iodine. The yield was 54 g. (68%) of XII distilling at 62–63° (13 mm.), n^{24}_{D} 1.4783.

Anal. Calcd. for $C_8H_{14}OS$: C, 60.71; H, 8.92; S, 20.26. Found: C, 60.84; H, 8.80; S, 19.98.

There remained 26 g. of residue from the above distillation which solidified on cooling and was polymeric in nature. On another run 2 moles of methacrylyl chloride was added dropwise at 0–10° to a stirred solution of 2 moles of *t*-butyl mercaptan in 1000 ml. of 10% sodium hydroxide. The organic phase was separated, washed with water, and dried over sodium sulfate. Distillation was carried out from 0.2 g. of iodine, yielding 187 g. (59%) of XII at 56–57° (8 mm.), followed by 65 g. (26% based on mercaptan) of **t-butyl 2-methyl-3-(2-methyl-2-thiopropoxy)-thiolpropionate (XIII)** at 128–129° (8 mm.), n^{24}_{D} 1.4865, leaving 7 g. of hard yellow residue.

Anal. Calcd. for $C_{12}H_{24}OS_2$: C, 58.01; H, 9.74; S, 25.81. Found: C, 58.35; H, 9.67; S, 25.50.

Illustrating the fact that the *t*-butyl mercaptide could react at the double bond of methacrylyl chloride prior to reaction at the acid chloride function was another 2-mole run in which the acid chloride was added in one portion to the chilled solution of mercaptan in 5% sodium hydroxide. The mixture was stirred with cooling for 2 hours and worked up in the usual manner. Fractionation from 0.1 g. of iodine gave a 47% yield of *t*-butyl thiolmethacrylate and a 21% yield of addition compound XIII. An intermediate fraction of 25 g. (6%) proved to be **2-methyl-3-(2-methyl-2-thiopropoxy)-propionyl chloride**, b.p. 91–92° (12 mm.), n^{24}_{D} 1.4740.

Anal. Calcd. for $C_8H_{15}ClOS$: C, 49.34; H, 7.77; Cl, 18.21; S, 16.46. Found: C, 49.55; H, 7.97; Cl, 18.29; S, 16.44.

Reaction of the *t*-Butyl Mercaptide with Acrylyl Chloride.—To 1000 ml. of 5% sodium hydroxide was added 90.2 g. (1 mole) of *t*-butyl mercaptan. The solution was maintained at 0–5° while 100 g. (1.1 moles) of acrylyl chloride was added dropwise with stirring. The organic phase was then separated and washed with 10% sodium carbonate, then with water, and run into a flask containing sodium sulfate and a trace of iodine. After drying, the material was decanted and fractionally distilled, yielding 29 g. (20%) of *t*-butyl thiolacrylate at 50–51° (12 mm.), n^{23}_{D} 1.4786 (lit.[2] b.p. 44.5–45° (8 mm.), $n^{21.2}_{\mathrm{D}}$ 1.4808). An intermediate fraction of 15 g. (8%) of **3-(2-methyl-2-thiopropoxy)-propionyl chloride** followed at 88–89° (11 mm.), n^{23}_{D} 1.4788.

Anal. Calcd. for $C_7H_{13}ClOS$: C, 46.53; H, 7.25; Cl, 19.62; S, 17.74. Found: C, 46.56; H, 7.10; Cl, 19.99; S, 17.65.

Continuation of the distillation yielded 63 g. (54%) of **t-butyl 3-(2-methyl-2-thiopropoxy)-thiolpropionate** at 135–136° (11 mm.), n^{23}_{D} 1.4900.

Anal. Calcd. for $C_{11}H_{22}OS_2$: C, 56.36; H, 9.46; S, 27.35. Found: C, 56.27; H, 9.34; S, 27.18.

Acknowledgments.—The authors are pleased to acknowledge the assistance rendered in this work by C. F. Hartman. The microanalyses were performed by Alfred Foulds.

PHILLIPSBURG, N. J.

