ture. For acidities where no maximum occurs the absorbency at 220 mμ is taken as a qualitative measure of the amount of hydrolysis. At these acidities the absorbency decreases with temperature, indicating again more extensive hydrolysis at the lower temperatures.

Rates of Reaction.—The work of Whitney and Davidson[3] pointed to the fact that the equilibria involving $SbCl_6^-$ are established at a measurable rate. In the extraction experiments already cited it became apparent that considerable time was required before equilibrium was attained, indicating that the rate of formation of $SbCl_6^-$ is slow, at least in 3.5 *M* acid.

The attainment of equilibrium in such cases results from a series of reactions, and interpretation in terms of the separate reactions is not possible. The only individual reaction that can be studied easily is the hydrolysis of $SbCl_6^-$. This can be done spectrophotometrically by observing the rate of change of absorbency at a wave length of 300 mμ after diluting a solution in concentrated HCl to some desired acidity. It may be argued that the absorption at 300 mμ is not solely due to $SbCl_6^-$ since we have seen that $Sb(OH)Cl_5^-$ also shows appreciable absorption at this wave length, and hence that the observed rate is not truly the rate of hydrolysis. The evidence, however, points to the fact that even though $Sb(OH)Cl_5^-$ may be the initial product of the hydrolysis of $SbCl_6^-$, it is itself hydrolyzed rapidly. This is illustrated by an experiment where a 12 *M* acid solution was diluted to 2 *M* and the rate of change of absorbency followed at wave lengths of 240, 250 and 300 mμ. There was no increase in absorbency at 240 and 250 mμ which would have been expected if appreciable amounts of $Sb(OH)Cl_5^-$ had accumulated; and in fact, all three absorbencies decreased at the same rate.

If one examines the entire spectrum at various times during such an experiment and plots these spectra, an isosbestic point occurs. The wave length at which the isosbestic point occurs will vary with the final acidity. These observations and the points raised in the previous discussion are consistent with the interpretation that once the initial step of hydrolysis is complete the products come to the equilibrium determined by the acidity. That is, under these conditions all of the species, with the exception of $SbCl_6^-$, are in equilibrium. For fairly low acidities there is then no contribution by hydrolysis products to the absorbency at 300 mμ, and the actual rate of hydrolysis is being measured. Preliminary experiments indicate the hydrolysis to have a half-time of two hours at 25°.

Only qualitative information is available on the rates of reactions that lead from the more hydrolyzed to the less hydrolyzed species. If a solution of low acidity is mixed with concentrated acid the rate of attainment of equilibrium is strongly dependent on the resulting acidity. If the final acidity is greater than 9 *M* equilibrium is reached within a few minutes; in a 6 *M* solution equilibrium is reached after a few hours. Several days are necessary for the formation of $SbCl_6$ (as determined by extraction experiments) when the acidity decreases to less than 3 *M*. Here again the qualitative evidence points to a rapid equilibrium between the hydrolyzed species, followed by a slow rate of formation of $SbCl_6^-$.

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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Relationships among the Absorption Spectra of the 5,7-Dihalo-8-quinolinol Chelates of Gallium(III) and Indium(III)

BY THERALD MOELLER, FRED L. PUNDSACK AND ALVIN J. COHEN

RECEIVED JANUARY 23, 1954

The absorption spectra of chloroform solutions of 5,7-dihalo-8-quinolinol (dichloro-, dibromo-, chloroiodo- and diiodo-) chelates of gallium(III) and indium(III) resemble those of comparable solutions of the unsubstituted 8-quinolinol chelates in that only three absorption bands, all lying in the near ultraviolet and violet regions, are detectable in the wave length range 300–600 mμ. Absorptions in the 392.5–417 mμ region are major and most characteristic and are apparently due to bathochromic shifts in the spectra of the chelating agents as a result of chelate formation. The wave lengths and equivalent extinction coefficients characterizing these absorption bands increase generally with increasing molecular weights of the chelates. Absorptions at the major peaks are in accord with Beer's law at low metal concentrations. Chloroform solutions of these chelates all undergo photochemical decompositions.

