THE REACTIVE NATURE OF ALDEHYDES FROM THE STANDPOINT OF THE APPARENT ELECTROMOTIVE FORCE

BY SAUL B. ARENSON, PLEASANT ERNEST ROLLER AND D. J. BROWN

Haber and Russ[1] were the first to show that for the reversible oxidation and reduction of organic compounds the same factors are involved as for the same type of inorganic reactions. Later work[2] confirms their conclusions for this class of organic compounds. For organic substances that are oxidized or reduced irreversibly, except to show that some of them develop an apparent electromotive force, very little appears in the literature. Baur[3] showed that the alkaline solutions of aldehydes show a large variation in the apparent electromotive force on standing. Stieglitz[4] demonstrated that alkaline solutions of formaldehyde may be used as the negative electrode of a cell to deposit silver from solution at the other electrode apparently reacting the same as a reversible reducing agent. Other alkaline solutions of aldehydes react the same. St. Bugarszky[5] found that the velocity of reduction by aldehydes is inversely proportional to the concentration of the hydrogen ions. While no quantitative measurements are available, apparently the other reactions of aldehydes are affected similarly by the relative concentration of the hydrogen ions.

The following observations were made to secure further information on the relation of the apparent electromotive force to the alkalinity of the solutions and the reactions of aldehydes.

Experimental

Since preliminary experiments indicated that the apparent electrode potentials of the aldehydes were approximately of the same value as the oxygen electrode, all operations from the preparation of the solutions to the final measurement of the electromotive force were made in an atmosphere of nitrogen. This nitrogen was prepared by passing air or commercial nitrogen thru a chain of bottles filled with copper foil in contact with a solution of ammonium chloride and quite concentrated ammonia, then with the ammonia vapor thru a silica tube containing a tightly wound copper gauze heated to 500-600°C. The excess ammonia was removed by passing the nitrogen thru solutions of sulfuric acid.

"Conductivity water" was used to prepare all solutions. The acid solutions were prepared by recrystallizing $H_2SO_4.H_2O$ twice from conductivity water and then diluting. The sodium hydroxide solutions were prepared by dropping metallic sodium into a two-phase mixture of ether and water, the ether was evaporated in vacuo, and the concentrated solution diluted.

[1] Haber and Russ: Z. physik. Chem., **47**, 257 (1904).
[2] Clark: Chemical Reviews, **2**, 127 (1925).
[3] Baur: Ber., **34**, 377 (1901).
[4] Stieglitz: Science, **27**, 775 (1907).
[5] St. Bugarszky: Z. physik. Chem., **48**, 63 (1904).

The acetaldehyde was prepared from paraldehyde by the method of McLeod[1]. The temperature of the condenser was maintained at 22° ± 2C. It was collected in an oxygen-free container, which in turn was emptied by pressure into a two-liter flask and diluted with conductivity water at 0°C. The strength of the acetaldehyde solution was determined by the method of Seyewetz and Bardwin[2], in which the aldehyde is titrated in the presence of sodium sulfite with a standard acid.
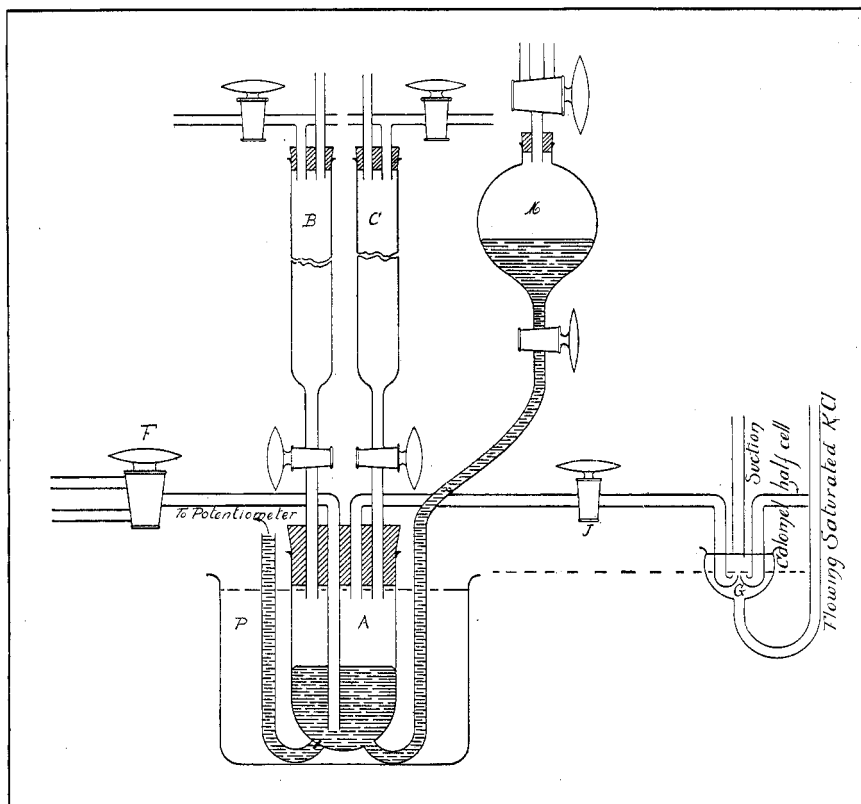