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

Reactions of Elemental Sulfur. II. The Reaction of Alkali Cyanides with Sulfur, and Some Single-Sulfur Transfer Reactions[1]

BY PAUL D. BARTLETT AND ROBERT EARL DAVIS[2]

RECEIVED DECEMBER 16, 1957

The reaction of sulfur, S_8, with cyanide has been studied kinetically in homogeneous solution. The reaction is of second order, first order in each reactant. The effects of salts and solvents upon the rate has been interpreted as evidence for the rate-determining step being the opening of the S_8 ring by cyanide ion. Two other forms, hexatomic sulfur and irradiated sulfur, react immeasurably fast with cyanide ion. Ferricyanide and ferrocyanide ions do not attack sulfur at a measurable rate. Several sulfur transfer reactions have been studied.

Introduction

When sulfur reacts with an ionic cyanide the product is exclusively the thiocyanate; the reaction has been used as an analytical method for sulfur. The thiocyanate produced can be titrated with silver nitrate[3,4] or measured spectrophotometrically as the ferric–thiocyanate complex.[5] The reaction is fast enough at 40° to permit the titration of sulfur with cyanide using potentiometric *p*H measurements.[6]

Triarylphosphines,[1] like cyanide ion, react cleanly with sulfur to yield a single product, the phosphine sulfide, which is produced in a second-order reaction. The rate of the reaction is markedly increased by anion-solvating solvents

$$8\mathrm{Ar_3P} + \mathrm{S_8} \longrightarrow 8\mathrm{Ar_3PS} \qquad (1)$$

and by electron-releasing substituents in the phenyl groups ($\rho = -2.5$ in the Hammett equation). Two other forms of sulfur, the hexatomic form[7] and the amorphous form produced by irradiation,[8] react immeasurably fast with triphenylphosphine in benzene. From these facts it was concluded that the rate-determining step was the opening of the sulfur ring on attack by the phosphine giving a dipolar ion which then reacts rapidly in a series of further displacement reactions.

The reaction of sulfur, S_8, with cyanide represents the attack of a strongly nucleophilic anion on sulfur–sulfur bonds. The reaction can easily be

$$8\mathrm{CN^-} + \mathrm{S_8} \longrightarrow 8\mathrm{SCN^-} \qquad (2)$$

followed using the strong ultraviolet absorption of sulfur.[9]

Another reagent which attacks elemental sulfur in similar fashion is the sulfite ion. We find that either triphenylphosphine or cyanide ion will take an atom of sulfur from thiosulfate ion, but there is no measurable reaction of sulfur transfer between

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triphenylphosphine and thiocyanate or between cyanide and triphenylphosphine sulfide.

Experimental

Materials.—Merck reagent grade anhydrous methanol was refluxed with magnesium turnings and then distilled through a one meter packed column. Triply distilled conductivity water was used in preparation of the aqueous solutions.

Mallinckrodt sublimed U.S.P. sulfur was crystallized three times from benzene and dried under vacuum. Mallinckrodt AR sodium cyanide and Fisher AR potassium cyanide were used from freshly opened bottles. The solutions were standardized against silver nitrate.[10]

The sodium thiosulfate (Mallinckrodt AR) was standardized against sodium iodate.

Merck reagent sodium chloride was dried at 120°. Mallinckrodt AR sodium thiocyanate was dried at 120°. Baker AR potassium ferricyanide and Mallinckrodt AR potassium ferrocyanide were used without further purification.

Kinetic Procedure.—The stock sulfur solutions (about 10^{-3} molar based upon S_8) were prepared by direct weighing and solution of the sulfur in anhydrous methanol (solution required one week). The solutions were stable for six months to a year when stored under nitrogen in the dark. The cyanide solutions were prepared daily, kept in the dark and standardized against silver nitrate[10] immediately before use. All solutions were kept and thermostated in the dark. After thermal equilibrium was attained, 1 or 2 ml. of the cyanide solution was delivered rapidly into an amount of the sulfur solution to bring the total volume to 10 ml. Complete mixing was achieved in a few seconds as tested with 20% aqueous ammonium sulfate and water,[11] which gave a visually homogeneous solution when mixing was complete.

