Attempts to prepare analogous compounds from acetophenone proved unsuccessful.

Trichloro-*tert.*-amyl Alcohol.—B. p., 110–113°, with decomposition, at 620 mm. (atm. press. Boulder); d_4^{20}, 1.2128; n_D^{20}, 1.4460; M_D, calc. 41.479, found 42.107.

Analysis. Calc. for $C_5H_9OCl_3$: C, 31.34; H, 4.69; Cl, 55.61. Found: C, 31.20; H, 4.75; Cl, 55.69.

Tribromo-*tert.*-amyl Alcohol.—B. p., 130–135° (40 mm.), with decomposition; d_4^{20}, 1.8788; n_D^{20}, 1.5130; M_D, calc. 50.226, found 53.23.

Analysis. Calc. for $C_5H_9OBr_3$: C, 18.46; H, 2.76; Br, 73.84. Found: C, 18.86; H, 2.71; Br, 73.15.

Tri-iodo-*tert.*-amyl Alcohol decomposes before the boiling point is reached even under diminished pressure; d_4^{20}, 2.1438; n_D^{20}, 1.5680; M_D, calc. 65.845, found 71.11.

Analysis. Calc. for $C_5H_9OI_3$: C, 12.88; H, 1.93; I, 81.76. Found: C, 12.99; H, 2.08; I, 79.12.

Summary

1. Three compounds, trichloro-*tertiary*-amyl alcohol, tribromo-*tertiary*-amyl alcohol, and tri-iodo-*tertiary*-amyl alcohol, homologs of the corresponding derivatives of acetone, have been prepared. This reaction is apparently a general one for the simple aliphatic ketones. The chloroform and bromoform derivatives are fairly stable in the dark, decomposing under the influence of light and heat.

2. The molecular refractions of the compounds as experimentally determined are considerably greater than those calculated from Eisenlohr's values, and the discrepancies increase with the increasing atomic weight of the halogens.

BOULDER, COLORADO

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE IRREVERSIBLE REDUCTION OF ORGANIC COMPOUNDS. I. THE RELATION BETWEEN APPARENT REDUCTION POTENTIAL AND HYDROGEN-ION CONCENTRATION

BY JAMES B. CONANT AND ROBERT E. LUTZ

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The irreversible reduction of organic substances has been often expressed in terms of a qualitative scheme of oxidation-reduction potentials of the various reagents employed, but except in the case of electrolytic reduction no attempt has been made to treat the subject quantitatively. The interpretations of the reduction processes which take place at the cathode during electrolysis are complicated by the two-phase system which is necessarily present and similar difficulties are encountered in considering the reducing action of metals and metallic combinations. In order to avoid these complications we have turned our attention at first to the development of a quantitative theory of those cases of reduction which take place in homogeneous solution. In a preliminary paper[1] we reported the results of some experiments carried out in alcoholic and acetone solutions as a result of which it was possible to make quantitative statements concerning the reduction of various types of organic substances under definite conditions and to develop a tentative theory of irreversible reduction. In order to study the effect of changes of hydrogen-ion concentration, we have now investigated the reduction of a number of compounds in aqueous "buffer" solutions. The results of this and our earlier work convince us that it is possible to interpret irreversible organic reductions in homogeneous solution in quantitative terms involving the conception of oxidation-reduction potentials. This being the case, it is necessary only to accumulate sufficient data concerning a variety of substances in order to be able to give a general account of the irreversible reduction of organic compounds. Such is the aim of this series of investigations; in this paper we shall consider the effect of the hydrogen-ion concentration, and in later papers the reduction of various types of organic compounds and the effects produced by introducing different atoms or groups into the molecule.

In the case of the quinones and certain other compounds, the process of reduction is strictly reversible and can be formulated in terms of an electrochemical equation; the reduction potential of such substances can be accurately defined and measured.[2] This is not true of compounds which are irreversibly reduced since the reaction runs to completion and therefore cannot be expressed in terms of any simple thermodynamical equation. It is possible, however, to determine experimentally, within certain limits, what we have called "the apparent reduction potential" of a compound which is irreversibly reduced by a soluble reducing agent. This apparent reduction potential may be defined as the oxidation-reduction potential[3] (on the hydrogen scale) of the particular reducing agent

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[1] THIS JOURNAL, **45**, 1047 (1923).

[2] (a) Haber and Russ, *Z. physik. Chem.*, **47**, 257 (1904). (b) Granger and Nelson, THIS JOURNAL, **43**, 1401 (1921). (c) Clark, *J. Wash. Acad. Sci.*, **10**, 255 (1920). (d) Biilmann and Lund, *Ann. chim.*, **16**, 321 (1921). (e) Conant, Kahn, Fieser and Kurtz, THIS JOURNAL, **44**, 1382 (1922). (f) La Mer and Baker, *ibid.*, **44**, 1954 (1922). (g) Conant and Fieser, *ibid.*, **44**, 2480 (1922). (h) Clark, *Public Health Repts.*, **38**, 366, 443, 933 (1923).

