resulting benzoic acid was precipitated on cooling, and melted at 118°. It was further identified by converting to its ferric salt and to benzanilide, m. p. 158°.

The amount of benzaldoxime crystals obtained is practically that calculated based upon the nitrosyl chloride used, about 3% by weight of the toluene. The time required is dependent upon the temperature and upon the intensity of the sunlight but in no case was it longer than 2 hours. Under the right conditions the reaction could undoubtedly be made to proceed more rapidly and probably continuously. Whether the process can be utilized commercially under the influence of some catalyst is a problem which is at present engaging our attention. Furthermore, we are studying the action of nitrosyl chloride on other substances and will report the results later.

Summary

Nitrosyl chloride readily reacts with toluene in the sunlight to produce crystals of benzaldoxime hydrochloride, from which benzaldoxime, benzaldehyde, benzoic acid and benzanilide can be prepared in the usual way.

SEATTLE, WASHINGTON

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

AN ELECTROCHEMICAL METHOD OF STUDYING IRREVERSIBLE ORGANIC REDUCTIONS

Preliminary Paper

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The reversible reduction of such organic substances as anthraquinone and benzoquinone can be studied easily by electrochemical methods and the experimental results can be quantitatively expressed in the terms of a general thermodynamic equation.[1] This has not been true, hitherto, of the *irreversible* reduction processes which are so common in organic chemistry. In a recent paper[2] it was pointed out that the irreversible reductions brought about by catalytic hydrogenation cannot be interpreted even qualitatively by means of an electrochemical explanation; on the other hand, the irreversible reductions which are caused by such reducing agents as titanous chloride and chromous chloride are in qualitative agreement with a definite scheme of oxidation-reduction potentials. We have con-

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[1] (a) Haber and Russ, *Z. physik. Chem.*, **47**, 257 (1904). (b) Granger and Nelson, THIS JOURNAL, **43**, 1401 (1921). (c) W. M. 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) LaMer and Baker, *ibid.*, **44**, 1954 (1922). (g) Conant and Fieser, *ibid.*, **44**, 2480 (1922).

[2] Conant and Cutter, THIS JOURNAL, **44**, 2651 (1922).

tinued the study of the irreversible reductions which are brought about by reducing agents which have a definite and measurable potential in solution. The list of common inorganic substances has been supplemented by the inclusion of quinones and related compounds which are reversibly reduced and whose potentials have been measured in this Laboratory. By means of a convenient electrochemical method it has been a relatively easy matter to determine whether or not a given substance, such as dibenzoyl-ethylene, is irreversibly reduced by one of these reducing agents. In this way an upper potential limit has been set for the irreversible reduction of a particular substance *under the conditions of our experiments.*

In this preliminary paper we shall consider the results so far obtained with a variety of compounds and discuss a probable theoretical interpretation of the reaction. In later papers we shall give the results of a more complete study of the irreversible reduction of each class of compounds and discuss the effects of substitution. We also hope to show the practical application of these measurements to the problem of the partial reduction of various substances and mixtures.

Method

Briefly, our method consists in measuring the potential of the following combination and then adding the material under investigation to the half-cell containing the reducing agent and noting whether or not the potential changes during a period of 30 minutes:

Pt | Solution A: reducing agent | Solution A: quinhydrone | Pt

The apparatus employed was similar to that described in a former paper[1g] except that the hydrogen electrode was replaced by a quinhydrone electrode[3] when the solvent employed contained acetone, since it was found that a hydrogen electrode could not be used in this solvent. The half-cell which contained the reducing agent was rapidly stirred and continually swept out with a stream of pure nitrogen. A gold-plated electrode and a platinized electrode were immersed in the solution; a siphon plugged with filter paper connected the 2 half-cells and was filled with the same solution as were the 2 cells; essentially identical ionic concentrations were thus present throughout the combination. The solvent employed in most of the work was a mixture of 75% of acetone and 25% of hydrochloric acid, the total concentration of acid being 0.2 *N*. In a few experiments an alcoholic hydrochloric acid solution was employed but was not found entirely satisfactory, as many of the compounds were not sufficiently soluble in it.

The organic compounds employed as reducing agents were the various hydroquinones whose potentials have already been measured in this

[3] Biilmann, *Ann. chim.*, **15**, 109 (1921). Ref. 1d. Sörensen, *ibid.*, **16**, 283 (1921).