Fig. 1
Aldehyde Half-cell.

Chloral hydrate best grade was recrystallized from carbon bisulfide which had been shaken with lead carbonate and then distilled.

The potentials of the aldehyde half-cell were measured in terms of the calomel electrode by means of a Weston cell, a Leeds and Northrup Type K potentiometer, and Type R galvanometer. Both electrodes were kept in beakers of distilled water which were in a thermostat at 25° ± .05 C. All work except the titrations was done in a room lighted by ruby lights.

[1] McLeod: Am. Chem. J., **37**, 20 (1907).
[2] Seyewetz and Bardwin: Bull., **33**, 1000 (1905).

The results were obtained by the use of the container for the aldehyde solutions shown in Fig. 1. Tube P was filled with mercury and sealed at the bottom with a platinum insert to complete the circuit from the mercury within the container to the potentiometer. When an observation was being made, the contents of the electrode chamber was caused to flow slowly into the flowing saturated potassium chloride bridge, G. The procedure was as follows:

Mercury from M was forced into A, the contents of A flowed thru J into G. "Oxygen-free" water was then admitted thru F to A while the surface of the mercury was lowered, J being kept closed. F was closed and the container emptied as stated in the first sentence. After A was completely washed, the balance of the water was removed by admitting nitrogen thru F. By means of nitrogen, solutions kept in thermostats were forced into burets, B and C, and then the measured quantity of each was forced into the electrode chamber, A, and immediately stirred by the nitrogen thru F for several seconds, F was closed and mercury from M was allowed to force sufficient of the solution thru J to make a circuit thru G with the calomel electrode—by rapid manipulation it was found possible to make the first observation of the electromotive force within one minute after the solutions were admitted to the electrode. After each reading J was closed. A little mercury was permitted to enter A before each subsequent reading, thus securing the flow while the reading was being made.

Results

For approximately molar solutions of acetaldehyde and chloral hydrate in normal sodium hydroxide the velocity of change in the observed electromotive force was very large. For this concentration with acetaldehyde the results check those given by Baur[1]. The results with the more dilute solutions of acetaldehyde in sodium hydroxide were as follows:

+.071 molar acetaldehyde,

2 min	−.1180	2 min	−.1186
4	.1255	4	.1286
7	.1280	6	.1300
10	.1179	12	.1290
22	.1112	30	.1253
		114	.1245

.0105 normal sodium hydroxide

3 min−	.1223	2 min	−.1179
5	.1263	5	.1183
17	.1285	9	.1199
29	.1275	19	.1193
107	.1229	89	.1110

The mean minimum results for the concentrations studied were

Acetaldehyde	Sodium hydroxide	E.M.F.
.071 molar	.0105 normal	− .128 volts
.017	.0105	− .113
.0121	.00525	− .092
.0263	.0525	− .155
1.0	1.0	− .239

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[1] Baur: Ber., **34**, 377 (1901).

An attempt was made to determine the effect of the added oxidized state as would be expected from the reactions studied by Evans[1]. For this reason the observations were made in the .0263 normal sodium hydroxide to determine the effect due to the addition of acetate and of oxalate. The average minimum values were,

.054 molar acetaldehyde		− .153
.054 ″ ″	+ sodium acetate, .020 N	− .158
.076 molar acetaldehyde		− .163
.076 ″ ″	+ potassium oxalate, .020 N	− .160

The variations in the presence and absence of the added salt with time were the same.

Since it was not possible to secure reproducible results in acid solutions of acetaldehyde, chloral hydrate was studied. The decomposition of chloral hydrate in water was observed by titrating the acid formed by 100 ml. of the following solutions:

Chloral hydrate	Ml. .014 base 1/3 hr.	2 hr.	20 hr.	Maximum H+
.0140 molar	1.4	1.4	2.2	.0003 N
.0280	2.6	2.7	2.8	.0004
.0560	2.7	3.9	4.2	.0006

The titration of hundredth normal acid after it had stood several days in the presence of chloral hydrate indicated that none of the chloral hydrate had decomposed.