[3] The term "oxidation-reduction potential of a substance" is used throughout this paper to signify the potential of equimolecular amounts of oxidant and reductant referred to the normal hydrogen electrode. This potential for substances of the quinone type varies in acid solution with the hydrogen-ion concentration according to the equation

$$\Pi_n = \Pi_0 + \frac{RT}{F} \log [H^+]$$

where Π_n is the oxidation-reduction potential as defined, and Π_0 is the normal potential, that is, the potential in a solution normal with respect to the hydrogen ion. When referring to the potential of a reducing agent we are, therefore, referring to the potential of which will just cause an appreciable amount of reduction of the substance in question; reducing agents of a higher potential will not reduce the compound under the same experimental conditions, whereas all reducing agents of lower potential will reduce it more or less rapidly. By a simple electrochemical scheme it is possible to determine easily whether or not a certain reducing agent causes the appreciable reduction of a given substance.

In order to apply this method successfully it is necessary to have available reducing agents whose potentials form a graded series with not more than 50 mv. difference between two successive members. Even if such a closely graded series of reducing agents is at hand it is probably not possible to determine the apparent reduction potential more accurately than 25 mv. as the definition of "appreciable reduction" is necessarily arbitrary; in some instances it is difficult to decide whether or not the slow reduction caused by a certain reducing agent is to be considered appreciable or not. A further refinement of the quantitative study of the process of irreversible reduction will undoubtedly have to discard this somewhat approximate conception of "apparent reduction potential" and in its place develop a more detailed and complicated theory of the mechanism of the reduction.[4] However, results which are in doubt by not more than 25 or even 50 mv. are significant enough for the first stage of the development of a consistent account of irreversible reductions. This is evident when one recalls that the reducing agents available in the laboratory cover a range of at least some 1,000 mv. (if one includes the so-called oxidizing agents, the range is nearly 3,000 mv.).

Method

The apparatus used consisted of a glass cell of 250cc. capacity (inside diameter about 55 mm.) closed by a rubber stopper carrying a glass stirrer working through a mercury seal and gas inlet and outlet tubes. The stirrer which was in the form of a glass propeller (about 7 × 25 mm.) at right angles to the shaft was located nearly at the bottom of the cell and when rotated at 900–1,300 r.p.m. agitated very vigorously the entire contents of the cell. The two electrodes were located a few centimeters above the bottom of the cell; they were of platinum foil (15 × 20 mm.) one bright, the other platinized. Connection with a calomel electrode was made by means of a saturated potassium chloride bridge of 5mm. diameter, plugged with filter paper at each end to decrease the rate of diffusion; a fresh bridge was used in each experiment. The stopper was also provided with an opening for admitting the inorganic reducing agent from a buret. The substance whose apparent reduction potential was to be measured was contained in a very small glass capsule resting on a circular wire support placed near the top of the cell in such a way that by the turn of a glass rod the capsule was dropped into the liquid below.

At the beginning of an experiment the oxidized form of the reducing agent (Table I) was dissolved in 200 cc. of the suitable buffer solution which was placed in the cell. After the cell had been carefully freed

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an equimolecular mixture of oxidant and reductant as is common electrochemical practice; the term normal potential we shall use *only* for the value Π_0 in the above equation.

[4] Compare Ref. 1, p. 1053.

from oxygen by sweeping it out with a stream of pure nitrogen, the usual electrometric titration was commenced. Sufficient sodium hydrosulfite solution was added in small increments (or at *P*H 0.76 titanous chloride solution) to reduce approximately one-half of the organic substance; the potential of the electrodes then corresponded within a few millivolts to the value given in Table I for the oxidation-reduction potential of the reducing agent in the particular buffer solution which was employed. As soon as it was evident that this potential was constant, the substance to be investigated was rapidly introduced into the liquid and the potential of each electrode determined at short intervals during 30 minutes. The substance in every case dissolved very rapidly and was completely in solution within a few minutes. In those cases in which no reduction occurred, the potential was constant within a few millivolts for half an hour; on the other hand if the substance was reduced a rapid rise of the potential was observed. Except in our attempts to obtain closely reproducible changes in potential in the "border line cases" referred to below, the rate of stirring was without appreciable effect. The solution of the oxidized form of the reducing agent was 0.002 *M* so that when this was half reduced the solution was 0.001 *M* in respect to its reducing power. The substance being investigated was taken in such amounts that a 0.002 *M* solution resulted; two molecular equivalents of compound were thus present for each molecular equivalent of reducing agent.

