Oesper and Smyth[20] measured the moments of dibenzoyl peroxide and dibenzoyl persulfide. For the former, they reported the value 1.58 D. at 45° in benzene, nearly the same value as reported here for 30° in the same solvent, and for the persulfide they obtained the values 1.1 D. at 25° and 1.4 D. at 45° in benzene. Taking all the other parameters the same as we have taken them for dibenzoyl peroxide, the moments for the persulfide correspond to a C → S moment of 0.94 D. in the one case and 0.7 D. in the other. The amounts by which these moments exceed the C → O moment lie in a reasonable range for the change from oxygen to sulfur.[20]

Acknowledgment.—The interest and advice given by Dr. Daniel Swern to this research is gratefully acknowledged.

PHILADELPHIA, PENNSYLVANIA

[20] P. F. Oesper and C. P. Smyth, THIS JOURNAL, **64**, 768 (1942).

[CONTRIBUTION FROM THE CHEMISTRY DIVISION, OAK RIDGE NATIONAL LABORATORY, OPERATED BY UNION CARBIDE CORPORATION FOR THE U. S. ATOMIC ENERGY COMMISSION]

Studies Involving Isotopically Labelled Formic Acid and its Derivatives.[1] III. Positive and Negative Ions Produced by Electron Impact in Formic Acid and Deuteroformic Acids

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The principal positive and negative ions in the mass spectra of formic acid and deuteroformic acids are reported. It is shown that the positive ions of mass 45 (CHO_2^+), 29 (CHO^+) and 13 (CH^+) are formed by reactions involving loss of hydrogen from either position in the formic acid molecule. Loss of the hydrogen attached to carbon occurs only a little more readily than loss of the other hydrogen in the formation of the ion CHO_2^+. Loss of the hydrogen attached to oxygen occurs more readily in the formation of the ions CHO^+ and CH^+. Negative ions of masses 45 (CHO_2^-) are formed almost exclusively by loss of the hydrogen attached to oxygen. The relative sensitivities for formation of negative ions from formic, acetic and propionic acids are approximately those predicted from the structures of these acids.

Introduction

As a part of an isotope fractionation study formic-*d* acid was synthesized and assayed mass spectrometrically. It was convenient at this time to compare the cracking patterns of the three possible deuteroformic acids with that of unlabelled formic acid. The deuterium labels served as indicators of the relative amounts of hydrogen lost from each of the two possible positions in the formation of several ions by fragmentation of formic acid during electron bombardment.

Mass spectrometric studies of positive ions from formic acid have been carried out by several investigators.[2-4] In addition to tabulating the positive mass spectra of formic acid, Mariner and Bleakney[2] reported the appearance potential for each of the fragment ions. They observed two values for approximately one half of the ions and suggested that this might be due to the existence of two isomeric forms of the acid, *cis* and *trans*. Approximate appearance potential studies were made for the ions at masses 29 (CHO^+) and 45 (CHO_2^+) in the present investigation, and the results are discussed in terms of structure of the ion rather than the form of the parent molecule.

Although much work has been done on the positive ion spectrum of formic acid, little information is available concerning the negative ions and only the OH^- ion has been previously reported.[2] In the present work a systematic study of the negative ion spectra was carried out in order to tabulate the principal ions and to seek information concerning their origin.

Experimental

Mass Spectrometer.—Data were obtained using a 6 in. radius 60° type of mass spectrometer described in detail elsewhere.[5,6] The temperature of the ionization chamber was reduced to 120° since the formic acid sample decomposed into hydrogen and carbon dioxide at higher temperatures.

Formic Acid.—The unlabeled acid used was Eastman Kodak $98^+\%$ formic acid.

Preparation of Deuteroformic Acids.—The deuteroformic acids used were above 95% pure and were synthesized by the following methods.