The values given below are representative of the observations made during the first few minutes. Since the velocity of change is very great, the time is indicated in seconds to the nearest multiple of 5. To show the effect of changing acidity, results for .005 molar chloral hydrate only are given, except one series of observations to show the effect in acid solutions of the oxidized state, trichlor acetate.

.0050 molar chloral hydrate, .180 normal sulfuric acid

45 sec.	+ .206	50 sec.	+ .209	50 sec.	+ .210
105	+ .229	80	+ .228	80	+ .223
135	+ .227	180	+ .229	110	+ .228
220	+ .224	270	+ .228	215	+ .229

.005 molar chloral hydrate, .0180 normal sulfuric acid

35 sec.	+ .181	35 sec.	+ .179	75 sec.	+ .188
90	.192	90	.192	120	.196
140	.198	130	.194	175	.199
290	.203	250	.199	220	.204
330	.204	495	.206		

[1] Evans: J. Am. Chem. Soc., 44, 1543, 1730 (1922).

Same as preceding + .0046 molar sodium trichlor acetate

45 sec.	+ .179	35 sec.	+ .180	30 sec.	+ .181
90	.190	85	.189	105	.196
165	.198	165	.196	160	.197
260	.202	265	.200	215	.198

.0050 molar chloral hydrate, .0062 N barium hydroxide

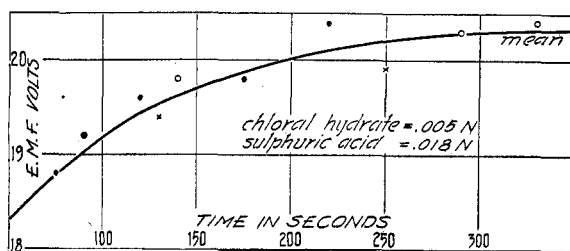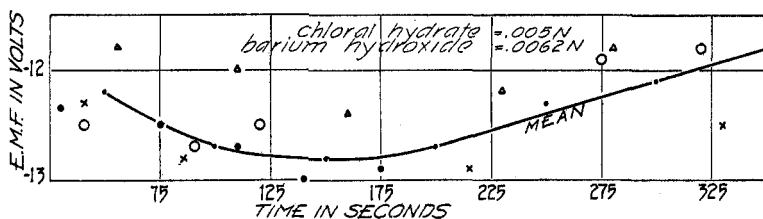| 55 sec.	+ .118	40 sec.	− .125	40 sec.	− .123
110	.120	90	.127	85	.128
160	.124	120	.125	215	.129
230	.123	275	.119	330	.125
280	.118	420	.116	650	.106
		900	.102	840	.103

FIG. 2

FIG. 3

Median curves to fit the data for the alkaline chloral hydrate solution, and the .018 normal acid solution are given in Figs. 2 and 3.

The velocity of decomposition of alkaline solutions of chloral hydrate was observed. The solutions were allowed to stand in the thermostat for the desired length of time, then the decomposition was stopped by adding an excess of standardized acid, and the excess acid was titrated with barium hydroxide solution, using phenol-phthalein as indicator. Since the reaction at this temperature was very rapid, especially for those in which the concentration of the base was relatively large, the results are not exceedingly accurate. The constants for reactions of the second order were calculated from the standard equations,

$$K_1 = \frac{1}{ta} \cdot \frac{x}{a - x}$$

and,

$$K_2 = \frac{1}{t(a - b)} \ln \frac{b(a - x)}{a(b - x)}$$

A third constant, K_x, was calculated on the assumption, for calculation only, that the concentration of the reactive aldehyde was equal to the concentration of the base.

a = concentration of chloral hydrate,
b = concentration of barium hydroxide,
x = decrease in concentration of the base.

For b = a

t	b	x	K_1	t	b	x	K_1
o	.0070	.0000		o	.0560	.0000	
90 sec.		.00106	.283	60		.0263	.264
150		.00168	.301	120		.0363	.274
200		.00206	.298	200		.0425	.280
660		.00406	.299	325		.0471	.290
1,140		.00493	.290				

For b = 2a

t	b	x	K_2	K_x
o	.00625	o		
15		.00050	1.94	.42
60		.00139	1.80	.61
180		.00241	1.77	.57
250		.00276	2.02	.51
o	.01135	o		
40		.00304	2.00	.80
50		.00339	1.94	.78
75		.00420	2.07	.69

For a = 2b

t	b	x	K_2	K_x
o	.00595	o		
40		.00037	.137	.27
60		.00039	.097	.21
110		.00056	.077	.16
250		.00103	.068	.14

For acetaldehyde in alkaline solution the following facts only were observed: The base on standing in presence of the aldehyde did not change its concentration. For .054 and .144 acetaldehyde in .0263 normal sodium hydroxide, for the same intervals of time the same fraction of the aldehyde had decomposed when determined by the method given above.

