Liquid Hydrogen Sulphide as an Ionising Solvent. Part II.[1] Reactions of Lewis Acids of Boron with Base Analogues

By J. D. Cotton and T. C. Waddington

Neutralisations of base analogues by volatile boron Lewis acids have been examined in liquid hydrogen sulphide. Salts containing the new anions BF_3SH^-, BCl_3SH^-, BBr_3SH^-, and BEt_3SH^- have been prepared. The reaction of diborane is more complicated but seems to proceed, at least initially, through the formation of the ion $BH_3{,}SH{\cdot}BH_3^-$, which subsequently loses hydrogen. The ions BF_3SH^- and BCl_3SH^- react with excess of boron trihalide to give tetrafluoroborate and tetrachloroborate ions, respectively.

Previous workers have shown that Lewis acids of boron can form adducts and react with hydrogen sulphide. Thus boron trifluoride and hydrogen sulphide form $BF_3{,}H_2S$ (m. p. $-137°$) and perhaps $BF_3{,}7H_2S$ (m. p. $-99°$).[2] Boron trichloride forms $BCl_3{,}H_2S$ (m. p. $-35°$)[3] and is not solvolysed by liquid hydrogen sulphide at room temperature.[4] However, boron tribromide is reported[5] to be thiohydrolysed in boiling carbon disulphide to $B_2S_3{,}H_2S$. A polymer of composition $(BSH)_x$ and hydrogen were slowly produced during the gas phase reaction of diborane and hydrogen sulphide at room temperature.[6]

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[1] Part I, J. D. Cotton and T. C. Waddington, preceding Paper.

[2] A. F. O. Germann and H. S. Booth, *J. Phys. Chem.*, 1926, **30**, 369.

[3] D. R. Martin, *J. Amer. Chem. Soc.*, 1945, **67**, 1088.

[4] A. W. Ralston and J. A. Wilkinson, *J. Amer. Chem. Soc.*, 1928, **50**, 258.

[5] A. Stock and O. Poppenberg, *Ber.*, 1901, **34**, 399.

[6] A. B. Burg and R. I. Wagner, *J. Amer. Chem. Soc.*, 1954, **76**, 3307.

The only sulphur-containing borate anions which have previously been prepared are the thioborates[7] and $B_{10}H_{13}S(CH_3)_2^-$.[8] This Paper reports the first formation of mixed thioloborates by the neutralisation of boron trifluoride, boron trichloride, boron tribromide, triethylboron, and diborane with tetra-alkylammonium hydrogen sulphides, and also deals with the reactions of these Lewis acids with amines and phosphines in the solvent.

EXPERIMENTAL

Apparatus and Techniques.—Many of the techniques have been described.[1] Weight changes accompanying reaction were often measured, and are quoted as percentages. The material was placed in a small vessel which could be attached to the vacuum line through a vacuum tap and a ground-glass cone. The vessel was evacuated, detached, and weighed. It was then re-attached to the vacuum line, liquid hydrogen sulphide condensed into it, and the reaction carried out. The vessel was again evacuated and allowed to warm to room temperature, detached, and reweighed. On reconnection to the vacuum line and evacuation, weighings were reproducible to 0·2 mg. Generally 50—150 mg. of starting material were taken; the percentage weight change should therefore be reproducible to better than 1%. The method has the great advantage that exposure to air, inevitable in microcombustion analysis, is avoided.

Materials.—Boron trifluoride, boron trichloride, and boron tribromide were commercial. Diborane was kindly donated by Dr. N. R. Thompson, and triethylboron by Dr. K. G. Wade. All gases were fractionally distilled before use.

Analytical Methods.—Boron was determined acidimetrically as the borate-mannitol complex. Fluorine was determined either potentiometrically[9] by means of the variation in potential of a cerous–ceric half-cell, or gravimetrically by the usual lead chloride–fluoride method. The potentiometric method required a much smaller sample, and was faster, but was very much more subject to interference than the gravimetric method. Hydrolysis of mixed thioloborates R_4NBX_3SH produced small amounts of lower alkanethiols which were not readily oxidised to sulphate.