The solution was then poured into a stoppered Beckman 1-cm. quartz cell previously thermostated and then placed in a thermostat compartment[12] built into a Beckman DU spectrophotometer. The thermostat was built from a hollow brass block, 5 × 10 × 10 cm., having two brass inserts holding the quartz cells. The block was so mounted that it could be moved back and forth into the light path of the Beckman. The outer stationary compartment was constructed of brass and black plastic and allowed dry air to be circulated slowly over the exposed optics. This allowed runs to be made at temperatures below the dew-point of air and below zero. The solutions within the Beckman cells maintained a constant temperature within 0.03° when water from a bath was circulated rapidly through the hollow brass block.

The reactions were followed by using the strong ultraviolet absorption of sulfur at several wave lengths between 250 and 300 mμ (see Table I). The rate of the cyanide-thiosulfate reaction was studied by following the ultraviolet absorption of the thiosulfate ion at 260 mμ and alternatively by quenching the reaction in acidified iodine solution (*caution:* HCN) and back-titrating the excess iodine with standard thiosulfate. The two methods gave identical results within 2%. The reaction of triphenylphosphine[1] and sodium thiosulfate was followed by means of the strong ultraviolet absorption of the phosphine at 260 mμ.

The reaction of triphenylphosphine sulfide[1] with sodium cyanide in 90 weight per cent. methanol with water was studied in sealed glass tubes. No thiocyanate ion was produced, even after several weeks at 70°, as tested with ferric ion or with cobaltous sulfate in acetone. The maximal rate was calculated assuming that the reaction produced thiocyanate at the limit of detection in the time interval studied.

The reaction of triphenylphosphine and sodium thiocyanate was studied in like manner. The sealed tubes were opened and an aliquot withdrawn. The aliquot was acidified with several drops of dilute sulfuric acid and heated. The evolved gases were passed through a filter paper moistened with the cupric acetate–benzidine reagent.[13] No cyanide was detected and the maximal rate constant (Table V) was calculated assuming that a second-order reaction produced an amount of cyanide equal to the limit of detection of the spot test.

Kinetic Equations.—It has been found experimentally that

$$-\mathrm{d}(\mathrm{S}_8)/\mathrm{d}t = k_2(\mathrm{S}_8)(\mathrm{CN}^-) \qquad (3)$$

If x, the reaction variable, is the amount of S_8 reacted in moles per liter then

$$\mathrm{d}x/\mathrm{d}t = k_2(a - x)(b - 8x) \qquad (4)$$

where a is the initial concentration of sulfur, S_8, b is the initial cyanide concentration and t is the time in seconds. Integration yields

$$\frac{1}{b - 8a} \ln \frac{a(b - 8x)}{b(a - x)} = k_2t \qquad (5)$$

for $8a \neq b$, and

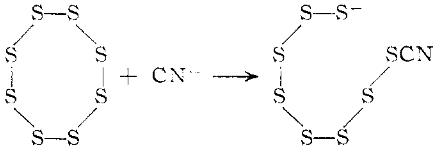
$$\frac{1}{8}\left[\frac{1}{a - x} - \frac{1}{a}\right] = k_2t \qquad (6)$$

for $8a = b$. The rate constants were calculated by fitting the integrated equation to the experimental points by the method of least squares. An entirely similar treatment was used in the other second-order reactions studied.

Results and Discussion

The rapid reaction between cyanide ion and sulfur is of the second order, the sulfur concentration being varied between 0.400 and 16.61 × 10^{-4} molar and the cyanide concentration between 0.516 and 8.40 × 10^{-4} molar. The strong ultraviolet absorption of sulfur allows investigation at quite low concentration and thus the rapid rate could be measured without resorting to flow techniques. Table I summarizes the data.

Aten and co-workers[14] have examined the exchange of ^{35}S between thiocyanate and sulfur in acetone and acetone–alcohol mixtures. The exchange detected after a period of one week at room temperature was so small that the bimolecular rate constant for reaction between sulfur and thiocyanate must be less than 10^{-6} l./mole sec. Likewise, there appears to be no exchange between CN^- and SCN^-.[15] Foss[16] has formulated the reaction of cyanide ion and sulfur as an initial attack of cyanide upon the sulfur with ring opening followed by a series of further displacement reactions.


