Calcd. for $C_6H_{14}O_2$: C, 60.97; H, 11.94. Found: C, 60.84; H, 12.04.

The Solubility Data.—The method of procedure was the same as that described in a previous paper.[14] The data are recorded in Table I and Fig. 1.

TABLE I

SOLUBILITY OF THE ISOMERIC *n*-PROPYL ETHERS OF 1,2-PROPYLENE GLYCOL IN WATER

1-Propoxy-propane-2-ol			2-Propoxy-propane-1-ol		
Ether, % by wt.	Lower soln., temp., °C.	Upper soln., temp., °C.	Ether, % by wt.	Lower soln., temp., °C.	Upper soln., temp., °C.
10.7	75.0	125.5	12.1	76.0	126.0
13.1	57.7	145.0	14.9	57.2	143.5
14.9	49.8	154.0	20.0	47.2	156.0
20.0	39.5	165.5	25.4	43.8	161.0
24.8	35.9	170.0	30.0	42.8	162.0
35.5	34.5	171.7	40.5	43.4	161.5
45.2	35.0	171.2	50.3	44.7	159.5
55.0	36.6	168.0	60.0	48.7	151.5
60.4	39.3	162.0	66.2	56.0	138.0
65.2	42.7	155.5	69.3	64.7	126.0
69.7	49.3	144.0	..	..	...
74.7	71.0	114.0	..	..	...

Summary

The isomeric *n*-propyl ethers of 1,2-propylene glycol have been prepared. Solubility data for these ethers and water have been determined.

PITTSBURGH, PENNSYLVANIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE IRREVERSIBLE REDUCTION OF ORGANIC COMPOUNDS

IV. THE APPARENT REDUCTION POTENTIAL OF UNSATURATED CARBONYL COMPOUNDS

BY JAMES B. CONANT AND ROBERT E. LUTZ

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In a preliminary paper published a few years ago[1] we outlined a convenient and rapid method of studying the *irreversible* reduction of organic compounds. By an electrochemical device, it was possible to decide what reversible reducing agents of a graded series would reduce a given compound. It was found that with the compound studied, the oxidation-reduction potential of the reagent appeared to be the governing factor. The method has since been applied to the study of the irreversible reduction of a variety of compounds, particularly in aqueous solution.[2] In this paper we shall report the results of a further study of unsaturated

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[14] Ref. 11, p. 452.

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

[2] Conant and Pratt, *ibid.*, **48**, 2468 (1926).

1,4 diketones and certain other carbonyl compounds and attempt to correlate "ease of reduction" with chemical constitution.

Since the carbonyl compounds in which we were interested were for the most part insoluble in water, we have employed a mixture of acetone and hydrochloric acid as a solvent. The series of reversible reducing agents which are now available for use in such a solvent are listed in Table I. With the exception of the three last, these are either leuco forms of dyestuffs or hydroquinones; when they function as reducing agents they are oxidized during the reaction to the corresponding dye or quinone, respectively. For reasons which have been discussed in earlier papers, an equimolecular mixture of the reducing agent and its oxidized form was always employed.[3] This was prepared as needed by the titration of the oxidized form of the reagent (for example, the quinone) with titanous chloride, the titration being continued only to the point of half reduction. The potential of the resulting mixture of leuco compound and dye or hydroquinone and quinone was compared with the quinhydrone potential by measuring the e.m.f. of the following cell at 25°: Pt | quinhydrone solvent | solvent | equimolecular mixture of the quinone and hydroquinone | Pt. (The solvent was 75% acetone, 25% water with a total concentration of 0.2 *M* hydrochloric acid.)

In order to express the potential in terms of the hydrogen electrode in the same solvent, we have assumed a value for the quinhydrone electrode of + 0.711, the value actually measured in alcoholic solution. We were not able to use the hydrogen electrode in our acetone solutions and were therefore forced to this approximation which can hardly be in error by more than a few millivolts.