RESULTS

Boron Trifluoride.—The conductivity curve for the titration of trimethylamine against a solution of boron trifluoride showed a break at a molar ratio of 1·0 : 1·0, but did not distinguish between the formation of an adduct or an insoluble salt. The analysis and infrared spectrum of the material formed by mixing equivalent amounts of both reactants indicated that a mixture of adduct Me_3N,BF_3 and salt $Me_3NH^+BF_3SH^-$ was formed.

A white precipitate formed on the addition of boron trifluoride to a mixture of phosphine and liquid hydrogen sulphide, and the conductivity rose only slightly. The white solid, isolated after removal of the solvent at −78°, melted with decomposition at 120°. The infrared spectrum showed absorptions at 1070—1030s,b and 524m cm.$^{-1}$ (characteristic of the tetrafluoroborate ion[10]), and at 2500w and 975m cm.$^{-1}$ (phosphonium ion[11]). The weight change indicated that *phosphonium tetrafluoroborate* had formed [Found: weight increase (from phosphine), 254. Calc. for H_4BF_4P: weight increase, 256%]. The infrared spectrum of the vapour above the solution showed, as well as the boron trifluoride and weak hydrogen sulphide absorptions, peaks at 1285 and 1275 cm.$^{-1}$, of about equal intensity, and at 1240 and 1230 cm.$^{-1}$ about three times as intense. The relative intensities of these two sets of absorptions remained unchanged after partial separation from the large excess of boron trifluoride.

The conductivity fell steadily during the addition of boron trifluoride to a $2·7 \times 10^{-2}$M solution of the tetra-n-propylammonium hydrogen sulphide, but no end point was detected up to a molar ratio, $BF_3 : SH^-$, of 2·7 : 1·0, when precipitation commenced. On mixing equivalent amounts of tetramethylammonium hydrogen sulphide and boron trifluoride in the solvent, and removing the solvent at −78°, white *tetramethylammonium trifluorothioloborate* was obtained (Found: C, 28·9; H, 7·1; B, 6·1; F, 31·8; N, 8·3. $C_4H_{13}BF_3S$ requires C, 27·5; H, 7·5; B, 6·2; F, 32·6; N, 8·0%). The product isolated after reaction of equivalent amounts of tetraethylammonium hydrogen sulphide and boron trifluoride ($9·65 \times 10^{-4}$ mole in 1·5 ml. of solvent) was *tetraethylammonium trifluorothioloborate* [Found: weight increase (from the hydrogen sulphide) 42; S, 12·6. $C_8H_{21}BF_3NS$ requires weight increase, 42; S, 13·9%]. The reaction of tetramethylammonium hydrogen sulphide ($9·76 \times 10^{-4}$ mole in 4·0 ml. of solvent) with excess of boron trifluoride showed that partial conversion into the tetrafluoroborate had occurred (Found: B, 6·6; F, 44·7. Calc. for $C_4H_{12}BF_4N$: B, 6·7; F, 47·2%).

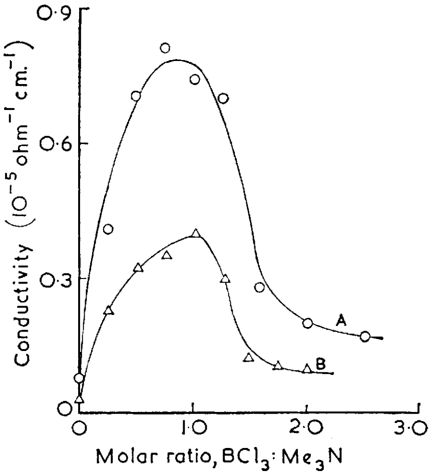

FIGURE 1 Conductimetric titration of BCl_3 against Me_3N A, $2·25 \times 10^{-2}$M-Me_3N; B, $1·09 \times 10^{-2}$M-Me_3N

Boron Trichloride.—Boron trichloride was only sparingly soluble in hydrogen sulphide, forming a white precipitate at concentrations above 5×10^{-2}M. No compound could be isolated at −78°. A rather indefinite conductivity maximum in the region of 1·0 : 1·0 was observed in the titrations of solutions of trimethylamine with boron tri-

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[7] P. Hagenmuller and F. Chopin, *Compt. rend.*, 1963, **256**, 5578.