(7)

$$^{-}\mathrm{S{-}S_5{-}S{-}SCN} + \mathrm{CN}^- \longrightarrow {}^{-}\mathrm{S{-}S_4{-}S{-}SCN} + \mathrm{SCN}^- \qquad (8)$$

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$$^{-}S{-}S_x{-}SCN + CN^- \longrightarrow {}^{-}S{-}S_{x-1}{-}SCN + SCN^- \quad (9)$$

$$^{-}S{-}SCN + CN^- \longrightarrow 2SCN^- \quad (10)$$

TABLE I

REACTION OF SODIUM CYANIDE WITH SULFUR, S_8, IN METHANOL

Temp.,[a] °C.	Solvent[b]	Other component	k_2, l. m.$^{-1}$ sec.$^{-1}$[c],[d]	
25.00	100		33.6	± 0.5[e]
14.88	100		15.3	.3[f]
4.50	100		7.88	.05[g]
4.50	91.3	Water	4.29	.05[h]
4.50	79.8	Water	3.47	.05[h]
4.50	100	0.002 *M* NaCl	7.50	.05[h]
4.50	100	.020 *M* NaCl	5.97	.05[e]
4.50	100	.002 *M* NaSCN	5.36	.05[h]
4.50	100	.020 *M* NaSCN	4.87	.05[e]
4.50	100	Light	>120[i] 7.90	
4.50	79.8	Water, light	>120[i] 3.49	

REACTION OF POTASSIUM CYANIDE WITH SULFUR, S_8, IN METHANOL

Temp., °C.	Solvent	Other component	k_2, l. m.$^{-1}$ sec.$^{-1}$	
25.00	100		32.0	± 0.5[j]
14.88	100		14.9	.4[e]
4.50	100		7.04	.06[e]

[a] ±0.03°. [b] Per cent. by weight methanol. [c] Rate constants with standard deviation. [d] Rates measured at 268 mμ, except some of those of (*j*). [e] Average of three runs. [f] Average of four runs. [g] Average of seven runs. [h] Average of two runs. [i] Irradiated with a tungsten light at 200 foot candles for 3 hours, about half of the sulfur reacts with a rate greater than can be measured, the remainder reacts at the normal dark rate. [j] Average of eight runs, four measured at 268 mμ, and one each at 250, 280, 290 and 300 mμ.

This reaction sequence and that proposed later for the triphenylphosphine reaction[1] are completely parallel. Two factors contribute to making reactions 8–10 so much faster than reaction 7 that the latter controls the rate. First, previous evidence[1] supports the idea that the S–S bond in a chain is more easily broken than in an 8-membered ring. Second, the energy of formation of the thiocyanate ion should contribute substantially to making it a favored departing group in a displacement reaction. That there are no intermediates of polysulfide character present in detectable concentration is indicated by the fact that the rate constants determined at five different wave lengths from 250 to 300 mμ are the same within experimental error; this means that the absorption spectrum remains the same throughout the reaction.

The effect of light on the reaction is also consistent with the Foss mechanism. As in the triphenylphosphine reaction, strong irradiation appears to produce another form of sulfur in the solution which disappears too fast to measure while the remaining S_8 reacts at the normal rate. In irradiated sulfur the 8-membered ring is already broken and long sulfur chains or large rings formed and the rate-determining step of the attack of cyanide is not the same as with S_8 in the dark (Table II).

TABLE II

Temp., °C.	Reaction in 100% methanol	k_2, l. m.$^{-1}$ sec.$^{-1}$
25.00	S_8 with $K_3Fe(CN)_6$	$< 10^{-7}$
25.00	S_8 with $K_4Fe(CN)_6$	$< 10^{-7}$
4.50	NaCN with S_6	>120[a]
4.50	NaCN with irradiated S	>120[a]
4.50	NaCN with S_8	7.88

[a] Limit of measurement.

The effect of solvent is in contrast to the reaction with triphenylphosphine, and this, too, supports the mechanism. The attack of triphenylphosphine, a neutral molecule, upon sulfur produces a dipolar ion and accordingly responds positively to the presence of a good ion-solvating solvent, especially an anion-solvating solvent, for the negative charge on the sulfur is more bare and solvatable than the positive charge on phosphorus. The cyanide reaction, however, is retarded by the addition of water to the methanol solvent (Fig. 1). This is normal for a reaction in which an anion with strongly localized charge is reacting through a transition state in which this negative charge is more dispersed by being on a larger atom and by being partially on the original carbon and partially on sulfur. Good solvation is more necessary to the initial reactant than to the transition state in this case, and the presence of about 20% water in the methanol cuts the rate constant slightly more than in half. This kind of solvent effect generally goes with a negative salt effect, as is here observed. As was to be expected, complexing with ferric or ferrous ion removes the nucleophilic activity of the cyanide ion toward sulfur.

