decoupling. Some preliminary spectra were obtained with a Varian A-56/60 spectrometer operating at 56.4 MHz. The fluorides were examined as prepared in methylene chloride solutions with $CFCl_3$ as an internal standard and lock. The fluorine chemical shifts of all the compounds in this paper are upfield from the reference. All alcohols and carbonyl compounds were available from commercial sources and were used as received. Multiplets are indicated in the tables as follows: d, doublet; t, triplet; q, quartet; p, pentet; s, septet.

Method A. Alcohol Plus (Diethylamino)sulfur Trifluoride (DAST).[18] A 5-mL vial with 1 mL of CH_2Cl_2 and 50–100 μL of alcohol was cooled to −78 °C. To this solution was added 50 μL of DAST. The solution was warmed to room temperature. For some alcohols, elimination to olefin occurred as the temperature was raised; these were examined in a precooled spectrometer at −80 °C.

Method B. Carbonyl Compound Plus DAST. A 5-mL vial with 1 mL of CH_2Cl_2 and 50–100 μL of ketone or aldehyde was treated with 50 μL of DAST at room temperature.

Method C. Alcohol Plus 2-Chloro-1,1,2-trifluoroethylamine (FAR).[19] A 5-mL vial with 1 mL of CH_2Cl_2 and 100 μL of alcohol was treated with FAR at −78 °C. The solution was warmed slowly to room temperature.

Registry No. 1a, 562-49-2; 1**b**, 19031-61-9; **2a**, 464-06-2; **2b**, 354-09-6; **3a**, 353-36-6; **3b**, 420-26-8; **3c**, 353-61-7; **3d**, 420-45-1; **3e**, 75-37-6; **4a**, 59006-05-2; **4b**, 2924-20-1; **4c**, 335-04-6; **4d**, 74185-61-8; **4e**, 53731-23-0; methyl fluoride, 593-53-3; propyl fluoride, 460-13-9; butyl fluoride, 2366-52-1; 3-methylbutyl fluoride, 407-06-7; 2-methylpropyl fluoride, 359-00-2; 2-methylpentyl fluoride, 62127-27-9; 2-ethylbutyl fluoride, 62127-36-0; 3,3-dimethylbutyl fluoride, 371-64-2; allyl fluoride, 818-92-8; propargyl fluoride, 2805-22-3; 2-methoxyethyl fluoride, 627-43-0; *tert*-2-butenyl fluoride, 920-35-4; 2-butyl fluoride, 359-01-3; 2-pentyl fluoride, 590-87-4; 3-pentyl fluoride, 41909-29-9; 3-octyl fluoride, 20469-83-4; 4-methyl-2-pentyl fluoride, 62127-32-6; 2-methyl-3-pentyl fluoride, 62127-33-7; cyclohexyl fluoride, 372-46-3; *cis*-3-methylcyclohexyl fluoride, 74185-62-9; *trans*-3-methylcyclohexyl fluoride, 74185-63-0; *cis*-4-methylcyclohexyl fluoride, 74185-64-1; *trans*-4-methylcyclohexyl fluoride, 74185-65-2; *trans*-2-phenylcyclohexyl fluoride, 74185-66-3; 1-buten-3-yl fluoride, 53731-19-4; 1-penten-4-yl fluoride, 66702-91-8; cyclohex-1-en-4-yl fluoride, 2266-53-7; 1-indanyl fluoride, 62393-01-5; *exo*-norbornyl fluoride, 765-92-4; cyclooctyl fluoride, 53731-16-1; 2-methyl-2-butyl fluoride, 661-53-0; 3-ethyl-3-pentyl fluoride, 649-80-9; 2-methyl-2-pentyl fluoride, 62127-30-4; 1-methyl-1-cyclohexyl fluoride, 66922-12-1; 1-adamantyl fluoride, 768-92-3; 3,3-dimethylpropargyl fluoride, 74185-67-4; methylene difluoride, 75-10-5; propylidene difluoride, 430-61-5; butylidene difluoride, 2358-38-5; pentylidene difluoride, 62127-40-6; hexylidene difluoride, 62127-41-7; 3-methylbutylidene difluoride, 53731-22-9; 3-methylpentylidene difluoride, 74185-68-5; 2-ethylbutylidene difluoride, 74185-69-6; 2-methylpropylidene difluoride, 62126-91-4; 2-methylbutylidene difluoride, 66688-67-3; 2-ethylhexylidene difluoride, 74185-70-9; cyclohexylmethylene difluoride, 329-29-3; 2-propylidene difluoride, 420-45-1; 2-butylidene difluoride, 353-81-1; 2-pentylidene difluoride, 371-65-3; 4-methyl-2-pentylidene difluoride, 371-70-0; 4-heptylidene difluoride, 53731-27-4; 3-methyl-2-pentylidene difluoride, 74185-71-0; 2-phenylcyclohexylidene difluoride, 57514-11-1; cyclohexylidene difluoride, 371-90-4; norbornylidene difluoride, 22847-05-8; 2-methylcyclohexylidene difluoride, 74185-72-1; 3-methylcyclohexylidene difluoride, 74185-73-2; 4-methylcyclohexylidene difluoride, 74185-74-3; 5,6,6-trifluorocholestane, 74185-75-4; 6,6-difluorocholestane, 74185-76-5; 1,1′-(1,1,2-trifluoro-1,2-ethanediyl)bisbenzene, 68936-77-6; 1,1′-(1,1-difluoro-1,2-ethanediyl)bisbenzene, 350-62-9; 1,1′-(1-fluoro-1,2-ethanediyl)bisbenzene, 74185-77-6; (R*,R*)-(±)-2,3-difluoropentane, 74185-78-7; (R*,S*)-(±)-2,3-difluoropentane, 74185-79-8; (*meso*)-2,4-difluoropentane, 22464-30-8; (±)-2,4-difluoropentane, 22464-29-5; $PhCH_2CH_2F$, 458-87-7; $PhCH_2F$, 350-50-5; $PhCH_2CHFCH_2Ph$, 74185-80-1; PhCHFEt, 19031-70-0; $PhCH_2CHFMe$, 40888-89-9; Ph_2CHF, 579-55-5; PhCHFMe, 7100-97-2; $PhCFMe_2$, 74185-81-2; Ph_2CFMe, 74185-82-3; Ph_3CF, 427-36-1; Ph_2CHCHF_2, 387-04-2; $PhCH_2CHF_2$, 10541-59-0; 2-Ph-c-HxF_2, 57514-11-1; $PhCHF_2$, 455-31-2; $PhCF_2Et$, 74185-83-4; $PhCH_2CF_2CH_2Ph$, 74185-84-5; $PhCH_2CF_2Ph$, 350-62-9; $PhCH_2CF_2Me$, 58325-18-1; Ph_2CF_2, 360-11-2; $PhCF_2Me$, 657-35-2; $PhCF_3$, 98-08-8.

Gaseous Anion Chemistry. Hydrogen–Deuterium Exchange in Mono- and Dialcohol Alkoxide Ions: Ionization Reactions in Dialcohols

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The subject of this work is H–D exchange in certain gaseous anions using D_2 as the exchanging agent. The anions involved are produced from ethylene glycol, 1,3-propanediol, 1,4-butanediol, ethanol, 1-propanol, and 1-butanol. Spectra and postulated ionization reactions for these mono- and dialcohols are given. Hydrogen–deuterium exchange occurs in the $(M-1)^-$ and $(2M-1)^-$ ions of ethylene glycol, 1,3-propanediol, and 1,4-butanediol. The amount of exchange occurring is 3–8 times greater in $(2M-1)^-$ than in $(M-1)^-$. The amount of H–D exchange occurring in ethanol, 1-propanol, and 1-butanol is small or zero in the $(2M-1)^-$ ions and in the $(M-1)^-$ ion for 1-butanol [the only $(M-1)^-$ ion which could be examined experimentally]. The amount of exchange occurring in the $(2M-1)^-$ and $(M-1)^-$ ions from ethylene glycol is not affected by the total pressure or composition of the reaction mixture in the ionization chamber of the mass spectrometer. A novel hydrogen-bridging mechanism is suggested to account for the observed exchange occurring in the dialcohols.

