to crystalline imperfections which in other methods are averaged in the result. The emphasis in this study has been upon a technique for the rapid examination of small quantities of material with respect to the density of the solid phases present. For the purposes of rapid survey, measurements to an accuracy of ±0.2% can be made in 5 minutes. The use of the centrifuge is largely responsible for this rapidity.

The limitations of the gradient column technique in the study of crystalline homogeneity have been discussed. Where it is applicable, the method appears to have several advantages. No severe changes in environment which might affect labile compounds are involved. Materials once crystallized need not be dissolved. The recovery, with care, may be made quantitative. It has been shown that a 1% impurity may be easily observed. Further investigations on the sensitivity have still to be made. The sensitivity has been limited in this study to the detection of a mass of crystalline fragments large enough to be visible to the naked eye. The microscopic examination of a microgradient tube should lead to the observation of a single very small crystal.

The sensitivity of the density determination as an indication of the purity and identity of a crystalline phase appears to have been neglected. Since the optically active and racemic forms of a compound almost invariably have different crystal densities, this method offers a rapid quantitative procedure for distinguishing between these two forms. Application of the method may establish the presence of a complex or a mixed crystal rather than a pure compound of known density.

Wet and dry protein crystal densities have been studied by the gradient column technique. This method provides a non-equilibrium procedure comparable in accuracy to, and more rapid than the flotation technique hitherto used. Small differences in density between crystals subjected to different media or drying procedures are visibly demonstrated by the use of a single gradient column for their comparison. The results demonstrate the speed with which protein crystals change in composition upon exposure to air and emphasize the value of an equilibrium method for their study. Non-equilibrium methods are only applicable to the study of large crystals. An equilibrium method for the study of smaller protein crystal densities has, therefore, been developed. It will be described elsewhere.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, BROOKHAVEN NATIONAL LABORATORY]

The Mass Spectra of Some Deuterated Isopropyl Alcohols[1]

BY LEWIS FRIEDMAN AND JOHN TURKEVICH

The mass spectra of $(CH_3)_2CHOH$, $(CH_3)_2CHOD$, $(CH_3)_2CDOH$ and $(CH_3)_2CDOD$ are reported and the mechanism of the formation of the more abundant fragment ions is discussed. The results support the concept of localized charge on the oxygen atom in the more abundant ions.

Introduction

The mass spectra of $(CH_3)_2CHOH$, $(CH_3)_2CHOD$ and $(CH_3)_3CDOD$ were needed in connection with studies on the mechanism of the catalytic reduction of acetone with deuterium. The mass spectrum of isopropyl alcohol has been previously reported[2] but no data are available on the mass spectra of deuterium substituted alcohols.[3]

Experimental

Isopropyl alcohol was prepared by hydrolysis with ordinary water of aluminum isopropoxide which had been previously purified by distillation. Isopropyl alcohol O–D was prepared by hydrolysis of the same compound with 99.8% D_2O. The absence of an O–H absorption band at 2.95 μ in the infrared absorption spectrum of the isopropyl alcohol O–D indicates less than 5% impurity of $(CH_3)_2CHOH$. Isopropyl alcohol 2-C–D–O–D was prepared by catalytic reduction of acetone with deuterium.[4] Isopropyl alcohol 2-C–D–OH was prepared by hydrolysis of the 2-C–D–OD with light water.

The isotopic content of these preparations was determined in the following way from the mass spectrometer data. The relative intensity of the parent ion is small and cannot be used as a criterion of purity under controlled electron bombardment. However in the mass region 45–48, the most intense ion corresponds to a fragment produced by the loss of a methyl group. In the case of the dideutero compound this ion has the mass 47 and its relative intensity is set at 100 units. Isopropyl alchol containing more than two D atoms may be estimated from the intensities of ions above mass 47 in this region of the spectrum. Ions of mass 48 are present to the extent of 3.64 units of which approximately 2.2 are ascribed to natural C^{13}. The remaining 1.4 units arise from the dissociation of a trideutero isopropyl alcohol formed by exchange in the reduction process. Since the probability of losing the CH_3 or CH_2D methyl group is approximately the same, the residual peak intensity of 1.4 units at mass 48 indicates an upper limit of 3% for trideutero isopropyl alcohol. The concentration of monodeutero isopropyl alcohol may be estimated from the relative intensity of ions of mass 46. In ordinary isopropyl alcohol the corresponding process, *i.e.*, the loss of CH_4 or $CH_3 + H$, gives rise to a peak of 4.3 units at mass 44. If we subtract 4.3 units for this process which normally occurs from the observed 23.7 units at mass 46 in the dideutero isopropyl alcohol spectrum, we obtain 19.4 units which may be due to mono-

