Kinetics of the Chlorine-36 Exchange Reactions between Gallium(III), Antimony(III), and Antimony(V) Chloride and Ethyl Chloride

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Abstract: Kinetic studies have been made of the chlorine-36 exchange reactions between radioactive gallium chloride and ethyl chloride and between radioactive antimony pentachloride and ethyl chloride in excess ethyl chloride. The first reaction is second order in gallium chloride; the second is first order in antimony pentachloride. Enthalpies and entropies of activation have been determined for each reaction. Chlorine exchange between radioactive antimony trichloride and ethyl chloride was too slow to permit a rate law determination. At 0° the relative rates of exchange are: $GaCl_3$, 170; $SbCl_5$, 1; $SbCl_3$, <1/1000. Reaction mechanisms are proposed for the gallium chloride and antimony pentachloride reactions.

In a previous paper,[3] we reported the kinetic results of the chlorine-36 exchange reaction between gallium chloride and methyl chloride in excess methyl chloride. In view of the contradictory reports which have appeared in the literature concerning the relative rates of exchange of methyl and ethyl halides,[4,5] we have extended our study to the gallium chloride–ethyl chloride exchange reaction.

As part of their program of investigating the function of metal halides in the Friedel–Crafts reaction, Brown and coworkers have made vapor-pressure studies of aluminum halides[6] and gallium chloride[7-9] dissolved in simple alkyl halides. Byrne[10] has continued this work through his investigation of the interaction of other common Lewis acid catalysts such as antimony pentachloride, antimony trichloride, tin tetrachloride, and titanium tetrachloride with methyl chloride. Addition complexes of the form $CH_3Cl{:}MCl_{3-5}$ were identified as the predominant solute species in each system (Table I). Because of the importance of such complexes in Friedel–Crafts alkylation and related reactions,[11] and because metal halide–alkyl halide exchange studies under homogeneous conditions have been limited essentially to group III halides,[3,12,13] we have extended Byrne's research to include the kinetics of halogen exchange involving a series of other common catalytic halides.

Table I. Addition Compounds of Lewis Acid Chlorides with Methyl and Ethyl Chloride

System	$GaCl_3$–CH_3Cl[a]	$GaCl_3$–C_2H_5Cl[b]	$SbCl_5$–CH_3Cl[c]	$SbCl_3$–CH_3Cl[c]	$SnCl_4$–CH_3Cl[c]	$TiCl_4$–CH_3Cl[c]
Compd in solution in excess RCl	1:1	1:1	1:1	1:1	1:1	1:1
Solid phases	1:1		1:1		1:1	1:1
	1:2	1:2		1:2		
Mp (calcd), °C	4.8	−29	90		−50	−42.8
Heat of solution, kcal/mol	2.15	5.0	1.96		1.22	6.69
Heat of formation, kcal/mol						
1:1 compd	−7.61[b]		−8.92		−4.69	−4.35
1:2 compd	−8.11[b]	−9.74		−8.83		

[a] Reference 8. [b] Reference 9. [c] Reference 10.

Results

Chlorine Exchange between Gallium Chloride and Ethyl Chloride in Excess Ethyl Chloride. The exchange reaction involving gallium chloride and ethyl chloride in excess ethyl chloride was conveniently carried out at −35.6 and −24.7°. All the solutions were clear and colorless when first brought to reaction temperature. After completion of reaction, some 12–14 hr later, runs 1, 3, and 4 exhibited a very pale yellow color. The others were colorless. In all cases the pressure of ethyl chloride above the solution remained constant throughout the entire reaction. Thus the dehydrohalogenation

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[1] Undergraduate research assistant, 1968, on a grant provided by the Research Corporation of America.

[2] Undergraduate research assistant, 1967, on a grant provided by the National Science Foundation–Undergraduate Research Participation.

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[11] G. A. Olah and M. W. Meyer, in "Friedel–Crafts and Related Reactions," Vol. I, G. A. Olah, Ed., Interscience Publishers, New York, N. Y., 1963, Chapter 8.

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[13] M. F. A. Dove and D. B. Sowerby in "Halogen Chemistry," Vol. I, V. Gutmann, Ed., Academic Press, New York, N. Y., 1967, Chapter 2.

observed by Wong and Brown[9] in this system at 0° is negligible at the lower temperatures.