It should be noted that the normal potential thus estimated is the potential of an equimolecular mixture of oxidized and reduced reagent against a hypothetical hydrogen electrode *in the same solvent.* Such potentials we have referred to elsewhere as normal reduction potentials[4] and we have shown that with a number of quinones the values obtained in water, aqueous alcohol and aqueous acetone are not very different. In aqueous solution they correspond to the normal potential (referred to the hydrogen electrode) at $P_H = 0$. If it were possible at present to evaluate the hydrogen-ion activity of 0.2 *N* hydrochloric acid in aqueous acetone, we should refer all the potentials given in this paper to the normal hydrogen electrode ($P_H = 0$) in aqueous acid. Since this is not yet possible, we shall arbitrarily take the hydrogen electrode in 0.2 *M* hydrochloric acid-acetone as our aqueous *acetone* standard and refer all the potentials to this basis. This is in effect what we have done by measuring and defining the normal potential as stated above.

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[3] Compare Conant, *Chem. Rev.*, **3**, 1 (1926).

[4] Conant and Fieser, THIS JOURNAL, **46**, 1858 (1924).

As in all our other work, the rate of reduction of the compound in question was followed by noting the change in potential of the reducing mixture to which it was added. The electrochemical cells were identical with those previously described. The quinhydrone electrode in the same hydrochloric acid-acetone mixture formed the other half cell. The temperature was 24° ± 2°.

Table I

Oxidation-Reduction Potentials of Equimolecular Amounts of Oxidant and Reductant Compared to the Hypothetical Hydrogen Electrode in the Same Solution (0.2 *N* Hydrochloric Acid-Acetone)

Symbol	Compound (oxidized form)	Oxidation-reduction potential, v.
A	Methylene blue	+0.491
B	1,4-Naphthoquinone	.433
C	Retenequinone	(.410)
D	Indigo tetrasulfonate	.354
E	Indigo disulfonate	.311
F	Anthraquinone-2,6-disulfonate	(.226)
G	Anthraquinone-2,7-disulfonate	.218
H	2,7-Dichloro-anthraquinone	.223
I	Naphthanthraquinone	.219
K	1-Chloro-anthraquinone	.166
L	Anthraquinone	.155
M	2-Methylanthraquinone	.142
T	Titanous chloride	(− .020)
V	Vanadous chloride	(− .150)
Cr	Chromous chloride	....

Values in parentheses are somewhat uncertain.

Chromous chloride ("Cr") was not used in any electrometric determination. Its potential is of the magnitude of —0.40 v. Reduction by this agent was indicated by a sharp color change.

The difficulties of measuring electrode potentials in solvents containing but little water are so great that we have not attempted to treat the results from the standpoint of the rate equations developed in the third paper of this series. We have contented ourselves merely with determining what reagents produced a rapid reaction and what reagents were without perceptible action in 30 minutes. Our probable error was 2 or 3 mv., which corresponds to about 8% reduction; our statement that a reagent is without perceptible action, therefore, means that not more than 8% reduction occurred in 30 minutes.

In every experiment the concentration of materials was as follows: oxidized form of the reagent, 0.001 *M;* reduced form of the reagent, 0.001*M;* material being examined, 0.002 *M*. In several experiments with dibenzoylethylene and di-(2,4-dimethyl)-benzoylethylene, the concentration of the reagent and material was increased 10-fold without materially affecting the results. We may thus conclude that the rate of the irreversible process is essentially independent of the dilution as in the case of the reduction of the azo dyes.[1]

The experimental results are given in Table II. The letters refer to the reagents listed in Table I. We have estimated the potential of the reagent which would just cause 20–30% reduction in 30 minutes and defined the potential of such a hypothetical reagent as the "apparent reduction potential" of the compound under investigation. In the present work we have arbitrarily taken the value of the apparent reduction potential (A.R.P.) as being halfway between the potentials of the weakest reducing agent which causes reduction and the next above in our series, which causes no appreciable reaction. Between values of + 0.35 and + 0.14, we are fortunate enough to have a series of reagents which enable us to estimate thus the A.R.P. within + 0.01 to + 0.03 v.; below + 0.14 there are only