TABLE I

OXIDATION-REDUCTION POTENTIAL OF AN EQUIMOLECULAR MIXTURE OF OXIDANT AND REDUCTANT IN VOLTS AT 24° AS COMPARED WITH THE NORMAL HYDROGEN ELECTRODE

	Compound (oxidized form)	*P*H 0.76	*P*H 3.76	*P*H 6.77	*P*H 9.6	*P*H 11.6	*P*H 12.7
A	1,4-Naphthoquinone	+0.426	+0.262	.....	.....	.....	.....
B	Chloranilic acid	+ .375	+ .123	.....	.....	.....	.....
C	Methylene blue	.....	+ .188	.....	.....	.....	.....
D	Sulfonated thioindigo scarlet	+ .320	+ .140	−0.005	.....	.....	.....
E	Sulfonated alizarin indigo	+ .315	+ .128	− .012	.....	.....	.....
F	Sulfonated Ciba scarlet	+ .275	+ .102	− .029	−0.139	−0.160	−0.198
G	Indigo disulfonate	+ .250	+ .090	− .100	− .212	− .240	− .300
H	Anthraquinone-1,5-disulfonate	+ .194	+ .017	− .161	.....	.....	− .485
I	Anthraquinone-2,7-disulfonate	+ .184	+ .007	− .171	.....	− .325	− .325
J	Anthraquinone-2,6-disulfonate	+ .183	+ .006	− .172	.....	− .325	− .325
K	Anthraquinone-2-sulfonate	+ .142	− .035	− .213	− .300	− .380	− .380
N	Sulfonated naphthanthraquinone	+ .180	+ .004	− .174	.....	.....	.....
T	Titanium chloride	+ .020	.....	.....	.....	.....	.....

Certain experimental difficulties were encountered in this work and must be guarded against if significant results are to be obtained. As in all electromotive-force measurements of oxidation-reduction systems, the electrodes may at times give erratic results. The source of this trouble is not always apparent but long contact with strong reducing agents is one common cause. After careful cleaning, heating to red heat and resurfacing (with platinum black or gold as the case may be) the electrodes are generally again ready to use. By using two electrodes and carefully noting the potentials of both during the titration, any difficulties due to poor electrodes can be detected before the introduction of the substance whose apparent reduction potential is to be measured. If both electrodes rapidly come to the same potential after each increment of reducing agent has been added, satisfactory results will be obtained throughout the experiment.

Not all the organic compounds which are reversibly reduced are equally well suited for use as reducing agents in this work. It is obvious that only those are of service which rapidly react with oxidizing and reducing agents and which rapidly come into equilibrium with the electrodes. The differences in the speed with which electrode equilibrium is attained vary greatly from substance to substance. For example, electrodes immersed in quinone itself, indigo disulfonate, β-anthraquinone-sulfonate and anthraquinone-2,6-disulfonate come to equilibrium within a few minutes during a titration with titanous chloride or other reducing agent. On the other hand, with the α-anthraquinone-sulfonate one must wait sometimes as long as 10 or 20 minutes after each increment of reducing agent has been added before the potentials of both electrodes are constant. Such compounds, which either do not cause an electrode to come to rapid equilibrium or are themselves somewhat slowly reduced, are not suitable for an investigation of irreversible reduction processes. The results obtained with them are erratic and inconsistent. We have carefully chosen, therefore, only those substances as reducing agents (Table I) which were found satisfactory in this regard. With them repeated experiments always gave reproducible and consistent results. It was, however, never deemed safe to trust only one experiment and several trials were always made in order to determine whether or not a given substance was appreciably reduced by a certain reducing agent.

In most experiments it was an easy matter to decide whether or not reduction had occurred; the potential either changed not more than 5 mv. in 30 minutes or else rose 30 to 150 mv. in the first five minutes. In certain instances, however, we were apparently dealing with border-line cases as there was a slow rise of 15 to 40 mv. in 30 minutes. The same compound when introduced into a reducing agent of higher potential caused no change but was rapidly reduced by reducing agents of a potential lower than that of the border-line reagent. These cases, therefore, merely represent special instances in which we have been able to detect slow changes between our usual limits of no reduction or appreciable reduction.

