though broad, diffraction band at 8.4 Å. cannot be assigned to either pure structure; (c) diffraction maxima corresponding to spacings below 3.5 Å., which should be most sensitive to changes in the configurational order of single chains, are relatively weak. In their X-ray diffraction analysis of the structure of poly-L-proline (I), Traub and Shmueli[15] have identified the major equatorial reflections. This leads to the conclusion that the major nonequatorial reflections, corresponding to Bragg spacings of 4.9 and 5.7 Å., are common to both forms. This is a surprising result since the conformations of the individual chains are deduced to be so distinctly different.

In addition to the above, it seems quite likely that, owing to the inherent broadness of the transition, both forms occur on either side of the transition midpoint; *i.e.*, the degree of "cooperativeness" is probably comparable to that observed in the order–disorder transitions of the α-helix type polypeptides.[19] If this is so, then it might be expected that in the transition region sequences of both the *cis* and *trans* types might co-exist over an observable solvent composition interval. We do however reiterate that the infrared absorption bands below 1400 cm.$^{-1}$ associated with form I cannot be observed in samples precipitated from solutions containing less than 56% alcohol and that conversely the diffraction maximum at 7.75 Å., which appears sharply in the 56% sample, appears only as a diffuse halo in the 50% sample and not at all in samples removed from solutions of lower alcoholic content. In this connection, it should also be noted that none of the precipitated samples exhibited diffraction patterns characteristic of virtually uncrystallizable molecules such as conventional (atactic) vinyl polymers. In the latter, the customary explanation for their inability to crystallize is that their chain structures are sterically disordered. Applying this line of reasoning to the poly-L-proline precipitates, and recalling that at some point in the mutarotation the number of *cis*- and *trans*-imide bonds must be equal, it follows that the transition from an all-*cis* to an all-*trans* structure must proceed in a manner tending to favor the *coordinated* isomerization of *cis* sequences whose lengths are sufficient to crystallize. If this were not the case and the isomerization were totally uncooperative, each bond isomerizing independently of its neighbors, then at the midpoint of the transition the average sequence length (either *cis* or *trans*) would be two and the total fraction of *cis*- or *trans*-imide bonds found in isoconfigurational sequences exceeding four in length would be less than one-fifth (0.1875, to be exact).

We conclude with the observation that the cooperative configurational transition described here occurs in an isolated polymer chain devoid of intramolecular hydrogen bonding. In synthetic polypeptides and proteins of the α-helix type, the abruptness of the transition between ordered helix and disordered coil has been ascribed[20] to the large difference between the entropic increase accompanying the first break in a sequence of intact hydrogen bonds and the entropic increase *per bond* in propagating the break once it is started. Stated alternatively, the formation of a break in an otherwise intact α-helical sequence is less effective in imparting rotational freedom to the chain than is the breaking of an equal number of hydrogen bonds located at the ends of such sequences. There appears to be no equally appealing explanation for the cooperativeness of the transition between forms I and II of poly-L-proline. It is hoped that further research will illuminate this problem.

(19) For a summary of these observations see P. Doty, *Rev. Mod. Phys.*, **31**, 107 (1959).

(20) B. H. Zimm and J. K. Bragg, *J. Chem. Phys.*, **31**, 526 (1959).

[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT DEPARTMENT, AMERICAN OIL CO., WHITING, INDIANA, AND THE DIVISION OF PURE CHEMISTRY, NATIONAL RESEARCH COUNCIL, OTTAWA, CANADA]

Organic Ions in the Gas Phase. XIV.
Loss of Water from Primary Alcohols under Electron Impact

BY SEYMOUR MEYERSON[1a] AND L. C. LEITCH[1b]

RECEIVED FEBRUARY 20, 1964

Loss of water from the parent ion is a prominent reaction in the mass spectra of primary alcohols. Such loss has been viewed as 1,2-elimination to form an olefin ion, but growing evidence favors 1,4- over 1,2-elimination. The hope of confirming the specificity of this reaction prompted study of the mass spectra of hexanol unlabeled, -4-d_2, -5-d_2, and -6-d_3. The extra hydrogen atom lost as water comes from C-4 in 91% of the reacting molecules, and from a position closer than C-4 in the remaining 9%. No measurable hydrogen comes from C-5 or C-6. Label retentions in secondary decomposition products suggest that loss of water is accompanied or followed by making of a new bond between the carbon atoms from which H and OH are removed.