Introduction

The ability of 8-quinolinol to form stable chelates with a variety of metal ions is well established.[1–3] Since such chelates result through substitution of metal ions for the acidic hydrogen in the parent compound, they are structurally similar to 8-quinolinol itself, and their properties may be expected to reflect those of 8-quinolinol with suitable modifications depending upon the metal ions themselves. Similar chelates are formed by many of the substituted 8-quinolinols.[4,5] Although the properties of these chelates again reflect those of the parent chelating agents, they differ somewhat from

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(1) F. L. Hahn, *Z. angew. Chem.*, **39**, 1198 (1926).

(2) R. Berg, *J. prakt. Chem.*, **115**, 178 (1927).

(3) R. Berg, "Das O-Oxychinolin 'Oxine'," F. Enke, Stuttgart, 1935.

(4) R. Berg, *Z. anorg. allgem. Chem.*, **204**, 208 (1932).

(5) L. L. Merritt and J. K. Walker, *Ind. Eng. Chem., Anal. Ed.*, **16**, 387 (1944).

TABLE I

MICROANALYTICAL DATA FOR CHELATES

Chelate	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found	X, % Calcd.	X, % Found
$Ga(C_9H_4Cl_2NO)_3$	45.75	45.71	1.71	1.90	5.93	6.03	30.0	30.8
$Ga(C_9H_4ClINO)_3$	32.98	32.86	1.23	1.28	4.27	4.30	49.6	..
$Ga(C_9H_4I_2NO)_3$	25.79	25.89	0.96	1.01	3.34	3.24	60.6	..
$In(C_9H_4Cl_2NO)_3$	43.01	42.67	1.60	1.72	5.57	5.44	28.3	..
$In(C_9H_4Br_2NO)_3$	31.77	31.83	1.19	1.08	4.12	4.15	47.0	..
$In(C_9H_4ClINO)_3$	31.54	31.46	1.18	1.20	4.09	4.10	47.4	..
$In(C_9H_4I_2NO)_3$	24.90	25.03	0.93	1.02	3.23	3.20	58.5	..

those of the comparable unsubstituted 8-quinolinol chelates. Such differences are functions both of the natures and positions of the substituted groups. Particularly common among substituted 8-quinolinols are the 5,7-dihalo derivatives. Because of the higher electronegativities of the halogens over hydrogen, the 5,7-dihalo-8-quinolinols are stronger acids than 8-quinolinol itself. This would probably render them less prone to chelate with metal ions, but the decreased solubilities of the chelates which they form so reduce the equilibrium concentrations of metal ions in solution that they appear to be rather strong chelating agents. A case in point is found with the 5,7-dichloro-8-quinolinol chelates of the tripositive rare earth metal ions.[6,7]

The utilities of the characteristic absorption bands in the spectra of chloroform solutions of the 8-quinolinol chelates of gallium(III)[8] and indium(III)[9] for spectrophotometric determinations of these metals have been established and, in a comparative study,[10] it has been shown that the absorption spectra of chloroform solutions of these chelates differ only slightly from each other. On the other hand, the absorption spectra of similar solutions of the 5,7-dibromo-8-quinolinol chelate of gallium(III) are characterized by enhanced absorption intensities and bathochromic shifts in characteristic bands.[11]

It has been of interest, therefore, to investigate the relationships existing between the absorption spectra of additional 5,7-dihalo-8-quinolinols and the chelates which they form and to extend earlier observations on the gallium(III) and indium(III) 8-quinolinol systems to those involving these halogen-substituted derivatives. The possible analytical applications of these materials have been considered also.

Experimental

Materials Used.—Gallium and indium compounds were prepared from samples of the metals which contained only spectroscopic traces of other materials. The dibromo-, diiodo- and chloroiodo-8-quinolinol samples used were commercial products. Each was recrystallized repeatedly from absolute ethanol prior to use. The dichloro-8-quinolinol sample employed was prepared and purified as previously described.[7] Chloroform was a reagent quality product containing 0.75% ethanol by volume. Other chemicals were of analytical reagent quality. Conductivity water was employed to eliminate traces of other metal ions.