TABLE II

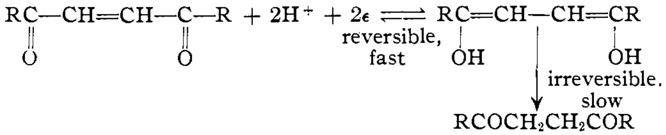
DETERMINATION OF THE APPARENT REDUCTION POTENTIAL IN 0.2 *M* HYDROCHLORIC ACID-ACETONE SOLUTION AT 24° ±2°

Substance	Not reduced by	Reduced by	A.R.P.
Di-[α-naphthoyl]-ethylene	E, (I)[a]	M, T, V	+0.22
Di-[4-chloro-5-methylbenzoyl]-ethylene	E, (I)[a]	G, T	+ .22
Dibenzoylacetylene	I	M, T	+ .18
Di-[2,4-dimethylbenzoyl]-ethylene	F, G, M	T, V	+ .06
Di-[2,4,6-trimethylbenzoyl]-ethylene	L, M	T, V	+ .06
Di-[2-chloro-5-methylbenzoyl]-ethylene	F, M	T, V	+ .06
Dibenzoylchloro-ethylene (β)	I, M	T	+ .06
Dibenzoylchloro-ethylene (α)	M	T	+ .06
Dibenzoylbromo-ethylene	M	T	+ .06
Dibenzoyldichloro-ethylene (α)	M	T	+ .06
Dibenzoyldichloro-ethylene (β)	M, T	V	− .10
Dibenzoyldibromo-ethylene (α)	M	T	+ .06
Dibenzoyldibromo-ethylene (β)	M	T	+ .06
Dibenzoylamino-ethylene	I,M	T, V	+ .06
Di-[4-methylbenzoyl]amino-ethylene	M	T	+ .06
Dibenzoylhydroxy-ethylene	M	T, V	+ .06
Dibenzoylmethoxy-ethylene	M	T, V	+ .06
Dibenzoylethoxy-ethylene	M	T, V	+ .06
Dibenzoylphenoxy-ethylene	M, T	V	− .10
Dibenzoyl[4-methylphenoxy]-ethylene	M, T	V	− .10
Ethylene tetracarbonic ester	M, T	V	− .10
Acetylene dicarbonic acid	V	Cr	ca. − .3
Diacetylfumaric ester	I, M	T, V	+ .06
Dibenzoylmaleic ester	I, M	T, V	+ .06
1,2-Dibenzoylcyclopropane	V, Cr	...	below − .4
1,2-Dibenzoylcyclobutane	Cr	...	below − .4

[a] These reagents produced very slow reduction and were regarded as "border-line cases." The A.R.P. was taken in these cases as being that of these reagents.

three reagents differing by about + 0.1 v. and the interpolation is correspondingly inaccurate.[5]

The carbonyl compounds which we have examined in this study all have the grouping —CO—C=C—CO—, which is also present in the quinones, indigoids and other compounds which undergo *reversible* reduction. According to the theory put forward in an earlier paper (Ref. 1), this conjugated dicarbonyl system is reduced by *soluble reducing agents* by the addition of two hydrogen atoms to the ends of the system. This process we imagine to be strictly reversible in all cases, and probably involves the simultaneous addition of 2 electrons and 2 hydrogen ions. The resulting di-enol may be stable; in this case the entire process is reversible, as in the case of quinone, since the hydroquinone (the di-enol) may be easily oxidized (dehydrogenated). If the di-enol is unstable and rearranges irreversibly to a saturated diketone, we have the case of the irreversible reduction of dibenzoylethylene. Such a mechanism accounts for all the known facts in regard to the behavior of such systems on reduction. If we imagine the reversible step to be fast and the irreversible ketonization to be relatively slow, an explanation of the success of the electrochemical formulation is at hand. The speed of the entire reaction depends on the amount of di-enol; this in turn is a function of the reducing agent.[4]



$$\underset{\underset{O}{\|}}{RC}-CH=CH-\underset{\underset{O}{\|}}{C}-R + 2H^+ + 2\epsilon \underset{\text{reversible, fast}}{\rightleftharpoons} \underset{\underset{OH}{|}}{RC}=CH-CH=\underset{\underset{OH}{|}}{CR} \xrightarrow[\text{slow}]{\text{irreversible,}} RCOCH_2CH_2COR$$