[8] E. L. Muetterties, *Inorg. Chem.*, 1963, **2**, 647.

[9] T. A. O'Donnell and D. F. Stewart, *Analyt. Chem.*, 1961, **33**, 337; 1962, **34**, 1347.

[10] N. N. Greenwood, *J. Chem. Soc.*, 1960, 2339.

[11] J. V. Martinez and E. L. Wagner, *J. Chem. Phys.*, 1957, **27**, 1110.

chloride as shown in Figure 1. The infrared spectrum and analyses of the solid isolated from equivalent amounts of trimethylamine and boron trichloride indicated that a mixture of the adduct Me_3N,BCl_3 and the salt $Me_3NH^+BCl_3SH^-$ had formed. Similar conductivity maxima were observed in the titrations of triethylamine and pyridine with boron trichloride.

The conductivity curve for the addition of boron trichloride to a 8·70 × 10^{-2}M solution of phosphine shows an end-point at a molar ratio of 1·0 : 1·0. The white solid, isolated after removal of the solvent at −78°, decomposed readily at room temperature. The *adduct* BCl_3,PH_3 decomposes below 20° into its components.[12]

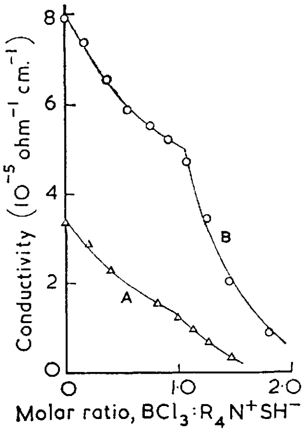

FIGURE 2 Conductimetric titrations of BCl_3 against A, Me_4NSH and B, Et_4NSH

A larger amount of material was prepared by mixing equivalent amounts of both reactants and analysed [Found: weight increase (on phosphine), 346; Cl, 69·5. H_3Cl_3BP requires weight increase 344; Cl, 70·4%].

The addition of boron trichloride to the white suspension, formed after mixing ammonia and hydrogen sulphide, caused only a slight increase in conductivity. The product isolated after the addition of a four-fold excess of boron trichloride and removal of the solvent was identified from its infrared spectrum as ammonium tetrachloroborate.[13]

Addition of boron trichloride to a 1·50 × 10^{-2}M solution of tetramethylammonium hydrogen sulphide caused precipitation and a decrease in conductivity. However, an end-point is apparent at a molar ratio of 1·0 : 1·0 (Figure 2A). On mixing equivalent amounts of both reactants and removing the solvent at −78°, *tetramethylammonium trichlorothioloborate* Me_4NBCl_3SH was formed [Found: weight increase (on the hydrogen sulphide), 103; C, 22·7; H, 5·8; B, 4·7; Cl, 47·3; N, 6·2; S, 13·1. $C_4H_{13}BCl_3NS$ requires weight increase 109; C, 21·4; H, 5·8; B, 4·8; Cl, 47·3; N, 6·3; S, 14·3%]. The infrared spectrum of the compound showed in addition to typical cation absorptions, strong peaks at 690 and 660, and a shoulder at 620 cm.$^{-1}$. The powder decomposed, in part, at 205° and the residue melted at 240° to a red liquid. The m. p. of BCl_3,Me_3N is 243°.[14] Alkanethiols were produced in the decomposition.

Analysis of the product isolated after the reaction of excess of boron trichloride with tetramethylammonium hydrogen sulphide showed that substantial conversion into the tetrachloroborate had occurred (Found: C, 20·1; H, 5·4; B, 4·8; Cl, 57·8; N, 6·2; S, 3·9. Calc. for $C_4H_{12}BCl_4N$: C, 21·2; H, 5·3; B, 4·8; Cl, 62·5; N, 6·2; S, 0·0%).