As in the case of our earlier study,[3] we continually monitored the increasing activity of the alkyl chloride vapor above the solution as it was circulated through a glass-jacketed Geiger tube. The count rate at infinite time and the rate of exchange was determined *via* computer analysis of the data.

The results of these reactions are shown in Table II.

Table II. Rate Data for the Chlorine-36 Exchange Reaction between Gallium Chloride and Ethyl Chloride in Excess Methyl Chloride

Reaction temp, °C	Concn, *M* $GaCl_3$	Concn, *M* C_2H_5Cl	Rate × 10^3, mol/(l. min)[a]	$k_2 \times 10^2$, l./(mol min)[b]
−35.6	0.335	14.7	1.38	1.23
	0.676	14.4	5.40	1.18
	1.05	14.0	11.9	1.08
			Av	1.16 ± 0.08
−24.7	0.374	14.5	4.71	3.36
	0.672	14.2	14.1	3.12
			Av	3.24 ± 0.12

[a] Calculated by means of a modified form of the quantitative exchange equation, as derived in ref 3. [b] Rate/$[GaCl_3]^2$.

Table III. Rate Data for the Chlorine-36 Exchange Reaction between Antimony Pentachloride and Ethyl Chloride in Excess Ethyl Chloride

Reaction temp, °C	Concn, *M* $SbCl_5$	Concn, *M* C_2H_5Cl	Rate × 10^4, mol/(l. min)[a]	$k_1 \times 10^3$, min^{-1} [b]
0.0	0.079	14.2	1.73	2.21
	0.378	13.7	8.24	2.18
	0.415	13.6	6.06	1.46
	0.663	13.2	12.0	1.81
	0.946	12.7	16.2	1.71
	1.38	12.0	19.2	1.39
			Av[c]	1.59 ± 0.14
−10.0	0.392	13.9	3.58	0.84
	1.23	12.4	10.4	0.91
			Av	0.88 ± 0.04

[a] Calculated by means of a modified form of the quantitative exchange law, ref 3. [b] Rate/$[SbCl_5]$. [c] From a least-squares analysis.

Like the exchange reaction involving methyl chloride reported earlier,[3] the gallium chloride–ethyl chloride exchange reaction is second order in gallium chloride (eq 1). From the average values of the rate constants

$$\text{rate} = k_2[GaCl_3]^2 \qquad (1)$$

and their uncertainties, the values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for this exchange reaction were calculated to be 10.6 ± 0.9 kcal/mol and −22 ± 4 eu, respectively.

Chlorine Exchange between Antimony Pentachloride and Ethyl Chloride in Excess Ethyl Chloride. Other than the precautions necessary to exclude mercury from the exchange system and thus from reacting with antimony pentachloride, this study proceeded in a manner similar to the gallium chloride–ethyl chloride system. We found the rate of exchange to be convenient for measurement at −10.0 and 0.0°. In all cases the pressure above the clear, pale yellow solutions remained sensibly constant, within the limits of the bath temperature fluctuation, throughout the reaction.

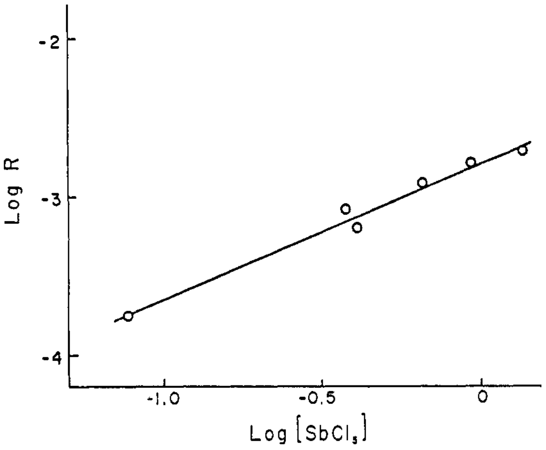

Figure 1. The effect of antimony pentachloride concentration on the rate of chlorine exchange between antimony pentachloride and ethyl chloride in ethyl chloride at 0°.

