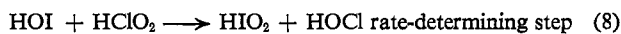
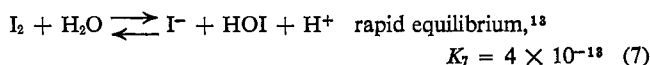


The autocatalytic term in eq. 3 can be accounted for by the reaction sequence



In the presence of sufficient iodide, the products of step 8 are promptly reduced, with a net yield of two iodine molecules per chlorite. At very low iodide concentration,  $\text{HIO}_2$  is instead oxidized to iodate.

We may now calculate  $k_8 = k_2/2K_5K_7 = 6 \times 10^7 \text{ M}^{-1} \text{ sec.}^{-1}$  at  $25^\circ$ . Since the frequency factor for a reaction between two uncharged species is not expected to lie much above the normal upper limit of about  $10^{12} \text{ M}^{-1} \text{ sec.}^{-1}$ , we may set an upper limit of about 6 kcal. mole<sup>-1</sup> on  $\Delta H_8^*$ . Correspondingly, we have

$\Delta H_7^\circ = \Delta H_2^* - \Delta H_8^* - \Delta H_5^\circ \geq 17 \text{ kcal.}$ , where we have taken the required enthalpies for reaction 5 from Latimer.<sup>14</sup> This inequality is inconsistent with the NBS heat of formation for  $\text{HIO}(\text{aq})$  of  $-38 \text{ kcal.}$ , a figure already branded as unreliable by Latimer,<sup>14</sup> so our result tends to confirm his suspicions. Proceeding in the reverse direction, if we accept the NBS figure we get  $\Delta H_7^\circ \cong 12 \text{ kcal.}$  and  $\Delta H_8^* \sim 11 \text{ kcal.}$ , in which case the frequency factor for reaction 8 has to be about  $10^{16} \text{ M}^{-1} \text{ sec.}^{-1}$ , a very unlikely value.

*Acknowledgments.* We wish to thank the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation Undergraduate Research Participation Program for support of this research.

(14) W. M. Latimer, "Oxidation Potentials," 2nd Ed., Prentice-Hall, Inc., New York, N. Y., 1952, Chapter 5.

## Reactions of Gaseous Brønsted Acids<sup>1</sup>

M. S. B. Munson

*Contribution from the Esso Research and Engineering Company, Baytown Research and Development Division, Baytown, Texas. Received July 12, 1965*

*Gaseous ionic reactions have been observed for a series of oxygenated compounds in the source of a mass spectrometer at pressures up to a few tenths of a torr. The major product ions were the solvated protons. Major differences in relative abundances were observed for the higher solvated protons which suggested differences in stability: no more than two molecules of dimethyl ether, acetaldehyde, or acetone will be strongly bound to a proton, but more highly solvated protons will be stable for methanol (three), formic acid (three), and water (four). There are general areas of agreement between ionic reactions in the gas phase and their macroscopic counterpart. Reactions of protonated molecule ions were observed in methanol, acetaldehyde, and acetone which may be considered as elementary steps of some of the acid-catalyzed reactions which occur in solution. Proton transfer was observed from  $\text{H}_3\text{O}^+$  to  $\text{HCOOH}$ , and the decomposition path of lowest energy for  $\text{HCOOH}_2^+$  is the one which gives  $\text{H}_3\text{O}^+$  and  $\text{CO}$ .*

### Introduction

Most of the recent work from this laboratory concerns mass spectrometric studies of ionic reactions in gaseous hydrocarbons. The work reported here is an extension to oxygenated hydrocarbon derivatives and shows the wealth of chemistry which can be developed. A study has been made of ionic reactions in some simple polar molecules to establish the types of reaction products which could be observed, with a primary concern for clustering of the polar molecules and reactions of the protonated species. A complete analysis of all of the reactions was not attempted, and only the dominant

processes are discussed. Individual reaction rate constants were not calculated since the pressures within the source of the mass spectrometer were not known with sufficient accuracy.