Preparation of Chelates.—The gallium(III) and indium(III) chelates were precipitated by adding acetone solutions of the chelating agents to hot aqueous metal sulfate solutions containing sufficient sulfuric acid to reduce the *p*H to 1.0, the procedure in all cases being essentially that already described for the dibromo gallium derivative.[11] The yellow precipitates were washed with 1:1 mixture of acetone and water and dried to constant weight at 110°. Microanalytical data summarized in Table I show the materials to have the expected 3 quinolinol to 1 metal ion stoichiometries. Further purifications by recrystallizations proved impractical because of solubility limitations. Solutions studied were prepared by dissolving weighed quantities of the chelates in chloroform and diluting to predetermined volumes. Because of their photosensitivities, these solutions were protected from light.[10]

Absorption Spectra Studies.—Absorption spectra were measured by means of an unmodified Beckman model DU quartz spectrophotometer for gallium compounds and with a Cary recording spectrophotometer for the indium compounds. In all cases, 5.0-cm. demountable cells with quartz windows were employed, and chloroform was used as the reference liquid. Molecular extinction coefficients were evaluated by use of the familiar relationship $\epsilon = (M/cl)\log_{10}(I_0/I)$, M representing molecular weight for the 8-quinolinols and atomic weight of the metal for the chelates, and equivalent extinction coefficients by dividing the molecular values by appropriate oxidation numbers (1 for the 8-quinolinols, 3 for the chelates). Measurements were made at wave lengths greater than 250–300 mμ.

Results and Discussion

Absorption Spectra of the 8-Quinolinols.—The absorption spectra of chloroform solutions of the 5,7-dihalo-8-quinolinols are comparable with the spectrum of chloroform solutions of 8-quinolinol[11] in that a single broad absorption peak appears in the 318–340 mμ region with other major absorption occurring in the vicinity of 250 mμ close to the lower limit of the useful wave length range of the solvent. Relationships among these spectra, as shown in Table II, indicate a general bathochromic shift in the 318–340 mμ region with increasing molecular weight of the 8-quinolinol. Except for the diiodo compound, however, the major change occurs upon the introduction of halogen into the 5- and 7-positions, the nature of the halogen being less important. Significant increases in molecular extinction coefficients paralleling increases in molecular weight

TABLE II

ABSORPTION SPECTRA DATA FOR 8-QUINOLINOLS

Compound	Molecular weight	Absorption peak, mμ	Molecular extinction coefficient × 10^{-3}
C_9H_6NOH	145.15	318	2.31
$C_9H_4Cl_2NOH$	214.06	326	2.57
$C_9H_4Br_2NOH$	302.97	328	2.95
$C_9H_4ClINOH$	305.51	326	2.76
$C_9H_4I_2NOH$	396.97	339	3.14

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(6) D. E. Jackson, Doctoral Dissertation, University of Illinois, 1950.

(7) T. Moeller and D. E. Jackson, *Anal. Chem.*, **22**, 1393 (1950).

(8) T. Moeller and A. J. Cohen, *ibid.*, **22**, 686 (1950).

(9) T. Moeller, *Ind. Eng. Chem., Anal. Ed.*, **15**, 270 (1943).

(10) T. Moeller and A. J. Cohen, THIS JOURNAL, **72**, 3546 (1950).

(11) T. Moeller and A. J. Cohen, *Anal. Chim. Acta*, **4**, 316 (1950).

indicate that absorption in this spectral region is enhanced by the heavier halogens. Why the dibromo compound is out of line here (and with the gallium and indium chelates) is obscure. Similarities in the over-all spectra indicate, however, that the fundamental 8-quinolinol arrangement is maintained. The halogens exert only slight modifying effects.

Absorption Spectra of the Chelates.—In the wave length range 300–600 mμ, the spectra of chloroform solutions of the 5,7-dihalo-8-quinolinol chelates of gallium(III) and indium(III) are strikingly similar to those of the unsubstituted chelates.[8–10] The absorption curves already reported for the 5,7-dibromo-8-quinolinol gallium(III) compound[11] and given in Fig. 1 for the dichloro indium chelate may be regarded as typical. Numerical data summarizing all of these spectra are given in Table III.