A number of investigations of the OH^- negative chemical ionization mass spectrometry of various compounds have recently been made.[1-5] In these studies, unusual and interesting reactions of gaseous anions have been observed, and we plan to make studies using deuterium labeling to elucidate their mechanisms. However, since with our high-pressure chemical ionization apparatus the gaseous anions to be investigated would suffer many collisions with gas molecules during the period of their residence in the ionization chamber, the stability of the labels with respect to exchange with the gas molecules must first be investigated before the mechanistic studies utilizing labels can properly be undertaken. We have made a number of studies of the exchange between the hydrogen atoms in various protium anions and D_2. We find that exchange does occur for certain compounds, and we report here our findings with mono- and dialcohols. The investigation

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entailed measuring the spectra of several dialcohols. These indicate that unexpected and interesting reactions of gaseous anions are occurring, so we give the spectra and our posulates concerning the reactions producing them.

Perhaps the first study of hydrogen–deuterium exchange under chemical ionization conditions was that of Hunt, McEwen, and Upham,[6] who pointed out that active hydrogens in positive ions would exchange with D_2O at a 1-torr pressure. The phenomenon was suggested as an analytical technique to determine the numbers of active hydrogens in small samples. Lin and Smith[7] have shown that the number of active hydrogens in positive ions can be determined by using ND_3, and Hunt, Sethi, and Shabanowitz[8] have shown that exchange occurs with active hydrogens in negative ions and that the number of active hydrogens can be determined by using a variety of deuterated reagent gases.

More general studies of exchange in positive ions have been made by Freiser, Woodin, and Beauchamp,[9] Martinsen and Buttrill,[10] and Hunt, Gale, and Sethi.[11] General studies of exchange in negative ions have been made by DePuy, Shapiro, and co-workers.[12-14]

To summarize these studies, it was found that both for positive and negative ions, certain hydrogens in the ions will exchange with certain deuterated reagents. Under some conditions and for some compounds, multiple exchange occurs. In the case of deuterated benzene, for example, all six of the benzene hydrogens exchange with D_2O,[9] and analogously, in the case of the $(M - 1)^-$ ion from 1-hexene, all 11 hydrogens in the ion exchange with D_2O.[12] Both Hunt and co-workers[8] and DePuy, Shapiro, and co-workers,[13,14] point out that in positive ions the occurrence of exchange depends upon the relative strengths of the base initiating the exchange and the conjugate base of the protonated ion undergoing the exchange and that in negative ions the exchange analogously depends upon the relative acidities of the acid promoting the exchange and the conjugate acid of the anion undergoing the exchange. The exchange will not occur in positive ions if the difference in basicities is too great or in negative ions if the difference in acidities is too great. Hunt and co-workers[8] attempt to provide some quantitation for this idea, for they estimate that exchange will not occur if a difference of 20–25 kcal/mol exists between the proton affinities of the two bases involved in the exchange in positive ions. Presumably a similar difference in the acid strengths of the acids involved determines whether exchange occurs in negative ions.

Experimental Section

The apparatus and techniques used for this work were very similar to those described by Smit and Field.[1] The mass spectrometer was a Biospect quadrupole mass spectrometer manufactured by the Scientific Research Instruments Co. The instrument was modified for negative ion detection by using the negative ion detection system previously developed in this laboratory.[15] The output signal from the mass spectrometer was introduced into a VG2040 data system for recording and storage of the mass spectra. The scan rate was such that 2 s was required to scan from zero mass to whatever upper mass limit was appropriate to the experiment being undertaken. Ionization was initiated by bombardment with electrons emitted from a filament; the emission current was maintained at 200 μA. The reagent gas consisted of 2 torr of nitrous oxide and 1 torr of either hydrogen or deuterium. For certain experiments where pressure was a variable, these values were changed appropriately. In a few experiments samples were introduced by means of the gas chromatograph, in which case the ionization chamber also contained 1 torr of helium. The source temperature was generally maintained at known values in the vicinity of 210 °C. Samples were generally introduced through the gas-handling system of the mass spectrometer, and a rough measure of the relative amounts of sample present in the ionization chamber was provided by measuring the volume in microliters of liquid sample injected into the gas-handling system.

All measurements reported in this paper were replicated at least once.

The reagent gases used were obtained from Matheson Gas Products and were of an appropriately high degree of purity: nitrous oxide, 98.5%; hydrogen, 99.95%; methane, 99.97%. Other materials used, their source, and their purity are as follows: deuterium, Merck Sharp and Dohme, 99.5%; ethanol, IMC Chemical Group, 100%; 1-propanol, Aldrich, >99%; isobutyl alcohol, Mallinckrodt, >99%; ethylene glycol, Aldrich, >99%; 1,3-propanediol, Matheson Coleman and Bell, >99%; 1,4-butanediol, Aldrich, >99%.

Results

(1) General Considerations. In these studies the anions which are to undergo hydrogen–deuterium exchange are produced by hydroxyl ion chemical ionization.[1] In a mixture containing 2 torr of N_2O and 1 torr of H_2, hydroxyl ions are produced by the reactions 1 and 2. When exchange with deuterium gas is to be investigated, the mixture in the ionization chamber is made up with N_2O and D_2, and hydroxyl ions (OD^-) are produced by reaction 3.

$$N_2O + e \rightarrow O^{-}\cdot + N_2 \qquad (1)$$

$$O^{-}\cdot + H_2 \rightarrow OH^- + H \qquad (2)$$

$$O^{-}\cdot + D_2 \rightarrow OD^- + D \qquad (3)$$

Anions of interest are produced by allowing the hydroxyl ions formed from the reagent gases to react with appropriate acids. The general reaction occurring is represented by eq 4. Fragmentation of A^- may occur. In some of our experiments the acid HA is added to the N_2O without the addition of H_2 or D_2, and in this case anions are produced by the reaction of $O^{-}\cdot$ ions with HA (eq 5). Fragmentation of A'^- may occur.

$$AH + OH^- \text{ (or } OD^-) \rightarrow A^- + H_2O \text{ (or HDO)} \qquad (4)$$

$$HA + O^{-}\cdot \rightarrow A'^- + OH \qquad (5)$$

In writing reaction 4, we imply that no significant amount of exchange of H and D occurs in the initial formation of the anion A^-. This is an assumption for which we have no proof since our single ionization chamber mass spectrometer does not permit us to make direct experiments concerning the matter. The other mechanism by

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(11) Donald F. Hunt, P. J. Gale, and Satinder K. Sethi, presented at the 26th Annual Conference on Mass Spectrometry and Allied Topics, St. Louis, MO, May 28–June 2, 1978.

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Table I. Spectra of Ethylene Glycol-N_2O System[a] with an $O^{-}\cdot$ Reactant Ion

			amt of $Et(OH)_2$,[b] μL							
			0.0		0.5		1.5		2.5	
m/z	ion	AI[c]	RI_1[d]	RI_2[e]	RI_1[d]	RI_2[e]	RI_1[d]	RI_2[e]	RI_1[d]	RI_2[e]
32	$O_2^{-}\cdot$	1436	64	64	62	71	52	68	46	67
45	HCO_2^{-}				3		4		7	
46	NO_2^{-}	652	29	29	20	23	18	24	13	19
58	$C_2H_2O_2^{-}\cdot$				9		19		19	
60	$N_2O_2^{-}\cdot$	146	7	7	6	6	7	9	10	15
94									5	

[a] Source temperature 220 °C; P_{N_2O} = 2.0 torr; $M_r Et(OH)_2$) = 62. [b] The volume (in microliters) of liquid $Et(OH)_2$ injected into the gas-handling system of the mass spectrometer. The pressure of $Et(OH)_2$ vapor in the ion source is proportional to this volume. [c] AI = absolute intensity in arbitrary units. [d] RI_1 = relative intensities based on sum of the intensities of all ions. [e] RI_2 = relative intensities based on sum of the intensities of only those ions attributed to N_2O (m/z 32, 46, and 60).

which exchange in ions might occur involves collisions of the ions sometime after their initial formation with isotope-containing molecules in the ionization chamber of the mass spectrometer. For the sake of brevity and simplicity we shall offer explanations of our observations only in terms of the second mechanism. However, we do not exclude the possibility that exchange can occur during the initial ionization process.

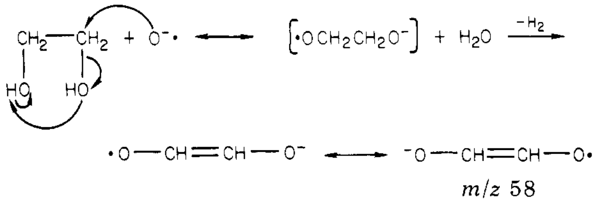
(2) Spectra of Ethylene Glycol in Mixtures of N_2O–H_2, N_2O–D_2, and N_2O Alone. Our order of procedure with our exchange results with alcohols is that we shall first present our results for ethylene glycol, 1,3-propanediol, and 1,4-butanediol. We then present our results on the corresponding monoalcohols (ethanol, 1-propanol, and 1-butanol) for comparison. We have measured spectra under several different conditions, and where possible we have made hypotheses concerning the ionic reactions occurring to produce the spectra.