Formic Acid-*d* (HCOOD).—Trideuterophosphoric acid was prepared by the reaction of phosphorus pentoxide with the calculated amount of $99^+\%$ deuterium oxide. Vacuum dried C.P. sodium formate was warmed to about 70° in an evacuated system with excess trideuterophosphoric acid and the formic acid-*d* was vacuum distilled into a trap cooled in liquid nitrogen. The trap could be removed from the line and attached to the mass spectrometer without permitting air to reach the acid. All of the glass apparatus was baked *in vacuo* before use to remove water which, if present, could exchange with the formic acid-*d*. A large sample of the formic acid-*d* (about 3 g.) was prepared in order further to minimize the effect of possible exchange with traces of water present during storage.

Formic-*d* Acid (DCOOH).—Thoroughly dried C.P. sodium cyanide was hydrolyzed with excess $99^+\%$ deuterium oxide in a sealed tube at 180° over a period of 18 hours. The tube was opened and attached to a vacuum line where excess deuterium oxide and deuteroammonia were distilled out leaving dry sodium formate-*d*. A sample of this salt gave a negative test for cyanide. The sodium formate-*d* was heated at 70° to 125° with excess 85% phosphoric acid. The aqueous formic-*d* acid which came over at a pressure of approximately 1 micron was then fractionated using a 40 inch Vigreux column. Formic acid-water azeotrope, b.p. 105-106° at 745 mm., d^{20} 1.170, was collected. It was shown to contain 72% formic-*d* acid by alkali titration. The azeotrope was neutralized with sodium hydroxide, and

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[1] Previous study, Gus A. Ropp, C. J. Danby and D. A. Dominey THIS JOURNAL, **79**, 4944 (1957).

[2] T. Mariner and W. Bleakney, *Phys. Rev.*, **72**, 792 (1947).

[3] G. P. Happ and D. W. Stewart, THIS JOURNAL, **74**, 4404 (1952).

[4] "Catalog of Mass Spectral Data," Amer. Pet. Inst. Res. Proj. 44, Nat. Bur. Stds., Washington, D. C., Serial No. 300.

[5] C. E. Melton and G. F. Wells, *J. Chem. Phys.*, **27**, 1132 (1957).

[6] G. F. Wells and C. E. Melton, *Rev. Sci. Instr.*, **28**, 1065 (1957).

the sodium formate-*d* was distilled to dryness in a vacuum line. Excess anhydrous phosphoric acid was added to the residue and anhydrous formic-*d* was vacuum distilled into a trap cooled in liquid nitrogen. This trap could be removed from the line and attached to the mass spectrometer without admittance of air. The deuterium in formic-*d* acid is not readily exchangeable and no special care was required for its handling.

Formic-*d* Acid-*d* (DCOOD).—Anhydrous sodium formate-*d* was distilled in a vacuum line with excess anhydrous trideuterophosphoric acid and the distillate, formic-*d* acid-*d* was collected in a liquid nitrogen cooled trap. This acid was handled with the precautions mentioned under formic acid-*d* as half of its deuterium exchanges rapidly with water.

Preliminary experiments indicated that formic acid had a very strong "memory"[7,8] in the mass spectrometer. To minimize this effect, the instrument was flushed with each new sample and evacuated for a minimum of five times or until subsequent flushing produced no change in the isotopic abundance. The analyzer tube and ion source were baked at 250° for 16 hours between samples.

Results and Discussion

Comparative data reported by various workers given in Table I show variations, as might be expected, because of different operating conditions for the different instruments. Values for the relative abundance of the low mass ions, 12–29, observed in this study, tend to be about a factor of two less than those reported by the other workers. The low values of relative abundance for the light ions observed in this study probably are caused by discrimination of the source used in this investigation. Collimating slits for the ion beam measured 250 × 5 thousandths of an inch and the customary beam centering plates were not used. However, this discrimination should not detract from the value of comparative spectra for formic and deuteroformic acids obtained on this instrument under constant operating conditions since comparisons were made for ions differing by one or two mass units. The large variations in the relative abundance of CO_2^+, CO^+, O^+ and C^+ shown in Table I are probably due to thermal decomposition of HCOOH into $H_2 + CO_2$.