### Experimental Section

The mass spectrometer and experimental procedure have been reported previously,<sup>2,3</sup> and will not be discussed in detail. The source temperature was  $200^\circ$ . A scan of the mass spectrum was made after the introduction of each successive pressure of the gases. The pressures were estimated from calibrations of structurally related compounds<sup>4</sup> or were taken as proportional to the pressures indicated on the ionization gauge in the envelope surrounding the source. The same qualitative behavior was observed using both pressures. To a reasonable approximation the rate constants for all of the reactions which are reported in this paper are very large, of the order of  $10^{-9} \text{ cc./molecule sec.}$

The compounds which were used in these experiments were obtained from several commercial sources and were purified by several single-stage distillations within the gas-handling system. The purities are not accurately known, but they should be about 99%, except for formic acid, which was somewhat less pure. No significant contamination was observed in preliminary experiments. Each compound will be discussed separately.

### Results

$\text{H}_2\text{O}$ . Ionic reactions were studied in pure water at pressures up to about 0.4 torr with electrons of

(2) F. H. Field, *J. Am. Chem. Soc.*, **83**, 1523 (1961).

(3) F. H. Field, J. L. Franklin, and M. S. B. Munson, *ibid.*, **85**, 3575 (1963).

(4) F. H. Field and M. S. B. Munson, paper presented at the ASTM E-14 Meeting on Mass Spectrometry, San Francisco, Calif., May 1963.

(1) Supported in part by Project SQUID under Contract Nonr-2623 (S-18).

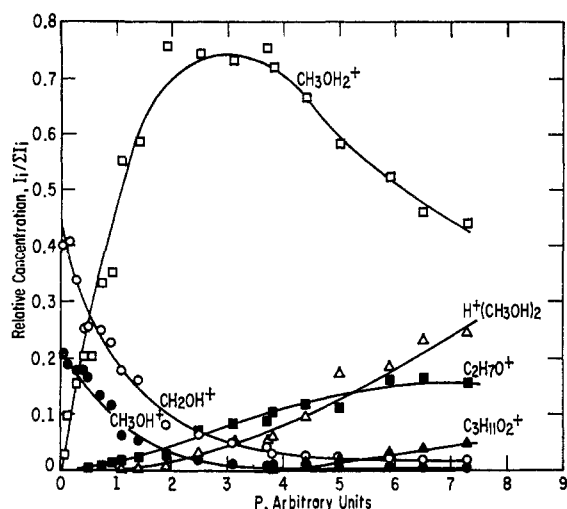
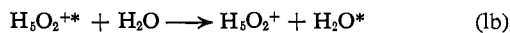
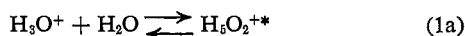


Figure 1. Ionic reactions in methanol.

energy sufficiently low that essentially only  $\text{H}_2\text{O}^+$  was formed as a primary ion by electron impact. Reaction of  $\text{H}_2\text{O}^+$  to form  $\text{H}_3\text{O}^+$  is very rapid,<sup>5</sup> and above 0.2 torr essentially all of the  $\text{H}_2\text{O}^+$  has reacted during the time of residence in the source, of the order of  $10^{-6}$  sec. The predominant ion under these conditions was  $\text{H}_3\text{O}^+$ , but smaller amounts of  $\text{H}_5\text{O}_2^+$ ,  $\text{H}_7\text{O}_3^+$ , and  $\text{H}_9\text{O}_4^+$  were observed as well. These gaseous hydrates have been reported previously.<sup>6</sup>

As an illustration of the extent of hydration under the present experimental conditions, at about 0.3 torr the relative concentrations of  $\text{H}_2\text{O}^+$ ,  $\text{H}_3\text{O}^+$ ,  $\text{H}_5\text{O}_2^+$ ,  $\text{H}_7\text{O}_3^+$ , and  $\text{H}_9\text{O}_4^+$  are  $1 \times 10^{-4}$ , 0.73, 0.23, 0.03, and  $1 \times 10^{-5}$ , respectively. The formation of  $\text{H}_5\text{O}_2^+$  from  $\text{H}_3\text{O}^+$  requires an additional water molecule to stabilize the complex (eq. 1a and 1b) since the ratio  $(\text{H}_5\text{O}_2^+)/(\text{H}_3\text{O}^+)$



( $\text{H}_3\text{O}^+$ ) increases linearly with the square of the pressure.