During the course of our measurements it became necessary to determine the spectrum of ethylene glycol in the presence of N_2O alone, and it is convenient to begin our discussion with these data. We give the N_2O spectra of ethylene glycol at three pressures in Table I. Note that we include in Table I two tabulations of the relative intensity, RI_1 and RI_2. The first constitutes relative intensities of all of the ions contained in the spectra; the second constitutes relative intensities of only those ions associated with nitrous oxide. From the spectrum obtained with no ethylene glycol we recognize that the ions to be attributed to nitrous oxide are those at m/z 32, ($O_2^{-}\cdot$), 46 (NO_2^{-}), and 60 ($N_2O_2^{-}\cdot$). The ions to be attributed to ethylene glycol are those at m/z 45 (HCO_2^{-}), 58 ($C_2H_2O_2^{-}\cdot$), and 94. One observes in Table I that the relative intensities (RI_1) of the ions associated with N_2O exhibit a general decline as the pressure of ethylene glycol increases; intensities of the ions associated with ethylene glycol show a corresponding increasing trend. An immediate question is what is the identity of the reactant ion producing the ions from ethylene glycol. As we have pointed out above, the primordial reactant ion in these systems is $O^{-}\cdot$, and it is the prime candidate for the reactant ion producing the ions from ethylene glycol. However, any of the ions from nitrous oxide could also serve this function, especially the intense $O_2^{-}\cdot$ and NO_2^{-} ions.

The RI_2 relative intensities given in Table I provide information on this question. Differing reactivities of the three ions from nitrous oxide will manifest themselves in different degrees of decrease of the RI_2 intensities as the pressure of ethylene glycol is increased. Considering only the two major nitrous oxide ions ($O_2^{-}\cdot$ and NO_2^{-}), the RI_2 values show that $O_2^{-}\cdot$ does not react with ethylene glycol. The RI_2 values for NO_2^{-} show a decline that is compatable with NO_2^{-} ions serving as a reactant to produce all or part of the ethylene glycol spectrum. We have no way of determining the extent to which $O^{-}\cdot$ and NO_2^{-} are involved in reacting with ethylene glycol, so the matter must be left open at the present.

Note from Table I that at the highest pressure of ethylene glycol an ion with small intensity appears at m/z 94. Since the relative intensity of this ion has a relatively high order of dependence on the pressure of ethylene glycol, it is almost surely formed by a reaction between an ion from ethylene glycol and one or more ethylene glycol molecules. However, we are unable to provide a reasonable hypothesis for the identity of the ion or the reaction(s) producing it. We shall see that analogous ions are found in the spectra of the other diols studied.

The most intense of the ethylene glycol ions given in Table I is that at m/z 58, which has the empirical formula $C_2H_2O_2^{-}\cdot$. This is an $(M - 4)^{-}\cdot$ ion, which is one that we have not observed in our previous work. The most reasonable hypothesis that we have conceived concerning the structure of this ion and the reaction by which it is produced is given in eq 6. We have written the reaction as

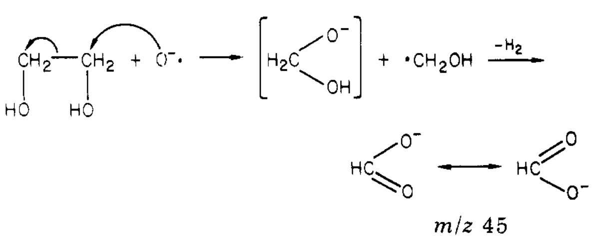


(6)

involving $O^{-}\cdot$ as the reactant ion; in the light of the discussion above we cannot exclude NO_2^{-} as a possible reactant. However, we suggest that NO_2^{-} might react to transfer an $O^{-}\cdot$ entity to its reaction partner, in which case the essential transformation of ethylene glycol is that represented in (6). The loss of hydrogen from the $C_2H_4O_2^{-}\cdot$ transient intermediate given in (6) is in accordance with behavior we have observed in the past[1] wherein the elements of H_2 are lost from alkoxide ions to produce resonance-stabilized enolate ions. The amount of resonance energy gained in producing $C_2H_2O_2^{-}\cdot$ by the loss of H_2 from $C_2H_4O_2^{-}\cdot$ must be rather large.

The m/z 45 ion appearing in the ethylene glycol spectrum and having a small intensity could have either $C_2H_5O^{-}$ or HCO_2^{-} as its empirical formula. We think that the production of the ion with the first formula is rather unlikely. We can write a plausible reaction which is analogous to (6) for the production of the HCO_2^{-} ion; thus we suggest eq 7. Exactly the same considerations applied to (6) apply to this reaction. The driving force for the loss of H_2 from the unobserved $CH_3O_2^{-}$ intermediate ion is the large carboxyl resonance in the formate anion.

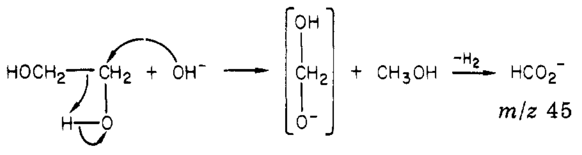
We give in Table II the spectra obtained at several pressures of ethylene glycol with OH^{-} produced in the



(7)

N_2O–H_2 system as the reactant. The ions observed with no ethylene glycol added comprise the reactant ions, and one observes the dominance of OH^- in this spectrum. One also observes vestigial amounts of the ions associated with N_2O ($O_2^-\cdot$ is produced in a large amount). The remaining ions in the spectra are those produced by ethylene glycol. As the ethylene glycol pressure is increased, the relative intensity of OH^- decreases monotonically, which attests to the fact that OH^- is reacting with the ethylene glycol. By contrast, the relative intensity of $O_2^-\cdot$ shows some fluctuation but no definite trend, indicating that this ion is not reacting significantly.

For ease of analysis we extract from Table II and list in Table III the relative intensities of the ions produced from ethylene glycol. In Table III we see ions at m/z 45 and 58, the formation of which we attributed to reactions involving $O^-\cdot$ ions. Residual reactions of $O^-\cdot$ ions (or possibly NO_2^-) probably adequately account for the ions at m/z 58 (reaction 6), but the ion at m/z 45 is present in Table III with an intensity roughly 2–3 times greater than that of the ion m/z 58, which is the inverse of the intensity relationship given in Table I. Thus some other process seems to be producing the m/z 45 ion listed in Table III, and since this process depends on the presence in the system of OH^-, we tentatively suggest the reaction given in eq 8. This ion and the other ions listed in Table III, namely, those at m/z 43, 59, 61, and 123, comprise the OH^- negative chemical ionization spectrum of ethylene glycol. The m/z 61 ion is the $(M - 1)^-$ ion produced by proton abstraction from ethylene glycol; this ion can lose H_2 to produce the $(M - 3)^-$ ion (m/z 59), a process which we have observed extensively in the past. The $(M - 1)^-$ ion can lose the elements of water to produce the m/z 43 ion (eq 9). The ion at m/z 123 is the $(2M - 1)^-$ ion, and as the pressure increases, one observes that the relative intensity of this ion monotonically increases, which is the behavior appropriate to an ion which must be second order in the pressure of ethylene glycol. It is of interest that as the pressure of ethylene glycol increases, the m/z 43 ion intensity steadily decreases, which constitutes evidence that this ion is undergoing some kind of reaction with ethylene glycol. Since no new ion which we can attribute to $C_2H_3O^-$ as a reactant appears in the spectrum, we assume that the product of this reaction with ethylene glycol is one of the ions already present in the spectrum, and the most likely possibility is the $(M - 1)^-$ ion. The reaction presumably involves an abstraction of a proton from ethylene glycol by the $C_2H_3O^-$ ion to produce $(M - 1)^-$ ions and acetaldehyde. It is of interest to note that, by contrast, the ions at m/z 45 and 58 do not seem to undergo any significant amount of reaction with ethylene glycol.