TABLE III

ABSORPTION SPECTRA DATA FOR GALLIUM AND INDIUM CHELATES

Gallium chelate	Absorption peak, mμ	Equiv. extinction coefficient × 10⁻³	Indium chelate	Absorption peak, mμ	Equiv. extinction coefficient × 10⁻³
$Ga(C_9H_6NO)_3$	320	1.11	$In(C_9H_6NO)_3$	320	1.03
	335	1.22		336	1.19
	392.5	2.16		395	2.22
$Ga(C_9H_4Cl_2NO)_3$	331	1.60	$In(C_9H_4Cl_2NO)_3$	334	1.55
	344	1.93		346	1.92
	409	2.54		412	2.38
$Ga(C_9H_4Br_2NO)_3$	331	2.04	$In(C_9H_4Br_2NO)_3$	334	2.42
	344	2.31		347	2.73
	410	2.91		413	3.10
$Ga(C_9H_4ClINO)_3$	335	1.92	$In(C_9H_4ClINO)_3$	338	1.79
	348	2.23		351	2.10
	414	2.61		417	2.36
$Ga(C_9H_4I_2NO)_3$	335	1.90	$In(C_9H_4I_2NO)_3$	337	2.25
	350	2.24		351	2.52
	416	2.91		416	2.79

Similarities among the spectra of the gallium complexes and among the spectra of the indium complexes suggest that any observed differences are due to the modifying effects of the halogen atoms rather than to any effect ascribable to the individual central metal ions. In each series, the effects of the halogens are comparable with those noted for the chelating agents themselves. Paralleling increases in molecular weights are general increases in intensities at absorption peaks and bathochromic shifts in peak wave lengths, results for the dibromo materials being slightly out of line. As regards band positions, once the 5- and 7-positions on the 8-quinolinol nucleus are substituted, alteration in the character of the halogen has little effect.

Comparison of the equivalent extinction coefficients for the absorption bands of the chelates in the 392–417 mμ region with those for the absorption bands of the chelating agents in the 318–340 mμ region, as shown in Table IV, suggests that the major absorption bands in the spectra of the gallium(III) and indium(III) chelates result from bathochromic shifts of the corresponding bands of the chelating agents as a result of replacement of acidic hydrogen by metal ion and the formation of a ring structure. It is probable that replacement of acidic hydrogen alone is not as important in this respect as is formation of the chelate ring involving the nitrogen and oxygen atoms. This view is supported by observations that the acidic species of 8-quinolinol, in which a comparable ring structure is presumably formed by hydrogen bonding between the nitrogen and oxygen atoms, gives an absorption spectrum similar to those for the 8-quinolinol chelates of the Group IIIb elements, whereas the absorption spectra of 8-quinolinol in sodium hydroxide solution and in "neutral" solvents are similar.[12] Similar relationships between the spectra of 8-quinolinol and its chelates with the tripositive Group IIIb elements exist.[10]

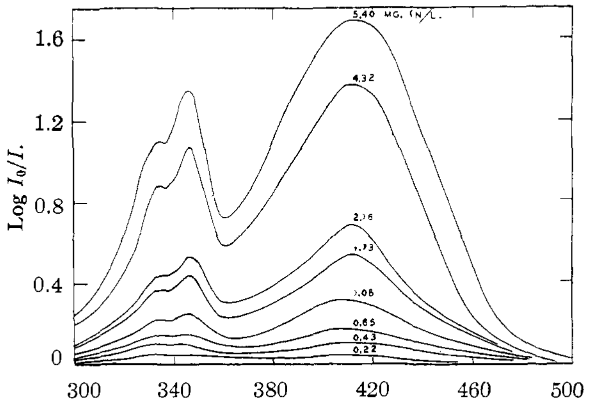

Fig. 1.—Absorption spectra of solutions of the 5,7-dichloro-8-quinolinol chelate of indium(III) in chloroform.