TABLE I

MASS SPECTRA OF FORMIC ACID

Mass	Ion	This study	Mariner[2]	Happ[3]	API[4]
12	C^+	0.93	2.2	10.5	5.5
13	CH^+	.56	2.9	2.6	4.8
14	CH^+_2	.08	0.22		
16	O^+	2.26	3.5	16.1	8.6
17	OH^+	3.23	8.3	13.8	28.1
18	HOH^+	14.17	28.5	46.1	....
22	CO_2^{++}	0.20			
28	CO^+	17.36	16.7	145.9	28.3
29	HCO^+	93.36	185.2	175.1	164.2
30	I	1.24	2.6	3.3	2.7
44	CO_2^+	25.91	9.8	159.5	16.4
45	HCO_2^+	77.01	67.7	80.4	78.2
46	$HCOOH^+$	100.0	100	100	100.00
47	I	2.09			

The positive mass spectra of formic acid and deuteroformic acids for 75 e.v. ionizing electrons and 5.1 Kev. ions are shown in Table II. Values shown are averages from at least ten separate determinations and have been normalized with the parent peak equal to 100. Assuming ion formation for mass 45 (CHO_2^+) in the spectrum of HCOOH to occur by simultaneous rupture of either the C–H or O–H bond and ionization of the radical, the resultant ion could have either the $HCOO^+$ or $COOH^+$ form. If the $COOH^+$ form is predominant, the relative abundance of the ion of mass 45 ($HCOO^+$) in the spectrum of HCOOD and 46 ($DCOO^+$) in the spectrum of DCOOH should be very small, assuming the break up of the deuterated acids to be qualitatively the same as that for the normal acid. Results shown in Table I for masses 45 and 46 indicate that cleavage of the C–H bond is favored in HCOOD but that the ion is formed by cleavage of either the C–H bond or the O–H bond. From these results one would expect two values for the appearance potential of the ion at mass 45 from formic acid, one corresponding to the rupture of the C–H bond to form $COOH^+$ and a second value corresponding to the rupture of the O–H bond[9] to form $HCOO^+$. Qualitative measurements of the appearance potentials at masses 45 ($COOH^+$) and 46 ($DCOO^+$) in the spectra of DCOOH confirmed the expected difference. Mariner and Bleakney[2] also reported two values for the appearance potential of the ion at mass 45; however, they suggested the results might be due to two forms of the acid, *cis*- and *trans*-, because the difference was greater than would be expected on the basis of bond energies.[9] It is entirely possible that the two observed values for the appearance potential correspond to ion pair formation according to the reactions

$$HCOOH + e \longrightarrow HCOO^+ + H^- + e \qquad (a)$$

and

$$HCOOH + e \longrightarrow COOH^+ + H^- + e \qquad (b)$$

These reactions together with the two

$$HCOOH + e \longrightarrow HCOO^+ + H + 2e \qquad (c)$$

and

$$HCOOH + e \longrightarrow COOH^+ + H + 2e \qquad (d)$$

could yield four values for the appearance potential of the ion at mass 45 (CHO_2^+) in the spectrum of HCOOH. However, the apparatus used here is not capable of distinguishing between these various possibilities. The difference of 0.8 e.v. between the appearance potentials observed by Mariner for mass 45 is very nearly equal to the electron affinity[10–13] of the hydrogen atom, 0.75 e.v. and therefore approximately the expected energy difference between reactions (a) and (c) or (b) and (d).

The fact that some mass 14 (CD^+) is formed (Table II) from HCOOD indicates that some rearrangement of the positions of the hydrogen and deuterium atoms accompanies the fragmentation process. However, the relative abundances of the

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[7] C. E. Melton, L. O. Gilpatrick, R. Baldock and R. M. Healy, *Anal. Chem.*, **28**, 1048 (1956).