The rate data for this exchange reaction are given in Table III. A plot of log *R* against log $[SbCl_5]$ is given in Figure 1. Since a least-squares analysis of this data yielded a value of the slope of the line of 0.86 ± 0.07, we conclude that the reaction is first order in antimony pentachloride (eq 2). Using the average

$$\text{rate} = k_1[SbCl_5] \qquad (2)$$

values of the rate constants as given in Table III, we obtained values of $\Delta H^{\ddagger} = 7.9 \pm 1.4$ kcal/mol and $\Delta S^{\ddagger} = -42 \pm 5$ eu.

Chlorine Exchange between Antimony Trichloride and Ethyl Chloride in Excess Ethyl Chloride. Our attempts to study the kinetics of this system were unsuccessful. Even at 15°, a few degrees above the boiling point of ethyl chloride, the reaction was too slow for measurement. On the basis of the small increase in the count rate after 6 days, we estimate the rate of this reaction at 15° to be approximately 10^{-6} mol $l.^{-1}$ min^{-1}.

Discussion

The bromine exchange reaction between aluminum bromide and ethyl bromide in carbon disulfide follows rate expression 3.[14] We have shown[3] that at the re-

$$\text{rate} = k_3[AlBr_3]^2[C_2H_5Br] \qquad (3)$$

action temperature of −26.3° and within the ethyl bromide:aluminum bromide (dimer) range of 5:1 to 80:1 at which Sixma worked, the concentration of the $C_2H_5Br{:}AlBr_3$ complex present in solution is essentially independent of excess ethyl bromide. Yet the reaction is first order in ethyl bromide. To explain this unusual result, we proposed a rate-determining attack by ethyl bromide on either two 1:1 addition compounds, or an ion-pair dimer formed from them.

On the basis of the evidence, it was reasonable to assume that large excesses of methyl chloride at −35.6° would convert essentially all the gallium chloride to the $CH_3Cl{:}GaCl_3$ addition compound. Thus a similar mechanism was proposed for the chlorine exchange reaction in this system.[3]

In order to discuss the mechanism of chlorine exchange between gallium chloride and ethyl chloride in

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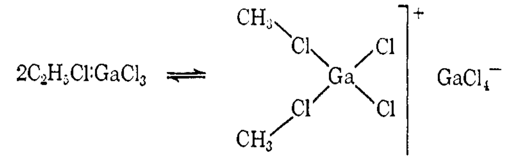
[14] F. L. J. Sixma, H. H. Hendriks, and D. Holtzapffel, *Rec. Trav. Chim.*, 75, 127 (1956).

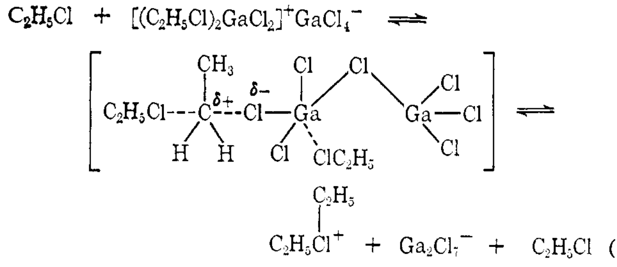
excess ethyl chloride, we must again consider the question of the identity and the concentration of the solute species.

Wong and Brown[9] have made a careful phase study of the ethyl chloride–gallium chloride system in the temperature range −78.5 to −36°. At the latter temperature their observations were made over the C_2H_5Cl:Ga_2Cl_6 mole ratio range of 13:1 to 45:1, which is the same range covered by our exchange reactions (Table I). From these data they conclude "it appears certain that the 1:1 addition compound exists as such in the ethyl chloride solutions, probably in equilibrium with minor amounts of the 1:2 compound."

We suggest the presence of minor amounts of an ion-pair dimer and the reaction mechanism



(4)



(5)

which follows the rate law

$$\text{rate} = k_3[C_2H_5Cl:GaCl_3]^2[C_2H_5Cl] \qquad (6)$$

in substantial agreement with (1).