The existence of these hydrated protons at 200° and these low pressures is evidence for the stability of these species. The successive hydration reactions must be exothermic, but no quantitative data are provided. Tentative estimates for heats of hydration for successive steps have been made from high-pressure mass spectrometric experiments.<sup>6c</sup> Unfortunately, the pressures attained in these experiments are not high enough to provide any information concerning the suggested special stability of  $\text{H}_9\text{O}_4^+$ .<sup>7</sup>

**CH<sub>3</sub>OH.** Figure 1 shows the relative concentrations of several of the most abundant ions of methanol as functions of pressure.  $\text{CHO}^+$  is not included in this figure, but its relative concentration decreases very rapidly as well as those of the other primary ions shown in this figure. The dominant reaction product from

(5) (a) M. M. Mann, A. Hustrulid, and J. T. Tate, *Phys. Rev.*, **58**, 340 (1940); (b) F. W. Lampe, F. H. Field, and J. L. Franklin, *J. Am. Chem. Soc.*, **79**, 6132 (1957).

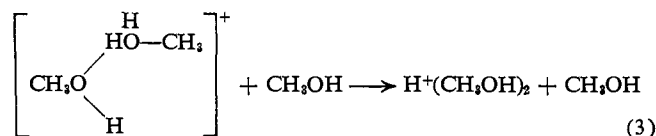
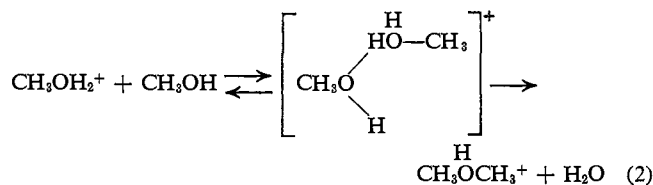
(6) (a) P. F. Knewstubb and A. W. Tickner, *J. Chem. Phys.*, **38**, 464 (1963); (b) H. D. Beckey, *Z. Naturforsch.*, **15a**, 822 (1960); (c) P. Kebarle and A. M. Hogg, *J. Chem. Phys.*, **42**, 798 (1965).

(7) M. Eigen and L. DeMaeyer in "The Structure of Electrolyte Solutions," W. J. Hamer, Ed., John Wiley and Sons, Inc., New York, N. Y., 1959, Chapter 5.

these primary ions is the protonated molecule ion,  $\text{CH}_3\text{OH}_2^+$ . These data provide excellent confirmation for other observations of proton transfer of the primary ions.<sup>8</sup> If one uses  $\Delta H_f(\text{CH}_3\text{OH}_2^+) = 138$  kcal./mole,<sup>9</sup> then proton-transfer reactions from  $\text{CH}_3\text{OH}^+$ ,  $\text{CH}_2\text{OH}^+$ , and  $\text{CHO}^+$  are exothermic.

More interesting than these reactions is the formation of the higher solvated protons  $\text{H}^+(\text{CH}_3\text{OH})_2$  and  $\text{H}^+(\text{CH}_3\text{OH})_3$ . The latter is not included in Figure 1, but it is present as 1.4% of the total ionization at the highest pressure of these experiments. No higher solvated protons were observed, but the pressures of these experiments were not high enough to establish with certainty that  $\text{H}^+(\text{CH}_3\text{OH})_{4,5,\dots}$  ions are not formed or that they are always formed to a very much smaller extent than the lower solvated protons. These ionic species are completely analogous to those observed in water. The existence of these solvated protons is an excellent indication of appreciable solvation energies.