Many classes of substituted alkanes $C_nH_{2n+1}X$ characteristically split out HX under electron impact in a mass spectrometer to produce an "olefin" ion $C_nH_{2n}^+$. Such loss of H_2O is especially prominent in the spectra of primary alcohols, where it has been ascribed to 1,2-elimination *via* a four-membered bridged cyclic intermediate.[2,3] Postulated 1,2-elimination in other classes of alkane derivatives[4-6] has rested in part on analogy with alcohols. Little evidence has been available until very recently on the mechanism by

(1) (a) American Oil Co.; (b) National Research Council.

(2) (a) F. W. McLafferty, 8th Annual Meeting of ASTM Committee E-14 on Mass Spectrometry, Atlantic City, N. J., 1960; (b) F. W. McLafferty in "Determination of Organic Structures by Physical Methods," Vol. 2, F. C. Nachod and W. D. Phillips, Ed., Academic Press, Inc., New York, N. Y., 1962, p. 93.

(3) See also F. W. McLafferty in "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press, Inc., New York, N. Y., 1963, p. 309.

(4) F. W. McLafferty, *Anal. Chem.*, **29**, 1782 (1957).

(5) E. J. Levy and W. H. Stahl, *ibid.*, **33**, 707 (1961).

(6) F. W. McLafferty, *ibid.*, **34**, 2 (1962).

which alcohols lose H_2O. Data available, however, are not compatible with 1,2-elimination. The mass spectrum of butanol-2-*d*[7] shows no loss of deuterium in forming the $C_4H_8^+$ ion. Similarly, 1,1-elimination is clearly ruled out by the spectra of butanol-1-*d*[7] and -1-d_2.[8] The $C_5H_8^+$ ion derived from cyclopentanol-2,5-d_4 by loss of H_2O retains all four deuterium atoms, ruling out 1,2-elimination.[9] Likewise, loss of H_2O from 2-butanol-1,3-d_5[8] and from 3-tetradecanol-2,4-d_4[10] entails no loss of deuterium. The preferred mechanism in a cyclic or a secondary acyclic alcohol is not necessarily the same as in a primary one; even so, the data would seem to be not altogether irrelevant. In 2-methyl-2-butanol-3-d_2,[11] about 37% of the water molecules lost from parent ions are HDO. However, this is the only alcohol larger than ethanol, to our knowledge, in which clear evidence exists for 1,2-elimination.

The spectra of propionitrile-2-d_2 and propanol-1,2-d_4 were recently measured by S. M. in connection with another investigation.[12] Loss of HCN from the former compound produces almost solely $C_2H_3D^+$ ions; loss of H_2O from the latter produces mainly $C_3H_2D_4^+$. These results, indicating 1,1- and 1,3-elimination, respectively, directed attention anew to the discrepancy between the postulated 1,2-elimination and available evidence. A further clue was uncovered by reexamining published spectra of straight-chain primary alcohols.[13] Relative intensity at the parent mass less 18 units, corresponding to loss of H_2O, increases sharply when the carbon number is raised from 3 to 4, and then decreases monotonically with further increase in carbon number; this trend is paralleled closely by relative intensity at the parent mass less 34 units, corresponding to loss of H_2S, in the spectra of straight-chain primary thiols.[5] The correlation suggests that a hydrogen atom on C-4 is needed for facile loss of H_2O, although an atom on C-3 can serve, as found in propanol. Progressive decrease of relative intensity of the $C_nH_{2n}^+$ ion so formed with increasing carbon number probably reflects simply an increasing likelihood of subsequent further decomposition. This interpretation is supported by the carbon-number dependence of the summed intensities of olefinic ions $C_jH_{2j}^+$ and $C_jH_{2j-1}^+$ for all values of j from 3 to n, which comprise a particularly large fraction of total ion intensity in the spectra of straight-chain primary alcohols.[13] In the spectrum of propanol, this series of ions accounts for 9% of total fragment-ion intensity; the value rises to nearly 40% in butanol and 50% in pentanol, remaining at about that value out to undecanol, beyond which no data are reported.