(8)

$$HOCH_2CH_2{-}O^- \longrightarrow H_2O + CH_2{=}CH{-}O^- \longleftrightarrow {}^-CH_2{-}CH{=}O \quad (9)$$
$$m/z\ 43$$

We give in Table IV spectra of ethylene glycol at four ionization chamber pressures using N_2O–D_2 as the reactant system. The spectra are in most ways identical with or very similar to those obtained in the N_2O–H_2 system given in Tables II and III. The significant difference is that the N_2O–D_2 system exhibits ions at m/z 62 and 124, which are not present in the N_2O–H_2 system. The N_2O–D_2 system also exhibits an ion of weak intensity at m/z 121 at the highest pressures of ethylene glycol. This is most likely $(2M - 3)^-$ ion formed by an association of the $(M - 3)^-$ ion with ethylene glycol. We believe that the ions with m/z 62 and 124 are produced by exchange with the deuterium gas in the reactant system. We point out that sometimes no m/z 62 and 124 ions were observed in the N_2O–H_2 system (as in the runs given in Tables II and III), and the reason that the ^{13}C isotope ions corresponding to the m/z 61 and 123 ions were not observed is that the data system operates with a minimum signal threshold. The ^{13}C isotope peaks expected to accompany the m/z 61 and 123 peaks were of intensities which were below the threshold of detectability. Unfortunately, the possibility of observing exchange in other ions in the spectra is precluded by various factors. The m/z 43 ion is always of relatively low intensity, and small amounts of exchange will lie below the limit of detectability. The N_2O–D_2 system contains NO_2^- ions at m/z 46 (not included in Table IV) which would obscure the observation of exchange in the ethylene glycol ion at m/z 45; similarly, the nitrous oxide ion at m/z 60 obscures the observation of exchange in the ion at m/z 59, which in turn obscures the observation of exchange in the ion at m/z 58.

We include in Table IV the values of the ratios I_{62}/I_{61} and I_{124}/I_{123}, and one observes that while the values of both ratios vary appreciably from one pressure to the next, no consistent trend with pressure appears to be occurring, which is what one would expect for exchange between $(M - 1)^-$ and $(2M - 1)^-$ ions and D_2 in the mass spectrometer. The variations that do appear are almost surely the results of experimental errors involved in the measurement of some relatively small quantities. We have made three replicate measurements of the N_2O–D_2–ethylene glycol system and two replicate measurements of the N_2O–H_2–ethylene glycol system. Each measurement involved multiple scans at each pressure of ethylene glycol. We have averaged all of the results obtained for the ion-intensity ratios at m/z 62 and 62 and at m/z 124 and 123. The values obtained are as follows: for the N_2O–H_2 system, $I_{62}/I_{61} = 0.030$ and $I_{124}/I_{123} = 0.052$; for the N_2O–D_2 system, $I_{62}/I_{61} = 0.093$ and $I_{124}/I_{123} = 0.32$. The number of experimental points included in these averages range from 7 to 29. These intensity ratios show that exchange between D_2 and ethylene glycol occurs. The amount of exchange in the $(2M - 1)^-$ ion is approximately 4 times larger than that in the $(M - 1)^-$ ion, and we can immediately draw several deductions from this observation. First, we have spoken earlier of the question of whether the hydrogen–deuterium exchange observed in the mass spectrometer occurs in the primary chemical ionization process or in subsequent reaction of the initially formed ion. Since the $(2M - 1)^-$ ion must of necessity be produced by reactions of the initially formed $(M - 1)^-$ ions, exchange in the $(2M - 1)^-$ ions must also of necessity occur after the initial chemical ionization. One can argue that $(M - 1)^-$ ions can exchange in the course of their initial formation and that these ions would then associate with ethylene glycol

Table II. Spectra of the Ethylene Glycol-N_2O-H_2 System[a] with an OH^- Reactant Ion

		amt of $Et(OH)_2$,[b] μL									
		0.0		0.5		1.5		2.5		3.5	
m/z	ion	AI	RI	AI	RI	AI	RI	AI	RI	AI	RI
17	OH^-	4095	67.9	3280	56.1	1128	28.0	582	16.6	273	8.9
26	CN^-	95	1.6	132	2.3	69	1.7	91	2.6	84	2.7
32	$O_2^{-}\cdot$	956	15.9	784	13.4	716	17.8	589	16.8	400	13.0
35	$H_2O \cdot OH^-$ (?)	350	5.8	208	3.6	115	2.9	111	3.2	119	3.9
42	N_3^- (?)	102	1.7	114	2.0	65	1.6	55	1.6	65	2.1
43	$C_2H_3O^-$			193	3.0	239	5.9	150	4.3	60	2.0
45	HCO_2^-			198	3.4	239	5.9	277	7.9	269	8.8
46	NO_2^-	388	6.4	188	3.2	288	5.7	232	6.6	164	5.3
58	$C_2H_2O_2^{-}\cdot$			73	1.2	106	2.6	121	3.5	139	4.5
59	$(M - 3)^-$			248	4.2	456	11.3	428	12.2	376	12.2
60	$N_2O_2^{-}\cdot$	44	0.7	71	1.2					53	1.7
61	$(M - 1)^-$			352	6.0	567	14.1	602	17.2	530	17.3
94										116	3.8
123	$(2M - 1)^-$					98	2.4	265	7.6	424	13.8
Σ*I*		6030		5841		4026		3503		3072	

[a] Source temperature 220 °C; $P_{N_2O} = 2.0$ torr; $P_{H_2} = 1.0$ torr; $M_r(Et(OH)_2) = 62$. [b] Volume of liquid $Et(OH)_2$.

Table III. Spectra of Ethylene Glycol[a] with an OH^- Reactant and an N_2O-H_2 System

		RI			
m/z	ion	0.5[b]	1.5[b]	2.5[b]	3.5[b]
43	$C_2H_3O^-$	18.1	14.0	8.1	3.1
45	HCO_2^-	18.6	14.0	15.0	14.1
58	$C_2H_2O_2^{-}\cdot$	6.9	6.2	6.6	7.3
59	$(M - 3)^-$	23.3	26.7	23.2	19.6
61	$(M - 1)^-$	33.1	33.2	32.7	27.7
94					6.1
123	$(2M - 1)^-$		5.7	14.4	22.2

[a] Conditions as described in Table II, $Et(OH)_2$ ions only. [b] *Volume of liquid* $Et(OH)_2$ *injected (in microliters).*

molecules to produce exchanged $(2M - 1)^-$ ions. However, this mechanism could produce an amount of exchange in $(2M - 1)^-$ ions not greater than that in $(M - 1)^-$ ions. Thus while we cannot rule out the possibility that exchange occurs during the course of the initial chemical ionization of ethylene glycol, we can assert that a preponderance of the exchange observed in the $(2M - 1)^-$ ions occurs subsequent to the initial ionization processes. Somewhat similarly, in any sort of exchange experiments in mass spectrometers, one worries about the possibility that the observed exchange occurs heterogeneously either on the walls of the ionization chamber or on the walls of the gas-handling system, but since the $(2M - 1)^-$ ions are gas-phase entities produced only after the initial ionization, the exchange observed in the $(2M - 1)^-$ ion in excess of that observed in the $(M - 1)^-$ ion cannot result from heterogeneous exchange processes on various surfaces. Similar arguments apply to the possibility that the exchange is a gas-phase phenomenon occurring with neutral species. Thus we believe that our results constitute evidence that exchange is occurring between gaseous anions and gaseous D_2.