Laboratory at 25° in alcoholic solution.[4] They were introduced into the cell in the form of the oxidized compound (the quinone) and were reduced by the usual titration method with titanous chloride or vanadous chloride. The potential was followed during the titration and the reduction continued until about 50% of the quinone had been reduced, as shown by the potential measurements. The potential of this mixture was then noted and after it was constant for 10 minutes (the equilibrium is rapidly reached with most quinones) the substance to be investigated was introduced into the mixture. This was accomplished by having the substance in a small glass cup suspended above the liquid; by means of a glass rod the cup could be dropped into the liquid and the substance was thus quickly introduced into the well-stirred mixture. The material rapidly dissolved and a homogenous solution of reducing agent and substance was thus present in the cell. The potential was then determined over a period of 30 minutes. In the cases in which reduction occurred there was a rise in the potential, in the other cases the potential remained essentially constant. The total concentration of the quinone was 0.001–0.003 *M*; the amount of substance under investigation was such that a 0.001–0.003 *M* solution of it resulted. Since only 1/2 of the total quinone was present in the cell as the hydroquinone, the irreversibly-reduced compound was present in about 100% excess. Thus, if a reaction took place the hydroquinone was almost completely oxidized and a considerable change in potential occurred. Experiments showed that it made little difference whether this large excess were 100 or 150%; since the ratio was kept within these limits in all this preliminary work, our results are strictly comparable. The temperature was 24°±2°.

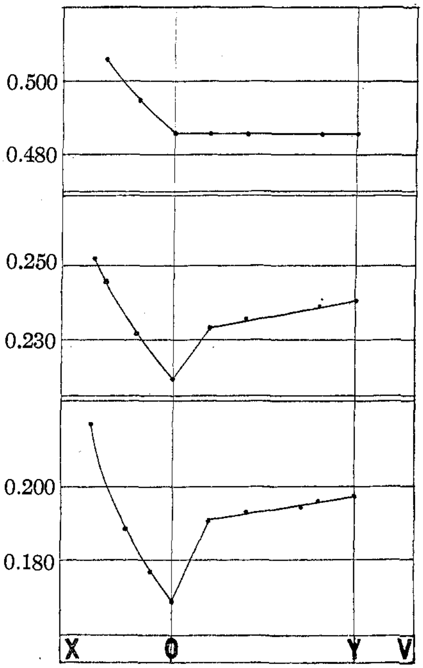

Fig. 1.—The action of reducing agents of different potential on dibenzoyl-ethylene in acetone-hydrochloric acid solution. Potentials are plotted vertically, and increments of reducing agent horizontally from X to O. Time is plotted from O to V; Y is a point 30 minutes after the addition of the dibenzoyl ethylene.

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[4] Refs. 1e and 1g. The potential measurements of some of the quinones used in this work have not yet been published, but soon will be in a series of papers dealing with the relation between structure and reduction potentials.

The curves shown in Fig. 1 represent three typical cases; one in which there was no appreciable reduction, a second in which a slow change in potential occurred, and a third in which there was a more rapid rise in potential. In Table I are listed the reducing agents we employed and their normal potentials measured against the hydrogen electrode at 25° in alcoholic solution. We found by several experiments that these normal potentials, when measured in acetone, were within 5 or 6 millivolts of the values found in alcoholic solutions. The actual potential of the mixture employed in an experiment was in a few cases 10 or 20 millivolts different from the values for the normal potential, since there was some variation in the proportions of the quinone and the hydroquinone present, due to the fact that the exact midpoint of the titration was not always reached. All the potentials of the organic reducing agents are, of course, dependent on the hydrogen-ion concentration (or really activity) as the following equation shows.

TABLE I

ORGANIC SUBSTANCES EMPLOYED AS REDUCING AGENTS

	Compound (oxidized form)	Normal potential in alcoholic hydrochloric acid (π_0) volts		Compound (oxidized form)	Normal potential in alcoholic hydrochloric acid (π_0) volts
A	1,4 Naphthoquinone	+0.483	F	Anthraquinone-2-sulfonate	+0.196
B	Retenequinone	+0.410	G	1-Chloro-anthraquinone	+0.174
C	Indigo-disulfonate	+0.310[a]	H	Anthraquinone	+0.155
D	Anthraquinone-2,7-disulfonate	+0.238	I	2-Methylanthraquinone	+0.150
E	2,7-Dichloro-anthraquinone	+0.226			

[a] π_0 in acetone-hydrochloric acid solution; +0.298 in aqueous solution.

$$\pi = \pi_0 + 0.0295 \log \frac{[A]}{[AH]_2} + 0.059 \log [\mathrm{H}^+] \qquad (1)$$