At −35.6°, we find ethyl chloride exchanges chlorine some 15 times faster with gallium chloride than methyl chloride. At this temperature the dielectric constants of the two solvents are very similar: 13.5 for methyl chloride[15a] and 13.0 for ethyl chloride.[15b] It is noteworthy that this order is contrary to that expected for typical bimolecular displacement reactions, but in agreement with that found for Friedel–Crafts alkylation reactions.[16] On this basis, a transition state similar to that proposed for alkylation, involving a nucleophilic attack by the alkyl halide (rather than an aromatic) on a strongly polarized alkyl halide–metal halide addition complex, seems reasonable.

The relative rate of gallium bromide exchange with ethyl and methyl bromide varies from 3.4 in 1,2,4-trichlorobenzene to 80 in nitrobenzene.[5] Although the solute species in this system have yet to be determined, it is conceivable that this large change reflects in part the larger difference expected in the concentration of CH_3Br:$GaBr_3$ and C_2H_5Br:$GaBr_3$ in solvents of high Lewis basicity.

It is difficult to reconcile these results with that of Polaczek and Halpern[4] who report a relative rate of Me > Et > *n*-Pr for the iodine exchange between Al(III), Ga(III), and In(III) iodides in excess alkyl iodide. Brown and Wallace[6] observed that the addition compound between aluminum bromide and methyl iodide was much less stable than the corresponding aluminum bromide–methyl bromide adduct. Furthermore, in the aluminum bromide catalyzed methylation of benzene and toluene, Brown and Jungk[17] found $k_{MeBr}/k_{MeI} = 200$, indicative of a more weakly polarized carbon–iodine bond. Perhaps the polarization in the alkyl iodide–methyl iodide systems is so small that these exchange reactions follow the order expected (Me > Et > *n*-Pr) for typical bimolecular displacement reactions. It should be noted, however, that in a more recent paper, Polaczek and coworkers[18] report appreciable zero time exchange (as high as 20–30% for aluminum) for the MI_3–EtI solutions, which seems to take place during the dissolution of the metal iodide. Since many of the alkyl iodide–metal iodide exchange reactions were complete in times as short as 1–2 min,[4] it is possible that a heterogeneous exchange as well as the rate of dissolution of the metal iodide are complicating their results. Further study is underway in our laboratory to clarify these matters.[19]

The first-order rate law dependence upon antimony pentachloride in the exchange reaction with ethyl chloride is surprising. In all the kinetic studies reported thus far involving homogeneous exchange between catalytic halides ($GaCl_3$, $GaBr_3$, $AlBr_3$) and simple alkyl halides,[3–5,14,20,21] the rate law has involved a second-order term in the metal halide. Jensen and Brown[22] found a second-order dependence upon gallium chloride and antimony pentachloride in the benzoyl chloride–MCl_{3-5} reaction with aromatics. Unfortunately little else is known kinetically concerning the role of antimony pentachloride in catalyzing Friedel–Crafts and related reactions[23] (see below).

In order to properly discuss the mechanism of the antimony pentachloride–ethyl chloride exchange reaction, the concentrations of the solute species must be ascertained. Byrne's vapor pressure lowering data for the $SbCl_5$–CH_3Cl system at −78.5, −64, and −50°[10] clearly indicate the 1:1 species to be the predominate solute species. Nelson[24] has presented ir evidence which supports the presence of considerable quantities of the CH_3Cl:$SbCl_5$ complexes in excess antimony pentachloride at temperatures as high as 28°. Since the ethyl chloride complex is probably more stable than that with methyl chloride,[25] we would expect appreciable quantities of antimony pentachloride to be tied up as the 1:1 complex in ethyl chloride at our reaction temperatures. This suggests a rate-determining attack by ethyl chloride on the polarized[24] C_2H_5Cl:$SbCl_5$ complex. However, since this is rather speculative, we will defer our discussion of the mechanism until further investigations have been completed.

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[15] (a) A. A. Maryott and E. R. Smith, "Table of Dielectric Constants of Pure Liquids," National Bureau of Standards Circular 514, U. S. Government Printing Office, Washington, D. C., 1951. (b) J. D. Nickerson and R. McIntosh, *Can. J. Chem.*, **35**, 1325 (1957).

[16] For example, C. R. Smoot and H. C. Brown, *J. Am. Chem. Soc.*, **78**, 6249 (1956).