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[1] Research carried out under the auspices of the U. S. Atomic Energy Commission. Presented before the Division of Physical and Inorganic Chemistry at the 116th Meeting of the ACS, September, 1949.

[2] (a) American Petroleum Institute, Research Project 44, National Bureau of Standards 76, 285; (b) B. W. Thomas and W. D. Seyfried, *Anal. Chem.*, **21**, 1023 (1949); (c) A. P. Gifford, S. M. Rock and W. J. Comaford, *ibid.*, **21**, 1027 (1949).

[3] Since this work has been completed a paper by F. E. Condon, H. L. McMurry and V. Thornton, *J. Chem. Phys.*, **19**, 1010 (1951), has been published containing the mass spectra of $(CH_3)_2CDOH$.

[4] L. Friedman and J. Turkevich, THIS JOURNAL, **74**, 1669 (1952).

TABLE I

MASS SPECTRA OF ISOPROPYL ALCOHOL AND DEUTERIUM DERIVATIVES

Mass 66	Isopropyl alcohol				NBS[e] #76	$(CH_3)_2CDOD$	$(CH_3)_2CDOH$		$(CH_3)_2CHOD$
	CN[a]	GE[b]	T & S[c]	GR & C[d]		GE[b]	GE[b]	CN[a]	CN[a]
62						0.30	...		
61						.37	0.4	0.39	0.4
60	0.5	0.5	0.47	0.44	0.5	2.2	.32	0.45	3.6
59	2.9	2.6	4.54	3.58	3.5	0.4	2.2	2.59	0.5
58	0.2	0.1	2.16	...	0.2	.38	0.3	1.4	0.6
57	.5		0.4	0.30	0.5				
48	...	...	...	...		3.64	.4	...	...
47	0.3	...		0.21	0.3	100.0	5.3	6.7	2.0
46	2.3	2.6	2.32	2.25	2.3	23.7	100.0	100.0	100.0
45	100.0	100.0	100.0	100.0	100.0	5.4	22.3	22.4	17.0
44	4.0	4.3	3.77	3.45	3.7	12.1	10.0	15.1	5.4
43	16.5	17.4	18.68	16.76	18.3	10.6	14.0	15.6	15.0
42	4.3	4.0	6.40	3.9	4.3	7.4	6.7	7.2	3.9
41	7.5	8.0	9.55	6.54	7.3	5.4	4.7	3.4	7.7
40	1.0	1.2	1.50	...	1.0	4.7	4.0	2.8	1.0
39	...	7.7	6.17	5.52		7.4	6.0	...	
33						1.8	0.1	...	...
32	0.3	0.8			0.3	7.5	1.9	1.8	5.4
31	5.65	7.1	5.0	5.75	5.6	1.3	6.3	3.8	1.7
30	0.7	0.6	0.30	0.60	0.7	7.43	6.3	4.2	1.5
29	11.0	13.4	5.45	9.49	10.7	10.4	11.7	6.1	6.7
28	2.2	8.8[f]	2.17	0.91	2.2	24.0[f]	14.0	26.0[f]	4.7
27	15.0	20.4	10.19	15.50	15.8	13.5	13.5	5.9	15.4
26	2.3	2.9	1.86	2.20	2.3	2.4	1.5	...	2.1

[a] Consolidated Nier Isotope Ratio Mass Spectrometer. [b] General Electric Mass Spectrometer. [c] B. W. Thomas and W. D. Seyfried, ref. 2. [d] A. P. Gifford, S. M. Rock and W. J. Comaford, ref. 3. [e] API Research Project #44, NBS #76, ref. 1. [f] Value at 28 uncertain because of background in mass spectrometer.

deutero isopropyl alcohol and in part to a rearrangement process on electron impact. The upper limit for the monodeutero compound concentration is approximately 16%.