The activity of the hydrogen ion in such solvents as we are using is not known, but since it affects the potential of the quinhydrone electrode or the hydrogen electrode in exactly the same manner as it affects the potential of our organic reducing agents, the potential of our combination gives the values for π_0 in Equation 1. For purposes of simplification we shall arbitrarily assume that the hydrogen-ion activity in our 0.2 *N* hydrochloric acid-acetone mixture is 1; this is probably in error by an amount corresponding to some 60 millivolts. At some later time, if the hydrogen-ion activity in such a solvent as we are employing is determined, our results can be easily corrected. If the irreversible reductions are also a function of the hydrogen-ion concentration, as seems probable from the considerations presented below, this correction will cancel out and not affect our final results. In any case, for the preliminary survey of this field, we are not attempting to differentiate between the various compounds more closely than about 50 millivolts, so that any error introduced by the above simplifying assumption will not vitiate our conclusions. The potentials given in this paper are, thus, all expressed in terms of the hypothetical potential of the hydrogen electrode in our 0.2 N hydrochloric acid—acetone mixture. The value of the quinhydrone electrode is taken as + 0.711 volts, the value for π_0 (Equation 1) in alcohol-hydrochloric acid solution; the actual potential of the entire cell subtracted from this number expresses the oxidation-reduction potential on the scale which we have adopted.

Table II gives the experimental results; the letters refer to the organic reducing agents listed in Table I. The actual potential of the cell is given as π° (on the arbitrary scale just defined). The following columns give the total change in potential (in millivolts) 5, 10, 20 and 30 minutes after the compound under investigation was added. The results with the inorganic reducing agents (titanous chloride and vanadous chloride) were much less satisfactory than those obtained with the organic reducing agents. It was difficult to obtain closely reproducible potentials and to decide what value was to be assigned to the oxidation-reduction potential of these inorganic substances under the conditions of our experiments.

In the table are given the results of a number of experiments for dibenzoyl-ethylene; for the other compounds only typical experiments are recorded. These show in most cases the lowest potential at which no appreciable reduction occurred in 30 minutes, the highest potential at which we noted reduction and a case of very rapid reduction. A value somewhere between the first and second cases represents the highest potential at which appreciable reduction would take place under the conditions of the experiment. We have estimated this value by interpolation and

TABLE II

DETERMINATION OF APPARENT REDUCTION POTENTIALS IN 0.2 N HYDROCHLORIC ACID-ACETONE AT 24°

Substance	Red. agent	Volts π°	Change in potential in millivolts			
			5 min.	10 min.	20 min.	30 min.
Dibenzoyl-ethylene (trans)........	A	+0.486	0	0	0	0
	C	+0.304	...	−2	−3	−2
	C	+0.298	0	0	0	0
	D	+0.220	21	21	22	23
	E	+0.223	10	12	15	16
	E	+0.226	2	7	13	14
	F	+0.213	17	19	18	19
	G	+0.161	28	37	45	57
	H	+0.162	...	27	31	33
	I	+0.147	38	60	62	74
		Apparent reduction potential = +0.270				
Di[p-chlorobenzoyl]-ethylene (trans)	C	+0.306	0	−1	−1	−1
	E	+0.225	9	14	21	26
	H	+0.159	...	...	28	35
			App. red. pot. = +0.270			

Table II (*Continued*)

