cury electrode whether dropping or quiet is completely useless. The value commonly accepted[10] for the oxidation potential of that couple is due to Grube and Schächterle.[3a] From the potential of a platinized platinum electrode in a strongly alkaline solution of cobalt(III)hexacyanide partially reduced at a cobalt cathode, they calculated a result in terms of a hypothetical hexacyanocobalt(II)ate–hexacyanocobalt(III)ate electrode reaction. In addition to the error in formulation of the electrode reaction, a more serious difficulty exists. Both hydroxide ions and platinum are known to catalyze the water oxidation of the cobalt(II) cyanide complex. The potential which was measured differed from the potential of a hydrogen electrode in a solution of the same alkalinity by only a few millivolts: undoubtedly no more than experimental error. The potential which was reported (−0.81 v. on the hydrogen scale, European sign convention) must therefore be considered only as a lower limit on the reducing strength of the couple involved.

Summary

Polarographic investigation of the reduction of cobalt cyanide complexes has led to the following conclusions.

1. Addition of excess alkali cyanide to a solution of a cobalt(II) salt results in the immediate formation of the aquopentacyanocobalt(II)ate ion, reducible at the dropping electrode to a cobalt(I) complex.
2. Oxidation of the cobalt(II) complex yields aquopentacyanocobalt(III)ate, also reducible at the dropping electrode to a cobalt(I) complex.
3. Prolonged treatment of the aquopentacyano complexes with excess cyanide ultimately yields the hexacyanocobalt(III)ate ion, not reducible at the dropping electrode.
4. The cobalt(I) complex is neither reducible nor oxidizable at the dropping electrode.
5. The commonly accepted value for the potential of the cobalt(II)–cobalt(III) couple in cyanide medium cannot be considered valid.

CAMBRIDGE, MASSACHUSETTS
MINNEAPOLIS, MINNESOTA RECEIVED OCTOBER 28, 1948

[10] W. M. Latimer, "Oxidation Potentials," Prentice-Hall, New York, N. Y., 1938.

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE OHIO STATE UNIVERSITY]

The Behavior of Oxygenated Organic Compounds in Acid Media[1]

BY MELVIN S. NEWMAN, RAYMOND A. CRAIG[2] AND ALFRED B. GARRETT

When oxygenated organic compounds are dissolved in strong protonic acids they generally accept a proton from the solvent to form a positively charged intermediate which may or may not undergo further change.[3] Evidence as to the fate of these conjugate acids has been obtained, among other sources, from the measurements of freezing point depression of solvent sulfuric acid[3,4] and from the nature of the reaction products isolated when the sulfuric acid solutions were poured into water or certain alcohols.[4] The further behavior of the species BH^+ forms the topic for the present discussion.

$$\mathrm{B + HA \longrightarrow BH^+ + A^-} \tag{1}$$

Alcohols[5]

In the case of solutions of alcohols in sulfuric acid three types of cryoscopic behavior have been noted.

$\mathrm{ROH + H_2SO_4 \rightleftarrows ROH_2^+ + HSO_4^-}$ [$i = 2$][6] (2)

$$\mathrm{ROH + 2H_2SO_4 \rightleftarrows RHSO_4 + H_3O^+ + HSO_4^-}\quad [i = 3] \tag{3}$$

$$\mathrm{ROH + 2H_2SO_4 \rightleftarrows R^+ + H_3O^+ + 2HSO_4^-}\quad [i = 4] \tag{4}$$

For example, *i*-factors of 2 have reported for *t*-butyl and *t*-amyl alcohols[7]; *i*-factors of about 3 for several primary alcohols,[7] and an *i*-factor of 4 for triphenylcarbinol.[3,8] It appears reasonable to suppose that the first step in each of these cases involves a proton transfer to yield an oxonium compound, ROH_2^+. Two questions arose as to the further behavior of such oxonium compounds. (1) Why should an *i*-factor of only 2 be obtained with *t*-alcohols[7] when in reactions in acid media *t*-compounds often react most rapidly? (2) Are the conjugate acids of alcohols, ROH_2^+, thermally unstable at ordinary temperatures, or is some solvent effect operative?

In order to obtain information on the first topic, we have re-investigated the behavior of *t*-butyl alcohol in sulfuric acid and have also studied triethylcarbinol. When these alcohols are *carefully* (see Experimental Part for details) dissolved in sulfuric acid initial *i*-factors of slightly

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[1] The work herein reported is taken from the Ph.D. thesis of R. A. Craig, The Ohio State University, March, 1948.

[2] Standard Oil Company of Indiana Fellow, 1946–1947. Present address: Experimental Station, du Pont, Wilmington, Delaware.