In certain of these special cases the magnitude of the slow reduction was fairly reproducible and we have studied them in some detail to throw more light on the influence of certain factors on the rate of reduction. What was actually measured, of course, was the rate of change of the potential of the electrodes so that factors influencing the speed at which the electrode comes into equilibrium with the solution also influence the result. It was found at the outset that the stirring of the solution must be at a constant speed in order to obtain reproducible results with these border-line cases; this is probably connected with the speed of solution of the material added and possibly of some diffusion process at the electrode and not with changes in the rate of the reaction between the substances in solution. On the other hand, the temperature had a definite though not very great effect on the rate of change of the potential and this is probably a measure of the temperature coefficient of the actual irreversible reduction process. The figures in Table II show the magnitude of this temperature effect; they were obtained in experiments carried out in an acetate buffer solution of *P*H 3.76 with sodium anthraquinone-2-sulfonate as the reducing agent.

TABLE II

RATE OF REDUCTION AT DIFFERENT TEMPERATURES

Substance	Temp. °C.	Increase of potential in mv. 5 min.	10 min.	20 min.	30 min.
Sodium	25	4	6	10	13
Nitrophenyl	25	5	6	10	13
Acetate	25	5	7	10	13
	0	1	3	4	6
	0	2	3	4	6
	0	3	5	7	9
Sodium	25	9	18	29	40
m-Nitrobenzoate	25	11	18	29	37
	0	5	8	14	18
	0	4	7	11	15

These border-line cases also gave us an opportunity of delicately testing the effect of certain substances usually active as catalysts—a point of considerable importance. To eliminate any possible effect of the platinized electrode it was removed in several experiments, but practically identical results were obtained in its absence as in its presence. In several other experiments small amounts of platinum black were introduced and in others several cubic centimeters of a colloidal platinum solution; both these catalysts were without effect. It should be mentioned in this connection that in other experiments with entirely different substances and reducing agents we attempted to cause reduction by introducing a catalyst with a reducing agent which would normally cause no reduction. Platinum black, palladium black and colloidal platinum were all tried and found to have no effect. Thus it seems fairly certain that these substances do not appreciably affect the rate of the reaction between a soluble reducing agent and the organic compounds we have been studying.

The effect of the temperature noted above illustrates the point we emphasized in our preliminary paper, namely, that while our results are comparable with each other, they concern only the effect of the reducing agent on the substance in question under the conditions of our experiments. At a temperature of 100°, for example, undoubtedly not only would the rate of the slow reduction of our border-line cases be much faster but in many instances our cases of no reduction would become cases of appreciable reduction.

The normal potentials of the majority of the substances used as reducing agents in this work (Table I) have already been published;[5] the potential of indigo disulfonate has been carefully determined by W. M. Clark,[6] while papers which will soon be published from this Laboratory will include a study of chloranilic acid and naphthanthraquinone. The sulfonated dyes, however, were especially prepared for this work and a study of them is, therefore, included in this paper. Since we were interested only in obtaining a water-soluble substance which would be reversibly reduced at a certain potential, no attempt was made to isolate and purify the actual sulfonates of the dyes. Instead, a standard solution of the sodium salts was prepared in each instance and used throughout the work.

Ciba Scarlet G.—Ciba Scarlet G (Schultz' No. 907) was treated with 16% fuming sulfuric acid, 14 g. of acid being used for 6 g. of dye; 10 g. of 50% fuming acid was then added and the mixture allowed to stand overnight. It was then poured into water, the solution neutralized with sodium hydroxide and made up to a volume of 500 cc. The values for the oxidation reduction potential in different buffer solutions at 24° were determined by the usual electrometric titration with titanous chloride or sodium hydrosulfite, and are listed in Table I; the values are significant within 3–5 millivolts.

Alizarin Indigo G.—Alizarin Indigo G (Schultz' No. 893) was sulfonated in a similar manner, the product diluted with water, neutralized and made up to a definite volume. The potentials are recorded in Table I.

Thioindigo Scarlet.—The sulfonation of thioindigo scarlet (Schultz' No. 905) was carried out in the same way; its potentials are also recorded in Table I.

The Effect of the Hydrogen-Ion Concentration

In our preliminary paper dealing with irreversible reductions in essentially non-aqueous solutions at one hydrogen-ion concentration, it was pointed out that it was a matter of importance to determine whether the apparent reduction potential of various substances would be essentially independent of the hydrogen-ion concentration or whether it would vary in the way the true reduction potential of the quinones vary. The change of the oxidation reduction potential of a reversible reduction of the type $A + 2H^+ + 2\epsilon \rightleftharpoons AH_2$, with changes in hydrogen-ion concentration

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[5] (a) This Journal, **44,** 1382 (1922); (b) **44,** 2480 (1922).