Substance	Red. agent	Volts π°	Change in potential in millivolts			
			5 min.	10 min.	20 min.	30 min.
Ditoluyl-ethylene (trans)	C	+0.304	...	−1	−2	−4
	E	+0.228	9	12	18	19
	G	+0.178	15	23	26	...
			App. red. pot. = +0.270			
Di-[2,4,6-trimethylbenzoyl]-ethylene (trans)	H	+0.161	...	...	2	3
	I	+0.151	...	...	...	0
	$TiCl_3$	+0.007	...	38	41	41
			App. red. pot. = +0.080			
Dibenzoyl-styrene	H	+0.159	...	2	4	7
	$TiCl_3$	+0.046	...	−1	−1	−4
	VCl_2	−0.127	3	3	3	2
			App. red. pot. below −0.130			
Benzoyltrimethyl-acetyl-styrene	VCl_2	−0.171	−1	−3	−3	−4
			App. red. pot. below −0.130			
Benzoyl-acrylic acid	H	+0.157	−1	2	4	...
	$TiCl_3$	+0.042	12	10	...	29
	VCl_2	−0.098	...	100	...	139
			App. red. pot. = +0.080			
Benzoyl-acrylic ester	I	+0.130	...	...	0	0
	$TiCl_3$	+0.003	34	34	...	34
	VCl_2	−0.139	...	56	...	89
			App. red. pot. = +0.080			
Methyl fumarate	$TiCl_3$	+0.010	...	−1	−5	−5
	VCl_2	−0.122	−4	−4	−4	−6
			App. red. pot. below −0.130			
Fumaric acid	VCl_2	−0.114	...	−3	−5	−5
			App. red. pot. below −0.130			
Benzil	H	+0.163	...	−1	0	...
	$TiCl_3$	−0.008	−2	−3	−1	−2
	VCl_2	−0.118	16	66	121	180
			App. red. pot. = −0.070			
Azobenzene	A	+0.488	...	−1	...	−1
	B	+0.410	0	−1	−1	−1
	C	+0.302	43	51	60	...
			App. red. pot. = +0.360			
1,3,5-Trinitro-benzene	C	+0.305	0	1	...	2
	E	+0.225	...	7	13	17
	H	+0.158	73	...	127	129
			App. red. pot. = +0.270			
1,3-Dinitro-benzene	G	+0.174	1	0	0	1
	I	+0.154	2	...	7	9
	$TiCl_3$	+0.085	105	111	124	126
			App. red. pot. = +0.162			
Nitrobenzene	H	+0.159	...	0	0	0
	$TiCl_3$	+0.092	24	29	34	37
			App. red. pot. = +0.080			

have recorded it as the "apparent reduction potential." This potential is probably accurate to within about 25 or 50 millivolts, except in the case of the inorganic reducing agents where the error may be greater. At some later time, when we have a greater choice of reducing agents, it should be possible to determine with greater accuracy the limits between the point at which no reduction occurs and the first point of appreciable reduction.

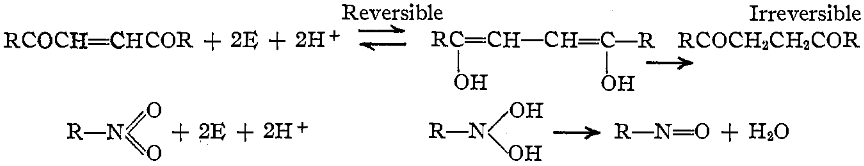
Discussion

The experimental values given above allow certain quantitative statements to be made in regard to the irreversible reductions of the substances investigated. If the sole factor which determines the reducing power of a substance like anthrahydroquinone is its potential, the action of this hydroquinone on any of the substances listed can be predicted from the potential of a particular quinone-hydroquinone mixture and Table II, *provided the experiment is carried out under the same conditions as we have employed.* The fact that we have found no inconsistencies in the action of our diverse series of reducing agents argues for the probability of the potential being the controlling factor in these reductions. The success of the application of the electrochemical point of view to these irreversible processes stands or falls with the consistency or inconsistency of the results obtained with a large number of reducing agents of known potential. We believe that sufficient facts are now at hand to make highly probable the success of the application of this point of view as applied to *reductions in homogeneous solutions.*

If the potential of the reducing agent is the determining factor, the question arises as to the effect of changes in concentration, temperature, solvent, etc., on the "apparent reduction potential." A closely allied problem is the relation between the "apparent reduction potential" and some real oxidation-reduction potential of the irreversible system. The following theory of irreversible reductions is put forward as a working hypothesis to answer these questions. It is based on an analogy with reversible reductions and seems to correlate in a satisfactory manner the experimental results we have obtained; more work, particularly along kinetic lines, will be necessary, however, to prove the correctness of this theory or to furnish the material for constructing another hypothesis if this should be necessary.

A Theory of Irreversible Reductions in Homogeneous Solutions

The irreversible reduction of $C_6H_5COCH{=}CHCOC_6H_5$ to $C_6H_5COCH_2CH_2COC_6H_5$ can be thought of as occurring in two stages, one reversible and one irreversible; the first would be exactly parallel to the reversible reduction of quinones, the other would involve some essentially irreversible process such as isomerization. In the case of dibenzoyl-ethylene this probably would be the change of a di-enol to the stable diketone; in the case of nitrobenzene, the loss of water.



$$RCOCH{=}CHCOR + 2E + 2H^+ \xrightleftharpoons{\text{Reversible}} \underset{OH}{RC}{=}CH{-}CH{=}\underset{OH}{C}{-}R \xrightarrow{\text{Irreversible}} RCOCH_2CH_2COR$$

$$R{-}N\begin{smallmatrix}\diagup O\\ \diagdown O\end{smallmatrix} + 2E + 2H^+ \qquad R{-}N\begin{smallmatrix}\diagup OH\\ \diagdown OH\end{smallmatrix} \longrightarrow R{-}N{=}O + H_2O$$