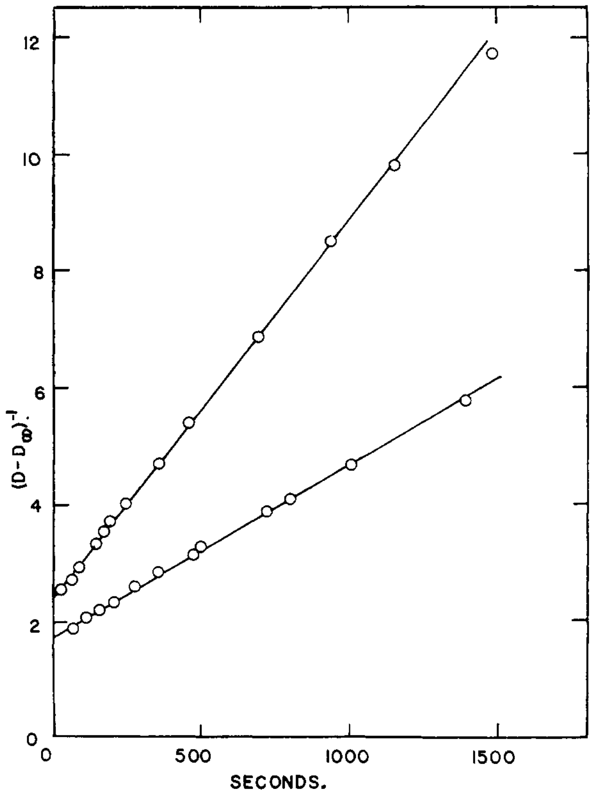

Fig. 1.—Reaction of sulfur (1.033 × 10^{-4} *M*) with sodium cyanide (8.26 × 10^{-4} *M*) at 4.50°: lower line, reaction in 79.8% methanol; upper line, reaction in 100% methanol; for the upper line the abscissa scale is $(D - D_\infty)^{-1} + 0.40$.

The near identity of the rates with sodium and potassium cyanides is normal for a reaction in a strongly ionizing solvent, in which the anion is able to function independently of the alkali cation attending it.

Reaction 10 above is one of a series of reactions in which a single sulfur atom is transferred from a donor to an acceptor, both reactants being basic in character. Other such reactions might be possible with thiocyanate, thiosulfate or triphenylphosphine sulfide as donors and with cyanide, sulfite or triphenylphosphine as acceptors. Of the nine possible exchange reactions involving these compounds, six have been studied. The exchange of sulfur between thiosulfate and sulfite has been shown to proceed at a measurable rate,[17] while the cyanide–thiocyanate exchange is immeasurably slow.[14] As another example of single-sulfur transfer we have measured the rate of the reaction between sodium cyanide and sodium thiosulfate in water, which proceeds irreversibly and establishes the cyanide ion as a stronger thiophile than the sulfite ion. The results are recorded in Table III; the activation parameters for this reaction, along with those of the sulfur exchange between thiosulfate and sulfite,[17] the reaction of trithionate and sulfite,[18] and the sulfur–cyanide reaction, are given in Table IV. The rate of the reaction between triphenylphosphine and sodium thiosulfate in aqueous methanol has been measured (Table V). The reaction is bimolecular and demonstrates that the phosphine is a stronger thiophilic reagent than sulfite. The reaction of cyanide with triphenylphosphine sulfide is immeasurably slow and only an upper limit on the rate can be estimated. Likewise, there seems to be no reaction between triphenylphosphine and thiocyanate. Therefore, the present data do not indicate the thiophilic order of triphenylphosphine and cyanide ion.