$\text{C}_2\text{H}_7\text{O}^+$ ,  $m/e$  47, is an ion whose relative concentration depends on the third power of the pressure, and the most probable precursor is  $\text{CH}_3\text{OH}_2^+$ . Its precursor must be a second-order product ion, and it seems most reasonable to consider the most abundant ion reacting with the neutral molecules. The structure of this ion cannot be determined, but it is very tempting to consider that it is protonated dimethyl ether, perhaps through an intermediate complex such as



The collision complex formed in (2) dissociates in two ways, either to give the original reactants or to give the rearranged products  $\text{C}_2\text{H}_7\text{O}^+ + \text{H}_2\text{O}$ . The formation of a stable disolvated proton,  $m/e$  65, requires collision with another methanol molecule as indicated in (3). This sequence explains the pressure dependence of ions of  $m/e$  47 and 65:  $I_{65}/I_{47}$  increases approximately linearly in pressure. The heats of formation of the protonated species are not very well known, but since the proton affinity of dimethyl ether is greater than the proton affinity of methanol,<sup>10</sup> the reaction is probably exothermal.

The other major product ion in Figure 1 which is shown to increase with a high power of the pressure is  $\text{C}_3\text{H}_{11}\text{O}_2^+$ ,  $m/e$  79. This ion is probably the mixed solvated proton,  $\text{H}^+(\text{CH}_3\text{OH})(\text{CH}_3\text{OCH}_3)$ , and its relative concentration is of a reasonable magnitude to be formed from solvation reactions of protonated dimethyl ether.

**CH<sub>3</sub>OCH<sub>3</sub>.** Figure 2 shows the relative concentrations of several of the major ions in dimethyl ether

(8) (a) P. Wilmenius and E. Lindholm, *Arkiv Fysik*, **21**, 97 (1962); (b) E. Lindholm and P. Wilmenius, *Arkiv Kemi*, **20**, 255 (1963); (c) K. R. Ryan, L. W. Sieck, and J. H. Futrell, *J. Chem. Phys.*, **41**, 111 (1964).

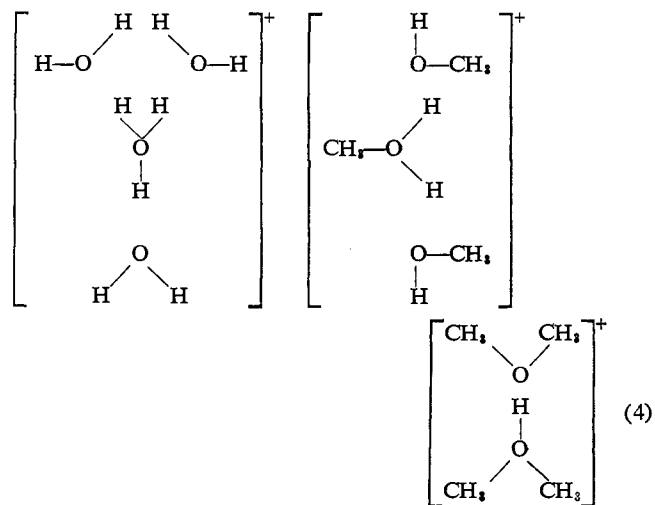
(9) V. L. Tal'roze, *Pure Appl. Chem.*, **5**, 455 (1962).

(10) M. S. B. Munson, *J. Am. Chem. Soc.*, **87**, 2332 (1965).

plotted as functions of pressure. The relative concentrations of the major primary ions decrease in a reasonable, exponential manner, except for  $C_2H_5O^+$ . There must be some process leading to the formation of  $C_2H_5O^+$  since its relative concentration does not decrease in the manner observed for other primary ions. Both proton transfer to form  $C_2H_7O^+$  and hydride transfer to form  $C_2H_5O^+$ , therefore, are occurring in this system. From the initial increases in relative concentrations of  $CH_3OHCH_3^+$  and  $C_2H_5O^+$ , it is apparent that proton transfer is dominant. No new information is provided for  $\Delta H_f(CH_3OHCH_3^+)$  from these experiments, but these reactions are compatible with recent observations that  $P(CH_3OCH_3) \geq 177$  kcal./mole, or  $\Delta H_f(CH_3OHCH_3^+) \leq 144$  kcal./mole.<sup>10</sup> Moran and Hamill<sup>11</sup> have previously reported the formation of protonated dimethyl ether and also observed that it is formed from more than one process.