[17] H. C. Brown and H. Jungk, *ibid.*, **77**, 5584 (1955).

[18] K. Krzywanska, A. Kaminski, and A. Polaczek, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*, **15**, 563 (1967).

[19] Polaczek[18] appears to have found an inverse first-order rate dependence upon the metal iodide in his exchange experiment. In his calculations, he has assumed that k in the equation $-\ln(1 - F) = kt + C$ is a rate constant, rather than the product of R times a concentration factor. Thus his conclusions are in error.

[20] S. U. Choi and J. E. Willard, *J. Am. Chem. Soc.*, **87**, 3072 (1965).

[21] M. J. Beers, Thesis, Amsterdam, 1958. See ref 3.

[22] F. R. Jensen and H. C. Brown, *J. Am. Chem. Soc.*, **80**, 3039 (1958).

[23] Reference 11, Chapters 4, 8, and 17.

[24] H. M. Nelson, *J. Phys. Chem.*, **66**, 1380 (1962).

[25] B. Rice and K. C. Bald, *Spectrochim. Acta*, **20**, 721 (1964).

From the enthalpy and entropy of activation, we calculate $k_2 = 2.7 \times 10^{-1}$ l. mol^{-1} min^{-1} for gallium chloride–ethyl chloride exchange at 0°. The relative rates of ethyl chloride exchange at 0°, assuming 1 *M* metal halide concentrations, are $GaCl_3$, 170; $SbCl_5$, 1; $SbCl_3$, <1/1000.

These values do not seem to agree with the heats of formation of the solid-phase addition compounds, Table I. Neither should they be expected to, since packing considerations and lattice energies would likely be major factors in the solid complexes, but not in solution. They are in agreement, however, with the order found by Russell[26] in the alkylation of benzene with alkyl halides, methyl cyclopentane → cyclohexane isomerization, and the polymerization of styrene: $AlBr_3 > GaBr_3 > GaCl_3 > FeCl_3 > SbCl_5 > ZrCl_4 > BF_3$, BCl_3, $SnCl_4$, $SbCl_3$. There are other reactions[27] which show our reactivity sequence of catalysts, and some which do not.[22] This is to be expected; as Olah[28] states, "in all probability in Friedel-Crafts-type reactions no simple monotonic series of catalytic activity of Lewis acid and related proton acid catalysts is possible." However, the general superiority of antimony pentachloride to antimony trichloride as a catalyst is well established.[12,22,26–29]

Experimental Section

Apparatus. All experiments were carried out using a glass high vacuum apparatus and the usual vacuum line techniques. The exchange reaction system is shown in Figure 1 of the previous paper.[3]

Materials. Matheson ethyl chloride was passed through a column of Mallinckrodt Aquasorb (P_2O_5 base), thoroughly degassed, and stored on the vacuum line. Subsequent gc analysis indicated a purity of 99.4%. The preparation and purification of radioactive gallium chloride was given earlier.[3] Radioactive antimony pentachloride was produced by the reaction at 65° between the metal and excess radioactive chlorine gas (prepared by the method of Brown, Gillies, and Stevens[30]) in the absence of mercury. The final product, a pale yellow solid which melted at about 3°, was sealed in break-tip ampoules at liquid nitrogen temperature after a series of sublimations *in vacuo* at 0° *via* Dry Ice slush baths. To produce radioactive antimony trichloride, an excess of the metal was heated with radioactive chlorine overnight at 200°. The product, a colorless, crystalline solid, was purified by sublimation *in vacuo* in exactly the same manner as gallium chloride.[3]

Kinetic Procedure. That for the gallium chloride and antimony trichloride reactions was described earlier.[3] To exclude mercury from the exchange apparatus for the antimony pentachloride study, the ethyl chloride is passed through trap E (Figure 1, ref 3) now at −36°, and into a cold finger attached to the exchange system at F *via* a Dry Ice bath. When transfer is complete, the stopcock on the cold finger is closed, and the residual ethyl chloride is withdrawn from the exchange system and measured. If mercury is absent from the cold finger, the reagents are sublimed to the bottom of the exchange system in the usual manner.[3]

Reaction temperatures were maintained by means of 1,2-dichloroethane slush baths, −35.6 ± 0.2°; a Lauda TK 30 ultrakryomat in conjunction with a Brinkmann thermoelectric cooler, −24.7 ± 0.07° and −10.0 ± 0.1°; and ice baths, 0.0 ± 0.2°.