While the present work was in progress, two communications reported spectra of additional deuterated species of butanol. From a spectrum of butanol-4-d_3, although isotopic purity was somewhat less than one might have wished, elimination of H_2O was estimated to be 80% 1,4 and 20% 1,3.[14] From spectra of butanol-3-*d* and -4-*d*, a lower limit of 80% was deduced for the contribution of 1,4-elimination.[15]

To confirm the occurrence and, even more so, the specificity of 1,4-elimination in primary alcohols as a class requires investigation of an alcohol containing more than four carbon atoms. We selected hexanol and have measured and studied the mass spectra of the 4-d_2, 5-d_2, and 6-d_3, as well as the unlabeled, species of this compound. Seventy-volt spectra were supplemented by measurements close to the respective appearance potentials of ions selected for study: $C_6H_{12}^+$, the product of H_2O elimination from the parent ion; and $C_5H_9^+$, $C_4H_8^+$, and $C_4H_7^+$, attributed to further decomposition of $C_6H_{12}^+$ by loss of CH_3, C_2H_4, and C_2H_5, respectively.

Results and Discussion

Partial spectra of the hexanols are shown in Table I; relative intensities are corrected for contributions of naturally occurring heavy isotopes.[16] Selected metastable peaks and the transitions denoted by them[17] are shown in Table II; these peaks support the postulated secondary loss of CH_3 and C_2H_4.

TABLE I

PARTIAL SPECTRA OF HEXANOLS

Scale of relative intensity defined by assigning value of 100.0 to total ion current at mass 36 and above

Mass	Ion[a]	Unlabeled	4-d_2	5-d_2	6-d_3
104		...	...	...	0.02
103		...	0.02	0.02	...
102		...	...	...	...
101	$C_6H_{13}O^+$	0.02	...	...	...
88		...	...	...	0.05
87		0.01	0.05	0.05	2.17
86		...	0.19	2.08	0.31
85		0.07	1.97	0.23	.05
84	$C_6H_{12}^+$	1.97	0.22	.12	.04
83	$C_6H_{11}^+$	0.30	.06	.03	.01
82		.02	.02	.01	.01
74		.01	.04	.04	.34
73		.35	.37	.67	.61
72		.06	.26	.26	3.18
71		.41	1.54	3.75	0.38
70		.33	3.35	1.81	0.35
69	$C_5H_9^+$	5.52	1.01	0.38	1.87
68		0.16	0.15	.11	0.15
60		...	.03	.02	0.46
59		0.17	.57	.65	19.6
58		0.04	3.49	16.9	5.81
57	$C_4H_9^+$	1.13	21.1	9.37	3.59
56	$C_4H_8^+$	22.8	10.3	5.62	1.64
55	$C_4H_7^+$	13.2	2.27	6.23	7.24
54		0.75	0.47	0.49	0.47

[a] Formulas shown correspond to unlabeled ions only.

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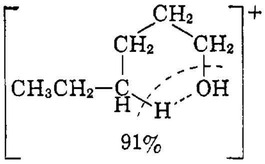
TABLE II

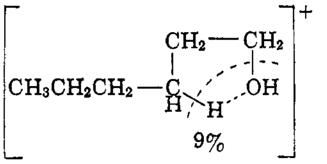
SELECTED METASTABLE PEAKS IN HEXANOL SPECTRA