The Relation between Structure and the A.R.P. of Substituted Dibenzoylethylenes

In Table III we have collected the data published in our first paper and those given in Table II, in regard to the A.R.P. of unsaturated 1,4 diketones. From Section 1 of this table, it is evident that *para* substitution by methyl or chlorine is without effect, but that *ortho* substitution of these groups lowers the A.R.P. In terms of our theory, the effect of this substitution might act in two ways. The potential of the reversible step might be affected or the rate of the irreversible ketonization. There is at present no way of measuring these two effects separately, but we are inclined to believe that the latter is by far the most important in the case of the diaryl unsaturated diketones listed in Group I. The known effects of nuclear substitution on the potential of reversible systems would indicate that most of the changes noted above are too large to be accounted for in terms of a change of potential of the reversible step. We suggest that substitu-

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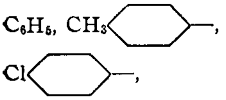
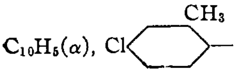
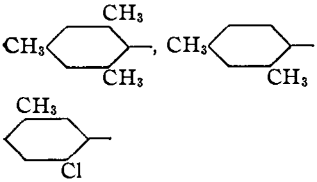
[5] For a more accurate method of formulating the A.R.P. when the actual rates of reduction can be followed (as in aqueous solution), see Ref. 2.

tion of a hydrogen by a larger atom or group in the *ortho* position decreases the rate of ketonization for much the same reason that similar substitution lowers the rate of addition reactions of carbonyl compounds. Such an effect is usually classed as steric hindrance.

TABLE III

THE RELATION BETWEEN STRUCTURE AND A.R.P. OF UNSATURATED 1,4 DIKETONES

(1) General formula, ACOCH=CHCOA

Group A	A.R.P.
 C_6H_5,	+0.27
 $C_{10}H_5(\alpha)$,	+ .22
	+ .06

(2) General formula, $C_6H_5COCR_1{=}CR_2COC_6H_5$

R_1	R_2	A.R.P.
H	Cl, Br, NH_2 OH, OCH_3, OC_2H_5	+0.06
H	OC_6H_5, $OC_6H_4CH_3$	− .10
H	C_6H_5	below − .4[a]
Cl or Br	Cl or Br	+ .06
$COOC_2H_5$	$COOC_2H_5$	+ .06

[a] Reduced by zinc and acetic acid.

It is interesting to examine the consequences of our theory in terms of the potential of the reversible step. We should imagine that the real oxidation-reduction potential of the system, unsaturated diketone-di-enol (the reversible step), might be about —0.03 v. If this were the case and the effects of substitution of this potential were negligible, the amount of di-enol formed in the reversible step with the critical reducing agent can be estimated by the approximate equation given below,[6] where X is the fraction of diketone reduced to the di-enol by the almost instantaneous reversible process: pot. of reversible step minus pot. of critical reducing agent (A.R.P.) = 0.03 log X. In the case of substances with an A.R.P. of about + 0.27 (for example, dibenzoylethylene itself), X would be about 10^{-10}; with the least easily reduced derivative (A.R.P., + 0.06), X would be about 5×10^{-2}. Since the actual rate of reduction is the same for all the critical reagents (by definition about 30% in 30 minutes), the actual rates of ketonization would vary in these cases by 10^{-8}. In this illustration we have assigned the value —0.03 to the potential of the reversible step merely for purposes of illustration. It cannot be higher than the lowest A.R.P. of the series of related compounds (+ 0.06), but we have no way of estimating how much lower it may be.

In the case of the compounds listed in Group 2, Table III, it is probable

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[6] See Ref. 3, p. 17, Equation 8.

that the substitution of the α-hydrogen atom affects *both* the potential of the reversible step and the rate of ketonization. If we include the α-phenyl derivative we should have to assign a value for the reversible step below —0.4 v. in this case. However, we should be unwilling to state that the reduction of this compound or the cyclic compounds is susceptible to an electrochemical formulation. With these compounds, soluble reducing agents may fail to act because the reversible 1,6 addition is no longer a rapid or even possible process. Their reduction with zinc and acid may proceed by an entirely different mechanism.[7] There seems to be no way at present to settle this problem of the reduction of compounds which are not attacked even by chromous chloride.