An end-point at a molar ratio of 1·0 : 1·0 was detected in the titration of boron trichloride against a 1·28 × 10^{-2}M solution of tetraethylammonium hydrogen sulphide (Figure 2B). The conductivity continued to decrease after the end-point, and precipitation commended at a molar ratio of 1·2 moles BCl_3 : 1·0 mole Et_4NSH. The material prepared by mixing equivalent amounts of the reactants was found to be *tetraethylammonium trichlorothioloborate* [Found: weight increase (on the hydrogen sulphide), 67; C, 34·4; H, 7·4; B, 3·7; Cl, 36·5; N, 5·1; S, 10·3. $C_8H_{21}BCl_3NS$ requires weight increase, 72; C, 34·3; H, 7·5; B, 3·9; Cl, 37·9; N, 5·0; S, 11·4%]. The infrared spectrum of the compound showed strong absorptions at 690 and 660, and a shoulder at 620 cm.$^{-1}$, in addition to the typical cation absorptions. The powder isolated after the reaction of a 13-fold excess of boron trichloride with tetraethylammonium hydrogen sulphide was found to consist almost entirely of the tetrachloroborate (Found: B, 3·8; Cl, 49·0; S, 0·8. Calc. for $C_8H_{20}BCl_4N$: B, 3·9; Cl, 50·1; S, 0·0%). The infrared spectrum contained only those peaks characteristic of the cation and the tetrachloroborate ion.[15]

Boron Tribromide.—Only a very slight increase in the conductivity of liquid hydrogen sulphide was caused by the addition of boron tribromide. The white powder remaining after the removal of the solvent at −78° melted with decomposition between −23° and room temperature (cf. boron tribromide,[16] m. p. −46°). A white solid and a gaseous mixture of hydrogen sulphide, boron tribromide, and an unknown thiohydrolysis product were formed. The conductivity curve (Figure 3) for the titration of boron tribromide against a 1·84 × 10^{-2}M solution of tetra-n-propylammonium hydrogen sulphide showed an end-point at a molar ratio of 1·0 : 1·0. By mixing equivalent amounts of both materials and removing the solvent at

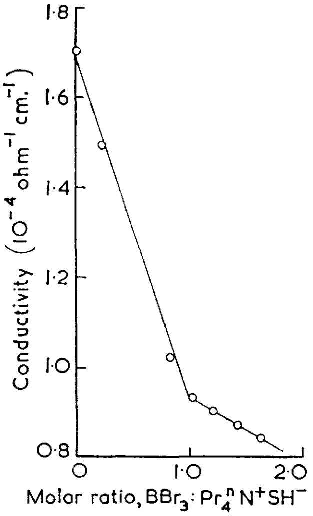

FIGURE 3 Conductimetric titration of BBr_3 against $Pr^n{}_4NSH$

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[12] D. R. Martin, *Chem. Rev.*, 1944, **34**, 461.

[13] W. Kynaston, B. E. Larcombe, and H. S. Turner, *J. Chem. Soc.*, 1960, 1772.

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[15] T. C. Waddington and F. Klanberg, *J. Chem. Soc.*, 1960, 2339.

[16] Handbook of Chemistry and Physics, Chemical Rubber Publishing Company, 39th edn., 1957.

–78°, *tetra-n-propylammonium tribromothioloborate* was prepared (Found: C, 14·3; H, 3·7; B, 3·1; Br, 69·1; N, 3·8. $C_{12}H_{29}BBr_3NS$ requires C, 13·4; H, 3·7; B, 3·0; Br, 67·0; N, 3·9%). It was not possible to test conclusively for the conversion of the tribromothioloborate ion into the tetrabromoborate ion because of the reaction of excess of boron tribromide with the solvent.

Triethylboron.—The conductivity of the solvent was unaffected by the addition of triethylboron, and no adduct or thiohydrolysis product could be detected at –78°. The conductrimetric titration (Figure 4) of triethylboron against a 2·41 × 10^{-2}M solution of tetra-n-propylammonium hydrogen sulphide showed an end-point at a molar ratio of 1·0 : 1·0. The white powder isolated at –78° decomposed in part on warming to room temperature, and melted in the dry box. Equivalent amounts of triethylboron and tetramethylammonium hydrogen sulphide reacted to give, on removal of the solvent at –78°, *tetramethylammonium triethylthioloborate* [Found: weight increase (on the hydrogen sulphide), 92; S, 15·8. $C_{10}H_{28}BNS$ requires weight increase, 91; S, 15·6%]. The compound had a decomposition vapour pressure of 16 mm. at room temperature. This vapour was shown by its infrared spectrum to be triethylboron.[17] Equivalent amounts of tetraethylammonium hydrogen sulphide and triethylboron reacted in hydrogen sulphide to give a colourless solution. The solvent was removed by evacuation at –78 and at –45° for 2 hr.; the material left was probably tetraethylammonium triethylthioloborate monothiohydrate [Found: weight increase (on the hydrogen sulphide), 80. Calc. for $C_{14}H_{38}BNS_2$: weight increase, 81%].