The disolvated proton,  $H^+(CH_3OCH_3)_2$ ,  $m/e$  93, is present in larger relative concentrations than the monosolvated proton at the highest pressures in these experiments; however, there were no detectable amounts of trisolvated protons. In this respect, dimethyl ether is different from both water and methanol, since for the latter compounds appreciable concentrations of trisolvated protons were observed at lower ratios of di- to monosolvated protons. The higher solvated protons are, therefore, markedly less stable than the disolvated protons in dimethyl ether than they are in water or methanol.

If one assumes that each hydrogen which is bound to an oxygen atom in the protonated molecule ion can bind strongly one other solvent molecule, then one would expect that the maximum number of strongly bonded solvent molecules about a proton (or the "primary cluster") would be four for water, three for methanol, and two for dimethyl ether.



This suggestion is perhaps a partial explanation for the differences in basic properties of these three compounds as liquid phase solvents.

Since the relative concentration of  $C_2H_5O^+$  passes through a maximum and the increase in relative concentration of  $m/e$  91 is approximately equal to the decrease in relative concentration of  $C_2H_5O^+$ , it seems reasonable to consider that this ion is  $(C_2H_5O^+ \cdot CH_3-$

(11) T. F. Moran and W. H. Hamill, *J. Chem. Phys.*, **39**, 1413 (1963);

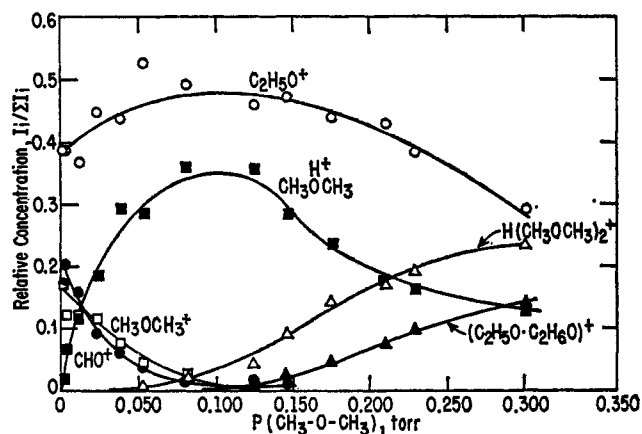


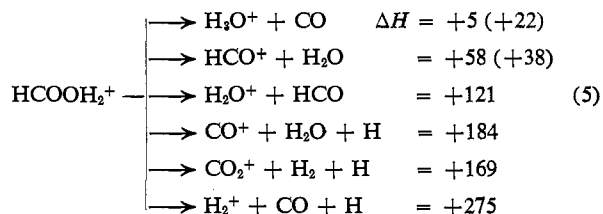
Figure 2. Ionic reactions in dimethyl ether.

$OCH_3$ ), that is,  $C_2H_5O^+$  solvated with a molecule of ether.

**HCOOH.** The relative concentrations of the primary ions of formic acid decrease rapidly with increasing pressure, and essentially the only second-order product ion is the protonated monomer,  $HCOOH_2^+$ . Hence the dominant processes are proton-transfer reactions from  $CHO^+$ ,  $CHO_2^+$ , and  $HCOOH^+$ . Both the di- and trisolvated protons were observed as one would expect from the considerations discussed previously, but the conversion to trisolvated protons is too small under these conditions to discuss the nonoccurrence of higher solvated protons.

No other ions are formed which can be established unequivocally as coming from  $HCOOH$  and not from impurities. Ions of  $m/e$  61 were observed, but these were probably protonated methyl formate, since methyl formate was an impurity in the formic acid.