The compounds which fall in Group 1 of Table III are all reduced to the corresponding ethanes by those reducing agents which are effective. The same is true of many of the substances of Class 2 in Table III, but the halogen and amino compounds are reduced by titanous chloride with loss of hydrogen halide (or ammonia). The probable mechanism of this reaction has been discussed in an earlier paper from this Laboratory,[8] which also deals with the preparation of many of the compounds listed in Table II.

It is interesting to compare the behavior of dibenzoylethylene, dibenzoylacetylene, dibenzoylcyclopropane and dibenzoylcyclobutane, even if the reduction mechanism of the last two may be different from that of the others. The "ease of reduction" of these substances is in the order given. The A.R.P. of dibenzoylethylene is + 0.27, of dibenzoylacetylene + 0.18, while the two cyclic compounds are not reduced even by chromous chloride (pot., —0.4). It is possible to differentiate between the compound containing the three-membered ring and the cyclobutane derivative, since the former is readily reduced to 1,3-dibenzoylpropane by boiling with zinc and acetic acid. Under similar conditions the cyclobutane compound is not attacked.

Experimental Part

Preparation of Materials

The unsaturated 1,4 diketones and their derivatives which were used in this work were carefully purified specimens of the substances whose preparation has been already described in a series of papers from this Laboratory.[8,9]

Dibenzoylacetylene, ethylene-tetracarbonic ester, acetylene-dicarbonic acid, diacetylfumaric ester and dibenzoylmaleic ester were all prepared by the standard methods given in the literature. They were all crystalline solids which were readily purified by repeated crystallization.

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[7] Compare Conant and Cutter, *J. Phys. Chem.*, **28**, 1096 (1924).

[8] Conant and Lutz, THIS JOURNAL, **47**, 881 (1925).

[9] Conant and Lutz, *ibid.*, **45**, 1303 (1923).

Preparation of Dibenzoylcyclopropane and Dibenzoylcyclobutane

1,3-Dibenzoyl-1,3-dibromopropane.—Dibenzoylpropane was prepared by the Friedel-Crafts reaction from glutaryl chloride[10] and was brominated with 4 moles of bromine in chloroform. The resulting solid was crystallized from alcohol. Ten g. of dibenzoylpropane yielded 9.7 g. of product; m. p., 115–115.5°.

Anal. Calcd. for $C_{17}H_{16}O_2Br_2$: Br, 39.0. Found: 38.8.

ISOMERIC DIBROMIDE.—An isomeric dibromide was isolated from the mother liquors. It melted at 89°. Unlike the dibromide which melted at 115°, it did not yield a cyclopropane compound on treatment with zinc and sodium iodide.

Anal. Calcd. for $C_{17}H_{16}O_2Br_2$: Br, 39.0. Found: 39.0.

1,2-Dibenzoylcyclopropane.—The dibromide melting at 115° was dissolved in purified acetone and warmed with a mixture of zinc dust and sodium iodide. After ten minutes' boiling, the mixture was filtered and diluted with water. The product was recrystallized with some difficulty from alcohol and after several crystallizations melted at 103–104°; yield, 24%.

Anal. Calcd. for $C_{17}H_{14}O_2$: C, 81.5; H, 5.6. Found: C, 81.1; H, 6.0.

The substance was reduced to dibenzoylpropane (identified by mixed-melting-point determination) on boiling for half an hour with zinc dust and glacial acetic acid. A solution of it in pure acetone did not decolorize a dilute solution of potassium permanganate in the same solvent.

1,4-Dibenzoyl-1,4-dibromobutane.—Dibenzoylbutane was prepared from adipyl chloride and benzene by the Friedel-Crafts reaction.[11] On bromination in chloroform it yielded two isomeric dibromides. The one obtained in larger amount could be transformed into a cyclic compound. It was therefore assigned the structure of a 1,4 dibromide. By using 4 moles of bromide, a 41% yield of this dibromide was obtained. It was purified by recrystallization from alcohol; m. p., 171°.