[3] For background discussion see Hammett "Physical Organic Chemistry," McGraw-Hill Book Company, New York, N. Y., 1940, pp. 45–48, 53–56 and 277–285.

[4] (a) Newman, THIS JOURNAL, **63**, 2431 (1941); (b) Newman, Kuivila and Garrett, *ibid.*, **67**, 704 (1945); (c) Newman, *ibid.*, **64**, 2324 (1942).

[5] In this paper monofunctional compounds containing only carbon, hydrogen and oxygen and a few silicon organic compounds will be considered.

[6] The *i* refers to the van't Hoff *i* factor which means essentially the number of particles produced from one particle of solute.

[7] Oddo and Scandola, *Gazz. chim. ital.*, **39**, II. 1 (1909).

[8] Hammett and Deyrup, THIS JOURNAL, **55**, 1900 (1933).

over 2 are obtained. On standing, however, these values gradually increase and eventually go over 5. If roughly extrapolated back to zero time, *i*-factors of 2.1 and 2.4 are obtained. On standing, sulfuric acid solutions of these alcohols gradually develop a hydrocarbon layer. The presence of sulfur dioxide was also established. The above findings are interpreted further below.

As for the second question, we have found that *n*-propyl and *t*-butyl alcohols each give *i*-factors of about 1.7 in methanesulfonic acid.[9] We interpret this to mean that the reaction indicated in equation 5 is only partly complete and that the oxonium salts, ROH_2^+, are not unstable *per se.*

$$ROH + CH_3SO_3H \rightleftharpoons ROH_2^+ + CH_3SO_3^- \quad (5)$$

The importance of the solvent in the further reactions of the species ROH_2^+ is attested by the fact that the *i*-factor of 1.7 for *t*-butyl alcohol is only slightly increased by heating the solution in question to 60° for fifteen minutes[9] (compare the behavior of *t*-butyl alcohol in sulfuric acid).

It is interesting to note that, in their further reactions with sulfuric acid, the oxonium compounds, ROH_2^+, appear to react analogously to the corresponding alkyl halides, RX, in nucleophilic displacement reactions.[10] For example, most primary alkyl halides react by the S_N2 mechanism,[10] which involves a backside approach.[11] The *i*-factors of 3 generally observed for primary (and some secondary) alcohols may be explained by the backside approach of a bisulfate ion to displace a water molecule from the oxonium salt of the alcohol, followed by the further ionization of water in sulfuric acid, as shown below.

$$ROH + H_2SO_4 \rightleftharpoons ROH_2^+ + HSO_4^- \quad (6)$$

$$HSO_4^- + ROH_2^+ \rightleftharpoons RHSO_4 + H_2O \quad (7)$$

$$H_2O + H_2SO_4 \rightleftharpoons H_3O^+ + HSO_4^- \quad (8)$$

Summation of equations 6, 7, and 8 yields equation 3.

t-Halides undergo displacement reactions at an appreciable rate only by a first order mechanism (S1 type) in which the rate determining step involves ionization of the halide.[10] The rate is slow for *t*-butyl halides but quite rapid for triphenylmethyl halides. When *t*-butyl alcohol and triethylcarbinol are carefully dissolved in cold sulfuric acid, the first measurement of *i*-factor gives values of slightly over two. Successive measurements give increasing *i*-factors which eventually reach over 5. We interpret these results as evidence that the oxonium salts formed in accordance with equation 6 undergo a slow spontaneous ionization as shown in equation 9.

$$ROH_2^+ \rightleftharpoons R^+ + H_2O \quad (9)$$

If nothing further happened the summation of equations 6, 9, and 8 would yield equation 4 and an *i*-factor of 4 would result. In the case where R is triphenylmethyl, this is actually the case.[8]

However, complicating side reactions set in with the aliphatic *t*-alcohols. These side reactions include polymerization (*i*-factor lowering), general oxidation (*i*-factor raising) and possibly others. The fact that triphenylcarbinol gives an immediate *i*-factor of 4 is not surprizing in view of the fact that triarylcarbinyl halides ionize much more readily than trialkylcarbinyl halides. In this connection it is interesting to note that in methanesulfonic acid we have shown[9] that triphenylcarbinol gives an *i*-factor of 3.8.