(3) Spectra of 1,3-Propanediol in Mixtures of N_2O-H_2 and N_2O-D_2. We give in Table V spectra of 1,3-propanediol at three source pressures of the diol. The reactant ion is OH^- produced from the N_2O-H_2 system. The ions observed when 1.0 μL of propanediol is injected into the mass spectrometer comprise the primary chemical ionization mass spectrum of this compound. The ion at *m/z* 75 is the $(M - 1)^-$ ion, which is produced by abstraction of a proton from one of the hydroxyl groups, and this can lose successive molecules of H_2 to produce the ions observed at *m/z* 73 and 71. The high intensity of the ions at *m/z* 71 is probably the consequence of the large amount of resonance stabilization that one expects in this symmetrical ion (see eq 10). The *m/z* 57 and 55 ions can also

$$HOCH_2CH_2CH_2OH + OH^- \longrightarrow HOCH_2CH_2CH_2O^- \xrightarrow{-2H_2}$$
$$O{=}CH{-}CH{=}CH{-}O^- \longleftrightarrow {}^-O{-}CH{=}CH{-}CH{=}O \quad (10)$$

m/z 71

be produced from the $(M - 1)^-$ ion. The loss of H_2O from

Table IV. Spectra of Ethylene Glycol[a] with an OD^- Reactant and an N_2O-D_2 System

		amt of $Et(OH)_2$, μL							
		0.5		1.5		2.5		3.0	
m/z	ion	AI	RI	AI	RI	AI	RI	AI	RI
43	$C_2H_3O^-$	239	10.3	237	7.9	112	3.2	34	10
45	HCO_2^-	467	20.1	552	18.3	551	15.9	628	17.7
58	$C_2H_2O_2^{-}\cdot$	312	13.5	440	14.6	434	12.5	501	14.1
59	$(M - 3)^-$	432	18.6	406	13.5	600	17.3	597	16.8
61	$(M - 1)^-$	771	33.3	959	31.8	746	21.5	659	18.5
62	$(M + D - H - 1)^-$	41	1.8	103	3.4	57	1.6	33	0.9
94		24	1.0	148	4.9	353	10.2	437	12.3
121	$(2M - 3)^-$					55	1.6	64	1.8
123	$(2M - 1)^-$	32	1.4	151	5.0	427	12.3	498	14.0
124	$(2M - D + H - 1)^-$			18	0.6	134	3.9	104	2.9
Σ*I*		2318		3014		3469		3555	
I_{62}/I_{61}		0.053		0.11		0.076		0.050	
I_{124}/I_{123}				0.12		0.31		0.21	

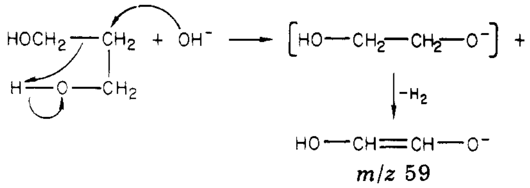
[a] Source temperature 220 °C, $P_{N_2O} = 2.0$ torr, $P_{D_2} = 1.0$ torr, $Et(OH)_2$ ions only.

Table V. Spectra of 1,3-Propanediol[a] with an OH^- Reactant and an N_2O-H_2 System

		amt of $Pr(OH)_2$, µL					
		1.0		2.0		3.0	
m/z	ion	AI	RI	AI	RI	AI	RI
43	$CH_2{=}CHO^-$	389	13.2	882	8.9	688	4.8
45	HCO_2^-	188	6.4	471	4.8	595	4.2
55	$CH_2{=}C{=}CHO^-$	374	12.8	347	3.5	52	0.4
57	$CH_2{=}CHCH_2O^-$	205	7.0	479	4.9	140	1.0
59	$HOCH{=}CH{-}O^-$	90	3.1	474	4.8	435	3.0
71	$(M-5)^-$	703	24.0	744	7.5	636	4.4
73	$(M-3)^-$	193	6.6	976	9.9	1120	7.8
75	$(M-1)^-$	790	26.9	4095	41.5	4095	28.6
76	$^{13}C(M-1)^-$			126	1.3	106	0.7
101						201	1.4
102						205	1.4
103				66	0.7	307	2.1
105				630	6.4	2643	16.4
108				157	1.6	821	5.7
137						136	1.0
138						246	1.7
151	$(2M-1)^-$			422	4.3	1732	12.1
152	$^{13}C(2M-1)^-$					136	1.0
ΣI		2932		>9869		>14294	

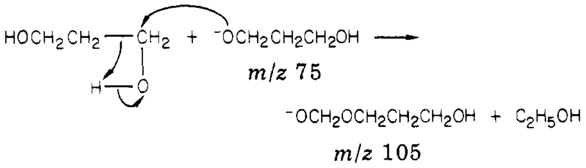
[a] $Pr(OH)_2$ ions only, source temperature 205 °C, $P_{N_2O} = 2.0$ torr, $P_{H_2} = 1.0$ torr, $M_r(Pr(OH)_2) = 76$.

$(M-1)^-$ yields the *m/z* 57 ion, and loss of H_2 from the *m/z* 57 ion produces the *m/z* 55 ion. All of these reactions are in keeping with behavior generally observed in hydroxylic compounds. The formation of the *m/z* 59 ion constitutes something of a problem. A possible structure for this ion is CH_3COO^-, that is, acetate ion, but we can conceive of no reasonable mechanism by which this ion can be produced from the 1,3-propanediol. Consequently, we suggest that the ion has the structure given in Table V and that the reaction producing it is as shown in eq 11. This reaction is analogous to reaction 8. The transient intermediate postulated in reaction 11 can lose water to produce the ion observed at *m/z* 43. The *m/z* 45 ion observed in the 1,3-propanediol spectrum can be produced by the exact analogue of reaction 8. Ethanol is lost in the case of 1,3-propanediol rather than the methanol produced in reaction 8. Thus we are able to account for all of the ions observed in the primary spectrum of 1,3-propanediol.



(11)

One observes from Table V that secondary ions are produced at higher pressures of 1,3-propanediol (2.0 and, especially, 3.0 µL injected into the mass spectrometer). A $(2M-1)^-$ ion appears at *m/z* 151, as one expects. One also observes ions at *m/z* 103, 105, and 108, and the relative intensities of these increase sharply with 1,3-propanediol pressure, which proves that the ions are produced by reactions of primary ions of 1,3-propanediol with 1,3-propanediol molecules. The relative intensities of several of the 1,3-propanediol primary ions decrease with increasing 1,3-propanediol pressure, which indicates that these ions are reacting. One particularly notes in this regard the ions with *m/z* 71, 55, and 43. The $(2M-1)^-$ ion must be produced by the association of an $(M-1)^-$ ion with 1,3-propanediol, but because the intensity of the $(M-1)^-$ ion overloaded the data system, conclusions about the behavior of this ion cannot be deduced from the relative intensity of the ion. The intensity of the ion at *m/z* 105 is the second highest in the spectrum at 3.0 µL of diol, and we suggest that it is produced by a reaction analogous to (8) and (11), namely, (12). The *m/z* 103 ion observed may be produced from the *m/z* 105 ion by loss of H_2.



(12)

The intensities at *m/z* 75 are high enough at the two higher 1,3-propanediol pressures that the ^{13}C isotope peak at *m/z* 76 appears. The values of I_{76}/I_{75} are 0.031 with 2.0 µL of 1,3-propanediol and 0.026 with 3.0 µL of 1,3-propanediol. These values are slightly low because the intensity at *m/z* 75 is not exactly known (data system overload), but the intensity at *m/z* 76 is approximately that to be expected from the naturally occurring ^{13}C abundance. The ratio I_{152}/I_{151} with 3.0 µL of 1,3-propanediol is 0.079, which is within experimental error of the intensity to be expected from naturally occurring ^{13}C.

We give in Table VI the spectra of 1,3-propanediol produced by OD^- as the reactant ion in the N_2O-D_2 system. The spectra are analogous to those produced in the N_2O-H_2 system, the main difference being that ions representing the occurrence of exchange with deuterium are observed at several mass numbers, namely, *m/z* 58, 72, 74, 76, 106, 109, and 152.

We have calculated the ratios of the several pairs of ions which differ only in the isotope content, and these results are given in Table VII. These results are the averages of the values obtained in approximately ten scans at each pressure of 1,3-propanediol in two separate replicate experiments. Thus the value given for the ratio *m/z* 76/75 is the average of 44 experimental determinations. Exchange was not observed in certain ions included in Table V for which exchange might be expected because of interference with other ions. Thus, for example, exchange occurring in the *m/z* 59 ion from 1,3-propanediol would be obscured by a residual amount of the *m/z* 60 ion produced from nitrous oxide. The ratios given in Table VII include contributions from naturally occurring ^{13}C, and the

Table VI. Spectra of 1,3-Propanediol[a] with an OD^- Reactant and an N_2O-D_2 System

		amt of $Pr(OH)_2$, μL					
		1.0		2.0		3.0	
m/z	ion	AI	RI	AI	RI	AI	RI
43	$CH_2=CHO^-$	330	13.9	309	4.2	244	2.6
45	HCO_2^-	248	10.4	449	6.2	499	5.4
55	$CH_2=C=CHO^-$	144	6.1				
57	$CH_2=CHCH_2O^-$	122	5.1	74	1.0		
58	$(57 + D - H)^-$	144	6.1	96	1.3	68	0.7
59	$HOCH=CHO^-$	125	5.3	204	2.8	170	1.8
71	$(M - 5)^-$	236	9.9	302	4.2	260	2.8
72	$(M - 5 + D - H)^-$	92	3.9	73	1.0	79	0.8
73	$(M - 3)^-$	172	7.2	531	7.3	480	5.2
74	$(M - 3 + D - H)^-$	117	4.9	105	1.4	144	1.5
75	$(M - 1)^-$	595	25.0	2269	31.2	1852	20.6
76	$(M - 1 + D - H)^-$	52	2.2	197	2.7	166	1.8
102				61	0.8	348	3.8
103						160	1.7
105				458	6.3	1024	11.1
106	$(105 + D - H)^-$					208	2.3
108				794	10.9	1398	15.1
109	$(108 + D - H)^-$			198	2.7	288	3.1
137						73	0.8
138				147	2.0	255	2.8
151	$(2M - 1)^-$			726	10.0	1215	13.1
152	$(2M - 1 + D - H)^-$			269	3.7	300	3.2
ΣI		2377		7272		9231	

[a] $Pr(OH)_2$ ions only, source temperature 205 °C, $P_{N_2O} = 2.0$ torr, $P_{D_2} = 1.0$ torr.