[8] M. Kilpatrick, C. A. Hutchinson, E. H. Taylor and C. M. Judson, "National Nuclear Energy Ser.," Vol. III-V, McGraw-Hill Book Co., New York, N. Y., 1952, pp. 357–358.

[9] T. L. Cottrell, "The Strengths of Chemical Bonds," Academic Press, Inc., Publishers, New York, N. Y., 1954, and E. S. Gould, "Inorganic Reactions and Structure," Henry Holt and Company, New York, N. Y., 1955.

[10] H. O. Pritchard, *Chem. Revs.*, **52**, 529 (1953).

[11] M. M. Mann, A. Hustrulid and J. T. Tate, *Phys. Rev.*, **58**, 340 (1940).

[12] W. W. Lazier, *ibid.*, **36**, 1417 (1930).

[13] S. Chandrasekar, *Rev. Mod. Phys.*, **16**, 301 (1944).

TABLE II

MASS SPECTRA OF FORMIC ACID AND DEUTEROFORMIC ACIDS

	HCOOH		HCOOD[a]		DCOOH[a]		DCOOD[a]	
Mass	Ion	Relative abundance	Ion	Relative abundance	Ion	Relative abundance	Ion	Relative abundance
12	C^+	0.93	C^+	1.03	C^+	0.93	C^+	0.96
13	CH^+	.56	CH^+	0.56	CH^+	.09	C_{13}^+	.02
14	CH^+_2	.08	CD^+	0.10	CD^+	.90	CD^+	.97
16	O^+	2.26	O^+	2.14	O^+	2.31	O^+	2.20
17	OH^+	3.23	OH^+	0.33	OH^+	2.94		
18	H_2O^+	14.17	OD^+	4.58	OD^+	4.48	OD^+	6.99
19			HOD^+	14.90	HOD^+	13.16		
20							D_2O^+	19.18
22	CO_2^{++}	0.20	CO_2^{++}	0.23	CO_2^{++}	0.19	CO_2^{++}	0.34
28	CO^+	17.36	CO^+	17.65	CO^+	17.83	CO^+	17.06
29	HCO^+	93.36	HCO^+	84.95	COH^+	12.87		
30	$HC_{13}O^+$	1.24	COD^+	15.24	DCO^+	91.52	DCO^+	90.85
44	CO_2^+	25.91	CO_2^+	21.88	CO_2^+	25.84	CO_2^+	21.51
45	CHO_2^+	77.01	$HCOO^+$	18.47	$COOH^+$	37.20		
46	$HCOOH^+$	100.00	$COOD^+$	61.25	$DCOO^+$	40.12	CDO_2^+	67.29
47	$HC_{13}OOH^+$	2.09	$HCOOD^+$	100.00	$DCOOH^+$	100.00		
48			$HC_{13}OOD^+$	2.05	$DC_{13}OOH^+$	1.74	$DCOOD^+$	100.00

[a] Values for the relative abundances have been corrected for contributions by unlabeled molecules.

TABLE III

NEGATIVE IONS FROM HCOOH, DCOOH AND HCOOD

	HCOOH		DCOOH		HCOOD	
Mass	Ion	RA	Ion	RA	Ion	RA
16	O^-	6.3	O^-	6.6	O^-	6.9
17	OH^-	3.4	OH^-	3.5	OH^-	0.6
18			OD^-	0.2	OD^-	3.5
44	COO^-	0.1	COO^-	0.1	COO^-	0.1
45	$HCOO^-$	100	$COOH^-$	1.2	$HCOO^-$	100
46	$HC_{13}OO^-$	1.3	$DCOO^-$	100	$HC_{13}OO^-$	3.7
47	$HCOO_{18}^-$	0.4	$DC_{13}OO^-$	1.2	$HCOO_8^-$	0.6
48			$DCOO_{18}^-$	0.6		
91	$HCOOH \cdot HCOO^-$	0.1				
92			$DCOOH \cdot COOH^-$	0.01	$HCOOD \cdot HCOO^-$	0.1
93			$DCOOH \cdot DCOO^-$	0.1		

positive ions of masses 29 (HCO^+), 30 (DCO^+ and COD^+), 13 (CH^+) and 14 (CD^+) in the spectra of the deuterated acids indicate that these ions are formed largely without cleavage of the C–H bond.