In general terms we can express these equations as, $B + 2E + 2H^+ \rightleftharpoons BH_2 \longrightarrow C$. According to this hypothesis the first process in every case would be strictly reversible and can be formulated, therefore, in the general terms of oxidation-reduction potentials. The potential between dibenzoyl-ethylene (B) and the di-enol form of dibenzoyl-ethane (BH_2) would be given[5] by an equation similar to Equation 1 above. The potentials of our organic reducing agents are given by the same general equation; the term 0.059 log $[H^+]$ occurs in both equations and, therefore, the equilibrium between the reducing agent and the substances to be reduced should be independent of the hydrogen-ion concentration; we will, therefore, at first neglect this factor in our discussion. When a substance such as a dibenzoyl-ethylene is treated with a reducing agent consisting of a mixture of a quinone and a hydroquinone there will be some reaction between the hydroquinone and the dibenzoyl-ethylene. According to the theory we are now presenting, this reaction will proceed rapidly and reach an equilibrium point. This relatively rapid reaction which comes to a definite equilibrium can be represented in the general terms, $AH_2 + B \rightleftharpoons BH_2 + A$, where A and AH_2 represent the quinone and hydroquinone, BH_2 the di-enol form of the reduced unsaturated ketone. The composition of the equilibrium mixture will depend on the oxidation-reduction potential of the quinone-hydroquinone mixture on the one hand and the potential of the reversible stage of the reduction of the dibenzoyl-ethylene on the other. If the potential of the reducing agent (the hydroquinone mixture) is far above that of the reversible potential of dibenzoyl-ethylene there will be very little of the di-enol form of reduced dibenzoyl-ethylene in the equilibrium; if the two potentials are near together there will be an appreciable fraction of the di-enol form (BH_2) in the equilibrium mixture. This equilibrium condition, however, is very transitory, since the di-enol form of dibenzoyl-ethane is continuously rearranging into the diketone form at a rate which is given by Equation 2.

$$\frac{dx}{dt} = k([BH_2]-x) \qquad (2)$$

A further reaction between the hydroquinone (AH_2) and dibenzoyl-ethylene (B) takes place at *this same rate* in order to compensate for the removal of BH_2 from the equilibrium. In the experiments which we are considering it is very probable that the first rapid reaction which results in the initial

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[5] The correction for differences in solubility and the changes which occur in alkaline solution are neglected in this discussion. Compare Ref. 1g.

equilibrium involves such a slight change as to be experimentally negligible, and that the reduction which is observed is the relatively slow reaction between the hydroquinone and the unsaturated diketone that follows and keeps pace with the isomerization of the di-enol. Since this relatively slow reduction proceeds at the same rate as the rearrangement of the di-enol form, its speed is dependent on the value of k in Equation 2, and the concentration of the di-enol form in the equilibrium mixture ($[BH_2]$ in Equation 2). This last factor in turn depends on the difference between the potentials of the reducing agent and the reversible stage of the irreversible reduction. Since we have not as yet been able to determine either the value for k or the potential of the reversible stage of these irreversible reductions, we cannot now apply this theory quantitatively to our experiments. We hope to do this at some later time.

Qualitatively, the considerations outlined above are useful in that they enable us to form a clear picture of what may be the cause of the behavior of unsaturated ketones towards reducing agents of different potential. For example, at a potential of +0.301 there is no reduction of dibenzoylethylene apparent in 30 minutes; according to our theory this is because the amount of the di-enol form present in the equilibrium mixture is so small that no appreciable amount of it will have isomerized during the 30 minutes, in spite of its probably high rate of rearrangement, and consequently no appreciable amount of substance will have been reduced. At a lower potential, such as +0.237, there is a much larger amount of the di-enol in the equilibrium, and this quantity is sufficient to show an appreciable isomerization and consequent reduction within the time of our experiment. There is no sharp line between these two cases, of course, but it can be shown from the shape of the potential curves that the amount of the di-enol in the equilibrium mixture decreases so rapidly with increasing differences in potential that one would expect a fairly definite experimental transition between reducing agents which cause reduction and those which do not.