Table VII. Isotope Ratios in 1,3-Propanediol with an N_2O-D_2 System

$(m/z)_1/(m/z)_2$	intens ratio	$I(+D - H)/I(H)$
	Primary Ions	
58/57	0.98	0.95
72/71	0.27	0.24
74/73	0.31	0.28
76/75	0.12	0.087
	Secondary Ions	
106/105	0.20	
109/108	0.22	
152/151	0.35	0.28

third column of Table VII gives intensity ratios corrected for ^{13}C content by using 1.1% as the naturally occurring abundance of ^{13}C. From Table VII one observes that the phenomenon observed in ethylene glycol also occurs in 1,3-propanediol; namely, the amount of exchange occurring in the $(2M - 1)^-$ ion is significantly larger than the amount occurring in the $(M - 1)^-$ ion. Thus in this compound, also, at least some exchange is occurring after the initial formation of the $(2M - 1)^-$ ion. The *m/z* 57, 71, and 73 primary ions also exchange and do so to an extent greater than $(M - 1)^-$. We guess that the *m/z* 57, 71, and 73 ions are of higher energy than the $(M - 1)^-$ ion, and it is possible that the larger amount of exchange is the result of the operation of the relationship mentioned earlier between the ion energy and the amount of exchange. Exchange is also observed in secondary ions at *m/z* 105 and 108.

(4) Spectra of 1,4-Butanediol in Mixtures of N_2O-H_2 and N_2O-D_2. We give in Table VIII spectra of 1,4-butanediol at two source pressures of the diol. The reactant ion is OH^- produced from the N_2O-H_2 system. The primary ion spectrum (ions with *m/z* values of 90 or less) is produced by reactions identical with or analogous to reactions previously postulated to occur in ethylene glycol and 1,3-propanediol. The secondary ions produced in 1,4-butanediol are the $(2M - 1)^-$ ion, as expected, and an ion at *m/z* 122, which is a homologue of the ion at *m/z* 108 observed in the spectrum of 1,3-propanediol. Since the relative intensity of the *m/z* 122 ion increases sharply with 1,4-butanediol pressure, it must be formed by reactions of an ion from 1,4-butanediol with a molecule of 1,4-butanediol. We are unable to advance a reasonable hypothesis for its structure or mode of formation. The ratio of the intensity of the ion with *m/z* 90 to that of the ion with *m/z* 89 is 0.040, which indicates that the *m/z* 90 ion is a $(M - 1)^-$ ion containing one ^{13}C atom.

Table VIII. Spectra of 1,4-Butanediol[a] with an OH^- Reactant and an N_2O-H_2 System

		amt of $Bu(OH)_2$, μL			
		3.0		6.0	
m/z	ion	AI	RI	AI	RI
45	HCO_2^-	324	6.5	487	6.5
59	$HOCH=CHO^-$	75	1.5	96	1.3
69	$CH_2=CHCH=CHO^-$	228	4.6	108	1.4
85	$(M - 5)^-$			107	1.4
87	$(M - 3)^-$	352	7.0	717	9.6
89	$(M - 1)^-$	3376	67.5	3861	51.8
90	$^{13}C(M - 1)^-$	136	2.7	158	2.1
122		376	7.5	1128	15.1
179	$(2M - 1)^-$	136	2.7	789	10.6
ΣI		5003		7451	

[a] $Bu(OH)_2$ ions only, source temperature 220 °C, $P_{N_2O} = 2.0$ torr, $P_{H_2} = 1.0$ torr, $M_r = 90$.

We give in Table IX spectra of 1,4-butanediol at two pressures with N_2O-D_2 as the reactant system. The spectra are identical with those shown in Table VIII except for the presence of ions resulting from incorporation of deuterium. Unlike the situation observed in 1,3-propanediol, only the $(M - 1)^-$, the $(2M - 1)^-$, and the *m/z* 122 ions exhibit exchange. We have no explanation for this difference in behavior. We have calculated average values for the ratios of intensities in the N_2O-D_2 system of the ions which undergo exchange, using all of the experimental measurements, and the values obtained are $I_{90}/I_{89} = 0.060$, $I_{180}/I_{179} = 0.20$, and $I_{123}/I_{122} = 0.14$. When the first two ratios are corrected for the naturally occurring ^{13}C content, they become 0.016 and 0.11, respectively, and the third

Table IX. Spectra of 1,4-Butanediol[a] with an OD^- Reactant and an N_2O-D_2 System

		amt of $Bu(OH)_2$, μL			
		3.0		6.0	
m/z	ion	AI	RI	AI	RI
45	HCO_2^-	626	11.1	864	10.5
59	$HOCH{=}CHO^-$	235	4.2	260	3.2
69	$CH_2{=}CHCH{=}CHO^-$	203	3.6	174	2.1
85	$(M - 5)^-$	171	3.0	168	2.0
87	$(M - 3)^-$	535	9.5	800	9.7
89	$(M - 1)^-$	3124	55.3	3071	37.2
90	$(M - 1 + D - H)^-$	288	5.1	271	3.3
122		471	8.3	1226	14.9
123	^{13}C			191	2.3
179	$(2M - 1)^-$			1007	12.2
180	$(2M - 1 + D - H)^-$			219	2.7
ΣI		5653		8251	

[a] $Bu(OH)_2$ ions only, source temperature 220 °C, $P_{N_2O} = 2.0$ torr, $P_{D_2} = 1.0$ torr.

Table X. Spectra of 1-Butanol[a] with an OH^- Reactant and an N_2O-H_2 System

		amt of BuOH, μL					
		1.0		2.0		3.0	
m/z	ion	AI	RI	AI	RI	AI	RI
43	$CH_2{=}CHO^-$			200	3.3	109	1.1
45	HCO_2^-			153	2.5	180	1.8
69	$(M - 5)^-$	77	1.4	128	2.1	260	2.6
71	$(M - 3)^-$	1098	19.7	1178	19.3	2866	28.5
72	isotope					200	2.0
73	$(M - 1)^-$	3339	59.8	2735	44.8	>4095	>40.7
74	isotope	200	3.6	130	2.1	403	4.0
91		207	3.7	85	1.4	91	0.9
117		519	9.3	751	12.3	665	6.6
147	$(2M - 1)^-$	139	2.5	746	12.2	1119	11.1
148	isotope					77	0.8
ΣI		5579		6106		10065	

[a] BuOH ions only, source temperature 215 °C, $P_{N_2O} = 2.0$ torr, $P_{H_2} = 1.0$ torr, $M_r = 74$.

Table XI. Spectra of 1-Butanol[a] with an OD^- Reactant and an N_2O-D_2 System

		amt of BuOH, μL					
		1.0		2.0		3.0	
m/z	ion	AI	RI	AI	RI	AI	RI
43	$CH_2{=}CHO^-$			102	2.0	119	1.9
45	HCO_2^-			210	4.2	116	1.9
69	$(M - 5)^-$	52	1.3	72	1.4	105	1.7
71	$(M - 3)^-$	949	23.2	1249	25.1	1794	28.7
72	isotope					136	2.2
73	$(M - 1)^-$	2735	66.8	2623	52.7	2279	36.5
74	isotope	218	5.3	108	2.2	170	2.7
117		140	3.4	377	7.6	686	11.0
147	$(2M - 1)^-$			235	4.7	781	12.5
148	isotope					57	0.9
ΣI		4094		4976		6243	

[a] BuOH ions only, source temperature 215 °C, $P_{N_2O} = 2.0$ torr, $P_{D_2} = 1.0$ torr.