The inability of *t*-halides to undergo S_N2 type reactions is commonly attributed to steric effects which hinder the approach of a substituting group from the face of the tetrahedron directly opposite to the carbon–halogen bond.[12] However, if the central atom involved were silicon instead of carbon, the steric effect should be less. We have found that triethylsilanol gives an *i*-factor of 3 in sulfuric acid and thus approximates the behavior of primary alcohols. We interpret this fact as support for the view that a bisulfate ion makes a backside attack to displace a water molecule from the initially formed silicon-containing oxonium salt, as shown below.

$$(R)_3SiOH + H_2SO_4 \rightleftharpoons (R)_3SiOH_2^+ + HSO_4^- \quad (9)$$

$$HSO_4^- + (R)_3SiOH_2^+ \rightleftharpoons (R)_3SiHSO_4 + H_2O \quad (10)$$

Summation of equations 9, 10, and 8 results in a calculated *i*-factor of 3.

In addition we have found that hexamethyldisiloxane,[13] hexaethyldisiloxane, and triethylethoxysilicon yield *i*-factors of about 4. The over-all equations are given below and may be derived by following the principles above outlined.

$$(R)_3SiOSi(R)_3 + 3H_2SO_4 \rightleftharpoons 2(R)_3SiHSO_4 + H_3O^+ + HSO_4^- \quad (11)$$

$$(C_2H_5)_3SiOC_2H_5 + 3H_2SO_4 \rightleftharpoons (C_2H_5)_3SiHSO_4 + C_2H_5HSO_4 + H_3O^+ + HSO_4^- \quad (12)$$

When added to water the trialkylsilicon bisulfate present in these solutions probably reacts with water as shown by the reverse of equation 10. In the acid medium the trialkylsilanols rapidly form disiloxanes and these compounds were obtained in high yield on pouring the sulfuric acid solutions above mentioned into water.[14]

The formation of trialkylsilicon chloride[15] by adding ammonium chloride to solutions which contain trialkylsilicon bisulfate probably involves the displacement of the bisulfate ion by a back-

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[9] A more complete discussion of our work in methanesulfonic acid is being prepared for publication.

[10] Hughes, *J. Chem. Soc.*, 968 (1946).

[11] For an excellent review of the evidence see Hammett "Physical Organic Chemistry," McGraw-Hill Book Company, Inc., New York, N. Y., 1940, Chapter VI.

[12] Evans, *Trans. Faraday Soc.*, **42**, 719 (1946); Hughes and Ingold, *ibid.*, **43**, 798 (1947).

[13] In agreement with Price, THIS JOURNAL, **70**, 871 (1948).

[14] Compare Ladenberg, *Ann.*, **164**, 320 (1872).

[15] Flood, THIS JOURNAL **55**, 1735 (1933).

side attack of chloride ion.[16] Because of the insolubility of the trialkylsilicon chlorides in sulfuric acid the reaction goes to completion and constitutes an excellent method of preparation for these chlorides.

$$Cl^- + (R)_3SiHSO_4 \rightleftarrows (R)_3SiCl + HSO_4^- \quad (13)$$

Esters[17]

Two types of behavior have been noted for solutions of methyl esters in sulfuric acid.

$$RCOOCH_3 + H_2SO_4 \rightleftarrows RCO_2CH_3 \cdot H^+ + HSO_4^- \; [i = 2] \quad (14)$$

$$RCOOCH_3 + 3H_2SO_4 \rightleftarrows RC^+O + H_3O^+ + CH_3HSO_4 + 2HSO_4^- \; [i = 5] \quad (15)$$

Some factors tending to cause esters to behave according to either of these courses have been discussed.[4a,b] In seeking to determine the effect of heating the sulfuric acid solution of methyl benzoate, a new type of behavior has been noted, as shown in equation 16.

$$RCOOCH_3 + 2H_2SO_4 \rightleftarrows RCO_2H_2^+ + CH_3HSO_4 + HSO_4^- \; [i = 3] \quad (16)$$

When solutions of methyl benzoate in sulfuric acid were heated to 45° or above for short times and then cooled for freezing point depression determinations, *i*-factors of about 3 were obtained. This behavior may be explained by postulating a backside attack of bisulfate ion on the conjugate acid of methyl benzoate as shown below.

$$RCOOCH_3 + H_2SO_4 \rightleftarrows RCO_2CH_3H^+ + HSO_4^- \quad (17)$$

$$HSO_4^- + CH_3O_2CR \cdot H^+ \rightleftarrows CH_3HSO_4 + RCOOH \quad (18)$$

$$RCOOH + H_2SO_4 \rightleftarrows RCO_2H_2^+ + HSO_4^- \quad (19)$$

Summations of equations 17, 18, and 19 yields equation 16.