Examination of Table II reveals that large deuterium isotope effects are affecting the relative abundances of various ions. These effects are not surprising on the basis of the discussion by Stevenson[14 15] of isotopic effects in mass spectra. From his discussion it is apparent that not all of the factors influencing the mass spectra of polyatomic molecules can be evaluated and, hence, one cannot predict what the isotopic effects on polyatomic molecules will be.

The mass spectra for the principal negative ions observed in formic acid and deuteroformic acids taken for 5.1 Kev. ions and 50 e.v. ionizing electrons are shown in Table III. In addition to the ions listed, C^- and CH^- were detected. No attempt was made to detect the positive and negative fragment H ions because of the different focusing conditions required. No attempt was made to determine the mode of formation for the various negative ions. It is possible, however, that the negative ion of mass 45 (CHO_2^-) is produced by ion pair formation[16] according to the reaction

$$HCOOH + e \longrightarrow HCOO^- + H^+ + e \qquad (e)$$

The relative abundance of the ions of masses 45 (CHO_2^-) and 46 (CDO_2^-) in the spectra of DCOOH and HCOOD, respectively, clearly show that deuterium migration[17] is not very probable during negative ion formation and that these negative ions are formed almost exclusively by cleavage of the O–H bond. The negative ions of masses 92 ($HCOOD \cdot HCOO^-$) and 93 ($DCOOH \cdot DCOO^-$) were at first believed to arise from loss of hydrogen from formic acid dimer. Their abundances are about the same as expected from the monomer–dimer equilibrium data reported by Coolidge.[18] However, evidence subsequently was found that these negative ions may be formed by ion molecule reactions.

Another interesting observation concerns the negative ion of mass 44 (CO_2^-) which appears in the mass spectra of the three acids. This ion reportedly[19] cannot be produced directly from car-

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[14] D. P. Stevenson, *J. Chem. Phys.*, **15**, 409 (1947).

[15] D. P. Stevenson and C. D. Wagner, *ibid.*, **19**, 11 (1951).

[16] V. H. Dibeler, R. M. Reese and F. L. Mohler, *J. Research Natl. Bur. Standards*, **57**, 367 (1956).

[17] W. A. Bryce and P. Kebarle, *Canad. J. Chem.*, **34**, 1249 (1956).

[18] A. S. Coolidge, THIS JOURNAL, **50**, 2166 (1928).

[19] L. B. Loeb, "Basic Processes of Gaseous Electronics," University of California Press, Berkeley and Los Angeles, 1955.

bon dioxide (CO_2). However, it has been detected[20] as a product from impact of CO_2^+ ions on metal surfaces. The mode of production may be electron attachment to an electronically excited state.

The relative abundances for all of the positive and negative ions measured in DCOOH are shown in Table IV. These data were taken for 50 e.v. ionizing electrons and 5.1 Kev. ions. Pressure[6] in the ionization chamber was 2×10^{-6} mm.