[6] Clark, *U. S. Pub. Health Repts.*, **38,** 1669 (1923).

is given by Equation 1, where Π_n is the potential of equimolecular amounts of A and AH_2 at a particular hydrogen-ion concentration and Π_0 is the normal potential, that is, the potential in a solution normal with respect to the hydrogen ion.

$$\Pi_n = \Pi_0 + 0.059 \log [H^+] \tag{1}$$

Such an equation holds very accurately for a number of quinones over a wide range of hydrogen-ion concentrations[2d,2e,2h] but in alkaline solution other factors affect the course of the reaction and the potential often deviates widely from this equation. On the other hand the potential of an equimolecular mixture of ferro- and ferricyanides is nearly independent of the hydrogen-ion concentration, since no hydrogen is actually involved in the reduction process.

The results of the present research tabulated in Table III show that the apparent reduction potential of the nine substances investigated decreases with decrease in hydrogen-ion concentration much as does the reduction potential of quinone. If the change of apparent reduction potential paralleled the change of a true quinone potential it would be expressed by the empirical Equation 2,

$$P_x = P_0 + 0.059 \log [H^+] \tag{2}$$

where P_x is the apparent reduction potential in a particular buffer solution and P_0 the corresponding apparent reduction potential in a solution normal with respect to the hydrogen ion. Under the heading ΔP, in Table III, there is given at every hydrogen-ion concentration studied

TABLE III

APPARENT REDUCTION POTENTIAL IN VARIOUS BUFFER SOLUTIONS

	*P*H 0.76	*P*H 3.76		*P*H 6.77		*P*H 9.6		*P*H 11.6	
Substance	P	P	ΔP (0.18)	P	ΔP (0.18)	P	ΔP (0.17)	P	ΔP (0.12)
Sod. *m*-nitrobenzene sulfonate	+0.06	+0.03	0.03	−0.06	0.09	−0.18	0.12	−0.31	0.13
m-Nitrobenzoic acid	+ .06	+ .05	.01	− .14	.19	− .18	.04	− .24	.06
m-Nitrophenol	+ .06	+ .05	.01	− .10	.15	− .22	.12	− .27	.05
p-Nitrophenylacetic acid	+ .06	+ .03	.03	− .14	.17	− .26	.12	...	..
Benzoylacrylic acid	+ .08	− .06	.14	− .13	.07	− .25	.12	− .43	.18
2,4-Dinitrobenzoic acid	+ .23	+ .05	.18	− .03	.08	− .09	.06	− .11	.02
Dinitro-α-naphthol sulfonate	+ .26	+ .05	.21	− .15	.20	− .22	.07	− .31	.09
Picric acid	+ .26	+ .05	.21	− .05	.10	− .18	.13	− .20	.02
Orange II (Schultz' No. 145)	+ .35	+ .06	.29	− .14	.20	− .22	.08	− .31	.09

The following solutions were employed:

*P*H 0.76, 0.2 *N* HCl; *P*H 3.76, acetic acid and sodium acetate; *P*H 6.77, monosodium and disodium phosphate; *P*H 9.6, sodium carbonate and sodium bicarbonate; *P*H 11.6, *N* ammonium hydroxide; the last two were chosen because they could be used later on a large scale and were reliable enough for the present purposes. The Sörensen values were determined in the usual way, except in the case of the ammonia solution where the value was taken from the tabulation of Michaelis' "Die Wasserstoffionen-Konzentration," [Julius Springer, **1914,** p. 23]; changes in the values of the *P*H of the carbonate and ammonia solutions, due to the bubbling through of nitrogen for some 40 minutes, were neglected, as they must be very slight in these relatively concentrated solutions.

(except the first) the decrease (in volts) in apparent reduction potential as compared with the value in the preceding buffer solution; if Equation 2 held, this decrease would be equal to the values given in parentheses at the very top of the column. It is evident that the change in apparent reduction potential in many instances is very far from this decrease calculated from Equation 2; thus, with the first compound the apparent reduction potential in *P*H 3.76 was only 0.03 volts less than in *P*H 0.76 as compared to the calculated value of 0.18. These discrepancies are in part due to experimental difficulties and in part represent real divergencies from Equation 2. We will consider the experimental difficulties first.