Anal. Calcd. for $C_{18}H_{18}O_2Br_2$: Br, 36.5. Found: 37.0.

ISOMERIC DIBROMIDE.—This compound was obtained in the mother liquors; m. p., 96°.

Anal. Calcd. for $C_{18}H_{18}O_2Br_2$: Br, 37.0. Found: 36.7.

1,2-Dibenzoylcyclobutane.—Two g. of the dibromide, m. p. 171°, was heated under a reflux condenser in acetone with 4 g. of zinc dust and 3 g. of sodium iodide for 30 minutes. The solution was filtered and diluted with water. After several recrystallizations from alcohol, 0.5 g. of material was obtained; m. p., 163°. Dibenzoylbutane was isolated from the mother liquors.

Anal. Calcd. for $C_{18}H_{16}O_2$: C, 81.75; H, 6.1. Found: C, 81.6; H, 6.3.

The substance did not decolorize a dilute solution of potassium permanganate in acetone. It was slowly attacked by bromine in chloroform solution with the evolution of hydrogen bromide. It was heated for two hours with zinc dust and acetic acid and after filtration and precipitation with water was recovered unchanged. The action of sodium amalgam yielded a resinous oil which failed to crystallize.

Summary

1. The apparent reduction potential of a series of unsaturated 1,4 diketones and related substances has been measured in acetone solution containing hydrochloric acid.

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[10] Auger, *Ann. chim. phys.*, [6] **22**, 358 (1891).

[11] Etaix., *ibid.*, [7] **9**, 370 (1896).

2. The substitution of groups in the *ortho* positions in the aromatic nuclei of dibenzoylethylene lowers the apparent reduction potential. The substitution of the α-hydrogen atom in the same compound by a variety of atoms or groups has the same effect.

3. Dibenzoylcyclopropane and dibenzoylcyclobutane have been synthesized. Neither compound is reduced by chromous chloride, but the former is reduced by boiling with zinc and acetic acid.

CAMBRIDGE 38, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA]

THE REACTION BETWEEN DICHLORO-ACETIC ACID AND AROMATIC AMINES

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In 1923 one of us[1] published a paper in which we stated that not only did dichloro-acetic acid react with aniline and similar amines to form salts, but also that salts of trichloro-acetic acid were formed if the amount of acid was increased and the temperature of the reaction allowed to rise. The trichloro-acetates of aniline, *o*-toluidine, *p*-toluidine, α-naphthylamine and *m*-nitro-aniline, were described as having been obtained from dichloro-acetic acid. These results were checked up by preparing the trichloro-acetates from trichloro-acetic acid. We supposed that two molecules of dichloro-acetic acid shifted to one molecule of monochloro-acetic acid and one of trichloro-acetic acid. To show that this could happen we treated *p*-nitro-aniline with dichloro-acetic acid in the presence of phosphorus pentoxide and obtained a solid product which was found to consist of *p*-nitro-monochloro-acetanilide and *p*-nitrotrichloro-acetanilide. In 1925 Doughty[2] repeated our experiments but was unable to obtain the trichloro-acetates from dichloro-acetic acid. We thereupon repeated our own experiments and were also unable to obtain the trichloro-acetates. This has greatly puzzled us because in carrying out our original work we felt we had taken every care to check up our observations. We purified our dichloro-acetic acid by redistillation, using that portion boiling at 191°. We also carefully examined the trichloro-acetate (1) by decomposing it with sodium hydroxide and obtaining aniline and (2) by treating an alcoholic solution with sulfuric acid, obtaining the ethyl ester of trichloro-acetic acid which was converted into the amide; m. p., 141°. Also, the analysis for chlorine gave excellent figures for three atoms: calculated, 41.52%; found, 41.44%. The conversion into a trichloro-acetate seemed to us to be proved in a thorough manner. Unfortunately, new samples of

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[1] Wheeler and Smith, THIS JOURNAL, **45**, 1994 (1923).

[2] Doughty, *ibid.*, **47**, 1095 (1925).