Discussion of the Results

The oxidized state has no effect on the apparent electromotive force, a contrast to the reversible type of electrode.

The reduced state affects the apparent electromotive force proportionally to its concentration and to the concentration of the hydroyl ion, the same as for a reversible electrode like $H_2S - S^\circ$. The difference in the two curves in Fig. 2 is due to the fact that the reactive form may be formed less rapidly than in the ionization of the hydrogen sulfide. The subsequent rise in the curve in alkaline solution is due to the decomposition of this reactive form. The rise in the curve for acid solutions of chloral hydrate to a maximum is due to the decrease in concentration of this reactive form to a minimum by the formation of the inactive form.

The velocity of decomposition of the chloral hydrate at first appears anomolous, but as shown by the approximation K_x, if we assume that the reaction is due to the active form whose equilibrium with the inactive form is determined by the concentration of the base, it may be possible to account for the variations of the constants for a dimolecular reaction.

The velocity of condensation of the acetaldehyde in a solution of a base of definite concentration is apparently a reaction of the first order.

The velocity of reduction, as reported by St. Bugarszky, for aldehydes is inversely proportional to the concentration of the hydrogen ion.

In all the preceding reactions of the reduced state and in the change of electromotive force, the concentration of the hydroxyl ion seems to be one of the determining factors.

By the assumption of the equilibrium reaction

$$R—C = O \rightleftharpoons R—C—OH \rightleftharpoons R—C—O^- + H^+$$
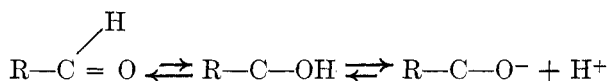
in which the bivalent carbon is the reactive form, all the preceding admit of simple interpretation,—the key is the fact that the bivalent carbon radical in solution is directly proportional to the concentration of the hydroxyl ion.

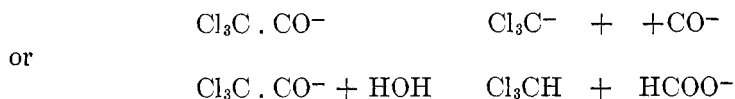Then the apparent electromotive force, E_a, would be at $25^\circ C$, assuming the effect to be due to the bivalent carbon,

$$E_a = E_o - .06/n \log [RCHO] \; [OH]$$

The changes of E_a as indicated by the curves for acid and alkaline solutions are due to the velocity of the change to equilibrium. This is reached in acid solutions of chloral hydrate in a few minutes, but in alkaline solutions the chloral hydrate, and the acetaldehyde decrease in concentration due to chemical reaction, and the curves reach a minimum value which would not be the true equilibrium values for the solutions as prepared.

In alkaline solutions, for the determinations made with one concentration of base, the velocity of condensation of the acetaldehyde is proportional to the concentration of the acetaldehyde. This indicates that the determining

factor in the velocity of the reaction may be the formation of the bivalent carbon, and the latter condenses comparatively rapidly.

In neutral solution the chloral hydrate decomposes until a certain degree of acidity is reached. This is due to the decrease in concentration of the bivalent carbon form in the equilibrium reaction as stated above on account of the formation of the formic acid. In molar solutions of a base the velocity of decomposition of chloral hydrate is almost instantaneous, but in the concentrations of base where fairly accurate observations could be made, the concentration of the base seems to be the determining factor. From the above equilibrium reactions this may be interpreted as due to the dissociation of the ionized bivalent carbon form and its reaction with the base or with the water of the solution as an instaneous reaction, thus

$$Cl_3C \, . \, CO^- \qquad\qquad Cl_3C^- \quad + \quad +CO^-$$

or

$$Cl_3C \, . \, CO^- + HOH \qquad Cl_3CH \quad + \quad HCOO^-$$

Summary

The apparent electromotive force of acetaldehyde and chloral hydrate was determined as affected by the concentration of the hydroxyl ion.

The velocity of decomposition of chloral hydrate in dilute alkaline solutions was studied.

A theory was advanced to correlate the observations,—the apparent electromotive force is due to the bivalent carbon radical in solution as the reduced state, which for this state has all the properties of the reduced state in an electrode that satisfies the conditions of a reversible electrode, but the oxidized state is passive.

University of Nebraska,
Lincoln, Nebraska.