It is of interest to note that proton transfer was observed from  $H_3O^+$ , formed from the water impurity, to  $HCOOH$ . One can then consider the possible modes of decomposition of protonated formic acid,  $HCOOH_2^+$



There is an uncertainty about the heats of formation of some of the ions,<sup>12</sup> but even considering this, it is apparent that the lowest energy decomposition is the one to give  $H_3O^+$  and  $CO$ . The value for the heat of reaction, 22 kcal./mole using  $\Delta H_f(H_3O^+) = 156$  kcal./mole, is probably fortuitously close to the activation energy, 20 kcal./mole, for the acid-catalyzed decomposition of formic acid in solution.<sup>13</sup> These

(12) Heats of formation of the ions are taken from F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press Inc., New York, N. Y., 1957, Table 45; however, the two values for  $H_3O^+$  are those of V. L. Tal'roze and E. L. Frankevich, *Dokl. Akad. Nauk SSSR*, **111**, 376 (1956) (139 kcal./mole), and D. Van Raalte and A. G. Harrison, *Can. J. Chem.*, **41**, 3118 (1963) (156 kcal./mole). Recent work seems to favor a value of 225 rather than 205 kcal./mole for  $\Delta H_f(HCO^+)$ : R. I. Reed and J. C. D. Brand, *Trans. Faraday Soc.*, **54**, 478 (1958).  $\Delta H_f(HCOOH_2^+) = 107$  kcal./mole: M. S. B. Munson and J. L. Franklin, *J. Phys. Chem.*, **68**, 3191 (1964).

(13) E. R. Schierz and H. T. Ward, *J. Am. Chem. Soc.*, **50**, 3240 (1928).

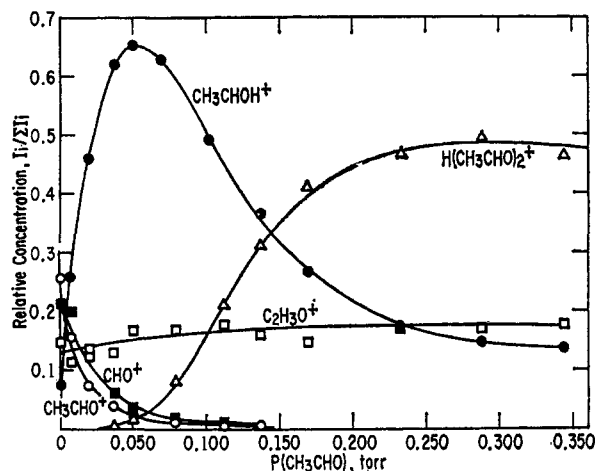
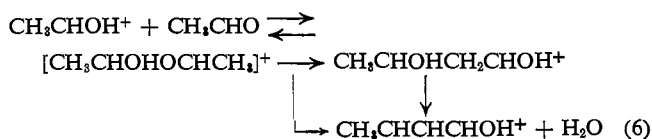


Figure 3. Ionic reactions in acetaldehyde.

data provide another example of agreement between gas phase and condensed phase, since from gas-phase data one would predict that the decomposition products of the acid-catalyzed reaction would be water and CO and that the reaction would be autocatalytic. Although the majority of the work on the acid-catalyzed decomposition of formic acid has been done in very strong acids, it has been reported that addition of  $H_2SO_4$  to formic acid causes evolution of CO even after enough water has been produced to form the dihydrate.<sup>14</sup> Furthermore, even dilute acid solutions catalyze the decomposition of formic acid.<sup>15</sup>

**$CH_3CHO$ .** Figure 3 shows plots of relative concentrations of several of the ions in acetaldehyde as functions of pressure. The relative concentrations of all of the primary ions decrease in the expected manner except for  $C_2H_3O^+$ . Because of the small increase in the relative concentration of this ion, there must be some hydride transfer occurring in this system; however, the dominant reaction is proton transfer, since the most abundant second-order product ion is the protonated monomer,  $CH_3CHOH^+$ .

Very large relative concentrations of the disolvated proton are formed, such that it is the most abundant ion at pressures above 0.2 torr. It is of interest to consider that this disolvated proton is isomeric with protonated acetalol. Since acetalol can be formed from acetaldehyde in condensed phase by acid- as well as base-catalyzed reactions,<sup>16</sup> it is possible that some of the ions at  $m/e$  89 are protonated acetalol molecule ions. Since acetalol is readily dehydrated to crotonaldehyde by acids in condensed phase,<sup>16</sup> one might expect to observe protonated crotonaldehyde,  $m/e$  71, in the gas phase. Ions of  $m/e$  71 constitute 1–2% of the total ion current at pressures above 0.2 torr. These observations suggest the occurrence in the gas phase of other elementary steps which have been postulated for solution reactions (eq. 6). Further, it seems reasonable



(14) R. E. DeRight, *J. Am. Chem. Soc.*, **55**, 4761 (1933).