The values for the apparent reduction potentials summarized in Table III are somewhat arbitrarily taken as the mean between the potential at which no appreciable reduction was observed and the highest potential which caused appreciable reduction. This is illustrated by the following typical data, which to save space are given in Table IV for only a few compounds measured in a few buffer solutions. The letters refer to the sub-

TABLE IV

THE DETERMINATION OF THE APPARENT REDUCTION POTENTIAL IN BUFFER SOLUTIONS

Typical Data

			Change in potential in Mv.			
*P*H	Reagent	Π°	5 min.	10 min.	20 min.	30 min.
		m-NITROBENZENE SULFONATE				
0.76	I	187	...	2	2	2
	I	188	1	0	...	0
	I	181	...	2	2	0
	K	146	0	0	0	0
	K	149	...	0	...	0
	T	005	41	49	57	...
	T	−062	70	77	90	104
	Apparent reduction potential = +0.06					
3.76	G	085	2	1	0	...
	G	084	0	1	1	2
	J*	−007	...	15	18	19
	J*	007	3	4	7	9
	I*	014	2	3	4	3
	I*	−004	...	7	8	8
	K	−053	19	34	51	63
	K	−046	13	19	26	36
	K	−032	5	9	14	19
	K	−027	6	10	14	18
	K	−032	...	11	21	28
	Apparent reduction potential = +0.03					
6.77	F	−045	0	..	0	0
	F	−028	1	1	2	2
	G	−104	8	11	18	25
	G	−084	5	..	...	21
	K	−205	163	..	239	271
	Apparent reduction potential = −0.06					

TABLE IV (*Concluded*)

*P*H	Reagent	Π°	Change in potential in Mv. 5 min.	10 min.	20 min.	30 min.
	m-NITROBENZOIC ACID					
	K	145	2	3	3	4
0.76	K	149	0	0	0	0
	T	−006	...	77	73	68
	Apparent reduction potential = +0.06					
	G	086	...	0	0	...
	J	−003	6	12	22	27
	J	−008	5	9	16	17
3.76	I	+005	4	6	12	16
	J	021	6	10	18	22
	K	−051	19	31	48	61
	K	−044	12	29	46	...
	Apparent reduction potential = +0.05					
6.77	F	−045	1	..	0	0
	G	−097	4	..	...	6
	G	−088	−1	−1	−1	0
	G	−085	2	2	4	6
	G	−096	...	2	3	3
	I	−173	65	138	203	241
	Apparent reduction potential = −0.14					

* = border line case.

stances listed in Table I; Π° is the potential of the reducing agent (on the hydrogen scale) as actually observed which differs slightly from the value for the oxidation-reduction potential given in Table I because not exactly equimolecular amounts of reduced and oxidized compound were always present. The changes in potential after the introduction of the substance in question are given in the last four columns. The border-line cases are marked with a star.

The accuracy of the estimate of the apparent reduction potential obviously depends in most instances on the range between the two successive reducing agents which cause no reduction and appreciable reduction, respectively. Thus, in the cases of the *m*-nitrobenzene sulfonate and the next three compounds listed in Table III the apparent reduction potential in *P*H 0.76 falls within the wide range of about 120 mv. between the anthraquinone-2-sulfonate and titanous chloride. The estimate of +0.06 for these compounds is much less accurate, therefore, than that for *m*-nitrobenzene sulfonate in *P*H 6.77, for example, where the apparent reduction potential falls between —0.039 for sulfonated Ciba scarlet and —0.10 for indigo disulfonate.

The numerical value of the apparent reduction potential is thus only a probable mean of a more or less wide range which for lack of suitable reagents we cannot at present investigate. This is clearly shown in Figs. 1, 2 and 3 where the broad and irregular bands represent the range between the potential of reduction and no reduction of the substances in question.

The narrower such a band the more accurate is the value of the apparent reduction potential.

Not all the divergence between the actual values of ΔP in Table III and those calculated from Equation 2 can be explained by taking into account the experimental difficulties. A study of Table III and Figs. 1, 2 and 3 shows that in many instances the change of apparent reduction potential with change of hydrogen-ion concentration does not follow Equation 2, and does not therefore parallel the potential of the hydrogen electrode. This is not surprising in view of the fact that the *reversible* reduction of many organic compounds is not represented by Equation 1 in its simple form. One type of such deviation has been studied in this Laboratory[5a] and an equation developed on theoretical grounds to account for it; this deviation occurs because in alkaline solution the reduced compound is present more or less as an ionized sodium salt and not as the undissociated hydroquinone. In general, if the basic or acidic ionization of any part of the molecule is different in the oxidized and reduced form, Equation 1 must be modified. Various types of such modified equations have been developed by Clark;[7] such equations correspond to curves which between certain values of the hydrogen-ion concentration have slopes