Table XII. Isotope Ratios in Monoalcohols

alcohol	ion	reactant system	$(m/z)_2/(m/z)_1$	intens ratio (IR)	IR − IR(^{13}C)
ethanol	$(2M - 1)^-$	N_2O-H_2	92/91	0.044	0.000
	$(2M - 1)^-$	N_2O-D_2	92/91	0.067	0.023
1-propanol	$(2M - 1)^-$	N_2O-H_2	120/119	0.071	0.005
	$(2M - 1)^-$	N_2O-D_2	120/119	0.084	0.018
1-butanol	$(M - 1)^-$	N_2O-H_2	74/73	0.047	0.003
	$(M - 1)^-$	N_2O-D_2	74/73	0.066	0.019
	$(2M - 1)^-$	N_2O-H_2	148/147	0.072	−0.016
	$(2M - 1)^-$	N_2O-D_2	148/147	0.098	0.010

value is indeterminate because we do not know the carbon content of the ion. The amount of apparent exchange in the $(M - 1)^-$ ion is only marginally above the experimental uncertainty. However, the exchange in the $(2M - 1)^-$ ion is large enough to be definite, and thus in 1,4-butanediol as in ethylene glycol and 1,3-propanediol the amount of exchange in the $(2M - 1)^-$ ion exceeds that in the $(M - 1)^-$ ion.

(5) Spectra of Ethanol, 1-Propanol, and 1-Butanol in Mixtures of N_2O-H_2 and N_2O-D_2. We have determined the spectra of these three monoalcohols using both N_2O-H_2 and N_2O-D_2 as the reactant systems. The spectra are all analogous, and it is sufficient for our purposes to give only the spectra of 1-butanol as an example. Table X gives spectra of this compound in the N_2O-H_2 system. The ions produced are those which our prior experience with alcohols leads us to expect. We cannot identify the ion appearing at *m/z* 91, but we suggest that the *m/z* 117 ion has the formula $C_4H_9OCH_2CH_2O^-$ and that it is formed by a reaction analogous to (12).

Table XI gives the spectra produced in the N_2O-D_2 system. The ions produced are those produced in the N_2O-H_2 system plus ions produced by exchange.

We give in Table XII the isotope ratios observed for the $(M - 1)^-$ and $(2M - 1)^-$ ions in the monoalcohols studied. The values tabulated are the averages of all of the individual experimental measurements made at the several different pressures of the alcohols in the several replicates. The numbers of replicates included in these values range from a low of 19 to a high of 58. The ratios showed no dependence on alcohol pressure, which permits the averaging of the values at the several pressures. No values are given for the $(M - 1)^-$ ions in ethanol and 1-propanol because of interferences. The ion from nitrous oxide at *m/z* 46 prevents the accurate observance of exchange in the $(M - 1)^-$ ion in ethanol; analogously, the nitrous oxide ion at *m/z* 60 prevents the observation of exchange in the $(M - 1)^-$ ion in 1-propanol. The rightmost column in Table XII gives the experimental intensity ratios corrected for the naturally occurring ^{13}C content. In the ions produced with N_2O-H_2 as a reagent system (no deuterium exchange possible), the quantity tabulated in this column provides a kind of figure of merit for our measurements of ionic intensities. One observes that the agreement between observed and calculated ratios is very good for the ions from ethanol and propanol and for the $(M - 1)^-$ ion from butanol. The agreement for the $(2M - 1)^-$ ion from butanol is not as good but is still quite acceptable. The values given in this rightmost column for the ions produced in the N_2O-D_2 system constitute the fractions of the ions which undergo H–D exchange. The values tabulated range from a minimum of 0.010 for the $(2M - 1)^-$ ion from 1-butanol to a maximum of 0.023 for the $(2M - 1)^-$ ion from ethanol. These values are very small, they are small differences between large numbers, and they do not constitute unequivocal evidence for the occurrence of exchange in these ions. However, one can state with certainty that exchange occurs at most to only a small extent.

(6) Effect of Total Pressure and Reactant Composition on the Amount of Exchange. In order to provide experimental evidence of interest in connection with certain mechanistic considerations, we have measured the effect of total pressure and reactant gas composition on the amount of exchange occurring in the $(M - 1)^-$ and $(2M - 1)^-$ ions from ethylene glycol. In Table XIII we give the

Table XIII. Effect of Total Pressure and Reactant Mixture Composition on Exchange in Ethylene Glycol[a]

mixture [substance (pressure in torr)]	P_{tot}, torr	I_{62}/I_{61}	I_{124}/I_{123}
N_2O (1.0), D_2 (1.0)	2.0	0.11	0.27
N_2O (2.0), D_2 (0.5)	2.5	0.11	0.24
N_2O (2.0), D_2 (1.0), N_2 (1.0)	4.0	0.11	0.24
N_2O (2.0), D_2 (2.0)	4.0	0.11	0.28
N_2O (4.0), D_2 (1.0)	5.0	0.080	0.25

[a] Source temperature 220 °C.

Table XIV. Summary of Exchange in $(M - 1)^-$ and $(2M - 1)^-$ Ions in Dialcohols

alcohol	ion	$(m/z)_2/(m/z)_1$	intens ratio (IR)	A[a]	B[b]
$C_2H_4(OH)_2$	$(M - 1)^-$	62/61	0.093	0.071	3.9
	$(2M - 1)^-$	124/123	0.32	0.28	
$C_3H_6(OH)_2$	$(M - 1)^-$	76/75	0.12	0.087	3.2
	$(2M - 1)^-$	152/151	0.35	0.28	
$C_4H_8(OH)_2$	$(M - 1)^-$	90/89	0.060	0.016	8.1
	$(2M - 1)^-$	180/179	0.20	0.13	

[a] $A = \mathrm{IR} - \mathrm{IR}(^{13}C) = \mathrm{IR}(+D - H)$. [b] $B = \mathrm{IR}(+D - H)_{(2M-1)^-}/\mathrm{IR}(+D - H)_{(M-1)^-}$.

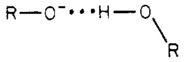
amount of exchange occurring with various mixtures of N_2O, D_2, and, in one experiment, N_2. The total pressure in the ionization chamber in these experiments ranged from 2.0 to 5.0 torr. One observes that neither in the $(M - 1)^-$ ion (I_{62}/I_{61}) nor in the $(2M - 1)^-$ ion (I_{124}/I_{123}) is any trend in the amount of exchange to be observed as a function of the different conditions in the ionization chamber. Such variations as are to be observed are random and are to be ascribed to experimental error. We also carried out an experiment wherein the pressures of N_2O and D_2 were each maintained constant at 1.0 torr and the pressure of N_2 was varied between 0.3 and 3.3 torr. The value of I_{124}/I_{123} obtained is constant within experimental error.

Discussion

We have found differing amounts of exchange occurring in the ions from monoalcohols and in those from dialcohols, and to facilitate comparisons, we summarize in Table XIV the exchange found in the $(M - 1)^-$ and $(2M - 1)^-$ ions from the dialcohols. If we compare the fifth column of Table XIV with the sixth column of Table XII, we see that in the diols the ratios of the intensities of the exchanged to nonexchanged $(2M - 1)^-$ ions range from 0.13 to 0.28, but in the monoalcohols the corresponding values range from 0.01 to 0.023, and we have some question that this small amount of apparent exchange in the monoalcohols is experimentally significant. The only comparison we can make between mono- and dialcohols for $(M - 1)^-$ ions is for 1,4-butanediol and 1-butanol, and for both of these compounds the amount of exchange occurring is small, and probably negligibly small. However, Table XIV shows that an appreciable amount of exchange is occurring in the $(M - 1)^-$ ions of ethylene glycol and 1,3-propanediol. The fact that we are unable to obtain reliable experimental values for exchange in $(M - 1)^-$ from ethanol and 1-propanol is unfortunate, for these quantities are important to our understanding of the exchange processes. However, in the four compounds for which exchange in $(M - 1)^-$ could be observed (1-butanol and the three diols), the amount of exchange in $(2M - 1)^-$ is always much greater than that in $(M - 1)^-$. Since the amount of exchange in $(2M - 1)^-$ in ethanol and 1-propanol is zero or small, we think that one can with considerable confidence take the amount of exchange in $(M - 1)^-$ in ethanol and 1-propanol to be zero.

The possible reasons for these differences in behavior offer an interesting subject for speculation. The negligible amount of exchange in the $(M - 1)^-$ ions from monoalcohols is quite to be expected. These ions are alkoxide ions, and we know of no evidence (either in gas or condensed phase) that the H atoms of the alkoxide ions are exchangeable.