The rate of the irreversible isomerization must be constant for any substance under given experimental conditions, but would be expected to vary with changes in temperature, solvent and the absence or presence of catalysts. Such possible variations in the value of k in Equation 2 make it unsafe to assume that results obtained under different experimental conditions are comparable. Thus, a reducing agent of a certain potential might in one solvent cause an "appreciable reduction" while in another solvent the value of k might be so much smaller that no reduction could be experimentally detected. We have carried out a few experiments in this direction by determining the "apparent reduction potential" of several compounds in alcoholic solution, as well as in the acetone solution. The results are summarized in Table III.

TABLE III

APPARENT REDUCTION POTENTIALS IN 0.2 N HYDROCHLORIC ACID-ALCOHOL

Substance	Red. agent	Volts π°	Change in potential in millivolts 5 min.	10 min.	20 min.	30 min.
Dibenzoyl-ethylene (trans)	A	+0.502	0	0	0	0
	C	+0.301	0	0	0	0
	E	+0.237	11	15	19	21
	I	+0.156	46	59	68	..
			App. red. pot. = +0.270			
Dibenzoyl-ethylene (cis)	A	+0.503	−1	−1	0	...
	C	+0.300	−1	−2	−3	−4
	E	+0.233	7	11	15	...
	I	+0.170	35	47	63	75
			App. red. pot. = +0.270			
Di [*p*-chlorobenzoyl]-ethylene (cis)	C	+0.302	−1	−1	−2	−1
	E	+0.227	2	4	9	12
	I	+0.147	7	11	18	20
			App. red. pot. = +0.270			
Ditoluyl-ethylene (trans)	C	+0.298	0	0	−1	0
	E	+0.227	4	6	10	12
	I	+0.151	...	33	62	...
			App. red. pot. = +0.270			
Di- [2,4,6 - timethylbenzoyl]-ethylene (trans)	I	+0.148	1	2	3	3
	TiCl$_3$	+0.034	...	137	213	...
			App. red. pot. = +0.080			
Benzil	I	+0.149	0	0	0	...
	TiCl$_3$	−0.031	37	85	128	178
			App. red. pot. = +0.080			
Methyl fumarate	I	+0.157	2	...	2	...
	TiCl$_3$	+0.000	0	0	0	...
			App. red. pot. below TiCl$_3$			
Fumaric acid	TiCl$_3$	+0.023	...	−3	−2	−1
			App. red. pot. below TiCl$_3$			
Benzoyl-acrylic acid	I	+0.156	0	0	2	...
	TiCl$_3$	+0.004	18	37	61	76
			App. red. pot. = +0.080			
Benzoyl-acrylic ester	I	+0.142	0	0	1	...
	TiCl$_3$	+0.034	18	37	63	80
			App. red. pot. = +0.080			
1,3,5-Trinitro-benzene	C	+0.285	0	0	0	0
	E	+0.220	10	18	28	38
	G	+0.176	45	83	102	111
			App. red. pot. = +0.270			
1,3-Dinitro-benzene	G	+0.175	1	0	0	1
	I	+0.151	7	10	18	26
	TiCl$_3$	+0.026	187	230	269	...
			App. red. pot. = +0.162			

A comparison with Table II shows that only in the case of benzil is there sufficient difference to affect the "apparent reduction potential" as we have at present measured it. Doubtless more accurate work may reveal further changes. A few experiments were carried out at 45° and essentially the same results were obtained as at 24°. Thus it seems as if the influences of solvent and temperature are not as great as might have been expected.

It is conceivable that the reversible stage of the irreversible reduction might involve only an electron transfer, the irreversible step being the addition of two hydrogen ions, $B + 2E \rightleftharpoons B^{--} + 2H^+ \longrightarrow C$. In this case the true potential would be given by Equation 3 in which the concentration of the hydrogen ion does not occur.

$$\pi = \pi_0 + 0.0295 \log \frac{[B]}{[B^{--}]} \qquad (3)$$

As we have pointed out above, the potential of our organic reducing agents is a function of the hydrogen-ion concentration (Equation 1); therefore, if Equation 3 represented the reversible stage of the reduction, the "apparent reduction potential" would not depend on the hydrogen-ion concentration. We have been unable to put this question to a successful experimental test in our acetone solutions as we have not been able to prepare suitable "buffer solutions" of a definite hydrogen-ion activity. A few experiments seemed to indicate that the interaction of the irreversibly reduced substance and the hydroquinone was independent of the hydrogen-ion concentration, as would be expected if Equation 1 held for the reversible phase. We are now starting an investigation of the irreversible reduction of certain water-soluble substances, and by working in aqueous solution of known hydrogen-ion concentration we hope to obtain a definite answer to this question.