Ultraviolet absorption spectrum of the alcohol indicates less than 0.1% acetone in this preparation.

The mass spectra were determined on a Consolidated Nier type Isotope Ratio spectrometer and in a General Electric mass spectrometer. Seventy-five-volt and 45-volt ionizing electrons were used in the Consolidated Nier and the GE, respectively. Magnetic scanning techniques were used in both machines with ion accelerating potentials of 1200 volts for the Consolidated Nier and 2000 volts for the GE.

Special care had to be taken to avoid the loss of the hydroxyl deuterium in running samples of $(CH_3)_2CDOD$ and $(CH_3)_2CHOD$. Exchange was observed between water adsorbed in the sample manifolds and mass spectrometer leaks, etc., and the alcohol OD. This difficulty was circumvented by saturating the spectrometer with heavy water prior to running the alcohols containing O–D bonds. Fifty lambda samples of 99.8% D_2O were introduced into the mass spectrometer and removal of light water was followed by observing the relative intensity of the peaks at masses 20 and 19 corresponding to D_2O^+ and HDO^+. The first four samples increased this ratio to a value of 94% D. After four additional samples had been introduced and evacuated the value rose to 97%. After this treatment the molecules $(CH_3)_2CDOD$ and $(CH_3)_2CHOH$ were run.

Discussion of Results

The mass spectral data on the isotopic molecules along with data available in the literature on isopropyl alcohol are presented in Table I. The most abundant ion in the isopropyl alcohol spectrum has the mass 45 and corresponds to 55% of all the ions formed. Its formation is for the most part due to the process

$$(CH_3)_2CHOH + e^- \longrightarrow CH_3CHOH^+ + CH_3 + 2e^-$$

whereby a methyl group drops off as a methyl radical. The hydrogen on the oxygen and the secondary hydrogen atom are involved only to a slight extent as can be seen from the fact that the highest positive ion current in this mass region shifts to mass 46 for the CHOD and CDOH compounds and to 47 in the CDOD. The presence of significant peaks at masses 45 for CDOH (22 units) and CHOD (17 units) and at mass 46 for CDOD (24 units) indicates either the presence of a material with lower D content or a dissociative rearrangement process whereby a departing methyl group exchanges one of its hydrogens for the hydrogen on the hydroxyl or the hydrogen on the secondary carbon. The light impurity argument is weak in the case of $(CH_3)_2CHOD$ since the infrared spectrum shows a negligible amount of OH absorption and the spectrometers were saturated with heavy water prior to running the compound.

The second most abundant ion in the isopropyl alcohol mass spectrum is at mass 43. Ions of this mass may be formed by loss of (a) an OH group forming $(CH_3)_2CH^+$; (b) a methyl and two hydrogens from another methyl group forming $CH{\equiv}CHOH^+$; (c) a methyl, a hydrogen from the methyl and the secondary hydrogen atom forming $CH_2{=}C{=}OH^+$; (d) a methyl, a hydrogen from the other methyl group and the hydroxyl hydrogen forming $CH_2{=}CHO^+$; (e) a methyl, the secondary and hydroxyl hydrogens forming $CH_3C{\equiv}O^+$.

The mass spectrum of the isopropyl alcohol OD strongly suggests that one of the hydrogen atoms removed in this process is the hydroxyl hydrogen. The intensity of ions of mass 43 in the CHOD spectrum is 15 units compared to 18.3 for the protium compound while at mass 44 (the mass of the fragment produced if the OD band were not ruptured) has the value of 5.4 units. Consequently processes (b) and (c) make only a minor contribution. Process (a), the formation of an isopropyl carbonium ion by loss of an OH group and an electron is considered improbable in view of the fact that similar processes in *n*-propyl, *n*-butyl, *s*-butyl and *t*-butyl alcohols are rather infrequent.[1] There is some evidence that processes (d) and (e) occur simultaneously. Thus in CD–OD the small peak at 45 and the higher peaks at 44 and 43 indicate that process (d), loss of a methyl group and an H and D atom, or (e), loss of a methyl group and both D atoms, are both taking place. The relative intensities of the peaks at 44 and 43 in the CDOH spectrum are consistent with this mechanism. It must be noted that the conclusions drawn concerning the mechanism of the formation of the ions would not be affected by the presence of as much as 16% light isopropyl alcohol impurity.