Apparent mass	Unlabeled	4-d_2	5-d_2	6-d_3	Transition denoted
		$C_6H_{12}^+ \rightarrow C_5H_9^+ + CH_3$			
59.6	..	..	..	0.02	$(87^+) \rightarrow (72^+) + 15$
58.6	..	..	0.02	..	$(86^+) \rightarrow (71^+) + 15$
57.6	..	0.02	..	..	$(85^+) \rightarrow (70^+) + 15$
56.7	0.04	..	..	..	$(84^+) \rightarrow (69^+) + 15$
		$C_6H_{12}^+ \rightarrow C_4H_8^+ + C_2H_4$			
40.0	..	..	..	0.04	$(87^+) \rightarrow (59^+) + 28$
39.1	..	..	0.03	..	$(86^+) \rightarrow (58^+) + 28$
38.2	..	0.02	..	..	$(85^+) \rightarrow (57^+) + 28$
37.3	0.04	..	..	..	$(84^+) \rightarrow (56^+) + 28$

The $C_6H_{12}^+$ ions derived from hexanol-5-d_2 and -6-d_3 retain essentially all the original deuterium. Essentially all the $C_6H_{12}^+$ ions derived from hexanol-4-d_2 retain one deuterium atom, except about 9%, which retain both. Moreover, this distribution is constant within experimental error over the entire range of ionizing voltages from the appearance potential to 70 v.; thus, the energies required to produce the d_1 and d_2 ions are identical or nearly so. The picture that emerges parallels closely that found for butanol. About 91% of the $C_6H_{12}^+$ ions arise by 1,4-elimination of H_2O and 9% probably by 1,3.



91%



9%

Neither 1,5- nor 1,6-elimination contributes to any measurable extent.

The structure of the resulting ion is uncertain. Two possible paths that would lead to conventional molecular structures can be readily suggested: making of a new bond between the carbon atoms from which H and OH are removed would lead to ethylcyclobutane and propylcyclopropane ions; or hydrogen migration concerted with or following loss of H_2O would lead to one or more isomeric hexene ions. Even if cycloalkanes are formed, they might be expected to have some tendency to isomerize to hexene, so that the distinction between the two alternatives may be blurred. Energetics[18] and labeling[19] evidence indicates that such isomerization occurs in the lowest-energy paths by which H and CH_3, respectively, are lost from cycloalkanes and methylcycloalkanes with rings smaller than cyclohexyl, and by which C_2H_5 is lost from ethylcyclopentane. Even so, deuterium retention in products of further decomposition can perhaps furnish some clues to the structure of the intermediate $C_6H_{12}^+$ ions.

By analogy with ethylcyclopentane,[19] C_2H_4 lost from an ethylcyclobutane ion would be expected to come solely from the ring. Thus, in the spectra of the three labeled hexanols studied, $C_4H_8^+$ ions derived from a $C_6H_{12}^+$ intermediate with this structure should retain all the deuterium atoms that were present in the intermediate. How much CH_3 and C_2H_5 would come from the ring and how much from the side chain will depend upon ring strain, dissociation energy of the bond to the side chain, vibrational energy available to drive the reactions, and isotope effects.

Partial isotopic distributions of the $C_5H_9^+$, $C_4H_8^+$, and $C_4H_7^+$ ions were estimated[20] from the spectra in Table I. Maxima of 28% of the $C_5H_9^+$ ions from hexanol-4-d_2 and 68% of those from hexanol-5-d_2 retain two deuterium atoms; about 58% of those from hexanol-6-d_3 retain all three. The bulk of the remaining $C_5H_9^+$ ions from the d_3 alcohol are unlabeled; yields of d_1 and d_2 ions are low. $C_4H_8^+$ ions derived from hexanol-4-d_2 are mainly d_1, but about 13% retain two deuterium atoms; 72% of those from the 5-d_2 alcohol retain two deuterium atoms, and 83% of those from the 6-d_3 species retain all three. Of the $C_4H_7^+$ ions derived from hexanol-4-d_2, -5-d_2, and -6-d_3, about 15, 45, and 53%, respectively, are unlabeled. At energies close to the appearance potential, two deuterium atoms are retained in about 13% of the $C_5H_9^+$ ions derived from hexanol-4-d_2 and 57% of those from hexanol-5-d_2, and all three are retained in 60% of those from hexanol-6-d_3. The corresponding values for $C_4H_8^+$ are 9, 50, and 70%. No estimates were made of retention in $C_4H_7^+$ at low voltage because of interference from $C_4H_6^+$ as well as $C_4H_8^+$.