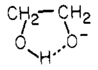
Table XII shows that the $(2M - 1)^-$ ions from the monoalcohols also undergo only a small or negligible amount of exchange with D_2. This is of interest from several points of view. First, the contrast with the large amount of exchange observed in the $(2M - 1)^-$ ions in the dialcohols is striking. Second, Kebarle[16] gives a value of −25 kcal/mol for the enthalpy of association of a molecule of water with OH^- to produce the $(2M - 1)^-$ ion from water. We estimate that the enthalpy change to produce a $(2M - 1)^-$ ion from a monoalcohol is somewhat less than this value, perhaps −20 kcal/mol. This energy has a negligible effect upon the rate of exchange in the $(2M - 1)^-$ ion. Finally, the $(2M - 1)^-$ association complex in monoalcohols must have a structure approximately like that shown in I, and we draw



I

the conclusion that exchange is not enhanced by the presence of the two oxygen atoms in separate molecular entities bound together by a hydrogen bond. This seems to us to be reasonable: we would not expect the association of the alkoxide ion with an alcohol molecule to enhance exchange with hydrogens on the R groups; we would expect that any exchange which might be postulated as involving the bridging proton in the hydrogen bond might destroy the bond and lead to the dissociation of the ion, or, as a minimum, have a high activation energy.

The $(M - 1)^-$ ions from ethylene glycol and 1,3-propanediol exhibit exchange in about equal amounts, while that in the $(M - 1)^-$ ion from 1,4-butanediol is present in a lower amount. The difference in the behavior of the butanediol seems to be large enough to be significant. The structure of the $(M - 1)^-$ ion from ethylene glycol (for example) may be approximated as II. Because of the fact



II

that the O atoms in II are constrained by the cyclic structure, the energy of the intramolecular hydrogen bond in II will be different from that of the intermolecular bond in I. We know of no quantitative measurements of strain energy in anions such as II, but Yamdagni and Kebarle[17] report significant strain energies (as high as 10 kcal/mol) in protonated α,ω-diaminoalkanes. Strain energies for some of these compounds have also been obtained recently in this laboratory.[18] The amount of strain decreases as the chain length increases. We believe that the strain energies in the alkoxide anions from 1,2-ethanediol, 1,3-propanediol, and 1,4-butanediol will be of similar magnitudes. A consequence of the presence of strain is probably that of raising the energy of the hydrogen-bonded

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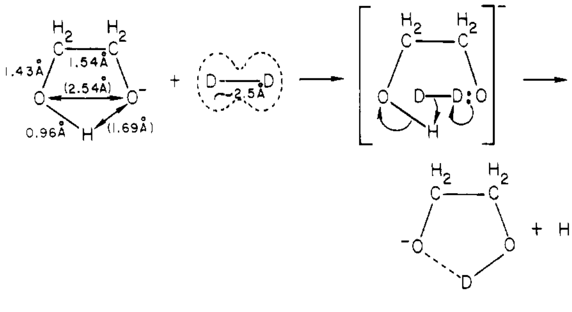
[16] P. Kebarle, *Annu. Rev. Phys. Chem.*, **28**, 445 (1977).

[17] R. Yamdagni and P. Kebarle, *J. Am. Chem. Soc.*, **95**, 3504 (1973).

[18] Unpublished data from this laboratory to be submitted for publication.

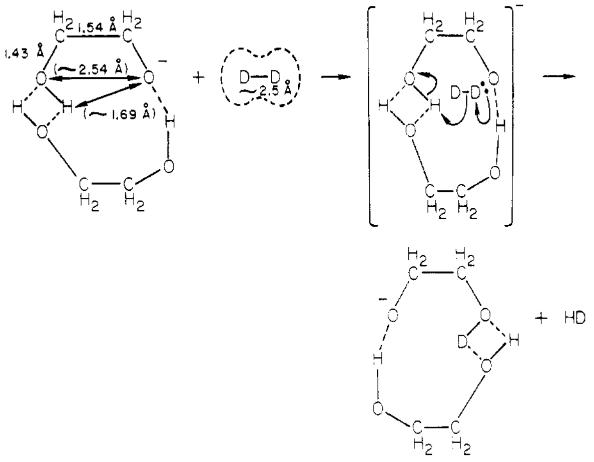
H atom, which in turn would enhance its exchangeability. Our observation of a significant amount of exchange in $(M - 1)^-$ from 1,2-ethanediol and a much smaller amount in $(M - 1)^-$ from 1,4-butanediol is compatible with this idea. We do not understand the significance (if any) of the approximately equal amounts of exchange in $(M - 1)^-$ from 1,3-propanediol and 1,2-ethanediol.

We suggest as a hypothesis a hydrogen-molecule bridging for the observed exchange, namely, eq 13. The bond distances given are taken from the list given by Pauling,[19] and the values included in parentheses are calculated by using appropriate values for the bond angles (which are represented approximately correctly in the drawing above). The van der Waals radius of H_2 given by Pauling is about 2.5 Å, and one observes that the dimensions for the molecular entities involved are such that reaction 13 is possible from a steric point of view.



(13)

The amounts of exchange occurring in the $(2M - 1)^-$ ions from the three dialcohols studied are appreciably greater than those in the $(M - 1)^-$ ions (Table XIV). The ratios of the exchange in the two kinds of ions are 3.9 and 3.2 for ethylene glycol and 1,3-propanediol, respectively, and the ratio for 1,4-butanediol is 8.1. We think that the significance of this last figure is dubious because of uncertainties in the significance of the figure for the small amount of exchange observed in the $(M - 1)^-$ ion for this compound. The $(2M - 1)^-$ ion has three potentially exchangeable H atoms, as compared to one in the $(M - 1)^-$ ion, and two of these will not be involved in strong hydrogen bonds (in this case a bond to an alkoxide anion). The hydrogen-bridging-mechanism hypothesis can also be applied to this exchange, i.e., eq 14.



(14)

A possible explanation for the larger amount of exchange observed in $(2M - 1)^-$ ions is that the exchange is promoted by the association energy involved in forming the $(2M - 1)^-$ ion; that is, the exchange occurs in a $(2M - 1)^-$ ion which contains as vibrational excitation all or part of the energy of association. To investigate this possibility, we determined the effect on the amount of exchange in $(2M - 1)^-$ of total pressure and gas composition. No perceptible changes were produced in the amount of exchange occurring (Table XIII). The total pressure was varied between approximately 2 and 5 torr, and the ratio of the pressure of stabilizing gas (N_2O and N_2) to the pressure of D_2 varied by a factor of 4. The following simple analysis is helpful in understanding the results of these experiments. If exchange were to occur only when a D_2 molecule collides with an excited association ion, we would write eq 15–17 for the reaction system, where P^- = a primary ion,

$$P^- + A \underset{k_d}{\overset{k_a}{\rightleftharpoons}} PA^{-*} \tag{15}$$

$$PA^{-*} + D_2 \xrightarrow{k_e} PAD^- + HD \tag{16}$$

$$PA^{-*} + m \xrightarrow{k_s} PA^- + m \tag{17}$$

i.e., $(M - 1)^-$, A = an alcohol molecule, PA^{-*} = an excited association ion, PA^- = a stabilized association ion, PAD^- = an exchanged (and stabilized) association ion, and m = a stabilizing molecule. A steady-state analysis of this set of reactions (based on $d[PA^{-*}]/dt = 0$), gives the result shown in eq 18. Equation 18 shows that if this mechanism

$$[PAD^-]/[PA^-] = \left(\frac{k_e}{k_s}\right)\left(\frac{[D_2]}{[m]}\right) \tag{18}$$

is operating, the factor of 4 change in the relative pressures of M and D_2 made experimentally should have changed the amount of exchange occurring in the $(2M - 1)^-$ ion also by a factor of 4. Our experiments would have shown this change in the amount of exchange if it were occurring, and we consider that the constancy of exchange found in our pressure experiments constitutes evidence against the possibility that the enhanced exchange in $(2M - 1)^-$ ions is the result of the energy release in the association ion formation.

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Registry No. Ethylene glycol, 107-21-1; 1,3-propanediol, 504-63-2; 1,4-butanediol, 110-63-4; 1-butanol, 71-36-3; ethanol, 64-17-5; 1-propanol, 71-23-8.

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[19] L. Pauling, "The Nature of the Chemical Bond", 3rd ed., Cornell University Press, Ithaca, NY, 1960, pp 224–226.