The conjugate acids of *t*-butyl esters undoubtedly undergo ionization as follows

$$RCO_2C(CH_3)_3 \cdot H^+ \rightleftarrows RCOOH + (CH_3)_3C^+ \quad (20)$$

Evidence for this type of reaction has been obtained in the formation of *t*-butyl methyl ether by the acid catalyzed decomposition of *t*-butyl esters in methanol.[18]

It is thus evident that the behavior of the conjugate acids of methyl and *t*-butyl esters in acid media can be compared to the behavior of the conjugate acids of methanol and *t*-butyl alcohol. How complete the analogy may be must await further experimentation.

It is a fact that *i*-factors of about 3 can be obtained from methyl benzoate on heating or on long standing at 25°. This might be explained by postulating an amount of ionization according to equation 15 sufficient to account for the *i*-factors observed. That such ionization does not occur is indicated by the fact that the amount of benzoic acid recovered on pouring the sulfuric acid solutions of methyl benzoate into water is far greater than that which would have been found if ionization according to equation 15 were taking place. Thus, when a solution of methyl benzoate in sulfuric acid was heated to 90° for fifteen minutes and then cooled, an *i*-factor of 3.32 was obtained. When an aliquot of this solution was poured into water 81% of the original ester was isolated as benzoic acid. If the benzoic acid had been formed by the reaction of the $C_6H_5CO^+$ ion (equation 15) with water, an *i*-factor of over 4 would have been expected. We have ruled out possible abnormalities derivable from the action of sulfuric acid on methanol by showing that *i*-factors of solutions of methanol in sulfuric acid do not change appreciably on heating to 90° for twenty minutes.

Experimental

Reagents

Sulfuric Acid.—C. P. concentrated sulfuric acid and thirty per cent. fuming sulfuric acid were mixed in the ratio twenty to thirteen by weight and sufficient water added to make the solution slightly less than 100% sulfuric acid. Acid with a freezing point between 10.2 and 9.6° was used in cryoscopic determinations.

Solutes.—All solutes were carefully purified and dried before use. Where the material was not otherwise available, preparation was by previously reported procedures. Physical constants were as follows:

Benzoic acid: m.p. 122.1–122.3° (uncor.)
Hexaethyldisiloxane: b.p. 103° (11 mm.); $n^{20}D$ 1.4338
Hexamethyldisiloxane: $n^{20}D$ 1.3780. Received through the courtesy of General Electric Research Labs.
Methyl alcohol: $n^{20}D$ 1.3294
Methyl benzoate: b.p. 112.5° (53 mm.); $n^{20}D$ 1.5170
Triethylcarbinol: b.p. 80° (70 mm.); $n^{20}D$ 1.4300
Triethylethoxysilicon: b.p. 152° (740 mm.); $n^{20}D$ 1.4135
Triethylsilanol: b.p. 74.5° (26 mm.); $n^{20}D$ 1.4329
t-Butyl alcohol: m.p. 25.43° (cor.)

Apparatus and Procedure.—Except where indicated in the data section, the apparatus used and procedures followed are essentially those previously described.[4a]

Data

A. Tertiary Alcohols.—Preliminary runs with *t*-butyl alcohol indicated that its *i*-factor rose rapidly with time, the rate of rise being temperature dependent. Care was taken in subsequent determinations to note the rate of this rise, making possible extrapolation of *i*-factor values to zero time. In all runs herein reported the solute was added after the freezing point apparatus and sulfuric acid had been in the cooling bath for some time, the addition being made when the temperature of the acid was about 13°. Use of this technique facilitated calculation of the *i*-factor at zero time since it not only cut the time that the alcohol was in the acid prior to the freezing

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[16] In line with the above concept, it was predicted that the alkaline hydrolysis of trialkylsilicon halides should be first order with respect to the base used. This prediction appears to be confirmed by a statement of Dr. Gardner Swain of M. I. T. made at the Chicago meeting, April, 1948, to one of us (M.S.N.) that he had observed kinetics in such replacement reactions to be first order with respect to alkali.

[17] In this discussion only the behavior of methyl esters will be discussed.

[18] Cohen and Schneider, THIS JOURNAL, **63**, 3382 (1941).

point determination, but also minimized the rate of i-factor change by maintaining a relatively constant low temperature.

The second column gives the time elapsing between addition of the solute and the time crystallization started in each run.

I. Alcohols

A. *t*-BUTYL ALCOHOL (0.03509 MOLAL SOLUTION)

Temperature of solution rose to a maximum of 180° between runs

No.	Time, min.	F. p., °C.	T	i
1	Pure solvent	10.024	...	..
2	20	9.473	0.551	2.56
3	76	9.322	.702	3.27
4	205	9.168	.856	3.99
5	1650	9.068	.956	4.46

Highest i-value observed was 5.46. Rough extrapolation to zero time gives $i = 2.1$.