TABLE IV

COMPARISON OF EQUIVALENT EXTINCTION COEFFICIENTS

Group	Chelating agent mμ	Chelating agent Equiv. extinct. coeff. × 10⁻³	Gallium (III) mμ	Gallium (III) Equiv. extinct. coeff. × 10⁻³	Indium (III) mμ	Indium (III) Equiv. extinct. coeff. × 10⁻³
$C_9H_6NO^-$	318	2.31	392.5	2.16	395	2.22
$C_9H_4Cl_2NO^-$	326	2.57	409	2.54	412	2.38
$C_9H_4Br_2NO^-$	328	2.95	410	2.91	413	3.10
$C_9H_4ClINO^-$	326	2.76	414	2.61	417	2.36
$C_9H_4I_2NO^-$	339	3.14	416	2.91	416	2.79

Light absorptions of chloroform solutions of the gallium(III) and indium(III) chelates at the three absorption peaks are in accord with Beer's law, the most useful concentration ranges being *ca.* 0.2–2.0 mg./l. of cation with the gallium chelates and *ca.* 1.0–5.0 mg./l. of cation with the indium chelates with 5-cm. cells. These major peaks are useful for spectrophotometric determinations of these elements, and because of the greater intensities noted for the dihalo materials these may be employed at lower metal concentration levels than the 8-quinolinol materials alone.[8,9,11] Since maximum absorption intensities are obtained with the diiodo compounds, these might be expected to be most useful for low level determinations. However, reduction in chloroform solubility, which accompanies introduction of heavier halogens, is a mitigating factor. It is probable that of the dihalo chelates studied, only the 5,7-dichloro or the 5,7-

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[12] T. Moeller and F. L. Pundsack, THIS JOURNAL, **76**, 617 (1954).

dibromo compounds can qualify for useful spectrophotometric determinations.

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URBANA, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF NOTRE DAME]

Formation of Hydrazine in Electric Discharge Decomposition of Ammonia[1,2]

BY JOHN C. DEVINS[3] AND MILTON BURTON

RECEIVED OCTOBER 22, 1953

In the decomposition of ammonia in a d.c. electric discharge in the pressure range 0.6-11 mm., hydrazine and nitrogen (as well as hydrogen) are produced by apparently unconnected processes. Nitrogen is produced uniformly throughout the discharge while hydrazine is produced significantly only in the positive column. Nitrogen yield is not substantially affected by back reaction while hydrazine yield is limited, at least in part, by back reaction which appears to involve atomic hydrogen. Catalysis of H atom removal (by platinum-coating the wall of the discharge tube) increases over-all hydrazine yield. Maximum 100 e.v. yields reported are $G(N_2) \sim 0.8$ and initial $G(N_2H_4) \sim 2.5$; the latter may have been exceeded. Effects of pressure, temperature, surface-to-volume ratio, X/p, and general character of discharge are discussed and suggestions are offered as to detailed mechanism and methods of modification of the yields. Substantially, all the primary chemical effects involve only relatively low excited states of ammonia, with energies far less than those required for ionization and probably below optically attainable levels.

Symbols Used Throughout Paper

H, hydrazine collected, mole $\text{sec.}^{-1} \times 10^9$
$\dot{\mathrm{N}}$, nitrogen collected, mole $\text{sec.}^{-1} \times 10^9$
$\dot{\mathbf{H}}$, $d\dot{\mathrm{H}}/dx$, mole $\text{sec.}^{-1}\ \text{cm.}^{-1} \times 10^9$
$\dot{\mathbf{N}}$, $d\dot{\mathrm{N}}/dx$, mole $\text{sec.}^{-1}\ \text{cm.}^{-1} \times 10^9$
$\dot{\mathrm{N}}_n$, nitrogen prod. in the cathode zones, mole $\text{sec.}^{-1} \times 10^9$
$G(\mathbf{H})$, number of molecules of hydrazine produced per 100 e.v. in positive column at $x = 0$
$G(\mathbf{N})$, number of molecules of nitrogen produced per 100 e.v. in positive column (this value is constant throughout the positive column unless otherwise specifically stated)
$G_n(\mathbf{N})$, number of molecules of nitrogen produced per 100 e.v. in negative glow
F, flow rate (cc. sec.^{-1}) measured at N.T.P.
i, discharge current, ma.
p, pressure, mm.
R, radius of discharge tube, cm.
T, temperature of discharge tube, °C.
V, discharge potential, volts
V_n, cathode fall, volts
x, interelectrode distance, cm.
X, dV/dx, volt cm.^{-1}
Y, initial energy yield of hydrazine at $x = 0$, g. k.w.h.^{-1}

