the scattering angle from s = 1.23 Å^{-1} to s = 15.09 Å^{-1} ($s = 4\pi\lambda^{-1} \sin \theta$) at increments in θ of 0.25°. At least three runs over the entire angular range were made for each solution. The average intensity at each scattering point was used in subsequent calculations.

Table I. Solution Compositions

Solution	Molality, mol/kg	Mole fractions				Density, g/ml
		La	Cl	O	H	
A	2.67	0.015	0.045	0.313	0.627	1.53
B	2.10	0.012	0.036	0.317	0.635	1.43
C	1.74	0.010	0.030	0.320	0.640	1.36
D	1.54	0.010	0.060[a]	0.300	0.630	1.40

[a] Excess chloride has been added in the form of hydrochloric acid.