A second solution of *t*-butyl alcohol (0.3411 molal), in which the temperature never was above 14°, gave i-factors of 2.30, 3.08 and 3.85 for the time intervals of 15, 86 and 312 minutes, respectively.

B. TRIETHYLCARBINOL (0.08017 MOLAL SOLUTION)

Temperature was below 16° for runs 1–4; at room temperature for runs 5–7

No.	Time	F. p., °C.	T	i
1	Pure solvent	9.686	...	..
2	25 minutes	8.432	1.254	2.55
3	63 minutes	8.360	1.326	2.71
4	252 minutes	8.201	1.485	3.04
5	27 hours	7.759	1.927	3.96
6	40 hours	7.412	2.274	4.68
7	160 hours	6.902	2.784	5.74

Extrapolation to zero times gives $i = 2.4$.

II. Organo-silicon Compounds

A. Triethylethoxysilicon.—The i-factors for 5 different increments of solute ranged in value from 3.98 to 4.44 with an average of 4.3. The time intervals ranged from a few minutes to fourteen hours and no drift in the value of i was noted with time.

B. Hexamethyldisiloxane.—The i-factors for 3 different increments of solute ranged in value from 3.98 to 4.23 with an average of 3.1. The time intervals ranged from a few minutes to twelve hours and no drift in the value of i was noted with time.

C. Hexaethyldisiloxane.—The i-factors for three different increments of solute ranged in value from 3.92 to 4.04 with an average of 4.0.

D. Triethylsilanol.—The i factors for 3 different increments of solute ranged in value from 2.84 to 3.10 with an average of 3.0. The time intervals ranged from a few minutes to three hours and no drift in the value of i was noted with time.

III. Effect of Heating on the i-Factors

A. METHYL BENZOATE

No.	m	F. p., °C.	T	
1	....	9.638	...	..
2	0.07803	8.645	0.993	2.07
3	At 14° for 40 minutes	8.642	0.996	2.08
4	At 45° for 15 minutes	8.171	1.467	3.05
5	At 45° for 50 minutes	8.125	1.513	3.15
6	At 45° for 35 minutes	8.119	1.519	3.16
7	New run	9.802	...	..
8	0.07329	8.891	0.911	2.02
9	At 65° for 15 minutes	8.289	1.513	3.35
10	At 65° for 35 minutes	8.328	1.474	3.27
11	At 25° for 10 hours	8.344	1.458	3.23
12	New run	9.627	...	..
13	0.6282	8.840	0.787	2.04
14	At 90° for 15 minutes	8.344	1.283	3.32
15	At 25° for 4 hours	8.385	1.242	3.21
16	At 45° for 30 minutes	8.353	1.274	3.30

B. METHYL ALCOHOL

No.	m	F. p., °C.	T	
1		9.535		
2	0.03682	8.895	0.640	2.85
3	At 15° for 40 minutes	8.913	.622	2.77
4	At 90° for 20 minutes	8.888	.647	2.88

C. BENZOIC ACID

No.	m	F. p., °C.	T	
1		9.971		
2	0.05385	9.304	0.667	2.10[a]

[a] This freezing point was measured after the benzoic acid solution had been held at 70° for thirty minutes.

Summary

i-Factors, calculated from measurements of the freezing point depression in sulfuric acid caused by solution of a number of organic compounds, have been determined.

The i-factors for *t*-butyl alcohol and triethylcarbinol are shown to change with time; extrapolation to zero time gives values of 2.1 and 2.4, respectively. An explanation of this phenomenon is proposed.

An hypothesis which attempts to correlate the behavior of oxonium salts, ROH_2^+, of alcohols in acid media with the nucleophilic displacement reactions of the analogous alkyl halides, RCl, is stated.

It is shown that the i-factor of a solution of methyl benzoate in sulfuric acid is raised from a value of 2 to 3 by heating at 90° for fifteen minutes. This i-factor is accounted for by postulating the following reaction

$$C_6H_5CO_2CH_3 + 2H_2SO_4 \rightleftharpoons C_6H_5CO_2H_2^+ + CH_3HSO_4 + HSO_4^-$$

Experimental evidence supporting this equation is presented.

Triethylethoxysilicon, hexamethyldisiloxane, hexaethyldisiloxane, and triethylsilanol were shown to give i-factors of about 4.3, 4.1, 3.9, and 3.0, respectively, in sulfuric acid.

COLUMBUS, OHIO RECEIVED SEPTEMBER 14, 1948