Calculations. Determination of Reactant Concentrations. The solutions were assumed ideal, *i.e.*, the total volume was taken to be equal to the sum of the component volumes. The density of gallium chloride was given earlier,[31] that of antimony trichloride was taken to be 2.55;[32] the values of ethyl chloride are: 0.923 at 0°, 0.938 at −10°, 0.959 at −24.7°, and 0.974 at −35.6°.[33] Corrections were made for the ethyl chloride vapor above the solution.[3]

Curve Fitting. The experimental data were fitted to a modified form of the exchange equation[3]

$$\ln [A_\infty/(A_\infty - A)] = Rt[(1 + \alpha)a + nb]/nab \quad (7)$$

where $n = 3$ for $GaCl_3$ and $SbCl_3$ and $n = 5$ for $SbCl_5$ by the method described previously. As a check of our results the experimental points and the theoretical points were computer plotted on the same graph.

Error Analysis. The uncertainty in the rate constants was calculated in the usual manner.[3] For the gallium chloride and antimony pentachloride reactions, the uncertainty in the curve-fitting process σ varied from 1.6 to 2.6% and 1.4 to 3.4%, respectively. The uncertainty in $\Delta H^\ddagger$ was determined from eq 8 when

$$\left[\frac{\Delta(\Delta H^\ddagger)}{\Delta H^\ddagger}\right]^2 = \left[\frac{T_2}{T_2 - T_1} - \frac{1}{L}\right]^2\left(\frac{\Delta T_1}{T_1}\right)^2 + \left[\frac{T_1}{T_2 - T_1} - \frac{1}{L}\right]^2\left(\frac{\Delta T_2}{T_2}\right)^2 + \left(\frac{1}{L}\right)^2\left[\left(\frac{\Delta k_1}{k_1}\right)^2 + \left(\frac{\Delta k_2}{k_2}\right)^2\right] \quad (8)$$

$L = \ln [(k_1)(T_2)/(k_2)(T_1)]$, and k_1 and k_2 are the rate constants at T_1 and T_2. The uncertainty in $\Delta S^\ddagger$ was given by eq 9.

$$[\Delta(\Delta S^\ddagger)]^2 = \left[\frac{\Delta H^\ddagger + RT}{T}\right]^2\left(\frac{\Delta T}{T}\right)^2 + R^2\left(\frac{\Delta k}{k}\right)^2 + \left[\frac{\Delta(\Delta H^\ddagger)}{T}\right]^2 \quad (9)$$

As further evidence that we were observing the true rates of exchange rather than a diffusion process, we found that increasing the rate of stirring and/or the temperature of the thermal pump had no effect on the observed rate of exchange.

Acknowledgment. We wish to acknowledge the support of the Research Corporation of America and the National Science Foundation. The assistance of E. Ralston and P. Ryan is also acknowledged.

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[26] G. A. Russell, *J. Am. Chem. Soc.*, **81**, 4834 (1959).

[27] For example, R. A. Coleman, M. S. Newman, and A. B. Garrett, *ibid.*, **76**, 4534 (1954).

[28] Reference 11, Chapter 11.

[29] For example, K. Bodendorf and H. Bohme, *Ann.*, **516**, 1 (1935); H. Meerwein, K. Van Emster, and J. Joussen, *Ber.*, **55B**, 2500 (1922).

[30] F. Brown, A. Gillies, and W. H. Stevens, *Can. J. Chem.*, **31**, 768 (1953).

[31] F. P. De Haan and H. C. Brown, *J. Am. Chem. Soc.*, **91**, 4844 (1969).

[32] S. M. Ohlberg, *ibid.*, **81**, 811 (1959).

[33] C. F. Jenkin and D. N. Shorthose, "The Thermal Properties of Ethyl Chloride," Department of Scientific and Industrial Research, Food Investigation Board, Special Report No. 14, London, 1923.