(15) G. E. K. Branch, *ibid.*, **37**, 2316 (1915).

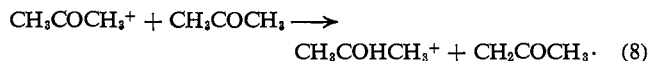
(16) C. R. Noller, "Chemistry of Organic Compounds," W. B. Saunders Co., Philadelphia, Pa., 1951, pp. 203–206.

to suggest that the mechanism involved is one in which protonated acetaldehyde reacts to form a disolvated proton with O–H–O bonds and that this ion may then either decompose to the reactants or it may rearrange to give C–C bond formation in the isomeric protonated acetalol, which may then eliminate water to give protonated crotonaldehyde.

In this system there are many other high molecular weight ions whose structure and origins cannot be established. However, ions of  $m/e$  87 are observed which can be considered as  $C_2H_3O^+$  ions solvated with acetaldehyde. Similarly, ions are observed at  $m/e$  = 115 which are perhaps protonated crotonaldehyde molecules solvated with acetaldehyde. However, since neither  $C_2H_3O^+$  nor  $C_4H_7O^+$  passes through a clearly discernible maximum with increasing pressure, it is not possible to say that these ions must be reacting.

Only traces of  $m/e$  133, the protonated trimer or trisolvated proton, were observed at the highest pressures of these experiments. This observation is in agreement with the previous suggestions concerning the stability of solvated protons: the disolvated proton is expected to be the most stable.

**$CH_3COCH_3$ .** In acetone the predominant second-order product ion is the protonated molecule ion,  $CH_3COHCH_3^+$ ,  $m/e$  59, and virtually no ions of  $m/e$  57 are formed, so essentially no hydride transfer occurs and the dominant processes are proton-transfer reactions. The most abundant primary ions, then, react as

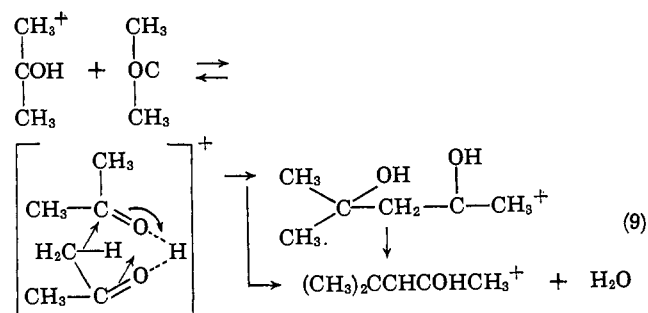


The relative concentration of protonated acetone passes through a maximum and the relative concentration of the disolvated proton,  $H^+(CH_3COCH_3)_2$ ,  $m/e$  117, increases continuously with increasing pressure (4th order, collision stabilized). At the highest pressure of these experiments the disolvated proton constituted about 50% of the total ion current and the monosolvated proton, about 20%, but no trisolvated protons were observed. From the model previously discussed, one would expect that the disolvated proton would be the most stable of the solvated protons, and that the trisolvated proton would be much less stable than the disolvated proton.

In a manner analogous to acetaldehyde, the disolvated proton is isomeric with protonated diacetone alcohol, and one may consider that some of the ions at  $m/e$  117 are protonated diacetone alcohol molecule ions. If this is the case, then one would also expect protonated mesityl oxide,  $m/e$  99 a third-order ion, to be formed by loss of water; and it is, to the extent of about 1% of the total ionization. These observations provide another area of agreement between gaseous and solution ionic reactions since the formation of diacetone alcohol and mesityl oxide from acetone in solution is catalyzed by acids as well as bases.<sup>16</sup>

One can consider that the reaction mechanism, as indicated in eq. 9, is one which involves the initial reversible reaction of protonated acetone with acetone to give a disolvated proton with O–H–O bonds. This complex may rearrange before or after collisional stabilization, by way of a six-membered ring and a hydro-

gen migration to give the isomeric protonated diacetone alcohol which contains C-C bonds. The protonated mesityl oxide may be formed from dehydration of protonated diacetone alcohol or the complex.