The most abundant ions in the lower mass range (26–32) in isopropyl alcohol are $C_2H_3^+$ at mass 27 and ions of mass 29. The spectrum of $(CH_3)_2$-CHOD indicates the loss of the hydroxyl hydrogen in the formation of ions of mass 29. The latter could conceivably have the following structures: (a) $C_2H_5^+$, (b) $HC\equiv O^+$ or (c) $C{=}O^+{-}H$. The formation of $C_2H_5^+$ involves a rearrangement on electron impact of the type that produces $C_2H_5^+$ from isobutane. $HC{=}O^+$ could be formed directly by the loss of two methyl groups and the hydroxyl hydrogen while $C{=}O^+H$ would require a rearrangement of hydrogen in view of the observed $(CH_3)_2$–CHOD spectrum. It is possible that all of the above ions are formed to a limited extent, with $H{-}C{=}O^+$ probably most abundant in view of its relative ease of formation.

Ions of mass 31 arise from a rearrangement. In the CHOD and CDOD spectra the peaks shift up one mass unit while in the CDOH spectrum the peak remains at 31. Thus the rearrangement involves the migration of the OH group from the secondary position to one of the primary carbon atoms followed by the formation of the CH_2OH^+ ion in isopropyl alcohol. It is possible to postulate an alternative more complicated mechanism of hydrogen rearrangements in which the secondary carbon–hydrogen and a CH_3 group is replaced by two of the methyl hydrogens permitting the formation of $CH_2{=}O^+{-}H$ by loss of the remaining CH_3 group. It is not possible to distinguish these processes from the data at hand but the latter seems to be a bit more complicated than the former and consequently less probable.

The molecular ions produced by electron bombardment of isopropyl alcohol are of low relative intensity. The ion produced by the loss of a hydrogen atom from the molecular ion is approximately seven times as abundant as the molecular ion. The CD-OH spectrum establishes quite conclusively that for the most part the secondary carbon–hydrogen bond is ruptured in the process and that the ion formed from isopropyl alcohol has the formula $(CH_3)_2COH^+$. The CHOD spectrum shows that the OD bond is not ruptured in the formation of the most abundant ion in the parent mass group, $(CH_3)_2COD^+$.

These results are consistent with the following general ionization mechanism for alcohols first proposed by Cummings and Bleakney.[5] An electron is removed from one of the non-bonding oxygen orbitals. The resulting O^+ seeks to compensate for its electron deficiency by forming an additional valence bond with the carbon atom to which it is already bound. This can happen only if one of the other substituents of this carbon atom is removed. Generally in alcohols the weakest bonded substituent will be lost forming the most abundant ion in the spectrum. Cummings and Bleakney investigated the appearance potentials of methanol and ethanol and found that the appearance potentials for CH_3O^+ and $C_2H_5O^+$ were approximately equal to the appearance potentials of the corresponding molecular ions in spite of the fact that additional energy to rupture a CH or OH bond was required in the formation of the fragment ion. The anomalously low values of these fragment ion appearance potentials were explained by assuming localized ionization of the molecule by removal of one of the oxygen electrons and pointing out that in the formation of trivalent positive oxygen $C{=}O^+{-}$ from normal divalent oxygen in alcohols–C–O– an additional C–O bond is formed which compensates for the energy required to rupture a C–H or C–C bond and leads to rational values of the appearance potentials of the molecular and fragment ions.

The deutero isopropyl alcohol spectra show that the secondary C–H bond is more frequently ruptured than the primary C–H bonds and that ions containing the structures $-C{=}O^+{-}H$ or $-C\equiv O^+$ account for approximately 75% of the observed ion yield. The fact that the spectrum of isopropyl alcohol and the spectra of alcohols in general are dominated by ions containing $=C{=}O^+{-}$ or $-C\equiv O^+$ groups suggests that the mechanism proposed by Cummings and Bleakney for threshold processes holds for ionization and dissociation with 45–75 volt electrons.

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(5) C. S. Cummings and W. Bleakney, *Phys. Rev.*, **58**, 787 (1949).