More than one process and more than one intermediate $C_6H_{12}^+$ structure are apparently involved in the paths leading to each of the secondary products, $C_4H_8^+$, $C_5H_9^+$, and $C_4H_7^+$. Comparatively high retentions of all the $C_6H_{12}^+$ deuterium in derived $C_4H_8^+$ suggest that ethylcyclobutane ion is an important intermediate in this system, although, alternatively, such retentions might arise simply by loss of the terminal $-CH_2CH_2\cdot$ group with no intervening bond making or rearrangement concerted with or following loss of H_2O. The isotopic distribution of $C_5H_9^+$ ions from hexanol-6-d_3 is strikingly reminiscent of the isotopic distribution of $C_5H_9^+$ ions derived from methyl-d_3-cyclopentane[19]; and the extent of loss of all deuterium in forming $C_4H_7^+$—low in hexanol-4-d_2 and close to 50% in hexanol-5-d_2 and -6-d_3—is also compatible with an intermediate having a cycloalkane structure. Loss of positional identity of atoms appears less extensive here than in those deuterium-labeled unsaturated aliphatic hydrocarbons that have been subjected to mass-spectral study: butene-1,[21] *cis*- and *trans*-butene-2,[22] propene,[23] and propyne.[24]

The three smaller fragments derived from hexanol-4-d_2 show higher retentions of two deuterium atoms than does $C_6H_{12}^+$. If the assumption that all three arise solely from $C_6H_{12}^+$ precursors is valid,[25] these

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(25) The assumption is most likely valid for $C_5H_9^+$ and $C_4H_8^+$, but not for $C_4H_7^+$. A weak metastable peak (relative intensity = 0.006) of apparent mass 36.7 in the spectrum of unlabeled hexanol is attributed to the transition $(83^+) \rightarrow (55^+) + 28$, *i.e.*, $C_6H_{11}^+ \rightarrow C_4H_7^+ + C_2H_4$. $C_6H_{11}^+$, in turn, most likely arises by loss of H from $C_6H_{12}^+$. Relative contributions to $C_4H_7^+$ yield by this and other possible reaction paths are not known.

statistics require at least two different chemical species of $C_6H_{12}^+$ ions that have different label retentions and contribute disproportionately to each of the secondary decomposition products. The requirement could be met by ethylcyclobutane and propylcyclopropane intermediates arising from 1,4- and 1,3-elimination, respectively. In consequence of the differences in geometry and in ring strain, propylcyclopropane ion would be expected to yield a different distribution of products of further breakdown than ethylcyclobutane. The difference in strain energy between the cyclobutyl and cyclopropyl rings is only about 2 kcal./mole,[26,27] exceedingly small beside the energy of the impinging electrons. However, similarly small differences between ring-strain energies in methylcyclopentane and methylcyclohexane and between dissociation energies of the alkyl–cycloalkyl bonds in methyl- and ethylcyclopentanes have been found to exert marked influence on relative rates of competing reactions leading to isomeric products.[19]

Multiple processes involving isomeric ions cannot be fully disentangled; details are not entirely clear. Even so, considerable specificity is evident in hexanol decomposition—especially in the primary loss of H_2O, but also, though to a lesser extent, in secondary reactions.[28]

Experimental

The hexanols were prepared by reaction of unlabeled and appropriately labeled 1-bromopropanes with trimethylene oxide,[29] which in turn was prepared from 3-chloropropanol[30] (27.5% yield).