Thus, by postulating that the irreversible reduction of organic substances in homogeneous solution proceeds in two stages we have been able to construct a theory which qualitatively accounts for the observed facts and serves as a basis for a possible future quantitative explanation. The same point of view may prove useful in interpreting other *irreversible* organic reactions which take place only after the reacting system has reached a certain "potential." We hope to show in a later paper that many cases of irreversible oxidation can be treated in this way; probably certain cases of irreversible addition and elimination reactions can also be profitably considered as proceeding through a reversible stage.

Reduction of Carbonyl Compounds

The results obtained place the unsaturated carbonyl compounds investigated[6] in the three following groups.

$$\left.\begin{array}{l} C_6H_5COCH{=}CHCOC_6H_5 \text{ (cis and trans)} \\ CH_3C_6H_4COCH{=}CHCOC_6H_4CH_3 \\ ClC_6H_4COCH{=}CHCOC_6H_4Cl \end{array}\right\} \text{App. red. pot.} = +0.270$$

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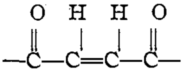
[6] The preparation of the unsaturated 1,4 diketones employed and a study of their reduction to the saturated 1,4 diketones by sodium hydrosulfite will be given in a future paper.

$$\left.\begin{array}{l}(CH_3)_3C_6H_2COCH{=}CHCOC_6H_2(CH_3)_3\\ C_6H_5COCH{=}CHCOOH\\ C_6H_5COCH{=}CHCOOC_2H_5\end{array}\right\}\text{App. red. pot.} = +0.080$$

$$\left.\begin{array}{l}C_2H_5OOCCH{=}CHCOOC_2H_5\\ HOOCCH{=}CHCOOH\\ C_6H_5COC(C_6H_5){=}CHCOC_6H_5\\ C_6H_5COC(C_6H_5){=}CHCOC(CH_3)_3\end{array}\right\}\text{App. red. pot. below } -0.130$$

The last group should be further subdivided, as Mr. Cutter in this Laboratory[7] has shown that the first two are rapidly reduced by chromous chloride (about —0.300) while the last two are not.

The relationship shown above is qualitatively what would be expected from our general knowledge of the reactivity of carbonyl compounds. The simple diketones are more easily reduced than the ketonic acid or ester and these substances in turn are more easily reduced than the dibasic acid or its ester; this is in agreement with the general reactivity of ketones, esters and acids. The extreme difficulty of reducing the diketones with an α-phenyl group is perhaps surprising, but some lowering of the apparent reduction potential would be expected from our knowledge of the effect of an α-phenyl group on addition reactions of ketones and the low oxidation-reduction potential of naphthoquinone as compared with benzoquinone. The lowering of the apparent reduction potential of dibenzoyl ethylene from +0.270 to +0.080 by introducing 3 methyl groups in the *ortho* and *para* positions of each phenyl group is in accordance with the lack of reactivity of the ketonic group in acetomesitylene, $CH_3COC_6H_2(CH_3)_3$. It should be noted that the cis and trans forms of the unsaturated ketones have the same "apparent reduction potential" within our present experimental error.

According to the views here presented, the difference between a quinone (reversibly reduced) and an unsaturated 1,4 diketone (reduced irreversibly) is to be traced to the relative stabilities of the di-enol (phenolic) forms. In general, it may be said that any compound containing the linkage  $-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{C}=\overset{\overset{H}{|}}{C}-\overset{\overset{O}{\|}}{C}-$ is reversibly reduced if the reduced form exists in a stable di-enol form. This generalization seems to be without exception when the entire class of quinones, indigoids and vat dyes is examined. It is probably unnecessary for the reduced form to be wholly enolic, but the equilibrium between the enol and keto forms would have to be mobile and the enolic form would have to be present in the equilibrium in sufficient amounts to cause the formation of metallic derivatives stable in solution.

The Reduction of Nitrogen Compounds

It is very important to establish at the outset whether or not a given reduction is reversible or irreversible. Evidence on this point can be

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[7] Unpublished results.

obtained by determining whether or not mixtures of the oxidized and reduced compounds give reproducible potentials which are in accord with the usual electrochemical equation. Another method is to investigate the behavior of the substance when titrated with a reducing agent according to Clark's method; when the potentials are constant and reproducible for each increment of reducing agent and lie on a smooth curve, the substance is very probably reversibly reduced. We have applied these tests to the substances mentioned in Table II and have established that their reduction is irreversible.