TABLE III

REACTION OF SODIUM CYANIDE WITH SODIUM THIOSULFATE IN WATER, IONIC STRENGTH 0.09

Temp., °C.	k_2, l. m.$^{-1}$ sec.$^{-1}$
25.00	3.9×10^{-5}
69.84	2.94×10^{-4}
90.00	8.62×10^{-4}

TABLE IV

ACTIVATION PARAMETERS AND RATE CONSTANTS AT 25°

Reaction	k_2, l. m.$^{-1}$ sec.$^{-1}$	E_a[a]	$\Delta H\ddagger$[a]	$\Delta S\ddagger$[b]
$KCN + S_8$[c]	32.0	12.0	11.4	− 4.7
$NaCN + S_8$[c]	33.6	11.5	10.9	− 5.7
$NaCN + Na_2S_2O_3$[d]	3.9×10^{-5}	13.0	12.4	−38
$Na_2SO_3 + Na_2S_2O_3$[d][17]	5.0×10^{-5}	14.5	13.8	−32
$Na_2SO_3 + Na_2S_3O_6$[d][18]	3.5×10^{-4}	11.1	9.5	−43

[a] ±0.5 kcal./mole. [b] Cal./mole degree. [c] Methanol. [d] Water.

TABLE V

SULFUR TRANSFER REACTIONS

$$X + SY \rightarrow XS + Y$$

X	SY	Solvent	Temp., °C.	k_2, l. m.$^{-1}$ sec.$^{-1}$
CN^-	$S\text{–}SO_3^{-2}$	H_2O	25	3.9×10^{-5}
$(C_6H_5)_3P$	$S\text{–}SO_3^{-2}$	80% MeOH[a]	25	3.3×10^{-3}
CN^-	$(C_6H_5)_3PS$	90% MeOH[a]	70	$<1 \times 10^{-7}$
$(C_6H_5)_3P$	SCN^-	90% MeOH[a]	70	$<4 \times 10^{-7}$
CN^-	SCN^-	H_2O[15]	25	$< 10^{-6}$
$SO_3^=$	SSO_3^{-2}	H_2O[17]	25	5.0×10^{-5}

[a] Weight per cent. methanol with water.

Table IV shows a great difference in rate between the reaction involving elemental sulfur and the others. This difference resides almost entirely in the entropy of activation which is responsible for a ratio of over six powers of ten between the rates.

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[CONTRIBUTION FROM THE WILLIAM ALBERT NOYES LABORATORY OF CHEMISTRY, UNIVERSITY OF ILLINOIS]

Some Properties of Tetraalkyl-2-tetrazenes[1]

BY WILLIAM E. BULL,[2] JACOB A. SEATON AND L. F. AUDRIETH[3]

RECEIVED NOVEMBER 27, 1957

Tetramethyl-2-tetrazene (TMT) and tetraethyl-2-tetrazene in ethanol reveal absorbancy maxima at 277 and 285 mμ with molar absorptivities of 8.3×10^3 and 7.6×10^3, respectively. Changes in absorption spectrum in various solvents have been related to the tendency for 2-tetrazenes to form protonated species in more acidic solvents. The basic nature of TMT has been characterized, using both analytical and titrimetric procedures, by formation of 1:1 compounds with the following protonic and non-protonic acids: $H_2C_2O_4$, $HOC_6H_2(NO_2)_3$, H_2SO_4, $HClO_4$, $CdCl_2$, $CdBr_2$, $HgCl_2$, $HgBr_2$, BF_3 and $AlCl_3$.

The search for a rapid and reliable procedure for the detection and estimation of the 2-tetrazenes led to a study of the ultraviolet absorption characteristics of these hydronitrogen derivatives along with a study of their chemical properties. The absorbancy maxima of compounds containing the azo chromophore generally lie between 240 and 290 mμ.[4] Alcoholic solutions of tetraethyl-2-tetrazene and tetramethyl-2-tetrazene were found to exhibit absorbancy maxima at 284 and 277 mμ, respectively. A linear plot of absorbancy *versus* concentration was obtained for 10^{-4} to 10^{-5} *M* ethanolic solutions of both tetrazenes measured at the respective wave lengths of maximum absorbancy. The molar absorptivities, a_M, of the tetraethyl- and tetramethyl-2-tetrazenes were found to

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[1] Abstracted in part from the doctoral dissertation submitted to the Graduate College of the University of Illinois by William E. Bull.

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