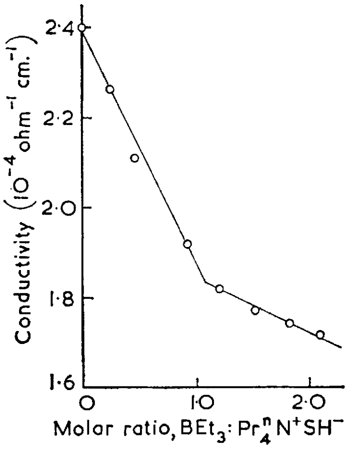

FIGURE 4 Conductimetric titration of BEt_3 against $Pr^n{}_4NSH$

Diborane.—Diborane caused very little change in the conductivity of liquid hydrogen sulphide. There was no evidence of adduct formation or thiohydrolysis at –78°. An end-point at a molar ratio of 1·0 : 1·0 of B_2H_6 : Me_4NSH was observed (Figure 5) in the titration of diborane against tetramethylammonium hydrogen sulphide (9·89 × 10^{-4} mole in 4·78 ml.). The large, initial increase in conductivity corresponded with the dissolution of the white solid to give a colourless solution. Hydrogen was evolved throughout the titration, the evolution reaching a maximum near the end-point. The total amount of hydrogen collected was 3·60 × 10^{-4} mole, *i.e.*, 36% of the base used. The white powder isolated after removal of the solvent was analysed (Found: B, 16·1; S, 23·6%; B : S ratio 2·01 : 1·00. Calc. for the direct adduct of tetramethylammonium hydrogen sulphide and diborane, $C_4H_{19}B_2NS$: B, 16 3; S, 24·2%).

A similar titration and 1 : 1 end-point was obtained in the titration of diborane against tetraethylammonium hydrogen sulphide (1·09 × 10^{-3} mole in 5·1 ml. of solvent). Hydrogen (3·7 × 10^{-4} mole, *i.e.*, 34% of the base used) was evolved throughout the titration. In a preparative experiment, a suspension of tetraethylammonium hydrogen sulphide (1·36 × 10^{-3} mole in 5·1 ml. of solvent) was treated with a two-fold excess of diborane to give a colourless 0·27M solution. A total of 9·1 × 10^{-4} mole of hydrogen, 67% of the base, was evolved. The white powder obtained after removal of the solvent at –78° was analysed (Found: C, 52·2; H, 11·6; B, 11·4; N, 6·7; S, 17·4%; B : S ratio 1·94 : 1·0. Calc. for the direct adduct of tetraethylammonium hydrogen sulphide and diborane, $C_8H_{27}B_2NS$: C, 51·1; H, 12·9; B, 11·5; N, 7·5; S, 17·1%.) A further experiment showed that after addition of diborane to tetraethylammonium hydrogen sulphide at –78°, hydrogen evolution was complete after about 30 min. Hydrogen was not evolved during removal of solvent at –78° but considerable amounts were produced while the product was coming to room temperature. The products decomposed slowly at room temperature to give polymers insoluble in hydrogen sulphide. The infrared spectra of the products from the reactions of diborane with tetramethylammonium and tetraethylammonium hydrogen sulphides showed the following absorptions, not due to cations: Me_4N^+: 2370s, 2280s, 2180sh, 1160m, 1070s, 625w cm.$^{-1}$; Et_4N^+: 2380s, 2280s, 2220sh, 1160m, 1070s, 625w cm.$^{-1}$. Such absorptions were very different from the anion absorptions of tetramethylammonium and tetraethylammonium borohydrides, prepared[18] by a standard method: Me_4NBH_4: 2240s, 2150s, 1065s cm.$^{-1}$; Et_4NBH_4: 2280s, 2210s, 1070s cm.$^{-1}$.