We have examined nitroso-benzene and nitroso-β-naphthol and found them to be reversibly reduced, though in the case of the latter compound we have not yet isolated the reduction product. The normal oxidation reduction potential at 25° for nitroso-benzene in 0.2 N hydrochloric acid-acetone was found by the titration method to be +0.605. An equimolecular mixture of phenyl-hydroxylamine and nitroso-benzene in the same solvent gave a definite potential which corresponded to a value of +0.606 ±0.005 for the normal oxidation-reduction potential. The value for nitroso-β-naphthol was found to be +0.523 ± 0.002. Since these potentials are measured against a quinhydrone electrode in the same solvent with the same acid concentration, these potentials are the values for π_0 (Equation 1) for these substances. The reversible reduction potentials of such compounds will be reported in more detail in another paper.

The apparent reduction potentials of the nitrogen compounds that are *irreversibly* reduced which we have investigated are as follows.

	App. red. pot.		App. red. pot.
Azobenzene[8]	+0.360	Dinitro-benzene	+0.162
1,3,5-Trinitro-benzene	+0.270	Nitrobenzene	+0.080

A discussion of the significance of this series of results and the connection between them and methods of reducing aromatic nitrogen compounds will be reserved for a later paper. We are now studying the reduction of a number of similar compounds including such water-soluble substances as the azo dyes, and we hope to present more complete data along these lines in a subsequent paper.

We wish to express our indebtedness to the Cyrus M. Warren Fund of the American Academy of Arts and Sciences for the electrical apparatus used in this work.

Summary

1. An electrochemical method of investigating the irreversible reduction of organic substances in homogeneous solution has been developed.

2. An upper potential limit for the reduction of certain substances under specified conditions in acetone and alcoholic solutions has been determined.

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[8] There is some possibility of this reduction being slowly reversible. This point is under investigation.

This "apparent reduction potential" is in every case, except one, essentially the same in the two solvents.

3. A theory of irreversible reductions has been put forward which connects the "apparent reduction potential" with a true oxidation-reduction potential of the substance in question.

4. A series of unsaturated carbonyl compounds has been studied. The results show that the potential at which the substance is irreversibly reduced is approximately proportional to the reactivity of the carbonyl group.

5. The reduction of nitroso-benzene to phenyl-hydroxylamine has been shown to be reversible and the potential has been measured.

6. A series of nitrogen compounds, which are irreversibly reduced, has been studied and preliminary values for their "apparent reduction potential" established.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

DERIVATIVES OF 2,4-DINITRO-BENZALDEHYDE. III

BY THOMAS B. DOWNEY[1] WITH ALEXANDER LOWY

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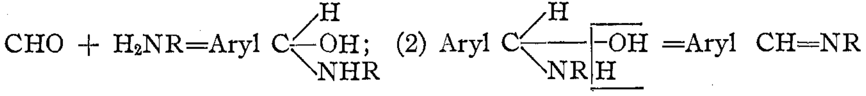
In the two previous reports,[2] the object of the research and references to the literature were given.

In the present study of 2,4-dinitro-benzaldehyde, two types of condensation reactions were investigated. The first type was the reaction between 2,4-dinitro-benzaldehyde and different aromatic amines producing the class of compounds known as "Schiff bases."[3] The reaction proceeds in two steps as represented by the following general equations: (1) Aryl



$$\text{CHO} + \text{H}_2\text{NR} = \text{Aryl C}\begin{cases}\text{H}\\ \text{OH}\\ \text{NHR}\end{cases};\quad (2)\ \text{Aryl C}\begin{cases}\text{H}\\ \text{—}\boxed{\text{–OH}}\\ \text{NR}\boxed{\text{H}}\end{cases} = \text{Aryl CH=NR}$$

$+H_2O$. In most cases, it was not found possible to isolate the intermediate addition product due to its tendency to eliminate water, as shown by Equation 2. However, the addition product of 2,4-dinitro-benzaldehyde and *o*-tolidine was isolated from a 95% alcoholic solution. The addition reaction takes place slowly even in an aqueous solution, while in the presence of acetic acid the condensation product is formed. Condensation products were formed by using 2,4-dinitro-benzaldehyde and the following substituted amines in unimolecular proportions: *o*-chloro-aniline, *p*-chloro-aniline, 2,4-dichloro-aniline, *p*-amino-azobenzene and *o*-tolidine.

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[1] This report is the abstract of a thesis presented by Thomas B. Downey, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] THIS JOURNAL, (a) **42,** 849 (1920); (b) **43,** 346 (1921).

[3] *Ber.,* **35,** 984 (1902).