1. Introduction

In the work here reported an investigation of the processes occurrent in the low pressure d.c. glow discharge through ammonia has yielded information on optimum conditions required for the production of hydrazine. In certain respects the conclusions agree with recent expressions of Ouchi and his colleagues.[4] We concur, for example, on the limited role of ions in the total chemical process but differ in more detailed considerations of the energetics and also in interpretation of the mechanism of the decomposition and of formation of products. We agree that the evidence clearly shows the reactions necessary for hydrazine production to occur in the positive column as contrasted with the negative glow.

Unlike the negative glow, the positive column of a glow discharge[5] is an essentially uniform plasma. The molecular temperature is close to ambient, while the ionic temperature is only slightly higher. The electrons have a drift velocity in the direction of the field of $\sim 10^5$ cm. sec.^{-1} superimposed upon a random velocity distribution, usually thought to be nearly Maxwellian[4a] with an average energy of the order of 1 e.v.[6] Chemical reaction is initiated by interaction of sufficiently energetic electrons with molecules at about room temperature.

In principle it is possible, with knowledge of the energy distribution of electrons in a discharge plasma and the pertinent collision cross-sections, to determine the relative rates of production of all states conducive to reaction. Lunt and Meek[4g] have performed such calculations for the relatively simple case of hydrogen, but they are excessively difficult for a gas like ammonia. By contrast, essentially simple experiments do, however, lead to some potentially valuable physical and chemical conclusions.

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(1) Paper presented before Division of Physical and Inorganic Chemistry, Meeting of American Chemical Society at Los Angeles, Calif., March 17, 1953.

(2) Detailed data of this paper have been deposited as Document number 4181 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting in advance $1.25 for photoprints, or $1.25 for 35 mm. microfilm, to Chief, Photoduplication Service, Library of Congress.

(3) Olin Research Fellow at the University of Notre Dame.

(4) Part I: (a) K. Ouchi and Y. Watanabe, *J. Electrochem. Soc. Japan*, **17**, 285 (1949); (b) K. Ouchi, *ibid.*, **20**, 164 (1952); (c) **20**, 168 (1952); (d) **20**, 209, 212 (1952); (e) K. Ouchi and T. Takamatsu, *ibid.*, **20**, 266, 268 (1952); (f) **20**, 378 (1952); (g) **20**, 381 (1952). These articles are in Japanese accompanied by introductions and abstracts in English. (h) Part I is also paraphrased in English; *cf.* K. Ouchi, *Science Reports of the Research Institutes, Tôhoku University*, **A-4**, 203 (1952). A wide variety of discharge phenomena is discussed. (i) Parts II and III of the same subject "The Chemical Reaction by the Glow Discharge in Ammonia Gas" have appeared accompanying a complete reprint of Part I (with different pagination) in a single report not identified as to source or publisher. Apart from introductions and abstracts, these parts are in Japanese.

(5) For extensive discussion of the glow discharge and its various details, and review of much pertinent literature, *cf.* L. B. Loeb, "Fundamental Processes of Electrical Discharge in Gases," John Wiley and Sons, Inc., New York, N. Y., 1939: (a) p. 585; (b) p. 578; (c) Chap. XI; (d) p. 566. (e) A more qualitative description including some recent literature is given in K. G. Emeleus, "The Conduction of Electricity through Gases," John Wiley and Sons, Inc., New York, N. Y., third edition, 1951; (f) M. J. Druvesteyn and F. M. Penning, *Rev. Modern Phys.*, **12**, 87 (1940); (g) R. W. Lunt and C. A. Meek, *Proc. Roy. Soc. (London)*, **A157**, 146 (1936).

(6) (a) H. Wiener and M. Burton, THIS JOURNAL, **75**, 5815 (1953). (b) See also section 4.2.