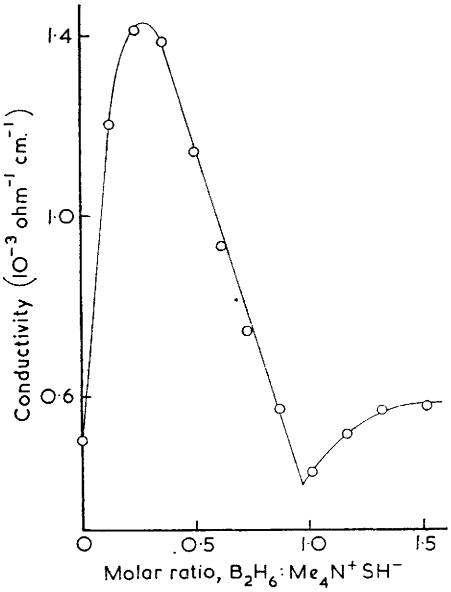

FIGURE 5 Conductimetric titration of B_2H_6 against Me_4NSH

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[17] W. J. Lehmann, C. O. Wilson, and I. Shapiro, *J. Chem. Phys.*, 1958, **28**, 781.

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DISCUSSION

The reactions reported in this Paper have demonstrated that the boron compounds may act as Lewis acids by the co-ordination of a hydrogen sulphide ion in liquid hydrogen sulphide:

$$BX_3 + R_4N^+SH^- = R_4N^+BX_3SH^-$$

or, in some cases, *via* the protonation of an amine or phosphine:

$$BX_3 + H_2S + R_3Y = R_3YH^+ + BX_3SH^- \text{ (Y = P or N)}$$

The boron compounds studied did not, however, cause substantial increases in conductivity when added to the pure solvent, and there seems to be little tendency for the reaction

$$BX_3 + 2H_2S \rightleftharpoons H_3S^+ + BX_3SH^-$$

to occur. Boron trifluoride and boron trichloride reacted with the trihalogenothioloborate anions to form tetrafluoroborate and tetrachloroborate anions, respectively. The exchange reactions must be accompanied by the formation of a thiohydrolysis product either of the form BX_2SH or $BX(SH)_2$, or polymers therefrom. The volatility of the compounds at −78° suggest that the product is probably a monomer of the type BX_2SH. BCl_2SH has already been reported.[19] A very volatile thiohydrolysis product, possibly BF_2SH, was detected by its infrared spectrum during the reaction of BF_3SH^- ions with BF_3. Exchange reations are quite common among the boron trihalides and their derivatives. A species $BX_4^- \cdots BY_3$ has been suggested to account for the exchange between tetrachloroborates and tetrafluoroborates in methylene chloride.[20] Triethylboron reacted with tetramethylammonium hydrogen sulphide to give the triethylthioloborate salt. Here, however, excess of triethylboron did not produce exchange.

The reactions of tetra-alkylammonium hydrogen sulphides with diborane indicate that an anion of stoicheiometry B_2H_6,SH^- is initially formed in solution, and that this anion gradually loses hydrogen. By comparison with the anion B_2H_6,PH_2^-, which has the structure $BH_3,PH_2{\cdot}BH_3^-$,[21] the anion may, initially, have the structure $BH_3,SH{\cdot}BH_3^-$. Comparison of infrared spectra showed that the freshly prepared B_2H_6,SH^- anion did not contain any borohydride, nor were there any peaks due to B–H–B bonds. This suggests that the formulation of the initial ions as $BH_3,SH{\cdot}BH_3^-$ is probably correct. The structure of the anion formed after loss of hydrogen is uncertain, but it is unlikely to be polymeric as the material remains soluble in liquid hydrogen sulphide. At room temperature further hydrogen is lost slowly, and an insoluble polymer is eventually formed. The loss of hydrogen can be compared with similar processes in the condensation of the adduct CH_3SH,BH_3 to give $(CH_3S,BH_2)_x$,[6] and in the formation of the compound $BH_2{\cdot}S{\cdot}[CH_2]_2{\cdot}S,BH_3$ from diborane and ethane-1,2-dithiol.[22]

UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE.
[Present addresses—see Part I]

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