The data for the temperature jump studies are summarized in Table III for both the RNO^{2-}–SO_3^{2-}–Na^+ and RNO^{2-}–SO_3^{2-}–Cs^+ systems. At constant $[Na^+]$, $1/\tau$ is independent of the concentrations and combinations of concentrations of RNO^{2-}, SO_3^{2-}, $NaSO_3^-$, and $[RNO(SO_3)]Na^{3-}$ (although not shown in Table III, this is also true for the Cs^+ case). Considering eq 6, $1/\tau$ then approximates k_{-4}. The values of k_{-4} at 25° and $[M^+] = 1.0\ M$ are $9.8 \times 10^2\ sec^{-1}$ (Na^+) and $1.8 \times 10^2\ sec^{-1}$ (Cs^+). The activation parameters have been measured for $1/\tau$ ($\sim k_{-4}$) at 1.0 M Na^+ and at 0.96 M Cs^+ and 0.04 M Na^+. In the former case $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are 10.4 ± 0.9 kcal/mol and −10 ± 3 eu and in the latter case 14.5 ± 0.6 kcal/mol and 0 ± 2 eu.

TABLE III
TEMPERATURE-JUMP DATA

t, °C	$[RNO^{2-}]$, M	$[SO_3^{2-}]$, M	$10^{-3}/\tau$,[a] sec^{-1}	λ, nm
$[Na^+] = 1.00\ M$				
35.0	1.0×10^{-3}	0.40	1.63	475
	1.0×10^{-3}	0.25	1.65	
	1.0×10^{-3}	0.10	1.65	
25.0	1.0×10^{-3}	0.40	0.99	
	0.05	0.01	0.96	
	0.10	0.01	1.02	
	0.40	0.01	0.99	
	0.10	0.01	0.87	450
	0.10	0.01	0.99	500
	0.10	0.01	0.95	550
	0.10	0.01	0.98	600
	0.10	0.01	0.99	650
10.0	1.0×10^{-3}	0.10	0.33	475
	1.0×10^{-3}	0.25	0.38	
	1.0×10^{-3}	0.40	0.33	
$[Cs^+] = 0.96\ M$, $[Na^+] = 0.04\ M$				
32.9	0.01	0.01	0.320	
			0.347	
23.2	0.01	0.01	0.142	
			0.149	
7.7	0.01	0.01	0.0365	
			0.0356	
			0.0379	

[a] Average of two measurements.

If the correct mechanism is indeed the one formulated as equilibria 1 and 2, where (1) equilibrates slowly compared to (2) for the reasons given previously and in ref 10, then the reciprocal of the relaxation time, $1/\tau$, equals

$$k_1([RNO^{2-}] + [SO_3^{2-}]) + k_{-1}\left\{\frac{1 + Q_2([M^+] + [RNO(SO_3)^{4-}])}{1 + Q_2[RNO(SO_3)^{4-}]}\right\}$$

If $1/\tau$ is independent of $[RNO^{2-}]$ and $[SO_3^{2-}]$ and consequently of the concentration of the complex $RNO(SO_3)^{4-}$, then $1/\tau$ may be approximated by $k_{-1} \cdot (1 + Q_2[M^+])$, and the rate constants and associated activation parameters are associated with this quantity.

Stopped-flow experiments were carried out to see if the formation of the complex could be observed. The formation of complex from nitroprusside and sulfite at $[Na^+] = 1.00\ M$ occurred with a bimolecular rate constant greater than $1 \times 10^3\ M^{-1}\ sec^{-1}$ at 1°. If, under Equilibrium Measurements, $Q_4Q_3[Na^+]/(1 + Q_3 \cdot [Na^+])$ is approximated by Q_4, then $k_4 = k_{-4}Q_4 = 160\ M^{-1}\ sec^{-1}$ from values of $k_{-4} = 190\ sec^{-1}$ and $Q_4 = 0.84\ M^{-1}$ at 1°. This value is well below the lower limit set on the rate constant for the formation of the complex, $1 \times 10^3\ M^{-1}\ sec^{-1}$. However, when $Q_4Q_3[Na^+]/(1 + Q_3[Na^+]) \approx Q_4Q_3[Na^+] = 0.84\ M^{-1}$, then $k_4 = 160/Q_3$. It has been shown that Q_3 decreases with increasing ionic strength and can be as low as $0.1\ M^{-1}$.[9] Thus k_4 can be of the order of or larger than $10^3\ M^{-1}\ sec^{-1}$, and it appears that $Q_4Q_3[Na^+]/(1 + Q_3[Na^+]) \approx Q_4Q_3[Na^+]$.