Since the relative concentration of protonated acetone passes through a maximum with increasing pressure in a manner similar to that indicated for the protonated molecules in Figures 1-3, it must react rapidly.

It seems unlikely that rate constants for any ionic reaction will be much larger than  $10^{-9}$  cc./molecule sec. so the neutral reactant must be the most abundant species, acetone in the ketone not enol form. It is, of course, not possible to say that the enol form of acetone is absent under these conditions for the formation of small amounts of protonated diacetone alcohol or protonated mesityl oxide; however, this alternative provides a plausible mechanism for condensation without the necessity of invoking reaction with a minor component.

Other product ions are formed, methylated and acetylated acetone being the most abundant, but the reactions forming these ions cannot be clearly established, so no further treatment will be given.

*Acknowledgment.* The author is very grateful to Mr. W. C. Gieger for performing these experiments with his accustomed competence, and to Drs. F. H. Field and W. H. Starnes for helpful discussions.

## Field Gradient and Magnetic Shielding at the Deuteron (Proton) in Ketene

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Contribution from the William A. Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois. Received June 1, 1965

The microwave spectra of  $D_2C_2O$  has been observed under high resolution in order to determine the deuterium quadrupole coupling constants. Line half-widths at half-heights of 20 kc. were obtained. The results in the principal inertial axis system are  $X_{aa} = -10 \pm 8$ ,  $X_{bb} = 64 \pm 8$ , and  $X_{cc} = -54 \pm 8$  kc. Assuming axial bond symmetry and coincidence of the principal inertial and principal field-gradient axis systems gives the quadrupole coupling constant along the C-H bond of  $X_{aa} = 120 \pm 12$  kc. compared to the much larger value of 171 kc. along the C-H bond in formaldehyde. The field gradient at the deuteron and diamagnetic shielding at the proton are calculated using normalized hybrid functions. The calculated electronic field gradients agree well with the experimental quantities. The calculated diamagnetic shielding and experimental total average shielding are used to predict the paramagnetic shielding and the functional dependence of the three proton spin-rotation constants. The predicted average paramagnetic shielding at the proton is  $\sigma^p = -80.4 \times 10^{-6}$ . The predicted value of the sum of spin-rotation constants is  $M_{bb} + M_{cc} = 5.0$  kc.

### I. Introduction

This paper is a discussion of the high-resolution microwave spectra of  $D_2C_2O$  leading to the deuteron quadrupole coupling constants. The resultant field gradients are also calculated using the hybrid orbital

method and the field gradient matrix elements given before for formaldehyde.

Previous work in this laboratory has involved the investigation of the electronic structure of the formaldehyde molecule. The field gradients at the deuteron<sup>2</sup> and the field gradients and spin-rotation interactions<sup>3</sup> at  $^{17}\text{O}$ , and the molecular magnetic moments,<sup>4</sup> which lead to the diamagnetic susceptibility in formaldehyde, have been investigated. We have also calculated the three independent deuteron field gradients, the diamagnetic shielding at the proton, the two independent oxygen field gradients and the diamagnetic susceptibility<sup>5</sup> in formaldehyde. The LCAO-SCF functions in formaldehyde gave reasonably poor agreement with experiment. A set of normalized hybrid orbitals were constructed and will be presented in a forthcoming paper which give much better agreement with experiment.

Therefore, one of the main reasons for studying the field gradients and magnetic shielding in ketene is to attempt an application of the hybrid orbitals similar to those proposed for formaldehyde. The hybrids and ionic character in the various regions in the ketene molecule will be quite different from those in the formaldehyde molecule and will therefore provide a good test of the method. It is also relevant to attempt a transfer of the molecular integrals used in calculating

(2) W. H. Flygare, *J. Chem. Phys.*, **41**, 206 (1964).

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