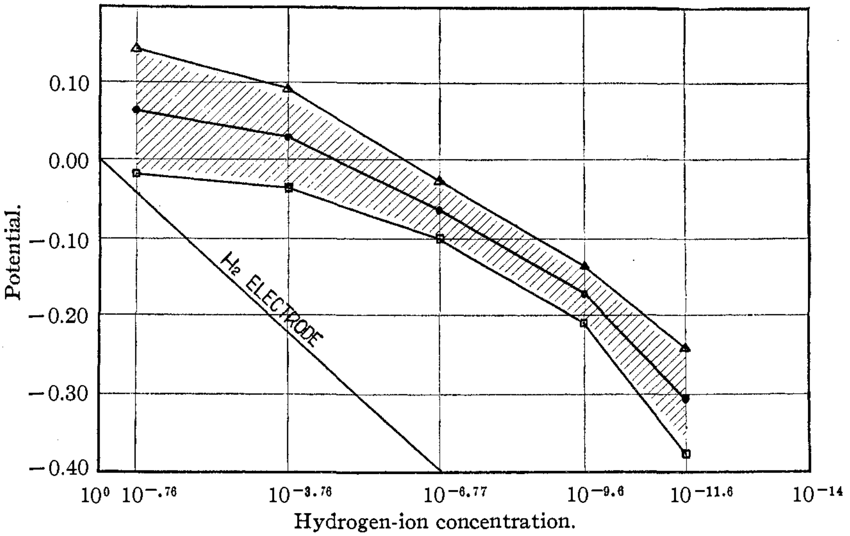

Fig. 1.—Apparent reduction potential of *m*-nitro benzene sulfonate. The upper boundary of the shaded band is drawn through the points representing the lowest potentials at which no reduction was observed; the lower boundary corresponds to the highest observed potentials at which appreciable reduction took place. The apparent reduction potentials lie on the median. The variations in the slope of this band from that of the line for the hydrogen electrode represent divergencies from Equation 2.

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[7] Clark, Ref. 6, p. 666.

either much less or much more than that given by Equation 1. Undoubtedly some similar influences are the cause of the more pronounced deviations of the apparent reduction potential from Equation 2. It is not profitable at present to speculate on the various possibilities which might cause these deviations, but in time it may be possible to express them in terms of some modified form of Equation 2, much as the potential

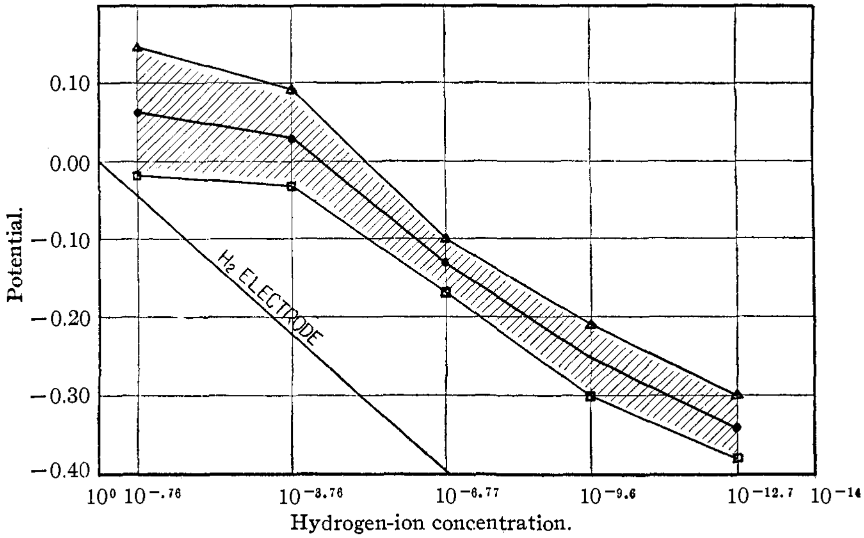

Fig. 2.—Apparent reduction potential of nitrophenylacetic acid.

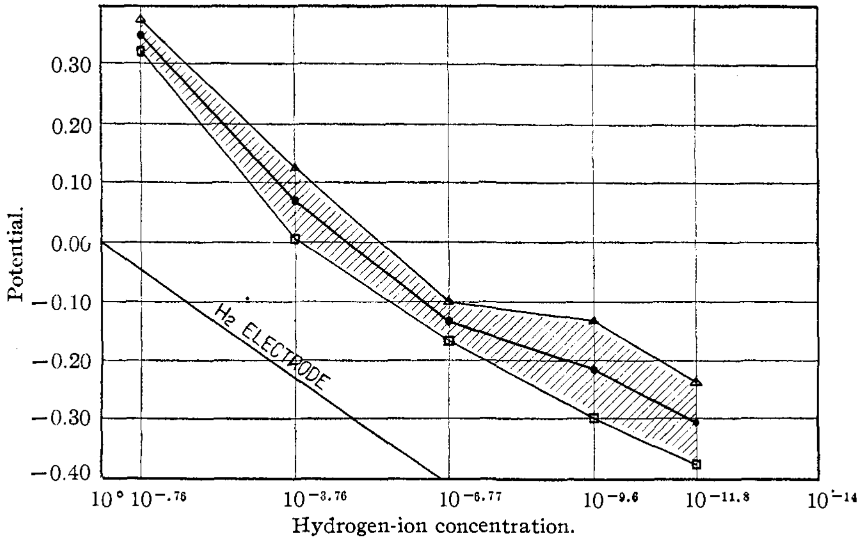

Fig. 3.—Apparent reduction potential of Orange II.

of certain reversible processes can be expressed in terms of a modified Equation 1.