To prepare unlabeled hexanol, 5.8 g. (0.1 mole) of trimethylene oxide was added with stirring to the Grignard reagent prepared from 12.3 g. (0.1 mole) of 1-bromopropane and 2.4 g. (0.1 g.-atom) of magnesium in 75 ml. of anhydrous ether. The reaction mixture was heated under reflux on a steam bath for 1 hr., 50 ml. of dry benzene was added, and the ether was distilled off. The benzene solution was then heated for 4 hr. on a steam bath, cooled, and poured into 50 ml. of ice-cold dilute hydrochloric acid. The benzene layer was separated and the aqueous solution was extracted with pentane. Evaporation of the organic solvents gave a pale yellow oil which was a mixture of hexanol and 3-bromopropanol. The crude product was added to a solution of 5.0 g. of potassium hydroxide in 10 ml. of methanol and 2 ml. of water and heated for 2 hr. under reflux on a steam bath. After cooling, the solution was poured into water and the oily layer was taken up in pentane. Evaporation of the pentane left an oil which was purified by distillation on a vacuum line at ambient temperature and 0.05 torr pressure. The 3.1 g. (31% yield) of hexanol so obtained was colorless and gave a negative Beilstein test.

Hexanol-4-d_2, -5-d_2, and -6-d_3 were prepared similarly from 5.0 g. (0.04 mole) of 1-bromopropane-1-d_2, -2-d_2, and -3-d_3, respectively, purchased from Merck Sharp and Dohme, Montreal, Canada. Yields were all about 35%.

Chemical purities (weight %) of the hexanols, estimated by gas chromatography, were: unlabeled, 92.5; -4-d_2, 84.5; -5-d_2, 90.3; -6-d_3, 90.8. Final purification by gas chromatography gave fractions, the mass spectra of which revealed no impurities. The labeled 1-bromopropanes were stated by the vendor to have minimum isotopic purities of 98 atom %. Mass spectra of the hexanols do not permit precise isotopic analysis; however, they suggest that isotopic purity is in every case close to 100 atom %.

Mass spectra were measured with 70-v. electrons on a modified[31] Consolidated Model 21-103c instrument with the inlet system at 250°. Low-voltage measurements were made with the repeller plates at an average potential of 3 v.; actual settings, adjusted for maximum ion current, were 4.00 v. on the inner repeller and 2.00 v. on the outer one.

Acknowledgment.—We are grateful to D. K. Albert for assistance with gas chromatography.

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[27] C. T. Mortimer, "Reaction Heats and Bond Strengths," Pergamon Press, New York, N. Y., 1962, p. 26.

[28] As this communication was being prepared to go to press, we learned of pertinent results reported by K. Biemann to the Welch Foundation Conference on Modern Developments in Analytical Chemistry, in Houston, Texas, Nov., 1963. In the respective mass spectra of butanol-2-d_2, pentanol-3-d_2, hexanol-4-d_2, and heptanol-5-d_2 <1, 3, 90, and 5% of the water lost from parent ions contained a deuterium atom—in essential agreement with our findings.

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[CONTRIBUTION NO. 7990 FROM THE DIVISION OF PURE CHEMISTRY, NATIONAL RESEARCH COUNCIL OF CANADA, OTTAWA, CANADA]

The Mercury-Photosensitized Decomposition of Propane at Temperatures above 300°

BY R. A. BACK AND S. TAKAMUKU[1]

RECEIVED JANUARY 31, 1964

A reinvestigation of the mercury-photosensitized decomposition of propane at temperatures from 300 to 400° has yielded results very similar to those obtained earlier by Bywater and Steacie, despite considerably improved conditions for kinetic measurements. It appears likely that an approximate equilibrium was established between *n*-propyl and isopropyl radicals. The resultant low concentrations of *n*-propyl radicals (3 to 6%) probably account for the abnormally low rate of formation of methane, which arose largely *via* the decomposition of *n*-propyl rather than isopropyl radicals. Rate constants for this decomposition, based on calculated values of [*n*-propyl], are in fair agreement at 300° with values obtained by extrapolation of the data of Calvert and Sleppy obtained at lower temperatures, but with rising temperature fall well below these values.

Introduction

Some of the earliest estimates of bond-dissociation energies in alkyl radicals come from studies of the mercury-photosensitized decomposition of alkanes at elevated temperatures. It has since become evident that some of these estimates are considerably lower than the correct values,[2] although the reason for this has never been clearly explained. About 12 years ago,

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[1] National Research Council of Canada Postdoctorate Fellow, 1961–1962.

[2] J. A. Kerr and A. F. Trotman-Dickenson, *Progr. Reaction Kinetics*, **1**, 107 (1961).