Table IV

Positive and Negative Ions from DCOOH

Mass	Ion	Relative abundance	Relative abundance (of negative ions only)
12	C^+	0.90	
13	CH^+	.10	
14	DC^+	.90	
15	HCD^+	.18	
16	O^+	2.04	
17	OH^+	3.79	
18	HOH^+, OD^+	8.03	
19	HOD^+	18.67	
20			
28	CO^+	15.51	
29	HCO^+	12.08	
30	DCO^+	88.61	
31	$DC_{13}O^+$	1.35	
44	CO_2^+	23.09	
45	$HCOO^+$	36.84	
46	$DCOO^+$	38.22	
47	$DCOOH^+$	100.00	
16	O^-	0.14	6.6
17	OH^-	.07	3.5
18	OD^-	.004	0.2
44	COO^-	.002	0.1
45	$HCOO^-$	.02	1.2
46	$DCOO^-$	2.06	100
47	$DC_{13}O_{18}O^-$	0.004	0.2

A brief investigation was undertaken to determine whether other aliphatic acids produced negative ions by loss of hydrogen. It was found that the major negative ion beams produced by 50 e.v. ionizing electrons for both acetic acid and propionic acid resulted from loss of one hydrogen from the parent molecule. The hydrogen loss in these cases was assumed to be from the carboxyl group as with formic acid. Relative sensitivities for negative ion formation for the three aliphatic acids studied are shown in Table V.

Table V

Sensitivity for Negative Ion Formation

Acid	Ion	Relative ease of ion formation
HCOOH	$HCOO^-$	100
CH_3COOH	CH_3COO^-	40
$CH_3CH_2 \cdot COOH$	$CH_3CH_2COO^-$	40

The estimated accuracy is ± 20%. These data indicate that the probability for negative ion formation is about equal for acetic acid (CH_3COOH) and propionic acid (CH_3CH_2COOH) but is much higher for formic acid.

As the mechanism of formation of these negative ions may involve loss of a proton from the carboxyl group, the inductive effect[21] of the methyl group in acetic acid or the ethyl group in propionic acid would tend to force electrons toward the carboxyl group and inhibit the ion formation. Accordingly, the negative ions would be formed in greatest abundance from formic acid as was actually observed. For a similar reason acetic acid would be expected to form the negative ion more readily than propionic acid although the difference should be much smaller than the difference between formic and acetic acids and was probably not detectable here because of the low accuracy of the method used. The trend in sensitivity to negative ion formation by the three acids is roughly comparable in magnitude to the relative tendencies of these acids to ionize in aqueous solution as measured by their ionization constants.[22]

The fact that the cracking of formic acid yields a positive ion at mass 45 (CHO_2^+) by loss of either hydrogen with about equal ease while the negative ion of the same mass (CHO_2^-) is formed almost entirely by loss of hydrogen attached to oxygen seems worthy of further discussion. Formation of the negative ion by loss of hydrogen from oxygen and not from carbon is analogous to the ionization of formic acid in aqueous solution. It is well known that organic acids containing the carboxyl group ionize in solution by loss of hydrogen from the oxygen attachment. Loss of hydrogen exclusively from the attachment to oxygen during ionization of carboxylic acids in solution is explained by two effects. These are: (a) a resonance effect[23] which stabilizes the carboxylate ion which remains after the hydrogen enters the solution and (b) the inductive effect[17] of the oxygen atoms of the carboxyl group which facilitates cleavage of the O–H bond. Loss of hydrogen exclusively from the oxygen during formation of the negative ion of mass 45 in the mass spectrometric cracking of formic acid also can be explained plausibly by these principles.

In the case of the formation of the positive ion of mass 45, there is little on which to base a prediction as to whether only one or both types of cleavage would occur except for consideration of the relative strength of the hydrogen to carbon and the hydrogen to oxygen bonds.

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[20] F. L. Arnot and C. Beckett, *Proc. Roy. Soc. (London)*, **A168**, 103 (1938).

[21] A. E. Remick, "Electronic Interpretations of Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1943, Chapter 11.

[22] See "Handbook of Chemistry and Physics," 38th Ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1956–1957.

[23] S. Glasstone, "Textbook of Physical Chemistry," D. Van Nostrand Co., Inc., New York, N. Y., 1946, p. 112, 113