It will be noted that three distinct types of compounds are represented in Table III; nitro compounds, an azo compound and an unsaturated ketonic acid. It may be safely stated that the apparent reduction potential of all three types is a function of the hydrogen-ion concentration, the potential decreasing with increase in Sörensen values. An exact equation for this relationship between apparent reduction potential and hydrogen-ion concentration cannot now be formulated but in general it appears to be similar to equations which are applicable to reversible reductions of the type, $A + 2H^+ + 2\epsilon \rightleftharpoons AH_2$. These conclusions make very probable the assumption that the course of these irreversible reductions is largely determined by some reversible reduction process similar to the reduction of quinones and certain nitrogen compounds, which is then followed by an irreversible reaction.

In connection with the problem of the relationship between apparent reduction potential and structure, it is interesting to note that the azo dye is reduced at a much higher potential than any of the other compounds in acid solution, the polynitro compounds being next in order while the ketonic unsaturated acid and the mononitro compounds are reduced only at a relatively low potential.

We are indebted to the Cyrus M. Warren Fund of the American Academy of Arts and Sciences for the electrical apparatus used in this work.

Summary

1. The "apparent reduction potential" may be defined as the oxidation-reduction potential of the particular reducing agent which will just cause an appreciable amount of reduction of the substance in question. The apparent reduction potentials of certain water-soluble nitro compounds, an azo dye, and a ketonic unsaturated acid have been measured in buffer solutions of various hydrogen-ion concentrations. The apparent reduction potential has been found to decrease with decreasing hydrogen-ion concentration in a manner more or less parallel to the change of the reduction potential of quinones with changing hydrogen-ion concentrations. Certain wide deviations from this parallelism are probably due to experimental difficulties, while others are probably due to complicating factors in the reduction process.

2. The results are in harmony with the assumption that the controlling factor in the irreversible reduction process is a reversible addition of both hydrogen ions and electrons followed by some irreversible change.

3. The addition of finely divided platinum to the solution has been found to be without effect. An increase of temperature causes a slight

increase in the speed of the reduction in those cases where it was possible to estimate this speed with any degree of accuracy.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE ADDITION REACTIONS OF CERTAIN PENTADIENONES

II. ADDITION OF MALONIC ESTERS

BY E. P. KOHLER AND C. S. DEWEY

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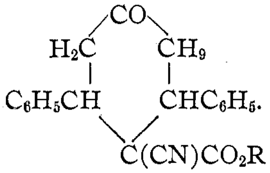
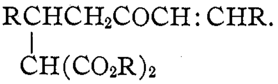
In the first paper[1] it was shown that in the presence of a little sodium methylate the esters of cyano-acetic acid combine very rapidly both with dibenzal acetone and with dianisal acetone. The products are saturated cyclohexanone derivatives formed by the addition of one molecule of ester to one of ketone: RCH: CHCOCH: CHR + $CNCH_2CO_2R$ = . No open-chained addition products of any sort could be detected and no appreciable difference was observed in the relative ease of the reaction with the two ketones.

This result is quite different from that which Borsche[2] reported after he had studied the addition of malonic ester, aceto-acetic ester and other substances containing active hydrogen to these same ketones and to others constituted like them. Thus, on condensing malonic ester and dibenzal acetone in the presence of piperidine he obtained only an unsaturated open-chained addition product: RCH:CHCOCH:CHR + $CH_2(CO_2C_2H_5)_2$ =  $RCHCH_2COCH{:}CHR$ with $CH(CO_2R)_2$ on the first carbon. Moreover, Borsche found that neither malonic ester nor aceto-acetic ester combines at all with dianisal acetone under conditions under which both combine with dibenzal acetone with the greatest ease. Since in these experiments both the ester and the condensing agent were different from those used in the work with the esters of cyano-acetic acid, it now became desirable to determine which of these was responsible for the marked difference in the results. We have, therefore, studied the addition of malonic esters to a number of unsaturated ketones of this type, and have employed both alcoholates and piperidine as condensing agents.

We have found that with dimethyl malonate as the substance to be added and sodium methylate as condensing agent the results are similar

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[1] Kohler and Helmkamp, THIS JOURNAL, **46,** 1018 (1924).

[2] Borsche, *Ann.*, **375,** 145 (1910).