The dependence of τ on $[Na^+]$ at 25° has been investigated from 0.20 to 1.00 M. The value of $1/\tau$ is found to vary from $1.4 \times 10^3\ sec^{-1}$ ($[Na^+] = 0.20\ M$) to $0.98 \times 10^3\ sec^{-1}$ ($[Na^+] = 1.00\ M$).

Table IV is a summary of kinetic data for the formation of various adducts of RNO^{2-}:[11] $RNO^{2-} + B^{n-} \rightarrow RNO(B)^{(2+n)-}$. The large negative values for the entropies of activation in all cases are consistent with the values expected for reactions between negatively charged ions, RNO^{2-} and B^{n-}. The enthalpy change for k_4Q_3 can be calculated from the enthalpy changes for k_{-4} (10.4 kcal/mol) and Q_4Q_3 (−4.6 kcal/mol) to be 5.8 kcal/mol (Table IV). If the enthalpy change for Q_3 is assumed to be 1.1 kcal/mol (using Na^+–SO_4^{2-} data),[9] then the enthalpy of activation for k_4 is 4.7 kcal/mol. This value is substantially smaller than the values measured for the RNO^{2-}–OH^- and RNO^{2-}–S^{2-} reactions and may reflect the fact that sulfite attacks at the oxygen end of the NO moiety while OH^- and S^{2-} attack at the nitrogen.

TABLE IV
SUMMARY OF KINETIC DATA FOR THE REACTIONS $RNO^{2-} + B^{n-} \rightarrow RNO(B)^{(2+n)-}$

B^{n-}	k[a]	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	Ref
SO_3^{2-}	450[b]	5.8[c]	−27[c]	*e*
OH^-	0.55[d]	12.6	−18	*f*
S^{2-}	170[d]	7.2	−24	*g*

[a] $\mu = 1.00$ (Na^+), temperature 298°K. [b] Units: $M^{-2}\ sec^{-1}$. [c] The values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ recorded are based on assumptions outlined in the section Results and Discussion: Kinetic Measurements. [d] Units: $M^{-1}\ sec^{-1}$. [e] This work. [f] J. H. Swinehart and P. A. Rock, *Inorg. Chem.*, **5**, 573 (1966). [g] P. A. Rock and J. H. Swinehart, *ibid.*, **5**, 1078 (1966).

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[11] The nomenclature $RNO(B)^{(2+n)-}$ does not mean B is necessarily attached to the oxygen of the NO moiety.

CONTRIBUTION FROM MOBAY CHEMICAL COMPANY,
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Trialkyl Phosphite–Boron Tribromide Coordination Compounds

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The system trialkyl(aryl) phosphite–boron trichloride has been investigated by Gerrard, *et al.*[1-4] These

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(1) W. Gerrard, "The Organic Chemistry of Boron," Academic Press, London and New York, N. Y., 1961, pp 189–190.

(2) M. J. Frazer, W. Gerrard, and J. K. Patel, *Chem. Ind.* (*London*), 90 (1959).

(3) W. Gerrard and M. Lindsay, *ibid.*, 152 (1960).

(4) M. J. Frazer, W. Gerrard, and J. K. Patel, *ibid.*, 728 (1959).

authors found that the alkoxy or phenoxy groups of the phosphite are successively exchanged by the chlorine atoms of the boron trichloride, the final products being trialkyl(aryl) borates and phosphorus trichloride. No coordination compounds involving a phosphorus–boron bond could be detected.[1,3] Boron tribromide was reported to behave similarly.[4] This is somewhat surprising since trialkyl phosphites have been shown to be about as nucleophilic as triethylamine[5] and should thus be expected to be good electron donators for boron trihalides. This communication describes the synthesis of stable trialkyl phosphite–boron tribromide coordination compounds by bromination of the corresponding trialkyl phosphite–borane[5] complexes in which the P–B bond is already present

$$\underset{\text{I}}{(RO)_3PBH_3} + 3Br_2 \longrightarrow \underset{\text{II}}{(RO)_3PBBr_3} + 3HBr$$

The syntheses, elemental analyses, and ^{31}P nmr spectra of compounds II are consistent with the proposed structure. It is interesting that the phosphite moiety in I survives the attack by bromine. This is evidenced by the titration[6] of the phosphorous acid which is formed on heating II overnight on a steam bath with concentrated hydrochloric acid and methanol. The presence of the phosphite moiety furthermore follows from the fact that II (R = i-C_3H_7) could be independently prepared by the direct reaction of triisopropyl phosphite with boron tribromide.

The ^{31}P nmr spectra of the compounds are in accord with the proposed structure. Compounds of the type $(RO)_3PBBr_3$ would be expected to exhibit a single ^{31}P resonance split into a 1:1:1:1 quartet by the boron nucleus. This quartet is indeed observed in all cases (centering in the range −33.5 to −40.9 ppm, relative to H_3PO_4). Similar quartets were found for trialkyl phosphite–boranes $(RO)_3PBH_3$.[7]

Table I lists the products and some of their properties.

TABLE I

TRIALKYL PHOSPHITE–BORON TRIBROMIDE COORDINATION COMPOUNDS

Formula	Yield, %	Mp, °C	^{31}P nmr, ppm, rel to H_3PO_4	J_{PB}, Hz	% decompn[a] in dioxane at room temp after 3 days
$(i\text{-}C_3H_7O)_3PBBr_3$	85	82	−33.5	285	1.9
$(n\text{-}C_4H_9O)_3PBBr_3$	82	42	. . .	. . .	7.0
$(C_2H_5O)_3PBBr_3$	92	33–34	−36.2	271	10.5
$(CH_3O)_3PBBr_3$	57	102–103	−40.9	271	33.0
$(i\text{-}C_3H_7O)_3PBH_3$	80	*b*	−111	80	No decompn

[a] The decomposition in dioxane was determined by precipitation with H_2O and recovery of the products. The extent of decomposition was checked by titration of the ionic bromine in the aqueous phase. [b] Bp 42° (1.1 mm).

It is interesting to compare the relative stabilities of the coordination compounds in dioxane solution. The rate of decomposition decreases with increasing alkyl substitution in the $P(OR)_3$ moiety. This may be due to steric hindrance in the assumed exchange of the bromine with the alkoxy group in II especially when the group R is the bulky isopropyl substituent. Preliminary attempts to chlorinate $(RO)_3PH_3$ led to crystalline products the identification of which is still to be performed.

Method of Preparation.—The bromine compounds were prepared by slowly adding a small excess of bromine to a mixture of trialkyl phosphite–borane[5] in an excess of finely divided ice (vigorous stirring!). The excess halogen was removed by treatment with sodium sulfite. The oily products crystallized and were filtered, washed with water, and dried in the air. The compounds were purified by dissolving in dioxane and treating with dilute sodium hydroxide. The precipitates were then washed with water, dried under vacuum, and recrystallized from methanol or hexane. Compound II, R = i-C_3H_7, was also prepared by adding a solution of boron tribromide in hexane to a solution of isopropyl phosphite in hexane at −40°.

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(5) T. Reetz, *J. Amer. Chem. Soc.*, **82**, 5039 (1960).

(6) Titrated with I_2 in $NaHCO_3$ solution. Back-titration with arsenite.

(7) We are indebted to Dr. M. M. Crutchfield for the spectra of $(i\text{-}C_3H_7O)_3PBBr_3$ and $(RO)_3PBH_3$ and their interpretation and to Mr. L. F. Johnson of the Varian Co. for the spectra of the other compounds listed in Table I.

CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY,
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Structural Ambiguity of the $B_{10}H_{14}^{2-}$ Ion

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The structure of $B_{10}H_{14}^{2-}$, not previously established, has been assumed[2] to be similar to that of $B_{10}H_{12}(NCCH_3)_2$, with which it is isoelectronic in the sense that the ligand CH_3CN is replaced by H^-. In this structure of 2632 topology[2] there are BH_2 groups at B_6 and B_9 (Figure 1) and hydrogen bridges between B_5 and B_{10} and between B_7 and B_8. However, the hydrogen atom arrangement observed in $B_{10}H_{14}$ is also a possibility in a structure of 4450 topology having bridges B_5HB_6, B_6HB_7, B_8HB_9, and B_9HB_{10}. This ^{11}B nmr study resolves this structural ambiguity and suggests relative emphasis on three-center resonance as compared with uniform charge distribution as a preferred criterion for resolving structural ambiguity when steric and other factors are comparable.

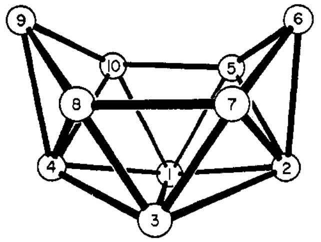

Figure 1.—Numbering system and the B_{10} fragment of the icosahedron seen in $B_{10}H_{14}$.

Experimental Section

Various salts of $B_{10}H_{14}^{2-}$ were prepared according to the pro-

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(1) Contribution No. 2875.

(2) W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, New York, N. Y., 1963, p 183.